Calculation of critical loads for cadmium, lead and mercury

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Background document to a Mapping Manual on Critical Loads of cadmium, lead and mercury

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ABSTRACT

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This report on heavy metals provides up-to-date methodologies to derive critical loads for the heavy metals cadmium (Cd), lead (Pb) and mercury (Hg) for both terrestrial and aquatic ecosystems. It presents background information to a Manual on Critical Loads for those metals. Focus is given to the methodologies and critical limits that have to be used to derive critical loads can be derived for Cd, Pb and Hg in view of : (i) ecotoxicological effects for either terrestrial or aquatic ecosystems.and (ii) human health effects for either terrestrial or aquatic ecosystems. For Hg, a separate approach is described to estimate critical levels in precipitation in view of human health effects due to the consumption of fish. The limitations and uncertainties of the approach are discussed including: (i) the uncertainties and particularities of the steady-state models used and (ii) the reliability of the approaches that are applied to derive critical limits for critical total dissolved metal concentrations in soil solution and surface water.

Keywords: heavy metals, critical loads, critical levels, leaching, critical limits, transfer functions, terrestrial ecosystems, aquatic ecosystems, lead, cadmium, mercury

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Preface

The development of methodologies to calculate critical loads for heavy metals has a long history and started about ten years ago. The first initiative was taken by the Ministry of Environment in the Netherlands, who approached the main author of this report to develop effects based calculation approaches for the calculation of critical loads of heavy metals in terrestrial and aquatic ecosystems. The idea was that, in analogy to critical loads for nitrogen and acidity, this approach would be valid for use in the context of the Convention on Long Range Transboundary Air Pollution (CLRTAP). In the mid of the 1990's, preliminary methods were presented at various meetings of the Coordinatation Centre of Effects of the ICP Modelling and Mapping, being part of the CLRTAP. This led in 1998 to two "Manuals" for calculation of critical loads of heavy metals in terrestrial ecosystems and aquatic ecosystems, headed by the main author of this document. These methods have been applied in national studies and discussed at international workshops in 1997 in Bad Harzburg and in 1999 in Schwerin. An "Expert Panel on Heavy Metals" was set up, focusing on the derivation of critical limits for heavy metals and on transfer functions for metals from soil solid phase to soil solution and vice versa. These methods were intensively discussed at various meetings in Bratislava (2000), Berlin (2002), Strausberg (2003) and Potsdam (2004). The final agreement achieved at the last meeting led to a chapter (5.5) on Critical Loads of cadmium, lead and mercury in the ICP's Manual for Modelling and Mapping Critical Loads & Levels (UBA 2004).

This report presents background information to that "manual" chapter. Major parts of the background information are included in the annexes of this report. The report was written by an interdisciplinary team of researchers in the "Expert Panel on Heavy Metals" under the co-ordination of Alterra. Institutes involved were:

- Alterra Green World Research, Droevendaalse steeg 3, P.O. Box 47, NL-6700 AA Wageningen, The Netherlands: Dr. Wim de Vries, Dr. Paul Römkens and Ir. Bert Jan Groenenberg.
- Federal Environmental Agency Berlin, P.O. Box 330022, D-14191 Berlin, Germany / ÖKO-DATA Strausberg. Ir. Gudrun Schütze
- Centre for Ecology and Hydrology (CEH), Lancaster Environment Centre, Library Avenue Bailrigg, Lancaster LA1 4AP, United Kingdom: Dr. Stephen Lofts and Prof. Dr. Edward Tipping.
- Stockholm University, Institute of applied Environmental research (ITM), SE-10691 Stockholm, Sweden. Dr. Markus Meili.

The overall co-ordination and editing of this report was carried out by Wim de Vries in close cooperation with Gudrun Schütze. For colleagues who like to know more specific details on several aspects, reference is made to the following co-authors:

- Stephen Lofts: Critical dissolved free Cd and Pb concentrations related to ecotoxicological effects: Part of Section 3.2.3 and Annex 8

- Edward Tipping: Calculation of critical total Cd and Pb concentrations in soil solution and surface water with the chemical speciation model WHAM: Part of Section 3.2.3, Annex 9 and 12.
- Markus Meili: Hg critical limits, critical loads (soils) and critical levels in precipitation (surface waters): Section 3.2.4, 4.2 and Annex 13.

This report has been written with the support of many other colleagues and we thus thankfully acknowledge the following Ministries, Institutes and Scientists:

- The Dutch Ministries of Housing, Spatial Planning and Environment (VROM) and of Agriculture, Nature and Food quality (LNV), the German Ministry of the Environment, Nature Conservation and Nuclear Safety and the UK Department of the Environment, Food and Rural Affairs for financial support.
- Dr. Ludwig de Temmerman of the "Centrum voor onderzoek in diergeneeskunde en agrochemie C.O.D.A" in Belgium for information on the relation between atmospheric deposition and plant metal contents.
- The "Expert Panel on Critical loads of Heavy Metals" consisting of Prof. Michael Ashmore, Dr. Lage Bringmark, Dr. Philipp Cambier, Dr. Wim de Vries, Dr. Régis Farret, Ir. Bert-Jan Groenenberg, Prof. J.-P. Hettelingh, Dr. Kjell Johansson, Dr. Stephen Lofts, Prof. Markus Meili, Dr. Tatiana Pampura, Dr. Anne Probst, Ir. Gudrun Schütze, Prof. Harald Sverdrup, Prof. Edward Tipping and Prof. Bjørn-Olav Rosseland for comments on previous drafts of parts of this background report.
- Prof. Marek Jakubowski of the Institute of Occupational Medicine in Poland for his information on human health critical limits.
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Summary

This report on heavy metals provides up-to-date methodologies to derive critical loads for heavy metals (Pb, Cd, Hg) for both, terrestrial and aquatic ecosystems. It presents background information to a Manual on Critical Loads of cadmium, lead and mercury that is part of a complete Manual for Modelling and Mapping Critical Loads & Levels. Major parts of the background information are included in the annexes of this report.

Chapter 2 presents general methodological aspects of mapping critical loads of the heavy metals cadmium (Cd), lead (Pb) and mercury (Hg). It first contains information on the different types of critical loads to be calculated in dependence on the receptors and regarded metals. Critical limits of these heavy metals, addressing either ecotoxicological ecosystem effects or human health effects, are derived with specific approaches. Critical loads on the basis of such limits have to be calculated separately for aquatic and terrestrial ecosystems. In consequence four types of critical loads can be derived for each metal:

- Ecotoxicological effects for all terrestrial ecosystems.
- Human health effects for all terrestrial ecosystems.
- Ecotoxicological effects for all aquatic ecosystems.
- Human health effects for all aquatic ecosystems.

Critical loads for terrestrial ecosystems addressing human health effects can be calculated, either in view of not violating food quality criteria in crops or in view of ground water protection (keeping quality criteria for drinking water of WHO 2004). An appropriate indicator for critical load calculations addressing human health effects via food intake is the Cd content in wheat. Such critical load calculations are in principle also possible for lead, and for other food and fodder crops, if the soil-plant transfer can be described with sufficient accuracy and can be done in addition on a voluntary basis. Among terrestrial ecosystems, critical loads of Cd and Pb are to be calculated from the viewpoint of ecotoxicology for areas covered by non-agricultural land (forests, semi-natural vegetation) or agricultural land (arable land and grassland). Organic forest (top)soils are considered as the only critical receptor with respect to atmospheric Hg pollution, based on knowledge on effects on microbial processes and invertebrates. Although it might be useful to calculate and map each of the different types of critical loads separately for comparison purposes, the aim is ultimately to provide maps for at most four critical loads as described above.

Chapter 2 also summarizes the main differences between a previous guidance document and the present manual. A main aspect to be mentioned is that this manual is limited to the calculation of critical loads for Cd, Pb and Hg for terrestrial and aquatic ecosystems using recommended critical limits (an effect-based approach), whereas the derivation of acceptable loads using a stand-still approach (not effects-based) is not included. Instead, information is given how to calculate the difference between present and critical metal concentrations in soil or surface water as an

important step in future dynamic modelling. Another important difference is that the critical limit for the metals Cd and Pb in soil solution is now described as a critical pH dependent free metal ion concentration instead of a constant critical total dissolved metal concentration. This implies further that use of a speciation (complexation) model (WHAM) is included in the manual (not in the guidance document) to calculate a critical total dissolved metal concentration from the free metal ion concentration. Furthermore transfer functions are now used that relate the reactive metal content to the free metal ion activity instead of the total dissolved metal concentration, as used in the guidance document. These improvements are all in accordance with increased insight in the effects of heavy metals on soil organisms and plants.

Chapter 3 describes the method to calculate critical loads of heavy metals for terrestrial ecosystems on the basis of a balance of relevant metal fluxes in and out of a considered ecosystem in a steady state situation. The assumption of a future steady state situation signifies that the concentration in the system does not change in time because the amount of heavy metal entering the system is equal to the amount that leaves the system. In order to keep the approach compatible with the simple mass balance approach used for nitrogen and acidity, the internal metal cycling within an ecosystem is ignored, such that calculations can be kept as simple as possible. In consequence the critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching. Natural inputs by weathering release is neglected because weathering causes only a minor flux of metals, while uncertainties of such calculations are very high. The described approach implies that the critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate.

Apart from deriving data on the removal of harvested crops or trees and the metal contents in it and on the water fluxes leaving the soil, the major challenge is to derive critical total concentrations of the heavy metals Cd, Pb and Hg in soil solution. This report describes how these critical total concentrations can be derived from either critical limits for metal contents in plants (Cd, Pb), metal concentrations in ground water (Cd, Pb), free metal ion concentrations in soil drainage water (Cd, Pb) or critical metal contents in the soil organic matter (Hg). For Hg, partitioning of soil organic matter is the basis of calculations rather than a free-ion approach.

Chapter 4 describes the method to calculate critical loads of the heavy metals Cd and Pb for aquatic ecosystems (lakes and rivers). Analogous to terrestrial ecosystems, the critical load of Cd and Pb for freshwaters corresponds to the sum of tolerable outputs from the catchment by harvest and metal outflow. For lakes the retention in the surface water, can be added. As with terrestrial ecosystems net weathering in soils is preliminarily assumed to be negligible, due to high uncertainties in its estimation. Similarly, the derivation of data focuses on the net removal of metals in a catchment, the water fluxes leaving the catchment and critical total concentrations of the heavy metals Cd and Pb in surface water. This report describes how these critical total concentrations can be derived from critical limits for dissolved metal concentrations in surface water, using the complexation model WHAM. The critical limits are based on an EU Risk Assessment Report for Cd and a substance data sheet for Pb.

For Hg, the critical loads approach for aquatic ecosystems, using a mass balance, is not practical because of the complexity of processes involved both within the water column and in the surrounding watershed. Alternatively, a concentration-based model is formulated to derive a critical level of Hg in precipitation, based on the steady state partitioning of Hg in a constant environment. This approach can be applied without any need for mass balance considerations or detailed understanding of ecosystem processes. Empirical transfer functions are used describing the relationship of Hg concentrations in fish (as a critical receptor) with the Hg immissions at steady state (represented by the most convenient atmospheric monitoring parameter). One transfer function is site-specific and links the (critical) Hg concentration in fish flesh directly to the (critical) Hg concentration in precipitation, using a 1-kg pike as the reference fish. An additional transfer function is organism-specific and describes how the Hg concentration in any fish, or any other organism serving as food for humans and fish-based wildlife, can be related to the Hg concentration in 1-kg pike, based on the typical Hg partitioning within food webs. In combination, the model and its two transfer functions permits calculations for any organism at any site, as well as conversions between regionally different approaches. The derivation of both transfer functions is described in detail in the last Annex (13).

An evaluation of the methodological approach is given in Chapter 5. This includes a methodology to calculate the critical soil content from a given critical limit function for the soil solution and compare this to the present soil metal content to assess the critical limit exceedance in the present situation (Section 5.1). The limitations and uncertainties of the critical load estimates are further discussed in Section 5.2. This includes: (i) an overview of sites where the calculations can not be carried out (ii), the uncertainties and particularities of the steady-state models used and (iii) the reliability of the approaches that are applied to derive critical limits for critical total dissolved metal concentrations in soil drainage water and surface water. Furthermore, possibilities to improve the model calculations and the derivation of critical total dissolved metal concentrations are presented.

1 Introduction

1.1 Background of the report

The UNECE Protocol on Heavy Metals, Article 6, encourages parties inter alia to develop "an effects-based approach … for the purpose of formulating future optimised control strategies …", primarily focussing on cadmium (Cd), lead (Pb) and mercury (Hg). This report describes in detail the most recent methods to calculate critical loads for cadmium, lead and mercury, as summarised in chapter 5.5 of the UNECE ICP Modelling and Mapping manual on this topic (UBA, 2004).

The methodologies described in this report are the result of a process of method derivation and scientific debate, which started already in the mid of the 1990's. A variety of effects based calculation approaches were first described in Manuals for calculation of critical loads of heavy metals in terrestrial ecosystems (De Vries & Bakker, 1996, 1998) and aquatic ecosystems (De Vries et al., 1998). These methods have been applied in national studies and discussed at international workshops in 1997 in Bad Harzburg (Gregor et al., 1997) and in 1999 in Schwerin (Gregor et al., 1999). For Hg several specific approaches have been developed (Meili et al., 1999; Sverdrup, 1999; De Vries et al., 2003; Meili et al., 2003a; Meili et al., 2003b; Sverdrup et al., 2003). In particular, intensive research and scientific discussion was necessary to develop methodologies and databases for the derivation of critical limits and necessary transfer functions. Expert meetings, 2000 in Bratislava (Curlík et al., 2000), and 2002 in Berlin (Schütze et al., 2003), dealt specifically with these items.

An important development was the first preliminary European mapping exercise on critical loads related to direct ecotoxicological effects of Cd and Pb (Hettelingh et al., 2002), which was conducted on a voluntary basis, following the decisions of the 20th Session of the Working Group on Effects (WGE) in 2001 in Geneva. The harmonised methodological basis for calculation and mapping in this exercise was a guidance document provided by De Vries et al. (2002a). A report on critical limits, and transfer functions (De Vries et al., 2002b), provided by expert groups (later the Expert Panel on Critical Loads of Heavy Metals) working under ICP Modelling and Mapping, described the scientific background on those aspects in more detail.

After the first mapping exercise, the methods were further developed. The most crucial steps were to include human health aspects, to develop the critical loads and levels for Hg, and to introduce critical limits (Pb, Cd) related to free ion activities and related transfer functions, the latter enabling also calculations for organic soil layers. Scientific papers have been prepared addressing:

- Solid-solution transfer functions, including validation (Groenenberg et al., 2003);
- pH dependent free metal ion derivation(Lofts et al., 2004);
- Critical limits for direct effects on soil and aquatic organisms, and indirect effects on animal health and human health (De Vries et al., 2003);

- Critical levels of atmospheric mercury pollution (Meili et al., 2003b).

According to the most recent findings the methodology was discussed again at a meeting of the Expert Panel in October 2003, in Strausberg (Germany) and in march 2004 in Potsdam (Germany) and agreement was achieved on tentatively final changes. This led to a chapter (5.5) on Critical Loads of cadmium, lead and mercury. This report presents background information to that "manual" chapter. Major parts of the background information are included in the annexes of this report

1.2 Aim and contents of the report

The aim of this report on heavy metals is to provide up-to-date methodologies to derive critical loads for heavy metals (Pb, Cd, Hg) for both, terrestrial and aquatic ecosystems, including background information that is not included in the relevant chapter (5.5) in the official mapping manual (UBA, 2004). Chapter 2 summarizes general methodological aspects of calculation and mapping critical loads of heavy metals. The methods to calculate critical loads for Cd, Pb and Hg for terrestrial ecosystems are summarized in Chapter 3. This includes (i) mass balance models and input data to calculate critical loads, (ii) critical limits for free metal ions, dissolved metal concentrations and/or contents of heavy metals in plants, that are essential to carry out the critical load calculations and (iii) transfer functions, describing the relationship between free metal ion concentrations or total dissolved metal concentrations and reactive contents of heavy metals, while accounting for the impact of soil chemical properties. Similarly, the methods to calculate critical loads for Cd, Pb and Hg for aquatic ecosystems are summarized in Chapter 4. For Hg, an alternative approach, focusing on the critical Hg level in precipitation, is included. The final chapter (5) includes an overview of the limitations in the present approach and possible future refinements

Most background information on the methodologies used to calculate critical limits and critical loads for Cd, Pb and Hg in terrestrial and aquatic systems is presented in Annexes. The definitions related to various expressions and the abbreviations used in the various critical load calculations are presented in Annex 1. The Annexes 2 and 3 focus on the derivation of critical limits from quality criteria for crops (Annex 2) and animal products (Annex 3), with a main emphasis on Cd. Considerations about an appropriate effects-based limit for the concentration of Cd in wheat, being the most relevant and sensitive crop, is given in Annex 4. Annex 5 describes a direct approach to derive critical loads for lead and mercury from food quality criteria for crops. Annex 6 presents methods to estimate heavy metal release by weathering in the mineral topsoil. Transfer functions used for conversion of metal concentrations in different soil phases are described in Annex 7. The methodology to assess critical free and total metal (Cd and Pb) concentrations in soil drainage water related to ecotoxicological effects are described in the Annexes 8 and 9, respectively. The Annexes 10 and 11 give information on the assessment of pH values, including relationships between various pH estimates, (Annex 10) and of DOC values (Annex 11). Annex 12 focuses on the calculation of critical total Cd and Pb concentrations in surface water, whereas Annex 13 gives background information on transfer functions for Hg in aquatic ecosystems.

2 General methodological aspects of mapping critical loads of heavy metals

The chapter contains information on: (i) the different types of critical loads to be calculated in dependence on the receptors and regarded metals (section 2.1) and (ii) the main differences between the previous guidance document and the present manual (UBA, 2004). A main aspect to be mentioned directly is that this manual is limited to the calculation of critical loads for Cd, Pb and Hg for terrestrial and aquatic ecosystems using recommended critical limits (an effect-based approach), whereas the derivation of acceptable loads using a **stand-still** approach (not effects-based) is not included. Instead, information is given how to calculate the difference between present and critical metal concentrations in soil or surface water as an important step in future dynamic modelling (see section 2.2).

2.1 Calculation of different types of critical loads in dependence on the receptors and regarded metals

Critical loads of cadmium (Cd), lead (Pb) and mercury (Hg) can be calculated in dependence on the receptors and the metal of concern. Critical limits of these heavy metals, addressing either ecotoxicological ecosystem effects or human health effects, are derived with specific approaches. Critical loads on the basis of such limits should be calculated separately for aquatic and terrestrial ecosystems. In consequence four types of critical loads can be derived for each metal. An overview is provided in Table 1, which is however not a complete review of possible effects of these metals.

Indicators of effects on ecosystems, listed in Table 1, are mainly ecotoxicological effects. Secondary poisoning through the food chain has also been studied (De Vries et al., 2003; De Vries et al., 2004b). These effects give partly more stringent critical limits, however their modelling includes more uncertainties and is therefore not considered in the manual (UBA, 2004).

Critical loads for terrestrial ecosystems addressing human health effects can be calculated, either in view of not violating food quality criteria in crops or in view of ground water protection (keeping quality criteria for drinking water of WHO 2004). An appropriate indicator for critical load calculations addressing human health effects via food intake is the Cd content in wheat. Keeping a conservative food quality criterion for wheat, as described in Section 3.3.1, protects at the same time against effects on human health via other food and fodder crops (including also the quality of animal products), since the pathway of Cd to wheat leads to the lowest critical Cd content in soils (De Vries et al., 2003; De Vries et al., 2004b). Such critical load calculations are in principle also possible for lead, and for other food and fodder crops, if the soil-plant transfer can be described with sufficient accuracy and can be done in addition on a voluntary basis.

Among terrestrial ecosystems, critical loads of Cd and Pb are to be calculated from the viewpoint of ecotoxicology for areas covered by non-agricultural land (forests, semi-natural vegetation) or agricultural land (arable land and grassland). Organic forest (top)soils are considered as the only critical receptor with respect to atmospheric Hg pollution, based on knowledge on effects on microbial processes and invertebrates (Meili et al., 2003b). The critical exposure of terrestrial ecosystems to atmospheric Hg pollution can be calculated in much the same way as for Pb and Cd by a simple mass balance, as discussed in Section 3.2.

Table 1 Four types of critical loads of heavy metals (HM), related receptors and indicators

Receptor ecosystem	Critical loads related to	Metals of concern	Land cover types to be considered	Indicator addressed by the critical limit *)
Terrestrial	Human health effects	Cd, Pb, Hg	Arable land	Metal content in food/*fodder* crops
		Cd, Pb, Hg	Grassland	*Metal content in grass, animal products (cow, sheep)*
		Cd, Pb, Hg	Arable land, grassland, non-agricultural land	Total metal concentration in soil water below the rooting zone (aiming at ground water protection)
	Ecosystem functioning	Pb, Cd	Non-agricultural land, arable land, grassland	Free metal ion concentration in soil solution in view of effects on micro-organisms, plants and invertebrates
		Hg	Forests only	Total metal concentration in humus layer in view of effects on soil micro-organisms and invertebrates
Aquatic	Human health effects**)	Hg	Freshwaters	Metal concentration in fish
	Ecosystem functioning	Pb, Cd, Hg	Freshwaters	Total metal concentration in freshwaters in view of effects on algae, crustacea, worms, fish, top predators

*) In italics: these calculations can be done in addition on a voluntary basis.

**) these are critical levels

In order to perform the voluntary calculations on human health and animal health effects for Cd, Pb and Hg in arable land and grassland more information is presented in the Annexes 2-5, respectively. The derivation of critical soil limits for Cd, based on critical metal contents in food/fodder crops and in animal products/organs is given in Annex 2 and 3, respectively. Annex 4 provides an argument for using a ceratin food quality criterium in wheat, being the most relevant crop in view of human health effects. Since for Pb and Hg in food crops, back calculation to soil content is not possible (there are no relationships between content of soil and contents in plants for those metals), critical loads can be derived using direct relationships between the Pb deposition or Hg concentrations in the air and Pb or Hg contents of plants (specifically vegetables). Methods for such calculations are provided in Annex 5.

For aquatic ecosystems the critical limits of Pb and Cd are related to ecotoxicological effects, while human health effects by this pathway are less relevant and therefore not considered here. Critical limits of Hg refer to both human health effects (Hg concentration in fish and other animals that serve as a food source to humans) and ecotoxicological effects, since fish and higher wildlife itself may also be affected.

Although it might be useful to calculate and map each of the different types of critical loads separately for comparison purposes, the aim is ultimately to provide maps for at most four critical loads (for Hg loads or levels) per metal related to:

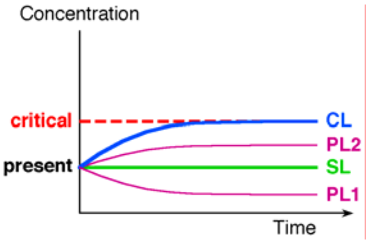
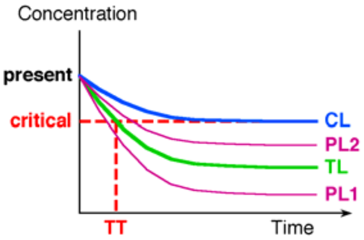
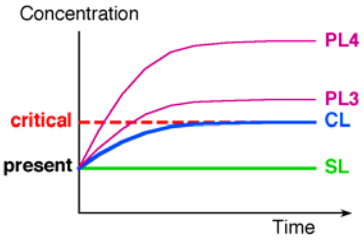
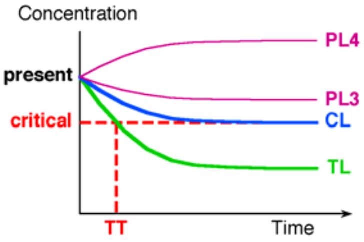
- Ecotoxicological effects for all terrestrial ecosystems.
- Human health effects for all terrestrial ecosystems.
- Ecotoxicological effects for all aquatic ecosystems.
- Human health effects for all aquatic ecosystems.

If different indicators within each category (map) have been considered (e.g. Cd in wheat and Cd in soil solution in view of ground water protection for human health), the final map should indicate the minimum critical Cd load for both effects to human health. The reason for providing different critical loads for different types of ecosystems is because the critical load for terrestrial ecosystems does not automatically protect aquatic ecosystems, receiving much or most of their metal load by drainage from the surrounding soils, and vice versa.

A critical load indicates only the sensitivity of an ecosystem against the anthropogenic input of the metal of interest. It implies a potential risk at sites where the critical load is exceeded. In agricultural ecosystems, the exceedance of critical loads of heavy metals is not only determined by atmospheric inputs (being generally the only source in non-agricultural ecosystems), but by total inputs, including fertilizer and animal manure inputs.

Exceedance of critical loads of heavy metals means that critical limits will be exceeded in the future, but not necessarily at present. It thus implies a potential risk. On the other hand non-exceedance of critical loads can include a present risk, if critical limits are already exceeded due to historical inputs (or geogenic high contents). This is explained in Figure 1. If the present soil metal content exceeds the critical concentration (limit), the metal input has to be less than the critical load to reach the critical concentration at a defined time period. In the reverse case, the metal input can be larger than the critical load for a defined time period not exceeding during that period the critical concentration (this load is called a target load; see Section 2.2). However, only keeping the critical load will not lead to exceedance of the critical limit in the long run.

Figure 1 shows, how the concentration in the ecosystems develops in individual cases of exceedance or non-exceedance of critical limits or critical loads of heavy metals, respectively.

	No critical limit exceedance	Critical limit exceedance
No critical load exceedance	No damage at present or foreseen:  ➔ Keep the Present Load (more stringent than Critical Load)	Present damage but recovery in progress:  ➔ Keep the Present Load (more stringent than Critical Load) or ➔ Consider Target Load to reach the critical limit in a defined time period (more stringent than Critical Load)
Critical load Exceedance	Future damage foreseen:  ➔ Consider Critical Load (emissions must decrease, even if concentrations in the ecosystem are allowed to increase further at critical load)	Present damage, no recovery foreseen:  ➔ Consider Critical Load (decrease of concentrations in the ecosystem down to critical limit in the long term) or ➔ Consider Target Load to reach the critical limit in a defined time period (more stringent than Critical Load)

CL - Critical load; PL - present load (2 cases); SL - Stand-still load; TL - Target load; TT - Target time

Figure 1 The predicted development of metal concentrations in ecosystems fir four cases of exceedance or non-exceedance of critical limits and of critical loads of heavy metals, respectively.

2.2 Differences between the guidance document and the manual

Main differences

The harmonised methodological basis for a first preliminary calculation and mapping of critical loads for Cd and Pb related to ecotoxicological effects (Hettelingh et al., 2002), was based on a guidance document (De Vries et al., 2002a). The methodological basis for calculation and mapping critical metal loads described in the manual (UBA, 2004) deviates in various aspects from the previous guidance document (De Vries et al., 2002a) as summarised in Table 2. In addition it includes human health aspects and the methodologies for Hg.

Table 2 Differences in the calculation of critical loads according to the guidance and the manual

Aspect	Manual	Guidance
Transfer function	Relation reactive metal content and free metal ion activity	Relation reactive metal content and total dissolved metal concentration
	Includes mineral and organic soils	Focus on mineral soil
Critical limits	pH dependent free metal ion activity	Constant total dissolved metal concentration
Method	Speciation model included	No speciation model included
	No weathering included	Weathering included
	Comparison of present and critical limits included	Stand still approach included

Transfer functions and critical limits

An important difference between the manual and the guidance document is that in the manual transfer functions are used that relate the reactive metal content to the free metal ion activity (see Annex 7), instead of the total dissolved metal concentration as used in the guidance document. This is related to the fact that the critical limit for the dissolved concentration of Cd and Pb in soil drainage water is now described as a critical pH dependent free metal ion concentration (see Annex 8) instead of a constant critical total dissolved metal concentration as used in the guidance document. This implies further that use of a speciation (complexation) model (WHAM) is included in the manual to calculate a critical total dissolved metal concentration from the free metal ion concentration (see Annex 9 and 12). Use of such a model was not needed and thus not mentioned in the guidance document, since critical limits already referred to total metal concentrations. These improvements are all in accordance with increased insight in the effects of heavy metals on soil organisms and plants.

Weathering

In the guidance document, the critical load of a metal was calculated from the sum of tolerable outputs from the considered soil layer by harvest and leaching minus the natural inputs by weathering release (De Vries & Bakker, 1998). In the manual, however, weathering inputs of metals are neglected due to (i) low relevance of such inputs and (ii) high uncertainties of respective calculation methods. It is, however, recommended to use estimates of weathering rate to identify sites with a high geogenic metal input, where natural weathering may already exceed the critical load. This should be considered, when critical limits and loads exceedances are to be interpreted. For methods to calculate weathering rates, see De Vries and Bakker (1998) and Hettelingh et al. (2002). More information on how sites with high geogenic contents of metals can be identified are described in Farret (2003). The most important information is summarised in Annex 6.

Stand-still approach versus calculation of critical limit exceedance

In the guidance document a stand-still approach, which aims at avoiding any (further) accumulation of heavy metals in the soil, was also included as an alternative to the effect-based approach. This method is, however, not included in the manual (UBA, 2004) since it implies the continued addition of metals on historically polluted soils with high leaching rates. The current leaching may then already imply significant effects, both on terrestrial as well as aquatic ecosystems receiving the drainage water from the surrounding soils, and is thus not per se acceptable in the long term. Furthermore, it does lead to critical load exceedance at soils which strongly adsorb heavy metals, whereas most effects occur through the soil solution.

Instead, it is suggested to calculate the critical soil content (from a given critical limit or a critical limit function for the soil solution) and compare this to the present soil metal content to assess the critical limit exceedance in the present situation. This implies that one has to map the present soil metal content in the country (expressed as total or reactive soil contents). Inversely, one may calculate the present total dissolved concentrations or even free ion concentrations from the present soil metal content, using transfer functions described later in this report and compare this to the critical limit function for the soil solution. Such a comparison can be seen as an intermediate step for dynamic models for heavy metals, as discussed before in Section 2.1 in view of Figure 1. If the present soil metal content exceeds the critical concentration (limit), the metal input has to be less than the critical load, whereas in the reverse case, the metal input can be larger than the critical load for a defined time period (target load). However, only keeping the critical load will not lead to exceedance of the critical limit in the long run and therefore target loads higher than critical loads are not accepted in the framework of the LRTAP Convention. More information on how to calculate the critical soil content is given in section 5.1.

As with terrestrial ecosystems, the stand-still principle, (no further increase of metal contents or concentration, respectively, in the catchment) is not advocated for aquatic systems. Instead one may compare the present concentrations and critical concentrations for metals in surface water to gain insight in the exceedance of critical metal concentrations at present.

3 Terrestrial ecosystems

3.1 Simple steady-state mass balance model and related input data

3.1.1 Steady-state mass balance model

The method to calculate critical loads of heavy metals is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a steady state situation. The assumption of a future steady state situation signifies that the concentration in the system does not change in time because the amount of heavy metal entering the system is equal to the amount that leaves the system. The time period before steady state is reached depends on how far the present situation is from equilibrium and the rate of change which is determined by the difference of the various input and output fluxes. If e.g. a metal sorbs very strongly to the soil, it may take a long time (up to hundreds of years), before a steady state is reached. This has to be kept in mind when comparing a present load with the critical load (De Vries & Bakker, 1998).

In order to keep the approach compatible with the simple mass balance approach used for nitrogen and acidity, the internal metal cycling within an ecosystem is ignored, such that calculations can be kept as simple as possible. In the first manual, the internal metal cycling within an ecosystem was included, but it was shown that the uncertainty in transfer functions and critical limits is much more important than the inclusion of this internal cycle (De Vries & Bakker, 1998). In consequence the critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching. As mentioned before in Section 2.2, the natural input by weathering release is neglected because weathering causes only a minor flux of metals, while uncertainties of such calculations are very high. The described approach implies that the critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate, according to:

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

where:

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

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

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

The notation has been related to the critical load equations for acidity and nutrient nitrogen: M stands for flux of a heavy metal and can be substituted by the chemical symbol of the individual metal (Cd, Pb, Hg) under consideration (see Annex 1). The critical metal leaching $M_{le(crit)}$ refers to the total vertical leaching rate, including dissolved free and complexed and particulate metal species in the drainage water. For a critical load, the critical metal leaching is based on a critical (toxic) metal concentration (free ion or total) metal concentration in soil drainage water. For simplification it can be assumed that the vertical flux of metals bound to suspended particulate matter is negligible.

In mass balance models for Hg, re-emission (volatilization) of deposited Hg occurs as an additional flux. This flux can, however, be ignored when calculating critical loads of Hg, because this re-emission is treated as part of the atmospheric net deposition in the modelling by EMEP MSC-E (Ryaboshapko et al., 1999; Ilyin et al., 2001). Therefore, in order to avoid double consideration in the calculation of critical load exceedances, re-emission should be excluded from the critical loads model. It might, however, be necessary to consider re-emission if other deposition data than those from EMEP are used for exceedance calculation.

Appropriate and consistent calculation critical loads for terrestrial ecosystems requires a consistent definition of the boundaries of the considered soil compartment. The depth can be variable. Relevant boundaries have been derived considering on one hand the expected probability of adverse impacts on the main target groups of organisms (plants, soil invertebrates, soil microbiota), or ground water quality, and on the other hand the occurrence and location of relevant metal fluxes within the soil profile:

- For **Pb** and **Cd** it is assumed that direct ecotoxicological effects as well as the main proportion of uptake by plants occur in (from) biological active humus rich (top)soil horizons (A_p, A_h, O). Therefore the depth (z_b) of these horizons should be considered for arable land, grassland, and forests as far as the critical load calculations are addressing ecotoxicological effects, or the protection of food/fodder quality, respectively. For forest soils covered by a humus layer, the critical loads for both the humus layer, and the upper mineral horizon should be calculated separately. In these cases the most sensitive of both layers should be presented in the critical loads map. For terrestrial ecosystems the maximum depth (z) to be considered is the lower boundary of the A-horizon.
- Regarding **Hg**, the critical receptor in terrestrial ecosystems is the organic topsoil (humus layer) of forest soils, where microbial processes are suspected to be affected. For calculating the critical load of Hg in forests, the topsoil is therefore defined as the humus layer, excluding underlying mineral soil layers.

Default values of z_b are:	forests:	0.1 m
	grassland:	0.1 - 0.2 m
	arable:	0.25 - 0.3 m

Note, that for calculations of critical loads with respect to protection of groundwater quality, the entire soil column has to be included. In a steady state calculation, the binding capacity of layers between rooting zone and the groundwater carrying layer does not need to be considered. Therefore, for simplification the critical leaching of metals from the view of ground water protection is calculated by multiplying the drainage water flux below the rooting zone (soil depth = z) with the critical limit for drinking water (see 3.2.2).

3.1.2 Heavy metal removal from the topsoil by net growth and harvest of plants

For critical load calculations, the removal of heavy metals refers to a future steady-state level where critical limits in the ecosystem compartments are reached (critical loads conditions). The calculation of a critical removal of metals on the basis of a critical limit for soil solution is hardly practicable, since for many metals there are no clear relationships between concentrations in soil solution (or even free metal ions) and the content of the metals in harvestable part of the plants. Reasons are amongst others the plant specific exclusion of metals from root uptake or accumulation in specific tissues (detoxification). Therefore a simplified approach is proposed here to describe the tolerable removal of heavy metals by biomass net uptake. An exception is the transfer of Cd from soil to wheat grains, in which a soil-plant transfer relationship is used to calculate critical loads related to food quality criteria (see Section 3.1.2)

The average yield (or growth increment) of harvestable biomass has to be multiplied with the heavy metal content in harvestable plant parts and with a factor to account for the metal uptake fraction from the soil layer considered relative to that from the total soil (Eq. 2):

$$M_u = f_{Mu,z} \cdot Y_{ha} \cdot [M]_{ha} \qquad (2)$$

where:

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

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

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

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

Data on yields for forests can in principle be obtained directly from the database of critical loads of acidity and nutrient nitrogen. Data on yields in agro-ecosystems are available from related statistics of the countries, the spatial pattern can be derived using information on land use as well as on soil quality and climate.

Data for the metal contents in harvestable biomass should be taken from relatively unpolluted areas. Median values (or averages) of metals contents in plants from such databases do in general not exceed quality criteria for food and fodder crops or phyto-toxic contents, respectively. Related fluxes can therefore be considered as tolerable. If appropriate national data are not available, default values as listed in Table 3 can be used.

Table 3 ranges of mean values (averages, medians) of contents of Pb, Cd, and Hg in biomass for various species (harvestable parts)

Land use	Species	Metal content in harvestable plant parts, $[M]_{ha}$ (mg.kg^{-1} dw)		
		Pb	Cd	Hg
Grassland	mixed grassland species	1.0 - 3.0	0.05 - 0.25	0.01-0.1
Arable land	wheat (grains)	0.1	0.08	0.01
	other cereals (grains)	0.1 - 0.3	0.02 - 0.06	0.01
	potato	0.73	0.23	0.02
	sugar beet	1	0.25	0.02
	maize	3.8	0.2	0.04
Coniferous forest	pine, fir, douglas, spruce			
	Central Europe	0.5- 10	0.1 - 0.5	0.01-0.05*
	Northern Europe	0.1 - 0.2**	0.02 - 0.04**	0.004-0.008**
Deciduous forest	oak, beech, birch, poplar	0.5 - 10	0.05 - 0.5	

**) Hg in spruce stems ≈ 10-20% of needle content (Schütze & Nagel, 1998)

***) Northern Sweden (Alriksson et al., 2002 and unpublished), for spruce stems without/with bark

other data sources: De Vries and Bakker (1998), Nagel et al. (2000), Jacobsen et al. (2002)

If critical loads related to quality criteria of food or fodder are to be calculated, these critical concentrations in the harvestable plant parts should be multiplied with the yields in order to calculate the tolerable output of metals by biomass harvest.

As a default approximation, a root uptake factor ($f_{Mu,z}$) of 1 can be used for all ecosystem types, assuming that most uptake of nutrients and pollutants occurs in the top soil. In forests values around 80 % have been reported for uptake from the humus layer alone (based on lead isotopes in Scots pine, Bindler et al., 2004). Thus, for calculations referring to the humus layer, $f_{Mu,z}$ may be 0.8, but, if the top of the underlying mineral soil is included in the calculations, $f_{Mu,z}$ is likely to approach 1, also in forests. If $f_{Mu,z}$ is 1, the uptake from the upper horizon is equal to that of the entire rooting depth. In this case there is no difference in the uptake calculation, whether it is done to calculate critical loads related to ecotoxicological effects or in view of ground water protection. Walther (1998) proposed a methodology to calculate the rooting depth, limiting it to the depth where 90 % of the root biomass is distributed. More detailed values of f_{Mu} may be used, if information is available.

When metal contents are available for different harvested parts of the plants, a weighted mean of both should be used. For example, if heavy metal concentrations of forest trees are an order of magnitude higher in the bark than within stems, metal concentrations in whole stems are about twice as high if including bark than without bark, since bark may account for about 10% of the stem dry mass.

Beware that only the net uptake is calculated. For instance, for agricultural land the amount of metals in stalks or the leaves of beets remaining on the field should not be considered. The removal of heavy metals in this case is the product of the yield of grains/beets and the mean contents in these parts of the plants. For forest ecosystems, only the net increment should be considered, but not the uptake into needles, leaves, etc., which also remain in the system.

In ecosystems with appreciable precipitation surplus the removal of metals by harvest may often be negligibly low compared to metal losses by leaching, in these cases the uptake calculation may not deserve high efforts for sophisticated calculations.

3.1.3 Critical leaching of heavy metals from the topsoil

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

$$M_{le(crit)} = c_{le} \cdot Q_{le} \cdot [M]_{tot,sdw(crit)} \qquad (3)$$

where:

$M_{le(crit)}$	= critical leaching flux of heavy metal M from the considered soil layer (see Eq. 1) ($g.ha^{-1}.yr^{-1}$)
Q_{le}	= flux of drainage water leaching from the considered soil layer ($m.yr^{-1}$)
$[M]_{tot,sdw(crit)}$	= critical total concentration of heavy metal in soil drainage water ($mg.m^{-3}$)
c_{lo}	= factor for appropriate conversion of flux units from $mg.m^{-2}.yr^{-1}$ to $ga.ha^{-1}.yr^{-1}$ ($10\ g\ mg^{-1}\ m^2\ ha^{-1}$).

In order to calculate critical loads in view of groundwater protection the data on precipitation surplus from the database on critical loads of acidity and nutrient nitrogen can be used. When critical loads with respect to ecotoxicological effects or to food/fodder quality are addressed, the proportion of transpiration removing water from the upper horizons (O and /or A_h, A_p) has to be accounted for by using a scaling factor $f_{Et,z}$. The drainage water flux leaching from the topsoil (with depth zb) at steady state can be calculated according to:

$$Q_{le,zb} = P - E_i - E_s - f_{Et,zb} \cdot E_t \qquad (4a)$$

where:

$Q_{le,zb}$	= flux of drainage water leaching from the topsoil z_b ($m.yr^{-1}$)
P	= Precipitation ($m.yr^{-1}$)
E_i	= Interception evaporation ($m.yr^{-1}$)
E_s	= Soil evaporation within the topsoil defined as above ($m.yr^{-1}$)
E_t	= Plant transpiration ($m.yr^{-1}$)
$f_{Et,zb}$	= Root uptake factor, fraction of water uptake within the topsoil (-)

This approach is based on the assumption that soil evaporation (E_s) only takes place at the soil surface (not further than the down to the depth z_b. Interception evaporation can be calculated as a function of the precipitation (De Vries, 1991). For the value of $f_{Et,zb}$ default values of 0.35 and 0.25 can be used for O horizons of coniferous and deciduous forest respectively. For a topsoil of 10 cm, default values of 0.65 and 0.50 can be used for soils with a rooting depth of 50-100cm. These data are based on a review of on the distribution of fine roots, mainly responsible for the

uptake of water as presented in De Vries (1991). This review shows that these roots mainly occur in the topsoil (humus layer and top 20 cm of soil).
For sites without detailed water balance data, the annual mean water percolation $Q_{le,zb}$ can also be determined by the long-term mean annual temperature (mainly determining the potential evapotranspiration, E_{pot}) and precipitation (mainly influencing the actual evapotranspiration, E_{act}) according to:

$$Q_{le,zb} = P_m - f_{E,zb} \cdot (P_m^{-2} + (e^{(0.063 \cdot T_m)} \cdot E_{m,pot})^{-2})^{-1/2} \qquad (4b)$$

where:

P_m	= Annual mean precipitation ($m.yr^{-1}$)
T_m	= Annual mean air temperature (°C)
$E_{m,pot}$	= Annual mean potential evapotranspiration in humid areas at T_m = 0°C.
$f_{E,zb}$	= Fraction of total annual mean evapotranspiration above z_b (-)

The value of $E_{m,pot} \approx 0.35$ $m.yr^{-1}$ in forests, possibly less in other terrestrial ecosystems. The value of $f_{E,zb} \approx 0.8$ for the organic top soil layer of forests. For forested areas, this relationship is supported by data not only on river runoff but also on soil percolation (e.g. based on Michalzik et al., 2001), which together suggest that about 80% or more of the total evapotranspiration takes place above or within the organic top soil layer. Thus, the mean water flux from the organic top layer (Q_{le}) can easily be estimated from annual means of precipitation (P) and air temperature (T), which are two traditional climate normals available in traditional climate maps.

In European forest regions, $Q_{le,zb}$ is typically 0.1-0.6 $m.yr^{-1}$, but may reach >2 $m.yr^{-1}$ in coastal mountain regions. The standard parameter uncertainty is approximately ±0.1 $m.yr^{-1}$ (i.e. about ±30%) at the landscape scale. Depending on climate, Q_{le} can account for 10 to 90% of P in temperate-boreal forests, but is usually close to half. In very dry regions the percentage of Q_{le} in P can become very low. With Eq. (4b), Q_{le} almost never drops below 0.1 $m.yr^{-1}$ in Europe (considering EMEP-50 km grid square means). For Eq. (4a), a suggested minimum value is 5 % of the precipitation. This seems a reasonable lower value since there are always periods during the year with downward percolation and a situation of no leaching hardly (or never) occurs on a yearly basis. The use of monthly water balances is not advocated as the effect of all seasonal variations is not included in the critical limits, since these represent annual or long-term means, in line with the critical load approach for acidity.

Critical total concentrations of heavy metals in soil drainage water

The critical total metal concentrations related to ecotoxicological effects in soils require some specific considerations. These critical dissolved metal concentrations in soil drainage water are determined as the sum of the critical concentration of the free metal ion M^{2+}, $[M]_{free\ (crit)}$, and the metals bound to inorganic complexes such as MOH^+, HCO_3^+, MCl^+, $[M]_{DIC}$, and to dissolved organic matter, $[M]_{DOM}$, according to:

$$[M]_{dis,sdw(crit)} = [M]_{free,sdw\,(crit)} + [M]_{DIC,sdw} + [M]_{DOM,sdw} \cdot [DOM]_{sdw} \qquad (5)$$

where:

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

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

$[M]_{DIC,sdw}$ = concentration of metal bound to inorganic species ($mg.m^{-3}$)

$[M]_{DOM,\ sdw}$ = concentration of metal bound to dissolved organic matter ($mg.kg^{-1}$)

$[DOM]_{sdw}$ = concentration of dissolved organic matter in soil drainage water ($kg.m^{-3}$)

The last part of Eq. (5) could also be written as the product of $[M]_{DOC} \cdot [DOC]_{ss}$, where:

$[M]_{DOC,sdw}$ = concentration of metal bound to dissolved organic carbon ($mg.kg^{-1}$)

$[DOC]_{sdw}$ = concentration of dissolved organic carbon in soil drainage water ($kg.m^{-3}$)

Geochemical equilibrium partitioning of the heavy metal between the different fractions is assumed. Furthermore, the water draining from the soil also contains metals bound to suspended particulate matter, $[M]_{SPM}$, according to:

$$[M]_{tot,sdw(crit)} = [M]_{dis,sdw\,(crit)} + [M]_{SPM} \cdot [SPM]_{sdw} \tag{6}$$

where:

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

$[M]_{SPM,sdw}$ = concentration of metal in suspended particulate matter ($mg.kg^{-1}$)

$[SPM]_{sdw}$ = concentration of suspended particulate matter in soil drainage water ($kg.m^{-3}$)

In the calculations, we suggest the latter fraction to be neglected to get comparable values of critical total concentrations for the different effects pathways (see Section 3.2.3). In the manual, the values used for $[M]_{tot,sdw(crit)}$ are thus all related to the critical dissolved metal concentrations,$[M]_{dis,sdw(crit)}$, implicitly assuming that the concentration of metals bound to suspended particulate matter is negligible ($[M]_{SPM,sdw} = 0$). In look-up tables critical total concentrations, $[M]_{tot,sdw(crit)}$ with SPM = 50 $mg.l^{-1}$ are also provided for ecotoxicological effects to enable the evaluation of the influence of this parameter.

The derivation of critical dissolved concentrations of the heavy metals Cd, Pb and Hg in soil drainage water, $[M]_{dis,sdw(crit)}$, based on either the critical limits for metal contents in plants (Cd, Pb), metal concentrations in ground water (Cd, Pb), free metal ion concentrations in soil solution (Cd, Pb) or critical metal contents in the soil organic matter (Hg) to be applied in Eq. 3, is explained in the next section (3.2).

3.2 Critical dissolved concentrations of Cd, Pb and Hg in terrestrial ecosystems

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

- Metal contents in plants (Cd, Pb, Hg) in view of human health or animal health effects through intake of plant products (Section 3.2.1).
- Metal concentrations in ground water (Cd, Pb, Hg) in view of human health effects through intake of drinking water (Section 3.2.2).
- Concentrations of free metal ions in soil solution (Cd, Pb) in view of ecotoxicological effects on soil micro-organisms, plants and invertebrates (Section 3.2.3).
- Metal contents in the soil (Hg) in view of ecotoxicological effects on soil micro-organisms and invertebrates in the forest humus layer (Section 3.2.4).

Specific attention is given to the derivation of the critical total concentration of the heavy metals Cd and Pb in soil drainage water, $[Cd]_{sdw(crit)}$ and $[Pb]_{sdw(crit)}$, from critical limits for free Cd and Pb ion concentrations in soil solution (section 3.2.3). In most cases this is the most sensitive critical limit for these metals, thus determining the critical Cd and Pb load (an exception can be the critical limit for Cd in wheat leading sometimes to lower critical dissolved Cd concentrations in soil solution than the ecotoxicological approach; see Section 3.2.1 and 3.2.3). Background information on the approaches for this derivation is given in the Annexes 7-9. Annex 7 provides information on the transfer functions used to calculate the heavy metal concentration in soil solution from reactive metal contents in the soil. Annex 8 describes how this information is used, in combination with NOEC data on reactive metal contents in the soil, to derive a critical free metal ion concentration in soil drainage water. Annex 9, finally, describes how this free metal ion concentration can be transferred to a total dissolved metal concentration in soil drainage water, using a special version of the chemical speciation model WHAM.

3.2.1 Critical dissolved metal concentrations in view of critical metal contents in plants

In order to derive critical dissolved Cd, Pb and Hg concentrations in soil drainage water related to human health effects, on the basis of critical limits for plant metal contents (food quality criteria) for food crops on arable land, De Vries et al. (2003) provided an overview on selected soil-plant relationships of Cd, Pb and Hg. It shows that only for Cd significant relationships (R^2 of ≥ 0.5) are available. For Pb and Hg, there is the possibility to derive directly critical loads (Pb) or levels (Hg) from critical limits for plant metal contents.

Cadmium

Wheat is a crop that is widely cultivated over Europe and has a relevant share in the total human food intake. Further there is a relatively large uptake of Cd into wheat grains, and sufficient good soil plant relationships ($R^2>0.7$, De Vries et al. 2004b), compared to other edible parts of agricultural crops, are available. Cd in wheat is therefore an appropriate indicator of human health effects of Cd on arable land. Phytotoxic concentrations of Pb and Cd in food crops were in all cases much higher than limits related to human health, thus there is no need to investigate critical loads of heavy metals related to phytotoxic effects.

Starting with a critical Cd content in plant one may derive a critical dissolved metal concentration by a plant -soil solution relationship. Such a relationship was derived by applying a regression of Cd contents in wheat in the Netherlands to calculated soil solution concentrations, that were derived by using measured total soil contents and soil properties and application of a transfer function, relating total concentrations in solution to the soil metal content (Römkens et al., 2004). By applying such a function, regression relationships were derived for Cd in plant (wheat grains) as a function of Cd in soil solution and vice versa as described in Table 4. The best estimate of a critical Cd concentration might be the mean of both estimates (from plant to soil solution and from soil solution to plant).

The EU regulation (EG) No.466/2001 uses a limit for Cd of 0.2 mg.kg^{-1} fresh weight in wheat grains. This limit was derived with the principle "**A**s **L**ow **A**s **R**easonably **A**chievable" (ALARA) and is therefore not based on effects (see Annex 4). There are however many indications that from the viewpoint of protection of human health, the critical limit of 0,1 mg.kg^{-1} fresh weight, which was used in the EU before 2001, is more appropriate (for these arguments see De Vries et al., 2003 and Annex 4). Table 4 provides the parameters for the transfer functions as well as results based on the critical limit of 0.1 mg.kg^{-1} fresh weight (results for the EU limit of 0.2 mg.kg^{-1} fresh weight are given in brackets). If the mean of both results of transfer function application is used, the resulting critical total concentration is approximately 0.8 mg.m^{-3} (or 4 mg.m^{-3}). The most conservative estimate equals approximately 0.6 mg.m^{-3} (or 1.75 mg.m^{-3}).

Table 4 Values for the intercept (int) and the parameter a in the regression relationships relating Cd in plant (wheat grains) as a function of Cd in soil solution and vice versa. The table also gives the percentage variation explained (R^2), the standard error of the result (se) and the resulting critical total dissolved Cd concentration when applying a critical Cd content in wheat of 0.1 mg.kg^{-1} fresh weight (0.12 mg.kg^{-1} dry weight) and in brackets the value when applying the limit of 0.2 mg.kg^{-1} fresh weight (EC, 2001)

Relationship	Intercept	a	R^2	se	log $[Cd]_{ss(crit)}$ (mmol.l^{-1})	$[Cd]_{ss(crit)}$ (mg.m^{-3})
Cd_{Plant} - $Cd_{solution}$[1]	1.05	0.39	0.62	0.25	-5.03 (-4.26)	1.05 (6.16)
$Cd_{solution}$ - Cd_{plant}[2]	-3.82	1.57	0.62	0.50	-5.28 (-4.81)	0.59 (1.75)

[1] log(Cd plant) = Int + a*log(Cd soil solution)

[2] log(Cd soil solution) = Int + a*log(Cd plant)

A more sophisticated and consistent way would be to:

- first derive a critical "pseudo" total soil metal content, by applying soil -plant relationships in the inverse way (derive a critical total soil content from a critical plant content).
- then apply a transfer function relating "pseudo" total metal contents to reactive metal contents (Annex 7, Equation A7.2a).

- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 7, Equation A7.3).
- followed by a calculation of total concentrations from free metal ion activities with a chemical speciation model (i.e. the W6S-MTC2 model).

Please note that the current version of W6S-MTC2 is designed to calculate $[M]_{sdw,crit}$ based on the critical limit functions related to ecotoxicological effects and not to food quality.

Lead and mercury
For Pb and Hg in food crops, back calculation to soil content is not possible, because there are no relationships between the contents in soil and in plants for those metals. For Pb and Hg, direct uptake from atmosphere to plant has to be considered. Assuming that for Pb, direct uptake is specifically relevant for vegetables, critical loads can be derived using direct relationships between the Pb deposition and Pb content of vegetables. Assuming that uptake of Hg is completely due to direct uptake from atmosphere, critical concentrations of Hg in air can be derived from critical limits of Hg in vegetation. Methods for such calculations, based on data from De Temmerman & de Witte (2003a; 2003b), summarized in De Vries et al. (2003), are provided in Annex 5.

3.2.2 Critical limits of Cd, Pb and Hg aiming at ground water protection

The critical total Cd, Pb and Hg concentration in soil solution related to human health effects can also be based on quality criteria (critical limits) for drinking water (WHO, 2004) for all terrestrial ecosystems (see Table 1). In line with the decisions of the Expert Meeting on Critical Limits (2002, in Berlin) the protection of ground water for potential use as drinking water resource should also be addressed in critical load calculations. The Technical Guidance Document for Risk Assessment (http://ecb.jrc.it) suggests in chapter 3.1.3 that in the first instance the concentration in soil pore water can be used as an estimate of the concentration in ground water. The WHO guideline includes the following quality criteria for Cd, Pb and Hg in view of drinking water quality:

Pb: 10 $mg.m^{-3}$
Cd: 3 $mg.m^{-3}$
Hg: 1 $mg.m^{-3}$

These values can directly be included as $[M]_{dis,sdw(crit)}$ in the critical load calculation.

3.2.3 Critical dissolved concentrations of Cd and Pb related to ecotoxicological effects

Critical limits related to the ecotoxicological effects of Cd and Pb are related to impacts on soil micro-organisms, plants and invertebrates for both agricultural land (arable land, grassland) and non-agricultural land (forests, natural non-forested ecosystems; see Table 1). The critical concentrations used in the manual are based on the following approach:

- Use of ecotoxicological data (NOEC and LOEC data) for the soil metal content using experiments with information on soil properties (clay and organic matter content and soil pH) as well;
- Calculation of critical free metal ion concentrations (critical limits) in soil solution on the basis of the ecotoxicological soil data (NOECs and LOECs) and soil properties, using transfer functions relating the reactive soil metal content to the free metal ion concentration;
- Calculation of the critical dissolved metal concentrations in soil $M_{dis,sdw(crit)}$ from critical limits for free metal ion concentrations using a chemical speciation model.

Calculation of critical free metal ion concentrations from critical soil reactive metal contents

Soil toxicity data collated and accepted under the terms of current EU Risk Assessment procedures (Draft Risk Assessment Report Cd (July 2003) see http://ecb.jrc.it, Voluntary Risk Assessment for Pb, were used. The data covered chronic population-level effects on plants, soil-dwelling invertebrates and microbial processes. The toxicity endpoints were quoted mainly in terms of an added metal dose. In using added doses, the assumption is made that the added metal is entirely in reactive forms over the course of the toxicity experiment.

The transfer functions for the calculation of free metal ion concentration from reactive soil metal content, used in the derivation of free ion critical limit functions, are given in Annex 7. Soil properties needed in this function are organic matter and soil solution pH. In the derivation, soil pH values measured by chemical extraction (by H_2O, KCl or $CaCl_2$) were used to estimate soil solution pH (pH_{ss}) by application of regressions given in Annex 10. EU Risk Assessment procedures do not require the organic matter content of the soil to be specified for data to be accepted. However, such data were not usable for the calculation of critical free metal ion concentrations from critical soil metal contents, since the transfer functions used do require organic matter contents (see Annex 7), and NOEC measurements without these data were thus removed from the databases.

The bioavailability of metals does not only depend on the free metal ion concentration but also on the concentration of other cations, such as H^+, Na^+, Ca^{2+}. This was taken into account in deriving critical limits as a function of the pH in soil solution (pH_{ss}). The derived critical limit functions were:

$$\log[Cd]_{free,sdw(crit)} = -0.32 \cdot pH_{sdw} - 6.34 \qquad (7)$$
$$\log[Pb]_{free,sdw(crit)} = -0.91 \cdot pH_{sdw} - 3.80 \qquad (8)$$

where

$[M]_{free,sdw(crit)}$ = critical free metal ion (Cd/Pb)concentration in soil solution ($mg.m^{-3}$)

More information on the approach and the toxicity data is given in Lofts et al. (2004)and in De Vries et al. (2004a). A summary can be found in Annex 8.

Calculation of total dissolved metal concentrations from free metal ion concentrations

To calculate critical loads for soils from the critical limit functions, it is necessary to know the total concentration of metal in soil drainage water that corresponds to the free ion critical limit. The metal in soil drainage water comprises the following metal species (Annex 9):

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

Here, DOM is dissolved organic matter, and SPM is suspended particulate matter. The total concentration of metal in soil drainage water does not refer simply to dissolved components ($[M]_{free}$, $[M]_{DIC}$, and $[M]_{DOM}$), but also includes $[M]_{SPM}$. Data on SPM concentration in soil drainage waters may be scarce, and in many cases the contribution of SPM to the metal leaching is only small. Thus this flux can be neglected preliminarily. The calculation model includes, however, the possibility of metal being leached from the soil in association with particulates.

Given the activity or concentration of M^{2+}, the concentrations of the other metal species can be estimated by applying an equilibrium speciation model. The calculation has to take into account the dependence of the metal speciation on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe. For this purpose a custom version of the Windermere Humic Aqueous Model version 6 (WHAM6, Tipping, 1998) speciation model, termed W6S-MTC2, has been produced. A detailed description of the model calculation steps is given in Annex 9. Results thus obtained with an assumed standard CO_2 pressure of 15 times the atmospheric pressure of 0.3 mbar (4.5 mbar) are given in Table 5 and Table 6. Annex 9 provides analogous tables for a wider range of 3 and 30 times the atmospheric CO_2 pressure.

WHAM includes also the fraction of suspended particulate matter, which strictly is not part of the soil solution. The total concentration is therefore related to soil drainage water. When $[SPM]_{ss}= 0$, the value of $[Cd]_{tot,sdw(crit)}$ equals that of $[Cd]_{dis,sdw(crit)}$ (see Eq. 6). For reasons of consistency with the other approaches (see before), in which the critical value refers to $[M]_{dis,sdw(crit)}$, it is advocated to apply the results with $[SPM]_{ss}= 0$. Furthermore, there are high uncertainties in the data on SPM in soil solution. Table 5 furthermore shows that in most cases, the impact of suspended particulate matter on the total Cd concentration in soil drainage water (even at a concentration of 50 $mg.l^{-1}$) is small, but for Pb it can be large (Table 6).

NFCs may calculate critical dissolved metal concentrations from the free ion concentration by one of three methods:

- Linear interpolation in the look-up tables given in Table 5 and Table 6 and in more detail in Annex 9. The look-up tables list critical dissolved metal concentrations (calculated using W6S-MTC2) for various combinations of pH, concentrations of soil organic matter, dissolved organic carbon ($[DOC]_{ss}$) and suspended particulate matter (SPM) and partial CO_2 pressure (pCO_2).

- Sending suitably formatted files to Ed Tipping (ET@CEH.AC.UK), who will perform the computations with W6S-MTC2. Instructions for preparing suitably formatted files for this purpose are given in Annex 9.
- Using the W6S-MTC2 program themselves. Instructions for use are given with the program.

Table 5 Look-up table to derive values of the total critical Cd concentrations in soil drainage water $[Cd]_{SDW(crit)}$ at a CO_2 pressure that equals 15 times the CO_2 pressure of the air

			$[Cd]_{tot,\ sdw(crit)}$ ($mg.m^{-3}$), being $[Cd]_{dis,sdw(crit)}$ ($mg.m^{-3}$) at SPM=0									
OM %dw	SPM $mg.l^{-1}$	DOC $mg.l^{-1}$	pH 3.5	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
10	0	0	4.04	2.79	1.92	1.34	0.94	0.68	0.51	0.43	0.47	0.75
10	0	5	4.04	2.80	1.93	1.38	1.04	1.08	0.91	0.66	0.61	0.80
10	0	15	4.04	2.81	1.97	1.47	1.23	1.83	1.68	1.13	0.88	0.91
10	0	50	4.05	2.86	2.12	1.80	1.89	4.08	4.03	2.74	1.85	1.30
10	0	100	4.07	2.94	2.36	2.29	2.80	6.76	6.86	4.94	3.22	1.85
10	50	0	4.06	2.82	1.95	1.38	1.00	0.76	0.61	0.57	0.67	1.02
10	50	5	4.06	2.82	1.96	1.42	1.10	1.16	1.02	0.81	0.80	1.07
10	50	15	4.06	2.84	2.00	1.51	1.29	1.91	1.79	1.28	1.08	1.18
10	50	50	4.07	2.89	2.15	1.85	1.94	4.15	4.14	2.88	2.05	1.57
10	50	100	4.08	2.96	2.39	2.33	2.85	6.84	6.97	5.08	3.42	2.12
50	0	0	3.98	2.74	1.91	1.34	0.94	0.68	0.51	0.43	0.47	0.75
50	0	5	4.02	2.81	2.02	1.52	1.26	1.09	0.91	0.66	0.61	0.80
50	0	15	4.11	2.94	2.24	1.89	1.85	1.86	1.68	1.13	0.88	0.91
50	0	50	4.45	3.48	3.01	3.06	3.69	4.16	4.03	2.74	1.85	1.30
50	0	100	5.06	4.29	4.07	4.59	5.96	6.89	6.86	4.94	3.22	1.85
50	50	0	4.03	2.81	2.00	1.45	1.11	0.90	0.81	0.84	1.03	1.51
50	50	5	4.07	2.87	2.10	1.64	1.42	1.31	1.21	1.08	1.17	1.57
50	50	15	4.16	3.00	2.32	2.01	2.01	2.08	1.98	1.54	1.44	1.68
50	50	50	4.50	3.54	3.09	3.18	3.85	4.38	4.33	3.15	2.41	2.06
50	50	100	5.11	4.35	4.16	4.71	6.12	7.11	7.16	5.35	3.78	2.61

Please note that it is necessary to recalculate values of soil pH (measured in KCl, $CaCl_2$, H_2O) to soil solution pH (Annex 10, section "Relationships between various pH estimates"), before applying the look-up tables or creating input files for W6S-MTC2.

Use of pH and DOC values to be considered in the calculation of critical metal concentrations

Some parameters in the critical load calculation depend on the status of the soil, in particular the acidification status (pH) and the concentration of DOC (see also the tables above). In the following recommendations are provided, which status of soil conditions (pH and DOC) should be considered, when deriving $M_{ss(crit)}$ from critical limits for free metal ion concentrations.

pH values: In principle the pH at steady state conditions assuming Gothenburg Protocol implementation, can best be taken as a basis. This may cause problems, as it has to be determined using dynamic models. Instead the pH at the critical acid load can be used. This pH is easier to calculate but it may strongly deviate from the pH at steady state assuming Gothenburg Protocol implementation. Furthermore, the calculation of the critical load pH is rather uncertain depending on arbitrary choices to be made. Therefore the use of the critical load pH is not recommended.

Table 6 Look-up table to derive values of the total critical Pb concentrations in soil drainage water $[Pb]_{SDW(crit)}$ at a CO_2 pressure that equals 15 times the CO_2 pressure of the air

			$[Pb]_{tot,sdw(crit)}$ ($mg.m^{-3}$), being $[Pb]_{dis,sdw(crit)}$ ($mg.m^{-3}$) at SPM=0									
OM	SPM	DOC	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
%dw	$mg.l^{-1}$	$mg.l^{-1}$	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
10	0	0	34.72	11.41	3.83	1.32	0.46	0.17	0.08	0.09	0.23	0.72
10	0	5	34.80	11.55	4.02	1.57	0.77	0.86	1.12	1.29	1.36	1.64
10	0	15	34.96	11.83	4.42	2.09	1.38	2.18	3.16	3.67	3.61	3.47
10	0	50	35.52	12.82	5.83	3.92	3.42	6.25	10.04	11.87	11.47	9.89
10	0	100	36.33	14.25	7.92	6.51	6.21	11.39	19.36	23.30	22.68	19.07
10	50	0	37.33	14.50	7.43	5.53	5.41	5.98	6.88	8.08	9.60	11.71
10	50	5	37.41	14.64	7.62	5.79	5.72	6.66	7.92	9.27	10.73	12.63
10	50	15	37.57	14.92	8.02	6.31	6.33	7.98	9.97	11.66	12.98	14.46
10	50	50	38.13	15.91	9.43	8.14	8.37	12.05	16.84	19.86	20.84	20.89
10	50	100	38.94	17.34	11.52	10.74	11.16	17.19	26.17	31.29	32.05	30.06
50	0	0	32.85	11.08	3.80	1.31	0.46	0.17	0.08	0.09	0.23	0.72
50	0	5	34.36	12.59	5.32	2.74	1.63	0.89	1.12	1.29	1.36	1.64
50	0	15	37.41	15.65	8.37	5.51	3.80	2.25	3.16	3.67	3.61	3.47
50	0	50	48.44	26.65	18.69	14.44	10.52	6.45	10.04	11.87	11.47	9.89
50	0	100	65.13	42.22	32.86	26.13	18.94	11.76	19.36	23.30	22.68	19.07
50	50	0	39.22	18.51	12.51	11.53	12.45	14.27	16.57	19.45	22.94	27.36
50	50	5	40.73	20.03	14.03	12.96	13.63	14.95	17.61	20.64	24.06	28.27
50	50	15	43.78	23.08	17.07	15.74	15.78	16.30	19.66	23.03	26.31	30.11
50	50	50	54.80	34.07	27.42	24.65	22.51	20.51	26.54	31.24	34.18	36.53
50	50	100	71.49	49.66	41.61	36.34	30.92	25.82	35.86	42.66	45.38	45.70

Assuming that it is likely that present pH is (almost) equal to future pH at steady state (under Gothenburg Protocol implementation conditions), the present pH is advised to use for pragmatic reasons. Because the present pH in soil solution is not always available, but rather measured as pH in water or in salt extracts, regression functions to relate several pH measurements to soil solution pH were derived. Relations are given in Table 7, assuming no effect of soil type on the relationship. These relations can be used to calculate the soil solution pH which is needed in the critical load calculations and also in the transfer functions relating reactive metal contents to free metal ion concentrations.

More detailed information is given in Annex 10. This includes relationships as a function of soil type. Ranges in the present and steady-state critical soil pH for various combinations of land use, soil type and soil depth are also provided there.

Table 7 Results of linear regression analyses of pH in soil solution against pH-H_2O, pH-$CaCl_2$ and pH-KCl

Explaining variable	N	Slope (α)[1)]	Intercept (β)[1)]	se $_{Yest}$	R_2adj
pH-H_20	1145	1.0462	-0.2847	0.453	0.84
pH-KCl	905	0.9692	0.6233	0.491	0.80
pH-$CaCl_2$	413	0.8834	1.317	0.741	0.49

1) All coefficients are significant at $p > 0,999$

DOC concentrations: The concentration of dissolved organic matter (DOM) in soils is nowadays frequently determined in climate-related studies. Concentrations of DOM are usually determined by analysis of carbon (DOC) which accounts for half of the weight of soil organic matter (DOM ≈ 2. DOC). However, long-term data on soil solutions are rarely available at sufficient density for mapping region-specific means and variability, and may need to be estimated from studies elsewhere. DOC values for major forest types and soil layers (5-, 50- and 95 percentiles) are presented in Annex 11 on the basis of measurements at approximately 120 Intensive Monitoring plots in Europe. In general, the results show a clear decrease in DOC concentrations with increasing soil depth, in particular from the humus layer (median value of 40 $mg.l^{-1}$) into the mineral subsoil. Furthermore, the values are slightly higher in coniferous forest compared to deciduous forests.

Relationships of DOC concentrations with vegetation type, hydrology, growth conditions or soil properties may be expected, which would be useful to improve estimates for different sites and regions. The data for the mineral soil (Annex 11) were thus used to derive relationships with available site characteristics and soil data that may affect the DOC concentrations, including the type of forest, (coniferous or deciduous forests), texture class (indication for soil type), temperature, pH and the contents of C and N, including the C/N ratio. Results thus obtained are given in Annex 11. The results show a good relationship with the site and soil characteristics in the subsoil (below 30cm) but the relationships were much worse in the topsoil (above 30cm). In the topsoil there was a clear positive relationship with C/N ratio and temperature, while the correlated values of the individual C and N concentrations were negatively and positively related to DOC, respectively. The relationships are, however, too weak to be very useful. This is in line with the limited number of studies in the literature, from which no significant relationship could be discerned (Michalzik et al., 2001).

Based on the available data the following default values for calculating critical loads of Pb and Cd, or critical levels of atmospheric Hg pollution, respectively, are suggested (see also Annex 11):

Forest organic layer (O horizon):	$[DOC]_{ss} = 35$ $mg.l^{-1}$ ($[DOM]_{ss} = 70$ $mg.l^{-1}$).
Forest mineral topsoil (0-10 cm):	$[DOC]_{ss} = 20$ $mg.l^{-1}$ ($[DOM]_{ss} = 40$ $mg.l^{-1}$).
Grass land (0-10) cm:	$[DOC]_{ss} = 15$ $mg.l^{-1}$ ($[DOM]_{ss} = 30$ $mg.l^{-1}$).
Arable land (0-30) cm:	$[DOC]_{ss} = 10$ $mg.l^{-1}$ ($[DOM]_{ss} = 20$ $mg.l^{-1}$).

3.2.4 Critical limits of Hg related to ecotoxicological effects in soils

Critical limit for the soil: With respect to Hg, critical limits refer only to effects on soil micro-organisms and invertebrates in the humus layer of forests. The suggested critical limit for Hg is that the concentration in the humus layer (O-horizon) of forest soils after normalization with respect to the organic matter content should not exceed 0.5 mg.(kg org)$^{-1}$ (Meili et al., 2003b). Because of the strong association of Hg with organic matter leaving virtually no free ions, the exposure of biota to Hg is controlled by the competition between biotic and other organic ligands, and the contamination of all types of organic matter is determined by the supply of organic matter relative to the supply of Hg at a given site (Meili, 1991 cf. biodilution; 1997). Therefore, the critical limit for Hg in soils is set for the organically bound Hg rather than for the free ion concentration, also in solution.

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

Transfer function for mercury: The critical leaching of Hg from the humus layer ($M_{le(crit)}$ in Eq. 1) is related to the mobility and Hg content of dissolved organic matter because of the strong affinity of Hg for living and dead organic matter and the resulting lack of competition by inorganic ligands in this layer (e.g. Meili, 1991, 1997). Because of the strong association of Hg with organic matter leaving virtually no free ions (apparently far less than one per km^2 of topsoil, based on Skyllberg et al. 2003), the biogeochemical turnover of Hg is controlled by the competition between biotic and other organic ligands. Therefore, Hg/OM ratios are a useful tool for calculating critical limits and loads and associated transfer functions (Meili et al., 2003b). This is the basis of the transfer function to derive total Hg concentrations in percolating (top) soil solution ($[M]_{dis,sdw(crit)}$ in Eq. 3, mg.m^{-3}) as follows:

$$[Hg]_{dis,sdw\ (crit)} = [Hg]_{[OM](crit)} \cdot f_f \cdot [DOM]_{dis,sdw} \cdot c_{sdw} \tag{9}$$

where

$[Hg]_{dis,sdw\ (crit)}$ = critical dissolved Hg concentration in soil drainage water (mg.m^{-3})

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

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

$[DOM]_{sdw}$ = concentration dissolved organic matter in soil drainage water (g.m^{-3}),

c_{sdw} = 10^{-3} kg.g^{-1}, factor for appropriate conversion of mass units.

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

Critical concentration for the soil solution: Based on the Hg limit of 0.5 mg.kg^{-1} OM and a DOM concentration of 70 mg.l^{-1} (DOC = 35 mg.l^{-1}), the critical steady state concentration of total Hg in soil solution is 35 ng.l^{-1} or 0.035 µg.l^{-1} (see Eq. 9). This concentration is consistent with that derived by a different approach at the watershed scale (Meili et al., 2003b) and is similar to high-end values presently observed in soil solutions and surface freshwaters (Meili, 1997; Meili et al., 2003a; Åkerblom et al., 2004). Note that this ecosystem limit for soil water is much lower than the drinking water limit above, but still higher than that for surface freshwaters where Hg limits for fish consumption usually are exceeded at surface water concentrations of 1-5 ng.l^{-1}.

4 Aquatic ecosystems

4.1 Critical Loads of lead and cadmium

4.1.1 Simple steady-state mass balance model and related input data

In principle, the simple steady-state mass balance approach can be used for Cd, Pb and Hg but it has been decided to restrict the approach in first instance to Cd and Pb and use a different, concentration based approach for Hg, as described in Section 4.2.

Steady-state mass balance model for lakes and stream waters
As with terrestrial ecosystems, the critical load of Cd and Pb for freshwaters is the acceptable total load of anthropogenic heavy metal inputs corresponding to the sum of tolerable outputs from the catchment by harvest and outflow, minus the natural inputs by weathering release in the catchment but adding the retention in the surface water (De Vries et al., 1998), the latter in particular for lakes. There is no need to consider net release in catchment soils, if the net weathering (weathering minus occlusion) is negligible. Since the estimation of net weathering in soils includes high uncertainties, it is preliminarily assumed to be negligible.

In the initial manual on the calculation of critical loads of heavy metals for aquatic ecosystems (De Vries et al., 1998), the default method presented to calculate critical loads of heavy metals for soils included in-lake metal retention, including all relevant metal fluxes, namely sedimentation, resuspension and exchange processes in the lake (infiltration, diffusion and bioirrigation), while assuming a steady state situation (De Vries et al., 1998). To keep the approach as simple as possible, and also to stay as close as possible to the simple mass balance approach for nitrogen and acidity, this model can be simplified by lumping transient exchange processes at the sediment-water interface and the net effect of sedimentation and resuspension in one retention term according to (see De Vries et al., 1998):

$$CL(M) = M_u + M_{ret(crit)} \cdot A_l / A_c + M_{lo(crit)} \qquad (10)$$

where:

M_u = removal of heavy metal by biomass harvesting or net uptake in forest ecosystems, respectively, in the catchment ($g.ha^{-1}.yr^{-1}$)

$M_{ret(crit)}$ = net retention of heavy metal in the lake at critical load ($g.ha^{-1}.yr^{-1}$)

$M_{lo(crit)}$ = critical lateral metal outflow from the whole catchment ($g.ha^{-1}.yr^{-1}$)

A_l = lake area (ha)

A_c = catchment area (ha)

As with terrestrial ecosystems the contribution of weathering to the potential available pool of a metal in the soil is also neglected here due to high uncertainties of such calculations, although the contribution might be considerable if the entire soil column (from top to the ground water level) is taken into consideration (for possible methods see Annex 6).

When critical loads of Pb and Cd for stream waters are calculated, there is no need to consider net retention, leading to the following critical load calculation:

$$CL(M) = M_u + M_{lo(crit)} \tag{11}$$

Because the estimation of net retention for lakes includes high uncertainties, it is recommendable to calculate preliminarily aquatic critical loads for stream waters only, for which the retention in surface water is term is negligible. It furthermore leads to the lowest critical loads and thus implies the protection of lakes as well. Finally, when calculating critical loads for lakes, one may also assume that net retention of metals in lakes is negligible, implying the assumption that the overall release or retention of metals in a catchment, including the lake sediment, is negligible.

Heavy metal removal by net uptake

The assessment of these data is comparable for those in forest ecosystems (see Eq. 2), but now the uptake or release refers to the complete catchment. This implies that no further reduction factors need to be applied to relate the uptake in the root zone/catchment to the mineral topsoil. The equation for net uptake is thus equal to Eq. (2) with f_{Mu} being equal to 1.

Critical output of heavy metals from the aquatic system

The critical lateral outflow can be described as the product of the lateral outflow flux of water and the critical total concentration of the heavy metal in the surface water according:

$$M_{lo(crit)} = c_{lo} \cdot Q_{lo} \cdot [M]_{tot,sw(crit)} \tag{12}$$

where:

Q_{lo} = lateral outflow flux of water from the catchment of the aquatic system (m.yr^{-1})

$[M]_{tot,sw(crit)}$ = critical total concentration (dissolved and in suspended particles) of heavy metal in surface water (mg.m^{-3})

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

The lateral outflow flux of water, Q_{lo}, sometimes denoted as the hydraulic load in the literature, can be derived from the flow Q (m^3.yr^{-1}) through the lake or river divided by the catchment are of the lake or river (m^2). The total concentration of metals can be calculated as:

$$[M]_{tot,sw(crit)} = [M]_{dis,sw(crit)} + [M]_{SPM(crit)} \cdot [SPM]_{sw} \tag{13}$$

where:

$[M]_{dis,sw(crit)}$ = critical dissolved concentration (critical limit) of a heavy metal in surface water ($mg.m^{-3}$)
$[M]_{SPM,sw(crit)}$ = critical total content of a heavy metal in suspended particles ($mg.kg^{-1}$)
$[SPM]_{sw}$ = concentration of suspended particles in surface water ($kg.m^{-3}$)

Data on the lateral outflow of lakes can be derived from the S&N critical loads database. If a country does not have data for aquatic systems, the multiplication of the average precipitation surplus in a catchment, multiplied by the catchment area provides an estimate for the lake outflow. The critical load depends on the critical limit used. In the manual for aquatic ecosystems (De Vries et al., 1998) it is argued that directly using a critical limit for the free metal ion activity in surface water is most appropriate. This idea has been further developed by Lofts et al. (unpublished data), but has not been adopted here, for reasons which will be given in 4.1.2. Instead, critical limits expressed as dissolved metal have been adopted. It is necessary to include a solid-solution transfer function (see Annex 7) to calculate the critical metal concentration in suspended particles and hence the critical total aqueous metal concentration.

Critical net retention of heavy metals in the aquatic system

The easiest way in order to get information on the (critical) net in-lake retention is to relate this retention to the total metal concentration in surface water (dissolved and in suspended particles) according to:

$$M_{ret(crit)} = c_{ret} \cdot r_{ret} \cdot [M]_{tot,sw(crit)} \qquad (14)$$

where:

r_{ret} = net retention rate in the lake system ($m.yr^{-1}$)
c_{ret} = factor for appropriate conversion of flux units from $mg.m^{-2}.yr^{-1}$ to $ga.ha^{-1}.yr^{-1}$ ($10\ g\ mg^{-1}\ m^2\ ha^{-1}$).

More sophisticated ways to derive net in-lake retention, distinguishing between sedimentation, resuspension and exchange processes in the lake (infiltration, diffusion and bioirrigation),are described in (De Vries et al., 1998).

4.1.2 Critical total cadmium and lead concentrations in aquatic ecosystems

Assessment of critical limits for dissolved concentrations in surface waters

Analysis of aquatic ecotoxicological data by Lofts et al. (unpublished) suggested overlap between aquatic and terrestrial toxic endpoint concentrations at a given pH. Hence it was suggested that common critical limits be applied for both soils and freshwaters, by using the critical limit functions derived in 3.3 for toxic effects on the soil ecosystem. However, although there is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar (assuming that uptake of the free ion from the aqueous phase is the significant mechanism leading to toxicity) this approach has not been adopted for the following reasons:

- The aquatic toxicity data for Cd covered a more restricted pH range than for the terrestrial toxicity data (pH 6.9 to 8.7 compared to pH 3.2 to 7.9). Therefore, although overlap of points was seen within the pH covered by the aquatic toxicity data, no data were available to validate the theory of overlap below pH 6.9.
- Observed overlapping of points for Pb was less than for any of the metals studied (Cu and Zn in addition to Cd and Pb). Most of the aquatic toxicity data gave free Pb endpoints higher than those observed for soils.

For these reasons, it was decided not to use the free ion approach for aquatic critical limits and instead to express the critical limits as the total dissolved metal (mg.m^{-3}). A summary of preliminary effect-based critical limits, suggested for use in the 2004 call for data on CL(M) by the Coordination Center for Effects (CCE), and "final" critical limits, suggested for a future call for data, is given in Table 8. Both the preliminary and "final" values for Cd are based on the EU Risk Assessment Report for Cd (Risk assessment Cadmium metal CAS-No. 7440-43-9) The preliminary value for Pb, suggested for use in the 2004 call for data, is based on Crommentuijn et al. (1997), whereas the "final" value, to be used after Annex 3 of the manual (UBA, 2004) is updated, is based on a substance data sheet on Pb and its compounds (2003). The reasons of needing this update are described below. The substitute for Annex 3 of the manual (UBA, 2004) is provided in Annex 12 of this background document, including detailed calculation examples. The values are all related to ecotoxicological effects. There are also critical limits related to secondary poisoning, but these values are not yet recommended for use because they do require further substantiation and discussion.

Table 8 Recommended critical limits for dissolved Cd and Pb concentrations surface waters

Metal	Critical dissolved concentration (mg.m^{-3})	
	Value to be used in the 2004 call for data by CCE	Value for update of Annex 3 of the heavy metals chapter in the manual (UBA, 2004)
Cd[1]	0.38 [2]	0.16 if H <100 [3] 0.30 if 100<H <200 and 0.50 if H >200
Pb[3]	11	5

[1] Both the preliminary and final value are based on the EU Risk Assessment Report for Cd (Risk assessment Cadmium metal CAS-No. 7440-43-9)

[2] A comparable critical limit is suggested in the RAR on Cd for the protection of top predators, namely 0.26 mg.m^{-3}. This value is based on a critical limit for the intake of Cd of 160 μg Cd /kg food (wet weight) of the predator, being the quality standard for biota tissue with respect to secondary poisoning. However, this value is yet considered too uncertain to be used in the critical load calculations

[3] H = hardness in mg $CaCO_3$.l^{-1}

[4] The preliminary value is based on Crommentuijn et al. (1997), whereas the final value is based on a substance data sheet on Pb and its compounds (2003).

The value of 0.38 mg.m^{-3}, taken from EU Risk Assessment Report for Cd, is based on the 5-percentile cut-off value of chronic toxicity data from 168 reliable tests on single species and 9 multi-species studies. An assessment factor of 2 is further introduced in EU Risk Assessment Report, leading to a critical limit of 0.19 mg.m^{-3}, but this approach was not accepted in the manual (UBA, 2004). For Cd, a relationship with water hardness has been reported. in the EU Risk Assessment Report. The influence of hardness on the toxicity of cadmium can be taken into account, using 3 hardness classes (with hardness H in mg $CaCO_3.l^{-1}$) according to 0.16 $mg.m^{-3}$ if H <100, 0.30 $mg.m^{-3}$ if 100<H <200 and 0.50 $mg.m^{-3}$ if H >200, when using no assessment factor. Since this approach has recently been accepted, it is advocated for future use in critical load assessments.

For Pb, the critical limit of 11 $mg.m^{-3}$ is based on Crommentuijn et al. (1997), whereas the value of 5 $mg.m^{-3}$ (range of 2.1- 9.3 $mg.m^{-3}$) is based on the 5-percentile cut-off value of chronic toxicity data, calculated with the method of Aldenberg & Jaworska, using 3 data sets of selected (i) freshwater and saltwater NOECs/EC10s (30 values), (ii) freshwater NOECs/EC10s (19 values) and (iii) saltwater NOECs/EC10s (11 values), described in a substance data sheet on Pb 92003). in the substance data sheet, an assessment factor of 3 is further introduced, but this approach was not accepted in the manual. At a workshop of ICP Waters on heavy metals, 2002, in Lillehammer (Skjelkvåle & Ulstein, 2002) a range of 1 - 11 $mg.m^{-3}$ was suggested in dependence on water chemistry, with low values referring to clear softwaters. The critical limit of 5 $mg.m^{-3}$ is in the middle of this range and thus consistent. A much lower critical limit is suggested in the substance data sheet on Pb for the protection of human health using a critical limit of 200 μg Pb /kg muscle meat of fish (food standard set by Commission Regulation (EC, 2001)) and the protection of predators in freshwater and saltwater environments from secondary poisoning (near 0.4 mg $Pb.m^{-3}$). However, this value is yet considered to uncertain to be used in the critical load calculations.

Although not presently used, a preliminary critical limit for Hg can be found in the substance data sheet on Hg and its compounds (2003). As with Pb, this value is based on the 5-percentile cut-off value of chronic toxicity data, using 3 data sets of selected (i) freshwater and saltwater, (ii) freshwater and (iii) saltwater, leading to a value of 0.142 $mg.m^{-3}$ (90 percentile range of 0.056- 0.281 $mg.m^{-3}$). In the substance data sheet on Hg, an assessment factor of 4 is further introduced, but this approach was not accepted in the manual. A reliable quality standard to protect top predators from secondary poisoning can not be given, but the value is much lower than those for ecotoxicological effects. The value of 0.035 $mg.m^{-3}$ presented earlier for soils is likely to be an upper limit for secondary poisoning.

Beware that the limits for Pb and Hg described above are still under discussion by the scientific community (e.g. the CSTEE) and should therefore used with precaution. Therefore the word “final” has been given between quotes in the case of Pb.

Calculation of critical total concentrations in surface waters

In order to calculate critical loads of metals for freshwater ecosystems it is necessary to know the total metal concentration at the critical limit, i.e. the concentration of dissolved metal and of metal bound to suspended particulate matter (SPM). There are various possible approaches to derive adsorbed metal contents on suspended particles in surface water ($[M]_{SPM,sw}$) from dissolved metal concentrations in surface water ($[M]_{dis,sw}$). The simplest approach is an empirical linear approach (K_d-value) relating both contents and concentrations, while accounting for the impact of major properties of the suspended particles influencing the sorption relationship. However, K_d values for a given metal may vary substantially from place to place and so the K_d approach is not appropriate when calculating metal contents on suspended particles from a large number of different locations.

An alternative approach, which uses as far as possible data and models is to take a two-stage approach:

1. Calculate the critical free ion concentration from the critical dissolved metal concentration.
2. Calculate the critical particle-bound metal from the critical free ion

Sum the critical particle-bound and dissolved metal to obtain the critical total metal.

Step 1 uses a complexation model (e.g. WHAM) to calculate the critical free ion concentration from the critical dissolved metal concentration. Step 2 uses a transfer function to calculate the particle-bound metal from the free ion. This transfer function is given in Annex 7. The calculation of the critical total concentration of Cd and Pb is presented in Annex 12.

Surface water chemistry data

Data needed to calculate the total dissolved metal concentration are the concentration of suspended particles in the water compartment, $[SPM]_{sw,}$ the pH and DOC concentrations of surface water. The concentration of SPM in the surface water ($kg.m^{-3}$ or $g.l^{-1}$) depends on the turbulence of the water, which in turn depends on the geological setting (incl. land use) and water flow velocity (i.e. wind speed for lakes). The concentration of suspended particles may thus vary considerably and generally ranges from 1 to 100 $g.m^{-3}$. The average concentration for Dutch surface waters, for example, is 30 $g.m^{-3}$, and for a dataset of lowland UK rivers (n = 2490) it is 30.6 $g.m^{-3}$ with a range of <0.1 to 890 $g.m^{-3}$, while Scandinavian waters typically show much lower values.

pH and DOC values for lakes largely depend on the landscape surrounding the lakes including the parent material (its sensitivity to acid inputs). Typical DOC values for clear water lakes are below 5 $mg.l^{-1}$, whereas for humic lakes, values can be higher than 50 $mg.l^{-1}$. Values for the pH generally vary between 5 and 7. Both pH and DOC are standard measurements in lake surveys and a wealth of data can be derived form those surveys

In deriving critical loads for lakes and rivers, data on the lake or river area and catchment area are needed. When calculating in-lake retention, the net retention rate has to be derived for each lake independently. In de Vries et al. (1998) several methods are described to estimate such a retention rate from measured metal concentrations in the lateral inflow to the lake and in the lake itself (De Vries et al., 1998 pp. 46-49). Another approximation can be derived from an annual average net sedimentation rate. Those rates vary in general from 1-25 $mm.yr^{-1}$.

4.2 Critical levels of mercury in precipitation

Critical loads of atmospheric pollution for aquatic ecosystems (lakes and rivers) may be approached by a mass balance approach involving a wide variety of processes both within the water column and in the surrounding watershed. Alternatively, the steady state partitioning of pollutants in a constant environment can be formulated without any need for mass balance considerations or detailed understanding of ecosystem processes. This can be achieved by linking critical receptors such as fish directly to the main immissions through transfer functions (TF) describing the relationship of their Hg concentrations at steady state, as described below.

First, we describe a simple model, which relates critical) Hg concentration in fish flesh to a (critical) Hg concentration in precipitation. This involves a site-specific transfer function, TF_{HgSite}, referring to a 1-kg pike as a standard receptor (Section 4.2.1). We then describe how the Hg concentration in any fish or other organism serving as food for humans and fish-based wildlife, can be related to the Hg concentration in 1-kg pike by using an organism-specific transfer function, addressing the typical Hg partitioning within food webs, TF_{HgBio} (Section 4.2.2). The model with its two independent transfer functions permits calculations for any organism at any site, as well as conversion between regional adaptations to differences in ecosystem types and data availability.

4.2.1 Derivation of critical levels of mercury in precipitation referring to a standard fish

Basic concept
Hg concentrations in fish show a wide variation, both within and among sites (about 30-fold each, Meili, 1997). A standardized value for a given site (lake or river) can be obtained by referring to a commonly caught piscivorous fish with a total body weight of 1 kg, in particular pike (Esox lucius). Using a 1-kg pike as a standard receptor, the mean Hg concentration in fish flesh can be related to the mean Hg concentration in precipitation at a given site as follows:

$$[Hg]_{Pike} = c_{bp} \cdot [Hg]_{Prec} \cdot TF_{HgSite} \qquad (15)$$

where:
$[Hg]_{Pike}$ = Hg concentration in the flesh of 1-kg pike ($mg.kg^{-1}$ fw).
$[Hg]_{Prec}$ = Hg concentration in precipitation ($ng.l^{-1}$).
TF_{HgSite} = site-specific transfer function ($l.kg^{-1}$ fw), referring to the transfer of atmospheric Hg to fish flesh in a watershed at steady state
c_{bp} = factor for appropriate conversion of units from $ng.kg^{-1}$ fw to $mg.kg.^{-1}$ fw (10^{-6} $mg.ng^{-1}$).

The critical level of atmospheric pollution ($[Hg]_{PrecCrit}$) can thus be calculated as:

$$[Hg]_{Prec(crit)} = 1/c_{bp} \cdot [Hg]_{Pike(crit)} / TF_{HgSite} \qquad (16)$$

where:

$[Hg]_{Pike(crit)}$ = critical Hg concentration in the flesh of 1-kg pike (0.3 $mg.kg^{-1}$ fw)
$[Hg]_{Prec(crit)}$ = critical Hg concentration in precipitation ($ng.l^{-1}$)
$1/c_{bp}$ = factor for appropriate conversion of units (10^6 ng. mg^{-1}).

For aquatic ecosystems, limits usually refer to the Hg concentration in fish and other animals that serve as a food source to humans, but wildlife itself may also be affected. A critical limit of 0.5 $mg.kg^{-1}$ fw (fresh weight) in edible tissues has been adopted in many countries, based on earlier recommendations by the UN-WHO/FAO. It should be noted, however, that the US Environmental Protection Agency (EPA) now recommends a lower fish Hg limit of 0.3 $mg.kg^{-1}$ fw referring to methyl-Hg alone, which constitutes virtually all Hg in fish-eating freshwater fish (US-EPA, 2001). Recently, also the UN-WHO/FAO has recommended to reduce the maximum weekly Hg intake to half (UN-FAO/WHO-JECFA, 2003), which would reduce the corresponding fish limit above to 0.25 $mg.kg^{-1}$ fw (fresh weight). All these limits are largely based on the potential exposure of fish consumers, usually focusing on humans, mammals and birds. Recent studies, however, also suggest behavioural and endocrine effects of low-level methyl-Hg exposure also in fish (Matta et al., 2001; Hammerschmidt et al., 2002; Drevnick & Sandheinrich, 2003). In the manual, we use the limit of 0.3 $mg.kg^{-1}$ fw on total Hg in fish which is consistent with recommendations by the US EPA and the UN-WHO/FAO.

The transfer functions TF_{HgSite}

TF_{HgSite} addresses the wide variation of Hg concentrations among ecosystems in response to a given atmospheric Hg input at steady state. It accounts for a variety of complex processes including both terrestrial and aquatic aspects related to the biogeochemistry of Hg in lakes and rivers (Meili et al., 2003b), thus accounting for both fluxes and transformations of Hg (e.g. sorption, volatilization, net methylation, bioavailability, biodilution, biomagnification). For mapping of watershed sensitivity, TF_{HgSite} is preferably expressed as a function of basic physical-chemical parameters. Hg concentrations in fish are generally highest in nutrient-poor softwaters in acidic watersheds rich in wetlands (e.g. Verta et al., 1986; Håkanson et al., 1988; Meili, 1991, 1994; Meili et al., 1996; Meili, 1997). Such differences can be described by empirical relationships to address regional and local differences in watershed biogeochemistry, based on variables for which data are commonly available (e.g. from other studies under CLRTAP), such as surface water pH or concentrations of organic carbon or nutrients (the latter being of particular relevance for mercury). Two alternative formulations capturing part of the large variation in TF_{HgSite} are:

$$TF_{HgSite} \approx TF_{HgRun} \cdot ([TOC]_{sw} + 1) / (400 \cdot [TP]_{sw} + 6) \qquad (17a)$$

$$TF_{HgSite} \approx TF_{HgRun} \cdot e^{-(pH_{sw}-6)/2} \qquad (17b)$$

where

$[TOC]_{sw}$ = concentration of total organic carbon in surface water ($mg.l^{-1}$).

$[TP]_{sw}$ = concentration of total phosphorus in surface water ($mg.l^{-1}$).
pH_{sw} = pH in surface water.
TF_{HgRun} = transfer function ($l.kg^{-1}$ fw) referring to the transfer of atmospheric Hg to fish flesh via runoff in a reference watershed at steady state.

The first formulation (17a) is most appropriate and should be used where concentrations of total organic carbon and total phosphorus in surface water are available, which is often the case from routine monitoring of surface waters. The alternative formulation based on pH alone (17b) is less adequate but may be used if data access is limited.

TF_{HgRun} can be quantified from adequate data sets in various ways (see Annex 13). An important aspect to consider when quantifying steady state parameter values from field data is that present environmental Hg concentrations are not in steady state with the present level of pollution (e.g. Meili et al., 2003a), as discussed in Annex 13. If such data are not available, a standard value of 250 000 $l.kg^{-1}$ fw can be used for TF_{HgRun} referring to the standard fish (1 kg, in particular pike, *Esox lucius*) at steady state (cf. Verta et al., 1986; Meili, 1991; Meili et al., 2003a).

4.2.2 Derivation of critical levels of mercury in precipitation referring to other organisms

Basic concept

The Hg concentration in any fish or other organism, serving as food for humans and fish-based wildlife such as birds and mammals, can be related to the Hg concentration in 1-kg pike according to:

$$[Hg]_{Bio} = [Hg]_{Pike} \cdot TF_{HgBio} \qquad (18)$$

where:
$[Hg]_{Bio}$ = Hg concentration in any biota, e.g. fish flesh ($mg.kg^{-1}$ fw)
TF_{HgBio} = organism-specific transfer function addressing the typical Hg partitioning within food webs (-)

The critical level of atmospheric pollution ($[Hg]_{PrecCrit}$) can thus be calculated from a combination of Eq. (16) and (18) as:

$$[Hg]_{Prec(crit)} = [Hg]_{Bio(crit)} / (TF_{HgBio} \cdot TF_{HgSite}) \qquad (19)$$

where:
$[Hg]_{Bio(crit)}$ = critical Hg concentration in any biota, e.g. fish flesh ($mg.kg^{-1}$ fw)

The transfer function TF_{HgBio}

TF_{HgBio} is useful for two purposes: (1) to estimate values for 1-kg pike for sites/regions in which only mercury concentrations in other organisms are available, (2) to convert critical load maps referring to 1-kg pike into maps for other target organisms of local/regional interest. TF_{HgBio} addresses the wide variation of Hg concentrations among organisms within food webs, by describing the typical deviation from the standard fish. Among commonly available variables, body weight is the most powerful single predictor of fish Hg levels, also across species. The variation in TF_{HgBio} can be described as follows:

$$TF_{HgBio} \approx f_{HgY} + f_{HgW} \cdot W^{2/3} \tag{20}$$

where:
f_{HgY} = value for very young fish and other small animals (-); $f_{HgY} \approx 0.13$
f_{HgW} = species-specific slope coefficient (-); $f_{HgW} \approx 0.2...2$ (Table 9)
W = total body fresh weight (kg fw)

For many freshwater fish used for human consumption, this will generate estimates of mean Hg concentrations at a given fish size that differ less than 2-fold from observed means for a given site, provided that the fish species is known. Species-specific slope coefficients (f_{HgW}) for some common freshwater fish are given in Table 9 for the typical case that the value for very young fish and other small animals (f_{HgY}) can be maintained at 0.13. For any fish species (e.g. for unexplored sites or for unknown future fish populations), a first approximation differing less than 3-fold from observed size-class means can be made based on body weight alone, using the parameter for the standard fish, pike ($f_{HgW} = 0.87$, Table 9). If total body fresh weight data for fish are not available, the value can be estimated from the total body length by applying a species specific shape factor according to:

$$W \approx f_{LW} \cdot L^{3.1} \tag{21}$$

where:
L = length of the fish (cm)
f_{LW} = species specific shape factor relating the length to the weight of a fish

Table 9 Coefficients for size conversion (f_{LW}) and normalization of Hg concentrations (f_{HgW}) in freshwater fish, some standard fish weights (W) for consumption and the related value for TF_{HgBio}

Fish taxa			f_{LW}	f_{HgW}	W	TF_{HgBio}
pike	*Esox lucius*	Esocidae	$3.8\ 10^{-6}$	0.87	1.0	1
pike-perch, zander	*Stizostedion lucioperca*	Percidae	$6.4\ 10^{-6}$	1.2	1.0	1.3
perch	*Perca fluviatilis*	Percidae	$7.9\ 10^{-6}$	1.9	0.3	1.0
trout	*Salmo trutta*	Salmonidae	$7.2\ 10^{-6}$	0.4	0.3	0.3
Arctic char	*Salvelinus alpinus*	Salmonidae	$6.8\ 10^{-6}$	0.7	0.3	0.4
whitefish	*Coregonus spp.*	Coregonidae	$6\ 10^{-6}$	<0.4...>2		
burbot	*Lota lota*	Lotidae	$5\ 10^{-6}$	0.9	0.3	0.5
bream	*Abramis brama*	Cyprinidae	$8\ 10^{-6}$	0.25	0.3	0.2
roach	*Rutilus rutilus*	Cyprinidae	$6.8\ 10^{-6}$	0.6...1.2		

Data for f_{LW} for various fish species are given in Table 9. By applying Eq. (18), using the parameters for fHgW and W as given in this table and keeping f_{HgY} at 0.13, reference values of TF_{HgBio} for various fish species are also given in Table 9. Note that for compatibility of transfer functions and for inter-regional comparisons, the value of TF_{HgBio} for the reference receptor (1-kg pike) needs to be maintained at 1.

5 Evaluation

As mentioned in Section 2.2, a stand-still approach, which aims at avoiding any (further) accumulation of heavy metals in the soil, was included in a in previous guidance document as an alternative to the effect-based approach. This method is, however, not included in the manual. Instead, it is suggested to calculate the critical soil content (from a given critical limit function for the soil solution) and compare this to the present soil metal content to assess the critical limit exceedance in the present situation (see Section 2.2). This aspect is further discussed in Section 5.1.

The limitations and uncertainties of the critical load estimates are further discussed in Section 5.2. This includes: (i) an overview of sites where the calculations can not be carried out (ii), the uncertainties and particularities of the steady-state models used and (iii) the reliability of the approaches that are applied to derive critical limits for critical total dissolved metal concentrations in soil solution and surface water. Furthermore, possibilities to improve the model calculations and the derivation of critical total dissolved metal concentrations are presented.

5.1 Derivation of critical Cd and Pb contents for soil

In Annex 8, it is shown that the reactive critical metal concentration in the soil can be related to the organic matter content and the pH according to:

$$\log[\mathrm{M}]_{\mathrm{re(crit)}} + (\mathrm{b}/\mathrm{c}) \cdot \log[\mathrm{OM}]_{\mathrm{s}} = \phi \cdot \mathrm{pH}_{\mathrm{ss}} + \psi + \varepsilon \qquad (22)$$

where ε is the 95%ile of the regression residuals.

By applying this approach and using toxicity data on chronic population-level effects on soil plants, soil-dwelling invertebrates and microbial processes, collated and accepted under the terms of current EU Risk Assessment procedures and limiting the data to those in which also the organic matter content of the soil is given, see also De Vries et al. (2004a), the following results were obtained:

$$\log\mathrm{Cd}_{\mathrm{soil,crit}}\,(\mathrm{mol.kg^{-1}}) = 0.33 \cdot \mathrm{pH} + 1.00 \cdot \log\,[\mathrm{OM}]_{\mathrm{s}} - 7.32 \qquad (23)$$

$$\log\mathrm{Pb}_{\mathrm{soil,crit}}\,(\mathrm{mol.kg^{-1}}) = 0.11 \cdot \mathrm{pH} + 0.66 \cdot \log\,[\mathrm{OM}]_{\mathrm{s}} - 4.74 \qquad (24)$$

Below tables of the critical reactive soil content of Cd and Pb are given, calculated from these two equations for pH 3.5-8 and % OM from 1 to 100%, that can be used as look up tables.

Generally, one will like to compare the results with present total (aqua regia extracted) metal concentrations. This requires the calculation of critical total metal concentrations from those critical reactive concentrations, using Eq. (A7.2b) described in Annex 7 and the parameters for this function given in Table A7.3. Applying this approach for a sandy soil with a clay content of 5% leads to the results presented in Table 12 and Table 13. Beware that in calculating these results, the transfer function (Eq. A7.2b) was sometimes applied outside its range of validity specifically in the case of Cd. This holds for example for total Cd concentrations above 40 mg.kg^{-1}. In this situation it did happen that the model calculated higher reactive than total metal concentrations. In that case both concentrations were set equal, which is reasonable in highly polluted soils.

Table 10 Critical reactive soil content of Cd (mg.kg^{-1}) as a function of pH in soil solution and soil organic matter content

pH	%OM												
	1	2	3	4	5	10	15	20	25	30	50	80	100
3.5	0.08	0.15	0.23	0.31	0.38	0.77	1.2	1.5	1.9	2.3	3.8	6.2	7.7
4.0	0.11	0.22	0.34	0.45	0.56	1.1	1.7	2.2	2.8	3.4	5.6	9.0	11
4.5	0.16	0.33	0.49	0.66	0.82	1.6	2.5	3.3	4.1	4.9	8.2	13	16
5.0	0.24	0.48	0.72	0.96	1.2	2.4	3.6	4.8	6.0	7.2	12	19	24
5.5	0.35	0.70	1.1	1.4	1.8	3.5	5.3	7.0	8.8	11	18	28	35
6.0	0.51	1.03	1.5	2.1	2.6	5.1	7.7	10	13	15	26	41	51
6.5	0.75	1.5	2.3	3.0	3.8	7.5	11	15	19	23	38	60	75
7.0	1.1	2.2	3.3	4.4	5.5	11	16	22	27	33	55	88	110
7.5	1.6	3.2	4.8	6.4	8.0	16	24	32	40	48	80	128	161
8.0	2.3	4.7	7.0	9.4	12	23	35	47	59	70	117	188	235

Table 11 Critical reactive soil content of Pb (mg.kg^{-1}) as a function of pH in soil solution and soil organic matter content

pH	%OM												
	1	2	3	4	5	10	15	20	25	30	50	80	100
3.5	9.1	14	19	23	26	42	55	66	77	86	121	165	191
4.0	10	16	21	26	30	47	62	75	87	98	137	187	217
4.5	12	19	24	29	34	54	70	85	99	111	156	213	246
5.0	13	21	28	33	39	61	80	97	112	126	177	241	280
5.5	15	24	31	38	44	69	91	110	127	143	201	274	317
6.0	17	27	36	43	50	79	103	124	144	163	228	311	360
6.5	20	31	40	49	57	89	117	141	164	185	259	353	409
7.0	22	35	46	55	64	101	133	160	186	210	294	400	464
7.5	25	40	52	63	73	115	151	182	211	238	333	454	526
8.0	29	45	59	71	83	131	171	207	239	270	378	516	598

The results show that present concentrations most likely exceed the critical concentrations in acidic sandy soils (low pH and organic matter content), but in this case the present metal concentration is generally also low.

Table 12 Critical total soil content of Cd (mg.kg^{1}) as a function of pH in soil solution and soil organic matter content for a sandy soil with a clay content of 5%

pH	%OM												
	1	2	3	4	5	10	15	20	25	30	50	80	100
3.5	0.13	0.24	0.34	0.44	0.53	0.99	1.4	1.8	2.2	2.6	4.1	6.2	7.7
4.0	0.18	0.33	0.47	0.61	0.74	1.4	2.0	2.5	3.1	3.6	5.7	9.0	11
4.5	0.25	0.46	0.66	0.85	1.0	1.9	2.7	3.5	4.3	5.1	8.2	13	16
5.0	0.35	0.64	0.92	1.2	1.4	2.7	3.8	4.9	6.0	7.2	12	19	24
5.5	0.49	0.90	1.3	1.7	2.0	3.7	5.3	7.0	8.8	11	18	28	35
6.0	0.68	1.3	1.8	2.3	2.8	5.2	7.7	10	13	15	26	41	51
6.5	0.95	1.7	2.5	3.2	3.9	8	11	15	19	23	38	60	75
7.0	1.3	2.4	3.5	4.5	5.5	11	16	22	27	33	55	88	110
7.5	1.8	3.4	4.9	6.4	8.0	16	24	32	40	48	80	128	161
8.0	2.6	4.7	7.0	9.4	12	23	35	47	59	70	117	188	235

Table 13 Critical total soil content of Pb (mg.kg^{1}) as a function of pH in soil solution and soil organic matter content for a sandy soil with a clay content of 5%

pH	%OM												
	1	2	3	4	5	10	15	20	25	30	50	80	100
3.5	16	23	29	35	39	58	74	87	98	109	146	191	217
4.0	17	26	33	38	44	65	82	96	109	121	162	212	240
4.5	19	29	36	43	48	72	90	106	121	134	179	234	266
5.0	21	32	40	47	54	79	100	118	134	149	199	260	295
5.5	24	35	44	52	59	88	111	131	148	165	220	288	327
6.0	26	39	49	58	66	98	123	145	164	182	244	319	362
6.5	29	43	54	64	73	108	136	160	182	202	270	353	409
7.0	32	48	60	71	81	120	151	178	202	224	299	400	464
7.5	36	53	67	79	89	133	167	197	224	248	333	454	526
8.0	40	59	74	87	99	147	185	218	248	275	378	516	598

5.2 Limitations in the present approach and possible refinements

Limitations in the present approach

Critical load calculations can not be carried out for sites with:

- Negative water balances, since there is no leaching but a seepage influx of water, leading to accumulation of salts and very high pH. Such regions do, however, hardly occur in Europe.
- Water logged soils where the simplified critical load calculation can not be applied because of a deviating hydrology. It should be noted that transfer functions do also not apply under reduced circumstances but transfer functions are presently not used in calculating critical loads but only in deriving critical limits for soil drainage water. Furthermore, the critical load calculations generally apply for the topsoil and completely reduced conditions hardly occur in the top 10 cm, even in wetlands.

Uncertainties in the present modelling approach and possible refinements

In general the uncertainties in measurement as well as in modelling are higher with respect to trace elements than for main nutrient elements. In particular the following uncertainties or particularities of the models should be mentioned:

- The steady-state of metal inputs and outputs on the level of the critical limit is a theoretical situation. In dependence of the actual status of a site (or area) it may take years to centuries (e.g. for calcareous soils) to reach this steady-state. This should be considered, when critical loads and their exceedances are to be interpreted. To consider the processes of metal accumulation or loss from soils (and sediments in case of aquatic ecosystems) over time, dynamic approaches would be needed.
- There is some inconsistency between the calculation of the critical leaching and the tolerable removal of the metals with biomass, because types of critical limits and their mode of use are different for both fluxes. For example, in case of a clear soil-plant relationship (e.g. for Cd), the uptake of heavy metals by plants should be related to the critical soil concentration (e.g. as assessed according to the methodology in Section 5.1).
- Possible effects of high biomass harvest (high yields) on the plant metal concentration are not considered due to missing knowledge.
- Weathering of heavy metals is excluded from the mass balance equation due to high uncertainties in the available calculation approach and the likely low impact, specifically for soils. However, if the same approach is used to identify sites with high natural weathering inputs it may happen that one site is excluded, while another site with a slightly lower weathering rate will stay in the database.
- The vertical flux of metals bound to particulate matter suspended in the drainage water is not considered in the calculation, whereas this might be significant in certain soils, particular for Pb. It was, however, recommended not to consider this flux in order to be consistent with other parts of the manual (UBA, 2004).
- In the steady state critical load models, seasonal variations in metal concentrations, due to e.g. seasonal variation of soil parameters, such as pH and DOC in both soils and surface waters can not be accounted for. Assuming that the critical dissolved metal concentrations are applicable on an annual basis, this aspect is not of crucial importance.
- Estimates of the DOC concentration, which is crucial in deriving critical total dissolved metal concentrations in soil drainage water from critical limit functions for the free metal ion concentration are very crude and only based on forest soils.

Possible refinements should focus on the implementation of dynamic models, considering processes of metal accumulation or loss from soils (and sediments) over time. Such models do allow the inclusion of various aspects considered in the above mentioned uncertainties, such as

- A clear relationship between dissolved metal concentrations (metal leaching) and uptake of heavy metals by plants, and their variation in time in response to changes in acid deposition and metal deposition.
- The interaction with changes in e.g. pH and DOC in response to changes in atmospheric deposition of acidity (N and S deposition) and land use change. In detailed models even the seasonal variations in metal concentrations, due to seasonal variation of these soil parameters can be included.

Furthermore, both the steady state and dynamic models may be used to investigate the uncertainties due to involvement or neglection of (i) weathering of heavy metals and (ii) leaching of metals bound to particulate matter suspended in soil drainage water.

Uncertainties in the critical metal concentrations and possible refinements

Regarding the use of critical limits for metals, specifically the critical dissolved metal concentrations in soil and surface water, the following uncertainties or particularities should be mentioned:

- The ecotoxicological limits for Cd and Pb, organisms are now assumed to be affected by soil solution only, whereas soil ingestion may be relevant for certain organisms, specifically in the organic layer of forests.
- The transfer functions have presently been used in deriving critical limits for soil drainage water and surface water need to be improved since (i) metal contents in soil were derived using different extraction techniques, (ii) the transfer function was derived over a range of soil metal concentrations which does not cover the range found in the toxic endpoint data and (iii) there is a difference between c-Q and Q-c relations.
- The approaches taken to calculate critical limits for ecotoxicological effects are different for terrestrial and aquatic ecosystems. Given the likelihood that terrestrial and freshwater organisms (with the exception of surface-dwelling soil invertebrates such as snails) are exposed to metal in a similar manner (i.e. via the solution phase), a common approach to deriving critical limits, if not common values or functions for the limits, is scientifically desirable.
- The critical limit derivation includes several uncertainties, as e.g. differences between results from laboratory or field, which are not taken into account by the use of "uncertainty factors as e.g. done in the OECD methodology.

Possible refinements should focus on the:

- Possible impact of ingestion of soil on the critical limit to be used, specifically for the organic layer of forests.
- Derivation of transfer functions based on reactive metal contents in soil only in a range which covers the range in of reactive soil metal concentrations using the K_f approach.
- Further assessment of NOEC data to evaluate the possibility of comparable approaches and critical limits for ecotoxicological effects in terrestrial and aquatic ecosystems.

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Appendix 1 Critical loads of heavy metals - definitions and symbols

Definitions

General definitions of critical loads, critical levels and exceedances, and others can be found in the related chapters of the Modelling and Mapping Manual. The following definitions refer specifically to applications related to critical loads of heavy metals.

Receptor = Target (used as synonyms)

The receptor is a living element of the environment that is subject to an adverse effect. It can be a species of interest, or several species considered representative of a larger group (e.g. plants, soil invertebrates, fish, algae, etc), or the whole ecosystem (typically the subject of interest in the critical load approach).

Critical Limit and critical Concentration

The critical limit is a concentration threshold within the ecosystem, based on adverse effects, i.e. it is a short expression of "effect-based critical limit". Below this critical limit significant harmful effects on human health or specified sensitive elements of the environment do not occur, according to present knowledge. To avoid confusion, limits that are not based on effects should not be called "critical limits". In this background document, the term "critical limit" is only used for a concentration, for which effects thresholds have been determined (free Cd and Pb ion concentration limits in soil solution, food quality criteria for Cd in wheat, food quality criteria for Hg in fish and critical limits for dissolved heavy metals in surface waters). All metal contents or concentrations, respectively, derived from these critical limits are named "critical (total) concentration" or "critical content".

Critical Load

The critical load is the highest total metal input rate (deposition, fertilisers, other anthropogenic sources) below which harmful effects on human health as well as on ecosystem structure and function will not occur at the site of interest in a long-term perspective, according to present knowledge. The critical load is derived from the critical limit through a biogeochemical flux model, assuming steady-state for the fluxes (which is a theoretical situation in an undetermined future, consistent with concepts of sustainability). For this purpose critical limits have to be transformed to a critical total concentration of the metal in the output fluxes by water (leaching from the soil or outflow from an aquatic ecosystem).

Present Load

The present load is the present total metal input. For natural ecosystems, including forests, the present load is generally equal to the atmospheric load.

Stand-still Load

The stand-still load is the total metal input that leads to no further increase (or decrease) of the metal concentration in the ecosystem according to the stand-still principle. The stand-still load is the total metal input that equals the sum of measured or modelled present output fluxes from the ecosystem (steady state). It does not say anything about the occurrence of effects at the present concentration level.

Symbols and abbreviations

Some general abbreviations:

M = a flux of a metal M
[M] = a content (in soil, plants) or a concentration (in a solution) of a metal M
f = a fraction
c = a factor for conversion of units
sdw = soil drainage water
sw = surface water

Regarding the metal concentrations in soil drainage water or surface water, the following notation can be used when neglecting the difference in compartments. In the Tables that follow hereafter, however, a distinction has been made in those tow compartments thus using these adding the symbols sdw or sw consistently.

Symbols	Short explanation	Basic units
$[M]_{free}$	concentration of free metal ion	[$mg.m^{-3}$]
$[M]_{DIC}$	concentration of metal bound to inorganic complexes	[$mg.m^{-3}$]
$[M]_{DOM}$, $[M]_{DOC}$	concentration of metal bound to dissolved organic matter (carbon)	[$mg.m^{-3}$]
$[M]_{dis}$	dissolved metal concentration	[$mg.m^{-3}$]
$[M]_{SPM}$	concentration of metal bound to suspended particulate matter	[$mg.kg^{-1}$]
$[M]_{tot}$	total metal concentration (dissolved and suspended particles)	[$mg.m^{-3}$]
$[M]_{free(crit)}$	critical concentration (or activity) of free metal ion	[$mg.m^{-3}$]
$[M]_{dis(crit)}$	critical dissolved metal concentration	[$mg.m^{-3}$]
$[M]_{SPM(crit)}$	critical concentration of metal bound to suspended particulate matter	[$mg.kg^{-1}$]
$[M]_{tot\ (crit)}$	critical total metal concentration (dissolved and in suspended particles)	[$mg.m^{-3}$]

Symbols	Short explanation	Basic units
Terrestrial ecosystems		
CLO fluxes		
CL (M)	Critical Load of a Metal (M)	[g.ha^{-1}.yr^{-1}]
M_u	Metal net uptake in harvestable parts of plants (under critical load conditions)	[g.ha^{-1}.yr^{-1}]
M_w	weathering rate of a metal	[g.ha^{-1}.yr^{-1}]
$M_{le(crit)}$	critical leaching flux of metal with drainage water	[g.ha^{-1}.yr^{-1}]
Uptake		
$[M]_{ha}$	metal content in harvestable biomass	[mg.kg^{-1} dw]
Y_{ha}	yield of harvestable biomass	[kg dw.ha^{-1}.yr^{-1}]
z_b	depth of the upper, biologically active soil layer (topsoil)	[m]
Hydrology		
$Q_{le,zb}$	leaching flux of water from the topsoil	[m.yr^{-1}]
$Q_{le,z}$	leaching flux of water from the rooting zone	[m.yr^{-1}]
Q_{lo}	lateral outflow flux of water from the aquatic system	[m.yr^{-1}]
P / E_i / E_s / E_t	symbols for water fluxes: Precipitation/ interception evaporation / soil evaporation / (plant) transpiration	[m.yr^{-1}]
$f_{Mu,zb}$	fraction of metal net uptake within the topsoil	[-]
$f_{Et,zb}$	fraction of water uptake by plants within the topsoil	[-]
c_{le}	conversion factor for units (leaching equation)	[g.mg^{-1}.m^2.ha^{-1}]
Metal concentrations in soil and soil drainage water		
$[M]_{re}$	reactive content of a metal in soil	[mg.kg^{-1}]
$[M]_{AR}$, $[M]_{HF}$, $[M]_{EDTA}$, $M]_{HNO3}$	concentration of a metal in soil, extracted with Aqua Regia, HF, EDTA, HNO_3 respectively.	[mg.kg^{-1}]
$[Hg]_{OM(crit)}$	critical limit of Hg, normalised to soil organic matter content	[mg.kg^{-1} OM]
$[M]_{free,sdw}$	concentration of free metal ion in soil drainage water	[mg.m^{-3}]
$[M]_{DIC,sdw}$	concentration of metal bound to inorganic complexes in soil drainage water	[mg.m^{-3}]
$[M]_{DOM,sdw}$ $[M]_{DOC,sdw}$	concentration of metal bound to dissolved organic matter (carbon) in soil drainage water	[mg.m^{-3}]
$[M]_{dis,sdw}$	dissolved metal concentration in soil drainage water (equal to total concentration in soil drainage water)	[mg.m^{-3}]
$[M]_{SPM,sdw}$	concentration of metal bound to suspended particulate matter in soil drainage water	[mg.kg^{-1}]
$[M]_{tot,sdw}$	total metal concentration (dissolved and in suspended particles) in soil drainage water	[mg.m^{-3}]
$[M]_{free,sdw(crit)}$	critical concentration (or activity) of free metal ion in soil drainage water	[mg.m^{-3}]
$[M]_{dis,sdw(crit)}$	critical dissolved metal concentration in soil drainage water	[mg.m^{-3}]
$[M]_{SPM,sdw(crit)}$	critical concentration of metal bound to suspended particulate matter in soil drainage water	[mg.kg^{-1}]
$[M]_{tot,sdw(crit)}$	critical total metal concentration (dissolved and in suspended particles) in soil drainage water	[mg.m^{-3}]
Soil (solution) properties		
$[OM]_s$	organic matter content of the soil	[kg OM.kg^{-1}] or [%]
[clay]	clay content of the soil	[(kg clay).kg^{-1}] or [%]
$[DOM]_{sdw}$, $DOC]_{sdw}$	concentration of dissolved organic matter (carbon) in soil drainage water	[g.m^{-3}] or [mg.l^{-1}]
$[SPM]_{sdw}$	concentration of suspended particulate matter in soil drainage water	[kg.m^{-3}]
pH_{sdw}	pH value in soil drainage water	[-]

Symbols	Short explanation	Basic units
Aquatic ecosystems		
CLO fluxes		
$M_{ret(crit)}$	net retention of heavy metal in the aquatic system at critical load	[$g.ha^{-1}.yr^{-1}$]
$M_{lo(crit)}$	critical lateral outflow of heavy metal from the aquatic system	[$g.ha^{-1}.yr^{-1}$]
Metal concentrations in suspended particles and surface water		
$[M]_{free,sw}$	concentration of free metal ion in surface water	[$mg.m^{-3}$]
$[M]_{DICsw}$	concentration of metal bound to inorganic complexes in surface water	[$mg.m^{-3}$]
$[M]_{DOM,sw}$ $[M]_{DOC,sw}$	concentration of metal bound to dissolved organic matter (carbon) in surface water	[$mg.m^{-3}$]
$[M]_{dis,sw}$	dissolved concentration of heavy metal in surface water	[$mg.m^{-3}$]
$[M]_{SPM,sw}$	concentration of metal bound to suspended particulate matter in surface water	[$mg.kg^{-1}$]
$[M]_{tot,sw}$	total metal concentration (dissolved and in suspended particles) in surface water	[$mg.m^{-3}$]
$[M]_{free,sw(crit)}$	critical concentration of free metal ion in surface water	[$mg.m^{-3}$]
$[M]_{dis,sw[crit)}$	critical dissolved concentration of heavy metal in surface water	[$mg.m^{-3}$]
$[M]_{SPM,sw(crit)}$	critical concentration of metal bound to suspended particulate matter	[$mg.kg^{-1}$]
$[M]_{tot,sw(crit)}$	critical total metal concentration (dissolved and in suspended particles) in surface water	[$mg.m^{-3}$]
Mercury model		
$[Hg]_{Pike}$	Hg concentration in the flesh of 1-kg pike	$mg.kg^{-1}$ fw)
$[Hg]_{Prec}$	Hg concentration in precipitation	[$ng.l^{-1}$]
$[Hg]_{Bio}$	critical Hg concentration in biota, e.g. fish flesh	[$mg.kg^{-1}$ fw]
$[Hg]_{Pike(crit)}$	critical Hg concentration in the flesh of 1-kg pike	$mg.kg^{-1}$ fw)
$[Hg]_{Prec(crit)}$	critical Hg concentration in precipitation	[$ng.l^{-1}$]
$TFHg_{Site}$	site-specific transfer function linking fish Hg to atmospheric Hg	[$l.kg^{-1}$ fw]
$TFHg_{Bio}$	organism-specific transfer function addressing Hg partitioning within food webs	[-]
f_f	fractionation or transfer factor describing the Hg contamination of organic matter in solution relative to that in solids	[-]
f_{HgRun}	fraction of total Hg input to surface waters contributed by runoff	[-]
Surface water characteristics		
A_l	lake area	[ha]
A_c	catchment area	[ha]
r_{ret}	net retention rate in the lake system	[$m.yr^{-1}$]
$[TOC]_{sw}$	concentration of total organic carbon in surface water	[$mg.l^{-1}$]
$[TP]_{sw}$	concentration of total phosphorus in surface water (mg.l-1)	($mg.l^{-1}$)
$[SPM]_{sw}$	concentration of suspended particulate matter in surface water	[$kg.m^{-3}$]
pH_{sw}	pH value in surface water	[-]

Appendix 2 Derivation of critical limits for soil from quality criteria for crops

Approach

Figure A2.1 shows how critical limits for the soil have been derived from critical limits in crops. A distinction was made 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 was included to ensure that critical loads related to food quality criteria do not lead to metal concentrations exceeding phytotoxic levels, having adverse effects on the food crops itself. Since metal uptake is crop specific and thus affects the level of the critical soil metal content, it is necessary to derive relationships for the most sensitive crops to assess critical soil contents. In this document a distinction was made between food crops (wheat, potato, lettuce and endive based on food quality criteria) and fodder crops (grass, maize and sugar beet using fodder criteria). Furthermore, critical limits related to phytotoxicity for all those crops were derived from the literature. The mathematical approach to calculate critical soil contents, the used critical limits for metal contents in plants and the results obtained are described separately below. More information on the approach is given in De Vries et al. (2004).

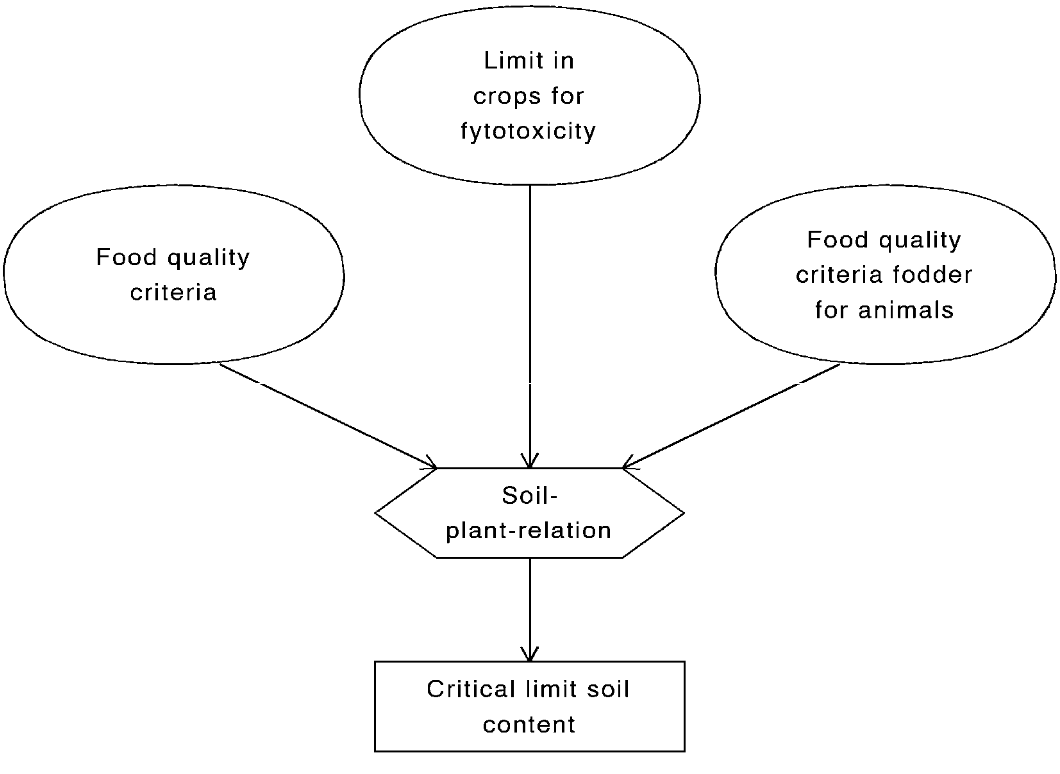

Figure A2.1 Procedure that has been applied to derive critical contents for heavy metals in the soil from quality criteria in food crops in view of effects on humans (arable land) and in fodder in view of effects on animals (grassland) and from critical limits in crops in view of phytotoxic effects (grassland and arable land).

Calculation of critical metal contents in soil from critical limits in crops

In most bioaccumulation models, including the model CSOIL, a simple bioconcentration factor (BCF or BAF, often denoted as bioaccumulation factor) is used to calculate critical soil contents from an acceptable daily intake by humans. Furthermore a simple BCF is also used to derive critical contents of heavy metals in soil from a critical limit for metal content in plant according to:

$$[M]_{s(crit)} = [M]_{p(crit)} / BCF_{sp} \tag{A2.1}$$

where:

$[M]_{p(crit)}$ = limit for metal concentration in plant ($mg.kg^{-1}$)
$[M]_{s(crit)}$ = 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 a (linear) relationship between plant and soil content exists, which is not the case for various metals, including Pb and Hg (see below). Reasons for this are amongst others that (i) crops are able to actively decrease the bioavailablity of metals in the rooting zone using ligands or by changing the rhizosphere pH and (ii) plant content metal content are also affected by above ground uptake of deposited metals (see Annex 5). For certain metals soil to plant transfer coefficients, like the BCF, are thus irrelevant and it is simply impossible to derive critical contents for soil from critical plant limits.

Even when a relationship does exist, use of BCF, assuming a linear relationship is not very adequate. Even then, use of e.g. a median BCF value for each considered agricultural crop, based on many plant and soil data, is not an adequate approach to derive a critical soil content since the relationship is not likely to be linear and furthermore depends on soil properties. If a significant relationship exists between the plant and soil content, this 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 (Brus et al., 2002; Adams et al., 2003):

$$[M]_p = K_{sp} \cdot [M]_s^{\,n} \tag{A2.2}$$

where:

$[M]_p$ = metal concentration in plant ($mg.kg^{-1}$)
$[M]_s$ = metal concentration in soil ($mg.kg^{-1}$)
K_{sp} = transfer constant from soil to plant ($mg.kg^{1-n}$)
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:

$$\text{Log}\,K_{sp} = a + b \cdot \text{pH-KCl} + c \cdot \log[\text{clay}]_s + d \cdot \log[\text{OM}]_s \quad \text{(A2.3)}$$

where:

OM = organic matter content (%)

Clay = clay content (%)

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

$$[M]_{s(crit)} = ([M]_{p(crit)} / K_{sp})^{1/n} \quad \text{(A2.4)}$$

A relationship was considered significant when $R^2 > 0.5$. Furthermore, inverse application is only warranted when the maximum measured metal content in plants, used in deriving the relationship, do approach (and preferably exceed) the critical limits for plants. Otherwise, the derivation of critical soil contents from critical limit for plant contents implies that the relationship is applied outside its range of derivation, which may lead to highly unreliable results (De Vries et al., 2004).

Critical limits for 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 A2.1. An overview of limits in view of phytotoxic effects on crops is also given in Table A2.1, based on literature information. In De Vries et al. (2004), more detail information is given on the background of all 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 in critical loads calculations.

Soil-plant relationships

Figure A2.2 gives an overview of relationships between Cd, Pb and Hg contents in crops (grass and wheat respectively) and soil. This clearly illustrates the absence of a simple direct relationship between metal contents in plants and soil, Only for Cd in wheat a weak relationship can be discerned. The fact that no relationship between the metal content in the soil and in the crop exists, implies that the BCF concept does not work.

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. A2.2 and A2.3):

Table A2.1 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)			Phytotoxicity 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]
	Sugar beet	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 sugar beet 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 Hg, 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

$$\log[\mathrm{M}]_p = a + b \cdot \mathrm{pH\text{-}KCl} + c \cdot \log[\mathrm{clay}]_s + d \cdot \log[\mathrm{OM}]_s + n \cdot \log[\mathrm{M}]_s \qquad \text{(A2.5)}$$

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., 2004). 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 A2.2. 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.

Based on the criterion of a minimum R^2 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, for Cd actual measured values in crops exceed the critical limit for wheat(food quality criteria). This also holds for Pb in wheat.

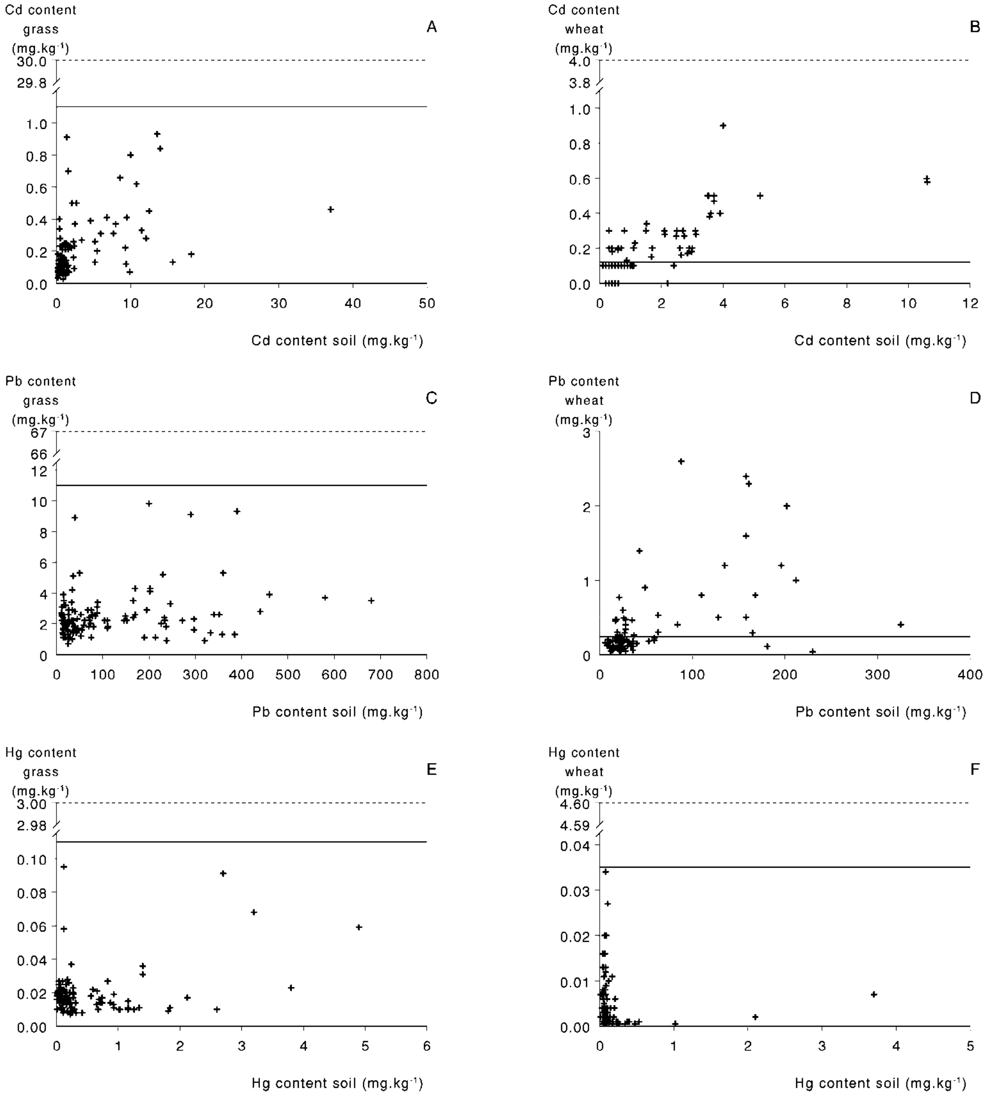

Figure A2.2 Relationships between Cd, Pb and Hg contents in grass and soil (A, C and E) and in wheat and soil (B, D, F). The solid line represents the fodder or food quality criteria and the dashed line represents limits in view of phytotoxic effects on crops.

Table A2.2 Overview of selected soil- plant relationships for Cd and Pb.

Crop	Soil- Plant relationship[1]	R^2
Grass		
Cd	$log[Cd]_p = 0.17-0.12*pH - 0.28*log [OM]_s + 0.49*log[Cd]_s$	0.53
Pb	No relationship found	-
Maize		
Cd	$log [Cd]_p = 0.9- 0.21*pH - 0.32*log [clay]_s + 1.08*log[Cd]_s$	0.62
Pb	No relationship found	-
Wheat		
Cd	$log [Cd]_p = 0.35- 0.15*pH - 0.39*log[OM]_s + 0.76*log[Cd]_s$	0.72
Pb	$log[Pb]_p = - 0.25*pH - 1.42*log[OM]_s + 1.14*log[Pb]_s$	0.24
Lettuce		
Cd	$log[Cd]_p = 2.55 - 0.33*pH - 0.19*log [clay]_s - 0.39*log[OM]_s + 0.85*log[Cd]_s$	0.71
Pb	$log [Pb]_p = -0.65 +0.59*pH - 0.30*log[OM]_s + 0.59*log[Pb]_s$	0.40

[1] pH is pH_{KCl}, $[clay]_s$ is clay content in the soil in% and [OM]s is soil organic matter content in %, and $[Cd]_s$ or $[Pb]_s$ is the aqua regia extractable "pseudo-total" Cd and Pb content in soil.

Derivation of critical limits for cadmium from food quality criteria

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 10. 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 A2.3).

Table A2.3 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

Critical soil contents have been calculated on the basis of food quality criteria for Cd for the following three soil types in agriculture:

- Sandy soils with an organic matter content of 3%, a clay content of 3% and a pH-KCl of 5.5.
- Clay soils with an organic matter content of 3%, a clay content of 25% and a pH-KCl of 6.5.
- Peat soils 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 A2.4).

Table A2.4 Calculated critical Cd contents in soil beyond which the food quality criteria for different crops are 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

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Appendix 3 Derivation of metal contents in soil from food quality criteria for animal products or acceptable daily intakes by animals

A3.1 Derivation of critical metal contents in soil from food quality criteria for animal products

Approach

Figure A3.1 shows how critical metal contents 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 requires 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 metals from plant to animal products and from soil to animal products is equal. The mathematical approach to calculate critical soil contents, the used critical limits for 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. (2004).

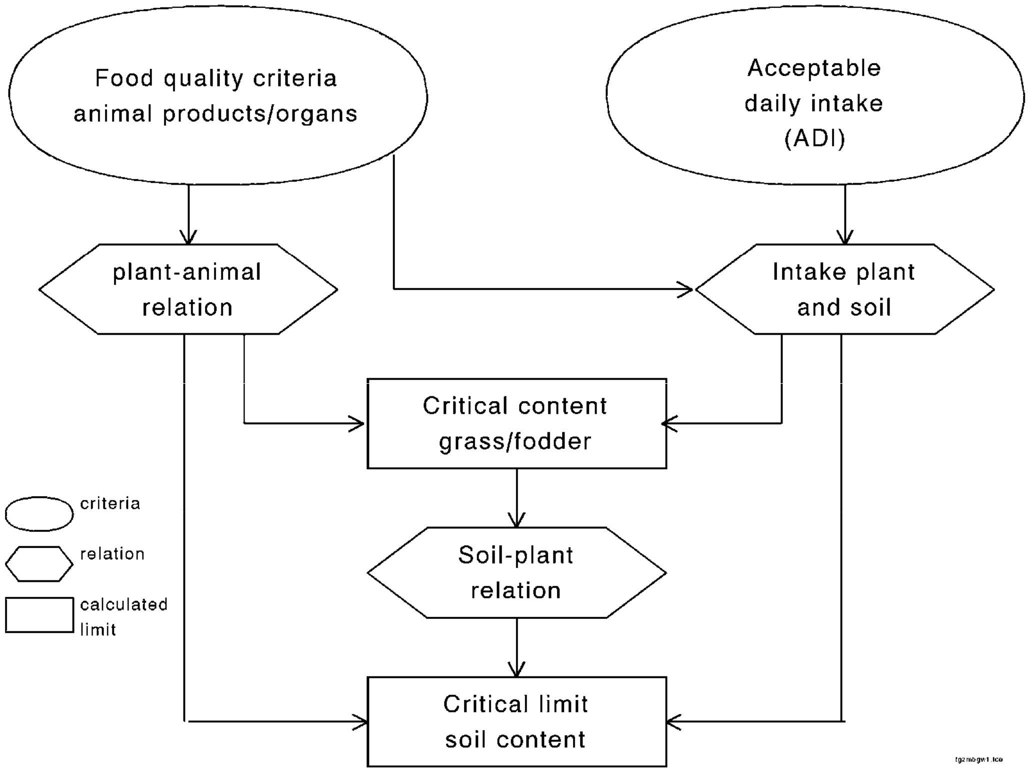

Figure A3.1 Procedure that has been applied to derive critical contents of heavy metals in the soil (on grassland) from food quality criteria in animal products/organs in view of effects on humans and from acceptable daily intakes in view of toxic effects on animals.

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

Based on available information on acceptable daily intakes (ADI) of metals for animals, the limits for metal contents in fodder (grass) and soil can be calculated according to:

$$[M]_{p(crit)} \cdot Ip + [M]_{s(crit)} \cdot Is = ADI \qquad (A3.1)$$

where:

ADI = Acceptable daily intakes of metals ($mg.d^{-1}$)
Ip = Intake of plants (fodder, dry mass) ($kg.d^{-1}$)
Is = Intake of soil dry mass ($kg.d^{-1}$)

and combining this equation with the relation between metal contents in the plant and the soil according to:

$$[M]_{p(crit)} = K_{sp} \cdot [M]_{s(crit)}{}^{n} \qquad (A3.2)$$

A combination of Eq. (A3.1) and Eq. (A3.2) gives:

$$K_{sp} \cdot [M]_{s(crit)}{}^{n} \cdot Ip + [M]_{s(crit)} \cdot Is = ADI \qquad (A3.3)$$

From Eq. (A3.3), the value of $[M]_{s(crit)}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp}, Ip and Is. 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 is used (by applying the median value in available data sets) and calculating the soil content, according to:

$$[M]_{s(crit)} = (ADI - [M]_{p} \cdot Ip)/Is \qquad (A3.4)$$

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

- The transfer coefficient of metals from soil to animal product and from plant to animal product is equal. 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. At the moment very little information is available that allows to distinguish between the availability of metals in plant material versus that in soil.
- There is a direct linear relationship between metal content in animal organs/products and metal content in fodder (use of a BCF_{pa}). This is a rather crude approach, but again, little or no information is available that can be used to derive a more realistic model linking uptake from soil and crops to internal levels in animals.
- The intake of metals by other sources (like intake of water and air) is negligible. This can actually be verified based on the consumption of water and prevailing

dissolved metal concentrations. In almost all cases, the contribution by drinking (or breathing) is less than a few percent compared to the intake by soil and crops.

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

$$[\mathrm{M}]_{\mathrm{ao(crit)}} = \left(\frac{[\mathrm{M}]_{\mathrm{p(crit)}} \cdot \mathrm{Ip} + [\mathrm{M}]_{\mathrm{s(crit)}} \cdot \mathrm{Is}}{\mathrm{Ip} + \mathrm{Is}} \right) \cdot \mathrm{BCF}_{\mathrm{pa}} \tag{A3.5}$$

where:

$[\mathrm{M}]_{\mathrm{ao(crit)}}$ = Food quality criteria for metal content in animal organ (mg.kg^{-1})

$\mathrm{BCF}_{\mathrm{pa}}$ = Bioconcentration factor from van plant to animal organ/product (-)

A combination of Eq. (A3.1) and (A3.5) gives:

$$\mathrm{ADI} = [\mathrm{M}]_{\mathrm{ao(crit)}} \cdot (\mathrm{Ip} + \mathrm{Is}) / \mathrm{BCF}_{\mathrm{pa}} \tag{A3.6}$$

This again allows the calculation of $[\mathrm{M}]_{\mathrm{s(crit),}}$ either iteratively from Eq. (A3.3) or directly from Eq. (A3.4).

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

In addition to soil-plant relationships, the calculation of critical soil limits contents requires information on: (i) food quality criteria in animal products/organs or ADIs, (ii) plant-animal product (target organ) relationships and (iii) intake data of grass and soil.

In Table A3.1, an overview is given of the critical limits of 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.

Table A3.1 Critical limits of 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.

An estimate of the acceptable daily intake based on these criteria is given in Table A3.2 using Eq. (A3.6) and the plant-animal bioconcentration factors given in the same table. The dry mass intake of grass by cows and sheep 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., 2004 and references therein)

Table A3.2 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	2380	28
	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	$3.3.10^{-3}$	$1.3.10^{-3}$	$9.2.10^{-4}$	262	1332	941	105	-	-
	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	$2.9.10^{-3}$	-	$9.4.10^{-4}$	45	-	138	-	-	-
	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 A3.3, an overview is given of critical soil contents of Cd, Pb and Hg in soil 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. In view of the absence of a significant soil-plant relationship (R^2 >0.5) for grass for all the metals involved, the calculation is based on a fixed median plant metal content found in grass in the datasets used to derive such relationships. Results show that those contents are generally much higher than those derived from impacts on soil organisms (see critical limit functions, chapter 3.2.3). More detailed information is given in De Vries et al. (2004).

Table A3.3 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

A3.2 Critical metal contents in soil related to impacts on animal health

This section describes approaches (simple food web models) to derive critical metal contents for soil based on accumulation in the food chain to animals (specifically Cd and Hg). Since critical contents of Cd and Hg related to impacts on terrestrial fauna may be lower than those related to soil organisms (see also De Vries & Bakker, 1998), this aspect is discussed in more detail in this Annex.

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 A3.2 shows the indicator- and target animals that have been used in this background document to calculate critical soil limits from critical values in animal organs in view of animal health impacts.

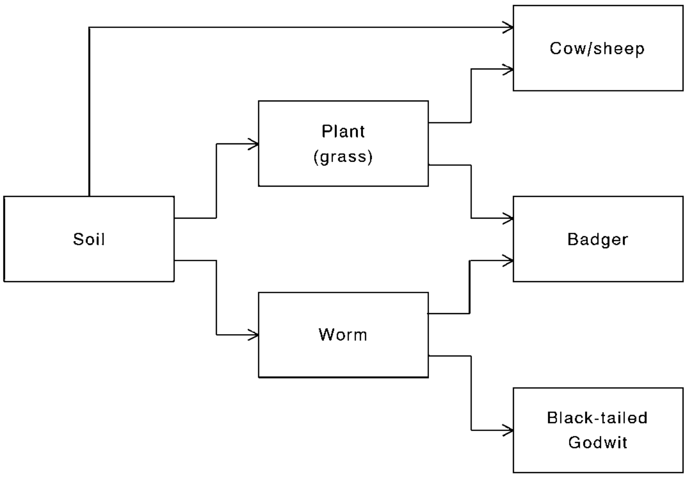

Figure A3.2 Indicator and target organism and procedure that has been applied to derive critical contents for heavy metals in the soil from criteria in animal organs in view of toxic effects on animals.

The food chain: soil ---> plant (grass) ---> cattle has been described in Annex 2. In this section we 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, $[M]_{s(crit)}$, based on this food chain is (Romijn et al., 1991a, b):

$$[M]_{s(crit)} = [M]_{in(crit)} / BCF_{sin} \qquad (A3.7)$$

in which:

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

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. (A3.7) 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.

Instead of using a fixed bioconcentration factor, a more sophisticated approach, is to use a BCF, which depends on soil characteristics, comparable to that of the soil-plant relationship as presented by Ma and Van der Voet (1993)for Cd in earthworms. The dependence of critical metal contents in 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 limits for 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 and its intake of earthworms is considered to be the dominant source of metals. 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:

$$[M]_{w(crit)} = ADI/Iw \tag{A3.8}$$

where:

$[M]_{w(crit)}$ = Critical limit for metal concentration in worm (mg.kg^{-1})

Iw = Daily intake of earthworms (kg.d^{-1})

Eq. (A3.8) 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:

$$[M]_{w(crit)} = K_{sw} \cdot [M]_{s(crit)}^{\ m} \tag{A3.9}$$

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

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

$$\text{Log } K_{sw} = a_o + a_1 \cdot \log(CEC) + a_2 \cdot \log[OM]_s + a_3 \cdot pH \qquad (A3.10)$$

where:
CEC = cation exchange capacity ($mmol_c.100g^{-1}$)

By combining Eq. (A3.9) and (A3.10), a critical soil content can thus be calculated from an ADI using an inverse non-linear soil-worm relationship according to:

$$[M]_{s(crit)} = (ADI/Iw)/K_{sw})^{1/m} \qquad (A3.11)$$

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., 2004):

$$[M]_{org\,(crit)} = [M]_{w(crit)} \cdot Iw \cdot f_{ass,org} \cdot T_{dy} \cdot T_{crit}/M_{org} \qquad (A3.12)$$

which by combination with Eq.(A3.8) leads to:

$$ADI = \frac{[M]_{org\,(crit)} \cdot M_{org}}{f_{ass,org} \cdot T_{dy} \cdot T_{crit}} \qquad (A3.13)$$

where
$[M]_{org\,(crit)}$ = critical limit for metal content in target organ (kidney) ($mg.kg^{-1}$)
M_{org} = dry weight of the organ (g)
$f_{ass,org}$ = 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 (yr)

Badger: Omnivores
The badger is taken as a representative of the omnivores. For badgers, the intake of earthworms (*Lumbricus terrestris*) from well-grazed pastures forms the largest part of the diet. Badgers also eat 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 their 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:

$$[M]_{p(crit)} \cdot Ip + [M]_{w(crit)} \cdot Iw = ADI \qquad (A3.14)$$

A combination of Eq. (A3.2), (A3.8) and (A3.14) leads to:

$$Ip \cdot K_{sp} \cdot [M]_{s(crit)}^{\ \ n} + Iw \cdot K_{sw} \cdot [M]_{s(crit)}^{\ \ m} = ADI \qquad (A3.15)$$

From Eq. (A3.3), the value of $[M]_{s(crit)}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp}, K_{sw}, Ip and Iw. 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:

$$[M]_{s(crit)} = ((ADI - Ip \cdot [M]_p)/(Iw \cdot K_{bw}))^{1/m} \qquad (A3.16)$$

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. (A3.13).

Critical limits for metal contents in target organs and acceptable daily intakes

In this study, the calculation of critical soil contents 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. (A3.14) and the needed parameters to perform the calculation are given in Table A3.4.

Table A3.4 Calculated acceptable daily intake of Cd and Pb by the black-tailed godwit and the badger

Animal	$[M]_{org(crit)}$ (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, $[M]_{org(crit)}$, 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. (2004).

[3] The critical limit of Cd in the kidney of vertebrates varies between 100-350 mg.kg^{-1} (Nicholson et al., 1983; Cooke & 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)

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).

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 ^{10}log relationship according to (see Eq. A3.10):

$$\log [M]_w = a_o + a_1 \cdot \log CEC + a_2 \cdot \log [OM]_s + a_3 \cdot pH + n \cdot \log [M]_s \qquad (A3.17)$$

where:

$[M]_w$ = metal content in earthworm (mg.kg^{-1})
$[M]_s$ = 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):

$$CEC = ((3.0 + 0.44 \cdot pH) \cdot [clay]_s + (5.1 \cdot pH - 5.9) \cdot [OM]_s / 2) / 10 \qquad (A3.18)$$

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 A3.5, both with and without the organic matter content.

Table A3.5 Overview of parameters in the transfer function for metal accumulation in earthworms, based on data by Ma (1983).

Metal	Parameters					
	a_0 -	a_1 (CEC) mmol$_c$.100 g^{-1}	a_2 $[OM]_s$ %	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

Despite its lower value of R^2, the relationship without organic matter was used to avoid unexpected effects of increasing metal contents in worms at increased organic matter contents (see Table A3.5). The reverse is namely expected, since an increase in organic matter contents decreases the bioavailability of metals (see Annex 7). 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.

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

Results of the critical contents of 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 A3.6. 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. 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 contents do become very low, specifically on sandy soils and peat soils, whereas the critical Pb contents are far above the generally observed present Pb contents (Table A3.6).

Table A3.6 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

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Appendix 4 Considerations about an appropriate effects-based limit for the concentration of Cd in wheat from the viewpoint of human health effects

Background:

In the UNECE Workshop on Critical Limits for Heavy Metals and Methods for their Application (Dec 2002, in Berlin) it was recommended to use official limits for metals in food as critical limits in the calculation of critical loads of heavy metals - CL(M) with respect to human health effects. The draft manual (version of 14 May 2004) suggested the use of the present EU limit of Cd in wheat (0.2 $mg.kg^{-1}$ (fw), following (EG) No 466/2001, of 8 March 2001). At the 20th meeting of the Task Force of ICP Modelling and Mapping the question was posed (as already in earlier workshops), whether this limit value was appropriate to calculate CL(Cd) with respect to human health effects, because the derivation of this value is not based on effects. The Task Force gave the mandate to the Expert Panel on Critical Loads of Heavy Metals to check again, whether there was a sound scientific basis for the use of an effects-based value, for instance the former EU value of 0.1 $mg.kg^{-1}$ (fw) in wheat.

Procedure

The following documents were checked in order to refresh/update the available information on effects of Cd in food on human health:

1. Sverdrup H (2000): Setting critical limits for mercury, cadmium and lead to be used in calculations of critical loads for different receptors, In: Ad-hoc international Expert Group on Effect-based Critical Limits, Bratislava, Slovak Republic, 11 - 13 Oct 2000, Proceedings, pp 93 - 97;
2. European Commission, DG Health and Consumer Protection, Information and Communication: Written information on the Scientific Background of Regulation (EG) No 466/2001, e-mail from SANCO-MAILBOX@cec.eu.int, 11 Feb 2003, 17:54
3. European Commission Food Science and techniques, Report of the Scientific Committee for Food /Thirty-sixt series) Opinion of the Scientific Committee for Food on Cadmium, DG Industry 1997
4. SCOPE - Scientific Committee on Problems of the Environment, Report on the SCOPE Workshop “Risk Assessment and Management of Environmental Cadmium, in particular: Working Group 3: Identifying Methodologies for Setting Standards for Cadmium, www.icsu-scope.org/cdmeeting/2003meeting/wg3.htm
5. WHO: Cadmium, In: www.who.int/docstore/water_sanitation_health/GDWQ/draftchemicals/cadmium2003.pdf
6. WGE (2004): Review and Assessment of Present Air Pollution Effects and their Recorded Trends**,** Report by The Working Group on Effects of the UN/ECE Convention on Long-Range Transboundary Air Pollution, in preparation
7. Final Draft Risk Assessment Report (RAR) Cadmium metal/Cadmium oxide, Status July 2003
8. Schütze et al. (2003): Risikoabschätzung der Cedmium-Belastung für Mensch und Umwelt infolge der Anwendung von cadmiumhaltigen Düngemitteln, In

Landbauforschung Völkenrode 2/3/2003 (53), Bundesforschungsanstalt für Landwirtschaft FAL, Braunschweig

9. European Commission Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE): Opinion on the result of the Risk Assessment of Cadmium Metal Human Health, Cadmium Oxide Human Health, Adopted by the CSTEE on 08 Jan 2004, http://europa.eu.int/comm/health/ph_risk/ committees/sct/documents/out220_en.pdf

Arguments pro 0.1 mg Cd/kg fw as critical limit for wheat

Arguments pro 0.1 mg Cd kg^{-1} (fw) as critical limit for wheat are:

- The limit of 0.2 mg.kg^{-1} (fw) in wheat is not effects-based. It is based on estimates from EU member countries to set the limit value “As Low As Reasonably Achievable” (ALARA). A critical load based on this type of standard leads to keeping what is currently achievable. It does not aim at diminishing human exposure to Cd, but an increasing risk would be prevented. The ALARA concept should only be explored as a possible alternative to risk assessment or as an interim measure (2), (4).
- The EU limit of Cd in wheat was doubled in 2001, although the WHO ADI/PTWI values did not change and there is no evidence that people eat less wheat than before. Furthermore, the limit for other grains than wheat and rice is still 0.1 mg.kg^{-1} (fw).
- Based on a symptom incidence of 0.01 - 0.02 % and a corresponding acceptable daily intake (ADI) of 9 - 15 μg Sverdrup (1) derived an acceptable Cd content in grains of 0.08 - 0.12 mg.kg^{-1} (fw). Basic assumptions were that half of the ADI can be filled by grains and a daily net intake of 60 g grains by an adult person (400 g.d^{-1} times a body uptake efficiency of 15 %).
- In the RAR Cd (7) a critical dietary Cd intake for adult non-smokers of 37 - 47 μg was used, based on the assumption of a Cd absorption rate by the human body of 3 %. Assuming that: (i) 50 % of the critical dietary Cd intake can be filled by (wheat) grain diets, and (ii) a daily intake of 200 g grains (8) the critical content in grain would be 0.09 - 0.12 mg.kg^{-1} (fw). These assumptions are based on an estimated: (i) 30 - 50 % of the dietary intake of Cd of the German population by consumption of flour and its products, breads and pastries (German studies on food consumption behaviour and data from the German food monitoring program (8) and (ii) a daily consumption of cereals in different European countries between 142 - 266 g. The critical content should be even considerably lower for smokers and persons with iron and other trace element deficiencies.
- In an opinion adopted at its 41st plenary meeting, the EC CSTEE (9) criticized several points in the EU RAR on Cadmium metal/Cadmium oxide, stating in particular that sensitive parts of the population are not sufficiently considered, that the exposure may be partly underestimated and that uncertainties are not enough considered. In its conclusions the CSTEE recommended the use of more conservative approaches for the risk assessment in general.
- A carcinogenic risk from dietary exposure to Cd cannot be completely excluded. Therefore a safe level of Cd in food cannot be established. There is a need to keep dietary exposure to cadmium as low as possible (3).

- The Task Force Health provided the following text (6) "Any further increase in the dietary intake of cadmium owing to an accumulation of the metal in agricultural soils will further narrow the gap to these critical levels. It is thus imperative to maintain a zero balance for cadmium in agricultural soils by controlling and restricting inputs from fertilizers (including sewage sludge) and atmospheric emissions. " This is in line with the statements in (4) that the need to reduce inputs of Cadmium into the environment is widely accepted and further accumulation of soil cadmium should be prevented. The critical load is different from a zero-accumulation approach (stand still). However, for most of the sites in Europe it can be assumed that a critical load based on 0.1 mg.kg^{-1} fw in wheat would be narrower to stand still than with 0.2 mg.kg^{-1} fw in wheat.
- If the limit of 0.2 mg.kg^{-1} (fw) is used, the calculation of related critical loads becomes unnecessary as far as the critical load to protect drinking water quality is calculated in parallel. The critical load with respect to drinking water would in any case be lower than that to protect the food. Therefore the critical load based on 0.1 mg.kg^{-1} (fw) in wheat could be suggested as a precautionary approach.

Arguments contra 0.1 mg Cd/kg fw as critical limit for wheat

The main arguments contra 0.1 mg Cd kg^{-1} (fw) as critical limit for wheat is that there are substantial data gaps at all stages in the food chain, particularly in assessing the risk to human health from exposure to dietary cadmium (4, 7). The high uncertainties in the assumptions may lead to an overestimation of the risk, e.g.: the risk assessment (7) is based on the assumptions that the humans are exposed to a 50 years constant daily Cd intake, or that all food origins from the region/continent of interest. Furthermore, the consumption behaviour of parts of the population is very different, what cannot be sufficiently considered.

Conclusions

Ultimately, it is a political decision, whether a more or less precautionary level of protection with respect to human health effects by dietary exposure to Cd is desired. There are, however, many arguments (listed above) to support the use of 0.1 mg.kg^{-1} (fw) as a precautionary approach. In particular there is high evidence that the critical dietary intake of Cd might be exceeded with the consumption of grains with constant Cd concentrations of 0.2 mg.kg^{-1} (fw) according to (EG) No 466/2001. Due to the high uncertainties this might include the possibility of overestimation of the risk. On the other hand, the considerations taking into account sensitive parts of the population strongly support the use of the lower limit for Cd in wheat. The Expert Panel on Critical loads of Heavy Metals thus supports the calculation of critical loads of Cd related to human health effects on the basis of a critical limit of 0.1 mg.kg^{-1} (fw). Cd inputs into agricultural soils at or below such critical loads will in the long term lead to the diminishing the risk of Cd via food uptake in line with the widely accepted requirement by scientists and policy in Europe.

Appendix 5 Derivation of critical loads for lead and mercury from food quality criteria

Food quality criteria can be back-calculated to critical contents in soils from critical limits for 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 content 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 A5.1 shows the relationship between Pb and Cd deposition (in ug.m^{-2}.d^{-1}) and Pb and Cd content of endive and lettuce (in mg.kg^{-1}), respectively based on results for one growing season in the year 2001 (De Temmerman & de Witte, 2003a).

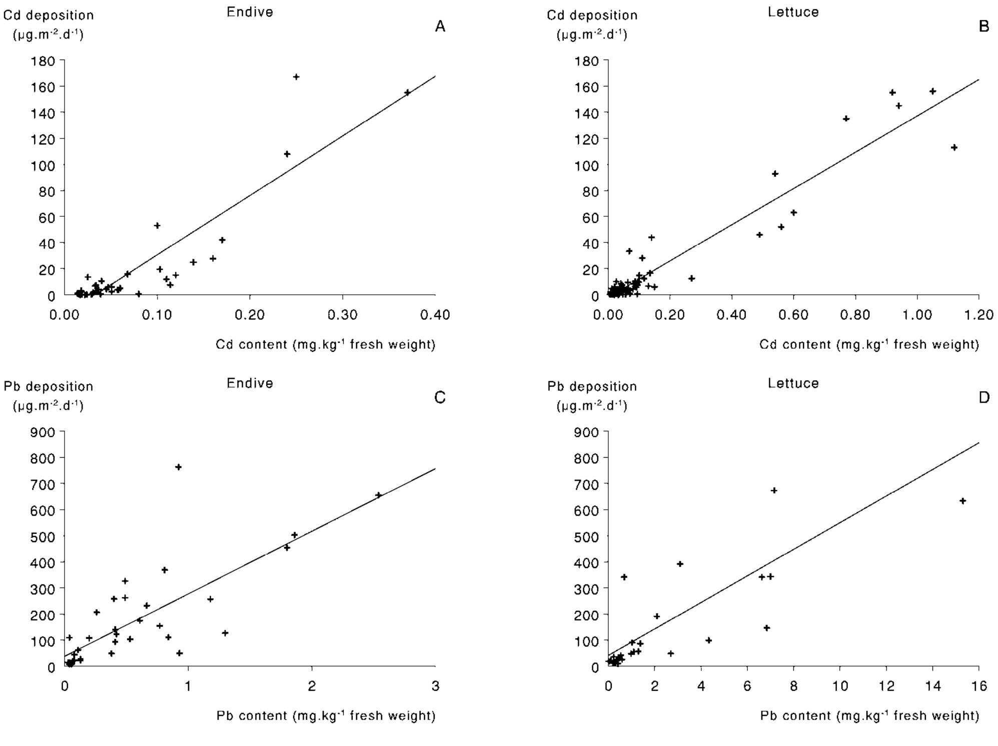

Figure A5.1 Relationships between inputs from the atmosphere in $\mu g.m^{-2}.d^{-1}$ *and plant contents in* $mg.kg^{-1}$ *for Cd in endive (A) and lettuce (B), Pb in endive (C) and lettuce (D).*

The resulting linear regression relationships that were derived are:

$Cd_{dep} = -15 + 456\ [Cd]_{endive}$ $R^2 = 0.81$
$Cd_{dep} = -1.8 + 139\ [Cd]_{lettuce}$ $R^2 = 0.92$
$Pb_{dep} = 39 + 240\ [Pb]_{endive}$ $R^2 = 0.58$
$Pb_{dep} = 42 + 50\ [Pb]_{lettuce}$ $R^2 = 0.52$

Those kind of relationships can be used to directly derive critical depositions from food quality criteria. For example, using a critical Cd limit of 0.2 mg.kg^{-1} fresh weight for vegetables leads to a critical Cd deposition of approximately 75 µg.m^{-2}.d^{-1} (274 g.ha^{-1}.yr^{-1}) for endive and of 25 µg.m^{-2}.d^{-1} (91 g.ha^{-1}.yr^{-1}) for lettuce. Similarly, using a critical Pb limit of 0.3 mg.kg^{-1} fresh weight for vegetables leads to a critical Pb deposition of approximately 110 µg.m^{-2}.d^{-1} (402 g.ha^{-1}.yr^{-1}) for endive and of 60 µg.m^{-2}.d^{-1} (219 g.ha^{-1}.yr^{-1}) for lettuce (see also De Temmerman & de Witte, 2003a).

Similarly, Figure A5.2 shows results of the relationship between Hg content in grass and the concentration of mercury in the atmosphere (after De Temmerman & 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 ion 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 of should not be higher than approximately 10 ng.m^{-3}.

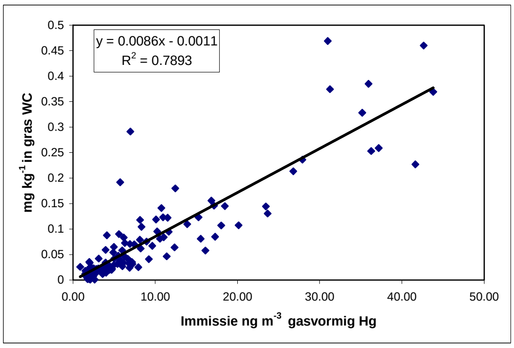

Figure A5.2 Relationships between inputs from the atmosphere and plant contents for Hg in grass.

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Appendix 6 Heavy metal release by weathering in the mineral topsoil

This annex provides guidance, how weathering rates of heavy metals can be estimated. The method, which was first suggested by Vrubel and Paces (1996) was formerly used as part of the critical load approach for heavy metals (De Vries & Bakker, 1998; De Vries et al., 1998; De Vries et al., 2002). While the results of such calculations show that the amount of heavy metal release from geogenic sources is irrelevant compared to the anthropogenic input fluxes to top soils at most of the sites, such calculations bear high uncertainties. It was recommended therefore to exclude them from the calculation of critical loads, but to use those estimates of weathering rates to:

- identify sites, where, geogenic (natural) sources are the main cause of exceedance of critical contents/concentrations by the recent metal concentrations in soil or soil solution, and
- evaluate the relevance of exceedances of critical loads by air pollution and/ or other anthropogenic sources.

It has to be mentioned, however, that the relevance of weathering as a contribution to the metal fluxes into aquatic ecosystems might by considerably higher, since the entire soil column above aquifers has to be considered as the source of weathering. This would mean to address also all the interactions of the drainage water passing through these layers, what is currently hardly possible for large scale studies due to a lack of data. Therefore, for the purposes mentioned, it is recommendable to limit estimates of weathering rates to the depth of the rooting zone (z), definitions of which are provided in Section 3.1.1 of this background document in line with the Modelling and Mapping Manual chapter 5.5 (UBA, 2004).

The method to estimate weathering rates of heavy metals is based on the idea to scale weathering rates of metals to those of base cations, using the molar ratio of the total metal content and the total base cation content in parent material (Eq. A6.1).

$$M_w = c_w \cdot f_w \cdot BC_w \cdot [M]_{pa}/[BC]_{pa} \qquad \text{(A6.1)}$$

where:

M_w = weathering release of the heavy metal M within the topsoil ($g.ha^{-1}.yr^{-1}$)
BC_w = weathering release of base cations from the parent material ($mol_c.ha^{-1}.yr^{-1}$)
$[M]_{pa}$ = content of the heavy metal in the parent material ($mg.kg^{-1}$)
$[BC]_{pa}$ = content of base cations in the parent material ($mol.kg^{-1}$)
f_w = fraction of the weathering release generated within the considered depth z or z_b (-)
c_w = 10^{-3} $g.mg^{-1}$, factor for appropriate conversion of units.

BC_w can be derived according to the methods described in Manual chapter 5.3.2 (Critical loads of acidity. For both, metals and base cations, the content in parent material is used since the content of heavy metal M in the (top)soil may be strongly influenced by accumulation on reactive sites due to pollution. This also holds for background values, which per definition in many countries include the ubiquitous historical pollution over the last centuries and are therefore often higher than pedogeogenic concentrations. Data for $[M]_{pa}$ and $[BC]_{pa}$ available in the literature vary widely as illustrated in Table A6.1 for of BC, Pb and Cd in parent materials, from German studies. Therefore it is recommended to use in national studies as far as possible investigations from the country of interest.

Table A6.1 Content of Pb and Cd in parent materials from German studies (Hindel et al., 1998) compared to values from a literature study (in brackets) as well as contents of base cations [BC] in parent Materials derived after Wedepohl (Ed.) (1978, in Schachtschabel et al., 1998) The literature study is a synthesis of Aubert and Pinta (1971), Wedepohl (Ed.) (1978), Bowen (Ed.) (1979), Krauskopf (1979), Guillet (1980), Alloway (1990), Ferguson (1990) and Merian (Ed.) (1991).

Parent material	[BC] $[mol_c.kg^{-1}]$	$[Pb]^{1)}$ $[mg.kg^{-1}]$	$[Cd]^{1)}$ $[mg.kg^{-1}]$
Sand	0.31	8.0	0.15
Calcareous stone	17.95	54.0 (3 - 10)	0.40 (0.035)
Clay stone	3.28	32.0 (18 - 40)	0.15 (0.22 - 0.3)
Loess	2.73	31.0	0.15
Boulder clay	4.52	19.0	0.30
Basic magmatites/ metamorphites	7.58	32.0 (3 - 8)	0.15 (0.13 - 0.22)
Acidic magmatites/ metamorphites	2.49	30.0 (15 - 24)	0.30 (0.09 - 0.2)
Sand stone	3.05	26.0 (5 - 10)	0.15 (0.05)
Bims tuff	7.58	27.0	0.40

The most simple approach to estimate f_w is by assuming vertical uniformity of weathering in which case f_w is the ratio between topsoil depth (z_b) and total soil depth (z). To be more precise with respect to weathering rates, the calculation can be done directly for the individual soil layers, i.e. involving the factor f_w becomes superfluous. A depth weighted mean should then be used to calculate M_w for the depth to be considered (z), if different layers appear within. The contents $[M]_{pa}$ and $[BC]_{pa}$ need to be quantified for the parent material of each layer. One has to be aware that the parent material on the surface is often not identical with the bedrock in deeper layers, which is provided in geological maps. Frequently mixtures occur, in particular mixtures with loess.

To avoid a uniform factor of 0.5 $mol.mol_c^{-1}$ for the sum of base cations (as proposed in De Vries et al., 1998) the ratio of the contents of individual base cations with their specific charges (Na^+, K^+, Ca^{2+}, Mg^{2+}) can be used by calculating a mass weighted mean for each layer. Such factors range between 0.5 and 1, depending on the chemical composition of the parent material. [BC] can then be used in terms of $[mol_c.kg^{-1}]$. Using the symbols accordingly, equation (A6.1) changes into (A6.2) as follows:

$$M_w = c_w \cdot BC_w \cdot [M]_{pa}/[BC]_{pa} \qquad (A6.2)$$

with terms defined as in Eq. A6.1, $c_w = 10^{-3}$ (g.mg^{-1}), and the unit for $[BC]_{pa}$ is mol$_c$.kg^{-1} instead of mol.kg^{-1}.

As an example, results of the quotient of [BC](mol.kg^{-1}) / [BC](mol$_c$.kg^{-1}) for German parent materials are provided in Tables A6.2 and A6.3. Table A6.2 presents data on the specific composition of base cations in an aeolic sand leading to a quotient of [BC](mol.kg^{-1})/[BC](mol$_c$.kg^{-1}) of 0,87 mol.mol$_c^{-1}$ for this soil type. Resulting quotients for other soil types are presented in Table A6.3.

Table A6.2: Consideration of specific composition of base cations in an Aeolic Sand (BC contents from Schachtschabel et al., 1998)

BC	[BC] (g.kg^{-1})	[BC] (mol.kg^{-1})	[BC] (mol$_c$.kg^{-1})
Ca	0,7	0,015	0,03
Mg	0,6	0,025	0,05
Na	0,0	0,00	0,0
K	8,8	0,23	0,23
Σ		0,27	0,31

Table A6.3: Consideration of specific average charge of base cation pools in soils from different parent materials, expressed as charge quotient of [BC](mol.kg^{-1}) / [BC](mol$_c$.kg^{-1})

parent material	X_bc (mol$_c$.kg^{-1})	charge quotient (mol.mol$_c^{-1}$)
Loess	1,63	0,60
Sand	0,31	0,87
Boulder clay	4,52	0,57
Clay stone	3,28	0,69
Sand stone	3,05	0,60
Calcareous stone	17,95	0,50
Basalt	7,58	0,55
Granite	2,49	0,92

Uncertainties:

The calculation approach in Equations A6.1 and A6.2 is based on the assumption that heavy metals only occur in primary minerals containing base cations, such as feldspars, pyroxenes, amphiboles, and micas (see Huang, 1977). This will be valid for soils where the mineralogical composition is mainly determined by these minerals, such as most sandy and loamy soils. The assumption will, however, not be valid for soils containing (heavy) minerals with high metal contents, that have a weathering rate that significantly deviates from the base cation containing minerals previously mentioned. This may be the case in heavy textured soils. The seeming benefit of using a refined quotient approach with Table A6.3 may be completely counteracted by these uncertainties The equations A6.1 and A6.2 give, however some insight in the order of magnitude of metal weathering rates.

Definitions:

Pedo-geogenic natural concentration

This is the concentration of metal in the soil which is inherited from the parent material above which the soil has developed. Several processes have concurrently contributed in the past to the present "natural" distribution of HM in soils :

- chemical alteration of the parent material ;
- migration and transfers (e.g. lixiviation), which may cause accumulations of metals.
- biological activity can also contribute to both alteration and transfers.

Background values

In Germany background values are defined as follows: "background values are representative values for common background contents of a substance or a substance group in top soils. The background content of a topsoil is composed of the naturally caused (geogenic/pedogenic) content and the ubiquitous substance distribution as consequence of diffuse man-made substance inputs in soils." This definition is similar to the ISO/11074 proposal for a norm on soil quality (draft). Information on how to determine the pedo-geogenic concentration of metals in the soil is provided in Schütze et al. (2003) on pp. 103-107.

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Appendix 7 Transfer functions for conversion of metal concentrations in different soil phases

A 7.1 Possible approaches and use of transfer functions

Possible transfer functions

This chapter provides an overview of transfer functions (regression relations) which describe the partitioning of heavy metals between soil and soil solution, while accounting for the impact of soil properties. Possibilities for the calculation of a solution concentration from solid phase data are presented in Figure A7.1.

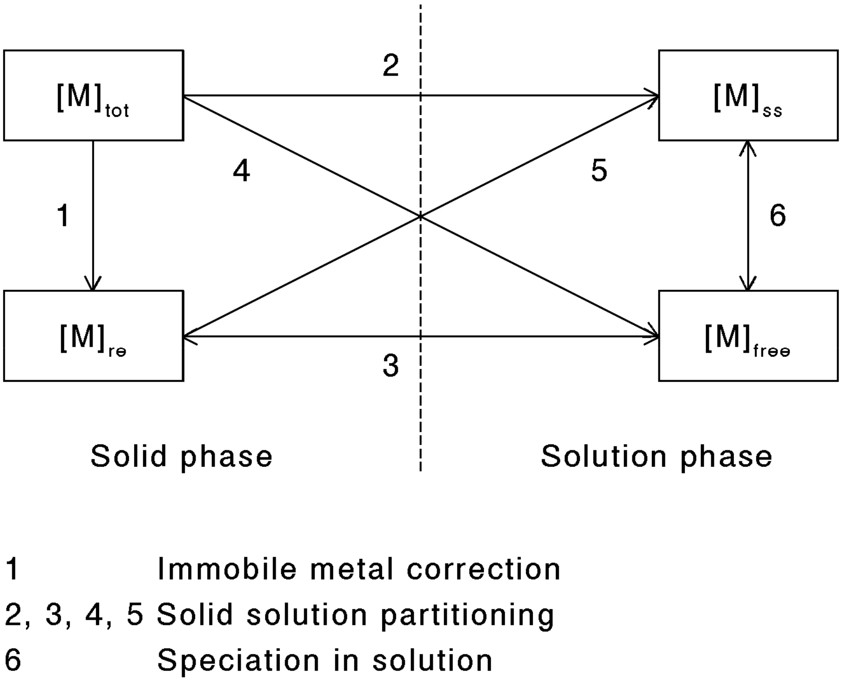

Figure A7.1 Overview of relations between solid and solution concentrations in soils:

The focus is on transfer functions for solid-solution partitioning relating reactive metal contents (M_{re}) in soil to free metal ion concentrations or activities (*relation 3* in Fig A7.1). In general only total metal contents are available and different extraction techniques are used to determine metal contents in soil. The data on present metal contents are mostly pseudo-total contents, based on aqua regia destruction $[M]_{AR}$ or a concentrated nitric acid destruction $[M]_{1N\text{-}HNO3}$. In some countries such data are provided as real total contents (e.g. HF destruction - $[M]_{HF}$). It is necessary to transfer these data (total and pseudo- total contents) to reactive metal contents based on mild HNO_3 (0.43N), EDTA or DTPA extractions (*relation 1* in Fig A7.1), because all transfer functions for solid-solution partitioning were derived on the basis of reactive metal contents. Possible calculations of either a total (free and complexed) concentration of metals in solution ($[M]_{ss}$ relation 2 in Fig A7.1) or the free metal ion concentration or activity ($[M]_{free}$; relation 4 in Fig A7.1) from a total concentration in the solid phase ($[M]_{tot}$, mostly as $[M]_{AR}$) are thus not described in this document.

To calculate the total dissolved metal concentration from the free metal concentration, chemical speciation models can be used which include the complexation of metals with DOC (*relation 6* in Fig A7.1). This aspect is further described in Annex 8. Although not used in the manual, one might also use direct relations between the reactive metal content and total metal concentrations in solution (*relation 5* in Fig A7.1). In this case the use of a speciation model is not needed. But this has shown to be less appropriate.

Possible approaches and types of transfer functions

A distinction can be made between transfer functions which directly relate the soil solution concentration to metal contents in the solid phase and soil and solution properties (further referred to as the direct approach) and transfer functions which relate adsorption constants to soil and soil solution properties (further referred to as the K_f approach). With the K_f approach calculations can be done in both directions. Furthermore the parameters derived using the K_f approach are more stable with respect to the data used in the derivation. The direct approach also has an analogy with the Freundlich isotherm, since the logarithmic form of the direct approach is equal to the logarithmised form of the Freundlich isotherm.

Within the direct approach a distinction can be made between relations in which the metal content in the solid phase is the explained variable and the solution concentration is the explaining variable (together with soil properties), which is often referred to as Q-c relations and relations in which the solution concentration is the explained variable and the metal content is the explaining variable which is often referred to as c-Q relations. In this case Q stands for the reactive metal content (M_{re}) and c for the dissolved (free)metal concentration in soil solution ($[M]_{free}$ or $[M]_{ss}$).

A pitfall in the use of direct methods can be the mistake that a Q-c relation is used the inverse direction to calculate the concentration in solution from the metal content in the soil and soil properties or inversely that a c-Q relation is used to calculate the content in the soil from the solution concentration and soil properties. Q-c and c-Q relations are not equal to each other and linear regression will give different estimates for the regression coefficients. In the case of a c-Q approach the sum of squares of $c_{regression}$-$c_{measured}$ (either $[M]_{ss,regression}$-$[M]_{ss,measured}$ or $[M]_{free,regression}$-$[M]_{free,measured}$) is minimized whereas the sum of squares for $Q_{regression}$-$Q_{measured}$ (more specifically $[M]_{re,regression}$-$[M]_{re,measured}$) is minimized for the Q-c approach. Incorrect use of these direct methods can lead to large errors.

Preferably one should thus have a relation which can be used in both directions. This is needed in the case when metal critical contents in soil are to be calculated from critical metal concentrations in soil solution to compare them with present contents Especially in the case of dynamic models, in which the partitioning of metals is calculated, this is a prerequisite. A possibility is to derive relations in which adsorption/partition constants are fitted to soil parameters instead of deriving relations in which Q or C are the explained variables. For the calculation of K_F however the value of the Freundlich exponent is not a priori known. Römkens et al (2004) developed a methodology to derive transfer functions for K_f. K_f-values were calculated from $[M]_{re}$ and $[M]_{free}$ (or $[M]_{ss}$) and unknown n. These Kf values are then regressed with soil properties while optimizing n iteratively at the same time (e.g. using the solver routine in MS-Excel The exponent n was optimized by maximizing the F-value (a measure for the significance of the model). Another possibility is to optimise all explaining variables simultaneously ($[M]_{re}$, $[M]_{ss}/[M]_{free}$) and soil properties), taking into account that all variables have variance, with an advanced statistical procedure, the total least squares method. More information on the methodology is given in Groenenberg et al. (2003).

Need of transfer functions in deriving critical dissolved metal concentrations

In principle, transfer functions are not needed in performing a critical load calculation. Transfer functions have been used to derive critical limits for free metal ion concentrations from NOEC data, referring to reactive soil metal contents. When applying critical limits for free metal ion concentrations, related to ecotoxicological effects, no transfer function is needed any more, since $[M]_{sdw(crit)}$ can be obtained directly, either by reference to the look up tables or by use of the W6S-MTC2 program (see Section 3.2.3 and Annex 9). In case of ground water protection, total dissolved critical concentrations can be used directly (see Section 3.2.2).

In the case of using critical limits referring to the metal content in plants, an empirical relationship can be used to derive total dissolved critical concentrations in soil solution, at least for Cd (See Table 4 in the main text). Using the more sophisticated and consistent way to derive soil solution concentrations from critical plant contents does however require transfer functions according to:

- first derive a critical *pseudo-total* soil metal content, by applying soil-plant relationships in the inverse way (derive a critical total soil content from a critical plant content)
- then apply a transfer function relating *pseudo-total* metal contents to reactive metal contents.
- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content.

Furthermore, all the transfer functions listed below are needed for the calculation of critical soil contents (from a given critical limit function for the soil solution) and to compare this to the present soil metal contents to assess the critical limit exceedance in the present situation (see Section 5.1). Inversely, one may calculate the present dissolved metal concentration form the present soil metal content, using the transfer functions described below and compare this to the critical limit function for the soil solution. For this purpose also transfer functions which relate different extraction techniques for the metal content in soils are to be used if the data on present metal contents are determined with other extraction techniques. Another use of transfer functions is described in Annex 12, i.e. in the derivation of critical total concentrations of Pb, Cd in surface waters.

Transfer functions described in this annex

An overview is given here of functions that are needed the total soil concentration to a dissolved free metal concentration, according to:

1 Relations between different extractable contents in the solid phase (Section A7.2)

- From total (HF) to *pseudo-total* (e.g. aqua regia) metal concentration (not in the figure)
- From *pseudo-total* (e.g. aqua regia, $[M]_{,AR}$) to reactive (e.g. 0.43N HNO_3 or EDTA extraction, $[M]_{re,HNO3/EDTA}$) metal concentration (relation 1). This relation possibly involves soil characteristics (e.g. clay and organic matter content).

2 Partition relations between solid phase and soil solution (Section A7.3)

- From reactive metal content ($[M]_{re}$, e.g. 0.43N HNO_3 or EDTA extraction) to free metal ion concentration or activity ($[M]_{free}$) in soil solution (relation 3).
- From reactive metal content to total dissolved metal concentration either directly via relation 5 in figure A7.1, or via relation 3 and 6.

A7.2 Relations between total, pseudo-total and reactive metal contents

The transfer functions for solid-solution partitioning were derived for reactive metal contents in soil. In general only total metal contents are available and different extraction techniques are used to determine metal contents in soil. In order to compare results obtained with different methods or to conduct calculations with a harmonised database, it is often necessary to transform contents/concentrations related to certain extraction methods into data related to another method. The data on present metal contents are mostly pseudo-total contents, based on aqua regia destruction $[M]_{AR}$ or a concentrated nitric acid destruction $[M]_{1N\text{-}HNO3}$. In some countries such data are provided as real total contents (e.g. HF destruction - $[M]_{HF}$). It is necessary to transfer these data (total and pseudo- total contents) to reactive metal contents based on mild HNO_3 (0.43N), EDTA or DTPA extractions, because all transfer functions for solid-solution partitioning were derived on the basis of reactive metal contents:

Transfer functions to derive pseudo-total from total contents of Cd and Pb and backwards

In some countries (e.g. Germany) true total metal concentrations (HF extractions) are measured, whereas most or nearly all countries use “pseudo-total” concentrations. Utermann et al. (2000) provided transfer functions to calculate *pseudo-total* contents of heavy metals (here aqua regia extract $[M]_{AR}$) from total contents (here $[M]_{HF}$) and backwards, according to:

$$\log_{10}[M]_{AR} = a_0 + a_1 \cdot \log_{10}[M]_{HF} \qquad (A7.1)$$

where:

M_{HF} = total content of heavy metal M in soil, provided as HF-extraction (HF, HCl and $HClO_4$) ($mg.kg^{-1}$)

M_{AR} = *pseudo-total* content of heavy metal M in soil provided as Aqua Regia extraction (mg.kg^{-1})

In order to calculate M_{AR} values for a_0 and a_1 are given in Tables A7.1 and A7.2. The correlations are depending on metal and substrate.

Table A7.1a Relation between cadmium (Cd) content in soils extractable by aqua regia ($[Cd]_{AR}$)and total contents ($[Cd]_{HF}$) in dependence on the parent material.

parent material	a_0	a_1	n	R^2	Range of validity $[Cd]_{HF}$ (mg.kg^{-1})	
basic and intermediate igneous rock	0.13	1.41	25	0,94	0.25	1.12
boulder clay	0.09	1.38	26	0.91	0.07	0.39
limestone	-0.15	1.24	25	0.91	0.26	1.86
loess or loessic loam	-0.15	1.26	25	0.91	0.07	0.88
marl stone	-0.05	1.24	25	0.93	0.10	0.98
sand	-0.02	1.26	37	0.89	0.04	0.65
sandy loess	0.29	1.78	36	0.82	0.06	0.29
acid igneous and metamorphic rock	-0.09	1.08	25	0.80	0.09	0.63
quartzitic sand stones and conglomerates	-0.11	1.23	25	0.81	0.07	0.60
clay stone, hard argillaceous and silty slates	-0.05	1.33	25	0.96	0.14	1.88
all parent materials	-0.12	1.19	274	0.91	0.04	1.88

Table A7.1b Relation between lead (Pb) content in soils extractable by aqua regia ($[Pb]_{AR}$) and total contents extractable ($[Pb]_{HF}$) in dependence on the parent material.

parent material	a_0	a_1	n	R^2	Range of validity $[Pb]_{HF}$ (mg.kg^{-1})	
basic and intermediate igneous rock	-0.20	1.11	25	0.97	5.6	113.6
boulder clay	-0.54	1.32	26	0.95	8.3	49.5
limestone	-0.02	0.99	22	0.88	24.8	132.7
loess or loessic loam	-0.42	1.22	24	0.91	15.1	91.8
marl stone	-0.03	0.95	25	0.94	5.5	124.0
sand	-0.54	1.31	49	0.91	2.7	76.7
sandy loess	-0.72	1.46	43	0.97	6.0	75.9
acid igneous and metamorphic rock	-0.84	1.44	25	0.84	14.6	106.1
quartzitic sand stones and conglomerates	-0.55	1.28	25	0.88	12.6	109.2
clay stone, hard argillaceous and silty slates	-0.11	1.05	25	0.98	13.9	270.3
all parent materials	-0.45	1.24	289	0.95	2.7	270.3

Because the transfer functions provided with the coefficients in tables A7.1a and A7.1b cannot be used in the reverse direction, other values have to be used to calculate total concentrations $[M]_{HF}$ from values for aqua regia exctractable contents $[M]_{AR}$, according to equation A7.1b with the a_0 and a_1 in Tables A7.2a and A7.2b:

$$\log_{10}[M]_{HF} = a_0 + a_1 \cdot \log_{10}[M]_{AR} \qquad \text{(A7.1b)}$$

Table A7.2a Relation between cadmium (Cd) total contents ($[Cd]_{HF}$) in soils and Cd content extractable by aqua regia ($[Cd]_{AR}$) in dependence on the parent material.

parent material	a_0	a_1	n	R^2	Range of validity Cd (AR) (mg.kg^{-1})	
basic and intermediate igneous rock	0.07	0.67	25	0.94	0.08	0.91
boulder clay	-0.13	0.66	26	0.91	0.03	0.32
limestone	0.09	0.73	25	0.91	0.13	1.55
loess or loessic loam	0.07	0.73	25	0.91	0.03	0.57
marl stone		0.75	25	0.93	0.05	0.88
sand	-0.12	0.71	37	0.89	0.02	0.61
sandy loess	-0.29	0.46	36	0.82	0.02	0.22
acid igneous and metamorphic rock	-0.06	0.74	25	0.80	0.06	0.62
quartzitic sand stones and conglomerates	-0.07	0.65	25	0.81	0.02	0.54
clay stone, hard argillaceous and silty slates	0.01	0.72	25	0.96	0.05	1.97
all parent materials	0.04	0.77	274	0.91	0.02	1.97

Table A7.2b Relation between lead (Pb) total content ($[Pb]_{HF}$) in soils and Pb content extractable by aqua regia ($[Pb]_{AR}$) in dependence on the parent material.

parent material	a_0	a_1	n	R^2	Range of validity Pb (AR) (mg.kg^{-1})	
basic and intermediate igneous rock	0.21	0.87	25	0.97	3.8	121.4
boulder clay	0.45	0.72	26	0.95	3.9	46.1
limestone	0.24	0.88	22	0.88	21.5	105.2
loess or loessic loam	0.45	0.74	24	0.91	7.0	97.3
marl stone	0.06	0.99	25	0.94	8.8	115.4
sand	0.47	0.70	49	0.91	1.2	73.6
sandy loess	0.52	0.66	43	0.97	2.3	77.9
acid igneous and metamorphic rock	0.76	0.58	25	0.84	5.0	100.0
quartzitic sand stones and conglomerates	0.56	0.68	25	0.88	6.6	110.8
clay stone, hard argillaceous and silty slates	0.13	0.94	25	0.98	13.2	280.2
all parent materials	0.41	0.77	289	0.95	1.2	280.2

Transfer functions to derive reactive from pseudo-total contents of Cd and Pb

The reactive metal concentration $[M]_{re}$ can be related to the *pseudo-total* concentration extracted with Aqua Regia $[M]_{AR}$ according to:

$$\log[M]_{re} = \beta_0 + \beta_1 \cdot \log[M]_{AR} + \beta_2 \cdot \log[OM]_s + \beta_3 \cdot \log[clay] \qquad (A7.2a)$$

where:

$[M]_{re}$ = the reactive metal content in the solid phase (mg.kg^{-1})
$[OM]_s$ = organic matter content in the soil (%)
$[clay]$ = clay content in the soil (%)

This is needed when starting with a present metal concentration that one wants to relate to a reactive concentration to compare with a critical reactive metal concentration (see Section 5.1). Inversely, the *pseudo-total* metal concentration can be derived from a critical reactive metal concentration, using the inverse relationship:

$$\log[M]_{AR} = \beta_0 + \beta_1 \cdot \log[M]_{re} + \beta_2 \cdot \log[OM]_s + \beta_3 \cdot \log[clay] \qquad (A7.2b)$$

This transfer function is needed when deriving a critical total metal concentration in either soil or suspended particles from a calculated critical reactive metal concentration. Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 $Mol.l^{-1}$ HNO_3 and Aqua Regia. The dataset consists of large variety of soil types with a relative wide variety in soil properties as the organic matter (median of 4% and 95% of 14%) and clay content (median of 13% and 95% of 36%). The dataset comprises both polluted and unpolluted soils. Results are shown in Table A7.3. Beware that the relationship holds for both M_{AR} and M_{re} in $mg.kg^{-1}$.

Table A7.3 Values for the coefficients β_0-β_3 in the relationships (Eq. A7.2a and A7.2b) between relating reactive, (0.43N HNO_3), and pseudo-total (aqua regia) soil concentrations of Cd and Pb, using a Dutch dataset (Römkens et al., 2004).The relationship hold for both M_{AR} and M_{re} in $mg.kg^{-1}$.

Metal	Relationship	β_0	β_1 $[M]_{re}$	β_2 $[OM]_s$	β_3 [clay]	R^2_{adj}	Se(Y)$^{1)}$
Cd	A7.2a (From AR to Re)	-0.089	1.075	0.022	-0.062	0.96	0.11
	A7.2b (From Re to AR)	0.028	0.877	0.009	0.081	0.96	0.10
Pb	A7.2a (From AR to Re)	-0.263	1.089	0.031	-0.112	0.92	0.16
	A7.2b (From Re to AR)	0.323	0.810	0.035	0.136	0.92	0.13

$^{1)}$ The standard error of the y-estimate on a logarithmic basis

When deriving the total critical metal concentration from a critical reactive metal concentration, using Eq. (A7.2b), it should be kept in mind that the critical soil metal concentrations are frequently higher than ambient soil concentrations, even for polluted soils. Therefore, the transfer function should preferably not be used outside its range of soil metal concentrations. The maximum values for the total (aqua regia extracted) concentrations of Cd and Pb were approximately 40 and 1600 $mg.kg^{-1}$, respectively, whereas the reactive (0.43 $mol.l^{-1}$ HNO_3 extracted) concentrations of Cd and Pb were approximately 20 and 1400 $mg.kg^{-1}$, respectively.

A7.3 Relations between free metal ion activities or concentrations and reactive metal contents

A distinction can be made between transfer functions relating free ion metal activity or concentration in solution (relation 3 in Figure A7.1) or total metal concentration in solution with reactive metal concentrations (relation 6 in Figure A7.1). Groenenberg et al. (2003) showed for metals which form strong complexes with DOC, such as Pb and Cu, the transfer functions with free ion metal activities or concentrations are always much better than the transfer functions with total concentrations. Therefore, the use of free metal activity or free metal concentration relations in combination with a speciation model is recommended. Because this second step introduces additional uncertainty which is not quantified and compared with the extra uncertainty caused by using a model for total concentrations, both relations are nevertheless described in this document.

Transfer functions for free metal ion activities can be divided into transfer functions which (i) directly relate free metal ion activities to reactive metal contents while accounting for the effect of soil properties (further referred as the Q-c or c-Q approach) and (ii) are based on the use of an adsorption constant which is related to soil properties, thus allowing the calculation of free metal ion activities indirectly (further referred as the K_f approach). Results of both approaches are presented below for reasons described in Section A7.1.

Direct transfer functions for free metal ion activities or concentrations

Calculation of free metal ion concentrations from soil reactive metal contents and vice versa

For calibration of direct transfer functions for Cd and Pb, data were drawn from four sources:

- Sauvé et al. (1997). Soil metal and labile Pb in Pb-contaminated soils of various origins. Free Pb concentrations were estimated by measurement of labile Pb using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations. Metal contents in soil were determined using a concentrated HNO_3 extraction.
- Sauvé et al. (2000). Soil metal and labile Cd in Cd-contaminated soils of various origins. Free Cd concentrations were estimated by measurement of labile Cd using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations. Metal contents in soil were determined using a concentrated HNO_3 extraction.
- Weng et al. (2002). Soil metal and free ion concentrations in sandy Dutch soils. Free Cd and Pb concentrations were estimated by the Donnan membrane technique. Metal contents in soil were determined using Aqua Regia extraction.
- Tipping et al. (2003a). Soil metal and free ion concentrations in UK upland soils. Free Cd and Pb were estimated by using the WHAM6 speciation model (Tipping, 1998) to speciate the soil solution. Metal contents in soil were determined using 0.43 $mol.l^{-1}$ HNO_3 extraction.

For the transfer functions derived here we have used the free ion concentration, since some of the data used (Sauvé et al., 1997; Sauvé et al., 2000) express the free ion as a concentration rather than an activity. Actual differences between free activities and concentrations in soil solutions will be small compared to the expected variation in the activity or concentration with soil properties. The data were fitted to the following expression:

$$\log[M]_{free} = a + b\cdot\log[OM]_s + c\cdot pH_{ss} + m\cdot\log[M]_{re} \qquad (A7.3)$$

where:

$[M]_{free}$ = the free metal ion concentration ($mol.l^{-1}$)
$[M]_{re}$ = the reactive metal content in the solid phase ($mol.g^{-1}$)
pH_{ss} = soil solution pH

This is entitled as a c-Q relation (a relation calculating c from Q), where c stands for the free metal ion concentration and Q stands for the reactive soil metal content. Calculated values of the parameters are given in Table A7.4.

Table A7.4 Values for the regression coefficients for the free ion concentration - reactive metal content relationship (Eq. A7.3) and statistical measures R^2 and se(Y) based on results of studies carried out in Canada, the Netherlands and the UK. Values in brackets are the standard errors for the coefficients.

Metal	a	b	c	m	R^2	se(Y)
		$[OM]_s$	pH_{ss}	$\log[M]_{re}$		
Cd	-0.08 (0.65)	-0.60 (0.08)	-0.53 (0.03)	0.60 (0.06)	0.624	0.53
Pb	4.32 (0.49)	-0.69 (0.07)	-1.02 (0.03)	1.05 (0.06)	0.854	0.60

The data mentioned above were also used to calculate Q-c relations (a relation calculating Q from c) according to:

$$\log[M]_{re} = a + b\cdot\log[OM]_s + c\cdot pH_{ss} + m\cdot\log[M]_{free} \qquad \text{(A7.4)}$$

Calculated values of the parameters are given in Table A7.5.

Table A7.5 Values for the regression coefficients for the reactive metal content - free ion concentration relationship (Eq.A7.4) and statistical measures R^2 and se(Y) based on results of studies carried out in Canada, the Netherlands and the UK. Values in brackets are the standard errors for the coefficients.

Metal	a	b	c	m	R^2	se(Y)
		$[OM]_s$	pH_{ss}	$\log[M]_{free}$		
Cd	-6.42 (0.41)	0.64 (0.07)	0.45 (0.04)	0.58 (0.06)	0.507	0.52
Pb	-5.42 (0.21)	0.55 (0.06)	0.70 (0.03)	0.61 (0.03)	0.698	0.45

Use of transfer functions in the manual

In the manual, the direct transfer function for the calculation of the free ion concentration from the soil reactive metal content (the c-Q relation) is used for the calculation of the pH-dependent critical limit functions (see Section 3.2 and Annex 8), in order to express the endpoint metal dose in toxicity experiments as the free ion concentration. The transfer function for the calculation of the soil reactive metal content from the free metal ion concentration (the Q-c relation) is used to calculate the critical SPM-bound metal ($[M]_{SPM\,(crit)}$) in surface waters (see Section 3.2 and Annex 12). The relation was used for this purpose since no calibration data for freshwaters covering a sufficiently wide range of pH were available for parameterisation.

Although the direct transfer functions have presently been used in deriving critical limits for soil drainage water and surface water, improvements are needed since:

- The dataset from which these transfer functions were derived is not consistent. Metal contents in soil were derived using 3 different extraction techniques.
- The coefficient m for the metal content in the relation for Cd is <1 which means that when the equation is written according to a Freundlich equation, n>1. This means that adsorption increases with an increasing concentration.
- Critical concentrations of soil metal ecotox experiments are higher than those used in deriving the transfer functions. This holds specifically for Cd, in which in the maximum metal content in the transfer function dataset (44 $mg.kg^{-1}$) is much lower than in the ecotox data set (2989 $mg.kg^{-1}$). For Pb, the difference is much less (max Pb is 14860 $mg.kg^{-1}$ while ecotox is 16573 $mg.kg^{-1}$).

Transfer functions for adsorption constants for free metal ion activities and total dissolved metal concentrations

Although not yet used in the manual, transfer functions were derived which relate the Freundlich coefficient to soil properties. These transfer functions are also based on the consistent use of reactive soil metal contents and the Freundlich coefficient n is always less than 1, thus accounting for the first two drawbacks of the transfer functions given above. However, as with the other transfer functions, the ranges for maximum metal content for Cd in soil (30 $mg.kg^{-1}$) does by far not meet the maximum metal content of the ecotox experiments (2989 $mg.kg^{-1}$) and this is also, although less pronounced, true for Pb (max is 9660 $mg.kg^{-1}$ while ecotox is 16573 mg.kg-1). The transfer function used is as follows:

$$\mathrm{LogK_f} = a + b\log[\mathrm{OM}]_s + c\log[\mathrm{clay}] + d \cdot \mathrm{pH} + e\log[\mathrm{DOC}]_{ss} \qquad \text{(A7.5)}$$

where:

K_f = the Freundlich constant defined as $Me_{re}/([M]_{ss})^n$ in case of a concentration relationship or as $[M]_{re}/([M]_{free})^n$ in case of an activity relationship
Me_{re} = the reactive metal content in the solid phase ($mol.kg^{-1}$)
$[OM]_s$ = organic matter content (% dw)
[clay] = clay content (% dw)
$[DOC]_{ss}$ = dissolved organic carbon concentration in soil ($mg.l^{-1}$)
n = Freundlich exponent

The DOC term is only used for total concentration relations. For free metal ion activity relations this term is not needed because in that case complexation with DOC is accounted for.

Free metal ion activities (M_{free}) or total metal concentrations in the soil solution (M_{ss}) can be calculated from reactive metal contents in the soil according to:

$$\log[M]_{free} = \frac{\log[M]_{re} - \log K_f}{n} \quad \text{(A7.6a) or} \quad \log[M]_{ss} = \frac{\log[M]_{re} - \log K_f}{n} \qquad \text{(A7.6b)}$$

where:

$[M]_{ss}$ = total metal concentration in the soil solution ($mmol.l^{-1}$)
$[M]_{free}$ = free metal concentration in the soil solution ($mmol.l^{-1}$)

Table A7.6 gives the parameters for the free ion metal activity relation derived from a combined UK-NL dataset (Groenenberg et al., 2004). The free ion concentrations used to derive the functions were estimated from total concentrations and soil solution chemistry data, using the WHAM/Model VI chemical speciation model as described in Tipping et al. (2003b). Metal contents in soils were determined using a 0.43 $mol.l^{-1}$ HNO_3 extraction No regression coefficients are given for the clay content because clay content data are absent in the UK dataset. Maximum Cd and Pb concentrations observed in the datasets used to derive these transfer functions were 44.9 $mg.kg^{-1}$ for Cd and 9660 $mg.kg^{-1}$ for Pb.

Table A7.6 Values for the regression coefficients for the free Cd and Pb activity - reactive Cd and Pb metal content (measured in 0.43M HNO_3 *extract) relationship (Eq. A7.6a) and statistical measures* R^2 *and se(Y) based on results of studies carried out in the Netherlands and the UK (after Groenenberg et al., 2003). Values in brackets are the standard errors for the coefficients.*

Metal	a	b	d	n	R^2	se(Y)
		(OM)	(pH)			
Cd	-2.82 (0.04)	0.68 (0.02)	0.30 (0.01)	0.57	0.82	0.30
Pb	-1.37 (0.09)	0.98 (0.04)	1.02 (0.02)	1.0	0.90	0.60

Table A7.7 gives the parameters for the total dissolved metal concentration relation derived from a Dutch dataset (Römkens et al., 2004). Relationships are given, with and without DOC, since the latter value is generally hard to be obtained on a regional scale In the case of Cd, the additional explaining influence of DOC was very low, but for Pb, DOC has a marked influence. Maximum Cd and Pb concentrations observed in the datasets used to derive these transfer functions were 20.3 mg.kg^{-1} for Cd and 1572 mg.kg^{-1} for Pb.

Table A7.7 Values for the regression coefficients for the total dissolved Cd and Pb concentration - reactive Cd and Pb metal content (measured in 0.43M HNO_3 *extract) relationship (Eq. A7.6b) and statistical measures* R^2 *and se(Y) based on results of studies carried out in the Netherlands (Römkens et al., 2004).*

Metal	a	b	c	d	e	n	R^2	se(Y)
		(OM)	(Clay)	(pH)	(DOC)			
Cd	-4.75	0.61	0.29	0.26	-0.05	0.54	0.80	0.33
	-4.85	0.58	0.28	0.27	-	0.54	0.79	0.33
Pb	-2.38	0.95	0.07	0.22	-0.23	0.73	0.59	0.55
	-2.96	0.83	0.02	0.25	-	0.68	0.57	0.55

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Appendix 8 Calculation of critical free Cd and Pb concentrations in soil drainage water related to ecotoxicological effects

Possible critical limits for metal concentrations for ecotoxicological effects

Critical limits related to the ecotoxicological effects of Cd and Pb are related to impacts on soil micro-organisms, plants and invertebrates for both agricultural land (arable land, grassland) and non-agricultural land (forests, natural non-forested ecosystems) (see Table 1 in the main text). Such limits can be related to either: (i) critical soil metal concentrations or (ii) critical free metal ion activities or concentrations in soil solution.

In the first case, such limits can directly be based on available No Observed Effect Concentrations (NOEC) for metals in soil related to adverse impacts on the mentioned organisms. When using critical soil metal contents, the critical total dissolved metal concentrations needed in the critical load calculation have to be calculated from those critical limits, using a solid-solution transfer function. In the second case, solid-solution transfer functions are only used to translate NOECs for reactive metals in soil solids, reported from ecotoxicological experiments, to free metal ion activities. The critical load calculations are then easier to conduct, although they still do require the use of a chemical speciation model to derive critical total dissolved metal concentrations from critical free metal ion activities.

In line with the outcome of the Expert meetings in Berlin (2002) and Strausberg (2003), there are strong arguments to prefer the second approach because it can be assumed that ecotoxicological effects for micro organisms and plants are related to the free ion, and the same is true for most soil invertebrates.

Calculation of critical free metal ion concentrations as a function of pH

The theoretical basis for calculating critical limits for free metal ion concentrations is that for organisms whose metal uptake is directly from their surrounding medium (soil water in the case of soil organisms), the concentration of the free metal ion (Cd^{2+}, Pb^{2+}) provides the best guide to bioavailability and thereby toxic effects. However, the bioavailability of the metal also depends upon the concentrations of other cations, such as H^+, Na^+, Ca^{2+} (Lofts et al., 2004). A theoretical expression for the toxicity of the metal may be given as:

$$\log[M]_{free(toxic)} = \alpha \cdot pH_{ss} + \gamma \tag{A8.1}$$

$[M]_{free(toxic)}$ = the concentration of free ion exerting a given level of toxic effect relative to a control soil of the same pH.

pH_{ss} = the pH of the soil solution.

Equation (A8.1) refers to the effect of a metal upon a single function (i.e. growth, reproduction) of a single organism. Since the concentrations of cations such as Na^+ and Ca^{2+} are expected to co-vary with pH across soils, the combined effects of these ions on toxicity may be expressed in a single pH term. In applying the equation to toxicity data for multiple species to calculate a critical limit, firstly a relationship between the median toxic metal and pH_{ss} is derived for the entire toxicity dataset, by regression:

$$\log[M]_{\mathrm{free(toxic,median)}} = \alpha_{EC} \cdot pH_{ss} + \gamma_{EC} \tag{A8.2}$$

Then, the distribution of regression residuals is analysed to derive the 95%ile, producing a function for a critical limit to protect 95% of ecosystem species and functions against adverse effect:

$$\log[M]_{\mathrm{free(crit)}} = \alpha_{EC} \cdot pH_{ss} + \gamma_{EC} + \delta = \alpha_{EC} \cdot pH_{ss} + \theta \tag{A8.3}$$

In practice, since $\log[M]_{free}$ values are derived from transfer functions including pH_{ss} as a variable, it is statistically invalid to regress calculated $\log[M]_{free}$ values against pH_{ss}. Therefore, an algebraically equivalent method is used. Combining the theoretical toxicity equation (Equation A8.1) with a transfer function directly relating the free metal ion concentration to the reactive soil metal content (see also Annex 7, Equation A.7.3):

$$\log[M]_{free} = a + b\cdot\log[OM]_s + c\cdot pH_{ss} + m\cdot\log[M]_{re} \tag{A.8.4}$$

and rearranging yields:

$$\log[M]_{re} + (b/m)\cdot\log[OM]_s = \varphi\cdot pH_{ss} + \psi \tag{A8.5}$$

Regressing Equation (A8.5) against toxicity data yields values of the unknown coefficients φ and ψ. Then by taking the 95%ile of the residuals in $\log[M]_{re}$ + $(b/c)\cdot\log[OM]_s$ an expression for the critical soil metal can be derived:

$$\log[M]_{\mathrm{re(crit)}} + (b/m)\cdot\log[OM]_s = \varphi\cdot pH_{ss} + \psi + \varepsilon \tag{A.8.6}$$

where ε is the 95%ile of the regression residuals. Values of the parameters α_{EC} and θ in the critical limit function can then be calculated:

$$\alpha_{crit} = c + m\cdot\phi \tag{A.8.7}$$

$$\theta_{crit} = a + m\cdot(\psi + \varepsilon) \tag{A.8.8}$$

Ecotoxicity data used and results obtained

The recommended critical limit functions for free ionic Cd, Pb, Cu and Zn in soil solution are based on NOEC and EC_{10} endpoints for: (i) organisms which are exposed to the metal via the soil solution (plants, micro-organisms and soft bodied soil invertebrates), (ii) accompanied by data on soil properties (pH and organic matter content) to allow evaluation using harmonised transfer functions and (iii) evaluated by a statistical approach deriving limits based on a 95% protection level, as described before. In the approach it is assumed that apart from the hard bodied invertebrates, where soil ingestion is the major intake route, soil solution is the major pathway for all soil organisms and plants. This assumption is certainly valid for plants and micro-organisms and for invertebrates living in soil water, such as nematodes, but is also a reliable assumption for soft bodied invertebrates living in soil, such as earthworms (e.g. Saxe et al., 2001). The use of transfer functions is based on the assumption that effects data from ecotoxicological investigations in laboratory can be related to a "reactive" heavy metal concentration in the soil, since the heavy metal applied in such tests is in a well available form.

In order to provide as far as possible consistency between the critical limits derived here and those derived under parallel EU Risk Assessment procedures for soils, the databases used were drawn from these procedures. The only modification of the databases required was the removal of those endpoints for which the soil organic matter content was not provided. Metal concentrations in the control soils were not considered in deriving toxic endpoints, i.e. the added metal endpoint was used. This was the most suitable approach since the transfer functions that were applied to derive free metal ion concentrations are based on reactive soil metal contents. Added metal is likely to be reactive whereas this is only partly true for the metal concentrations already occurring in the control soils Furthermore, the toxic endpoint (NOEC/EC10) is always calculated by considering the effect on the organism relative to the effect in the control soil, i.e. the soil containing the background metal concentration. So the effect endpoint is effectively expressed as an added metal dose.

The ecotoxicological datasets used to derive critical free metal ion concentrations for cadmium and lead as a function of pH are summarized in Table A8.1.

Table A8.1. Summary of ecotoxicological datasets used to derive critical free metal ion concentrations for cadmium and lead as a function of pH

Receptors considered	Cadmium	Lead
Plants		
Studies	6	4
Species/Groups	7	5
Endpoints	26	5
Invertebrates		
Studies	7	6
Species/Groups	5	3
Endpoints	13	8
Microbial Processes		
Studies	9	14
Processes	4	10
Endpoints	18	35
Total		
Studies	22	24
Species/Processes	16	18
Endpoints	57	48

The ranges in the chemical parameters in the toxicological test soils for both metals are summarized in Table A8.2.

Table A8.2. Ranges of chemical parameters in the toxicological test soils for cadmium and lead. Values in brackets are the medians of the parameters.

Metal	pH	OM (%)	$M_{soil,toxic}$ (mg/kg soil)
Cd	3.2-7.9 (6.1)	1.2-80 (4.2)	1.8-2989 (29)
Pb	3.7-7.9 (6.0)	1.0-80 (6.2)	10-16573 (767)

The derived critical limit functions were (see also main text):

$$\log[Cd]_{free(crit)} = -0.32 \cdot pH_{ss} - 6.34 \quad (A.8.9)$$

$$\log[Pb]_{free(crit)} = -0.91 \cdot pH_{ss} - 3.80 \quad (A.8.10)$$

References

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Appendix 9 Calculation of critical total Cd and Pb concentrations in soil drainage water related to ecotoxicological effects

Following several workshops, wide-ranging discussions, and analysis of published toxicity data, the “Expert Panel on Critical Loads of Heavy Metals” has decided to recommend the use of metal free ion concentrations (M_{free}) to define the critical metal contents in soils. In this approach, the critical limits depend upon pH, according equations of the form:

$$\log M_{free,crit} = \alpha_{crit}\, pH + \gamma_{cri} \tag{A9.1}$$

which are referred to as critical limit functions (Lofts et al., 2004). To calculate critical loads for soils from the critical limit functions, it necessary to know $M_{tot,SDW,crit}$ - the total concentration of metal in soil drainage water that corresponds to the free ion critical limit. Knowledge of $M_{tot,SDW,crit}$ permits calculation of the leaching loss of the metal at the Critical Limit, by combination with the run-off.

The metal in soil drainage water comprises the following metal species:

Metal free ion	M^{2+}
Inorganic complexes	MOH^+, $MHCO_3^+$, MCl^+ etc
Metal bound to DOM	M-DOM
Metal bound to SPM	M-SPM

Here, DOM is dissolved organic matter, and SPM is suspended particulate matter. The term $M_{tot,SDW,crit}$ does not refer simply to dissolved components (M^{2+}, inorganic complexes, and M-DOM), but also includes M-SPM. Thus the calculation includes the possibility of metal being leached from the soil in association with particulates.

Given the activity or concentration of M^{2+}, the concentrations of the other metal species can be estimated by applying an equilibrium speciation model. The calculation has to take into account the dependence of the metal speciation on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe (Tipping et al., 2002; Tipping, 2004). In the present work, a customised program (W6-MTC), based on the Windermere Humic Aqueous Model, Version 6 (WHAM6, Tipping, 1994, 1998) was used.

This annex covers the following topics:
- Details of the calculation of $M_{tot,SDW,crit}$ using W6-MTC
- Example calculations of $M_{tot,SDW,crit}$
- Creation of input files for the W6-MTC program
- Look-up tables of $M_{tot,SDW,crit}$ values including a range of values for pCO_2 (Tables 3 and 4)

Colleagues who wish to calculate $M_{tot,SDW,crit}$ values for their own soils can interpolate manually within the Look-up Tables. Alternatively, they can send suitable input files to Ed Tipping, who will perform the computations with W6-MTC.

Calculation of the critical total metal concentration in soil drainage water

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

1. The inputs to the calculation are: pH, % soil organic matter, pCO_2, [DOC] in $mg.l^{-1}$, and [SPM] in $mg.l^{-1}$. The relevant concentrations of DOC and SPM are those in water draining from the soil zone of interest. The calculations refer to a temperature of 10°C.
2. The concentration ($g.l^{-1}$) of "active" fulvic acid (FA) is obtained by multiplying [DOC] in $mg.l^{-1}$ by $1.3x10^{-3}$. This conversion factor is based on application of the WHAM6 model to field and laboratory data for waters and soils involving Al (Tipping et al., 1991; Tipping et al., 2002), Cu (Dwane & Tipping, 1998; Vulkan et al., 2000; Bryan et al., 2002), and Cd (Tipping, 2002).
3. The critical free ion concentration - M_{free} - is computed from the soil pH and the Critical Limit Function (equation A8.9; A8.10).
4. The activity of Al^{3+} is calculated from the pH, using equations derived by Tipping (2004). One equation applies to soils low in Al, and high in organic matter. A second equation applies to high-Al mineral soils. In the present exercise, soils with less than 20% organic matter are considered to be high in Al, and those with more than 20% organic matter are considered low in Al.
5. The activity of Fe^{3+} is obtained by assuming a solubility product at 25°C of $10^{2.5}$ and an enthalpy of reaction of -107 $kJ.mol^{-1}$ (Tipping et al., 2002).
6. As a starting-point, Na is assumed to be present in the soil solution at a concentration of 0.001 $mol.l^{-1}$, balanced by equal concentrations, in equivalents, of the three major acid anions Cl^-, NO_3^- and SO_4^{2-}. Thus, the concentrations of Cl^- and NO_3^- are each 0.000333 $mol.l^{-1}$, while that of SO_4^{2-} is 0.000167 $mol.l^{-1}$.
7. The concentration of M^{2+} and the activities of Al^{3+} and Fe^{3+} are fixed at the values obtained in steps 2-4, and the activity of H^+ is fixed from the pH. The WHAM6 model is then run to make an initial computation of inorganic solution speciation and metal binding by FA. As part of the computation, concentrations of carbonate species are obtained from pH and pCO_2. Possible metal inorganic complexes are with OH^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}.
8. If the result from Step 7 gives an excess of positive charge, which occurs for acid solutions, the total concentrations of NO_3^- and SO_4^{2-} are increased to compensate. Then the WHAM6 program is run again.
9. If the result from Step 7 gives an excess of negative charge (less acid to alkaline solutions), it is assumed that Ca provides the required additional positive charge. The WHAM6 model is run iteratively to find the total concentration of Ca that gives the correct charge balance.
10. The binding of metal to SPM is computed, by applying multiple regression equations ("transfer functions") derived for whole soils. These equations describe metal binding as a function of free ion concentration, pH, and organic matter. The transfer function used here is Equation (A7.4) with the parameters mentioned in Table A7.5.
11. The concentrations of dissolved inorganic metal species (including M^{2+}), metal bound to dissolved organic matter, and metal bound to SPM, are added together to obtain $M_{tot,SDW,crit}$.

Example calculations of critical total metal concentration in soil drainage water

Table A9.1 shows input data and the results of example calculations for five soil waters, representing a range of soil chemistries. The features of the Table are:

Lines 1-5	Input data.
Line 3	30× atmospheric for pCO_2 is typical (Freeze & Cherry, 1979; Drever, 1982), in Potsdam we agreed on 15 x atmospheric for consistency with the S+N Manual chapters, at least we should explain deviations.
Lines 6	Activity of Al^{3+}, computed from empirical equations (Tipping, 2004)
Line 7	Activity of Fe^{3+}, from $Fe(OH)_3$ solubility
Lines 8-9	Activities of carbonate species, from pH and pCO_2
Line 10	Total [Na], fixed
Line 11	Total [Ca], adjusted to achieve charge-balance for non-acid solutions
Line 12	Total [Cl], fixed
Line 13	Total $[NO_3]$ adjusted above 3.3E-04M to achieve charge balance in acid solutions
Line 14	Total $[SO_4]$ adjusted above 1.7E-04M to achieve charge balance in acid solutions
Line 15	Saturation index of $CaCO_3$ - if > 0, solution is oversaturated
Line 16	Critical concentration of Cd^{2+}
Lines 17-20	Concentrations of inorganic solution complexes of Cd
Line 21	Sum of inorganic Cd species concentrations
Line 22	Concentration of Cd bound to dissolved organic matter (fulvic acid)
Line 23	Concentration of Cd bound to suspended particulate matter
Line 24	Critical total Cd in soil solution
Line 25	Critical concentration of Pb^{2+}
Lines 26-29	Concentrations of inorganic solution complexes of Pb
Line 30	Sum of inorganic Pb species concentrations
Line 31	Concentration of Pb bound to dissolved organic matter (fulvic acid)
Line 32	Concentration of Pb bound to suspended particulate matter
Line 33	Critical total Pb in soil solution

The main factors governing $M_{tot,SDW,crit}$ are as follows:

- The pH dependence of the critical free ion concentration (equation 1)
- Complexation of M^{2+} by carbonate species, increasing with pH and dependent upon pCO_2
- Complexation of M^{2+} by dissolved organic matter, which tends to increase with pH, but is subject to competition by Al, Ca and Fe^{III} species
- Binding of M^{2+} by suspended particulate matter

The saturation index of $CaCO_3$ is computed to draw attention to the choice of input values for high-pH soils. If the pCO_2 is fixed at a certain value, the maximum soil pH is limited by $CaCO_3$ precipitation, unless oversaturation is allowed. Thus in example S4, the soil solution is considerably oversaturated with respect to $CaCO_3$. This means that competition by Ca for trace metal binding is greater than would be the case if $CaCO_3$ solubility control were operating.

Table A9.1 Example soil aqueous phases and aqueous phase compositions

			S1	S2	S3	S4	S5
1	pH		4	6	6	8	8
2	% OM of soil	%	50	10	10	10	10
3	pCO_2	× atmospheric	30	30	30	30	1
4	DOC	$mg.l^{-1}$	50	15	15	5	5
5	SPM	$mg.l^{-1}$	0	0	50	0	0
6	$\{Al^{3+}\}$	$mol.l^{-1}$	9.6E-07	9.4E-09	9.4E-09	9.4E-15	9.4E-15
7	$\{Fe^{3+}\}$	$mol.l^{-1}$	3.0E-09	3.0E-15	3.0E-15	3.0E-21	3.0E-21
8	$\{HCO_3^-\}$	$mol.l^{-1}$	1.9E-06	1.9E-04	1.9E-04	1.9E-02	6.5E-04
9	$\{CO_3^{2-}\}$	$mol.l^{-1}$	6.3E-13	6.3E-09	6.3E-09	6.3E-05	2.1E-06
10	Tot-Na	$mol.l^{-1}$	1.0E-03	1.0E-03	1.0E-03	1.0E-03	1.0E-03
11	Tot-Ca	$mol.l^{-1}$	0	1.3E-04	1.3E-04	1.3E-02	3.6E-04
12	Tot-Cl	$mol.l^{-1}$	3.3E-04	3.3E-04	3.3E-04	3.3E-04	3.3E-04
13	Tot-NO_3	$mol.l^{-1}$	3.4E-04	3.3E-04	3.3E-04	3.3E-04	3.3E-04
14	Tot-SO_4	$mol.l^{-1}$	1.7E-04	1.7E-04	1.7E-04	1.7E-04	1.7E-04
15	SI $CaCO_3$		-	-3.8	-3.8	2.0	-0.8
16	$[Cd^{2+}]$	$mol.l^{-1}$	4.2E-08	5.8E-09	5.8E-09	8.0E-10	8.0E-10
17	$[CdOH^+]$	$mol.l^{-1}$	9.2E-15	1.3E-13	1.3E-13	1.3E-12	1.7E-12
18	$[CdCl^+]$	$mol.l^{-1}$	1.2E-09	1.5E-10	1.5E-10	1.3E-11	2.0E-11
19	$[CdSO_4]$	$mol.l^{-1}$	1.3E-09	1.6E-10	1.6E-10	5.8E-12	2.0E-11
20	$\Sigma[Cd\text{-}CO_3]$	$mol.l^{-1}$	3.1E-11	4.2E-10	4.2E-10	5.7E-09	2.7E-10
21	[Cd-inorg]	$mol.l^{-1}$	4.2E-08	6.4E-09	6.4E-09	6.5E-09	1.1E-09
22	[Cd-FA]	$mol.l^{-1}$	1.4E-08	6.9E-09	6.9E-09	1.4E-10	1.7E-09
23	[Cd-SPM]	$mol.l^{-1}$	0	0	1.1E-09	0	0
24	$[M]_{tot,SDW(crit)}$ Cd	$mol.l^{-1}$	5.6E-08	1.3E-08	1.4E-08	6.7E-09	2.8E-09
25	$[Pb^{2+}]$	$mol.l^{-1}$	7.1E-09	1.6E-10	1.6E-10	3.4E-12	3.4E-12
26	$[PbOH^+]$	$mol.l^{-1}$	3.7E-13	8.0E-13	8.0E-13	1.3E-12	1.7E-12
27	$[PbCl^+]$	$mol.l^{-1}$	5.6E-11	1.2E-12	1.2E-12	1.6E-14	2.4E-14
28	$[PbSO_4]$	$mol.l^{-1}$	5.2E-10	1.1E-11	1.1E-11	5.9E-14	2.1E-13
29	$\Sigma\ [Pb\text{-}CO_3]$	$mol.l^{-1}$	6.0E-14	1.3E-11	1.3E-11	1.8E-09	9.2E-11
30	[Pb-inorg]	$mol.l^{-1}$	7.3E-09	1.8E-10	1.8E-10	7.0E-10	9.7E-11
31	[Pb-FA]	$mol.l^{-1}$	1.1E-08	1.8E-09	1.8E-09	7.0E-10	4.6E-09
32	[Pb-SPM]	$mol.l^{-1}$	0	0	5.2E-09	0	0
33	$[M]_{tot,SDW(crit)}$ Pb	$mol.l^{-1}$	1.9E-08	2.0E-09	7.2E-09	3.2E-09	5.2E-09

Creation of input files for the W6-MTC program

Colleagues who wish values of $M_{tot,SDW,crit}$ to be calculated should submit files to Ed Tipping (ET@CEH.AC.UK). The data should simply be entered into an Excel workbook, under the following headings.

code	pH	% OM	pCO_2	DOC	SPM

code	the user's identifier of the site
pH	soil solution pH
% OM	the soil organic matter content
pCO_2	the soil pCO_2 expressed as a multiple of the atmospheric value
DOC	concentration of dissolved organic carbon in $mg.l^{-1}$
SPM	concentration of suspended particulate matter in $mg.l^{-1}$.

- Please see the notes on the Look-up Tables A9.2 and A9.3 (below) regarding the selection of pH and pCO_2 values.
- Land use dependent default values for DOC are provided in chapter 3.2.3. and Annex 11. If data on DOC concentration are not included in the database sent, a value of 15 $mg.l^{-1}$ will be assumed for soils with % OM < 20%, and a value of 40 $mg.l^{-1}$ for soils with % OM ≥ 20%.
- If data on pCO_2 are not available, a value of 15× atmospheric will be assumed.
- If data on SPM are not available, a value of zero will be assumed.

Look-up tables of Mtot,SDW,crit values

Values of $M_{tot,SDW,crit}$ have been calculated for a range of soil conditions, and these are presented in Tables A9.2 and A9.3. The Tables can be used to estimate the total dissolved soil metal concentrations needed to compute Critical Loads. When using the Tables, attention should be paid to the correct choice of pH and pCO_2. The best pH value should be that estimated for the soil solution *in situ*. A table based on the mean value of $pCO_2 = 15$ is provided in chapter 3.2.3 of this background document.

- One way in which the measured soil pH values may differ from the *in situ* values is because it refers to a "standard" extract (e.g. $CaCl_2$ or KCl). In this case the measured value will be **lower** than the true value, to an extent depending upon the pH itself, and also soil properties.
- Another source of error arises from the difference in pCO_2 between the solution used for pH measurement and the *in situ* soil solution. This leads to measured pH values that are **higher** than the field values, the differences being greatest at higher pH.
- The Look Up Tables contain a column showing the saturation index of $CaCO_3$. If this number is positive, the solution is calculated to be oversaturated with respect to $CaCO_3$. This means that the dissolved Ca concentration is greater than could occur if it were controlled by solid-phase $CaCO_3$. If oversaturation of $CaCO_3$ is to be avoided, the pH and pCO_2 must be chosen accordingly. The following graph shows the relationship between pH and pCO_2 in the presence of $CaCO_3$. To avoid oversaturation of $CaCO_3$, the choice of pH for a given pCO_2 should not exceed the plotted value.

Table A9.2 Look-up table to derive values of the total critical Cd concentrations in soil drainage water $Cd_{tot,SDW,crit}$

OM	pCO_2	SPM	DOC	$[Cd]_{tot,SDW(crit)}$ (mg.m^{-3})									
				pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
%dw	× air	mg.l^{-1}	mg.l^{-1}	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
10	3	0	0	4.04	2.79	1.92	1.33	0.93	0.66	0.47	0.35	0.28	0.30
10	3	0	5	4.04	2.80	1.93	1.38	1.03	1.15	1.39	0.97	0.71	0.50
10	3	0	15	4.04	2.81	1.97	1.47	1.23	2.01	2.83	2.10	1.57	0.91
10	3	0	50	4.05	2.86	2.11	1.80	1.89	4.48	6.26	5.37	4.43	2.32
10	3	0	100	4.07	2.94	2.36	2.29	2.81	7.33	9.77	9.14	8.20	4.30
10	3	50	0	4.05	2.82	1.95	1.38	0.99	0.73	0.57	0.49	0.47	0.57
10	3	50	5	4.06	2.82	1.96	1.42	1.09	1.23	1.50	1.11	0.91	0.77
10	3	50	15	4.06	2.84	2.00	1.51	1.29	2.09	2.94	2.25	1.77	1.18
10	3	50	50	4.07	2.89	2.14	1.84	1.95	4.56	6.37	5.51	4.63	2.59
10	3	50	100	4.08	2.96	2.39	2.33	2.87	7.41	9.87	9.29	8.40	4.57
10	30	0	0	4.04	2.79	1.92	1.34	0.96	0.70	0.55	0.53	0.68	1.22
10	30	0	5	4.04	2.80	1.94	1.38	1.05	1.03	0.81	0.68	0.76	1.25
10	30	0	15	4.04	2.81	1.97	1.48	1.24	1.67	1.30	0.98	0.92	1.31
10	30	0	50	4.05	2.86	2.12	1.81	1.88	3.68	2.95	2.03	1.46	1.53
10	30	0	100	4.07	2.94	2.36	2.29	2.77	6.16	5.11	3.52	2.24	1.84
10	30	50	0	4.06	2.82	1.95	1.38	1.01	0.78	0.66	0.67	0.88	1.49
10	30	50	5	4.06	2.82	1.97	1.43	1.11	1.11	0.91	0.83	0.96	1.52
10	30	50	15	4.06	2.84	2.00	1.52	1.30	1.75	1.41	1.13	1.11	1.58
10	30	50	50	4.07	2.89	2.15	1.85	1.94	3.76	3.05	2.18	1.66	1.80
10	30	50	100	4.08	2.96	2.39	2.33	2.83	6.24	5.21	3.66	2.44	2.11
50	3	0	0	3.98	2.74	1.91	1.33	0.93	0.66	0.47	0.35	0.28	0.30
50	3	0	5	4.02	2.80	2.01	1.52	1.27	1.17	1.39	0.97	0.71	0.50
50	3	0	15	4.11	2.94	2.24	1.89	1.88	2.06	2.83	2.10	1.57	0.91
50	3	0	50	4.45	3.48	3.01	3.07	3.76	4.59	6.26	5.37	4.43	2.32
50	3	0	100	5.06	4.29	4.08	4.61	6.07	7.48	9.77	9.14	8.20	4.30
50	3	50	0	4.03	2.81	2.00	1.45	1.10	0.88	0.77	0.76	0.84	1.06
50	3	50	5	4.07	2.87	2.10	1.64	1.43	1.39	1.69	1.38	1.28	1.27
50	3	50	15	4.16	3.00	2.32	2.01	2.04	2.28	3.14	2.51	2.13	1.67
50	3	50	50	4.50	3.54	3.10	3.19	3.92	4.81	6.56	5.78	4.99	3.08
50	3	50	100	5.11	4.35	4.16	4.73	6.23	7.71	10.07	9.56	8.76	5.07
50	30	0	0	3.98	2.74	1.91	1.34	0.96	0.70	0.55	0.53	0.68	1.22
50	30	0	5	4.02	2.81	2.02	1.53	1.25	1.04	0.81	0.68	0.76	1.25
50	30	0	15	4.11	2.94	2.24	1.89	1.82	1.70	1.30	0.98	0.92	1.31
50	30	0	50	4.45	3.48	3.01	3.05	3.60	3.75	2.95	2.03	1.46	1.53
50	30	0	100	5.06	4.29	4.07	4.57	5.82	6.27	5.11	3.52	2.24	1.84
50	30	50	0	4.03	2.81	2.00	1.46	1.12	0.93	0.85	0.94	1.24	1.98
50	30	50	5	4.07	2.87	2.10	1.64	1.41	1.26	1.11	1.09	1.32	2.01
50	30	50	15	4.16	3.00	2.32	2.00	1.98	1.92	1.61	1.39	1.48	2.08
50	30	50	50	4.50	3.54	3.09	3.17	3.76	3.97	3.25	2.44	2.02	2.30
50	30	50	100	5.11	4.35	4.16	4.69	5.99	6.49	5.41	3.93	2.81	2.61

Table A9.3 Look-up table to derive values of the total critical Pb concentrations in soil drainage water $Pb_{tot,SDW,crit}$

OM	pCO$_2$	SPM	DOC	[Pb]$_{tot,SDW(crit)}$ (mg m^{-3})									
				pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
%dw	× air	mg.l^{-1}	mg.l^{-1}	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
10	3	0	0	34.72	11.42	3.83	1.32	0.46	0.16	0.06	0.04	0.06	0.17
10	3	0	5	34.80	11.55	4.02	1.58	0.77	1.00	1.44	2.13	2.06	2.32
10	3	0	15	34.96	11.83	4.42	2.09	1.39	2.48	3.96	6.14	6.03	6.60
10	3	0	50	35.53	12.82	5.83	3.92	3.45	6.81	11.74	18.84	19.56	21.55
10	3	0	100	36.33	14.25	7.92	6.52	6.27	12.11	21.85	35.05	38.10	42.72
10	3	50	0	37.33	14.51	7.43	5.53	5.40	5.96	6.88	8.07	9.43	11.16
10	3	50	5	37.41	14.65	7.62	5.79	5.71	6.81	8.25	10.12	11.43	13.31
10	3	50	15	37.57	14.93	8.02	6.31	6.34	8.28	10.76	14.12	15.41	17.60
10	3	50	50	38.13	15.91	9.43	8.14	8.40	12.62	18.55	26.83	28.93	32.54
10	3	50	100	38.94	17.34	11.52	10.75	11.21	17.92	28.66	43.04	47.47	53.71
10	30	0	0	34.72	11.41	3.83	1.31	0.46	0.17	0.10	0.15	0.42	1.39
10	30	0	5	34.80	11.55	4.02	1.57	0.76	0.78	0.99	1.04	1.27	1.99
10	30	0	15	34.96	11.83	4.42	2.09	1.37	1.94	2.76	2.81	2.96	3.20
10	30	0	50	35.52	12.82	5.83	3.91	3.38	5.73	8.86	8.98	8.90	7.44
10	30	0	100	36.33	14.25	7.92	6.50	6.15	10.65	17.32	17.72	17.37	13.50
10	30	50	0	37.33	14.50	7.42	5.53	5.41	6.01	6.90	8.14	9.79	12.38
10	30	50	5	37.41	14.64	7.62	5.79	5.72	6.58	7.80	9.03	10.64	12.98
10	30	50	15	37.57	14.92	8.01	6.31	6.32	7.75	9.57	10.80	12.33	14.19
10	30	50	50	38.13	15.91	9.42	8.14	8.33	11.53	15.66	16.96	18.27	18.43
10	30	50	100	38.94	17.34	11.51	10.73	11.09	16.45	24.13	25.70	26.73	24.49
50	3	0	0	32.85	11.08	3.81	1.32	0.46	0.16	0.06	0.04	0.06	0.17
50	3	0	5	34.36	12.59	5.32	2.75	1.68	1.03	1.44	2.13	2.06	2.32
50	3	0	15	37.41	15.65	8.37	5.54	3.93	2.56	3.96	6.14	6.03	6.60
50	3	0	50	48.44	26.65	18.71	14.51	10.79	7.04	11.74	18.84	19.56	21.55
50	3	0	100	65.13	42.23	32.89	26.24	19.31	12.51	21.85	35.05	38.10	42.72
50	3	50	0	39.22	18.52	12.52	11.53	12.44	14.23	16.59	19.51	22.76	26.80
50	3	50	5	40.73	20.03	14.03	12.97	13.66	15.11	17.94	21.49	24.77	28.95
50	3	50	15	43.78	23.08	17.08	15.76	15.91	16.62	20.45	25.49	28.74	33.24
50	3	50	50	54.80	34.07	27.44	24.73	22.77	21.10	28.24	38.20	42.27	48.18
50	3	50	100	71.49	49.67	41.64	36.46	31.29	26.57	38.35	54.41	60.81	69.35
50	30	0	0	32.85	11.07	3.80	1.32	0.46	0.17	0.10	0.15	0.42	1.39
50	30	0	5	34.36	12.59	5.32	2.73	1.57	0.80	0.99	1.04	1.27	1.99
50	30	0	15	37.41	15.65	8.36	5.48	3.66	2.00	2.76	2.81	2.96	3.20
50	30	0	50	48.43	26.65	18.67	14.35	10.22	5.91	8.86	8.98	8.90	7.44
50	30	0	100	65.13	42.21	32.82	25.99	18.51	11.00	17.32	17.72	17.37	13.50
50	30	50	0	39.22	18.51	12.51	11.53	12.47	14.32	16.59	19.50	23.12	28.02
50	30	50	5	40.73	20.03	14.03	12.95	13.55	14.85	17.49	20.39	23.97	28.63
50	30	50	15	43.78	23.08	17.07	15.71	15.64	16.06	19.26	22.16	25.67	29.84
50	30	50	50	54.80	34.07	27.40	24.56	22.20	19.98	25.36	28.33	31.60	34.08
50	30	50	100	71.49	49.65	41.58	36.20	30.49	25.06	33.82	37.07	40.07	40.13

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Appendix 10 Calculation of a critical steady state pH, assessment of actual pH values and relationships between various pH estimates

Calculation of a critical steady state pH

The critical pH at steady state was calculated for sandy soils and loess soils in view of the impact of a low pH on root uptake of Al. The critical H concentration was derived from the critical Al concentration using empirical equilibrium relations between Al and H in the soil solution according to:

$$[\mathrm{H}]_{\mathrm{crit}} = \left(\frac{[\mathrm{Al}]_{\mathrm{crit}}}{\mathrm{K}_{\mathrm{emp}}} \right)^{1/n} \qquad \text{(A10.1)}$$

where $[\mathrm{H}]_{\mathrm{crit}}$ and $[\mathrm{Al}]_{\mathrm{crit}}$ are the critical H and Al activities ($\mathrm{mol.l^{-1}}$), $\mathrm{K}_{\mathrm{emp}}$ is an empirical equilibrium constant and n is the reaction stoichiometric constant (Van der Salm & de Vries, 2001). Values used for $\mathrm{K}_{\mathrm{emp}}$ and n are given below in Table A10.1.

Table A10.1 Overview of the values of K_{emp} and n used to calculate a critical Al concentration.

Soil type	Depth (cm)	Total Al concentrations log *K*	n	R^2_{adj}	N	Free Al^{3+} concentrations log *K*	n	R^2_{adj}	N
All	Humus layer[1]	-3.28	0.29	25.0	275	-1.03	1.17	53.1	275
Sandy soils	0-10	-2.81	0.34	46.2	275	3.54	2.26	86.4	274
	10-30	-2.58	0.33	44.2	376	5.59	2.68	88.6	377
	30-100	-2.64	0.28	30.8	266	7.88	3.13	95.4	271
Loess soils	0- 10	-3.62	0.11	6.8	45	-0.38	1.04	60.9	45
	10- 30	-1.76	0.53	65.1	46	3.14	1.83	85.1	46
	30-100	-1.89	0.49	51.9	38	4.97	2.21	91.8	40
Clay	all depths	-2.32	0.44	56.4	142	4.68	2.15	82.0	152
Peat	all depths	-3.55	0.25	32.7	160	1.41	1.85	84.5	163

The critical Al leaching flux for root protection was calculated using a criterion for the maximum tolerable Al/BC ratio in the root zone:

$$\mathrm{Al}_{\mathrm{crit}} = \left(\frac{\mathrm{Al}}{\mathrm{BC}} \right)_{\mathrm{crit}} \cdot \mathrm{BC}_{\mathrm{ss}} \qquad \text{(A10.2)}$$

where $(\mathrm{Al/BC})_{crit}$ is the acceptable molar Al/BC ratio in the root zone and $\mathrm{BC}_{\mathrm{ss}}$ is the base cation concentration ($\mathrm{mol.m^{-3}}$) at steady state that can be calculated as :

$$\mathrm{BC}_{\mathrm{ss}} = (\mathrm{BC}_{\mathrm{td}} + \mathrm{BC}_{\mathrm{we}} - \mathrm{BC}_{\mathrm{gu}}) / 2000 \cdot \mathrm{PS} \qquad \text{(A10.3)}$$

where $\mathrm{BC}_{\mathrm{td}}$, $\mathrm{BC}_{\mathrm{we}}$ and $\mathrm{BC}_{\mathrm{up}}$ are the total deposition, weathering and uptake fluxes, respectively in $\mathrm{mol_c.ha^{-1}.yr^{-1}}$ and PS is the precipitation surplus in $\mathrm{m^3.ha^{-1}.yr^{-1}}$. the value of 2000 is used to convert units from $\mathrm{mol_c.m^{-3}}$ to $\mathrm{mol.l^{-1}}$

The critical Al/BC ratios are in principle a function of the BC concentration as given by Sverdrup and Warfvinge (1993), but for this calculation, we used the standard values given by those authors as presented in Table A10.2. Values given by Sverdrup and Warfvinge (1993) are based on a low BC concentration of 0.05 mmol.l^{-1} and those data are generally used in the calculation of critical loads submitted to the CCE. More information is given in Van der Salm and de Vries (2001).

Table A10.2 Critical limits used for the Al/BC ratios.

Tree Species	Al/BC ratio (mol./mol)
Pine	0.8
Spruce[3]	2.0
Deciduous[4]	1.7

Values for BC_{td}, BC_{we} and BC_{up} depend on area (deposition), the kind of soil (weathering) and kind of tree species (uptake). For BC_{ss} we made calculations with values of 0.05, 0.15 and 0.25 mmol.l^{-1} which could relate to situations as described below in Table A10.3.

Table A10.3 Possible BC concentrations at steady-state for different combinations of net base cation input (deposition plus weathering minus uptake) and precipitation surplus.

BC_{td}	PS	Soil	Input (mol$_c$.ha^{-1}.yr^{-1})				PS	BCss
			BC_{td}	BC_{we}	BC_{up}	BC_{in}	m^3.ha^{-1}.yr^{-1}	(mmol.l^{-1})
Low	Average	sand	250	200	250	200	2000	0.05
		loess	250	500	250	500	2000	0.125
High	Low	sand	500	200	250	450	1500	0.15
		loess	500	500	250	750	1500	0.25

Predicted pH values at steady state, using a BC concentration of 0.05 mmol.l^{-1} and applying the relationship between the pH value and the total and free Al^{3+} concentration, are presented in Table A10.4. The results show widely varying pH values due to differences in critical Al/BC ratios for trees and different K and n values for different soils and soil depths. This becomes even stronger when different BC values are used. Considering the uncertainties in local values for the steady-state BC concentration, critical Al/BC ratio, K and n value, it does not seem very wise to use any predicted steady-state pH value.

Table A10.4 Overview of calculated pH values for different combinations of soil types, layers and BC concentrations at steady-state

Soil type	Depth (cm)	pH values with relation total Al			pH values with relation Al^{3+}		
		Pine	Spruce	Deciduous	Pine	Spruce	Deciduous
All	Humus layer[1]	3.9	2.5	2.7	2.9	2.5	2.6
Sandy soils	0-10	4.7	3.5	3.7	3.5	3.3	3.4
	10-30	5.5	4.3	4.5	3.7	3.6	3.6
	30-100	6.3	4.9	5.1	3.9	3.8	3.8
Loamy soils	0- 10	7.1	3.5	4.1	3.9	3.5	3.5
	10- 30	5.0	4.2	4.4	4.1	3.9	3.9
	30-100	5.1	4.3	4.5	4.2	4.1	4.1

Assessment of actual pH values

The steady-state base cation concentrations and thereby the critical Al concentrations are strongly dependent on the base cation weathering rates. The model thus calculates high critical Al concentrations in e.g. clay soils with high weathering rates and consequently high critical H concentrations or low pH values. Such limits for those soils imply an acceptable (strong) decrease in base saturation and decline in pH leading to possible adverse effects, such as Mg deficiency in the vegetation. To avoid a decrease in base saturation for high base saturation (e.g. clay) soils, the criterion of no base saturation change is more relevant implying that the critical pH equals the actual pH of the soils.

An inventory of pH values based on soil solution data in the Netherlands and approximately 120 Intensive Monitoring plots in Europe (e.g. De Vries et al., 2003) are given in Table A10.5. Results are presented as a function of major forest type, soil type and soil layer in terms of average values and standard deviations and ranges by means of the 5-, 50- and 95 percentile. More information on the Dutch plots used is given below. In general, the results show a clear increase in pH going from the humus layer to the mineral subsoil. The pH values for clay soils are clearly higher than those for sandy/loamy soils and peat soils, specifically those under deciduous trees.

Table A10.5 Mean and standard deviation and ranges (5%, 50% and 95%) of pH values in forests on various non calcareous soils

Soil type	Depth (cm)	pH							
		Conifers				Deciduous			
		N	5%	50%	95%	N	5%	50%	95%
All soils	Humus layer	50	3.5	4.1	5.2	31	3.7	5.1	7.1
Sandy soils[1]	0-10	202	3.4	3.7	5.3	95	3.3	3.7	4.5
	10-30	297	3.4	3.9	5.7	148	3.4	3.9	4.8
Clay soils	0-10	12	3.8	4.0	4.8	57	3.7	5.5	7.1
	10-30	49	3.7	4.5	7.2	87	3.8	5.3	7.6
Peat soils	0-10	7	3.5	4.0	4.7	34	3.2	3.6	5.3
	10-30	1	3.8	3.8	3.8	40	3.2	3.7	5.5

[1] Includes loamy soils

Relationships between various pH estimates

In the transfer function relating dissolved metal concentrations or free metal ion activities to reactive soil metal contents, use is made of the pH of the soil solution. Many countries only do have data on the pH in a certain solution extraction such as pH-H_2O, pH-$CaCl_2$ or pH-KCl. To allow application of the transfer functions in these cases, relationships were derived between the various expressions of the soil pH. Data sets that were used to calculate the relationships between pH soil solution and pH H_2O and pH-KCl were:

- more than 120 forest stands out of the database of the Intensive Forest Monitoring programme of the European Commission and ICP Forests at 3 -5 depths (483 data points).

- 12 forest stands on non-calcareous sandy soils sampled in 1992: the humus layer and the depths of 0-10 cm, 10-30cm, 30-60 cm and 60-100 cm.
- 48 stands on non-calcareous sandy soils in the Dutch dune area sampled in 1991: the depths of 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm (De Vries, 1993).
- 150 forest stands on non-calcareous sandy soils sampled in 1990: the depth of 0-30 cm (De Vries & Leeters, 2001).
- 200 forest stands on non-calcareous sandy soils sampled in 1995: the humus layer and the depths of 0-10 cm (Leeters & de Vries, 2001).
- 100 forest stands sampled between 1992 and 1993 in approximately 40 loess soils, 30 clay soils and 30 peat soils: the depths of 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm (Klap et al., 1999).

The data set of the Intensive Forest Monitoring programme was also used to derive relationships between pH soil solution and pH-$CaCl_2$. Results of the regression analyses are given in Table A10.6. In general, the relationship is good between pH soil solution and both pH H_2O and pH-KCl and one may use a general relationship independent of soil type. For pH-$CaCl_2$ the relationship is much worse.

Table A10.6 Results of linear regression analyses of the pH in soil solution against pH-H_2O, pH-$Cacl_2$ and pH-KCl

Soil	Explaining variable	N	Slope (α)$^{1)}$	Intercept (β)$^{1)}$	se Y_{est}	R^2_{adj}
Sandy soils	pH-H_2O	643	0.9582	-0.0246	0.352	0.78
	pH-KCl	549	0.7811	1.0950	0.306	0.81
	pH-$CaCl_2$	169	0.6218	2.327	0.695	0.26
Loamy soils	pH-H_2O	122	0.9673	-0.020	0.362	0.83
	pH-KCl	118	1.0595	0.175	0.345	0.84
Clay soils	pH-H_2O	261	0.9311	0.570	0.567	0.79
	pH-KCl	119	0.7125	2.567	0.479	0.75
	pH-$CaCl_2$	239	0.9910	0.917	0.739	0.60
Peat soils	pH-H_2O	116	1.3630	-1.334	0.389	0.81
	pH-KCl	116	1.1390	0.485	0.328	0.86
All soils	pH-H_2O	1145	1.0462	-0.2847	0.453	0.84
	pH-KCl	905	0.9692	0.6233	0.491	0.80
	pH-$CaCl_2$	413	0.8834	1.317	0.741	0.49

$^{1)}$ All coefficients are significant at $p > 0,999$

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Appendix 11 Assessment of DOC concentrations

The concentration of dissolved organic matter (DOM) in soils is nowadays frequently determined in climate-related studies. Concentrations of DOM are usually determined by analysis of carbon (DOC) which accounts for half of the weight of soil organic matter (DOM ≈ DOC/50%). However, long-term data on soil solutions are rarely available at sufficient density for mapping region-specific means and variabilities, and may need to be estimated from studies elsewhere. A recent review of long-term percolation data from 42 studies all over Europe and the USA (Michalzik et al., 2001) covers both coniferous and deciduous forests in a wide variety of climatic regimes (mean temperature 1 to 16°C, precipitation 0.5 to 1.9 $m.yr^{-1}$). Complementing these data with recent Swedish data covering also the boreal region (Bringmark, 2002; Fölster et al., 2003; Fröberg et al., 2003; Fröberg et al., 2004) suggests that long-term means of DOC concentrations in organic soil layers typically are in the range of 20-50 $mg.l^{-1}$ and rarely may reach 100 $mg.l^{-1}$ (depending among other on extraction methods used). A decline with temperature and forest productivity to comparatively low values in cold regions with an annual mean temperature $<5°C$ has been reported recently (Bringmark, 2002; Fröberg et al., 2004). However, the range of long-term means is surprisingly narrow, given the wide range of sites and the wide small-scale variability of DOM concentrations.

An inventory of DOC values, measured in lysimeter studies in approximately 120 Intensive Monitoring plots in Europe (e.g. De Vries et al., 2003), given in Table A11.1 confirms the above mentioned ranges. Results are presented as a function of major forest type and soil layer in terms of ranges by means of the 5-, 50- and 95 percentile. In general, the results show a clear decrease in DOC concentrations going from the humus layer to the mineral subsoil. DOC values are much higher in peat soils, although the number of plots to substantiate the data is small.

Table A11.1 Mean and standard deviation and ranges (5%, 50% and 95%) of DOC concentrations in forests on various non-calcareous soils.

Depth (cm)	DOC concentration ($mg.l^{-1}$)											
	Conifers				Deciduous				All			
	N	5%	50%	95%	N	5%	50%	95%	N	5%	50%	95%
Humus layer	44	16	40	82	30	14	32	66	74	14	36	73
0-10	90	3.2	23	49	58	4.7	21	37	148	4.0	21	47
0-30	377	3.0	16	52	210	1.2	12	42	587	2.0	15	50
30-60	517	2.0	6.7	37	177	1.1	6.6	21	694	1.6	6.7	33
60-100	286	1.4	5.8	29	221	1.1	4.3	22	507	1.3	5.2	26

Relationships of DOM concentrations with vegetation type, hydrology, growth conditions, or soil properties may be expected, which would be useful to improve estimates for different sites and regions. However, from the limited number of studies, no such relationship of significance could be discerned (Michalzik et al., 2001). The above mentioned data for the mineral soil were thus used to derive relationships with available site characteristics and soil data that may affect the DOC concentrations, including the type of forest, (coniferous or deciduous), texture class (indication for soil type), temperature, pH and the contents of C and N including the C/N ratio. Results thus obtained are given in Table A11.2.

Table A11.2 Results of a regression analyses of DOC concentrations on site and soil characteristics (5%, 50% and 95%) in forests on various non-calcareous soils (-- implies a highly significant negative relationship with a predictor and ++ a highly significant positive relationship, whereas 0 implies no significant relationship).

Depth	n	C	N	C/N	Temp	pH	Texture	Tree	$R_{2, adj}$
0-10	142	--	++	++	++	0	0	0	0.34
0-30	564	--	++	++	++	--	--	0	0.22
30-60	52	--	++	++	0	--	++/--	--[1]	0.74
60-100	39	++	--	--	++	++	--	--[1]	0.83

[1] This means that deciduous is lower than coniferous

The results show a good relationship with the site and soil characteristics in the subsoil (below 30cm) but the relationships were much worse in the topsoil (above 30cm). The number of data is, however, much less in the subsoil In the topsoil there was a clear positive relationship with C/N ratio and temperature, while the correlated values of the individual C and N concentrations were negatively and positively related to DOC, respectively. Using the concentrations of C and N only, without the C/N ratio, decreased the value of $R_{2, adj}$ significantly. A comparison of predicted values using the above mentioned statistical approach, and measured values is given in Fig. A11.1. The results show that the correlation is reasonable to good for the subsoil but nearly absent for the topsoil.

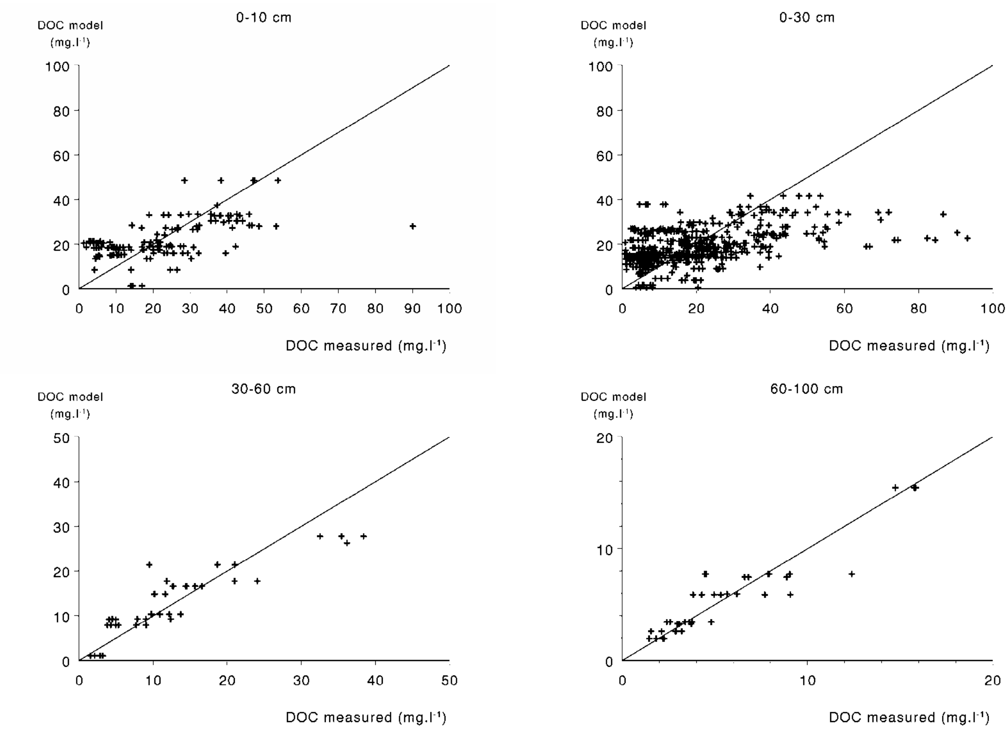

Figure A11.1 Comparison of predicted and measured DOC concentrations.

Based on the available data the following default values for DOC concentrations, to be used in calculating critical loads of Pb and Cd or critical levels of atmospheric Hg pollution, are suggested:

Forest organic layer (O horizon):	$[DOC]_{ss}$ = 35 mg l^{-1} ($[DOM]_{ss}$ = 70 mg l^{-1}).
Forest mineral topsoil (0-10 cm):	$[DOC]_{ss}$ = 20 mg l^{-1} ($[DOM]_{ss}$ = 40 mg l^{-1}).
Grass land (0-10) cm:	$[DOC]_{ss}$ = 15 mg l^{-1} ($[DOM]_{ss}$ = 30 mg l^{-1}).
Arable land (0-30) cm:	$[DOC]_{ss}$ = 10 mg l^{-1} ($[DOM]_{ss}$ = 20 mg l^{-1}).

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Appendix 12 Calculation of critical total Cd and Pb concentrations in surface water related to ecotoxicological effects

The calculation of the critical total aqueous concentration comprises the following steps:

1. Estimate the critical free metal ion concentration from the critical dissolved concentration (critical limit).
2. Calculate the metal bound per unit mass of SPM.
3. Calculate the water hardness.
4. Sum the total dissolved and particulate concentrations.

Step 1

The critical free metal ion concentrations ($[M]_{free,\ crit}$) are calculated using WHAM6, for waters of different pH, DOC and pCO_2, making the same assumptions as are used for calculating total metal from free-ion critical limits (for the Look Up Tables). These assumptions also lead to hardness values (H = hardness in mg $CaCO_3.l^{-1}$). In the calculations the critical dissolved concentrations used depend on the water hardness in case of Cd (0.16 $mg.m^{-3}$ if $H < 100$, 0.30 $mg.m^{-3}$ if $100 < H < 200$ and 0.50 $mg.m^{-3}$ if $H > 200$), whereas a value of 5 $mg.m^{-3}$ was used for Pb. Note that, here, all waters are assumed to be "normal" with respect to dissolved Al (i.e. acid bog-waters are not included).

Free ion activities corresponding to these limits (taking into account the variation in the Cd critical limit with water hardness) were calculated with WHAM6 for a range of solution conditions covering most natural freshwaters. They can be expressed in terms of multiple regression equations at different pH values, according to:

$$\log [M]_{free,crit} = A \cdot [DOC] + B \cdot pCO_2 + C \qquad \text{(A12.1)}$$

where [DOC] is in $mg.l^{-1}$ and pCO_2 is a multiple of the atmospheric pCO_2. Root mean square errors in $\log [M]_{free,crit}$ between the WHAM6 values and the regression values are < 0.12 for Cd and < 0.18 for Pb. The regression coefficients are given in Tables A12.1 and A12.2. Linear interpolation can be performed to obtain coefficients for intermediate pH values.

Table A12.1 Regression coefficients for estimating critical free Cd^{2+} concentrations

pH	A	B	C
4	-0.0004	0.0000	-8.87
5	-0.0053	-0.0001	-8.87
6	-0.0258	0.0040	-8.93
7	-0.0344	0.0189	-9.05
8	-0.0196	0.0466	-9.18
9	-0.0010	-0.0742	-9.44

Table A12.2 Regression coefficients for estimating critical free Pb^{2+} concentrations

pH	A	B	C
4	-0.0020	0.0000	-7.66
5	-0.0231	0.0000	-7.70
6	-0.0546	0.0062	-8.19
7	-0.0681	0.0261	-9.33
8	-0.0641	0.0349	-10.33
9	-0.0160	-0.1303	-11.41

Step 2

The critical SPM-bound metal ($[M]_{SPM\ (crit)}$, $mol.g^{-1}$) is calculated using the Q-c relations derived in Annex 7, Eq. A7.4 (Table A7.5). In this way we do calculate the critical reactive metal content on the suspended particles. This is considered appropriate by limitng the critical load approach to processes and fluxes of geochemically reactive metals. This implies that actual loads should also be related to the reactive fraction of the total input. Deposition measurements practices aim at extraction of reactive species (not total metal). Therefore we assume that, since EMEP models are calibrated to measurements, the currently mapped concentration/ deposition data (called "total") can be regarded as geochemically reactive metals.

Before proceeding to Step 3 $[M]_{SPM\ (crit)}$ must be converted to units of $mg.kg^{-1}$ by multiplying with the molar weight and a factor 10^6 to transfer from $g.g^{-1}$ to $mg.kg^{-1}$

$$[Cd]_{SPM(crit)}\ (mg.kg^{-1}) = [Cd]_{SPM(crit)}\ (mol.g^{-1}) \cdot (112 \cdot 10^6) \qquad (A12.2a)$$
$$[Pb]_{SPM(crit)}\ (mg.kg^{-1}) = [Pb]_{SPM(crit)}\ (mol.g^{-1}) \cdot (207 \cdot 10^6) \qquad (A12.2b)$$

Step 3

Using the assumptions about water composition (see Step 1), water hardness (mg $CaCO_3.l^{-1}$) is given by regression equations of the following form:

$$\text{hardness} = A \cdot [DOC] + B \cdot pCO_2 + C \qquad (A\ 12.3)$$

where [DOC] is in $mg.l^{-1}$ and pCO_2 is a multiple of the atmospheric pCO_2. The regression coefficients are given in Table A12.3. Linear interpolation can be performed to obtain coefficients for intermediate pH values.

Table A12.3 Regression coefficients for estimating water hardness

pH	A	B	C
4	0.00	0.00	0.00
5	0.11	0.02	-0.37
6	0.23	0.34	-0.14
7	0.31	3.4	-0.12
8	0.36	38.2	-6.84
9	0.43	1020	-966

Step 4

The total metal concentration in surface water at the critical limit is given by:

$$[M]_{tot,\ sw(crit)} = [M]_{dis,sw(crit)} + [M]_{SPM\ (crit)} \cdot [SPM]_{sw} \qquad \text{(A12.4)}$$

where $[M]_{dis,\ sw(crit)}$ is the critical dissolved concentration ($mg.m^{-3}$ or $\mu g.l^{-1}$) (See Table 7 in the main text), $[M]_{SPM(crit)}$ is the critical concentration bound to SPM calculated in Step 2 ($mg.kg^{-1}$), and $[SPM]_{sw}$ is the SPM concentration in surface water ($kg.m^{-3}$).

FULL CALCULATION EXAMPLE #1

pH = 6
DOC = 8 $mg.l^{-1}$
pCO_2 = 4 times atmospheric
SPM = 50 $mg.l^{-1}$
% OM = 20

Step 1

$$\begin{aligned}
\text{Log } [Cd]_{free,crit} &= (-0.0258 \cdot 8) + (0.0040 \cdot 4) + (-8.93) \\
&= -0.206 + 0.016 - 8.93 \\
&= \underline{-9.12}
\end{aligned}$$

$$\begin{aligned}
\text{log } [Pb]_{free,crit} &= (-0.0546 \cdot 8) + (0.0062 \cdot 4) + (-8.19) \\
&= -0.437 + 0.025 - 8.19 \\
&= \underline{-8.60}
\end{aligned}$$

Step 2

$$\begin{aligned}
\text{log } [Cd]_{SPM\ (crit)} &= -6.42 + (0.45 \cdot 6) + (0.64 \cdot 1.30) + (0.58 \cdot -9.12) \\
&= -6.42 + 2.70 + 0.832 - 5.29 = -8.178 \\
[Cd]_{SPM\ (crit)} &= 6.64 \cdot 10^{-9}\ (mol.g^{-1}) \cdot 112 \cdot 10^{6} = 7.43\ mg.kg^{-1}
\end{aligned}$$

$$\begin{aligned}
\text{log } [Pb]_{SPM\ (crit)} &= -5.42 + (0.70 \cdot 6) + (0.55 \cdot 1.30) + (0.61 \cdot -8.60) \\
&= -5.42 + 4.20 + 0.715 - 5.25 = -5.755 \\
[Pb]_{SPM\ (crit)} &= 1.76 \cdot 10^{-6}\ (mol.g^{-1}) \cdot 207 \cdot 10^{6} = 364\ mg.kg^{-1}
\end{aligned}$$

Step 3

$$\begin{aligned}
\text{HARDNESS} &= (0.23 \cdot 8) + (0.34 \cdot 4) + (-0.14) \\
&= 1.84 + 1.36 - 0.14 = 3.1
\end{aligned}$$

Therefore

$$\begin{aligned}
[Cd]_{sw(crit} &= 0.16\ \mu g.l^{-1} \\
[Pb]_{sw(crit} &= 5\ \ \mu g.l^{-1}
\end{aligned}$$

Step 4

$$\begin{aligned}
[Cd]_{tot,\ sw(crit)} &= 0.16 + (50\ /\ 1000) \cdot 7.43)\ \mu g.l^{-1} \\
&= 0.20\ \mu g.l^{-1} \\
[Pb]_{tot,\ sw(crit)} &= 5 + (50\ /\ 1000) \cdot 364)\ \mu g.l^{-1} \\
&= 23\ \mu g.l^{-1}
\end{aligned}$$

FULL CALCULATION EXAMPLE #2

pH = 8
DOC = 1 $mg.l^{-1}$
pCO_2 = 10 times atmospheric
SPM = 10 $mg.l^{-1}$
% OM = 20

Step 1

Log $[Cd]_{free,crit}$ $= (-0.0196 \cdot 1) + (0.0466 \cdot 10) + (-9.18)$
$= -0.020 + 0.466 - 9.18$
$= \underline{-8.73}$

log $[Pb]_{free,crit}$ $= (-0.0641 \cdot 1) + (0.0349 \cdot 10) + (-10.33)$
$= -0.064 + 0.349 - 10.33$
$= \underline{-10.05}$

Step 2

log $[Cd]_{SPM\ (crit)}$ $= -6.42 + (0.45 \cdot 8) + (0.64 \cdot 1.30) + (0.58 \cdot -8.73)$
$= -6.42 + 3.60 + 0.832 - 5.06 = -7.048$
$[Cd]_{SPM\ (crit)}$ $= 8.95 \cdot 10^{-8}\ mol.g^{-1} \cdot 112 \cdot 10^{6} = 10.0\ mg.kg^{-1}$

log $[Pb]_{SPM\ (crit}$ $= -5.42 + (0.70 \cdot 8) + (0.55 \cdot 1.30) + (0.61 \cdot -10.05)$
$= -5.42 + 5.60 + 0.715 - 6.13 = -5.235$
$[Pb]_{SPM\ (crit)}$ $= 5.82 \cdot 10^{-6}\ mol.g^{-1} \cdot 207 \cdot 10^{6} = 1205\ mg.kg^{-1}$

Step 3

HARDNESS $= (0.36 \cdot 1) + (38.2 \cdot 10) + (-6.84)$
$= 0.36 + 382 - 6.84 = 376$

Therefore

$[Cd]_{sw(crit}$ $= 0.50\ \mu g.l^{-1}$
$[Pb]_{sw(crit}$ $= 5\ \mu g.l^{-1}$

Step 4

$[Cd]_{tot,\ sw(crit)}$ $= 0.50 + (10/1000) \cdot 10)\ \mu g.l^{-1}$
$= 0.60\ \mu g.l^{-1}$
$[Pb]_{tot,\ sw(crit)}$ $= 5 + (10\ /\ 1000) \cdot 1205)\ \mu g.l^{-1}$
$= 17\ \mu g.l^{-1}$

Appendix 13 Transfer functions of Hg in aquatic ecosystems

In section 4.2, the derivation of critical levels of Hg in precipitation is given, focusing on the use of two separate transfer functions, namely TF_{HgSite} and TF_{HgBio} TF_{HgSite} is a site-specific transfer function, referring to the transfer of atmospheric Hg to fish flesh in a watershed at steady state, whereas TF_{HgBio} is an organism-specific transfer function, addressing the typical Hg partitioning within food webs. In this annex, more background information is given on both transfer functions.

The transfer function TF_{HgSite}

The transfer function TF_{HgSite}, which relates Hg concentrations in biota to the Hg concentration in precipitation at watershed steady state, can be described as a function of watershed properties, including both terrestrial and aquatic aspects related to the biogeochemistry of Hg in lakes and rivers. The properties of river waters are largely determined by the specific combination of influences during the passage of the catchment, including weathering, vegetation and soil processes, and hydrological flow patterns. The resulting chemical and biological environment influences not only the concentration but also the bioavailability of Hg. The combined effect can be expressed in terms of basic mapping and monitoring variables: Hg concentrations in fish are generally highest in nutrient-poor softwaters in acidic watersheds with extended wetlands (e.g. Verta et al., 1986; Håkanson et al., 1988; Meili, 1991a, 1994; Meili et al., 1996a; Meili, 1997). Such differences can be described by empirical relationships based on variables for which data are commonly available (e.g. from other studies under CLRTAP), such as surface water pH or concentrations of cations or nutrients.

In lakes, a variable proportion of pollutants enters by direct deposition on the lake surface, and this input may have a substantially different bioavailability. Therefore, an important difference among lakes is the proportion of Hg biouptake that is controlled by influences of the watershed (see above) as opposed to direct deposition on the water surface. This proportion is related but not proportional to the fraction of land and water surfaces in the watershed, largely because of differences in Hg transformation (e.g. net methylation and volatilisation). However, the transfer of airborne Hg to fish and other aquatic biota can be expressed as the sum of the two mentioned transfer pathways, if TF_{HgSite} is separated into TF_{HgRun} referring to the Hg transfer via soil runoff and TF_{HgPrec} referring to the Hg transfer via deposition on water surfaces (Meili, 1991a; Meili et al., 2003):

$$TF_{HgSite} = TF_{HgRun} \cdot f_{HgRun} + TF_{HgPrec} \cdot (1-f_{HgRun}) \qquad \text{(A13.1)}$$

where:

TF_{HgRun} = the ratio between the standard fish Hg concentration in runoff-fed waters (such as rivers and humic lakes) and the Hg concentration in precipitation at steady state

TF_{HgPrec} = the ratio between the standard fish Hg concentration in deposition-fed waters and the Hg concentration in precipitation at steady state.

f_{HgRun} = the fraction of total Hg input to surface waters contributed by runoff at steady state

Beware that all TFs are defined as Hg concentration ratios between biota ($ng.kg^{-1}$ fresh weight) and precipitation ($ng.l^{-1}$) at steady state. The equation describes the Hg burden in aquatic organisms as a mixture composed of a component controlled by terrestrial processes in the watershed and a component related to direct input to the aquatic system. These components can be quantified most easily if the terrestrial Hg runoff equals wet deposition at steady state, which appears to be a viable approximation at least for boreal and alpine watersheds where soils are shallow and pollution sensitivity is high. This implies that the sum of other watershed fluxes is near zero (dry deposition minus volatilization of Hg at the soil surface, plus weathering release minus net retention of Hg in deep soils, minus vegetation harvest). In this case, f_{HgRun} is equal to the fraction of land in a watershed, which for rivers is close to 100%, and for lakes typically 80 to 98% at steady state. At present, the terrestrial fraction of Hg input is likely lower because it may take centuries for soils to equilibrate with a given level of atmospheric Hg pollution, but the steady state routing (f_{HgRun}) can be derived from a suitable set of survey data (e.g. Meili et al., 2003) or by adopting the resulting scaling factors (see below).

Biotic Hg levels in lakes and rivers depend not only on the fluxes of Hg but vary widely with the biogeochemistry of waters and watersheds, depending on the abundance and distribution of organic and inorganic Hg binding sites in soils, sediments and waters, and on microbial and other ecological processes influencing the concentrations, bioavailability and bioaccumulation of Hg. However, biotic Hg levels often follow well-established patterns (e.g. Meili et al., 1996a; Meili et al., 1996b; Meili, 1997). For lakes, TF_{HgRun} is usually higher than TF_{HgPrec}, since runoff waters often contribute far more to the levels of bioavailable (e.g. methylated) Hg than does precipitation. With $f_{HgRun} > 80\%$ and $TF_{HgRun} > TF_{HgPrec}$, the contribution of direct deposition to fish Hg at steady state may be negligible not only in rivers but also in many lakes (even though it may be significant at present). Accordingly, Eq. (13.1) can be simplified to an expression considered sufficient to quantify the critical Hg exposure when focusing on sensitive ecosystems:

$$TF_{HgSite} \approx TF_{HgRun} \qquad \text{(A13.2)}$$

Further, Hg concentrations in fish are generally highest in nutrient-poor softwaters in wetland-rich acidic watersheds exposed to industrial pollution. These features also promote surface water acidity, which may be the most powerful single predictor of differences in fish Hg concentrations among freshwaters (TF_{HgSite}). As a first approximation, such patterns can be condensed into an empirical relationship with surface water pH alone, which is a convenient parameter reflecting a diversity of aspects such as weathering rates, cation concentrations, buffering capacity, binding site density, nutrient concentrations, terrestrial and aquatic productivity, humus concentration, sedimentation velocity, as well as Hg pollution via acid rain. Swedish data from hundreds of lakes ranging in pH from 4.6 to 8.0 (typically 5.5-7.0) suggest that present biotic Hg concentrations (total or methylated) increase with present surface water acidity by about 60% per pH unit and thus are proportional to $e^{-pH/2}$ in fish (Håkanson et al., 1988), zooplankton (Meili, 1991b), zoobenthos (Parkman & Meili, 1993) and at the microbial level (Meili, 1994). It should be noted that such covariations are useful as indicators, but are not evidence of any chemical link between pH and the Hg cycle (Meili, 1991a, 1994). An ongoing expansion based on Nordic surveys of data from several thousand lakes in Norway, Sweden and Finland confirms an expected link of fish Hg levels to nutrient levels in the water (Meili, 1991a), which can be used to improve TF_{HgSite}. After expansion of equation (A13.1) to address regional and local differences in watershed biogeochemistry, the transfer functions proposed in the main text, based on combined findings including data from over thousand sites, can be derived (Section 4.2.1, Eq. 15a and 15b).

Since the Hg transfer varies greatly among the biota within a lake or river, TF_{HgSite} needs to be specified, for example with respect to a given species and size of fish. Here, TF_{HgSite} is chosen to refer to a commonly caught piscivorous fish with a total body weight of 1 kg, in particular pike (*Esox lucius*). This is the most commonly used indicator species for monitoring fish Hg in boreal lakes since the beginning in the 1960's, and large databases with Hg concentrations in pike have already been compiled both in northern Europe and overseas. Referring to this standard fish, the transfer function TF_{HgSite} can be parameterised as for boreal lakes of south Sweden, where TF_{HgRun} was found to be around 250 000 $l.kg^{-1}$ fw at steady state, and thus many fold higher than TF_{HgPrec} which was found to be on the order of 20.000 $l.kg^{-1}$ fw (cf. Verta et al., 1986; Meili, 1991a; Meili et al., 2003).

TF_{HgSite} can be viewed to contain a transfer function linking the Hg contamination of living organic matter (e.g. a standard fish) to that of dead organic matter (e.g. sediments or soils). This is an important aspect of ecosystem sensitivity to Hg pollution, accounting among other for the Hg methylation potential in watersheds and the methyl-Hg biomagnification within rivers and lakes. Alternatives to Eq. (15) in the main text can thus be based for example on the ratio between Hg/OM in standard fish and Hg/OM in organic soils (which is conceptually compatible with the factor f_f in the solid-solution transfer function for Hg in organic soils). In south Sweden, this ratio is around 10 on a regional level, but varies with watershed characteristics (Meili et al., 2003) and among regions (Meili, 2001). Corresponding values for Pb and Cd are much lower.

If a generic parameterisation of the transfer function TF_{HgRun} of around 250 000 $l.kg^{-1}$ fw at steady state appears inappropriate, a regional formulation may be derived, using present survey data as described below.

The transfer function TF_{HgRun}

Quantifying the future (critical) steady state of a watershed from present survey data requires not only adequate data but also adequate interpretation of such data. One important aspect to consider here is that present environmental Hg concentrations are not in steady state with the present level of pollution. This is particularly true for the Hg transfer across watershed soils (TF_{HgRun}), which may take centuries to reach steady state. Accordingly, the Hg concentrations in runoff and river waters and associated biota (including most freshwater fish) are expected to increase substantially before steady state with the present atmospheric Hg pollution is reached (typically 2- to 10-fold, if referring to the year 2000, not accounting for local direct Hg emissions, see below). Since critical load concepts refer to a sustainable steady state in the future, survey data of present Hg levels in rivers and most lakes cannot be adopted directly but need to be scaled appropriately to a steady state situation before calculating steady state transfer factors such as TF_{HgRun} (Meili et al., 2003):

$$TF_{HgRun} = TF'_{HgRun} / e_{HgRun} \qquad (A13.3)$$

where:

TF'_{HgRun} = the present ratio between the standard fish Hg concentration in runoff-fed waters (such as rivers and humic lakes) and the Hg concentration in precipitation,

TF_{HgRun} = the corresponding ratio at steady-state

e_{HgRun} = an equilibration state coefficient

The equilibration state coefficient e_{HgRun} is defined as the ratio between the contamination factors q (the present contamination relative to natural conditions) for runoff-fed waters and for precipitation (Meili et al., 2003) according to:

$$e_{HgRun} = q_{HgRun} / q_{HgPrec} \qquad (A13.4)$$

where:

q_{HgRun} = present contamination of Hg in runoff-fed waters relative to natural conditions

q_{HgPrec} = present contamination of Hg in precipitation relative to natural conditions

e_{HgRun} describes the response of Hg concentrations in aquatic biota relative to the change in the atmospheric Hg pollution level and assumes values of 1 at steady state, <1 after onset of pollution, and >1 after remediation. This scaling factor, which varies regionally with ecotype, pollution history and pollution level, can be quantified in three ways:

I) e_{HgRun} can be quantified based on a suitable set of region-specific field data (Meili et al., 2003), including (1) several historical records of ecosystem pollution (e.g. natural archives such as lake sediments) from waters ranging widely in f_{HgRun}, and (2) present concentrations of Hg in precipitation that have been measured or modelled (e.g. Ilyin & Travnikov, 2003, see below). Note that f_{HgRun} refers to steady state.

II) A simplified but less region-specific alternative to above is to estimate q_{HgPrec} by adopting a generic value of 2 ng.l^{-1} for the natural $[Hg]_{Prec}$ in Europe (see below), and to estimate q_{HgRun} as the mean Hg concentration ratio between surficial and deep layers of suitable lake sediment cores collected in waters receiving mostly runoff Hg (cf. Meili, 1995, Meili et al., 2003).

III) e_{HgRun} can be calculated without region-specific field data as

$$e_{HgRun} = (d_{HgRun}\ [q_{HgPrec} - 1] + 1)\ /\ q_{HgPrec} \tag{A13.5}$$

with

$$d_{HgRun} = (q_{HgRun} - 1)\ /\ (q_{HgPrec} - 1) \tag{A13.6}$$

where

d_{HgRun} = the degree of equilibration between natural and future steady states

This degree of equilibration is based on the accomplished fraction of the change from the natural steady state to a future steady state if the current level of pollution is maintained (Meili et al., 2003). d_{HgRun} and e_{HgRun} are both related to the regional emission history and vary among ecotypes and over time. In contrast to e_{HgRun}, however, d_{HgRun} is independent of the regional pollution level and thus spatially fairly constant around an emission source. Therefore, e_{HgRun} can be quantified by adopting d_{HgRun} values from neighbouring regions. Accordingly, d_{HgRun} is more suitable than e_{HgRun} for mapping critical levels of atmospheric pollution.

For convenience or reference, e_{HgRun} is exemplified in Table A13.1 for various types of watersheds in European regions in the year 2000, based on initial findings on d_{HgRun} (Meili et al., 2003) combined with present European Hg concentrations in precipitation.

Table A13.1 Estimated equilibration state coefficient for runoff Hg, e_{HgRun}, in European regions in the year 2000 as a function of mean pollution level (from background to high) and the degree of equilibration between natural and future steady states, d_{HgRun}.

d_{HgRun}[1]	e_{HgRun} at different pollution levels[2]			
	background[3]	low[4]	moderate[5]	high[6]
≈ 1	1	1	1	1
≈ 0.3	≤0.60	0.44	0.37	0.31
≈ 0.15	≤0.55	0.32	0.24	0.17
≈ 0.05	≤0.50	0.24	0.15	0.07

[1] Degree of equilibration between two steady states.
d_{HgRun} ≈ 1 refers to minimal watershed retention of Hg as in bare sandy soils
d_{HgRun} ≈ 0.3 refers to watershed retention of Hg as found in boreal forests
d_{HgRun} ≈ 0.15 refers to longer watershed retention of Hg as expected in thicker soils
d_{HgRun} ≈ 0.05 refers to very long watershed retention of Hg as expected in very thick soils

[2] Pollution levels are defined by the Hg concentration in precipitation, $[Hg]_{Prec}$, in the year 2000 and a corresponding contamination factor in precipitation, q_{HgPrec}, in the year 2000

[3] $[Hg]_{Prec} \geq 4$ ng.l^{-1}and q_{HgPrec}, ≥ 2.

[4] $[Hg]_{Prec} = 10$ ng.l^{-1} and q_{HgPrec}, ≈ 5.

[5] $[Hg]_{Prec} = 20$ ng.l^{-1} and q_{HgPrec}, ≈10.

[6] $[Hg]_{Prec} = 100$ ng.l^{-1} and q_{HgPrec} ≈ 50.

The latter have increased from natural levels of about 2 ng.l^{-1} to present values of about 4 ng.l^{-1} at hemispheric background (Meili et al., 2003), but are despite a recent decline still at 10-30 ng.l^{-1} over large areas of Europe and >100 ng.l^{-1} in the most polluted areas (Ilyin & Travnikov, 2003). Note that all these values change over time with changes in atmospheric Hg pollution and with the gradual loss of mobile Hg from watersheds.

The transfer function TF_{HgBio}

Once the Hg concentration in the standard fish is established for an ecosystem, the Hg concentration in other fish types (or other biota) can be addressed by means of the transfer function TF_{HgBio} describing the deviation from the standard fish. Hg concentrations vary by several orders of magnitude among different biota within a lake or river food web, and up to 100-fold among fish alone (Meili, 1997). However, much of this variability follows predictable patterns and can be addressed by empirical, bioenenergetic or other transfer functions, which are preferably based on traditionally available data such as the species and size of fish. In fish, Hg concentrations increase with body size, trophic level, age and sexual maturity (e.g. Meili et al., 1996b; Meili, 1997). Among commonly available variables, body weight is the most powerful single predictor of fish Hg levels (TF_{HgBio}), also across species. Furthermore, the relationship between Hg concentrations and body weight in typical fish catches is often approximately linear after log-transformation of both variables, which is less likely for other variables, and which facilitates statistical evaluations.

For unknown future fish populations, or if no adequate fish Hg data are available for other reasons, a first approximation for any fish species can be made based on their body weight alone (W = total body fresh weight in kg) using an empirical relationship to describe the deviation in Hg concentration from that in any 1-kg fish, as given in Section 4.2.2 (Eqs. 17 and 18). Generic or empirical formulations of TF_{HgBio} are particularly useful for harmonising critical limits and exceedances irrespective of fish community compositions, and for statistical evaluations involving a multitude of species, sites or regions after converting observed Hg concentrations into normalised Hg concentrations for individual fish. Further development of the transfer functions TF_{HgSite} and TF_{HgBio} based on accumulating data is desirable to improve the site- and species-specific resolution. Among others, work supported by the Nordic Council of Ministers is currently in progress to quantify and validate transfer functions for fish Hg in Fennoscandia.

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