**Report 259101011/2002** J-P Hettelingh, J Slootweg, M Posch, S Dutchak, I Ilyin

# Preliminary modelling and mapping of critical loads for cadmium and lead in Europe

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EMEP - Meteorological Synthesizing Center - East

**wge**

**Working Group on Effects**
**of the**
**Convention on Long-range Transboundary Air Pollution**

**RIVM** reportno. **259101011/2002**

# Preliminary modelling and mapping of critical loads for cadmium and lead in Europe

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This investigation has been performed by order and for the account of the Directorate for Climate Change and Industry of the Dutch Ministry of Housing, Spatial Planning and the Environment within the framework of RIVM-project M259101, “UNECE-LRTAP”; and for the account of the Working Group on Effects within the trustfund for the partial funding of effect oriented activities under the Convention.

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# Acknowledgements

The methods and resulting maps contained in this report are the product of collaboration within the Effects Programme of the UNECE Convention on Long-range Transboundary Air Pollution, involving many institutions and individuals throughout Europe. National Focal Centres, whose reports regarding modelling and mapping activities appear in Part II are gratefully acknowledged for their contribution.

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# Preface

The Working Group on Effects (WGE) of the United Nations Convention on Long-range Transboundary Air Pollution (UNECE-CLRTAP), at its 20th session, “noted the need to further develop and test the methodology for mapping critical loads for heavy metals (Pb, Cd) and, to this end, invited the International Co-operative Programme on the Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends ICP Mapping (ICP-M&M) and the Coordination Center for Effects (CCE) to issue, by the end of 2001, a call for relevant data to be provided by the NFCs on a voluntary basis” (EB.AIR/WG.1/2001/2 para. 37f).

In response to this invitation the CCE issued a call for data on critical loads for lead and cadmium on 18 December 2001 requesting its twenty four National Focal Centres (NFCs) to respond not later than 11 March 2002.

This report summarises the results of this call to which 17 parties responded. Maps of critical loads for lead and cadmium presented in this report are tentative and preliminary.
The report is produced in collaboration with EMEP/MSC-E to enable the preliminary comparison of critical load maps to maps of lead and cadmium deposition in 2000 and 2010.
An executive summary including critical load and exceedance maps is provided in chapter 1.

Maps of critical loads are a first illustration of the application of available data and methods. Eleven NFCs sent data while six NFCs indicated not to be able to respond to the call at this point in time. Detailed NFC reports are provided in Part II.

The International Co-operative Programme on the Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends agreed that the results should only be used for testing the currently available methodology and data.
The results have been presented at the 12th CCE workshop (15-17 April 2002) and the 18th Task Force on Modelling and Mapping (18-19 April 2002) in Sorrento (Italy).

The work performed by NFCs used results from preparatory work conducted under the Convention since 1995. In 1998, two manuals were published, presenting guidelines for calculation methods, critical limits and input data for the calculation of critical loads of heavy metals for terrestrial and aquatic ecosystems. The development of those manuals started in 1994 and several drafts were discussed at CCE workshops in 1995, 1996 and 1997. Together with other background documents they were also discussed at the “International Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and POPs” in November 1997 in Bad Harzburg, Germany. In those two manuals various possibilities are described to calculate critical loads for heavy metals in view of the use of:

- Simple or (more) complex models, based on a mass balance approach for metals
- Different types of critical limits
- Different types of transfer functions between metals in the soil solid phase and soil solution

Since the publication of the manuals a “Workshop on Effects-based Approaches for Heavy Metals” was held in Schwerin, Germany, 12–15 October 1999, focusing on the use of methods and transfer functions and on critical limits to calculate critical loads. Furthermore, an “Ad-hoc International Expert Group Meeting on Effect-based Critical Limits for Heavy Metals” was held 11–13 October

2000 in Bratislava, Slovak Republic focussing specifically on the derivation of critical limits for heavy metals. This work is not yet finalised and is continued into 2003 by two expert groups, i.e. on transfer functions and critical limits.

Results of this historic work were boiled down to a “guidance” document summarising the state the methodology and the required data. This guidance document was provided to each of the NFCs and also made available through the CCE website *www.rivm.nl/cce*. This guidance document is included in this report as chapter 2.

Chapter 3 provides a detailed overview of the national submissions regarding ecosystems, and background data including a tentative inter-country comparison of data statistics.

Chapter 4 describes the methodology and data involved in the modelling of atmospheric dispersion of lead and cadmium, which have been used in this study to compute critical load exceedances.

The report is finalised with two Annexes. Annex 1 provides an update of the guidance document (chapter 2) which have evolved since results of the call were presented at the 12th CCE workshop and 18th Task Force on Modelling and Mapping meeting in Italy (Sorrento, 15-19 April 2002). Annex 2 consists of the effect-based critical load maps for cadmium and lead using a uniform background database, as an update of what has been presented in the CCE Status Report 2001.

# Summary

At its 20th session the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UNECE-CLRTAP), noted the need to further develop and test the methodology for mapping critical loads for cadmium and lead. To this end, the WGE invited the International Cooperative Programme on Modelling and Mapping (ICP M&M) and its Coordination Center for Effects at the RIVM (RIVM-CCE) to issue, by the end of 2001, a call for relevant data to be provided by its network of National Focal Centers (NFCs) on a voluntary basis.

This report describes the results of this call for data. NFCs were requested to apply (1) an *effect-based* methodology, identifying atmospheric deposition (critical loads) that will not lead to concentrations of heavy metals above critical limits for microbiota, plants and invertabrates and/or (2) a *stand-still* approach identifying atmospheric deposition (stand-still loads) that will not lead to any further accumulation of heavy metals in the soil. Seventeen NFCs responded of which eleven provided data.

The report, includes
- the methodological guidance provided to the NFCs at the time of the call.
- preliminary European maps of both critical and stand-still loads loads based on the response from Bulgaria, Belarus, The Czech Republic, Germany, Italy, The Netherlands, Russia, Slovakia, Switzerland, Ukrain, and the United Kingdom.
- preliminary exceedance maps produced in collaboration with the EMEP-Meteorological Synthesizing Centre East under the UNECE-CLRTAP.

The results of the call for data described in this report have been presented and discussed at the 12th CCE workshop and the 18th Task Force of the ICP M&M which were held back-to-back in Italy (Sorrento, 14-19 April 2002). Main recommendations include the further review of methods and national data, the review of atmospheric as well as other heavy metal inputs (in particular on agricultural soils), the exploration of critical limits including those related to human health and the exploration of effect-based approaches for mercury.

The ICP M&M recommended the work of the Expert Group on Critical Limits and the Expert Group on Transfer Functions to continue its work in 2003, using the results of the preliminary call for data on critical loads of cadmium and lead.

# Samenvatting

De “Working Group on Effects” (WGE) van de “Convention on Long-range Transboundary Air Pollution” onder de “United Nations Economic Commission for Europe” (UNECE-CLRTAP) heeft tijdens haar 20$^e$ bijeenkomst besloten dat de methode om kritische depositiewaarden voor cadmium en lood in kaart te brengen verder ontwikkeld moet worden. De WGE heeft daarom de “International Cooperative Programme on Modelling and Mapping” (ICP M&M) en het bijbehorende “Coordination Center for Effects” van het RIVM (RIVM-CCE) gevraagd om eind 2001 een verzoek te richten aan het netwerk van “National Focal Centres” (NFC’s) om de relevante data te verstrekken, op vrijwillige basis. Dit rapport beschrijft de resultaten van dit RIVM-CCE werk.

Aan NFC’s is verzocht om een *effect-georiënteerde* – en/of een *stand-still* methode toe te passen. De eerste methode geeft kritische depositiewaarden voor cadmium en lood die het risico van schade aan planten beperkt. De tweede methode begrenst verdere toename van de metalen in de bodem.

Zeventien NFC’s reageerden, waarvan elf gegevens hebben opgestuurd die zijn verwerkt.

Het rapport bevat:
- de methodologische leidraad die door het RIVM-CCE aan NFC’s werd verstrekt,
- de eerste voorlopige Europese kaarten van kritische – en stand-still waarden gebaseerd op de respons van Bulgarije, Duitsland, Italië, Nederland, Oekraïne, Rusland, Slowakije, Tsjechië, het Verenigd Koninkrijk, Wit-Rusland en Zwitserland en
- de voorlopige overschrijdingskaarten gemaakt in samenwerking met het EMEP-Meteorological Synthesizing Centre East onder de UNECE-CLRTAP.

De resultaten zijn gepresenteerd en bediscussieerd op de 12$^e$ CCE-workshop en de 18$^e$ Task Force van de ICP M&M die, op uitnodiging van Italië, in Sorrento werden gehouden (14-19 april 2002). Daar werd door deskundigen aanbevolen meer aandacht te besteden aan methoden en data, met name de evaluatie van atmosferische - en andere belastingen door zware metalen (van met name landbouwgronden), verder onderzoek naar kritische grenzen voor milieu en gezondheid en de verkenning van effect-georiënteerde methoden voor kwik depositie.

De ICP-M&M heeft verder aanbevolen het werk van de “Expert Group on Critical Limits” en de “Expert Group on Transfer Functions” in 2003 voort te zetten mede op basis van de hier gerapporteerde resultaten.

# Part I Modelling and Mapping of Critical Loads for Cadmium and Lead

Part I consists of four chapters focussing on methods and data for the modelling and mapping of critical loads and exceedances, and presents a preliminary analysis of the NFC response.

Chapter 1 is an executive summary of the response results including preliminary maps of critical loads and exceedances.

The methodology for the computation of critical loads for cadmium and lead is based on extensive preparatory work in past years. This was boiled down to a “guidance” document which was sent to NFCs as background information to the call. This guidance document is included here as chapter 2. Chapter 3 provides a data analysis of the response to the call for data. Finally, chapter 4 provides a description of the modelling of deposition fields of the two heavy metals.

# 1 Preliminary Modelling and Mapping of Critical Loads for Cadmium and Lead and their Exceedances – Executive Summary

Jean-Paul Hettelingh, Jaap Slootweg, Maximilian Posch, Sergey V. Dutchak[1], Ilia Ilyin[1]

## 1.1 Introduction

The Working Group on Effects (WGE) at its 20th session “noted the need to further develop and test the methodology for mapping critical loads for heavy metals (Pb, Cd) and, to this end, invited the ICP Mapping and the CCE to issue, by the end of 2001, a call for relevant data to be provided by the NFCs on a voluntary basis” (EB.AIR/WG.1/2001/2 para. 37f). In response to this invitation the CCE issued such a call for data on 18 December 2001 requesting its National Focal Centres (NFCs) to respond not later than 11 March 2002. In support of this call NFCs were provided with a Guidance document (reprinted in chapter 2).

The call requested parties to provide effect-based critical loads and stand-still loads using the 50x50 $km^2$ EMEP grid system. Effect-based critical loads in the context of the Convention equal the atmospheric deposition that will not lead to concentrations of heavy metals above critical limits in defined compartments in a steady-state situation. These critical loads can be derived using (a) critical limits of heavy metal concentrations in the soil solution which will not harm microbiota and plants and/or (b) critical limits of (reactive) soil metal concentrations which will not lead to adverse impacts on soil functioning, such as soil invertebrates that ingest soil. Stand-still loads in the context of the Convention equal the atmospheric deposition that will not lead to any further accumulation of heavy metals in the soil. In fact, stand-still loads should also include other than atmospheric inputs.

Finally, parties were encouraged to provide ecosystem information using the European Nature Information System (EUNIS) to enhance cross-border comparison of ecosystems (see also Hall, 2001).

Following recommendations from a joint meeting of the bureaux of the EMEP Steering Body and the Working Group on Effects, a collaboration was started between the EMEP/MSC-E and the CCE. The aim of the collaboration is to use MSC-E results of modelled deposition of cadmium and lead deposition fields in 1990, 2000 and 2010 (see chapter 4) for the computation of preliminary exceedance maps. MSC-E and CCE also agreed to attempt the assessment of ecosystem dependent exceedances.

Preliminary results of the call for data and exceedance maps have been shown and discussed at the 12th CCE workshop and the 18th Task Force of the ICP M&M which were held back-to-back in Italy (Sorrento, 15-19 April 2002).
This chapter summarises the NFC response and shows 5th percentile critical load maps for cadmium and lead and their exceedances.

[1] EMEP Meteorological Synthesizing Centre East, Moskow, Russia.

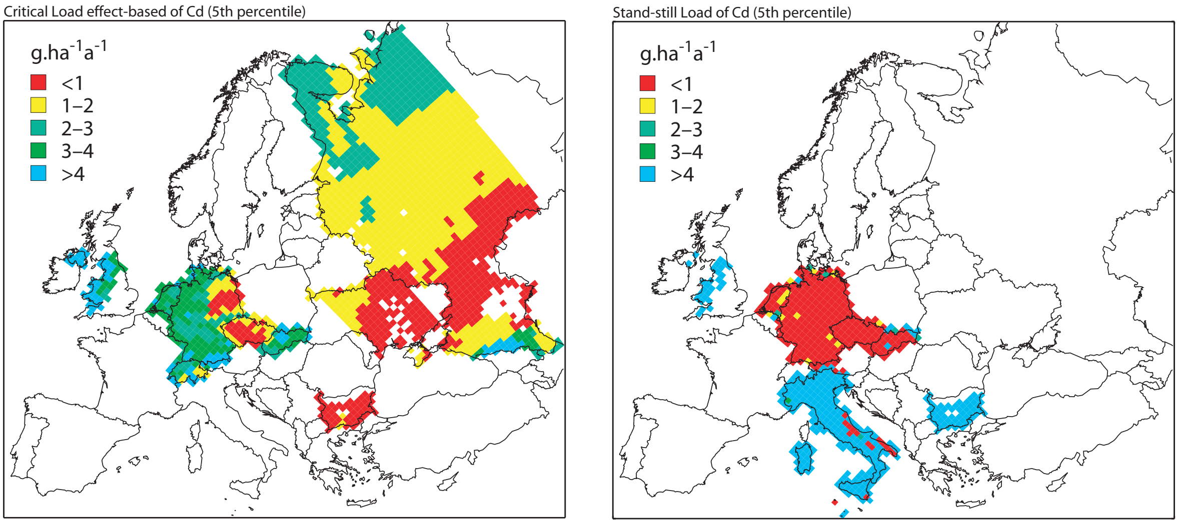
## 1.2 Preliminary critical load results

Critical load data were received from National Focal Centres (NFCs) of Bulgaria, Belarus, Czech Republic, Germany, Italy, The Netherlands, Russia, Slovakia, Switzerland, Ukraine and the United Kingdom. Effects-based critical loads (protecting microbiota and plants) were submitted by ten NFCs. Germany also submitted critical loads, which protect soil organisms (e.g. invertebrates). Stand-still loads were submitted by Bulgaria, Czech Republic, Germany, Italy, The Netherlands, Slovakia and the United Kingdom. Italy only provided loads based on semi-dynamic calculations, which are shown on European maps of stand-still loads. Austria, Belgium (Flanders), Finland, France, Sweden and Norway informed the CCE not to be able to participate at this time.

All NFCs provided critical loads for forest ecosystems, three NFCs also included natural vegetation. Three NFCs also provided critical loads for arable land, implying that atmospheric deposition is a major contributor to heavy metals input to these soils. See Chapter 3 for details on the ecosystems for which data have been submitted.

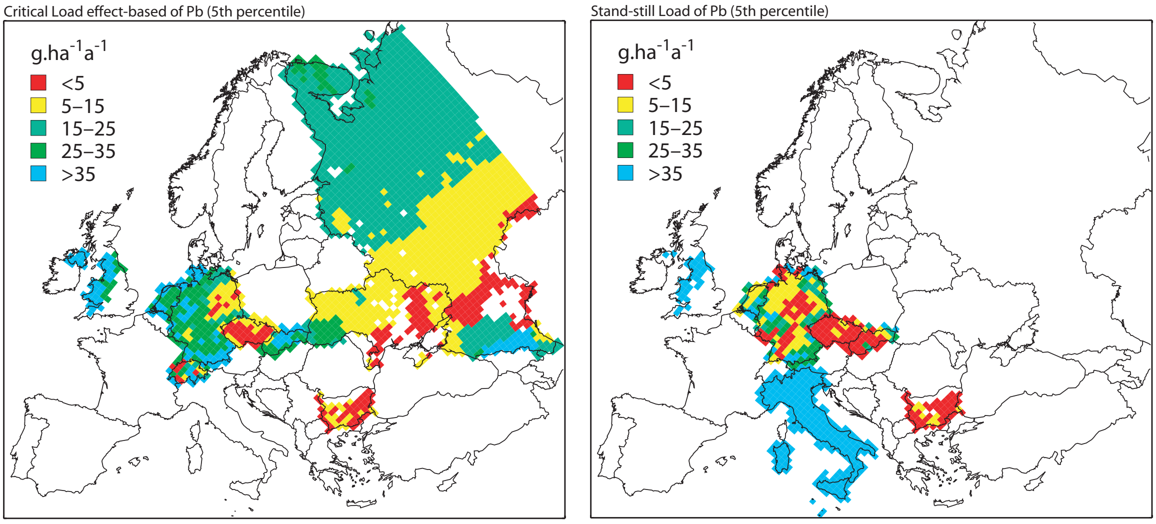
Preliminary European critical and stand-still load maps of cadmium and lead have been produced using data of the participating countries. Due to the preliminary and exploratory nature of the modelling and mapping exercise, no European databases have been used by the CCE to fill regional gaps of critical loads.

Critical load/stand-still load maps of cadmium and lead are shown in Figures 1-1 and 1-2, respectively. The maps show 5th percentile critical loads in each 50x50 km$^2$ EMEP grid cell. A 5th percentile critical load implies that 95% of the mapped ecosystems will be protected from adverse effects if the atmospheric deposition of cadmium in that grid cell is equal to this critical load value. Similarly, the 5th percentile stand-still load addresses protection against accumulation. Figure 1-1 shows the maps of the 5th percentile of effect-based critical loads (left) and stand-still loads (right) for cadmium. Comparison of the two maps shows that the stand-still approach may lead to lower values for cadmium in the Czech Republic, Germany, The Netherlands, and the United Kingdom while higher values occur in Bulgaria and Slovakia. Figure 1-2 shows the maps of the 5th percentile of effect-based critical loads (left) and stand-still loads (right) for lead. Comparison of the two maps shows that the stand-still approach may lead to lower values for lead in the Czech Republic, Germany, The Netherlands and the United Kingdom and to higher values in Bulgaria and Slovakia.



**Preliminary maps - Do not quote!**

**Figure 1-1: Preliminary maps of the 5th percentile of effect-based critical loads (left) and stand-still loads (right) for cadmium. Comparison of the two maps shows that the stand-still approach generally leads to lower values for cadmium in CZ, DE, NL, UK and SK and to higher values in BG.**



**Preliminary maps - Do not quote!**

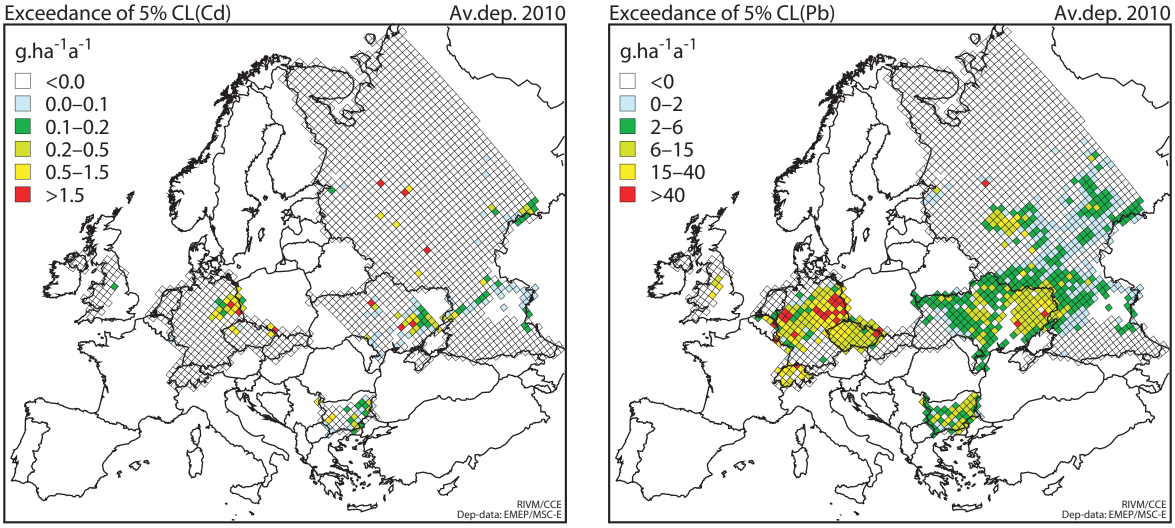
**Figure 1-2: Preliminary maps of the 5th percentile of effects-based critical loads (left) and stand-still loads (right) for lead. Comparison of the two maps shows that the stand-still approach generally leads to lower values for lead in e.g. DE, NL and SK.**

## 1.3 Preliminary exceedance computation results

Using estimates of emissions in 2010, EMEP/MSC-E computed both mean and ecosystem dependent depositions (see chapter 4) in 50x50 km$^2$ grid cells. These depositions are used to compute and map exceedances described below.

### 1.3.1 Preliminary exceedance maps using mean depositions

Figure 1-3 shows the result of comparing the 5th percentile critical load maps for cadmium and lead with the mean depositions of these metals. As can be seen the deposition of lead exceeds the preliminary critical loads in a wider area than cadmium deposition.

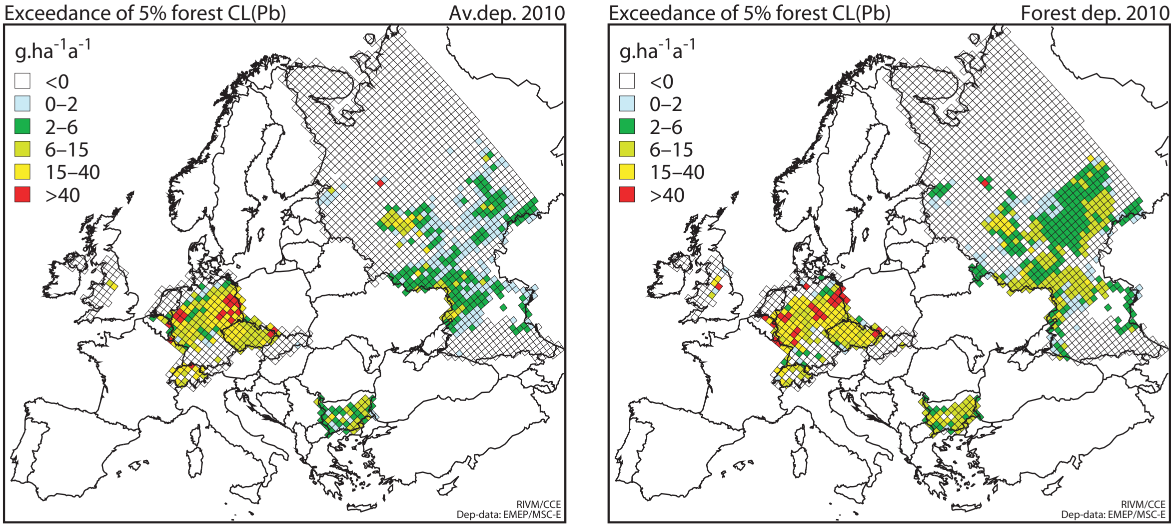


**Preliminary maps - Do not quote!**

**Figure 1-3: Exceedance of the 5th-percentile critical loads (effect-based) for cadmium (left) and lead (right) in 2010 using the mean deposition of these metals in 50x50 km$^2$ EMEP grid cells.**

### 1.3.2 Preliminary exceedance maps using ecosystem-dependent depositions

EMEP/MSC-E tentatively produced ecosystem dependent depositions (see chapter 4) using CCE land cover information (De Smet and Heuvelmans 1997)[2]. First results suggest that ecosystem dependent exceedances do not lead to striking changes in comparison to mean exceedances in Figure 1-3. Tentative results, focussing on lead, are shown in Figure 1-4. Figure 1-4 compares the average deposition of lead to the 5th-percentile forest critical load of lead (left) and the conifer dependent deposition of lead to the 5th-percentile forest critical load of lead (right). The result shows an increase in the area of exceedances, especially in Russia, and an increase of the exceedance magnitudes in distributed grid cells in the countries who submitted preliminary critical loads.



**Preliminary maps - Do not quote!**

**Figure 1-4: Ecosystem dependent exceedances in 50x50 km$^2$ EMEP grid cells using the average deposition of lead to the 5th-percentile forest critical load of lead (left) and the conifer dependent deposition of lead to the 5th-percentile forest critical load of lead (right).**

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[2] In the future an updated CCE land cover map (de Smet and Hettelingh 2001) will be considered.

## 1.4 Recommendations

Preliminary critical load and exceedance maps have been produced on the basis of data submissions of 11 NFCs. Inspection of the data, as reported in chapter 3, and subsequent discussions at the 12th CCE workshop and at the 18th Task Force lead to the following recommendations to:

(a) review total heavy metal inputs (i.e. atmospheric deposition and other sources, taking present concentrations in soil/soil solution into account),
(b) review methods to identify regions where the application of the stand-still approach might be more appropriate than an effects-based approach,
(c) review cross-border variability of the heavy metal content in soils and the exploration of methods to establish natural and anthropogenic shares of heavy metals in present soil content data,
(d) explore whether atmospheric deposition of heavy metals significantly influences the metal content in agricultural soils,
(e) analyse possible inconsistencies of critical load parameter values across borders,
(f) review critical limits and transfer functions,
(g) explore critical limits which can be related to human health,
(h) explore effects-based approaches for mercury.

The 18th TF M&M recommended the work of the Expert Group on Critical Limits and the Expert Group on Transfer Functions to continue its work in 2003, using the results of the preliminary call for data on critical loads of cadmium and lead, described in this report.

## References

Hall J (2001) *Harmonisation of Ecosystem Definitions*. In: M Posch, PAM de Smet, J-P Hettelingh, RJ Downing (eds) Modelling and Mapping of Critical Thresholds in Europe. Status Report 2001, RIVM-Coordination Center for Effects, pp.67-71. (available at *www.rivm.nl/cce*)

De Smet PAM, Heuvelmans E (1997) *Development of the European land cover map*. In: M Posch, J-P Hettelingh, PAM de Smet, RJ Downing (eds) Modelling and Mapping of Critical Thresholds in Europe. Status Report 1997, RIVM-Coordination Center for Effects, pp. 41-46. (available at *www.rivm.nl/cce*)

De Smet PAM, Hettelingh J-P (2001) *Intercomparison of Current European Land Use/land Cover Databases*. In: M Posch, PAM de Smet, J-P Hettelingh, RJ Downing (eds) Modelling and Mapping of Critical Thresholds in Europe. Status Report 2001, RIVM-Coordination Center for Effects, pp. 41-52. (available at *www.rivm.nl/cce*)

# 2. Guidance for the Calculation of Critical Loads for Cadmium and Lead in Terrestrial and Aquatic Ecosystems

Wim de Vries[1], Gudrun Schütze[2], Paul Römkens[1], Jean-Paul Hettelingh
with contributions by Regis Farret[3], Mike Ashmore[4] and Bert Jan Groenenberg[1]

## 2.1. Background and aim

This chapter is a reprint of the guidance document that was distributed to NFCs in the autumn of 2001 to assist them with their response to the call for data on preliminary critical loads for cadmium and lead.

**Background**

During its 20th session, the Working Group on Effects (WGE) decided to have the Coordination Center for Effects (CCE) issue a call for data to allow preliminary mapping of European critical loads of cadmium and lead. The call was issued by the end of 2001, leading to results which were presented at the 12th CCE workshop, at the 18th TFM meeting and which will be presented at the 21st session of the WGE.

In view of this call, the CCE requested the preparation of the guidance document (reprinted here), summarising the following published information. In 1998 two manuals were published, presenting guidelines for calculation methods, critical limits and input data for the calculation of critical loads of heavy metals for terrestrial ecosystems (De Vries and Bakker, 1998) and aquatic ecosystems (De Vries et al., 1998). The development of those manuals started in 1994 and several drafts were discussed at CCE workshops in 1995, 1996 and 1997. Together with other background documents they were also discussed at the "International Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and POPs" in November 1997 in Bad Harzburg, Germany (De Vries et al., 1997a,b). In those two manuals various possibilities are described to calculate critical loads for heavy metals in view of the use of:

- Simple or (more) complex models, based on a mass balance approach for metals
- Different types of critical limits
- Different types of transfer functions between metals in the soil solid phase and soil solution

Since the publication of the manuals a "Workshop on Effects-based Approaches for Heavy Metals" was held in Schwerin, Germany, 12–15 October 1999, focusing on the use of methods and transfer functions and on critical limits to calculate critical loads (Gregor *et al*., 1999). Furthermore, an "Ad-hoc International Expert Group Meeting on Effect-based Critical Limits for Heavy Metals" was held 11–13 October 2000 in Bratislava, Slovak Republic (Curlik *et al*., 2000), focussing specifically on the derivation of critical limits for heavy metals. At the 17th Task Force of the ICP on Modelling and Mapping in Bratislava in 2001, it was concluded that further harmonisation of critical limits and transfer functions is an urgent need. Two expert groups were set up, which should:

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[1] Alterra Green World Research, Wageningen, The Netherlands.

[2] OEKO-Data, Strausberg, Germany.

[3] INERIS, Verneuil en Halatte, France.

[4] University of Bradford, Bradford, United Kingdom.

- Review the transfer functions and critical limits provided in the manual and, more recently, at the workshop in Bratislava.
- Suggest a harmonised set of transfer functions and critical limits, which can be used in first mapping exercises to gain experience in the use of different approaches.

***Aim***

The aim of this chapter (at the time of the call for data) is to provide an up-to-date guidance to derive critical loads for heavy metals for both terrestrial and aquatic ecosystems, summarising the:

- Mass balance models and input data to calculate critical loads
- Transfer functions, describing the relationship between dissolved and adsorbed concentrations of heavy metals, while accounting for the impact of soil properties
- Critical limits for dissolved and adsorbed concentrations of heavy metals, that are essential to carry out the critical load calculations

This guidance is a summary of the two previous manuals and an update of Gregor *et al*. (2000). It also includes transfer functions and critical limits proposed in a joint report by the two expert groups (De Vries *et al*., 2001).

In general, this chapter has not been updated with information becoming available only after the call was made. Therefore, new findings following the presentation of the results of the call for data at the 12th CCE workshop (14-17 April 2002) and at the 18th Task Force on Modelling and Mapping (18-19 April 2002) in Sorrento (Italy) have not been included in this chapter. In stead, new information on the derivation of critical limits for lead and cadmium is included in Annex I of this report.

One exception has been made with respect to the naming of loads computed using the stand-still approach. It was agreed at the 18th TF M&M to use the term stand-still loads rather than critical loads for results of the stand-still approach. This convention has been adopted in this chapter, while also minor textual and layout changes have been made in comparison to the original guidance document.

This chapter provides information on the equations and data that are needed to compute (a) critical loads for terrestrial and aquatic ecosystems using **recommended critical limits**, i.e. an **effect-based** approach, and (b) **stand-still** loads for terrestrial and aquatic ecosystems using a stand-still approach. For the computation of critical and stand-still loads a sequence of equations needs to be assessed. This has been summarised in flowcharts (see Figures 2-1 and 2-2) at the beginning of the sections on terrestrial and aquatic ecosystems respectively.

## 2.2 Terrestrial ecosystems

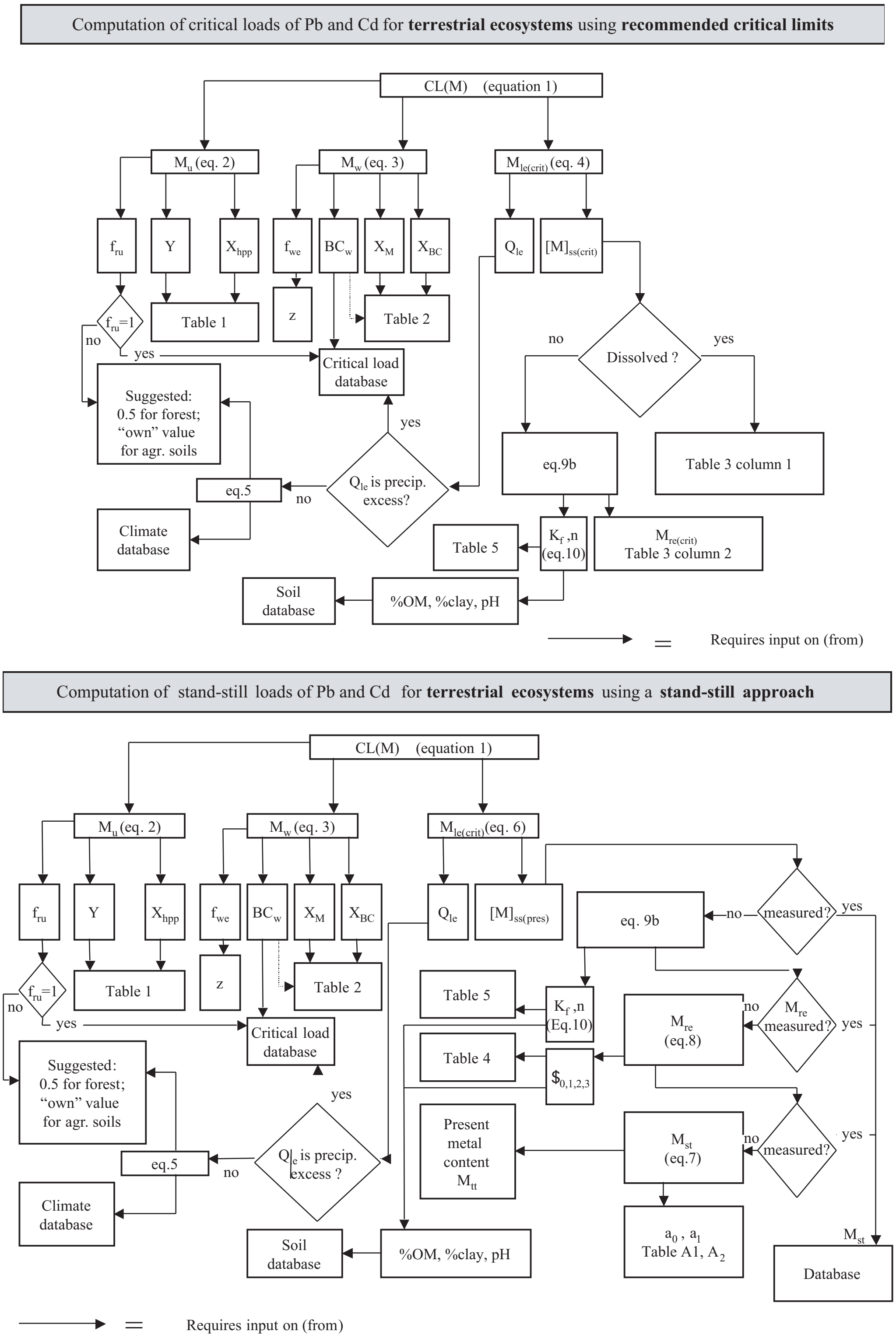


**Figure 2-1: Flowchart of equations and databases required to compute the critical load of Pb and Cd for terrestrial ecosystems using an effect-based approach (top) and a stand-still approach (bottom).**

### 2.2.1 Simple steady-state mass balance model and related input data

**Steady-state mass balance model**

The critical load is the acceptable total load of anthropogenic heavy metal inputs (deposition, fertilisers, other anthropogenic sources). It corresponds to the sum of tolerable outputs from the system by harvest and leaching minus the natural inputs by weathering release. In the manual for terrestrial ecosystems (De Vries and Bakker, 1998), the default method presented to calculate critical loads of heavy metals for soils includes all relevant metal fluxes in or out of the considered system, while assuming a steady state situation (Manual, page 45, Eq 5). This method is specifically relevant when calculating critical loads for the humus layer. The problem, however, is that transfer functions relating metal concentrations in the soil to those in soil solution are up to now limited to the mineral layer. This implies that any estimate of a critical load for the humus layer is highly uncertain. In order to keep this first approach as simple as possible and also stay as close as possible to the simple mass balance approach for nitrogen and acidity, we simplified this model by neglecting the metal cycling within a terrestrial ecosystem according to (see Manual, page 62, Eq. 34):

$$CL(M) = M_u - M_w + M_{le(crit)} \qquad (1)$$

where:

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

$M_u$ = removal of heavy metals by biomass harvesting or net uptake in forest ecosystems, respectively, from the mineral topsoil (g ha$^{-1}$ a$^{-1}$)

$M_w$ = weathering release of heavy metals in the mineral topsoil (g ha$^{-1}$ a$^{-1}$)

$M_{le(crit)}$ = critical leaching of heavy metals from the mineral topsoil (g ha$^{-1}$ a$^{-1}$)

The notation has been adapted to that in the critical load equations for acidity and nutrient nitrogen. M stands for a heavy metal and can be substituted by the chemical symbol of the individual metal (Cd, Pb) under consideration. The model can be even more simplified by neglecting weathering outside volcanic or ore-rich areas ($M_w = 0$ in Eq.1). This approach, which was already used by different countries, implies that the critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate.

The considered depths for the calculation are 10 cm for forest soils, 20 cm for grassland and 30 cm for arable land (plough layer), which are generally quite homogeneous. Furthermore, adverse impacts on plants and soil organisms, which are the main target groups considered, is mainly related to these layers (De Vries and Bakker, 1998; p.44).

Heavy metal removal by harvest of plants in the mineral topsoil

The most simple approach to describe the removal of heavy metals by biomass is to combine the average yield (or increment) of biomass with the heavy metals content in harvested parts:

$$M_u = f_{ru} \cdot Y \cdot X_{hpp} \qquad (2)$$

where:

$f_{ru}$ = root uptake factor, to scale the net uptake in the root zone to the depth considered (-)

$Y$ = annual average removal of biomass (dry weight) (kg ha$^{-1}$ a$^{-1}$)

$X_{hpp}$ = content of the heavy metal in the harvested parts of the plants (g kg$^{-1}$)

Since critical loads for forests are calculated for the mineral topsoil (0-10 cm), the total net uptake is multiplied by the root uptake fraction (fraction of fine roots) in this layer and the overlying humus layer as compared to the total root zone. As a first approximation, this root uptake factor, fru, could be taken equal to 0.5. For agricultural soils, where the whole root zone is considered, this factor can be set equal to 1.0.

Data on biomass removal for forests can in principle directly be derived from the S&N critical loads database. Metal contents in biomass will in principle depend on the critical limit chosen. Using the stand still principle, it refers to present concentration and using an effect-based approach it is best to use results from investigations on relatively unpolluted areas. Since those contents in most cases not normally distributed, the median value (instead of the mean) should be used. It can be expected that those values do not exceed limits or guidance values for use as food or feed, thus the export from the area can be regarded as tolerable. If in a country no content values are available from own studies, the ranges of values given in the Table 2-1 may be used. If contents are available for different harvested parts of the plants (e.g. stem and bark of forest trees), a weighted mean of both should be used.

**Table 2-1: Ranges for the annual biomass removal and the contents of Pb and Cd in biomass for various land use types in a temperate climate at relatively unpolluted sites. More information on the background of these data is given in De Vries and Bakker (1998)**

| Land use | Biomass removal Y (kg.ha$^{-1}$.yr$^{-1}$) | Metal content in harvested parts, $X_{hpp}$ (mg.kg$^{-1}$) | |
|---|---|---|---|
| | | Pb | Cd |
| Grassland | 5000 – 20000 | 1.0 - 3.0 | 0.05 - 0.25 |
| Arable land | 1000 – 6000 | 0.1 - 0.5 | 0.01 - 0.10 |
| Coniferous forest | 2000 – 7000 | 1 - 10 | 0.1 - 0.5 |
| Deciduous forest | 2000 – 6000 | 1 - 10 | 0.1 - 0.5 |

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.

**Heavy metal release by weathering in the mineral topsoil**
The weathering rate of a heavy metal can be estimated by the following equation:

$$M_w = 5 \cdot 10^{-4} \cdot f_{we} \cdot BC_w \cdot \frac{X_M}{X_{BC}} \qquad (3)$$

Where:
$M_w$ = weathering release of heavy metals in the mineral topsoil of 10cm (g ha$^{-1}$a$^{-1}$)
$BC_w$ = weathering release of base cations from the parent material (molc ha$^{-1}$a$^{-1}$m$^{-1}$)
$X_M$ = content of the heavy metal in the parent material (mg kg$^{-1}$)
$X_{BC}$ = content of base cations in the parent material (mol kg$^{-1}$)
$f_{we}$ = factor to scale the weathering rate from 1 m to the depth considered (m)

The factor of $5.10^{-4}$ is needed to convert the result to the appropriate units. To obtain a molar ratio in Eq.3 one has to divide the value of $X_M$ (in mg $kg^{-1}$) by its molar weight times 1000. This leads to a metal weathering rate in molc $ha^{-1}a^{-1}m^{-1}$, which has to be multiplied by the equivalent weight of the metal, being equal to the molar weight divided by 2. These considerations lead to the factor of $5.10^{-4}$. The most simple approach to estimate fwe is by assuming uniform weathering, leading to a value equal to z, where z is the considered depth in m, resulting in, e.g., $f_{we}$=0.1 for forest soils. For both metals and base cations, the content in parent material is used, since the total content of heavy metal M in the (top)soil may be strongly influenced by accumulation on reactive sites due to pollution.

The ratio of heavy metals and base cations in the parent material ($X_M/X_{BC}$) must be derived from geological survey data. The term of weathering may vary from insignificant to several times the deposition rate in ore-rich areas. If the weathering rate of heavy metals is exceeding the outputs by harvest and the critical leaching rate (see below), the area should be excluded as being naturally polluted. An overview of typical ranges of metal contents in parent material that could be used in combination with ranges in base cation weathering rates is given in Table 2-2. Data on base cation weathering rates can in principle directly taken from the S&N critical loads database.

**Table 2-2: Ranges for the base cation weathering rates and the total contents of base cations and of Pb and Cd in the parent material of major clusters of soil types (source are partly results for Dutch soils)**

| Soil type | $BC_{we}(mol_c.ha^{-1}.yr^{-1}.m^{-1})$ | $X_{BC}$ (mol.$kg^{-1}$) | Metal content in parent material (mg.$kg^{-1}$) | |
|---|---|---|---|---|
| | | | $X_{Pb}$ | $X_{Cd}$ |
| Poor sandy soil | 200–400 | 0.2-0.4 | 3-7 | 0.007-0.013 |
| Rich sandy soil | 400–800 | 0.8-1.2 | 5-15 | 0.01-0.03 |
| Loamy soil | 500–1000 | 0.6-1.0 | 15-25 | 0.07-0.13 |
| Heavy clay soil | 1000–2000 | 1.0-1.4 | 40-60 | 0.20-0.30 |

**Critical leaching of heavy metals**

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

$$M_{le(crit)} = 10 \cdot Q_{le} \cdot [M]_{ss(crit)}$$

where:

$Q_{le}$ = flux of leaching water leaching from the mineral topsoil (m.$a^{-1}$)

$[M]_{ss(crit)}$ = critical limit for the total concentration of heavy metal in the percolating soil solution (mg.$m^{-3}$)

The factor of 10 in Eq.4 is needed to convert the unit from mg.$m^{-2}$.$a^{-1}$ to g.$ha^{-1}$.$a^{-1}$. The total concentration of heavy metal in the soil solution is the most appropriate value to calculate the tolerable leaching flux. In this term both the free metal ions and the metals bound in dissolved complexes are included. Both parts are relevant to the leaching process.

The water flux leaching from the mineral topsoil at steady state is calculated according to:

$$Q_{le} = P - E_i - E_{se} - f_{ru} \cdot E_t \qquad (5)$$

where:

$P$ = precipitation (m $a^{-1}$)

$E_i$ = interception evaporation (m $a^{-1}$)

$E_{se}$ = soil evaporation (m $a^{-1}$)

$E_t$ = plant transpiration (m $a^{-1}$)

$f_{ru}$ = root uptake factor (see Eq.2)

In principle, the value of $Q_{le}$ can be derived from the S&N critical loads database, but one has to be aware that if the latter value refers to the total precipitation excess, a scaling is needed to take into account the partial plant transpiration.

The critical load depends to a large extent on the critical limit used. It is assumed that for Cd and Pb, soil biota (microbial processes, soil fauna) and plants are the most sensitive receptors, while secondary poisoning and impacts on food quality (in case of agricultural soils) is not (yet) considered. This means that in the case of Cd and Pb, protection of food quality, higher fauna and ground water is not a decisive point for the derivation of the critical limits, but the conservation of the soil function to act as a biotope. The critical limit can either be included directly or has to be derived from critical limits or present values for the metal concentration in the soil, as described in more detail in the next Section.

### 2.2.2. Assessment of critical limits for terrestrial ecosystems

In the workshop in Schwerin (Gregor, 1999), it was decided that the critical metal load equals the load that will not lead to concentrations of heavy metals above critical limits in defined compartments in a steady-state situation (effect-based approach). At the 18th TFM&M meeting it was agreed that a stand-still load is a load that will not lead to accumulation of heavy metals in the upper soil layer (stand-still approach).

In the effect-based approach, the critical limits for either the soil or the soil solution are based on adverse effects on (parts of) the ecosystem. In the stand-still approach, no further metal increase is accepted, implying that the present total metal concentration in the soil is considered the critical limit. In Schwerin it was suggested to take the minimum of both the stand-still and effect-based approaches, implying that the critical load either causes a stand-still or a decrease in the present metal concentration. The “expert group on critical limits”, however, decided to calculate and present stand-still as well as critical loads, but not to take the minimum of the two (De Vries et al., 2001).

**Effect-based approach**

In calculating a critical load for terrestrial ecosystems, a critical metal leaching rate is derived by multiplying the flux of leaching water with a critical dissolved metal concentration. Using the effect-based approach in view of the ideas mentioned above, this limit can be related to either:

- Critical **reactive soil metal concentrations** based on available NOEC toxicity data related to adverse impacts on soil functioning, such as soil invertebrates, that ingest soil. The implicit assumption is that NOEC data for metals can be regarded as reactive soil metal concentrations, since metal is added to the soil in the experiment and thus readily available.

- Critical **metal concentrations in soil solution** view of impacts on plants or microbiota, which are also relevant for soil functioning.

In the first case, one has to calculate a critical dissolved metal concentration for the critical reactive metal content, using a transfer function as described in Section 4. In the second case, the critical metal leaching rate can directly be calculated. A summary of preliminary effect-based critical limits that was agreed upon by the "expert group on critical limits" is given in Table 2-3.

**Table 2-3: Recommended critical limits including ranges for uncertainty assessment (± 20 %deviation from the recommended value)**

| Metal | Critical dissolved concentration $[M]_{ss(crit)}$ (mg $m^{-3}$) | Critical reactive concentration $M_{re(crit)}$ (mg $kg^{-1}$) |
|---|---|---|
| Cd | 0.8 (0.6 - 1) | 0.9 (0.7 – 1.1) |
| Pb | 8 (6 – 10) | 30 (25 – 35) |

The critical dissolved metal concentrations, $M_{ss(crit)}$, including the range for uncertainty assessments, are based on:

- NOEC toxicity data for soil in view of impacts on plants and microbiota, organisms from which you can be sure that the effect is only through the soil solution
- Data gathered in Germany, France and The Netherlands (Schütze and Throl, 2000; Farret and Magaud, pers.comm.; Klepper and Van de Meent, 1997); Crommentuijn et al., 1997).
- In which both NOECs and soil properties regulating metal availability (organic matter content, clay content and pH) are available
- Harmonised general transfer functions for Pb and Cd given in Section 4 to calculate related NOECs for soil solution from the soil solid phase and
- Statistical approaches, deriving limits based a log-logistic fit of the NOEC data (Aldenberg and Slob, 1991) and applying a 95% protection level ($HC_5$)

More information on the approach and the data sets used is given in De Vries et al. (2001). Also the uncertainties of the derivation and points to be further discussed in the future are described there.

The critical reactive metal concentrations, $M_{re(crit)}$, are based on the NOEC data for soil fauna data, using all available data from Schütze and Throl (2000), Farret and Magaud , pers.comm. (in connection with an EC Technical Guidance document on risk assessment) and Klepper and Van de Meent (1997), who mainly included data from Crommentuijn et al. (1997).
It was assumed that these organisms mainly get their metal intake through soil ingestion (e.g. hard-bodied soil invertebrates). In reality, most of those organisms do take up metals both from the soil and solution. Again, more information on the approach and the data sets used is given in De Vries et al. (2001).

### Stand-still approach

As an alternative to the effect-based approach a stand-still approach may be used (Gregor, 1999), which aims at avoiding any (further) accumulation of heavy metals in the soil. Note, however, that the current leaching may already imply significant effects, and is thus per se not acceptable in the long term. In the stand-still approach the critical leaching term is calculated as:

$$M_{le(crit)} = 10 \cdot Q_{le} \cdot [M]_{ss(pres)} \qquad (6)$$

where:

$[M]_{ss(pres)}$ = present total concentration of heavy metal in the percolating soil solution ($mg.m^{-3}$)

A limitation of the stand-still approach is that data on current concentrations of heavy metals in the leaching water are scarce, thus hampering the calculation of critical loads[1] on a large spatial scale. Therefore the current leaching can be mapped only on the basis of transfer functions to transform total contents of Cd and Pb in the upper soil layers, which are often available, into concentrations of the soil solution. Calculation of stand-still loads thus implies that present soil metal concentrations need to be assessed and mapped in each country.

There are several possibilities with respect to the availability of present metal concentration data. The data might be total concentrations based on a HF destruction or “so-called” total concentrations, based on aqua regia destruction or a concentrated nitric acid destruction. It is also possible that countries do have data sets on reactive metal concentrations based on mild $HNO_3$ (0.43N), EDTA or DTPA extractions.

In all cases, the soil concentration has to be translated to a dissolved concentration using a certain transfer function, as discussed in the following section. To avoid confusion the following abbreviations (subscripts) are used:

- tt = total (destruction by HF plus mineral acids under pressure)
- st = “so-called” total (e.g. aqua regia or other strong acids)
- re = reactive (e.g. extraction by 0.43N $HNO_3$, other mild acids, complexing agents like EDTA, DTPA, or mineral salt solutions)
- ss = soil solution (refers to the total dissolved metal concentration)

## 2.2.3 Transfer functions

**Possible approaches**

There are various approaches to derive total dissolved metal concentrations ($[M]_{ss}$) from total soil metal concentrations ($M_{tt}$ or $M_{st}$). The simplest approach is a direct empirical approach relating both concentrations, while accounting for the impact of major soil properties influencing the sorption relationship. This approach is, however, not suggested here, because there is no real process mechanism involved in this approach, since part of the metals extracted by e.g. HF or aqua regia do not interact with the soil solution (inert or immobile part, being equal to the total minus the reactive part). Starting from total concentrations, it is essential to (i) first derive the reactive metal concentration, $M_{re}$, from the total soil metal concentration (generally $M_{st}$) and (ii) derive the total dissolved metal concentration, $[M]_{ss}$, from the reactive metal concentration, $M_{re}$, accounting for the impact of soil properties. The most fundamental approach is to relate the free metal ion activity to $M_{re}$, accounting also for the impact of major ions in soil solution competing with the metals and then calculate the total dissolved metal concentration, $[M]_{ss}$, from the free metal ion activity, using a (simple) complexation model (De Vries and Bakker, 1998). This approach does, however, require more data and is therefore not suggested yet.

Taking into account the above-mentioned aspects, the following sequence of transfer functions is considered in this guidance:

- from total ($M_{tt}$) to “so-called” total metal concentration ($M_{st}$)
- from “so-called” total metal concentration ($M_{st}$) to reactive metal concentration ($M_{re}$)
- from reactive metal concentration ($M_{re}$) to dissolved metal concentration ($[M]_{ss}$)

These different transfer functions are discussed next.

**Transfer functions from total to “so-called” total metal concentrations**

Utermann et al. (2000) provided transfer functions to calculate “so-called” total contents of heavy metals ($M_{st}$; here aqua regia (AR)) from total contents ($M_{tt}$; HF), according to:

$$\log_{10} M_{st} = a_0 + a_1 \cdot \log_{10} M_{tt} \qquad (7)$$

where:

$M_{tt}$ = total concentration of heavy metal M in soil (mg kg$^{-1}$)
$M_{st}$ = “so-called” total concentration of heavy metal M in soil (mol kg$^{-1}$)

Values for $a_0$ and $a_1$ are given in Appendix 1. The correlations are depending on metal and substrate. For back-calculations of total contents from AR different functions are to be used. These functions are not provided here, since those calculations are not needed in the present calculation procedure.

**Transfer functions from “so-called” total to reactive metal concentrations**

The reactive metal concentration ($M_{re}$, here: 0.43N $HNO_3$) can be related to the so called total concentration (Mst, here: aqua regia digestion) according to:

$$\log_{10} M_{re} = \beta_0 + \beta_1 \cdot \log_{10} M_{st} + \beta_2 \cdot \log_{10}(\%OM) + \beta_3 \cdot \log_{10}(\%clay) \qquad (8)$$

where:

$M_{re}$ = reactive concentration of heavy metal M in soil (mol kg$^{-1}$)

Values for the various coefficients were derived from 49 soils with a large range in metal contents and soil properties, in which the reactive metal concentration was approximated by mild (0.43N) $HNO_3$ extraction. Results are shown in Table 2-4.

**Table 2-4: Values for the coefficients ß$_0$-ß$_3$ in the relationship between relating reactive, $M_{re}$, and “so-called” total soil concentrations, $M_{st}$, of cadmium and lead (Eq.8).**

| Metal | ß$_0$ | ß$_1$ | ß$_2$ | ß$_3$ | $R^2$ | se-$y_{est}$ 1) |
|---|---|---|---|---|---|---|
| Cd | 0.225 | 1.075 | 0.006 | -0.020 | 0.82 | 0.26 |
| Pb | 0.063 | 1.042 | 0.024 | -0.122 | 0.88 | 0.17 |

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

**Transfer functions from reactive to dissolved total metal concentrations**

Freundlich isotherms that relate the reactive metal content ($M_{re}$) to the total concentration in soil solution ($[M]_{ss}$) can be expressed as:

$$M_{re} = K_f \cdot [M]_{ss}^{\ n} \qquad (9a)$$

or inversely

$$[M]_{ss} = (M_{re} / K_f)^{1/n} \qquad (9b)$$

where:

$M_{re}$ = reactive metal concentration (here 0.43 N $HNO_3$ extractable) (mol $kg^{-1}$)
$[M]_{ss}$ = total metal concentration in soil solution (mol $m^{-3}$)*
$K_f$ = Freundlich coefficient ($mol^{1-n}$ $m^{3n}$ $kg^{-1}$)
n = Freundlich exponent (-)

To obtain an equation that can be used for a range of soils, $K_f$ can be written as:

$$\log_{10}K_f = \alpha_0 + \alpha_1 \cdot \log_{10}(\%OM) + \alpha_2 \cdot \log_{10}(\%clay) + \alpha_3 \cdot pH \qquad (10)$$

The values of $\alpha_0$, $\alpha_1$, $\alpha_2$ and $\alpha_3$ are obtained by multiple linear regression. As stated before, more (soil) parameters can be included, but often a lack of data on larger scale levels (national, international) limits the approach to the ones mentioned here (i.e. organic matter, clay and pH). Results of such a fit, based on two data sets of 114 soil samples and 1466 complete records of both solid phase and solution composition, are given in Table 2-5. The results are based on a regression in which the dissolved concentration is given in mol m-3. More information on the data set and the optimisation of the parameters is given in Römkens *et al*. (2001). Table 2-5 gives also the estimated values of the Freundlich exponent n.

**Table 2-5: Values for $\alpha_0$, $\alpha_1$, $\alpha_2$ and $\alpha_3$, and n in the transfer function between reactive and dissolved cadmium and lead concentration (Eq.10).**

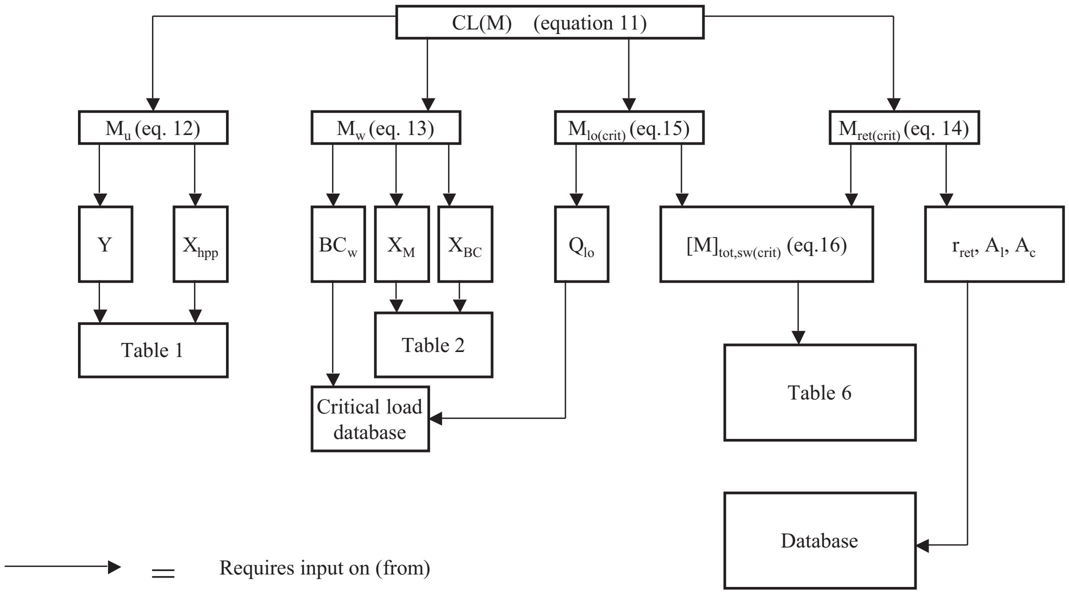
| Metal | $\alpha_0$ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | n | $R^2$ | se-$y_{est}$ 1) |
|---|---|---|---|---|---|---|---|
| Cd | -5.01 | 0.65 | 0.27 | 0.29 | 0.54 | 0.77 | 0.37 |
| Pb | -3.06 | 0.85 | 0.02 | 0.26 | 0.67 | 0.58 | 0.55 |

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

***Note:** In Eqs.9,10 it is crucial to use proper units. First the molar reactive concentration has to be derived from concentrations that are generally given in mg.$kg^{-1}$, by first dividing them by 1000 and then dividing them by the molar weight of Cd (112.4) or Pb (207.2). The resulting metal concentration in solution in mol.$m^{-3}$ has to be multiplied by 1000 and then by the molar weight of Cd or Pb to get the concentration in mg.$m^{-3}$ used in the critical load calculations.

## 2.3. Aquatic ecosystems

Computation of critical loads of Pb and Cd for **aquatic ecosystems** using **recommended critical limits**



Computation of stand-still loads of Pb and Cd for **aquatic ecosystems** using a **stand-still approach**

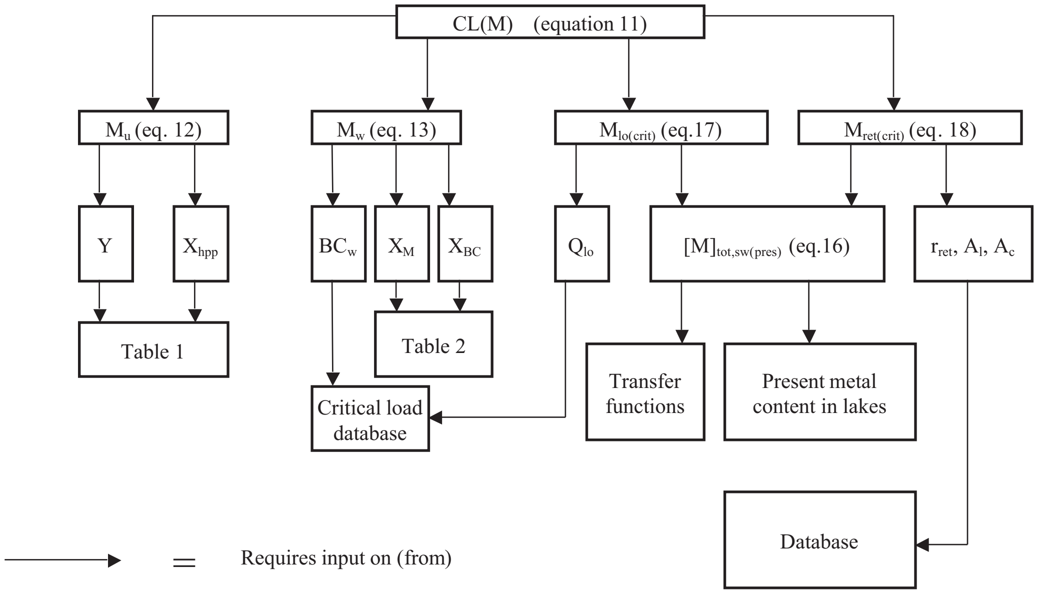


**Figure 2-2: Flowchart of equations and databases required to compute the critical load of Pb and Cd for aquatic ecosystems using an effect-based approach (top) and a stand-still approach (bottom).**

### 2.3.1 Simple steady-state mass balance model and related input data

**Steady-state mass balance model**

As with terrestrial ecosystems, the critical load is the acceptable total load of anthropogenic heavy metal inputs that now corresponds to the sum of tolerable outputs from the catchment by harvest and outflow plus the in-lake metal retention minus the natural inputs by weathering release. In the manual for aquatic ecosystems (De Vries *et al.*, 1998) the default method presented to calculate critical loads of heavy metals for soils includes all relevant metal fluxes in or out of the considered system. The in-lake metal retention thus includes sedimentation, resuspension and exchange processes in the lake (infiltration, diffusion and bioirrigation), while assuming a steady state situation (ibid., p.28, Eq.4). To keep the present approach as simple as possible, and also to stay as close as possible to the simple mass balance approach for nitrogen and acidity, we simplified this model by lumping transient exchange processes at the sediment-water interface and the net effect of sedimentation and resuspension in one retention term according to (ibid., p.62, Eq.34):

$$CL(M) = M_u - M_w + M_{ret(crit)} \cdot A_l / A_c + M_{lo(crit)} \qquad (11)$$

where:

$M_u$ = removal of heavy metal by biomass harvesting or net uptake in forest ecosystems, respectively, in the catchment (g $ha^{-1}a^{-1}$)
$M_w$ = weathering release of heavy metal in the catchment (g $ha^{-1}a^{-1}$)
$M_{ret(crit)}$ = net retention of heavy metal in the aquatic system at critical load (g $ha^{-1}a^{-1}$)
$M_{lo(crit)}$ = critical lateral outflow of heavy metal from the aquatic system (g $ha^{-1}a^{-1}$)
$A_l$ = lake area (ha)
$A_c$ = catchment area (ha)

**Heavy metal removal by net uptake and release by weathering in the catchment**

The assessment of these data is comparable for those in forest ecosystems, 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 or weathering in the root zone/catchment to the mineral topsoil. The equations for net uptake and weathering thus become:

$$M_u = Y \cdot X_{hpp} \qquad (12)$$

$$M_w = 5 \cdot 10^{-4} \cdot BC_w \cdot \frac{X_M}{X_{BC}} \qquad (13)$$

**Critical output and net retention of heavy metals from the aquatic system**

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

$$M_{ret(crit)} = 10 \cdot r_{ret} \cdot [M]_{tot,sw(crit)} \qquad (14)$$

where:

$r_{ret}$ = net retention rate in the lake system (m $a^{-1}$)
$[M]_{tot,sw(crit)}$ = critical limit for the total concentration (dissolved and in suspended particles)of heavy metal in surface water (mg $m^{-3}$)

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

$$M_{lo(crit)} = 10 \cdot Q_{lo} \cdot [M]_{tot,sw(crit)} \qquad (15)$$

where:
$Q_{lo}$ = lateral outflow flux of water from the aquatic system (m $a^{-1}$)

In the manual for aquatic ecosystems, $Q_{lo}$, is denoted as the hydraulic load to comply with the literature on this subject. The hydraulic load is often described as the ratio of the lake depth, z (m), and the hydraulic residence time, $\tau_w$ (a), where the residence time equals the ratio of the lake volume, V ($m^3$), and the flow through the aquatic system, Q ($m^3a^{-1}$).

The total concentration of metals can be calculated as:

$$[M]_{tot,sw} = [M]_{sw} + M_{sus,tot} \cdot c_{sus} \qquad (16)$$

where:
$[M]_{sw}$ = dissolved concentration of a heavy metal in surface water (mg $m^{-3}$)
$M_{sus,tot}$ = total content of a heavy metal in suspended particles (mg $kg^{-1}$)
$c_{sus}$ = 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. 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. For the sake of simplicity we here use only critical limits for the total dissolved concentration of heavy metal to avoid the need of using complexation reactions. Nevertheless, it is still necessary to include a transfer function to calculate the concentration in suspended particles.

**Catchment characteristics**
Relevant catchment characteristics are the lake and catchment area, which should be available for those lakes for which critical loads for acidity have been calculated. 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 measure metal concentrations in the lateral inflow to the lake and in the lake itself (*Ibid.*, pp.46-49). Another approximation can be derived from an annual average net sedimentation rate. Those rates vary in general from 1-25 mm $a^{-1}$.

The concentration of suspended particles in the water compartment depends on the turbulence of the water, which in turn depends on wind speed and water flow velocity. The concentration of suspended particles may thus vary considerably and generally ranges from 1-100 g $m^{-3}$. The average concentration for Dutch surface waters, for example, is 30 g $m^{-3}$.

### 2.3.2 Assessment of critical limits for aquatic ecosystems

As with terrestrial ecosystems, a critical metal load can be derived that will not lead to:

- Concentrations of heavy metals above critical limits in surface water in a steady-state situation and/or
- Accumulation of heavy metals in the catchment.

In the first effect-based approach, the critical limits for surface water are based on adverse effects on (parts of) the ecosystem. In the second stand-still principle, no further metal increase is accepted, implying that the present total metal concentration in the lateral outflow from the lake is considered the critical limit.

**Effect-based approach**

A summary of preliminary effect-based critical limits, based on an EU document for Cd and on Crommentuijn et al. (1997), that was agreed upon by the "expert group on critical limits", is given in Table 2-6. Those data were also mentioned in the manuals on terrestrial and aquatic ecosystems. Compared to terrestrial ecosystems, the values are higher for Pb and lower for Cd. The critical limits are related to the dissolved concentration, thus requiring the use of transfer functions to calculate

**Table 2-6: Recommended critical limits for surface waters including ranges for uncertainty assessments (±20% deviation from the recommended value).**

| Metal | Critical dissolved concentration (mg m$^{-3}$) |
|---|---|
| Cd | 0.3(0.2 – 0.4) |
| Pb | 11(9 – 13) |

**Stand-still approach**

In the stand-still approach, the leaching and in-lake retention fluxes become (see Eqs.14,15):

$$M_{lo(crit)} = 10 \cdot Q_{lo} \cdot [M]_{tot,sw(pres)} \qquad (17)$$

and

$$M_{ret(crit)} = 10 \cdot r_{ret} \cdot [M]_{tot,sw(pres)} \qquad (18)$$

where:

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

### 2.3.3 Transfer functions

There are various possible approaches to derive adsorbed metal concentrations on suspended particles ($M_{sus,tot}$) from total dissolved metal concentrations in surface water ($[M]_{tot,sw}$). The simplest approach is an empirical linear approach ($K_d$-value) relating both concentrations, while accounting for the impact of major properties of the suspended particles influencing the sorption relationship. There is no good reason to assume that this relationship will differ from those derived for the soil (Eq. 9), using values for $K_f$ and n that can be derived by using Eq.10 and Table 2-5. The problem, however, is that total concentrations can not be obtained from the inverse of Eq.8, since heavy metal analyses by acid extraction in sediment or suspended particles also includes precipitates. Consequently, there is no real relationship between dissolved metal concentrations in surface water and total concentrations in sediment or suspended particles. A pragmatic solution, used in the manual for aquatic ecosystems is to apply a linear approach, according to:

$$[M]_{sus,tot} = K_d \cdot [M]_{sw} \qquad (19)$$

where:

$K_d$ = partition coefficient between the total concentration of a heavy metal M in in suspended particles and the dissolved concentration in surface water ($m^{-3}$ $kg^{-1}$)

Reported $K_d$ values are 430 for Pb and 85 for Cd (De Vries *et al.*, 1998).

## 2.4. Summary of the present approach

In general, a critical load is calculated by first selecting a receptor of interest, followed by the determination of a critical limit and then calculating a critical load (see the flow charts for calculating critical loads in the two manuals). Following this approach, the above mentioned approach for terrestrial ecosystems can be summarised as presented in the flow chart given in Figure 2-3. For terrestrial ecosystems, the most important point is to derive a critical limit, either directly (Table 2-3) or indirectly using various transfer functions. If this value is available, the assessment of a critical load is simple, as summarised in the Figure 2-3. For aquatic ecosystems, the figure can be simplified since a critical dissolved concentration can directly be derived from Table 2-6. The other parts remain the same, but the various fluxes are now given by Eqs.12-15 and in-lake metal retention has to be accounted for.

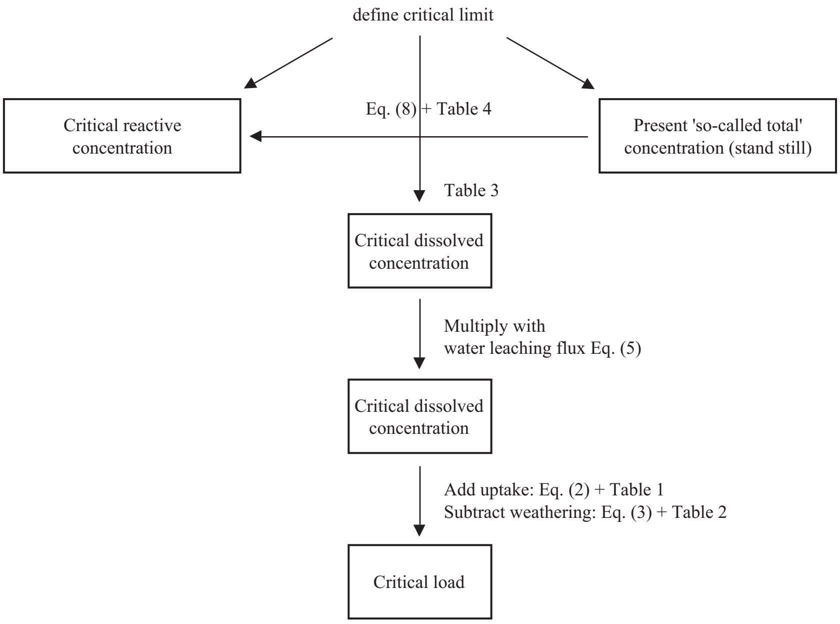


**Figure 2-3: Flowchart describing the assessment of a critical load for terrestrial ecosystems**

## 2.5. Limitations in the present approach and possible future refinements

The guidance for the calculation of critical loads for cadmium and lead in terrestrial and aquatic ecosystems provided here is based on the following assumptions:

- Critical limit values for terrestrial ecosystems are derived from statistical analysis of effects data on plants, microbiological processes and soil invertebrates. Secondary poisoning, including human health aspects, is not considered. For agricultural systems, we do not include criteria with respect to food quality that can be back calculated to soil quality criteria.
- Critical and stand-still loads can be calculated on the basis of a steady-state effect-based or stand-still approach respectively. For terrestrial ecosystems this implies that the critical load calculations will either be rather independent of the soil (the effect-based approach based on critical limits for dissolved metal concentrations) or always lead to the situation that critical loads are lower for clay and peat soils than for sandy soils (the effect-based approach based on critical limits for reactive metal concentrations and the stand-still approach), since the adsorption of metals is higher in clay and peat soils than in sandy soils. This seems counter-intuitive to the common belief of effects and is related to the fact that heavy metals in soil are far from equilibrium with metal inputs. Using a target load, however, the situation reverses. The calculation of a target load implies the use of a (simple) dynamic approach, including an acceptable net accumulation in the soil (based on the difference from background values of total contents to critical limits for total contents), according to the Eqs.7 and 8 in the Manual (De Vries and Bakker, 1998) and considering the simplifications of this guidance[5].

In general this guidance has to be further reviewed following the results of the first call for data. Also the discussions about critical limits and transfer functions are not yet finished, and an update is to be foreseen in the future (see also Annex I for an first update following the 12th CCE workshop and the 18th TFM&M meeting in Italy (Sorrento, 14-19 April 2002).

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[5] The 18th Task Force on Modelling and Mapping (Sorrento 2002) decided not to focus on the calculation of target loads in connection with effect-based work.

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# Appendix 1: Relations between cadmium and lead contents in soils extractable by aqua regia and total contents determined by HF extraction or x-ray fluorescence analysis

The relationship between Cd and Pb extracted by aqua regia (AR) and total content was approximated by (see Eq.7):

$\log_{10}$ Cd (AR)= $a_0 + a_1 \log_{10}$ Cd (HF) and $\log_{10}$ Pb (AR)= $a_0 + a_1 \log_{10}$ Pb (HF)

Values for $a_0$ and $a_1$ for Cd are given in Table A1 and for Pb in Table A2.

**Table A1: Relation between cadmium (Cd) content in soils extractable by aqua regia (AR) and total contents in dependence on the parent material.**

| parent material | $a_0$ | $a_1$ | n | $r^2$ $\alpha \leq 0.05$ | 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 |
| General | -0.12 | 1.19 | 274 | 0.91 | - | - |

**Table A2: Relation between lead (Pb) content in soils extractable by aqua regia (AR) and total contents extractable by HF in dependence on the parent material.**

| parent material | $a_0$ | $a_1$ | n | $r^2$ $\alpha \leq 0.05$ | 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 |
| General | -0.45 | 1.24 | 289 | 0.95 | - | - |

# 3. Summary of National Data

Jaap Slootweg, Maximilian Posch

## 3.1 Introduction

In response to the request by the WGE, the CCE issued a call for data on critical loads for cadmium and lead on 18 December 2001. NFCs were asked to submit data before 11 March 2002. The results were presented on the 12th CCE workshop in Sorrento (Italy). After the workshop several NFCs improved their data sets before the deadline of this report (15 May 2002). This chapter presents a summary and analysis of the results of both the critical loads data and their auxiliary variables.

## 3.2 Requested critical loads and auxiliary paramaters

The critical load data and parameters the NFCs were asked to submit are listed in the following box.

**1. Longitude:**

**2. Latitude:**

The geographical co-ordinates of the site or a reference point of the polygon (sub-grid) of the receptor under consideration (in decimal degrees, i.e. 48.5 for 48º30’, etc.)

**3. EMEP50-i (horizontal) grid index:**

**4. EMEP50-j (vertical) grid index:**

Indices (integers) of the 50km x 50km EMEP-grid cell in which the receptor is located. See “Appendix A” of the CCE Status Report 2001 for details on this grid.

**5. Ecosystem area:**

The area (weight) of the ecosystem, within its EMEP-grid cell, for which the critical loads are computed (in km$^2$).

**6. Critical load of heavy metal using an effect-based approach, $CL_{effb}(M)$** [g ha$^{-1}$ a$^{-1}$]

**7. Critical load of heavy metal using the stand-still principle, $CL_{stst}(M)$** [g ha$^{-1}$ a$^{-1}$]

**8. Net uptake of heavy metal, $M_u$** [g ha$^{-1}$ a$^{-1}$]

**9. Weathering rate of heavy metal, $M_w$** [g ha$^{-1}$ a$^{-1}$]

**10. Flux of leaching water, $Q_{le}$** [m a$^{-1}$]

For aquatic ecosystems this should be $Q_{le}$

**11. Critical limit for the concentration of heavy metal in solution, $[M]_{ss(crit)}$** [mg m$^{-3}$]

For aquatic ecosystems this should be $[M]_{ss(crit)}$

**12. Present concentration of heavy metal, $[M]_{ss(pres)}$** [mg m$^{-3}$]

The present concentration is used to calculate $CL_{stst}(M)$. For aquatic ecosystems this should be $[M]_{sw(pres)}$

**13. Layer thickness, $z$** [m]

**14. Annual yield (or increment) of biomass (dry weight), $Y$** [kg ha$^{-1}$ a$^{-1}$]

**15. Content of heavy metal in the harvested parts of the plants, $X_{hpp}$** [g kg$^{-1}$]

**16. Content of heavy metal in the parent material, $X_M$** [mg kg$^{-1}$]

**17. Content of base cations in the parent material*, $X_{BC}$** [mol$_c$ kg$^{-1}$]

**18. Clay content oftop soil, *clay*** [%]

**19. Soil organic matter, *OM*** [%]

**20. Acidity, *pH*** [-]

**21. Ecosystem code, *ecosystem***

Preferably use the code of the European Nature Information System (EUNIS) habitat classification (version 2.2 from May 2001 or later). For a discussion see Part II, Chap. 2 “Harmonisation of Ecosystem Definitions” in the CCE Status Report 2001. For a full overview of the classification look at *mrw.wallonie.be/dgrne/sibw/EUNIS/home.html*. Also codes for agricultural classes are mentioned there. Other codes should be explained in the explanatory document.

* We should have used the unit [mol kg$^{-1}$], because this is how it is used in formula (3) of the Guidance

These auxiliary parameters are used for checking the consistency in the calculation of the critical loads and for inter-country comparisons. All parameters are defined in the Guidance document (See Chapter 2).

NFCs were also asked to submit a documentation together with their data, with information on used methodology, assumptions on parameter values, as well as deviations from the Guidance (if any). Several countries did not submit data, but sent a document explaining the reasons. All these documents can be found in Part II of this Report.

## 3.3 Data submissions from the participating countries

Eleven NFCs submitted data, and six informed the CCE that they would not send any data in response to this call. As can be read in the Guidance document three approaches could be used for calculating critical loads. Two approaches are effect-based: The first is related to a critical metal concentration in the soil solution (a); the second is based on a critical reactive soil metal concentrations (b). The third is the so-called stand-still approach, aiming at preventing further accumulation of heavy metals. Of the 11 countries that submitted data, only Germany provided data for all three approaches. Ten submitted data for effects in the soil solution, of which six also used stand-still. Italy submitted only results from a semi-dynamic model, depending on present concentrations, but including accumulation. An overview of the countries that submitted data, with the number of ecosystems for each approach, is given in Table 3-1.

**Table 3-1: Number of ecosystems (records) per country for different approaches.**

| Country code | Country | Effects in solution (a) | Effects in soil (b) | Stand-still |
|---|---|---|---|---|
| BG | Bulgaria | 55 | - | 55 |
| BY | Belarus | 17 | - | - |
| CH | Switzerland | 691 | - | - |
| CZ | Czech Republic | 41,257 | - | 34,599 |
| DE | Germany | 1,222,695 | 1,222,695 | 870,238 |
| GB | United Kingdom | 1,086 | - | 186 |
| IT | Italy | - | - | 250* |
| NL | Netherlands | 17,807 | - | 17,807 |
| RU | Russian Federation | 14,748 | - | - |
| SK | Slovakia | 320,891 | - | 320,891 |
| UA | Ukraine | 1,603 | - | - |

*semi-dynamic model results are here classified as stand-still.

For the first time NFCs were asked to use the European Nature Information System (EUNIS) land use/land cover classification; and after some extra communication data could be classified in that way for all countries, except Belarus and Ukraine. As can be seen from Table 3-2, the detail and the type of ecosystems considered by countries varies. Belarus and Ukraine submitted data without any ecosystem classification and therefore are missing from the table. Note that the number of ecosystems is for cadmium only; for lead the numbers are almost identical. In the Guidance formulas are also given for calculating critical loads for surface waters, but no country has submitted data for that ecosystem type.

**Table 3-2: Number of ecosystems (records) per ecosystem type per country.**

| Ecosystem | BG | CH | CZ | DE | GB | IT | NL | RU | SK |
|---|---|---|---|---|---|---|---|---|---|
| C3 Littoral zone of inland waters | | | 945 | | | | | | |
| D Mire, bog and fen | | | | 944 | | | | | |
| E Grassland, tall forb | | | 1,115 | 6,906 | | | | | |
| E2.6 Agricultural grassland | | | | 139,778 | 571 | | | | |
| F Heathland, scrubs, tundra | | | | 3,800 | | | | | |
| FB Shrub plantations | | | | 9,978 | | | | | |
| G Forest | | | | 250 | | | | | |
| G1 Broadleaved deciduous | 54 | 189 | | 88,479 | | | 9,457 | | 208,451 |
| G3 Coniferous | 29 | 460 | 6,132 | 221,755 | | | 8,349 | 7,372 | 112,440 |
| G4 Mixed conif and decid | 1 | | | 89,560 | 515 | | | 7,367 | |
| G5 Sparse woodland | | 42 | | | | | | | |
| G5.6 Early and regrowth | | | | 1,041 | | | | | |
| I1 Arable land | | | 34,010 | 556,729 | | 250 | | | |
| X08 Rural Mosaics | | | | 102,780 | | | | | |

To enable easy comparison between countries we grouped critical loads into three major classes: forest (all classes G), agricultural (classes I1 and X08), and “vegetation” (classes other classes). To indicate the part of the country covered, the area of the ecosystems submitted is shown in Fig. 3-1 as fraction of the total country area.

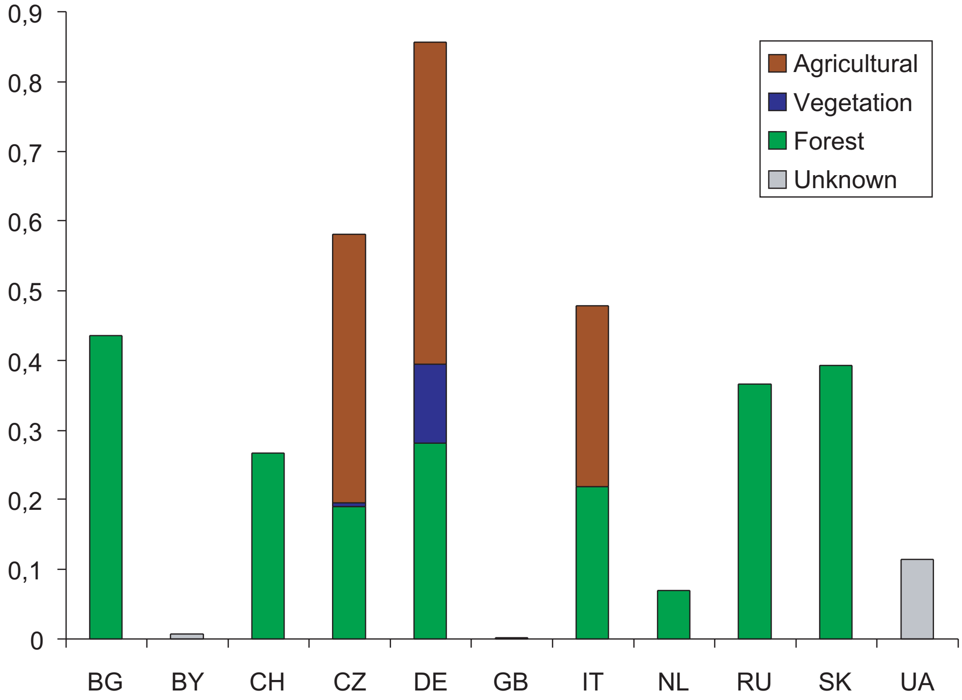
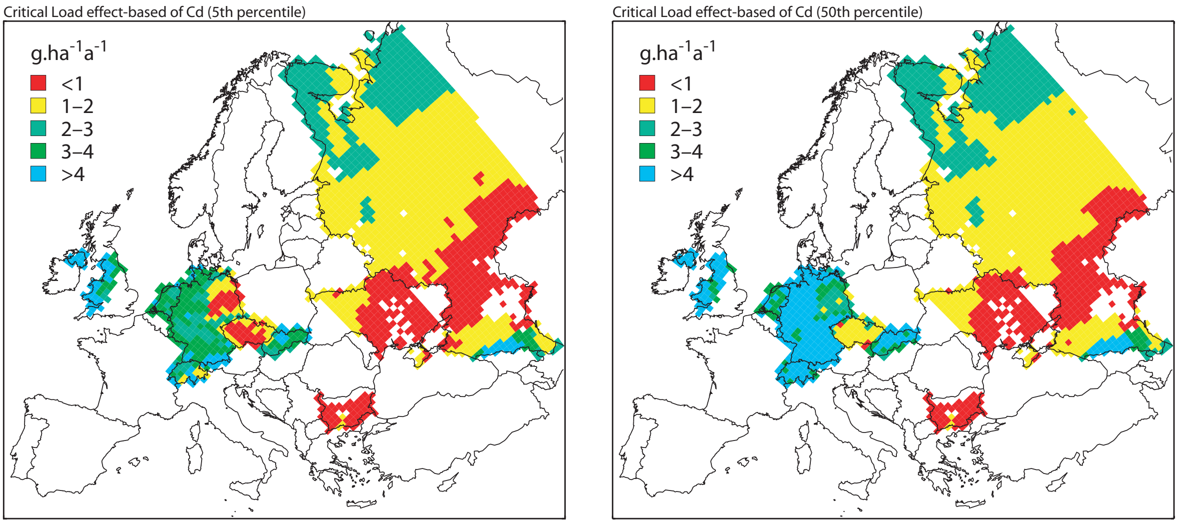


**Figure 3-1: Fraction of total country area for which critical loads are submitted per ecosystem type.**

## 3.4 Results

### Maps of critical loads

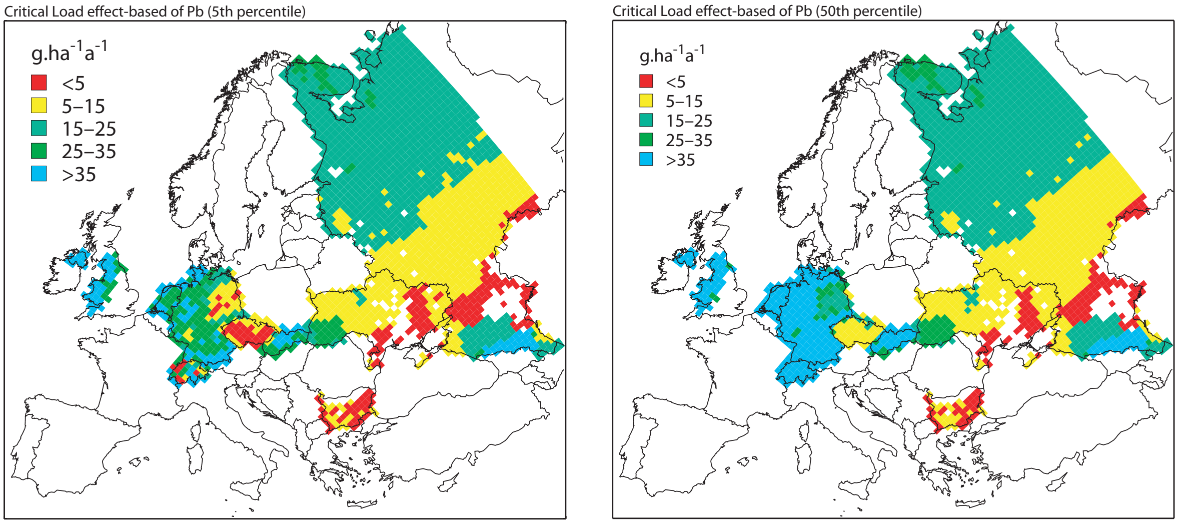
Each type of critical load is presented in two ways: As maps and as cumulative distribution functions (CDFs). In Fig. 3-2 the 5th and 50th (median) effect-based (soil solution criterium) critical loads of cadmium end lead are shown on the EMEP 50x50 grid; and Fig. 3-3 shows the same for the stand-still load.



Critical Load effect-based of Cd (5th percentile)

Critical Load effect-based of Cd (50th percentile)

**Preliminary maps - Do not quote!**

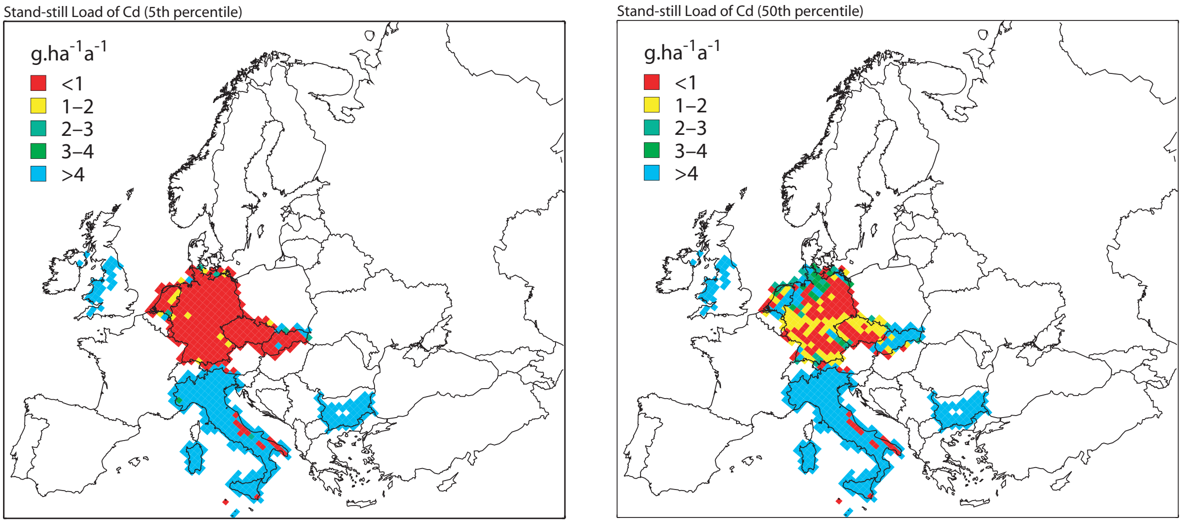


Critical Load effect-based of Pb (5th percentile)

Critical Load effect-based of Pb (50th percentile)

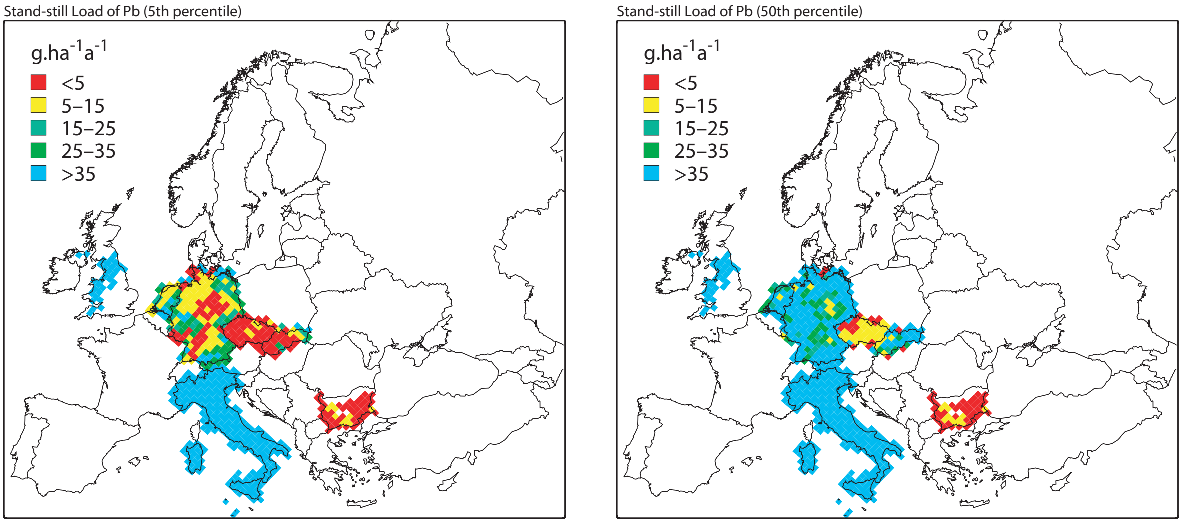
**Figure 3-2: Fifth percentile (left) and median (right) effect-based critical loads of cadmium (top) and lead (bottom) on the 50x50 EMEP grid.**

For the effect-based approach (Fig. 3-2) the more sensitive areas are found in Bulgaria, Ukraine, the south of Russia and some areas in Germany and the Czech Republic for both metals. Fig. 3-3 shows that the stand-still principle would result in much higher sensitivity in The Netherlands and


Stand-still Load of Cd (5th percentile)

Stand-still Load of Cd (50th percentile)

**Preliminary maps - Do not quote!**


Stand-still Load of Pb (5th percentile)

Stand-still Load of Pb (50th percentile)

**Figure 3-3: Fifth percentile (left) and median (right) stand-still loads of cadmium (top) and lead (bottom) on the 50x50 EMEP grid.**

Germany for both metals.

Germany submitted critical load data for both effects related to the reactive concentration in the soil and related to the concentration in the soil solution. In Fig. 3-4 the 5th percentile critical load of these two effect-based approaches, as well as 5th percentile after taking the minimum of the two critical loads at every site, are presented. Clearly, effects for soil are in different areas than effects in soil solution. Taking the minimum obviously leads to much bigger areas that are sensitive. Note, that in all other effect-based maps and graphs only the data for soil solution are taken.

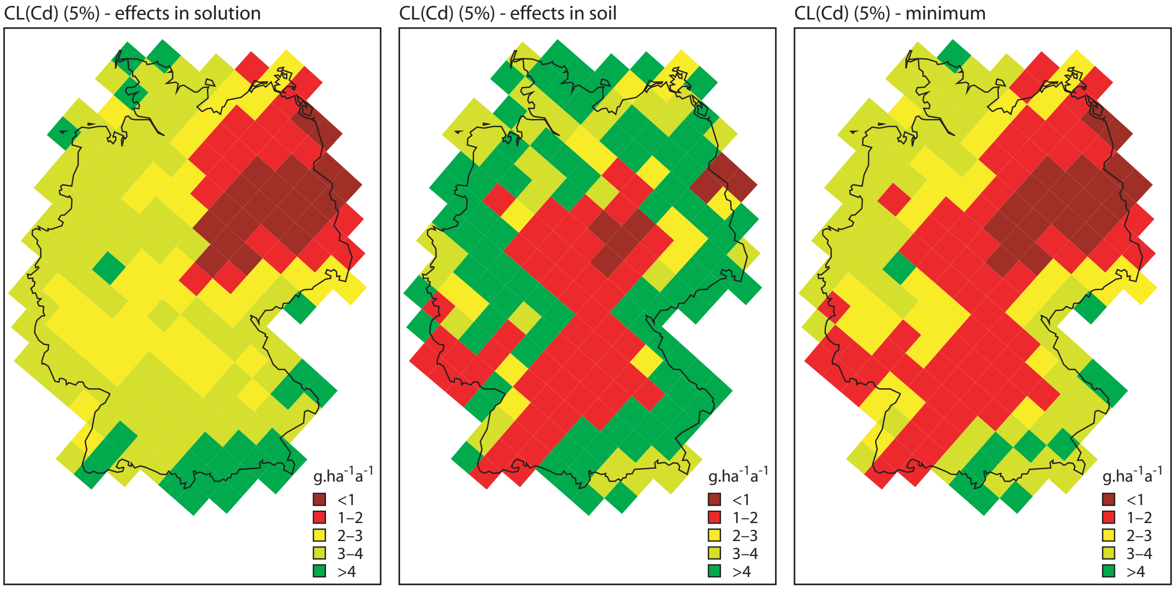


**Figure 3-4: Effect-based critical load for Germany (5%) for effects in solution (left), soil (centre) and the minimum of both (right).**

## Analysis of critical loads

Maps are an excellent way of gaining insight into the spatial distribution of data. Another way of analysing the data is with cumulative distribution functions (CDFs). A graph with a CDF shows the (area-weighted) distribution of a variable. The displayed variable is on the horizontal axis, the vertical axis represents the area of the ecosystems, normalised for each country individually. This means that, e.g., at half the height of the graph the median value (i.e. the 50th percentile) is found.

The steeper the slope of a CDF the less difference there is in the values of the respective variable. For example, in Fig. 3-5 the critical loads for The Netherlands have a steeper slope than Germany's. Not only is The Netherlands smaller, but Germany also submitted a wider range of ecosystem types.

The main results of this call for data are the (critical) loads (Figs. 3-5 and 3-6). The graphs with CDFs are shown separately for forests (green), agricultural land (red) and other vegetation ecosystem types (blue). Unfortunately Belarus and Ukraine did not submit any ecosystem types, consequently the ecosystem-dependent graphs do not show data for these two countries. Also not all countries submitted data for all ecosystem types. With the EUNIS classification a comparison is facilitated, but only if properly classified data are submitted.

In Fig. 3-5 CDFs of effect-based critical loads for cadmium and lead are shown. Looking at the countries separately it appears that the distribution of critical loads is very similar for both metals. But the differences *between* countries are quite large, also for some adjacent countries such as the Czech Republic and Slovakia. From these graphs one can see how much the submitted ecosystems differ within a country. If the slope of a CDF is steep, there is little difference between a 5% map and a 50% map.

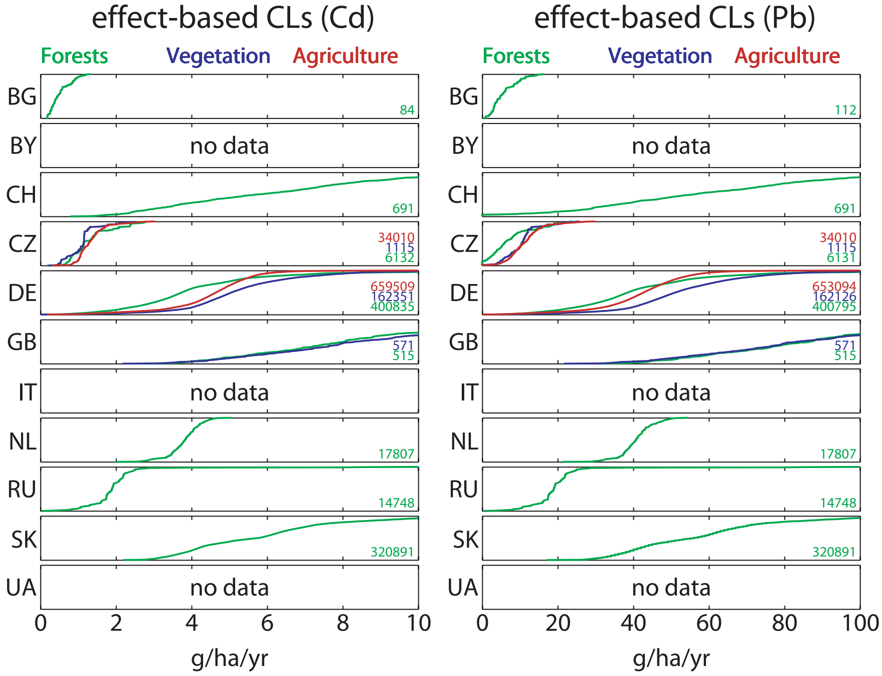


Figure 3-5: CDFs of effect-based critical loads of cadmium and lead.

Fig. 3-6 shows the stand-still loads of cadmium and lead. There are quite some differences between countries. Differences between ecosystem-CDFs seem to be larger than in fig. 3.5 (e.g. Czech Republic and Germany for lead).

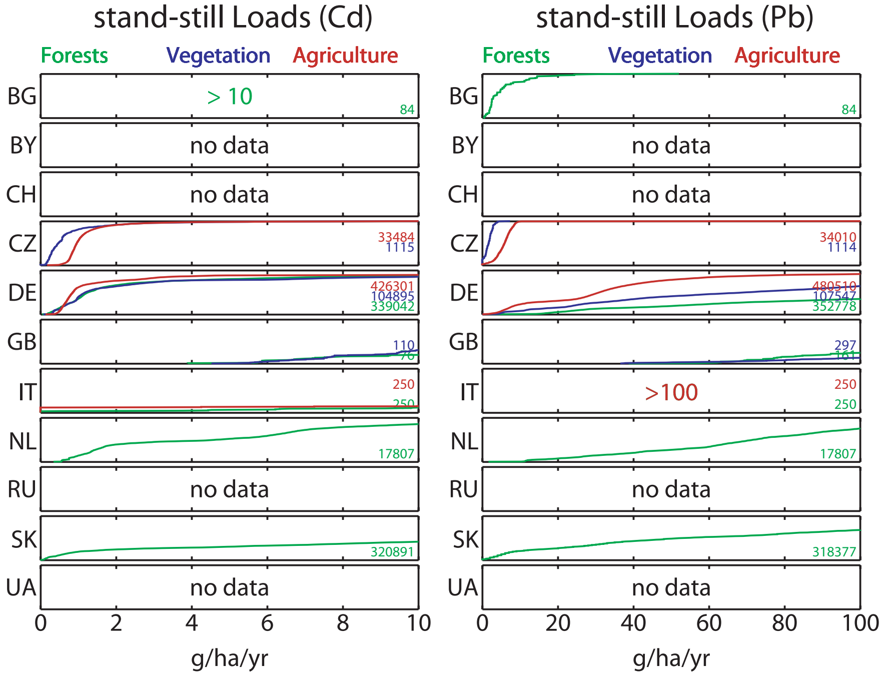


Figure 3-6: CDFs of stand-still loads of cadmium and lead.

## Fluxes

To get more insight in the background of the critical loads, we also show cumulative distribution functions of the main fluxes (Figs. 3-7 to 3-9). The three fluxes comprising the critical loads are leaching, net uptake and weathering. Note that the colours in these graphs do not reflect ecosystem types, but refer to the different fluxes.

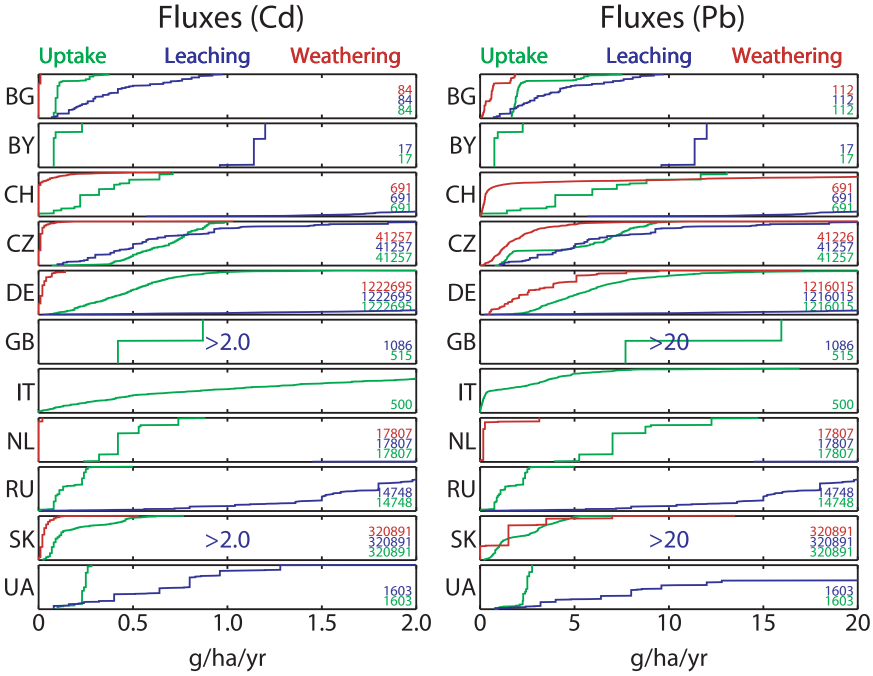


**Figure 3-7: The three fluxes comprising critical loads of cadmium and lead.**

Leaching is the most important flux. This explains the similarities between lead and cadmium. The leaching of both metals is directly related to the flux of water leached. Compared to leaching, the uptake and weathering fluxes are generally smaller, with weathering mostly the smallest. In fact, most countries neglected it, but entered it as missing into the database, instead of setting it to zero. The relative differences between cadmium and lead are small. The leaching flux of a metal M is calculated from formula (4) in the Guidance document (see Chapter 2):

$$M_{le} = 10 \cdot Q_{le} \cdot [M]_{ss(crit)}$$

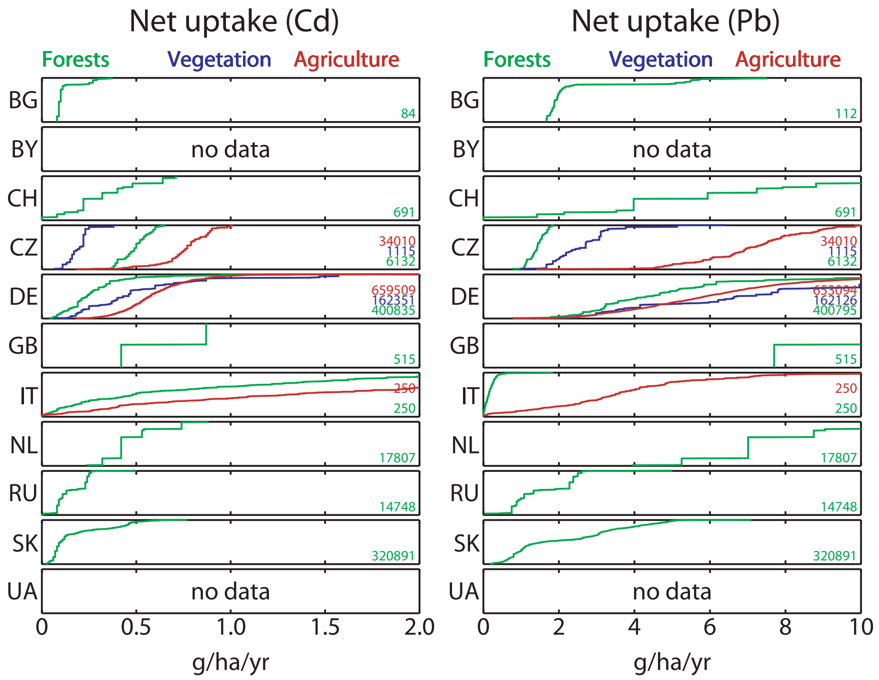


**Figure 3-8: Net uptake fluxes of cadmium and lead.**

The net uptake is the (long-term average) annual quantity that is removed from a site, neglecting cycling processes within the system. Uptake of the metals is higher for harvested areas (Fig. 3-8). Note that vegetation also contains agricultural-improved, re-seeded grassland. In general the agricultural areas are harvested most. Uptake depends on yield and metal content in the harvested parts.

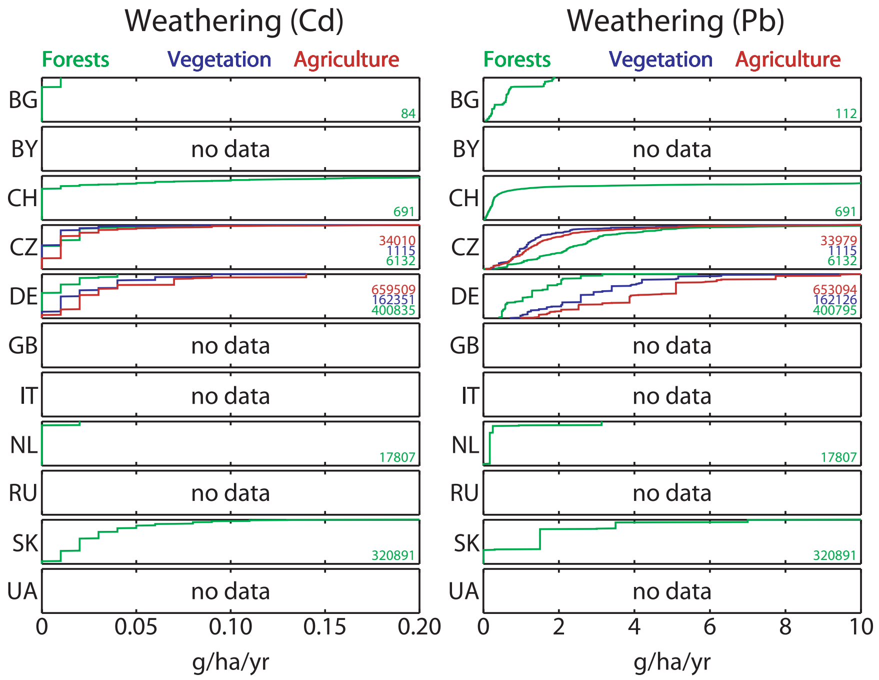


**Figure 3-9: Weathering fluxes of cadmium and lead.**

The weathering of the two metals is low compared to leaching and uptake (Fig. 3-9). This is especially true for cadmium. Weathering of a metal depends on the weathering release of base cations and the ratio between metal content and base cation content in the base material.

## Other input parameters

Figs. 3-10 to 3-12 show other parameters used in the calculation of critical loads. Fig. 3-10 shows the metal content in the parent material, which should reflect the geology within country.

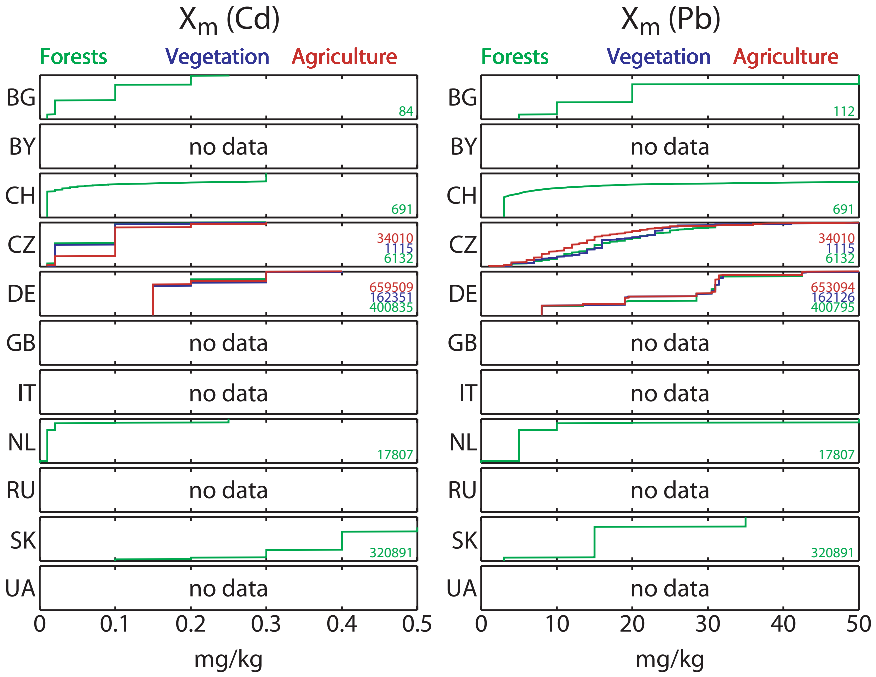


**Figure 3-10: Content of cadmium and lead in the parent material.**

For the stand-still approach the present concentration of the Cd and Pb (Fig. 3-11) is an important factor, because leaching is the dominant flux, and this flux is linearly related to this concentration. These concentrations are related to the deposition history and the geological background. Both vary a lot over Europe, but also per ecosystem type. Special attention needs to be paid to harmonising methodologies for measuring these concentrations and the use of transfer functions.

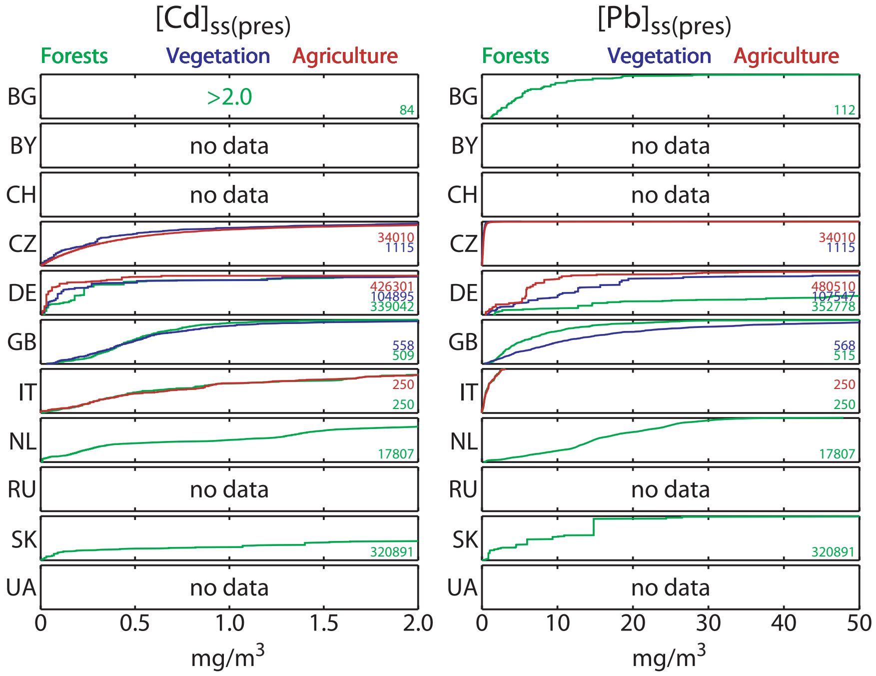


**Figure 3-11: Present concentrations of cadmium and lead in soil solution.**

In Fig. 3-12 no distinction is made between cadmium and lead since the variables do not depend on the metal. The data from the cadmium files were used, but for lead the figures are nearly identical (differences only caused by less ecosystems in Germany for lead).

The flux of leaching water is the driving force for leaching, and therefore an important factor. There are big differences between the countries, also for neighbouring countries. The differences are also shown in the 2001 CCE Status Report, Chapter 2 “Summary of National Data”, Figure 2-6. In general, for heavy metals leaching is a more important flux than for nitrogen or sulphur. Therefore, extra attention is needed for the careful derivation of this variable.

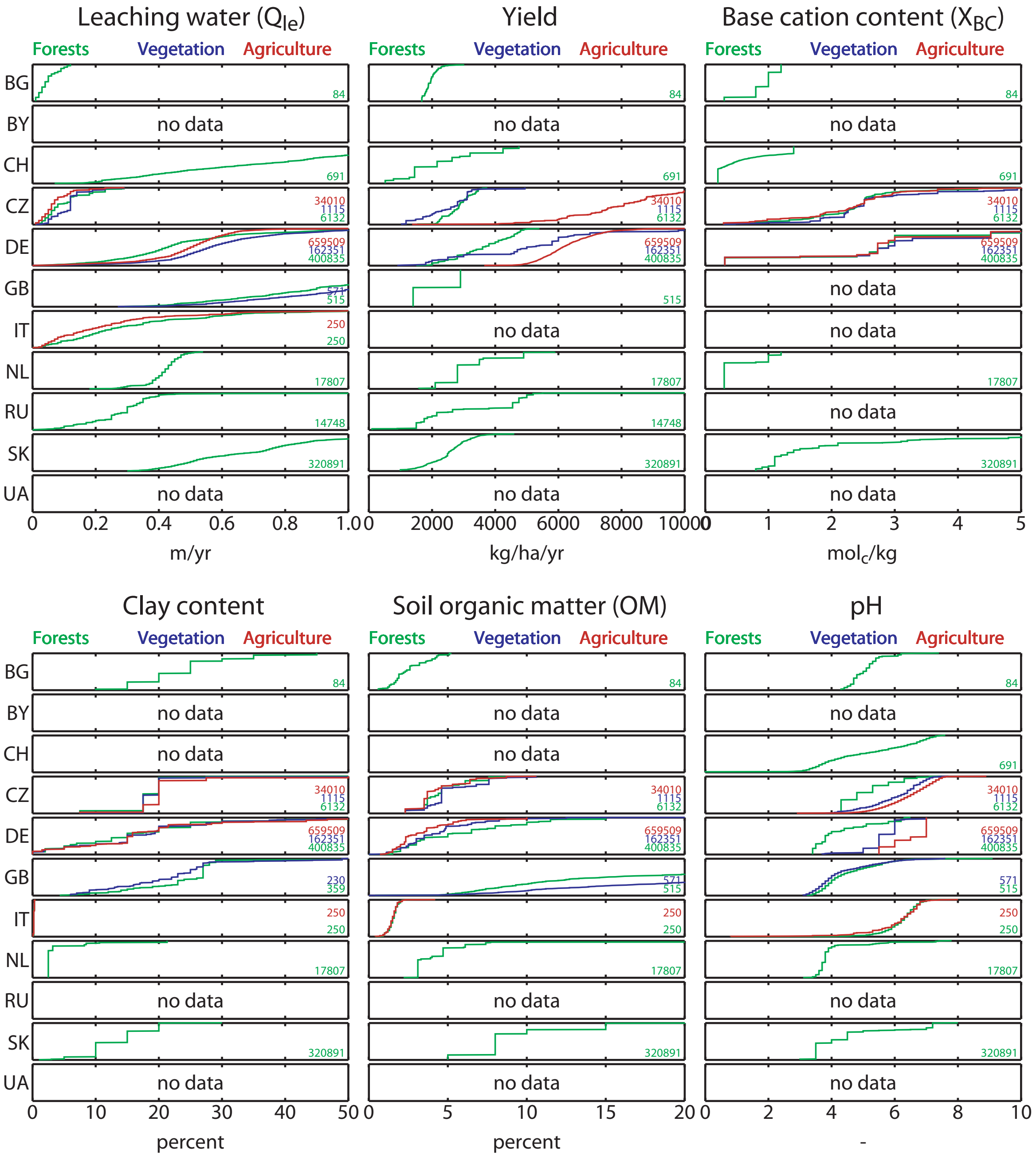


**Figure 3-12: Other non-metal related parameters.**

All countries used the recommended Guidance values for the critical concentrations, except for Belarus, Russia and Ukraine. These three countries adjusted the concentration to compensate for snow melting in springtime (see Part II).

Concerning the soil depth, most countries choose 0.1 meters. For other ecosystems then forests, some countries, e.g. Germany, use a thicker layer (e.g. 0.2 m for natural areas and 0.3 m for agricultural areas).

## 3.5 Concluding remarks

This chapter describes the results of the NFC response to the call for data, including a detailed comparison between countries of input data.

We see many similarities between the critical loads of cadmium and lead within the countries. But there are large differences between countries for most of the variables, which require further investigation.

The flux of leaching water is the most important factor and extra attention is needed for the careful derivation of this variable.

A more widespread use of EUNIS codes would be very beneficial, not only for heavy metals but also for other critical loads.

Although this call for data was on a voluntary basis, 11 countries made the effort to collect data and make the calculations. Also other countries contributed to progress in the field of critical loads for heavy metals.

# 4. Modelling Deposition Fields of Lead and Cadmium for Critical Load Exceedance Estimates

Sergey Dutchak[1], Ilia Ilyin[1]

Following recommendations from a joint meeting of the bureaux of the EMEP Steering Body and the Working Group on Effects, a collaboration was started between the EMEP/MSC-E and the CCE. The aim of the collaboration is to use MSC-E results of modelled deposition of cadmium and lead deposition fields for the computation of preliminary exceedance maps. MSC-E and CCE also agreed to attempt the assessment of ecosystem dependent exceedances. Calculations of depositions were carried out for 1990, 2000 and scenario 2010. The spatial resolution of the depositions is 50x50 km. To fulfil this task, MSC-E significantly modified its transport/deposition model. Basic modifications of the model are connected with improved parameterisation of dry deposition, necessary for the calculation of depositions to different land-use categories.

## 4.1 Emission data

Emission data are one of the key parameter in the long-range transport modelling. The quality of the modelling results depends to a high extent on the quality of the emission data. Currently two types of emission data are available. The first type of data are officially submitted by Parties to the Convention (so-called official data), and the second one is based on expert estimates. The main problem concerning official data is their incompleteness. Some countries do not provide a full set of emission sources. In addition to this, the data on the emission projections (in particular, for 2010) are needed. For the purpose of this report, expert estimates of lead and cadmium emissions were applied for the calculation of depositions.

In the framework of an UBA project, TNO prepared emission data for 1990 and 2010 (Berdowski *et al.*, 1998). Three possible emission scenarios have been designed for 2010: (a) no measures for emission reduction are undertaken; (b) only local (autonomous) measures are applied following national policies regarding emission management and control, and (c) measures prescribed by the international protocol on the reduction of heavy metal emissions are applied. Considering the preliminary nature of this study, it was agreed with the CCE to select scenario (c). In addition, data for 2000 were derived by interpolation between estimates for 1990 and 2010. It is necessary to mention that the number of countries submitting their data to EMEP has been increasing, and in future calculations of depositions and exceedances of critical loads, official emission data will be used.

The maps of spatial distributions of lead and cadmium emissions for 1990 are shown in Figures 4-1 (a) and (b), respectively. As seen from the Figures, the United Kingdom, Belgium, Spain, central Russia, south-eastern Europe and the eastern Ukraine are characterised by relatively high lead emissions in 1990. As for cadmium, the most pronounced emission country-source according to the expert estimates, is Poland. Elevated emission levels are located in the eastern Ukraine, Belgium, Romania and other countries.

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[1] EMEP/Meteorological Synthesizing Centre East, Moscow, Russia.

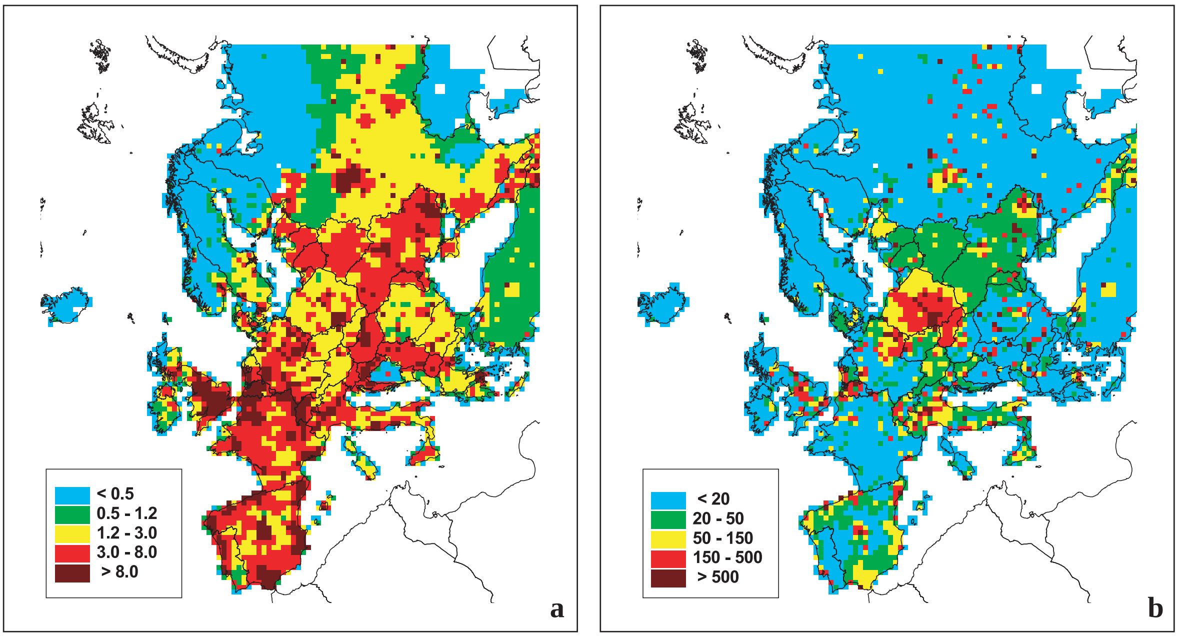

**Figure 4-1. Emissions in 1990 of (a) lead (kg/km$^2$/yr) and (b) cadmium (g/km$^2$/yr) in Europe.**

In comparison to 1990, emission reductions are expected in most countries in 2010. For Europe as a whole the reduction of lead will make up about 60% and of cadmium - more than 30%. This should lead to a general decrease of depositions in general and of lead in particular. However, for different countries different rates of emission reductions are prescribed (Berdowski *et al.*, 1998), and deposition reductions are not supposed to be uniform.

In addition to anthropogenic inputs, lead and cadmium can enter the atmosphere due to natural mechanisms. J. Nriagu (1989) carried out estimates of natural emissions of heavy metals and identified most important natural sources of lead and cadmium. These are wind resuspension, sea-salt aerosols, volcanoes, aerosol particles of biogenic origin. However, it is often mentioned in the scientific community that the heavy metal content in the environment (e.g., soils) has increased significantly because of long-term anthropogenic pollution (Renberg *et al.*, 2000, Shotyk *et al.*, 1998, Cortizas *et al.*, 2000, Brännvall *et al.*, 2000). Therefore, in this work higher emission fluxes, conditioned by some natural processes (so-called quasi-natural emission), were used. In Figures 4-1 only anthropogenic emissions are mapped, while quasi-natural emissions are discussed in detail elsewhere (Ilyin *et al.*, 2001).

## 4.2 Brief description of the transport model

To compute deposition fields of lead and cadmium in Europe the Eulerian transport and deposition model developed at EMEP/MSC-E was applied. The geographical scope of this model is the EMEP region. It includes Europe, the north of Africa, north-west Atlantic and the western part of the Middle East. The spatial horizontal resolution is 50x50 km in stereographic projection at 60º N latitude. A detailed description of the EMEP grid is given in Posch *et al.* (1997). Along the vertical the modelling domain consists of five non-uniform layers up to about four-km height. Therefore, it encompasses the boundary layer and part of the middle troposphere.

The model includes basic processes governing atmospheric transport and the formation of the spatial pattern of depositions such as advection, turbulent diffusion, wet and dry removal and the inflow of pollutants from outside of the EMEP domain. Lead and cadmium in the model are considered as particulate compounds with mass median diameters of 0.55 and 0.84 mm, respectively.

The advection scheme has been developed by Pekar (1996). The scheme is conservative, stable and positively defined. The horizontal diffusion is described according to the approach suggested by Izrael *et al.* (1980). The model description of vertical turbulent diffusion is based on a classical law: a substance flux is proportional to the concentration gradient. The proportionality factor is the coefficient of turbulent diffusion calculated by the boundary layer parametrisation described in Pekar (1996). Vertical diffusion is described by an implicit scheme (Samarsky, 1977).

The model allows an inflow of pollutants from outside of the EMEP domain both by advective flows and by large-scale vertical motions. The concentrations of pollutants at model boundaries are set based on data from field experiments in background regions (Ilyin *et al.*, 2001; Ryaboshapko *et al.*, 1999).

A detailed description of the model can be found in (Ryaboshapko *et al.*, 1999). In this section attention is mainly paid to description of the deposition processes - wet removal and dry uptake. In addition to this, questions concerning the quality of the modelling results are discussed.

Wet removal of aerosol particles containing heavy metals is described as a process of a first order:

$$\frac{\partial C}{\partial t} = -\Lambda \cdot C \qquad (4.1)$$

where C - air concentration, t - time, $\Lambda$ - washout coefficient which calculated in the following way:

$$\Lambda = \frac{W \cdot I}{\Delta z_i} \qquad (4.2)$$

where $I$ = precipitation intensity;
$\Delta z_i$ = layer depth where washout takes place;
$W$ = the washout ratio representing the ratio of pollutant concentration in precipitation to its concentration in the air.

On the basis of monitoring data on lead and cadmium content both in precipitation and air obtained at EMEP stations (Berg et al., 1996), washout ratios were calculated for individual months and for the whole year. The obtained minimum, maximum and mean values of the washout ratios for the whole set of stations are presented in Table 4-1. The estimated washout intensity of both metals varies with seasons reaching its maximum during summer. Also note that particles containing cadmium are more intensively washed out from the atmosphere.

**Table 4-1: Washout ratios for lead and cadmium ($\cdot 10^5$)**

| Characteristic | Lead | Cadmium |
|---|---|---|
| Mean annual | 3.3 | 7.0 |
| Maximum | 5.0 (summer) | 9.0 (summer) |
| Minimum | 1.7 (autumn) | 3.6 (autumn) |

## 4.3 Modification of dry deposition scheme for the effect-oriented tasks

Dry uptake flux of the metals is computed as follows:$F_{dry} = -C \bullet v_d$, where C is a pollutant air concentration. The parameter which characterises dry uptake is dry uptake (dry deposition) velocity $v_d$. Dry uptake velocity of the pollutants is described by an analogy to electrical resistance. According to this approach, the classical expression for dry deposition velocity is computed as follows:

$$v_d = \frac{1}{r_a + r_b + r_c} \qquad (4.3)$$

In equation (4.3) $r_a$ is the aerodynamic resistance. A pollutant has to overcome this resistance when transported within the surface boundary layer, $r_a$ is a property of the atmosphere and does not depend on properties of the pollutant. The term $r_b$ is the resistance of the near-surface laminar layer, which, together with external parameters (wind velocity, roughness etc), strongly depends on properties of a pollutant, e. g, diffusivity in air. Therefore, for different pollutants this term should also be different. The term $r_c$ is the surface resistance and it comprises contributions from a number of resistances of various surface elements like stomata, cuticule, soil etc. (Wesley and Hicks, 2000).

Unlike gaseous compounds, particles are also deposited due to gravitation. Equation (4.4) describes dry deposition velocity for particles (Wesely and Hicks, 2000; Hicks *et al.*, 1987):

$$v_d = \frac{1}{r_a + r_{ds} + r_a \cdot r_{ds} \cdot v_g} + v_g \qquad (4.4)$$

where $v_g$ is the velocity governed by gravitation, and surface resistance ($r_c$) is replaced by the term $r_{ds}$, the reciprocal of which is called surface deposition velocity: $v_{ds} = 1/r_{ds}$.

Following the request of the CCE, the MSC-E developed deposition schemes taking different types of land-use into consideration. Eight categories were taken into account: (1) deciduous forests, (2) coniferous and mixed forests, (3) arable land, (4) permanent crops, (5) grassland, (6) inland waters, (7) urban area, and (8) other areas (extensive agriculture and natural areas) (Posch *et al.*, 1997). Since different types of land-use manifest different capacities of dry uptake, dry deposition to these land-use categories was computed in different ways.

To compute dry deposition velocity to forested areas (land-use categories “coniferous forests” and “mixed and deciduous forests”) a model developed by Ruijgrock *et al.*, (1997) was applied. According to (Ruijgrock et al., 1997), the surface deposition velocity was assumed to be:

$$v_{ds} = E \cdot \frac{u_*^2}{u_h} \qquad (4.5)$$

where $u_*$ is the friction velocity and $u_h$ – the wind velocity at a canopy top. E characterises the total collection efficiency, which depends on meteorological parameters (Ruijgrock *et al.*, 1997).

To compute dry uptake for surfaces with low vegetation, the approach suggested by M. Wesley *et al.*, (1985) was taken. A similar approach was used in other regional-scale models, e. g. (Brook *et al.*, 1999). Following Wesley *et al.* (1985) the following expressions were applied to evaluate $v_{ds}$:

$$\begin{aligned} v_{ds} &= 0.002 \cdot u_*, & if\, L > 0 \\ v_{ds} &= 0.002 \cdot u_* \cdot \left[1 + \left(-\frac{300}{L}\right)^{2/3}\right], & if\; L < 0 \end{aligned} \qquad (4.6)$$

In (4.6) parameter $L$ (expressed in m) is the Monin-Obukhov length scale, and it characterises the stability of the atmosphere, and $v_{ds}$ has the same dimension as $u_*$. This parameterisation was released to compute deposition velocity to land-use categories called “grasslands”, “arable lands” and “permanent crops”. To compute dry deposition to land-use class “other areas” and “inland waters”, parameterisation developed by Pekar (1996) was applied. Dry deposition velocity for urban areas was taken 0.5 cm/s independent of season, time of a day or meteorological conditions.

Different types of land-cover are characterised by different roughness lengths $z_0$, which, in turn, influence dry deposition velocity. Typically, the higher the vegetation the greater the roughness length. The vegetation cover undergoes seasonal changes. These, in turn, affect roughness length and dry uptake velocity. For example, temperate deciduous forests shed leaves, thus reducing the area of dry uptake. In northern Europe large areas are covered with snow during winter time, which also both reduces the capacity of dry uptake of particles and makes the underlying surface smoother. In this connection the consideration of seasonal changes is important for the parameterisation of dry uptake. Three types of seasons are considered in the model: cold, warm and transitional. It was proposed that transitional season takes place twice a year and its duration is one month each time.

In the following, a scheme for the latitudinal dependence of a season is suggested. The number of a transitional month, at which a seasonal change takes place, is determined using the following formulae:

$$\mathrm{N_{SW}} = 12 - \frac{(\cos\varphi - \cos 40^\circ) \cdot (\mathrm{M_{SW40}} - M_{SW75})}{\cos 75^\circ - \cos 40^\circ} \qquad (4.7)$$

$$\mathrm{N_{WS}} = 3 + \frac{(\cos\varphi - \cos 40^\circ) \cdot (\mathrm{M_{WS75}} - M_{WS40})}{\cos 75^\circ - \cos 40^\circ} \qquad (4.8)$$

In (4.7) and (4.8) symbols $N_{SW}$ and $N_{WS}$ are integer numbers of months at which a warm season changes to a cold one and a cold to a warm, respectively, and φ is geographical latitude. A number of assumptions were made for these formulae. It was assumed that north of the 75° latitude the cold season prevails, and south of 40° - always a warm season occurs. At the 40° latitude a seasonal change is supposed to occur at the 12th month (“fall”, December) and at the 3rd (“spring”, March).

At 75º the corresponding seasonal changes are assumed to take place in August and June. Determination of a transitional month at other latitudes is made by linear interpolation between cosines of 40º and 75º latitude. The terms $M_{SW40}$ and $M_{SW75}$ indicate the numbers of the months at which a transition between a warm and a cold season is established at 40º and 75º latitude, respectively. Obviously, $M_{SW40}$ = 12 (December), and $M_{SW75}$ = 8 (August). The terms $M_{WS75}$ and $M_{WS40}$ have a similar meaning indicating the transition from a cold to a warm season, i.e. $M_{WS75}$ = 6 (June) and $M_{WS40}$ = 3 (March).

For each land-use class and each season type, the roughness length was determined based on literature data (Brook *et al.*, 1999; Davidson and Wu, 1988; Civerolo *et al.*, 2000; Garrat, 1999). The values used in the model are summarised in Table 4-2. In the Table $z_0$ for forests always is set to be 2.0 m. However, in order to account for a possible reduction of dry uptake in a cold season, dry uptake velocities are multiplied by reduction factors. These factors are given in Table 4-3 for different types of forests. It is important to mention that these factors are arbitrary and they are used because of lack of research data on aerosol dry deposition to forests in cold seasons.

**Table 4-2: Roughness lengths ($z_0$, m) for different land-use categories and season types used in the model**

| **Land-use class** | **Season type** | | |
|---|---|---|---|
| | **warm** | **transitional** | **cold** |
| Deciduous forests | 2.0 | 2.0 | 2.0 |
| Coniferous/Mixed forests | 2.0 | 2.0 | 2.0 |
| Arable lands | 0.10 | 0.05 | 0.01 |
| Permanent crops | 0.10 | 0.05 | 0.01 |
| Grassland | 0.10 | 0.05 | 0.01 |
| Inland waters | 0.005 | 0.005 | 0.005 |
| Urban area | 0.5 | 0.5 | 0.5 |
| Other areas | 0.05 | 0.05 | 0.05 |

**Table 4-3: Reduction factors used for dry uptake velocities computed for forests**

| **Forest type** | **Season type** | | |
|---|---|---|---|
| | **warm** | **transitional** | **cold** |
| Deciduous forests | 1.0 | 0.75 | 0.50 |
| Coniferous/Mixed forests | 1.0 | 0.85 | 0.75 |

Computed dry deposition velocities to forested areas and to areas with low vegetation differ significantly. In Figures 4-2 (a - c) monthly mean deposition velocities for these two different surface types are demonstrated. The data presented in the Figure refer to single grid-cells in Central Germany (a), the southern part of Spain (b) and central Romania (c). As can be seen, the dry uptake velocity to forests is an order of magnitude higher than that to low vegetation areas. This ultimately results in a greater total deposition flux to forests, which, in turn can lead to greater accumulation of lead and cadmium for long-term period.

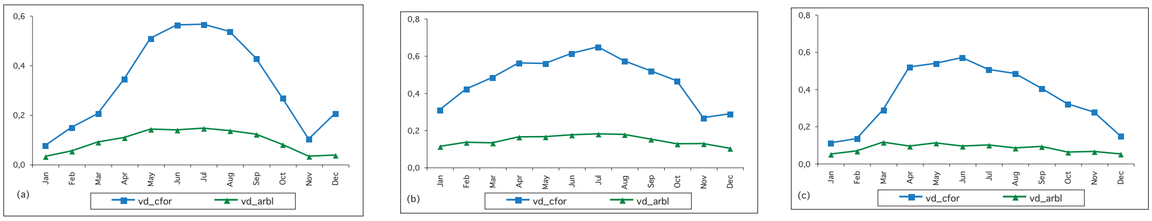

**Figure 4-2: Monthly mean deposition velocities, cm/s, to coniferous forests (vd_cfor) and to arable lands (vd_arbl) in arbitrary grid cells in Central Germany (a), the southern part of Spain (b) and central Romania (c).**

The effect on the introduction of a new parameterization of the dry deposition scheme is exemplified in Table 4-4. In the Table two kinds of dry deposition fluxes are given: one is specified for different land-use categories in an arbitrary grid-cell, and anther one is averaged for the grid-cell. As one can see, dry deposition flux within a grid-cell can vary substantially with regard to land-use type. For example, dry deposition to coniferous forests is 3.5 times higher than the average value, and dry deposition flux to inland waters is twice lower.

**Table 4-4. Annual dry uptake flux of Pb, kg/$km^2$/yr, at an arbitrary EMEP grid cell**

| Land-use type | Dry flux (per area unit) | Dry flux averaged for a grid cell |
|---|---|---|
| 1. Deciduous/mixed forests | 0.7 | 0.2 |
| 2. Coniferous forests | 0.7 | |
| 3. Arable lands | 0.2 | |
| 4. Grasslands | 0.2 | |
| 5. Permanent crops | 0.2 | |
| 6. Inland waters | 0.05 | |
| 7. Urban | 1.4 | |
| 8. Other | 0.1 | |

Dry deposition of lead and cadmium accounts for first tens of a per cent with regard to the total (wet and dry) deposition. In Figure 4-3 (a) differences in total deposition resulted from the introduction of the modified scheme is demonstrated. It is clear from the Figure that over land total deposition is mostly increased, especially in forested regions. Over some marginal seas such as the Baltic Sea, the Adriatic Sea, the western part of the Mediterranean, the Barents Sea and the Bay of Biscay total deposition is decreased from 5 to 15%. Over other areas the differences are within ±5%.

The increase of total deposition in areas covered by specific land-use types can be even greater than that averaged over the entire grid cell. In Figure 4-3 (b) the increase of total deposition to forested areas is shown. As can be seen, the highest increase takes place in the southern part of Iberian Peninsula, in Ireland, along the southern coast of the North and Baltic Seas as well as in the southern part of Italy.

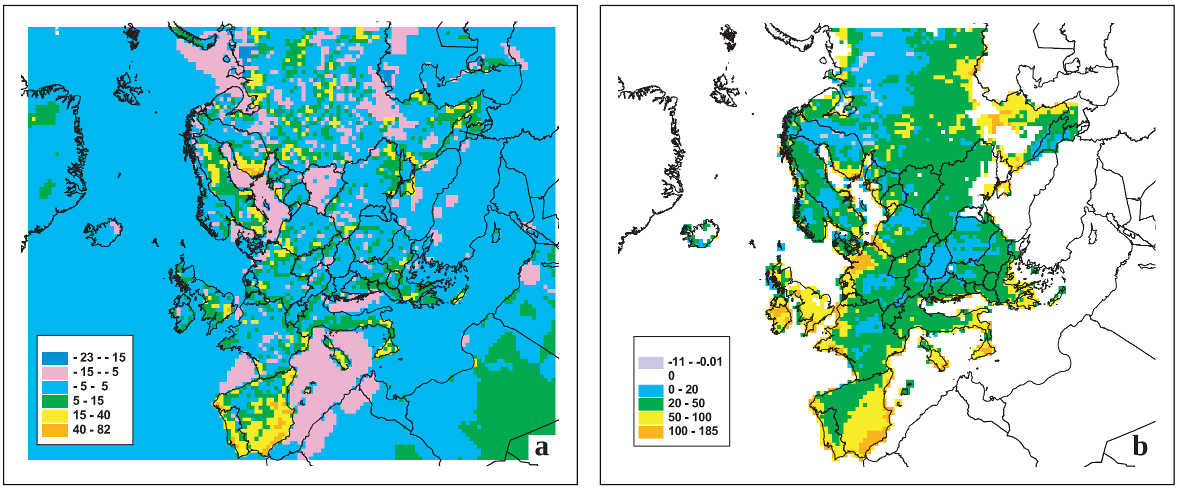

**Figure 4-3: Relative increase, %, in total deposition to Europe as a whole (a) and to forested areas (b) after modification of dry deposition scheme.**

Uncertainty analysis of the model results was carried out by Travnikov (2000). This analysis revealed that the most important source of uncertainty is emission data. If the uncertainty of the emission data is excluded from the analysis the overall model uncertainty for air concentrations and depositions is within 25%.

For the comparison, measurement data prepared by the CCC were used (Berg et al., 1996). It could be useful to note, that measuring data have some degree of uncertainty. Intercomparisons of the analytical methods used by chemical laboratories in Europe, have recently been carried out (Berg and Aas, 2000; Uggerud and Skjelmoen, 2001). These intercomparisons revealed that the error of analytical methods, which characterises European laboratories, is about 25% both for lead and for cadmium.

The comparison of modelled and measured concentrations of lead and cadmium in air in 1990 is given in Figure 4-4 and 4-5 respectively. As can be seen, not many sites are available where heavy metal air concentrations have been monitored in the early 90-s. Figure 4-4 shows that for 1990, the model reasonably reproduced measured lead concentrations. Some underestimation of measured lead concentrations occurs for the Czech sites CZ1 and CZ3.

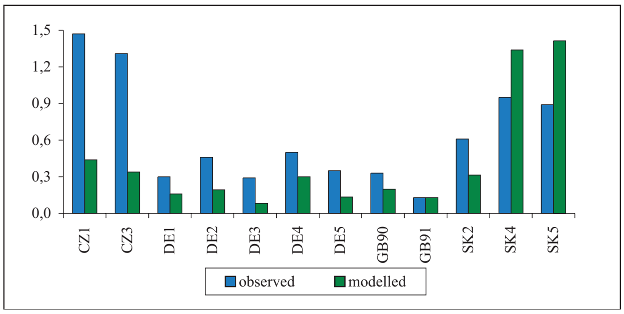

**Figure 4-4: Comparison of lead air concentrations, ng/m$^3$, for 1990.**

The comparison of cadmium concentrations in air is shown in Figure 4-5. In the case of cadmium general underestimation of measured concentrations in air is indicated. High underestimation for lead and cadmium can be noted for Czech sites and could be connected with the underestimation of expert estimates on emissions and other reasons (model uncertainties, quality of the measurement data, etc.).

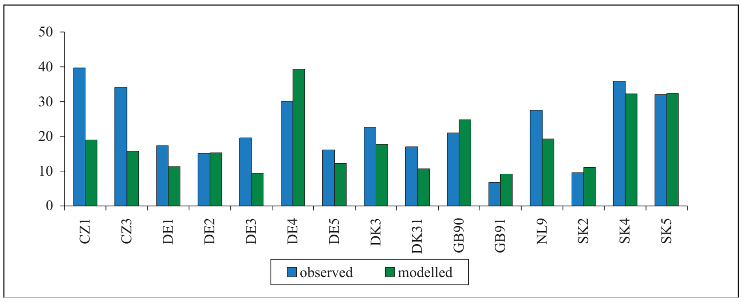

**Figure 4-5: Comparison of cadmium air concentrations, ng/m$^3$, for 1990.**

The underestimation of the heavy metal emission data as well as the fact that the emission data are the main source of model results uncertainty was confirmed at the EMEP workshop on emission estimates and emission factors, held in Moscow (November 2001). This workshop was jointly organised by the MSC-E and the Task Force on Emission Inventories and Projections (TFEIP) and brought together both people working in the field of modelling as well as national emission experts.

## 4.4 Lead and cadmium depositions for 1990, 2000 and 2010

On the basis of emission data for 1990, 2000 and 2010 deposition fluxes to different land-use categories of EMEP region were calculated. Deposition data obtained for these three years indicate a trend in deposition in response to current and expected emission reduction measures. However, meteorological parameters also undergo multi-annual variations, and this can play some “masking” role in assessment of the budget of lead and cadmium in soils or water bodies. That is why it was suggested to use meteorological data for 1990 in calculations of depositions for 1990, 2000 and 2010.

Deposition fluxes can vary with respect to different types of the underlying surface. Therefore, depositions of lead and cadmium were computed applying a subdivision of different land-use categories. At present, depositions as well as critical loads to eight types of land-use were computed. Therefore, currently it is possible to estimate the exceedances for eight land-use categories. However, a more detailed CCE land cover map including 16 land-use classes has meanwhile become available. This extended land-use data base will be applied in future simulations.

In accordance with recommendations of CCE, special attention was paid to coniferous forests. In Figure 4-6 maps of total (wet and dry) lead depositions in 1990 and map of the emissions for the same year are given. Figure 4-6(a) demonstrates the deposition flux per square kilometre of forested area. Hence, depositions are shown only for grid cells containing coniferous forests. As one can see, 1990 depositions of lead range from 3 to 8 kg/km$^2$/yr in broad areas. These areas occupy about 1 million km$^2$. Some areas, such as the centre of Russia, Germany, the north of France, Spain, and the south of Poland, have depositions even exceeding 8 kg/km$^2$/yr. The total area of coniferous forests with depositions exceeding 8 kg/km$^2$/yr is about 0.1 million km$^2$.

It is interesting to note that areas with relatively high depositions are not necessarily located in areas with relatively high emissions. For example, the southern part of Norway or Austria are characterised by moderate or even somewhat low levels of the emissions, but depositions in these areas are greater than 3 kg/km$^2$/yr. These comparatively high depositions are originating from the long-range transport from relatively large sources and were amplified by forests.

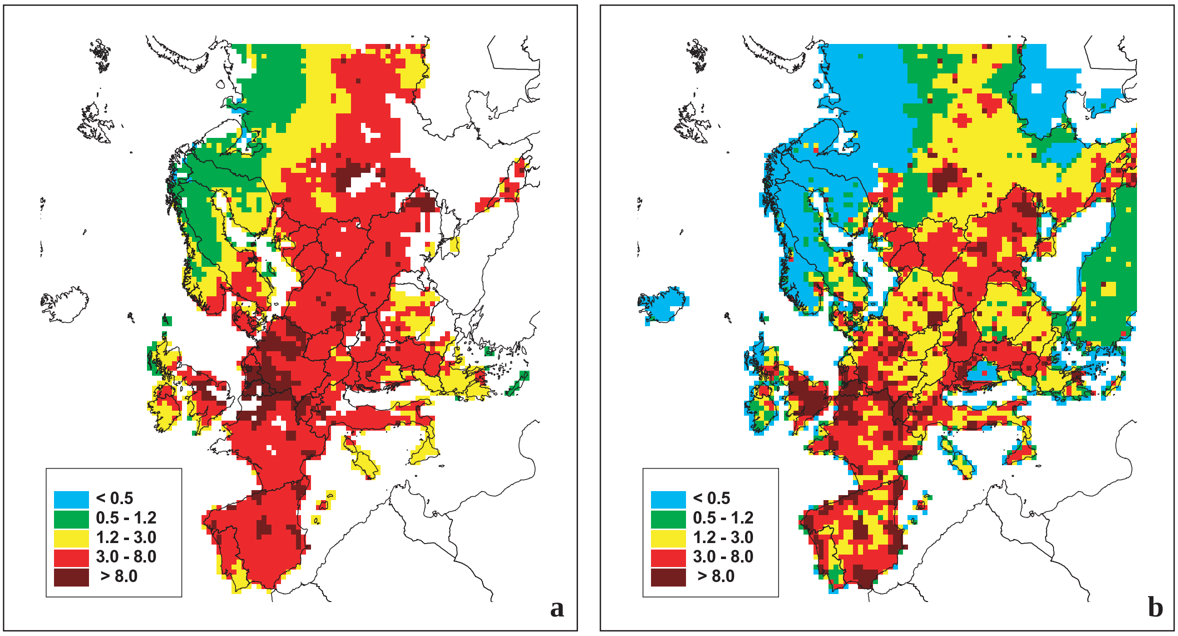

**Figure 4-6: Maps of total lead deposition to coniferous forests (a) and emissions (b) in 1990, kg/km$^2$/yr. It can be seen that areas with relatively high depositions are not necessarily located in areas with relatively high emissions.**

Similar maps for cadmium are shown in Figures 4-7 (a) and (b). It is seen from Figure 4-7 (a) that areas of the highest cadmium depositions for 1990 are located in Poland, the Czech Republic, the eastern part of Germany, the central part of Russia, Italy, the Ukraine, and The Netherlands. Some of these countries are also characterised by a relatively high percentage of areas covered by coniferous forests. Therefore, in these countries high deposition fluxes encompass extensive areas. For example, areas where depositions exceed 50 g/km$^2$/yr occupy about 1.4 million km$^2$.

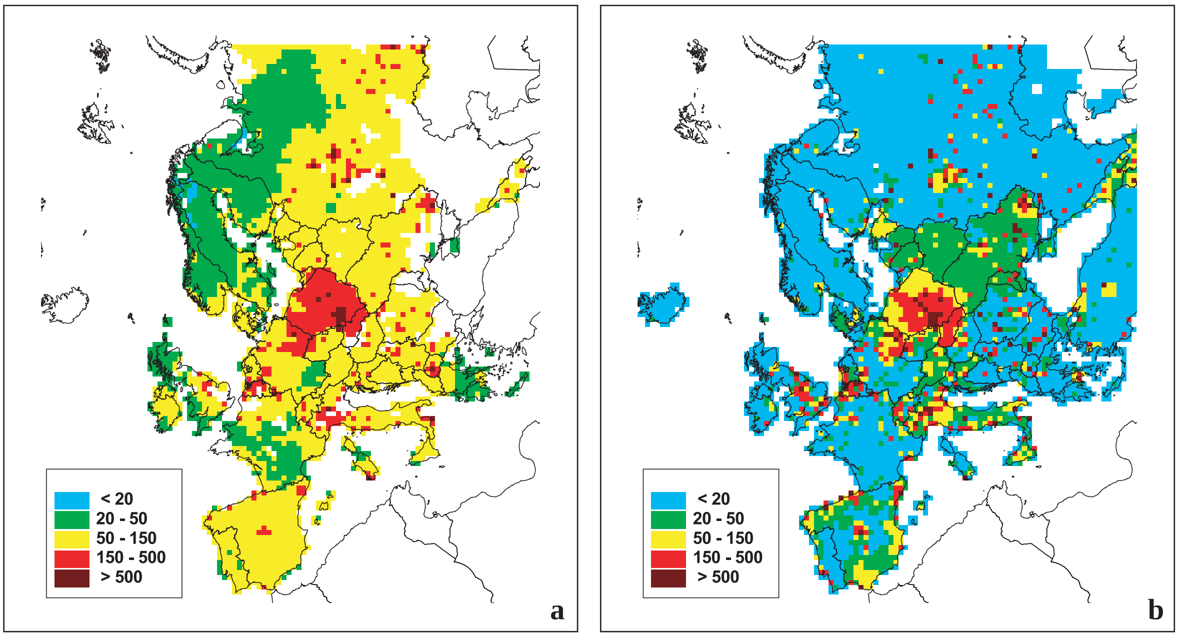

**Figure 4-7: Maps of total cadmium deposition to coniferous forests (a) and emissions (b) in 1990, g/km$^2$/yr.**

In Figures 4-8 (a) and (b), depositions of lead and cadmium to coniferous forests in 2010 are shown. Figure 4.8 illustrates that the area with relatively high depositions of lead are significantly reduced following emission reductions, estimated by TNO (Berdowski *et al.*, 1998). Areas of relatively high lead depositions (more than 3 kg/km$^2$/yr) encompass about 250 thousand km$^2$. As for cadmium, the reduction of depositions is not so pronounced as that for lead. This is partly due to relatively low emission reductions in 2010, according to TNO estimates (Berdowski *et al.*, 1998).

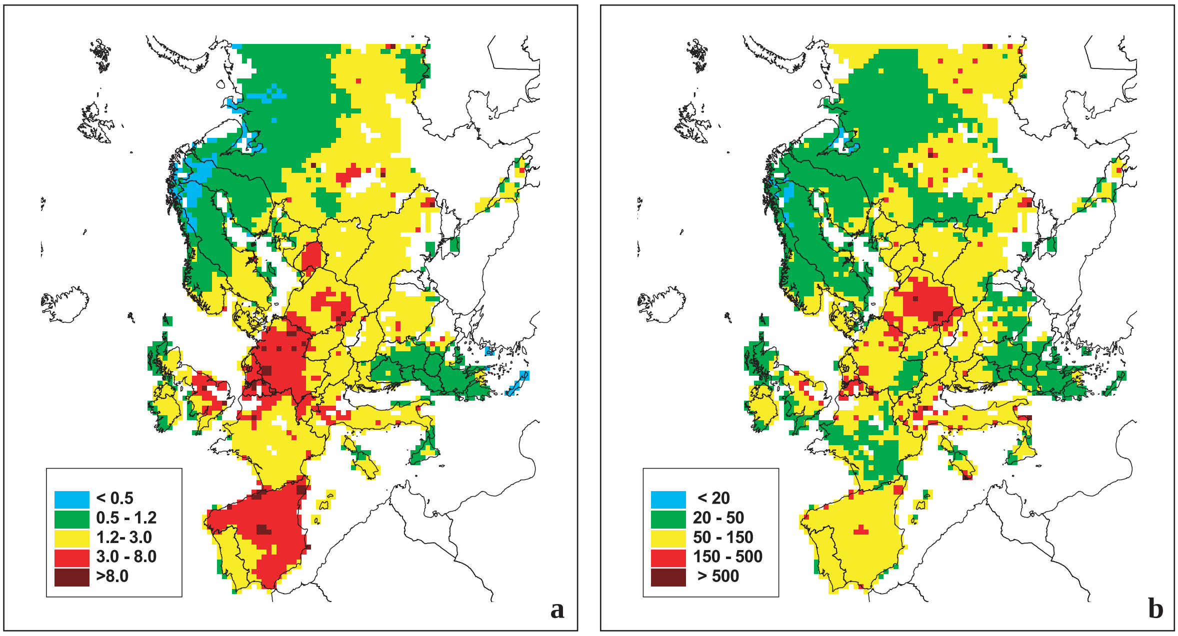

**Figure 4-8: (a) total lead depositions, (kg/km$^2$/yr), and (b) cadmium depositions, (g/km$^2$/yr), to coniferous forests in 2010.**

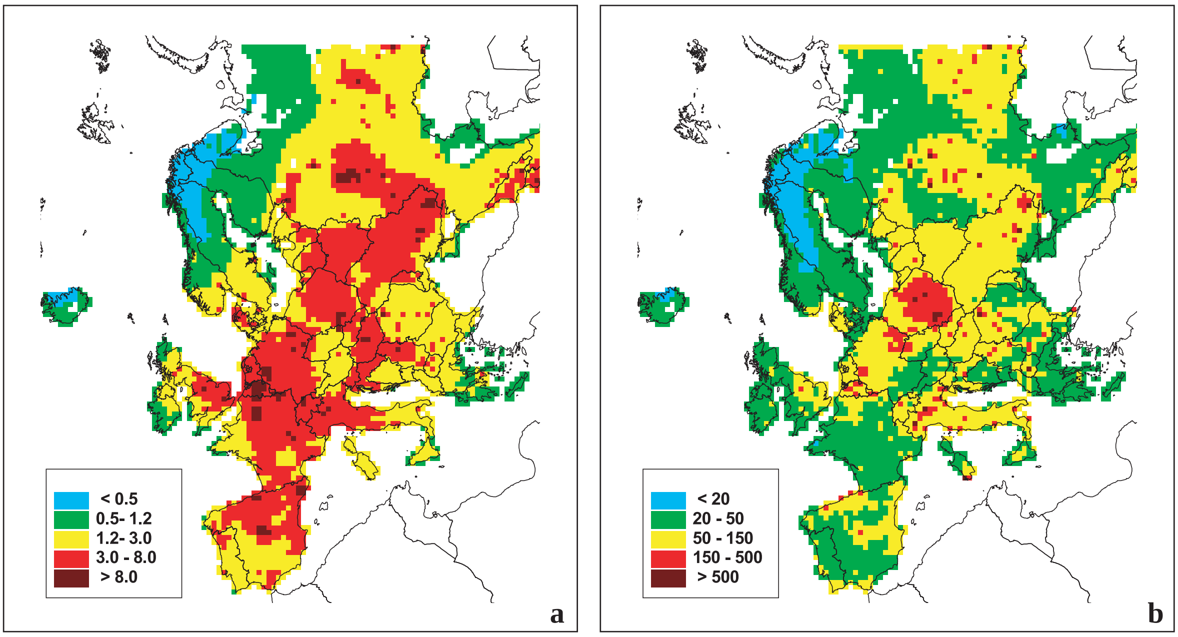

**Figure 4-9: (a) total lead deposition (kg/km$^2$/yr) and (b) cadmium deposition (g/km$^2$/yr) to grasslands in 1990.**

Similar maps were also computed for other land-use categories. In Figures 4-9 (a, b) total depositions of lead and cadmium to grasslands in 1990 are shown. Over large parts of Europe depositions of lead to grasslands vary between 1.2 and 8.0 kg/km$^2$/yr (Figure 4-9, a). In relatively polluted areas, lead depositions can exceed 8 kg/km$^2$/yr. These areas are in the south of Poland, the western part of Germany, and the central part of Spain. As can be seen from the comparison of Figure 4-9(a) and Figure 4-6(a), specific lead deposition flux to an area unit of grassland is lower than that to forests due to lower dry uptake velocity. For example, over most of the Czech Republic, Austria and southern Sweden, total forest-specific lead deposition ranges between 4.0 - 8.0 kg/km$^2$/yr, whereas grassland-specific lead deposition ranges between 1.2 - 3.0 kg/km$^2$/yr. Zones of depositions greater than 8 kg/km$^2$/yr are seen both in forests as weell as in grasslands. In the case of depositions to forests, the total area of these zones reaches 110 thousands km$^2$. In the case of grasslands the area is significantly lower amounting to about 25 thousands km$^2$.

The highest depositions of cadmium to grasslands are obtained in Poland where they can reach 500 g/km$^2$/yr or even more. Over the most part of Europe the deposition values range between 50 - 150 g/km$^2$/yr. Zones of relatively low depositions are located in northern Scandinavia, Russian Karelia and Kola Peninsula, where these depositions usually do not exceed 50 g/km$^2$/yr. Similarly to lead, the effect of forests on the total cadmium deposition is obvious from the comparison of Figures 4-9(b) and 4.7(a). For example, coniferous forest-specific depositions of cadmium in the northern part of Sweden is about 20 - 50 g/km$^2$/yr, however often exceeding 50 g/km$^2$/yr in the southern part. The grassland-specific depositions in the same parts of Sweden are usually below 20 g/km$^2$/yr and between 20 and 50 g/km$^2$/yr, respectively.

Data on depositions to other land-use categories are also available[2]. The effects of the introduction of a new parameterisation to the EMEP/MSC-E model on total deposition values with respect to land-cover has been described in section 4.3 of this chapter.

[2] The data on lead and cadmium depositions to different land-use types can be provided by MSC-E upon request.

## 4.5 Future activities

Heavy metals such as lead and cadmium have a tendency to be accumulated in the first several centimetres in the soil. Therefore, knowledge of historical depositions of heavy metals is important. Dynamic models, which can take historical depositions into consideration, are under development. MSC-E has started preparatory work for the calculations of historical depositions. The importance of the focus on accumulation trends is confirmed by the fact that over the past decades emissions (and, consequently, depositions) were several times higher, peaking in the late 60-s and 70-s (Olendrzynski *et al.*, 1995).

Mercury, as well as lead and cadmium, is also a priority metal identified by he Protocol. MSCE is currently working on the evaluation of depositions (wet and dry) of various mercury forms (elemental, gaseous oxidised, particulate) and concentrations in the atmosphere and in the atmospheric precipitation.

The modelling on a hemispheric scale is becoming more and more important. For the purpose of the evaluation of exceedances of critical loads, a hemispheric model can be helpful in two ways. First, it can help to evaluate the inflow of pollutants, into the EMEP domain via lateral boundaries. This, in turn results in more accurate evaluations of deposition fields. Secondly, territories of new parties under the Convention such as Kazakhstan and Kyrgyzstan are incorporated into an hemispherical modelling domain. This will enable the assessment of depositions and exceedances (provided that critical loads are mapped) for these countries.

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# Part II National Focal Centre Reports

This part consists of the documents accompanying the data submissions to the Coordination Center for Effects (CCE) by the National Focal Centres (NFCs). Also included are the reports of the NFCs that indicated not to submit data, stating the reasons for not submitting.

The reports received are not reviewed, only the layout is standardised to a certain extent and a few editorial changes were made for clarity.

The latest call was for the purpose of developing and testing the methodology for mapping critical loads of heavy metals (Cd, Pb). Therefore the reports of some countries also have information on their difficulties achieving results. The call was on a voluntary basis, eleven countries submitted data (Belarus, Bulgaria, Czech Republic, Germany, Italy, The Netherlands, Russian Federation, Slovakia, Switzerland, Ukraine and the United Kingdom).
Six countries informed the CCE that they would not submit any data this time (Austria, Belgium, Finland, France, Norway, and Sweden).

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The Austrian NFC believes that the modelling and mapping of critical loads for heavy metals is an important extension of the Mapping Programme.

However, the establishment of a critical loads data set for heavy metals is a very demanding task. For the time being the Austrian NFC has not been able to timely create a complete, consistent and reliable set of data.

Therefore, the Austrian NFC has initiated an internal project at the Austrian Federal Environment Agency to be able to comply with future needs for national critical loads data for cadmium and lead.

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### Calculation methods

Belarus has executed their calculations in close corporation with Russia. They applied exactly the same methodology.

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Following the call for voluntary submission of critical loads of lead and cadmium, we did some research and found that some basic data are still missing, such as transfer-functions for the Flemish soil types and the quantities released by weathering. We hope that in the future there will be better opportunities to meet the need for critical loads. Information from the Forest Soil Co-ordination Centre showed that within ICP-forest a soil survey has been planned for 2004-2006, also regarding heavy metals. This survey can contribute to fill the data gaps for calculating of critical loads.
Conclusion therefore is that the calculation of critical loads for Flanders will not be possible at short notice.

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## Calculation methods

The calculation of critical loads for cadmium and lead are executed for coniferous and for deciduous forests. In order to keep the steady state mass balance approach as simple as possible and also stay as close as possible to the simple mass balance approach for nitrogen and acidity, the critical loads for both Pb and Cd have been calculated using the follow equation:

$$CL(M) = M_u - M_w + M_{le(crit)}$$

Where:
$CL(M)$ = critical load of heavy metal (Pb, Cd), (g ha$^{-1}$ a$^{-1}$);
$M_u$ = removal of heavy metals by biomass harvesting or net uptake in forest ecosystems, respectively, from the mineral topsoil (g ha$^{-1}$ a$^{-1}$);
$M_w$ = weathering release of heavy metals in the mineral topsoil (g ha$^{-1}$ a$^{-1}$);
$M_{le(crit)}$ = critical leaching of heavy metals from the mineral topsoil (g ha$^{-1}$ a$^{-1}$).

### Uptake

Heavy metal removal by harvest of plants in the mineral topsoil has been calculated by combining the average yield of the biomass with the heavy metals content in harvested parts:

$$M_u = f_{ru} \cdot Y \cdot X_{hpp}$$

Where:
$f_{ru}$ = root uptake factor, to scale the net uptake in the root zone to the depth considered (10 cm);

$Y$ = annual average removal of biomass (dry weight) (kg $ha^{-1}$ $a^{-1}$)
$X_{hpp}$ = content of the heavy metal in the harvested parts of the plants (g $kg^{-1}$)

Since critical loads for forests are calculated for the mineral topsoil (0-10 cm), the total net uptake is multiplied by the root uptake fraction in this layer and the overlying humus layer as compared to the total root zone. This root uptake factor, $f_{ru}$, have been taken equal to 0.5.

## Weathering

Heavy metal release by weathering in the mineral topsoil was estimated by the following equation:

$$M_w = 5 \cdot 10^{-4} \cdot f_{we} \cdot BC_w \cdot \frac{X_M}{X_{BC}}$$

Where:
$M_w$ = weathering rate of heavy metals in the mineral topsoil of 10 cm (g $ha^{-1}a^{-1}$);
$BC_w$ = weathering release of base cations from the parent material ($mol_c$ $ha^{-1}a^{-1}m^{-1}$);
$X_M$ = content of the heavy metal in the parent material (mg $kg^{-1}$);
$X_{BC}$ = content of base cations in the parent material (mol $kg^{-1}$);
$f_{we}$ = factor to scale the weathering rate from 1 m to the depth considered (0.1 m).

Data on base cations weathering rates have been directly taken from the Acidity, Sulphur and Nitrogen critical loads database (Ignatova *et al.*, 1999). In the absence of more specific data on the production of basic cations through mineral weathering for most of study regions, weathering rates were calculated according to the dominant parent material obtained from the lithology map of Bulgaria and the texture class taken from the FAO soil map for Europe, according to the clay contents of the Bulgarian forest soils (UBA, 1996). The ratios of heavy metals and base cations in the parent material ($X_M/X_{BC}$) have been derived from the national geological survey data.

## Critical leaching of heavy metals

The critical leaching flux of Pb and Cd was calculated according to the follow equation:

$$M_{le(crit)} = 10 \cdot Q_{le} \cdot [M]_{ss(crit)}$$

Where:
$Q_{le}$ = flux of leaching water from the mineral topsoil (m $a^{-1}$)
$[M]_{ss(crit)}$ = critical limit for the total concentration of heavy metal in the percolating soil solution (mg $m^{-3}$)

The factor of 10 was used to convert the unit from mg $m^{-2}a^{-1}$ to g $ha^{-1}a^{-1}$.
Runoff of water under root zone has been measured in grid cells of 10 x 10 $km^2$ for the entire country.
The total concentration of heavy metal in the soil solution is the most appropriate value to calculate the tolerable leaching flux. In this term both the free metal ions and the metals bound in dissolved complexes are included. Both parts are relevant to the leaching process. There is an agreement that both direct and indirect effects of heavy metals on terrestrial organisms are more directly related to the soil solution and groundwater concentration than to the total soil content (Lamersdorf *et al*., 1991; Tyler, 1992; Wilkens, 1995; Crommentuijn *et al.*, 1997).

## Assessment of critical limits for terrestrial ecosystems

### Effect-based approach

In calculating a critical load for terrestrial ecosystems, a critical metal leaching rate is derived by multiplying the flux of leaching water with a critical dissolved metal concentration. Using the effect-based approach the critical metal concentrations in soil solution have been taken from the CCE guidance e.g. $[Pb]_{ss(crit)}$ = 8 mg $m^{-3}$ and $[Cd]_{ss(crit)}$ = 0.8 mg $m^{-3}$ (Vries *et al.*, 2001).

### Stand-still approach

In the stand-still approach the critical leaching term is calculated as:

$$M_{le(crit)} = 10 \cdot Q_{le} \cdot [M]_{ss(pres)}$$

Where:
$[M]_{ss(pres)}$ = present total concentration of heavy metal in the percolating soil solution (mg $m^{-3}$)

The present total concentration of Pb and Cd in the percolating soil solution (mg $m^{-3}$) was computed by means of the available present soil metal concentrations ($Pb_{st}$, $Cd_{st}$) in the country in a grid cells 16 / 16 km using the transfer functions recommended by the CCE guidance.

The reactive metal concentration ($M_{re}$) was related to the total soil concentration ($M_{st}$) according to:
$\log Pb_{re} = 0.063 + 1.042 \log Pb_{st} + 0.024 \log (\% OM) - 0.122 \log (\% clay)$;
$\log Cd_{re} = 0.225 + 1.075 \log Cd_{st} + 0.006 \log (\% OM) - 0.020 \log (\% clay)$

Where:
$Pb_{re}$, $Cd_{re}$ = reactive concentration of heavy metal Pb, Cd in soil (mol $kg^{-1}$)

Freundlich isotherms that relate the reactive metal content ($M_{re}$) to the total concentration in soil solution ($[M]_{ss}$) have been expressed as:

$$[M]_{ss} = (M_{re} / K_f)^{1/n}$$

Where:
$M_{re}$ = reactive metal concentration (mol $kg^{-1}$);
$[M]_{ss}$ = total metal concentration in soil solution (mol $m^{-3}$);
$K_f$ = Freundlich coefficient ($mol^{1-n}$ $m^{3n}$ $kg^{-1}$);
n = Freundlich exponent

To obtain an equation that can be used for a range of soils, $K_f$ was calculated as follow:
For Pb : $\log K_f = -3.06 + 0.85 \log (\% OM) + 0.02 \log (\% clay) + 0.26 pH$;
For Cd : $\log K_f = -5.01 + 0.65 \log (\% OM) + 0.27 \log (\% clay) + 0.29 pH$;

**Data sources**

A) National monitoring data
  - Critical loads for Pb and Cd have been calculated for all major tree species in grid cells of 16 km x 16 km. A total of 208 forest soil profiles have measured values for the Pb and Cd total soil concentration, the content of the organic mater (%), the clay content for the fraction

0.01 mm in the soil (%) and the pH of the soil.

- Runoff of water under root zone has been measured in grid cells of 10 x 10 $km^2$ for the entire country.
- Data on biomass removal for forests have been derived from the Acidity, Sulphur and Nitrogen critical loads database, taken from the National Forests Survey Agency. The content of the heavy metal in the biomass ($X_{hpp}$, g/kg) has been taken from the literature for different harvested parts of the plants (stem and bark of forest trees) (Jorova, 1992; Ignatova, 2001; De Vries and Bakker, 1998; De Vries *et al.*, 2001).

B) National synthetic maps
  - Soil type information on the FAO soil map of Bulgaria;
  - Geological map of Bulgaria 1 : 500 000
  - Vegetation map of Bulgaria 1 : 500 000

C) Calculation data
  - In the absence of more specific data on the production of basic cations through mineral weathering for most of study regions, weathering rates were calculated according to the dominant parent material obtained from the lithology map of Bulgaria and the texture class taken from the FAO soil map for Europe, according to the clay contents of the Bulgarian forest soils (UBA, 1996).

## Results, comments and conclusion

In order to protect surface waters and soils in deciduous and coniferous forested catchments, critical loads of heavy metals (Lead and Cadmium) have been calculated using a steady state mass balance approach. This approach is based on the concept of equilibrium partitioning between dissolved and adsorbed phases in soil and soil solution compartments. It also takes into account the environment quality objectives as well as the growth uptake, leaching by the runoff and weathering rates at a catchment scale in real geographical grid cells.

Coniferous and deciduous forest species have been selected as receptors in view of the different effects of heavy metals on forests. Effect-based ecological critical limits of Pb and Cd for the receptors of concern have been calculated. All data needed to calculate critical loads for Pb and Cd in accordance with the resolution and standards were collected and archived. Software for calculating critical loads for Pb and Cd with a spatial resolution of 50 x 50 km in EMEP grid cells was produce to facilitate further calculating procedure. Calculated critical loads of Pb and Cd for deciduous and coniferous-forested geographical units 50 x 50 km have been mapped using GIS systems and Arcview Programme.

All critical loads of heavy metals and their compartments were computed for both deciduous and coniferous forests in separate records for each EMEP grid cell 50 x 50 km.

The maximum lose of Pb by runoff for deciduous forested catchment was estimated as 9.21 g $ha^{-1}a^{-1}$ with a minimum of 0.72 g $ha^{-1}a^{-1}$. The leaching of this metal by runoff for coniferous forests was similar and ranged between 9.21 g $ha^{-1}a^{-1}$and 1.62 g $ha^{-1}a^{-1}$. The Cd lose by runoff for coniferous forests was between 0.92 and 0.10 g $ha^{-1}a^{-1}$ which was very close to the deciduous ones (0.92 and 0.07 g $ha^{-1}a^{-1}$ respectively).

Biomass uptake of Pb by the stem of deciduous forests was homogenous and obtained values ranged from 1.67 to 2.49 g $ha^{-1}a^{-1}$. Concerning coniferous-forested catchments the diversity of biomass uptake of Pb was higher and the values were situated between 4.13 and 7.49 g $ha^{-1}a^{-1}$. The Cd biomass uptake was between 0.21 and 0.37 g $ha^{-1}a^{-1}$ for coniferous forests and between 0.08 and 0.12 g $ha^{-1}a^{-1}$ for deciduous ones.

There were not significant differences between the input of lead by weathering processes for deciduous and coniferous receptors. In addition, the estimated input of lead by weathering was very low in comparison with the leaching by runoff and biomass uptake at the same grid cell. Values of weathering rates of Pb were situated between 0.07 and 1.91 g $ha^{-1}a^{-1}$ for deciduous forests and between 0.07 and 1.88 g $ha^{-1}a^{-1}$ for coniferous ones. The values for the Cd input by weathering were for coniferous forests between 0.0001 and 0.0094 g $ha^{-1}a^{-1}$, and between 0.0001 and 0.0076 g $ha^{-1}a^{-1}$ for deciduous forests.

Computed values for critical loads of Pb using effect based approach ranged from 0.53 to 11.02 g $ha^{-1}a^{-1}$ for deciduous forests and from 6.53 to 15.70 g $ha^{-1}a^{-1}$ for coniferous forested units (See Fig. BG-1).

Critical loads of Cd were lower than the values of Pb and they were situated between 0.15 and 1.05 g $ha^{-1}a^{-1}$ for deciduous forests and between 0.47 and 1.33 g $ha^{-1}a^{-1}$ for coniferous ones (See Fig. BG-1).

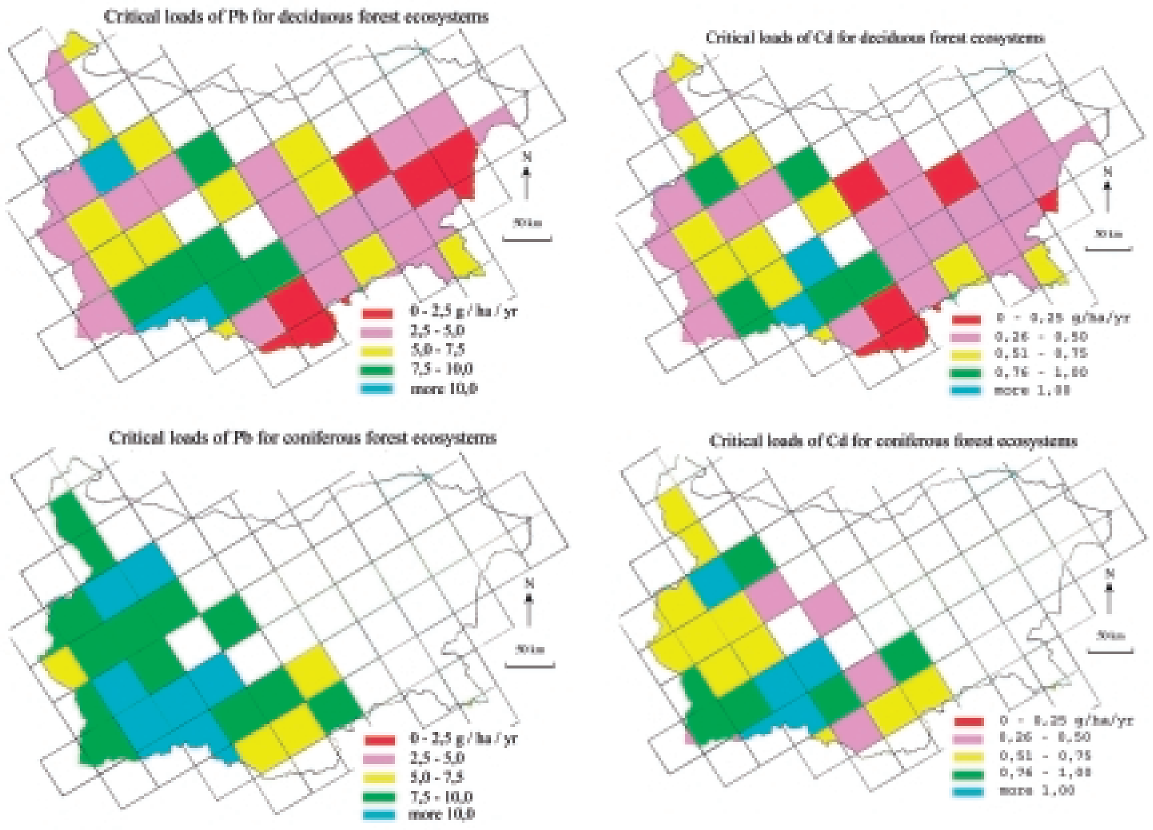

**Figure BG-1 Effect-based critical loads for lead (to the left) and cadmium (to the right)**

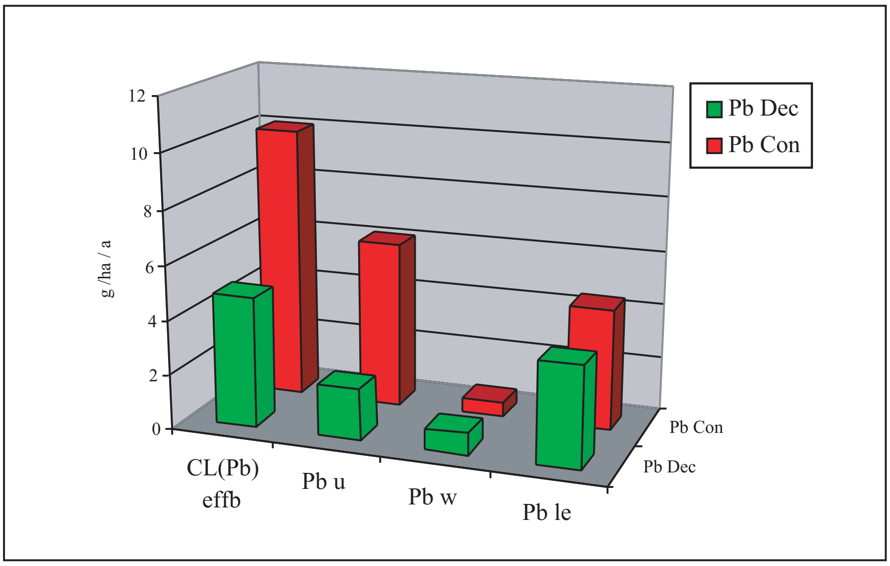

**Figure BG- 2 Average values of critical leaching ($M_{le}$), biomass uptake ($M_{gu}$), weathering rates ($M_{we}$) and critical loads ($M_{tl}$) of Cd (top) and Pb (bottom) for both deciduous and coniferous forests in Bulgaria, g ha$^{-1}$ a$^{-1}$.**

Comparing the average values of critical loads calculated by means of effect based approach and its compartments it could be stress that all values are higher for coniferous forested catchments than for deciduous ones (Fig. BG-2). The average critical leaching of lead for deciduous forested catchments was about 3.70 g ha$^{-1}$ a$^{-1}$ against 4.46 g ha$^{-1}$ a$^{-1}$ for coniferous forests.

Biomass uptake by the stems of coniferous as average annual value ranged 6.11 g ha$^{-1}$ a$^{-1}$ when for deciduous forested catchments this value was only 1.90 g ha$^{-1}$ a$^{-1}$. For Cd these values were 0.306 g ha$^{-1}$ a$^{-1}$ for coniferous and 0.095 g ha$^{-1}$ a$^{-1}$ for deciduous forests. Only the average annual weathering rates of lead for deciduous forested catchment were higher than for coniferous, but the values were very close. The average annual input of lead for deciduous covered areas by weathering was 0.79 g ha$^{-1}$ a$^{-1}$ and for coniferous 0.56 g ha$^{-1}$ a$^{-1}$.

Finally the average critical load of both lead and cadmium for all over the country were higher for coniferous forested areas (for Pb10.01 g ha$^{-1}$ a$^{-1}$ and for Cd 0.75 g ha$^{-1}$ a$^{-1}$) than for deciduous (for Pb 4.81 g ha$^{-1}$ a$^{-1}$ and for Cd 0.46 g ha$^{-1}$ a$^{-1}$) (Fig. BG-2).

Calculated critical loads by means of stand still approach for Cd were much higher than when using effect based approach. The values obtained for Pb was dispersed between 0.2 and 12 g ha$^{-1}$ a$^{-1}$ for deciduous forested grid cells and between 8.5 and 52 g ha$^{-1}$ a$^{-1}$ for coniferous ones. Comparing these values with the critical loads of Cd it could be stress that the computed maximum value was 63158 g ha$^{-1}$ a$^{-1}$ with a minimum of 62 g ha$^{-1}$ a$^{-1}$ for deciduous forests. The critical loads of Cd obtained for coniferous forested grid cells were respectively 2582 g ha$^{-1}$ a$^{-1}$ as a maximum and 64 g ha$^{-1}$ a$^{-1}$ as a minimum values.

## Conclusion

The critical loads of both Pb and Cd for deciduous forested catchments were lower than those for the coniferous at similar ecological and climatic parameters due mainly to the lower leaching by the runoff and lower growth uptake by the biomass of deciduous forest species which demonstrates the higher sensitivity of deciduous forest ecosystems to the heavy metals pollution than the coniferous ones.

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### Data submission

The database in six files involves critical loads for Cd and Pb and related data (Table CZ-1). The evaluation of critical loads was carried out for each heavy metal (HM) and each ecosystem type separately. Three ecosystem types have been investigated:

- coniferous forest ecosystems – “G3” (Cd1.dbf and Pb1.dbf files),
- grassland ecosystems with meadows and pastures – “E” (Cd2.dbf and Pb2.dbf files),
- agricultural ecosystems with arable land – “I1” ( Cd3.dbf and Pb3.dbf files).

The co-ordinates in the database for grassland and agricultural ecosystems belong to the measured localities. The co-ordinates for forest ecosystems represent the reference points of polygons in the CORINE map. For lack of measured data on heavy metal soil contents in the coniferous forest ecosystem the “effect-based” critical loads were evaluated, only. Both the “effect-based” critical loads and “stand-still” critical loads were calculated for the ecosystems with agricultural arable land and for meadows and pastures.

**Table CZ-1: Data included in the national database on heavy metals**

| Values | Names | Unites |
|---|---|---|
| Co-ordinate X | Longitude | |
| Co-ordinate Y | Latitude | |
| I | EMEP50-i grid index | |
| J | EMEP50-j grid index | |
| Areakm$^2$ | Ecosystem area | km$^2$ |
| CLeffb(M) | Critical load of HM using an effect based approach | g.ha$^{-1}$.a$^{-1}$ |
| CLstst(M) | Critical load of HM using the stand-still principle | g.ha$^{-1}$.a$^{-1}$ |
| Mu | Net uptake of HM | g.ha$^{-1}$.a-$^{-1}$ |
| Mw | Weathering rate of HM | g.ha$^{-1}$.a$^{-1}$ |
| Qle | Flux of leaching water | m.a$^{-1}$ |
| Mss(crit) | Critical limit for the concentration of HM in solution | mg.m$^{-3}$ |
| Mss(pres) | Present concentration of HM | mg.l$^{-1}$ |
| Z | Layer thickness M | |
| Y*) | Annual yield of biomass (dry weight) | kg.ha$^{-1}$.a$^{-1}$ |
| Xhpp*) | Content of HM in the harvested parts of the plants | g.kg$^{-1}$ |
| XM | Content of HM in the parent material | mg.kg$^{-1}$ |
| XBC | Content of base cations in the parent material | mol$_c$.kg$^{-1}$ |
| Clay% | Clay content in the soil layer | % |
| OM% | Soil organic matter content in the soil layer | % |
| PH | Acidity | |
| CORINE_class | Ecosystem code according to CORINE | |

*) for arable land the annual yield of biomass and the content of HM present fresh biomass

## Calculation methods

The equation (1) for the evaluation of heavy metal critical loads is based on a simple steady-state mass balance model presented in the Guidance (De Vries *et al.*, 2001).

$$CL(M) = M_u – M_w + M_{le(crit)} \quad (1)$$

Where CL(M) is the critical load of HM, $M_u$ is the removal of HM by biomass harvesting or increments in forest ecosystems, Mw is the weathering release of HM in the soil layer z, $M_{le(crit)}$ is the critical leaching of HM from the soil; all values are in g.ha$^{-1}$.a$^{-1}$.

The critical loads of HM using the effect-based approach, $CL_{effb}(M)$, were derived from the critical dissolved concentration $[M]_{ss(crit)}$ included in Table 3 of the Guidance. The critical loads of HM based on the stand-still principle, $CL_{stst}(M)$, were calculated with the use of “present” soil metal concentrations $[M]_{ss(pres)}$. The derivation of $[M]_{ss(pres)}$ is also suggested in the Guidance and involves the following equations:

$$[M]_{ss(pres)} = (M_{re} / K_f)^{1/n} \quad (2)$$

$$\log Kf = \alpha_0 + \alpha_1 . \log (\%OM) + \alpha_2 . \log (\%clay) – \alpha_3 . pH \quad (3)$$

with parameters given in Table 5 of the Guidance.

$[M]_{ss(pres)}$ is the “present” soil metal concentration in $mol.m^{-3}$ , $M_{re}$ is a reactive metal content in $mol.kg^{-1}$ , $K_f$ is the Freundlich coefficient in $mol^{1-n} .m^{3n} .kg^{-1}$ .

The reactive metal content (concentration) $M_{re}$ is related to the so-called total concentration $M_{st}$. The $M_{st}$ values were calculated from actual metal contents determined in 2 M $HNO_3$ leachate of soil samples and with the use of factors determined experimentally (Beneš, 1999).
The calculations were undertaken according to the following equations (4) and (5). The total concentrations, $Cd_{st}$ and $Pb_{st}$, should represent the total metal concentrations identified with the use of the aqua regia digestion.

$$Cd_{st} = Cd_{2MHNO3} * 100 / 75.5 \quad (4)$$

$$Pb_{st} = Pb_{2MHNO3} * 100 / 82 \quad (5)$$

Then $M_{re}$, the reactive metal concentration, can be related to the $M_{st}$ according to the equation (6) as proposed in the Guidance:

$$\log M_{re} = \beta_0 + \beta_1 . \log M_{st} + \beta_2 . \log (\%OM) + \beta_3 . \log (\%clay) \quad (6)$$

With parameters in Table 4 of the Guidance.

The results of “effect-based” and “stand-still” critical loads are only different in the values of $M_{le(crit)}$, while $M_u$ and $M_w$ values remain the same in the both cases.

## The assessment of input data on $M_u$, $M_w$ and $M_{le(crit)}$

The uptake of HM was assessed on the base of biomass uptake multiplied by the metal content in the harvested parts of plants (wood, grass or crops). The biomass uptake, Y, in the coniferous forest ecosystems represents average annual increments taken by district (NUTS) in the last decade (Report 2000, the Forest Management Institute, Brandys and Labem). The increments (in $m^3$) were recalculated to the dry biomass (with use of volume density) and divided by the forested area (in ha) in each district. P. Krám (the Czech Geological Survey, Prague) provided Table CZ-2 contents of Cd and Pb in wood – Table CZ-2. The biomass heavy metal contents used in the database include a bark composition (bole : bark = 12 : 1).

**Table CZ-2: Contents of Cd and Pb in coniferous trees in two localities of the Czech Republic**

| TYPE | LOCALITY | TREE | Cd | Pb |
|---|---|---|---|---|
| | | | ppm | ppm |
| BARK | Lysina | 1 | 0.3143 | 0.812 |
| | Lysina | 2 | 0.3729 | 1.425 |
| | Lysina | 3 | 0.7166 | 0.704 |
| | Lysina | 4 | 0.4483 | 0.629 |
| | Pluhuv Bor | 1 | 0.6883 | 0.3378 |
| | Pluhuv Bor | 2 | 0.6235 | 0.6355 |
| | Pluhuv Bor | 3 | 1.414 | 0.4242 |
| | Pluhuv Bor | 4 | 0.536 | 0.6924 |
| BOLE | Lysina | 1 | 0.1225 | 0.4248 |
| | Lysina | 2 | 0.1305 | 0.4821 |
| | Lysina | 3 | 0.1704 | 0.2679 |
| | Lysina | 4 | 0.1268 | 0.1696 |
| | Pluhuv Bor | 1 | 0.15 | 0.3472 |
| | Pluhuv Bor | 2 | 0.1243 | 0.8078 |
| | Pluhuv Bor | 3 | 0.1124 | 0.6591 |
| | Pluhuv Bor | 4 | 0.1452 | 0.694 |

Sampled: Slavkov Forest, Czech Republic, Summer 1994
(Pavel Kram, Jakub Hruska, Pavel Baresh)
Analyzed: Cornell University, New York, USA
More details in P. Kram 1997 (PhD Dissertation, Syracuse University, New York, USA)

The biomass uptake from grassland ecosystems (meadows and pastures) is in dry weight as well. The amount of harvested biomass per district was taken from the Czech Statistics (ČSÚ, 2000) and related to the areas of perennial meadows and pastures (in ha). The biomass contents of Cd and Pb for perennial meadows are 0.06 mg.kg$^{-1}$ and 0.63 mg.kg$^{-1}$, respectively. The higher contents of Cd and Pb were used for pastures; 0.13 mg.kg$^{-1}$ and 2.32 mg.kg$^{-1}$, respectively (Beneš, 1994; Cibulka *et al.*, 1991).

The biomass uptake from agricultural ecosystems on arable land (data from the statistics) comprises the area of arable land in km$^2$ and the total annual harvest of 20 crop types (in tons) by districts, their main and secondary products. The biomass uptake from agricultural ecosystems given in the database represents biomass in fresh weight. Contents of Cd in plants are in the range from 0.04 mg.kg$^{-1}$ (e.g. seeds of sunflower or rye) to 0.22 mg.kg$^{-1}$ (e.g. main product of turnip, its secondary product up to 0.652 mg.kg$^{-1}$); contents are in dry weight. The lowest content of Pb also shows the sunflower (0.02 mg.kg$^{-1}$) and the highest contents of Pb were observed in one-year fodder plants (up to 2.5 mg.kg$^{-1}$).

The weathering rates of lead were derived from the contents of Pb, Ca, Mg, K and Na in the underlying rocks (Skořepová et al., 1998). The relationship (7) was used for the calculation of molar$_c$ base cation contents, $X_{BC}$ (De Vries and Bakker, 1996, p. 91). The weathering rate of lead, $Pb_w$, was calculated according to the Guidance (equation 3, p. 4). Cadmium contents in parent materials given in Table 2 (the Guidance) were used for the assessment of cadmium weathering rates. This method for the assessment of weathering rates was applied to all types of ecosystems.

$X_{BC} = 10 * [ (\%CaO/56) + (\%MgO/40) + (\%K_2O/47) + (\%Na_2O/31) ]$ (7)

Where %CaO, %MgO, $\%K_2O$ and $\%Na_2O$ are contents of these oxides in the rocks in percentages, $X_{BC}$ is the content of base cations in rocks in $mol_c.kg^{-1}$.

$M_w = 5.10^{-4} . BC_w . ( X_M / X_{BC})$ (8)

Where $M_w$ is the weathering rate of HM in $g.ha^{-1}.a^{-1}$ , BCw is the weathering release of base cations from rocks (parent materials) corresponding to the soil layer Z in $mol_c.ha^{-1}.a^{-1}$ , $X_M$ is the content of $H_M$ in the rocks in $mg.kg^{-1}$ and $X_{BC}$ is the content of base cations in rocks in $mol.kg^{-1}$.

The Water Management Institute, Prague, provided the annual flux of water in m, $Q_{le}$. The data represent the 20-year average of water basic runoff by hydrogeological regions. The critical leaching of heavy metals was calculated according to the equation (9):

$M_{le(crit)} = 10 . Q_{le} . [M]_{ss(crit)}$ (9)

Where $M_{le(crit)}$ is the flux of HM by waters from soils in $g.ha^{-1}.a^{-1}$, $Q_{le}$ is the flux of water leaching from the soil in $m.a^{-1}$ and $[M]_{ss(crit)}$ is the critical limit for the total concentration of HM in the soil solution ( $[M]_{ss(crit)} = [M]_{ss(pres)}$ for a stand-still approach).

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Finland has decided not to contribute to the voluntary mapping call at this stage, due to reasons listed below.

The call set a very short period to data submission deadline, and the NFC was not able to find sufficient resources and data to fulfil the requirements. However, there was some interest in SYKE and collaborators to study the problem in more detail, if necessary resources were available. The proposed heavy metal mapping would have required new types of input data (both parameter-specific and regional), compared to the earlier mappings of acidity and eutrophication. The observed airborne loads of Pb and Cd have declined deeply during recent years in Finland. Especially in case of Pb the reduced concentrations in receptors indicate little need to allocate considerable amounts of newresources for regional mapping. As for Cd, the methodologies (concentration thresholds in soil solution) suggested in the mapping manual may not reflect the best approach for Finland, since the lakewater concentrations are already very low compared to e.g. other Nordic countries. Rather, the accumulation to biological receptors might provide a more feasible approach, as in case of Hg. This would require another type of research concentrating more on specific areas, not to
regional mapping. Finland may carry out case studies focusing on specific sites to clarify the potential threats of heavy metals. This, and possible future regional applications, would call for externalresources, since bulk of the data resides outside our institute (the Finnish Environment Institute) in the Finnish Forest Research Institute (FFRI) and in the Geological Survey of Finland (GSF).

# FRANCE

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## Data produced

### Heavy metals weathering rates for bedrock

Heavy metal calculations are still in progress. Heavy metal database have been improved particularly regarding heavy metals content in soils, bedrock and surface waters for semi-natural areas. Several regional or local (small catchment and soils) studies have been performed in order to determine specific transfer functions between solid and solutions and the parameters of their control in acidic areas (Février-Vauléon, 2000; Semlali, 2000; Hernandez, in progress).

Weathering rates for base cations and some heavy metals have been determined (Table FR-1) at the country scale for geo-pedological units (Party *et al.*, 1999 ; Février-Vauléon, 2000), according to Vrubel and Paces (1996).
The data generally show wider ranges compared to the values proposed by De Vries and Bakker (1998).

As soon as critical limits and transfer functions should be more calibrated and defined more accurately for French ecosystems, a first tentative map of critical load for heavy metals might be available.

## Critical load calculation in the Strengbach catchment

The Strengbach catchment (Vosges mountains) has been intensively studied since 1985 regarding acid, nitrogen and heavy metal atmospheric pollution. In this reference site, we have managed hydrochemical investigations that allow calculating critical loads of heavy metals.
According to Vrubel J. and Pačes T. (1996), two Pb critical load values have been calculated for the soil humus layer (0-10cm) (Février-Vauléon, 2000) considering $Pb_{we}$= 0.1mg.m$^{-2}$.a$^{-1}$; Dr=820mm; Kp=9
-In case of a “protective” value for vegetation (“stand-still approach”):
[$Pb_{crit}$]=12 mg.m$^{-3}$ CCPb=12 g.ha$^{-1}$.a$^{-1}$

-In cases of another much higher critical limit (micro-organisms protection for ex.) :
[$P_{bcrit}$]=50 mg.m$^{-3}$ CCPb=41 g.ha$^{-1}$.a$^{-1}$

The new protection limits recommended for Pb by De Vries *et al*. (2002) are lower but they do not apply for humus layers.

## Exceedances

Exceedances can be calculated comparing critical load values to present-day Pb deposition (11.2 g.ha$^{-1}$.a$^{-1}$) (Février-Vauléon, 2000). In this catchment, in case of the stricter Critical Limit, the critical load for vegetation is not yet exceeded but tolerance zero must been applied to prevent Exceedances in the future. In case of the higher limit however, the ecosystem would not be endangered by increased Pb deposition.
The investigations have also shown that Pb is accumulating in surface horizons of the soils in relation to great absorption capacity of the organic matter. This buffering effect can however change in the future and Pb could migrate into the soil profiles.

## Further Research

Research is in progress, and needs further international co-ordination, concerning:
Ecotoxicology : choice of critical limits
The methodology: several options to calculate the critical load, once the critical limit is defined
Absolute necessity to take into account high natural concentrations of metal.
Distinction of soil categories for transfer functions, possibly for critical limits

**Table FR-1 Weathering rates for base cations and heavy metals for French geo-pedological units (Party, 1999; Février-Vauléon, 2000)**

| Main Soil-Bedrock associations | BC$_w$ | Pb$_w$ | Cr$_w$ | Cu$_w$ | Ni$_w$ | Zn$_w$ |
|---|---|---|---|---|---|---|
| | Keq.ha$^{-1}$.a$^{-1}$ | µg.ha$^{-1}$.a$^{-1}$ | µg.ha$^{-1}$.a$^{-1}$ | µg.ha$^{-1}$.a$^{-1}$ | µg.ha$^{-1}$.a$^{-1}$ | µg.ha$^{-1}$.a$^{-1}$ |
| Tertiary sandy materials and podzolic soils (podzoluvisols) | 0.0-0.1 | - | 26<br>43 | 41<br>129 | 6<br>29 | 90<br>272 |
| Sandstones and podzolic soils (podzoluvisols) | 0.1-0.2 | - | 17<br>550 | 0<br>269 | 0<br>641 | 19<br>416 |
| Acid granites and podzolic soils (podzoluvisols) | 0.2-0.4 | 83<br>1978 | 65<br>961 | 6<br>830 | 8<br>699 | 131<br>1086 |
| Alkali granites, gneiss, micaschists, schists and acid or ochreous brown soils (dystric cambisols) | | | | | | |
| • with low Mg and K content | 0.4-0.6 | - | 1554<br>30621 | 91<br>7320 | 133<br>18430 | 285<br>3427 |
| • with mean content for all elements | 0.6-1.0 | - | 24<br>3099 | 16<br>1156 | 24<br>1576 | 875<br>4619 |
| Sandy loamy materials and hydromorphic leached out soils (gleyic luvisols + eutric luvisols) | 1.0-1.6 | - | 4454<br>6960 | 1272<br>3335 | 971<br>2224 | 3560<br>10214 |
| Volcanic rocks and brown soils (eutric cambisols) | 1.6-2.0 | - | 785<br>8671 | 103<br>1972 | 217<br>16763 | 1467<br>9860 |
| De Vries and Bakker (1996) | | 170<br>3100 | 330<br>4700 | 33<br>1300 | 67<br>1600 | 170<br>5000 |

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## Introduction

At the 20th meetings of the UN/ECE Working Group on Effects and the 17th Meeting of the Task Force on ICP Modelling and Mapping a first “call for national critical loads data” of heavy metals (M) was agreed to gain experience with those calculations. Supporting the Heavy Metals Protocol to the 1979 Convention on Long-range Transboundary Air Pollution. (ECE/EB.AIR/61).

The German NFC provides its respond to this call (file structure see table DE-2) with 1,222,695 records (Cd) and 1,216,015 records (Pb) covering different types of ecosystems (arable land, intensive used grassland, extensive used (= semi-natural) grassland and forest), following the desired format by the Coordination Center for Effects.

A detailed description of data is given in the following:

**Table DE-1: Data set overview**

| No. | Header | parameter | unit | Explanation |
|---|---|---|---|---|
| 1 | LONGITUDE | Longitude | dec. ° | - |
| 2 | LATITUDE | Latitude | dec. ° | - |
| 3 | EMEP50_I | Emep50-I | - | - |
| 4 | EMEP50_J | Emep50-J | - | - |
| 5 | ECO_AREA | Ecosystem area | km$^2$ | - |
| 6 | CLeffb_a or CLeffb_b | Critical Load (effect-based) | g ha$^{-1}$ a$^{-1}$ | Guidance eq. (1), based on critical limits for soil or soil solution a and b, see field 11 and table DE-2 |
| 7 | CLstst | Critical Load (stand-still) | g ha$^{-1}$ a$^{-1}$ | Guidance eq. (1), based on calculated present concentrations in soil and soil solution |
| 8 | Mu | net uptake of M | g ha$^{-1}$ a$^{-1}$ | Guidance eq. (2) |
| 9 | Mw | weathering rate of M | g ha$^{-1}$ a$^{-1}$ | Guidance eq. (3), small methodological deviations are described in the text below |
| 10 | Qle | flux of leaching water | g ha$^{-1}$ a$^{-1}$ | Guidance eq. (5), methodological deviations are described below |
| 11 | Mss_crit_a or Mss_crit_b | Critical concentration of M in soil solution | mg m$^{-3}$ | a directly derived, b derived on the basis of critical limits for reactive concentrations using transfer functions (9a,b; 10), see also table DE-2 |
| 12 | Mss_pres | Present concentration of M in soil solution | mg m$^{-3}$ | derived on the basis of present total content (50 percentiles of background values, Mtt), using gradual transfer functions (eq 7 + Appendix 1; 8; 9a,b; 10) |
| 13 | Z | thickness of the relevant layer | m | forest: 0.1; grassland: 0.2; arable: 0.3 |
| 14 | Y | Annual yield of biomass (dry weight) | kg ha$^{-1}$ a$^{-1}$ | area weighted mean, explanation see text, chapter 1 |
| 15 | X_hpp | content of M in the harvested part of the plant | g kg$^{-1}$ | area weighted mean, explanation see text, chapter 1 |
| 16 | X_m | Content of M in parent material | mg kg$^{-1}$ | literature data, see below |
| 17 | X_bc | content of base cations in parent material | mol$_c$ kg$^{-1}$ | literature data, see below |
| 18 | Clay | clay content in top soil | % | General Soil Map of Germany (Hartwig et al. 1995), updated in 1998 |
| 19 | OM | Soil organic matter | % | General Soil Map of Germany (Hartwig et al. 1995), updated in 1998 |
| 20 | PH | Acidity (pH-value) | - | see below |
| 21 | ECO_CODE | | - | see below |

Guidance = Guidance for the calculation of Critical Loads for cadmium and lead in terrestrial and aquatic ecosystems (DeVries *et al*., 2001)

The data set is split into five files (table DE-2). The *.dbf-files are packed and named as *_ger.zip (sm_cd_a.dbf becomes sm_cd_a_ger.zip)

**Table DE-2: File structure of the dataset**

| File | distinguishing field | Content |
|---|---|---|
| sm_cd_a.dbf | 6 | critical loads (Cd) protecting terrestrial plants/microbiota, |
| | 11 | critical limit (Cd) for soil solution (0.8 mg $m^{-3}$ according to Table 3 of the Guidance) |
| sm_cd_b.dbf | 6 | critical loads (Cd) protecting soil ingesting invertebrates, |
| | 11 | critical limit (Cd) for soil solution based on transfer calculation from the critical reactive Cd content of soil (0.9 mg Cd $kg^{-1}$ according to Table 3 of the Guidance) |
| sm_pb_a.dbf | 6 | critical loads (Pb) protecting terrestrial plants/microbiota, |
| | 11 | critical limit (Pb) for soil solution (8 mg Pb $m^{-3}$ according to Table 3 of the Guidance) |
| sm_pb_b.dbf | 6 | critical loads (Pb) protecting soil ingesting invertebrates, |
| | 11 | critical limit (Pb) for soil solution based on transfer calculation from the critical reactive Cd content of soil (30 mg Pb $kg^{-1}$ according to Table 3 of the Guidance) |
| descr_ger.doc | | explanatory document |

## Calculation methods

### Net uptake of heavy metals

The calculation is conducted according to equation (2) from the Guidance. For agricultural used land (arable, intensively used grassland and semi-natural grassland) the net uptake from the entire rooting zone has been calculated as

$$M_u = Y \cdot X_{hpp}$$

The calculation of the net uptake of lead and cadmium for forest ecosystems has been done applying the following equation:

$$M_u = Y_{stem} \cdot X_{hpp(stem)} + Y_{bark} \cdot X_{hpp(bark)}$$

$M_u$ = net uptake of M (X = Pb or Cd) [g $ha^{-1}$ $a^{-1}$]
$Y$ = average overall increment in dry mass [kg $ha^{-1}$ $a^{-1}$]
$Y_{stem}$ = average increment of stem wood
$Y_{bark}$ = average increment of bark
$X_{hpp(stem)}$ = content of M in stem wood [mg $kg^{-1}$]
$X_{hpp(bark)}$ = content of M in bark [mg $kg^{-1}$]

To consider the portion of the relevant soil layer (z) of the entire rooting zone, the factor $f_{ru}$ is implemented in the calculation of $M_u$ for all grids.

$$f_{ru} = z / d_{root} \cdot 2$$

$f_{ru}$ depends on land use type and rooting depth and is limited to a maximum value of 1. The factor of 2 is a mean to consider that i) fine roots density is often (not ever) higher in the upper soil layers and ii) there is frequently more cadmium and lead in plant available form than in deeper layers. Growth rates for all ecosystem types have been derived from abiotic site conditions.

The metal contents ($X_{hpp}$) in harvested parts of plants as well as ratios between content in stem and bark are provided in Tables DE-3, DE-4 and DE-5.

**Table DE-3: Average concentrations in the stem wood of coniferous and deciduous trees after a literature review (Nagel and Schütze, 1998)**

| | Pb | Cd |
|---|---|---|
| Coniferous | 5 | 0.25 |
| Deciduous | 2 | 0.1 |

**Table DE-4: Ratio between metal contents in stemwood and bark of coniferous and deciduous trees**

| | Pb | Cd |
|---|---|---|
| Coniferous | 0.5 | 4.0 |
| Deciduous | 9 | 1.5 |

**Table DE-5: Heavy metal concentrations (median) of the main agricultural crops and grass, measured in background areas and on control parcels (Nagel and Schütze, 1998)**

| | Summer wheat | Winter wheat | Rye | Winter barley | Summer barley | Pulses | Sun-flowers | Potato | Sugar beet | Rape | Maize | Clover, grass |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 0.08 | 0.08 | 0.03 | 0.02 | 0.06 | 0.04 | 0.04 | 0.23 | 0.25 | 0.04 | 0.20 | 0.15 |
| Pb | 0.19 | 0.10 | 0.20 | 0.20 | 0.30 | 0.20 | 0.20 | 0.73 | 1.00 | 0.20 | 3.80 | 2.49 |

Please note that in the delivered dataset the data on heavy metal content in the harvested part of the plant from arable land are area-weighted means. The spatial share of different crop species grown in each district (Landkreis) of Germany have been multiplied with the specific yield in this area and the species depending content of the metal in the crop. The dataset contains recalculated values according to

$$X_{hpp(recalc)} = \frac{M_u}{Y \cdot f_{ru}}$$

The same is true for average contents in forest trees (containing stem wood and bark).

**Weathering rates of Lead and Cadmium**

The weathering rates of lead and cadmium are calculated on the basis of equation (3) of the Guidance. Slightly deviating from this the weathering rates are calculated directly for the relevant soil layer (z), which makes the use of $f_{we}$ unnecessary. Therefore only the base cation weathering rates (derived according to the methods for acidification), base cation and heavy metals contents of the parent material in this top soil layer have been included.

The ratio of the particular base cations (Na, K, Ca, Mg) with their specific charges (1, 1, 2, 2, resp.) also is considered, thus the mass weighted factor to calculate [mol] from [$mol_c$] of the sum of base cations is ranging between 0.5 and 1 in dependence on the chemical composition of the parent material. $X_{BC}$ and $X_M$ are data from literature (Schachtschabel et al., 1998; Hindel et al., 1999)

For cadmium the calculated weathering rates in some regions (302,320 datasets) are so low that for reasons of rounding they have been included in the calculation as zero.

For lead in 6641 records the weathering rates exceeded the sum of $M_u$ and $M_{le(crit)}$. These grids are assumed to be naturally polluted. According to the recommendation in the guidance such records have been deleted. Natural pollution for Cd was not detected.

**Critical leaching of Lead and Cadmium**

The critical leaching flux of cadmium and lead has been calculated according to equation (4). Three different concentrations in the leaching water had to be inserted in this equation:

$[M]_{ss(crit)\_a}$: Related to effects on microbiota and plants

$[M]_{ss(crit)\_b}$: Derived by transfer calculations from a critical limit for reactive contents of heavy metals in the soil which are related to effects on soil invertebrates

$[M]_{ss(pres)}$: Derived by transfer calculations from the present content of heavy metals in the soil.

The transfer functions from the chapter 2.3 of the guidance have been used without changes. In general the calculated concentrations of lead in soil solution $[M]_{ss(crit)\_b}$ and $[M]_{ss(pres)}$ seem to be relatively high in comparison to data measured in the field. For particular units of the soil map in combination with land use specific acidic conditions they are much too high. For cadmium for most grids the values for $[M]_{ss(pres)}$ are plausible, however, also for this metal for some soil/land use combinations $[M]_{ss(crit)\_b}$ and $[M]_{ss(pres)}$ are much too high. Extreme values occur when clay content is zero. To enable the calculation of log10 we set the clay content to 0.01 % in these cases. This phenomenon is clearly determined by the transfer functions. Because transfer functions are only related to mineral soils, the critical leaching and thus critical loads for organic soils could not be calculated.

Sufficiently representative background values are not yet available for certain combinations of soil/parent material classes and land use types in Germany. Thus only about 70 % of the countries area could be covered with data on present heavy metal leaching fluxes and related stand-still critical loads.

$Q_{le}$ has been estimated from data on subsurface runoff, because specific data on interception, soil evaporation and transpiration (as required in equation 5) of the Guidance were not available in the short term. Transpiration was assumed to be 75 % of evapotranspiration, for which the magnitudes could be derived from the map of annual precipitation amount and the map of runoff. According to different land use types and orography the ratio of transpiration to subsurface runoff may differ considerably from this rough estimate. This is neglected in this dataset but should be proved in future calculations.

The following equation has been used to calculate $Q_{le}$:

$$Q_{le} = Q_{sub} + E_t - f_{ru} \cdot E_t$$

With:

$Q_{le}$ = leaching flux of water [m $a^{-1}$]

$Q_{sub}$ = flux of subsurface water runoff [m $a^{-1}$]

$E_t$ = transpiration flux [m $a^{-1}$]

$f_{ru}$ = factor to consider the share of transpiration from the relevant soil layer [-]

$f_{ru}$ was set to 1 for agricultural land and 0.5 for forest, because more detailed information with respect to the contribution of the relevant soil layer to the transpiration flux could not yet be found.

Ecosystem types (ECO_CODE)

The ecosystem code compares to main classes of the EUNIS habitat classification (table DE-6).

### Table DE-6: Ecosystem types used as receptors for the critical load approach

| ECO_CODE | Description |
|---|---|
| I1 | Arable land and market gardens |
| FB | Shrub plantations |
| E2.6 | Agriculturally-improved, re-seeded and heavily fertilised grassland, including sports fields and grass lawns |
| X08 | Rural mosaics, consisting of woods, hedges, pastures and crops |
| G1 | Broad-leaved deciduous woodland |
| G3 | Coniferous woodland |
| G4 | Mixed deciduous and deciduous woodland |
| E | Grassland and tall forb habitats (exc.: like E2.6) |
| F | Heathland, shrub and tundra habitats |
| G5.6 | Early-stage natural and semi-natural woodlands and regrowth |
| C3 | Littoral zone of inland surface water bodies |
| D | Mire, bog and fen habitats |

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## Calculation methods

In our work we used a steady-state mass balance, with the introduction of a dynamic term ($\Delta MPs$), that consider a temporal variable. For a first evaluation of critical loads we used the following mass balance

$$MP_{TL} + MP_{LF} + MP_{WE} = MP_{FU} + MP_{SR} + MP_{BP} + MP_{RU} + MP_{LE} + \Delta MP_{S}$$

Where:
$MP_{TL}$ = total critical load
$MP_{LF}$ = flux of heavy metal by litterfall
$MP_{WE}$ = flux of heavy metal due to weathering
$MP_{FU}$ = flux of heavy metal by foliar uptake
$MP_{SR}$ = flux of heavy metal by surface runoff
$MP_{BP}$ = flux of heavy metal due to bypass
$MP_{RU}$ = flux of heavy metal by root uptake
$MP_{LE}$ = flux of heavy metal by leaching waters
$DMP_{S}$ = the accumulation of heavy metal in soil

In this mass balance equation there are any differences between various oxidation states of metals. For lead and cadmium we assumed that are present in soil like bivalent cation.

Many simplifications can be made, because

$MP_{RU}$ is a function of $MP_{GU}$ (flux of heavy metal due to growth uptake), $MP_{LF}$ and $MP_{FU}$ are slight, $MP_{WE} = 0$, $MP_{SR}$ and $MP_{BP}$ are negligible.

The simplifications lead to

$MP_{TL} = MP_{GU} + MP_{LE} + \Delta MP_{S}$

The calculation of $MP_{GU}$ is variable for different ecosystems. In particular we have that for agriculture soils

$$MP_{GU} = \frac{\sum\left(area * yield * C_{plant}\right)}{\sum area}$$

Where:

$C_{plant}$ = concentration of heavy metals in plants (mg $kg^{-1}$);
area = hectares of considered species;
yield = production of agricultural considered species (q);
$C_{plant}$ = concentration of heavy metals in plants is obtained by the following formulation:

$$C_{plant} = \left(AV * K_{transf}\right)$$

Where:

AV = actual value of concentration of heavy metals in soil (mg $kg^{-1}$)
$K_{transf}$ = transfer coefficient of heavy metals by soil to plants

Actual value of concentration of Lead and Cadmium in soil has been calculated utilising the composition of various kind of rock of Italian soils.
For Cadmium $K_{trasf}$ is 1.12 for broad-leaved trees and 1.23 for conifer trees.
For Lead we have 0.032 for broad-leaved trees and 0.034 for conifer trees.
For forest soils we have this formulation

$$MP_{GU} = \sum\left(utilization * C_{trunk}\right) * \delta / area$$

Where:

utilization = total of cuts in $m^3$
$C_{trunk}$ = concentration of heavy metals in wood of trees. That concentration is obtained by AV multiplied for $K_{transf}$ that is a coefficient (mg $kg^{-1}$) ;
$\delta$ = trunk density
area = forest area

The second term of our mass balance is the concentration of heavy metals in leaching waters. Where:

$$MP_{LE} = FLU * M_{tot,ss} = \left(RU + I\right) * M_{tot,ss} = (P - E_v) * M_{tot,ss}$$

FLU = total leaching flux

$M_{tot,ss}$ = total concentration of heavy metals in soil.
RU = surface runoff (mm/year)
I = Infiltrated water (mm/year)
P = precipitation (mm/year).
$E_v$ = evapotranspiration (mm/year);
Data relative to evapotranspiration are calculated in accordin with Turc formulation:

$$E_v = \frac{P}{\sqrt{0.9 + \frac{P^2}{L^2}}} \quad \text{With} \quad L = 300 + 25T_{air} + 0{,}05T_{air}^3$$

For the calculation of total concentration of heavy metals it was been applied the following balance:

$$M_{TOT,SS} = \frac{AV}{K_P}$$

where AV = actual value of concentration of heavy metal in soil
$K_P$ = partition coefficient between soil and solution of soil

To calculate $K_p$ we used the following dependency on pH of soil

For cadmium $a_0$ = -3.43 ; $a_1$ = 0.48 and $a_2$ =-0.71
For lead there are not $a_2$; $a_0$ = -0.95 and $a_1$ = 0.35.

The annual accumulation is based on a linear increase in concentration from present values up to the legal value over a period of 200 years.

$$\Delta MP_S = \frac{(LV - AV) * h * \delta}{T}$$

where :
δ = is dry density of soil, calculated like average between the composition of soil in percentage (sand, clay, organic matter, silt) in function of the pH of soil (g/cm$^3$);
h = is layer thickness (25 cm for agriculture soils and 10 cm forest soils);
LV = legal value of heavy metals concentration in soils (D.Lgs 99/92; 100 mg kg$^{-1}$ for lead and 1.5 mg kg$^{-1}$ for cadmium).
AV = present value of heavy metal concentration (mg kg$^{-1}$)
T = time in years
For this kind of model heavy metals accumulation is a variable very important for the accumulation of critical loads, as we discuss in our file of explication.
For calculation of soil dry density we used the following formulation:
δ = 1.85*(%Sand)+1.55*(%silt)+1.35*(% clay)+0.5*(%Organic Matter)

**Data sources:**

For the calculation of critical loads we utilised the following data:

- Production of fruit and vegetables and Utilised agricultural area (ISTAT 1995-1997)
- Total wood production and forest area (ISTAT 1995-1997)
- Precipitations and temperature (Airforce 1950-1998)
- Evapotraspiration (INEA 1955-1998)
- Soil granulometry and acidity (FAO 1974)
- Soil composition (CESI 1995)

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## National Maps Produced

Critical loads for cadmium and lead were computed as loads that will not lead to: concentrations of Cd and Pb above critical limits in the soil solution in a steady-state situation (effect-based approach) and accumulation of Cd and Pb in the upper soil layer (stand-still approach).
The four maps (Figures NL-1 and NL-2) have been submitted to the CCE. The methods and results of the individually derived critical loads are discussed below.

### Calculation Methods

Critical loads for lead and cadmium for Dutch soils were calculated according to the guidelines (De Vries al., 2001). The calculations are limited to the mineral soil layer, with a depth of 10 cm. In contrast to the Dutch critical loads for nitrogen and acidity (Van Hinsberg *et al.*, 2001), critical loads for lead and cadmium were only calculated for forest soils.

Vegetation and soil types: Similar to the calculation procedure for the derivation of Dutch critical loads for nitrogen and acidity (Van Hinsberg *et al.*, 2001), critical loads were calculated on a 250x250m grid scale. Table NL-1 describes the soil and vegetation types distinguished. Critical loads based on soil and vegetation/forest type specific parameters were calculated for each individual 250x250 grid. The soil and vegetation maps used are described in Van Hinsberg *et al*. (2001) and Van Hinsberg and Kros (2001).

Uptake rates: The removal of heavy metals by the harvest of plants was calculated by multiplying the average yield of biomass during the rotation period and the heavy metals content in harvested parts (De Vries *et al*., 2001, equation 2).

### Table NL-1.Ecosystems for which critical loads were calculated

| | |
|---|---|
| Soil type[1] | Sand poor (Carbic Podzols, Arenosols) |
| | Sand rich (Gleyic Podzols, Gleysols) |
| | Sand calcareous (Arenosols) |
| | Peat (Histosols) |
| | Loess (Luvisols) |
| | Clay non-calcareous (Fluvisols) |
| | Clay calcareous (Fluvisols) |
| Vegetation/forest type | Deciduous forest (Broadleaved deciduous) |
| | Spruce forest (Coniferous) |
| | Pine forest (Coniferous) |

[1] the soil types were further sub-divided into five hydrological classes depending on the height and the seasonal fluctuations of the water table.

Since critical loads for forests were calculated for the mineral topsoil (0-10 cm), this total net uptake was further multiplied by the root uptake fraction of 0.5 (see De Vries *et al*., 2001). Yields are soil and forest-type specific (Table NL-2). Metal contents were assumed constant, independent of forest type, i.e. 0.3 mg.kg$^{-1}$ for Cd and 5 mg.kg$^{-1}$ for Pb. Uptake rates for Cd and Pb thus used are given in Table NL-3.

### Table NL-2. Estimated yields (kg.ha$^{-1}$.a$^{-1}$) for the forest-type and soil-type combinations considered

| Soil type | Forest type | | |
|---|---|---|---|
| | Deciduous | Pine | Spruce |
| Clay calcareous | 4900 | 1581 | 3498 |
| Clay non-calcareous | 3500 | 1581 | 3498 |
| Loess | 4900 | 3621 | 5883 |
| Peat | 3500 | 1581 | 3498 |
| Sand calcareous | 4900 | 1581 | 3498 |
| Sand rich | 4900 | 3621 | 5883 |
| Sand poor | 2100 | 2805 | 3498 |

### Table NL-3. Calculated uptake rates for Cd and Pb (g.ha.$^{-1}$.a$^{-1}$) for the forest-type and soil-type combinations considered

| Soil type | Cd uptake | | | Pb uptake | | |
|---|---|---|---|---|---|---|
| | Deciduous | Pine | Spruce | Deciduous | Pine | Spruce |
| Clay calcareous | 0.74 | 0.24 | 0.53 | 12.3 | 3.95 | 8.75 |
| Clay non-calcareous | 0.53 | 0.24 | 0.53 | 8.8 | 3.95 | 8.75 |
| Loess | 0.74 | 0.54 | 0.88 | 12.3 | 9.05 | 14.71 |
| Peat | 0.53 | 0.24 | 0.53 | 8.8 | 3.95 | 8.75 |
| Sand calcareous | 0.74 | 0.24 | 0.53 | 12.3 | 3.95 | 8.75 |
| Sand rich | 0.74 | 0.54 | 0.88 | 12.3 | 9.05 | 14.71 |
| Sand poor | 0.32 | 0.42 | 0.53 | 5.3 | 7.01 | 8.75 |

Weathering rates: According to the guidelines (De Vries *et al.*, 2002), the weathering rates for metals in a layer of 0-10 cm were scaled to base-cation weathering rates (Table NL-4). Base-cation weathering rates for the soil types distinguished were calculated from pedotransfer functions, relating weathering rates to the silt and clay contents of the soils (Van der Salm, 1999). The pedotransfer functions for loess and clay soil were based on laboratory experiments. Weathering rates for the other soil types were estimated from the pedotransfer functions for clay soils and the clay content of peat soils. Base cation contents in the subsoil were based on total analysis data for Dutch sandy soils (De Vries and Breeuwsma, 1986) and loess and clay soils (Van der Salm, 1999). Values used for the Cd and Pb content in the mineral subsoil were derived from available data sets in The Netherlands for 12 sandy soils (De Vries *et al.*, 1994), 40 loess soils, 30 clay soils and 30 peat soils (Klap *et al.*,1999).

**Table NL-4. Calculated weathering rates for Cd and Pb for the soil types considered**

| Soil type | $BC_{we}$ $mol_c.ha^{-1}.a^{-1}.m^{-1}$ | $X_{BC}$ $mol.kg^{-1}$ | $Cd_M$ $mg.kg^{-1}$ | $Pb_M$ $mg.kg^{-1}$ | $Cd_{we}$ $g.ha^{-1}.a^{-1}$ | $Pb_{we}$ $g.ha^{-1}.a^{-1}$ |
|---|---|---|---|---|---|---|
| Clay calcareous | 1500 | 1.2 | 0.25 | 50 | 0.0156 | 3.125 |
| Clay non-calcareous | 1500 | 1.2 | 0.25 | 50 | 0.0156 | 3.125 |
| Loess | 750 | 0.8 | 0.1 | 20 | 0.0047 | 0.9375 |
| Peat | 0 | 1 | 0 | 0 | 0 | 0 |
| Sand calcareous | 500 | 1 | 0.02 | 10 | 0.0005 | 0.25 |
| Sand rich | 500 | 1 | 0.02 | 5 | 0.0005 | 0.1667 |
| Sand poor | 200 | 0.3 | 0.01 | 10 | 0.0003 | 0.25 |

Leaching rates: The critical leaching flux was calculated according to the guidelines (De Vries *et al.*, 2001; equation 4) The water-flux leaching from the mineral topsoil was calculated according to:

$$Q_{le} = (1 - fr_i)P - f_{ru} \cdot E_t$$

Where:
P = precipitation ($m.a^{-1}$)
$fr_i$ = interception fraction (-)
$E_t$ = transpiration ($m.a^{-1}$)
$f_{ru}$ = root uptake factor.

Precipitation estimates have been derived from 280 weather stations in the Netherlands, using interpolation techniques to obtain values for 10x10 km grids. The interception fraction, relating interception to precipitation, was derived from literature data for the forest types considered. Values used were 0.4 for spruce, 0.3 for pine and 0.2 for deciduous forests. Data for forest transpiration were calculated for all combinations of forest types and soil types with a hydrological model (De Vries, 1996). As with metal uptake, the transpiration values were multiplied by a root uptake factor of 0.5, being the ratio of fine roots up to 10 cm divided by the fine root biomass in the complete root zone. As a result of this approach, the leaching rate varies as a function of location and the combination of forest type and soil type, as shown in Table NL-5.

**Table NL-5. Calculated ranges (minimum, average and maximum) in leaching rates for the forest type-soil type combinations considered**

| Soil type | Forest type | $Q_{le}$ (m.a$^{-1}$) | | |
|---|---|---|---|---|
| | | Min | Avg | Max |
| Clay calcareous | Deciduous | 0.38 | 0.42 | 0.48 |
| | Pine | 0.33 | 0.35 | 0.38 |
| | Spruce | 0.22 | 0.22 | 0.22 |
| Clay non-calcareous | Deciduous | 0.35 | 0.42 | 0.52 |
| | Pine | 0.31 | 0.35 | 0.39 |
| | Spruce | 0.2 | 0.22 | 0.28 |
| Loess | Deciduous | 0.41 | 0.46 | 0.54 |
| | Pine | 0.37 | 0.4 | 0.44 |
| | Spruce | 0.25 | 0.27 | 0.29 |
| Peat | Deciduous | 0.36 | 0.42 | 0.5 |
| | Pine | 0.31 | 0.34 | 0.41 |
| | Spruce | 0.18 | 0.23 | 0.25 |
| Sand calcareous | Deciduous | 0.42 | 0.45 | 0.48 |
| | Pine | 0.37 | 0.39 | 0.41 |
| | Spruce | 0.26 | 0.26 | 0.27 |
| Sand poor | Deciduous | 0.4 | 0.46 | 0.54 |
| | Pine | 0.36 | 0.4 | 0.47 |
| | Spruce | 0.24 | 0.29 | 0.33 |
| Sand rich | Deciduous | 0.4 | 0.46 | 0.53 |
| | Pine | 0.35 | 0.4 | 0.46 |
| | Spruce | 0.25 | 0.28 | 0.32 |

Critical dissolved metal concentrations: The critical limits used for dissolved metal concentrations were 0.8 mg.m$^{-3}$ for Cd and 8 mg.m$^{-3}$ for Pb. When using the standstill principle, dissolved metal concentrations were calculated from present soil concentrations according to equations 8, 9b and 10 from the guidelines. Values for the various coefficients are given in Tables NL-6 and NL-7.

**Table NL-6. Values for the coefficients $\beta_0$-$\beta_3$ in the relationship between reactive, $M_{re}$, and "so-called" total soil concentrations, $M_{st}$, of cadmium and lead ($\log_{10}M_{re} = \beta_0 + \beta_1\log_{10}M_{st} + \beta_2\log_{10}(\%OM) + \beta_3\log_{10}(\%clay)$[De Vries et al., 2001, equation 8].**

| Metal | $\beta_0$ | $\beta_1$ | $\beta_2$ | $\beta_3$ | $R^2$ | se-$y_{est}$$^{1)}$ |
|---|---|---|---|---|---|---|
| Cd | 0.225 | 1.075 | 0.006 | -0.020 | 0.82 | 0.26 |
| Pb | 0.063 | 1.042 | 0.024 | -0.122 | 0.88 | 0.17 |

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

**Table NL-7. Values for $\alpha^0$, $\alpha^1$, $\alpha^2$ and $\alpha^3$, and n in the transfer function between reactive and dissolved cadmium and lead concentration ($\log_{10}K_f = \alpha_0 + \alpha_1\log_{10}(\%OM) + \alpha_2\log_{10}(\%clay) - \alpha_3pH$. [De Vries et al., 2001, equation 10].**

| Metal | $\alpha_0$ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | n | $R^2$ | se-$y_{est}$[1]) |
|---|---|---|---|---|---|---|---|
| Cd | -5.01 | 0.65 | 0.27 | 0.29 | 0.54 | 0.77 | 0.37 |
| Pb | -3.06 | 0.85 | 0.02 | 0.26 | 0.67 | 0.58 | 0.55 |

[1]) The standard error of the y-estimate on a logarithmic basis

The pH, organic matter content, and Cd and Pb content in the mineral topsoil were estimated from such environmental factors, as metal deposition and soil characteristics, based on results of regression analysis on available data sets in the Netherlands for 200 sandy soils (Leeters and de Vries, 2001), 40 loess soils, 30 clay soils and 30 peat soils (Klap *et al.*,1999). Table NL-8 lists the results from the regression analysis.

**Table NL-8. Overview of the predictor variables explaining pH in soil solution, clay content and metal concentrations in mineral topsoil (0-10 cm) and the percentage variance accounted for ($R^2_{adj}$).**

| Predictor variable | PH | Org matter | Clay | Cd | Pb |
|---|---|---|---|---|---|
| Metal deposition | | | | x | x |
| Soil type | x | x | x | x | x |
| Forest type | | x | | x | x |
| Acid deposition | x | | | | |
| Ca deposition | x | | | | |
| | | | | | |
| n | 300 | 299 | 271 | 207 | 207 |
| $R^2_{adj}$ (%) | 54 | 74 | 79 | 34 | 68 |

The variation in the content of clay, organic matter and Pb (around 70%) could be well explained, whereas the result was slightly less for pH (54%) and rather poor for Cd (34%). Furthermore, Cd and Pb contents were hardly available for clay soils and loess soils; consequently, the results for these soils are based on a very limited data set. An overview of calculated average content of the necessary soil parameters and metal contents is given in Table NL-9. An overview of the range in resulting concentrations in soil solution is given in Table NL-10.

**Table NL-9. Derived average soil properties and initial content of Cd and Pb for the soil types considered**

| Soil type | PH | Org Matter (%) | Clay (%) | Cd ($mg.kg^{-1}$) | Pb ($mg.kg^{-1}$) |
|---|---|---|---|---|---|
| Clay calcareous | 7.2 | 4.7 | 29 | 0.14 | 13 |
| Clay non-calcareous | 5.3 | 7.3 | 28 | 0.06 | 20 |
| Loess | 4.0 | 7.9 | 12 | 0.10 | 23 |
| Peat | 3.7 | 91 | 10 | 0.95 | 76 |
| Sand calcareous | 5.7 | 3.4 | 2 | 0.06 | 13 |
| Sand rich | 3.7 | 5.3 | 3 | 0.15 | 17 |
| Sand poor | 3.8 | 4.6 | 3 | 0.12 | 14 |

**Table NL-10. Calculated ranges (minimum, average and maximum) for dissolved Cd and Pb concentrations for the forest type - soil type combinations considered**

| Soil type | Forest type | $C_{dss}$ (mg.m$^{-3}$) | | $P_{dss}$ (mg.m$^{-3}$) | | | |
|---|---|---|---|---|---|---|---|
| | | Min | Avg | Max | Min | Avg | Max |
| Clay calcareous | Deciduous | 0.003 | 0.009 | 0.043 | 0.183 | 0.65 | 1.688 |
| | Pine | 0.035 | 0.061 | 0.094 | 0.233 | 0.599 | 0.875 |
| | Spruce | 0.013 | 0.013 | 0.013 | 0.266 | 0.266 | 0.266 |
| Clay non-calcareous | Deciduous | 0.004 | 0.015 | 0.054 | 0.728 | 3.455 | 7 |
| | Pine | 0.043 | 0.101 | 0.222 | 0.997 | 2.641 | 5.707 |
| | Spruce | 0.012 | 0.022 | 0.052 | 0.749 | 1.548 | 3.25 |
| Loess | Deciduous | 0.01 | 0.038 | 0.129 | 11.846 | 26.279 | 36 |
| | Pine | 0.097 | 0.26 | 0.779 | 12.115 | 18.744 | 27.769 |
| | Spruce | 0.026 | 0.061 | 0.209 | 8.975 | 14.254 | 20.571 |
| Peat | Deciduous | 0.232 | 1.104 | 20.517 | 1.799 | 7.8 | 19.005 |
| | Pine | 2.12 | 12.709 | 137.983 | 2.39 | 8.541 | 13.424 |
| | Spruce | 0.564 | 1.336 | 7.272 | 1.763 | 3.474 | 8.995 |
| Sand calcareous | Deciduous | 0.01 | 0.041 | 0.106 | 0.779 | 4.117 | 8.06 |
| | Pine | 0.101 | 0.27 | 0.4 | 0.842 | 3.489 | 5.68 |
| | Spruce | 0.052 | 0.06 | 0.065 | 1.386 | 1.642 | 1.803 |
| Sand poor | Deciduous | 0.065 | 0.285 | 5.628 | 3.938 | 19.779 | 47.448 |
| | Pine | 0.439 | 2.49 | 25.778 | 3.179 | 18.256 | 38.699 |
| | Spruce | 0.156 | 0.495 | 6.905 | 3.117 | 10.321 | 22.315 |
| Sand rich | Deciduous | 0.072 | 0.295 | 5.71 | 5.807 | 22.724 | 47.891 |
| | Pine | 0.625 | 2.722 | 38.875 | 6.199 | 21.361 | 43.376 |
| | Spruce | 0.158 | 0.403 | 4.883 | 4.469 | 9.918 | 25.562 |

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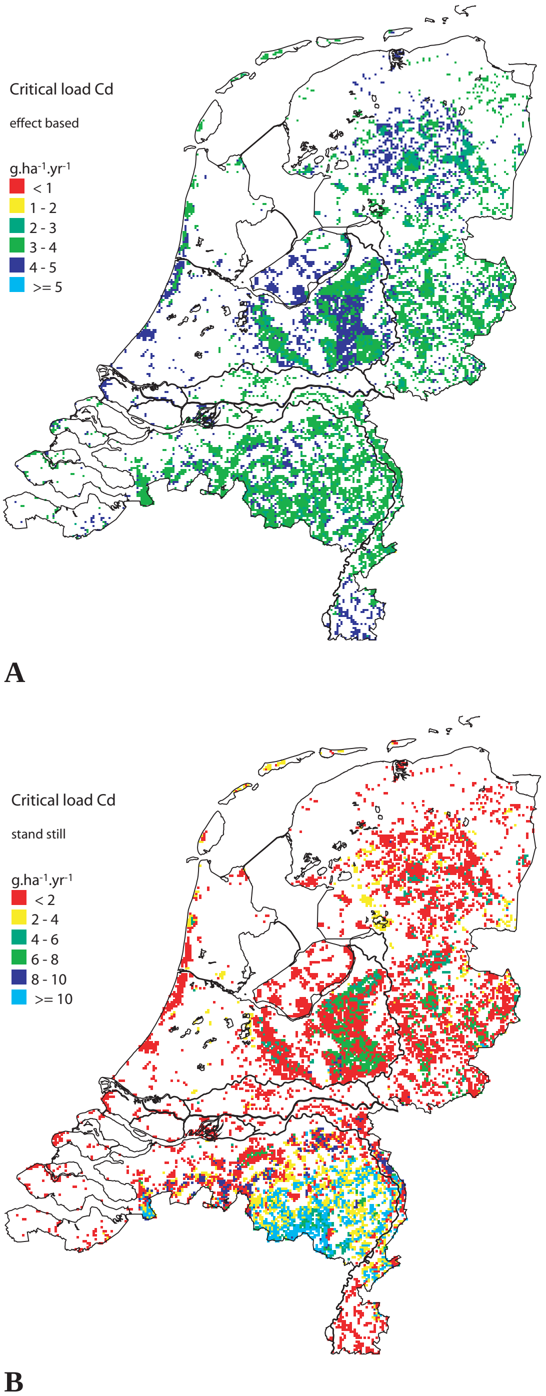
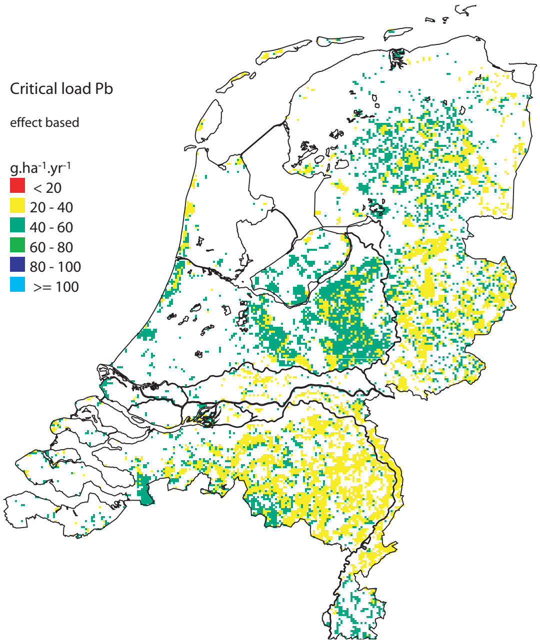
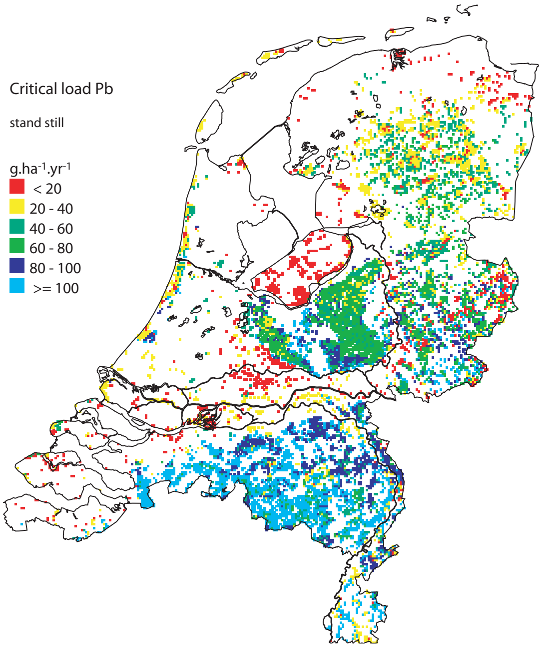


**Fig NL-1. Critical loads for Cd using the effect-based (A) and the stand- still approach (B).**



**A**



**B**

**Fig NL- 2. Critical loads for Pb using the effect-based (A) and the stand- still approach (B).**

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The official Norwegian policy is suggesting not to use the critical loads concept for heavy metals.

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## Calculation methods

### Preliminary calculations of Critical Loads for Pb and Cd in Forest Ecosystems of European part of Russia

The calculation of critical loads of Lead and Cadmium is in accordance to the guidance (De Vries *et al.*, 2002). It is based on one of the suggested approaches, namely effect-based approach, accounting the possible negative HM influence on biota under definite (critical) concentrations of these metals in the environmental media (soil, soil solution, vegetation, etc). The calculations are based on the simplified mass balance of metals in 0-10 cm soil layer suggesting that the airborne input of HM into the forest ecosystem must not exceed the total fluxes of these metals from the system.

$$CL(M) = M_{gu} + M_{le}$$

Where:
CL(M) is the critical loads of metal (g/ha per year);
$M_{gu}$ is the output of metals by annual net primary production for wood biomass of forests (g/ha per year);
$M_{le}$ is metal output by soil-ground leaching (g/ha per year).

Each member of the right side of equation was estimated based in turn on the relevant equations accounting the peculiarities for the formation of definite biogeochemical flux.

The metal plant uptake by forest wood biomass was estimated as follows:

$$M_{gu} = 0.5 * Y * 10^{-3} * [M_g]$$

Where:
0.5 is a coefficient, accounting the metal uptake from the upper 0-10 layer of soil;
Y is the net primary production of wood biomass (kg/ha per year);
$[M_g]$ is the metal content in the relevant part of wood forest biomass (mg/kg);
$10^{-3}$ is a coefficient recalculating mg/kg to g/kg.

The relevant data for net primary production in the forest ecosystems were based on national results (Basilevich, 1993). The Pb content in wood were considered to be equal to 1 mg/kg on dry weight, and Cd, 0.1 mg/kg, using the national experimental results (Zolotareva *et al*, 1983; Elpatievsky, 1993; Dobrovolsky, 1994; Uchvatov, 1995; Zolotareva and Uchvatov, 1996, etc.) and the manual (De Vries *et al.*, 2002). Using these data we have estimated that at present the accumulation of Pb and Cd in wood biomass of “unpolluted” forests in the East Europe area is lower than in West Europe.

Metal output by soil-ground runoff was estimated as follows:

$$M_{le} = 10 * Q_{le} * 10^{-3} * [M]_{ss}$$

Where:
$Q_{le}$ is the annual runoff in accordance to NASA DB (mm/yr);
$[M]_{ss}$ is HM content in soil solution (mg/m$^3$);
10 and $10^{-3}$ is the relevant coefficient for getting the final values in g/ha per year.

The critical (permissible) content of metals in soil solution was based on De Vries *et al.* (2002). We were considered that at $Q_{le} > 200$ mm, this content is 6 (Pb) and 0.6 (Cd) mg/m$^3$, and at $Q_{le} <$ 200 mm, 8 and 0.8 mg/m$^3$, respectively. This hypothesis was based on the speculations that the runoff value is the averaged parameter for the hydrological fluxes in the watersheds of minor and middle rivers, including the total surface, sub-surface (gravitation water) and groundwater runoff from both forested and open parts of watersheds. In the northern areas of the European part of Russia (and partly in Belarus), the predominant hydrological runoff is owed to the snow melting waters and accordingly its chemical composition is more formed by snow and accumulated during the winter period pollutants than the soil-geochemical parameters themselves. Reasonably, the application of unique value for critical content of heavy metal in soil solution (capillary water) would too much enlarge the permissible value of output by surface-ground runoff and the final value of critical load.

At the moment, the value of soil weathering $M_{we}$ was not accounted for due to uncertainties in spatial distribution of soil granulometric composition. Nevertheless, we have estimated the relevant parameters for various soils and this will be taken into account during future calculations of critical loads. One can see that these values are similar to those for HM plant uptake and should be accounted.

**Table RU-1 Weathering rates for lead and cadmium for different soil types**

| Soil texture type | Weathering rate | |
|---|---|---|
| | Pb, mg/ha/yr | Cd, mg/ha/yr |
| Poor sand | 0.25 | 0.5 |
| Sand with high base cation content | 0.3 | 0.6 |
| Sand loam | 0.9-0.95 | 4.6-4.7 |
| Heavy clay | 3.125 | 15.625 |

Other parameters and items:

Land use, IGBP Map of EDC DAAC;
Soil, FAO UNESCO soil map;
Runoff, NASA Global DB (1989).

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## Calculation methods

Calculations of CLs for Cd, Pb have been carried out according to the “Guidance” for voluntary submission of CLs of lead and cadmium.

## Data sources:

### Table SK-1 Source of information for input variables

| Variable | Source of the data | Notes |
|---|---|---|
| root uptake factor (fru) | Generalised data from the forest soil surveys according to the soil types | |
| Annual average removal of biomass | Values from the CL(S,N) database have been used | |
| Content of HM | Median values from the bark and wood direct estimates at the 111 ICP Forests monitoring plots according to individual tree species | Direct chemical analyses |
| BCw | Values from the CL(S,N) database have been used | |
| Content of HM in parent material | Values from „Geochemical atlas of the Slovak Republic – Soils“ have been used combined with the Table 2 from the Guidance | |
| Content of BC in parent material | Data based on the results from ICP Forest monitoring plots and forest soil surveys combined with the Table 2 from the Guidance | |
| Flux of leaching water | Values from the CL(S,N) database have been used with recalculations on the top 10 cm soil layer | |
| Mss(crit)<br>Organic matter, Clay content, pH | Values from the Table 3 (Guidance) have been used<br>Data based on the results from ICP Forest monitoring plots and forest soil surveys according to the soil types | |
| Ecosystems | Calculations have been carried out for coniferous (code 1) and broad-leaved forest ecosystems (code 2) | |

# SWEDEN

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Sweden will not deliver any critical loads data for heavy metals this time. We suffer from budget restrictions and so far we have not been able to get started with this task. Swedish priority is mercury, and in this field the work will continue and hopefully also be expanded.

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## Calculation methods

The submitted data are provisional. They are based on the methods and equations presented in the “can do” document from the CCE(Guidance for the Calculation of Critical Loads for Cadmium and Lead in Terrestrial and Aquatic Ecosystems).
Due to lack of time and data, only the effect-based approach has been applied. For the same reasons, the determination of critical loads was done only for forest areas: 691 points representing 11.000 km$^2$ of Swiss forest areas are considered.
The results are presented in 2 dbase-files (ch_clcd_020510.dbf, ch_clpb_020510.dbf). Structure, contents and units of the data in the 2 dbase-files respond exactly to the CCE format description (Instructions for the Submission of HM CL Data to the CCE, Dec. 2001).
27 records have negative CL values for Pb. This means, the calculation method or input data are not adequate, or the soils are very sensitive due to natural Pb contents in the bedrock. If the negative values lead to problems, the CCE should set them to zero.

**Description of input data and references:**
**CL(M)**: Critical Load of Heavy Metal (HM), CL(M) [g/(ha·yr)] = $M_u - M_w + M_{le(crit)}$ (equ.1)
**$M_u$**: HM removal by harvest of plants in the mineral topsoil, $M_u = f_{ru} \cdot Y \cdot X_{hpp}$ (equ.2)

- $f_{ru}$: since critical loads for forests are calculated for the mineral topsoil (0-10 cm) the root uptake factor, $f_{ru}$, has been taken equal to 0.5
- Y: data on biomass removal for forests have directly been taken from the S&N critical loads database. There is no biomass removal (Y=0) for some of the considered points. Therefore $M_u$ is zero in these points.
- $X_{hpp}$: average values of the ranges given for forests (“can do” document, table 1) have been used => $X_{hpp\ Pb}$: 0.0055 $g_{Pb}$/kg and $X_{hpp\ Cd}$: 0.0003 $g_{Cd}$/kg.

**$M_w$**: HM release by weathering in the mineral topsoil, $M_w = 0.0005 \cdot f_{we} \cdot BC_w \cdot X_M / X_{BC}$ (equ.3)

$BC_w$: data on base cation weathering rates has been taken from the S&N critical loads database. Remark: the $BC_w$ values for the considered data points vary from 8 to almost 33000 [$mol_c$ /(ha·yr·m)], that is a much larger data range than the one given in table 2 (“can-do” document).

$f_{we}$: the $BC_w$ values have been determined for a soil depth of approximately 0.5 m. Therefore a scale factor $f_{we}$ equal to 0.2 has been chosen.

$X_{BC}$: the values for $X_{BC}$ have been deduced form the $BC_w$ values by interpolation (using the values from table 2). The main problem with this approach was, that more than half of the $BC_w$ values (circa 400 out of 691) are out of the range of the values given in table 2. Since no other data was available the minimum value has been fixed at 0.2 (mol/kg) and the maximum at 1.4 (mol/kg).

$X_M$: the values for $X_M$ have been deduced form the $BC_w$ values by interpolation (using the values form table 2). As for the $X_{BC}$ values, minimum and maximum values for $X_M$ have been fixed: $X_{Pb\ min}$ equal to 3, $X_{Pb\ max}$ equal to 60 (mg/kg) and $X_{Cd\ min}$ equal to 0.007, $X_{Cd\ max}$ equal to 0.30 (mg/kg).

**$M_{le(crit)}$**: critical leaching of HM, $M_{le(crit)} = 10 \cdot Q_{le} \cdot [M]_{ss(crit)}$ (equ.4)

$Q_{le}$: the values of $Q_{le}$ are derived from the S&N critical loads database.

$[M]_{ss(crit)}$: the critical metal concentration in soil solution applied is equal to 0.8 ($mg_{Cd}/m^3$) resp. 8 ($mg_{Pb}/m^3$). These values correspond to the recommended critical limits given in table 3 (“can-do” document).

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### Methodology

The Ukraine has executed their calculations in close corporation with Russia. They applied exactly the same methodology.

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## Introduction

In the spirit of this “call for data”, which aims to provide an initial test of the proposed methods for calculating and mapping critical loads for metals, the UK NFC has submitted critical load values using both an effect-based approach and the stand-still approach. In both cases, we follow the recommended instructions for the submission of critical-loads data. Nevertheless, we must express considerable reservations about the use of the standstill approach and would not choose to submit data calculatedusing this method to any formal call for data. In particular, we do not believe that the stand-still approach should be applied to areas where the present concentrations are below the critical limits, for which an effects-based critical load is clearly appropriate. Therefore, we have only submitted stand-still values in response to this ‘call for data’ for areas where the critical limits are already exceeded.

Our models suggest that the critical limit of lead, in particular, is already exceeded over large areas of the UK uplands. The research conducted in the UK strongly indicates that these exceedances are due to the effects of long-term deposition over the last two centuries. The high values of current soil and modelled soil solution concentrations in these areas lead to very high critical load values if the stand-still approach is adopted. It is clear that the policy objective should be to reduce metal concentrations in these areas rather than to set critical loads to allow the current concentrations to be maintained in these areas. Hence, even in those areas for which we have submitted stand-still data, we see the stand-still approach as only a first step towards abatement, and would prefer a semi-dynamic or dynamic approach to be applied in such cases.

### Calculation methods

Critical loads for Cd and Pb have been calculated for two ecosystem types: (i) upland forest and (ii) upland non-forest. These ecosystems can be assigned to the following EUNIS habitat classes:
G4 mixed coniferous and deciduous woodland
E/F grassland and tall forbs/heathland scrub and tundra
The ecosystem areas submitted are derived from our national land cover map only for those 1km

grid squares for which we hold all the data required for both the effects-based and standstill methods, and not for the total ecosystem area. In the future we will consider how representative the model input data are for application to larger areas. At the current time, Scotland is also excluded from the data submitted.

A summary of the minimum, maximum and mean values of the input parameters and the critical loads is given in Table UK-1.

**Table UK-1. Minimum, maximum and mean values for input parameters and critical loads for Pb and Cd.**

| Parameter | Data Source | Pb | | | Cd | | |
|---|---|---|---|---|---|---|---|
| | | Minimum | Maximum | Mean | Minimum | Maximum | Mean |
| kd (ml $g^{-1}$) | | 7617 | 48478 | 19209 | 802 | 8495 | 2680 |
| CLeffb non-forest ecosystems (g $ha^{-1}$ $year^{-1}$) | | 21.6 | 297 | 84.9 | 2.16 | 29.7 | 8.49 |
| CLeffb forest ecosystems (g $ha^{-1}$ $year^{-1}$) | | 31.1 | 228 | 84.7 | 2.76 | 22.1 | 8.01 |
| CLstst non-forest ecosystems (g $ha^{-1}$ $year^{-1}$) | | 36.5 | 3977 | 300 | 3.46 | 90.3 | 15.4 |
| CLstst forest ecosystems (g $ha^{-1}$ $year^{-1}$) | | 38.7 | 1494 | 192 | 3.89 | 57.2 | 13.8 |
| Mu (g $ha^{-1}$ $year^{-1}$) forest ecosystems only | | 7.7 | 16.0 | 10.0 | 0.42 | 0.87 | 0.55 |
| Qle (m $year^{-1}$) | (a) | 0.27 | 3.71 | 1.0 | 0.27 | 3.71 | 1.0 |
| $[M]_{ss(crit)}$ (mg $m^{-3}$) | (b) | 8.0 | 8.0 | 8.0 | 0.8 | 0.8 | 0.8 |
| $[M]_{ss(pres)}$ (mg $m^{-3}$) | | 0.29 | 402 | 12.0 | 0.03 | 8.14 | 0.56 |
| z (m) | | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| Y (kg $ha^{-1}$ $year^{-1}$) forest ecosystems only | (c) | 1400 | 2900 | 1825 | 1400 | 2900 | 1825 |
| $X_{hpp}$ (g $kg^{-1}$) forest ecosystems only | (d) | 0.0055 | 0.0055 | 0.0055 | 0.0003 | 0.0003 | 0.0003 |
| Clay % | (e) | 4.34 | 57.0 | 23.0 | 4.34 | 57.0 | 23.0 |
| OM % (LOI) | (e) | 0.38 | 125 | 35.5 | 0.38 | 125 | 35.5 |
| PH | (e) | 3.1 | 9.1 | 4.6 | 3.1 | 9.1 | 4.6 |

**Partition co-efficients (kd)**

Calculations for kd are based on regression analysis of soil samples collected from upland areas across the UK.

Pb: log kd = 3.44651 + 0.134421 * pH + 0.00047808 * LOI

Cd: log kd = 2.34347 + 0.171818 * pH + 0.00101403 * LOI

LOI = loss on ignition values of organic matter. Since LOI values are not nationally available, they have been calculated using the relationship between organic matter and organic carbon, for which Broadbent (1965) suggests, that although the ratio of organic matter to organic carbon is variable, it usually falls in the range of 1.8 to 2.0 for surface horizons of mineral soils. In this application a mid-range value of 1.9 was used, ie, LOI (%) = 1.9 * organic carbon (%), and an upper limit of 99.9% was used where organic carbon content exceeded 50%. This conversion may not be suitable for organic soils.
The unit of kd is ml $g^{-1}$.

**Soil solution concentrations $[M]_{ss(pres)}$**
Soil solution concentrations derived from the total concentrations in soil (McGrath and Loveland, 1992; Jordan *et al*., 2000) and the above calculated kd values:

Soil solution concentration (mg $l^{-1}$) = total soil concentration (mg $kg^{-1}$) / kd (ml $g^{-1}$)

Values converted to mg $m^{-3}$ for data submission.

It should be noted that the soil solution concentrations exceed the critical limits see (ie, Pb 8 mg $m^{-3}$, Cd 0.8 mg $m^{-3}$) in some upland areas of England, Wales and Northern Ireland (Figure 6b-1). The critical limit for Pb is exceeded in 41% of grid squares and the critical limit for Cd is exceeded in 17% of grid squares.

It is important that exceedance of the critical limits is considered in addition to exceedance of the critical loads.

**Effects based steady-state critical loads $CL_{effb}(M)$**
The steady-state equation for the calculation of heavy metal critical loads is as follows:

$CL(M) = M_u - M_w + M_{le(crit)}$

Where:
$M_u$ = removal of heavy metals by biomass harvesting or net uptake in forest ecosystems from the mineral topsoil
$M_w$ = weathering release of heavy metals in the mineral topsoil
$M_{le(crit)}$ = critical leaching of heavy metals from the mineral top soil

However, we have not included $M_w$ in our calculations as we believe the weathering rate to be negligible in most upland areas, This conclusion is supported by a sensitivity analysis carried out in an earlier stage of our work.

In addition, in our calculations for upland non-forest areas we assume there is no significant removal of metal from the ecosystem. Over the timescale required for the calculation of a critical load, the processes of uptake, litterfall and decomposition (ie, internal cycling) are ignored. Therefore, we have used the following equations:

For upland non-forest ecosystems:
$CL(M) = M_{le(crit)}$

For upland forest ecosystems:
$CL(M) = M_u + M_{le(crit)}$

$M_{le(crit)}$ = runoff ($Q_{le}$) * critical limit in soil solution ($[M]_{ss(crit)}$
$Q_{le}$ is in m $year^{-1}$
$[M]_{ss(crit)}$ is in mg $m^{-3}$

The critical limits as provided in the guidance notes (De Vries et al) have been used in the above calculations, ie, 8 mg $m^{-3}$ for Pb and 0.8 mg $m^{-3}$ for Cd.

$M_u$ has been calculated using the same methods as used in the UK for deriving base cation uptake in forest ecosystems:

$M_u$ (mg $m^{-2}$ $year^{-1}$) = average annual yield (kg $m^{-2}$ $year^{-1}$) * content of metal in tree (mg $kg^{-1}$)

The average yield data are provided by Forest Research in the UK, with an average value of 0.29 kg $m^{-2}$ $year^{-1}$ for coniferous trees and 0.14 kg $m^{-2}$ $year^{-1}$ for deciduous trees. No UK data are currently available on the metal content in trees, so mid-range values from Table 8, page I-168 of UBA 1998 have been used, ie, Pb 5.5 mg $kg^{-1}$ and Cd 0.3 mg $kg^{-1}$.

Critical load values converted from mg $m^{-2}$ $year^{-1}$ to g $ha^{-1}$ $year^{-1}$ for data submission.

## Stand-still loads $CL_{stst}(M)$

The critical load equations used are basically as for the steady-state method, but with the critical limit being replaced by the concentration of metal in soil solution, on the premise that no further metal accumulation will be allowed. However, the concerns raised in the introduction about the applicability of stand-still critical loads for the UK must be taken into consideration if these data are used. Stand-still critical loads have not been calculated for areas where the critical limit is not exceeded by present-day concentrations. In areas where the critical limit is already exceeded by present day soil solution concentrations, there is a need to focus on dynamic modelling of the response of soil and leachate concentrations to reduced emissions of heavy metals.

$CL(M) = M_{le(crit)}$ for non-forest areas
$CL(M) = M_u + M_{le(crit)}$ for forest areas

$M_{le(crit)}$ = runoff ($Q_{le}$) * concentration of metal in soil solution
$Q_{le}$ in m $year^{-1}$
Soil solution concentrations in mg $m^{-3}$

Critical load values converted from mg $m^{-2}$ $year^{-1}$ to g $ha^{-1}$ $year^{-1}$ for data submission.

## References

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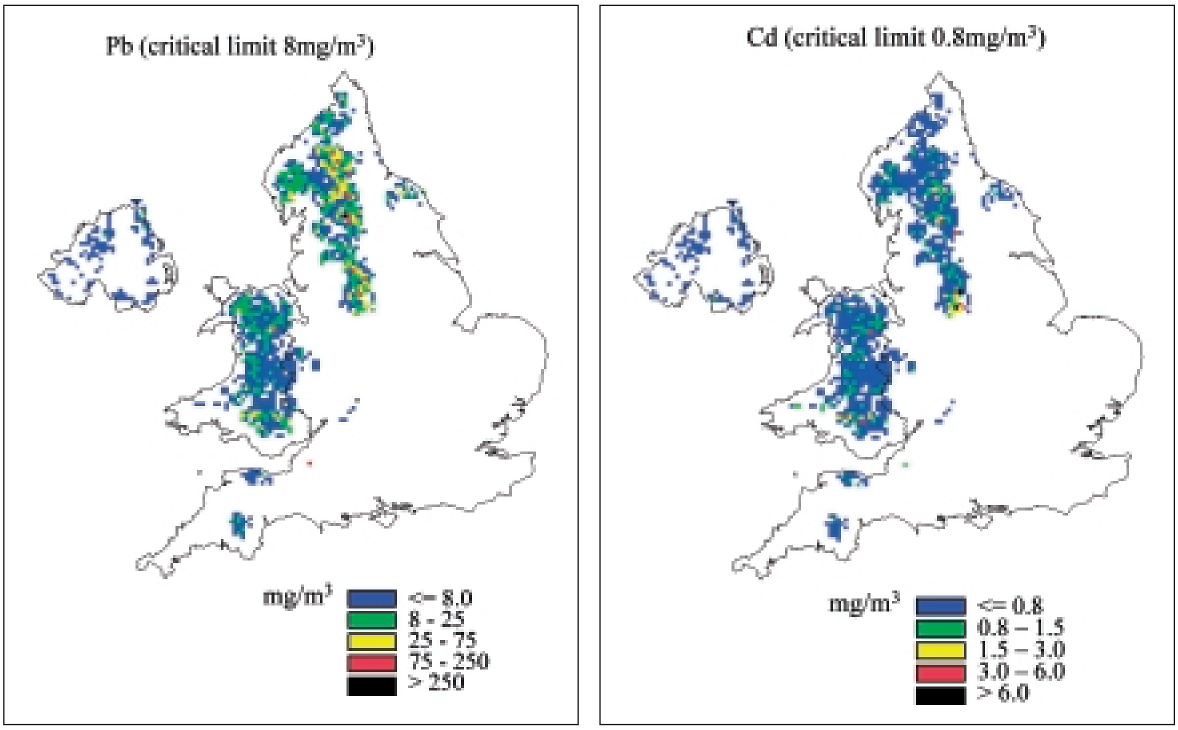

**Cd (critical limit 0.8mg/m$^3$)** **Pb (critical limit 8mg/m$^3$)**

**Figure UK-1 Modelled soil solution concentrations ($M_{ss(pres)}$) for upland areas of England, Wales and Northern Ireland**

**Data sources:**

(a) Centre for Ecology and Hydrology, Wallingford, UK.

(b) De Vries, W., Schutze, G., Romkens, P. & Hettelingh, J.-P. Guidance for the calculation of critical loads for cadmium and lead in terrestrial and aquatic ecosystems.

(c) Forest Research, Alice Holt Lodge, UK.

(d) UBA. 1998. Proceedings of Workshop on Critical Limits and Effect Based Approaches for Heavy Metals and Persistent Organic Pollutants, Bad Harzburg, Germany 3-7 November 1997. UNECE Task Force on Mapping. Umweltbundesamt, Berlin.

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# Annex 1: Background Information on the Derivation of Critical Limits for Lead and Cadmium

This Annex provides an update of elements of the guidance document (chapter 2 in this report) which was distributed to NFCs at the time of the call for data. This update is a results of discussions following the presentation of the results of the call for data at the 12th CCE workshop (14-17 April 2002) and 18th Task Force on Modelling and Mapping (18,19 April 2002) in Sorrento (Italy).

A recommended set of Critical Limits to be used in a first assessment of critical loads, including ranges for uncertainty assessment (deviation from the recommended value ± 20 %), is given in Table 1 (see Table 2-3 in chapter 2). More information on the derivation of those limits is given below.

**Table 1: Recommended set of Critical Limits including ranges for uncertainty assessment**

| Metal | Critical dissolved concentration [µg.l$^{-1}$] | Critical reactive soil concentration [mg.kg$^{-1}$] | Critical surface water concentration [µg.l$^{-1}$] |
|---|---|---|---|
| Pb | 8 (6 – 10) | 30 (25 – 35) | 0.3 (0.2-0.4) |
| Cd | 0.8 (0.6 - 1) | 0.9 (0.7 – 1.1) | 11 (9-13) |

### Critical dissolved metal concentration

The recommended Critical Limits for solution are based on (i) data that are limited to those organisms from which you can be sure that the effect is only through the soil solution (certainly plants and micro-organisms), (ii) data on NOEC and soil properties, which are available in the literature, (iii) a statistical approach deriving limits based on a 95% protection level and (iv) harmonised transfer functions.

The following work steps have been conducted to derive the Critical Limits:

- Combining the available data by Schütze and Throl (2000), Farret and Magaud , pers.comm.) and Klepper and Van de Meent (1997) or Crommentuijn *et al.*, (1997).
- Separate them in NOECs for soil for plants, micro-organisms (and soil fauna for interest, assuming that this is also partly related to soil solution effects).
- Apply the harmonised general transfer functions for Pb and Cd given in the guidance document and calculate related NOECs for soil solution
- Apply a log-logistic fit and calculate the critical limits ($HC_5$)

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

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

where:

$HC_p$ = Hazardous Concentration for p% of the species

p = Percentage of unprotected or potentially affected species at a given logarithmic concentration value of a certain compound.

$\mu$ = mean value of the log-logistic distribution (the value where p = 50%).

$\beta$ = scale parameter, which determines the width or shape of the log-logistic distribution.

Results of the log-logistic fit are given in Table 2, with the number of measurements plus the results of the fit using a 95% protection

**Table 2: Fitted parameter values and resulting critical limits for dissolved metal on concentrations in soil, based on a compilation of NOEC data for various receptors.**

| Metal | Receptor | N | $\mu$ | $\beta$ | $R^2_{adj}$ | Critical limit $HC_5$ ($\mu g.l^{-1}$) |
|---|---|---|---|---|---|---|
| Cd | Microflora | 83 | 2.802 | -0.9893 | 95 | 0.78 |
| | Soil fauna | 67 | 3.176 | -0.8857 | 93 | 3.7 |
| | Plants | 86 | 1.869 | -0.8143 | 86 | 0.30 |
| Pb | Microflora | 31 | 1.369 | -0.8270 | 91 | 1.7[1] (0.09) |
| | Soil fauna | 52 | 2.409 | -0.6535 | 96 | 32 (3.1) |
| | Plants | 10 | 2.739 | -0.5280 | 90 | 15[1] (1.5) |

[1] Values presented for Pb are $HC_{20}$ values. $HC_5$ values are likely to be too low, especially for microflora and plants since the transfer function for lead is unreliable at low concentrations.

The results are in the same range as previously given in the manual and also for those related to impacts on aquatic systems. The values of 8 $\mu g.l^{-1}$ for Pb and 0.8 $\mu g.l^{-1}$ for Cd (originally derived by Germany on the basis of the range of Critical Limits in Curlik *et al.* (2000), using German transfer functions and assuming pH values 6 – 7) are nicely in the centre of the range of calculated Critical Limits for soil solution. Thus there is sufficient reason to use them in first harmonised mapping exercises, although those values have not been justified yet.

### Critical reactive metal concentration

As reactive fraction, the adsorbed fraction of metals can be regarded. This share of the total content may be determined by extraction using weak acids like e. g. 0.43N $HNO_3$, complexing agents like EDTA, DTPA, or neutral salt solutions like 1 M $NH_4NO_3$, $CaCl_2$ and others. It is preliminarily assumed that effects data from ecotoxicological tests are best related to this reactive fraction, because in those tests the metals are added in a well available form. This aspect needs further investigation. Besides, the reactive fraction is supposed to be better related to the concentration in soil solution (calculations with transfer functions) than total contents.

A first approximation of Critical Limits of reactive metal contents was derived by:

- Combining the available data by Schütze and Throl (2000), Farret and Magaud , pers.comm.) and Klepper and Van de Meent (1997), who mainly included data from Crommentuijn *et al.*, (1997).
- Separate them in NOECs for soil for plants, micro-organisms and soil fauna
- Apply a log-logistic fit and calculate the critical limits ($HC_5$ )

Results, based on the same data set as those used in Table 2, are given in Table 3.

**Table 3. Fitted parameter values and resulting critical limits for reactive metal concentrations in soil based on a compilation of NOEC data for various terrestrial taxonomic groups, including microflora, soil invertebrates and plants.**

| Metal | Receptor | N | μ | β | $R^2_{adj}$ | Critical limit $HC_5$ (μg.l$^{-1}$) |
|---|---|---|---|---|---|---|
| Cd | Microflora | 83 | 1.567 | -0.4097 | 96 | 2.3 |
| Cd | Soil fauna | 67 | 1.747 | -0.3466 | 93 | 5.3 |
| Cd | Plants | 86 | 1.203 | -0.2886 | 97 | 2.3 |
| | | | | | | |
| Pb | Microflora | 31 | 2.932 | -0.3809 | 90 | 65 |
| Pb | Soil fauna | 52 | 2.459 | -0.3738 | 93 | 23 |
| Pb | Plants | 10 | 2.941 | -0.4807 | 87 | 34 |

The problem with using those values is that the critical limits for microflora and plants are unclear, since the effect is only through the soil solution. The proposed values are thus based on the NOEC data for organisms from which we can assume that metal effects work through the soil. This will partly be the soil fauna; specifically the hard bodied who mainly get their intake through ingestion. The problem is that it is always a matter of two pathways (partly soil and partly solution) but it can be preliminarily assumed the extreme of only ingestion. In this case one does not have to correct for soil type any more.

Enclosed is Table 4 summarising the results with soil fauna data, using the data from Crommentuijn *et al.*, (1997), Schütze and Throl, (2000) and an EC Risk assessment in support of regulation (CEE) 793/93 on existing substances 2002 in preparation (Farret and Magaud, pers. comm.). This table suggests a critical limit based on all data of 0.9 mg.kg$^{-1}$ for Cd and of 30 mg.kg$^{-1}$ for Pb. It is very well possible that for a certain effect, namely the effect on an organism that only ingest soil, the critical limit can be high, whereas it is lower if organisms are regarded, for which the effect takes place through the soil solution. It is thus suggested preliminarily to use those data without any difference for sand, loam, clay and peat. These differences are not relevant, if ingestion of reactive metal is the pathway, but if exposure and effects are caused by soil solution.

**Table 4. Fitted parameter values and resulting critical limits for reactive metal concentrations in soil based on a compilation of NOEC data for various terrestrial taxonomic groups, including soil invertebrates.**

| Metal | Data source | N | μ | β | $R^2_{adj}$ | Critical limit $HC_5$ ($mg.kg^{-1}$) |
|---|---|---|---|---|---|---|
| Cd | Crommentuijn *et al.* (1997) | 13 | 1.10 | 0.41 | 93 | 0.78 |
| | Schütze and Throl (2000) | 30 | 1.82 | -0.35 | 93 | 6.0 |
| | (Farret and Magaud, , pers. comm.) | 12 | 1.64 | -0.41 | 90 | 2.7 |
| | All | 67 | 1.57 | -0.46 | 91 | 0.9 |
| Pb | Crommentuijn *et al.*, (1997) | 13 | 2.71 | 0.30 | 93 | 66 |
| | Schütze and Throl (2000) | 10 | 2.94 | -0.48 | 87 | 34 |
| | (Farret and Magaud, pers. comm.) | 12 | 2.48 | -0.37 | 93 | 33 |
| | All | 52 | 2.64 | -0.41 | 90 | 30 |

### Critical metal concentration in surface water

Critical limits for surface water for Pb and Cd were derived from a literature compilation given in (Crommentuijn *et al.*, 1997). In Table 5 results are given of a fitted log-logistic distribution based on these results. The data refer to various taxonomic groups (including algae, crustacea, macrophyta and oligochaeta). Comparison with the limits for soil solution shows that the critical limit for Cd in surface water is lower, whereas the critical limit for Pb is higher. In an EC Technical Guidance document on risk assessment 2002 in prep; (Farret and Magaud, pers. comm.), an $HC^5$ of 0.31 $ug.l^{-1}$was derived. Consequently, a value of 0.3 $\mu g.l^{-1}$ was suggested for Cd and 11 $\mu g.l^{-1}$ for Pb.

**Table 5. Fitted parameter values and resulting critical limits for metal concentrations in surface water at different protection percentages, based on a compilation of NOEC data for various taxonomic aquatic groups (data after Crommentuijn et al. (1997).**

| Metal | Effect | N | μ | β | $HC_p$ ($\mu g.l^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | | | | p = 5% | p = 20% | p = 50% |
| Cd | Freshwater and Marine species | 87 | 1.2 | 0.56 | **0.36** | 2.7 | 16 |
| Pb | Freshwater and Marine species | 42 | 2.2 | 0.39 | **11** | 46 | 158 |

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# Annex 2: Updated Assessment of Critical Loads of Lead and Cadmium for European Forest Soils

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## 1. Background

As a follow up on the paper in last years CCE Status Report (Reinds *et al.*, 2001), an updated assessment was made of the critical loads for Cd and Pb on the European scale. In this new assessment, critical loads were computed exactly according to the guidance document (De Vries *et al.*, 2002) which means that, compared to the assessment of Reinds *et al.* (2001), different critical limits were used, metal cycling was neglected and metal adsorption was computed using other equations.

Critical loads were calculated for the mineral topsoil for a situation where (i) no further accumulation of heavy metals occurs (stand-still principle) and (ii) the concentration of heavy metals is below critical limits in the soil solution (effect-based approach) in agreement with recommendations made in the guidance document. In the first case ‘critical’ limits for the soil solution are derived from present metal concentrations and in the second case use was made of the critical limits for the soil solution given in the guidance document. Values used in this study (in $mg.m^{-3}$) were 8 for Pb and 0.8 for Cd. In the assessment of Reinds *et al.* (2001) critical limits were based on Tyler (1992), using the second lowest LOEC data from laboratory studies with culture solutions reported by Balsberg-Påhlsson (1989) divided by a safety factor of 10. This lead to substantially higher values for the critical limits of 15 $mg.m^{-3}$ for lead and 2 $mg.m^{-3}$ for Cd.

## 2. Methods

This chapter describes the methods that were used to compute the critical loads and the data that were used. Emphasis is put on the differences to the previous assessment (Reinds *et al.*, 2001) were more details on methods and spatial data are provided.

### 2.1 Geographical data

Input data for the critical load computations include parameters describing precipitation, evapotranspiration, root uptake, weathering, adsorption and complexation. The input data mentioned above vary as a function of location and receptor (the combination of forest type, soil type and climate). As a basis for the critical load computations, an overlay was made of maps on soil, climate zones, forest distribution and altitude (Reinds *et al.*, 2001). The resulting map contains about 80,000 different units for which critical load computations were made.

### 2.2 Critical load equations

Critical loads for Cd and Pb were computing according to the guidance document (thus neglecting the metal cycling) within a terrestrial ecosystem according to:

$$CL(M) = M_u - M_w + M_{le(crit)} \qquad (1)$$

where:

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

$M_u$ = removal of heavy metals by biomass harvesting or net uptake in forest ecosystems, respectively, from the mineral topsoil (g $ha^{-1}$ $a^{-1}$)

$M_w$ = weathering release of heavy metals in the mineral topsoil (g $ha^{-1}$ $a^{-1}$)

$M_{le(crit)}$ = critical leaching of heavy metals from the mineral topsoil (g $ha^{-1}$ $a^{-1}$)

In Reinds *et al.* (2001), the metal cycling was not neglected, but an analysis for major forest-soil combinations in the Netherlands showed that the effect of neglecting metal cycling has an influence of only about 10-30 % on the calculated critical loads which can be regarded a minor uncertainty compared to the other uncertainties in the critical load computations (De Vries *et al.*, 2002).

## 2.3 Input data and transfer functions

***Uptake rates:*** The removal of heavy metals by harvest of plants was calculated by multiplying the average yield of biomass during the rotation period and the heavy metals content in harvested parts ( De Vries *et al.*, 2001). Since critical loads for forests were calculated for the mineral topsoil (0-10 cm), this total net uptake was further multiplied by a root uptake fraction of 0.5 (see De Vries *et al.*, 2001). Forest growth was computed as a function of tree type, climate zone and site quality using an update of the procedure described by Klap *et al.*, (1997).

***Weathering rates:*** According to the guidance document (De Vries *et al.*, 2001), the weathering rates for metals for a layer of 0-10 cm were scaled to base cation weathering rates. Base cation weathering rates for the distinguished soil types were calculated from pedotransfer functions, relating weathering rates to the soil texture class and parent material type corrected for temperature (De Vries, 1993). Values used for the Cd and Pb content in the mineral subsoil were derived from De Vries *et al.*, (2002).

***Leaching rates:*** The critical leaching flux and the water flux leaching from the mineral topsoil were calculated according to the guidance document (De Vries al., 2001). Precipitation was derived from a European data base available for the 1.0° longitude x 0.5° latitude grid described by Leemans and Cramer (1990), who interpolated selected records of monthly meteorological data from 1678 European meteorological stations. Actual evapotranspiration was calculated according to a model that is essentially the same as used in the IMAGE Global Change Model (Leemans and Van den Born, 1994). The interception fraction, relating interception to precipitation, was derived form literature data for the forest types considered. Values used were 0.4 for spruce, 0.3 for pine and 0.2 for deciduous forests.

***Initial metal concentrations***

Initial metal concentrations are needed to calculate steady-state critical loads based because metal concentrations in the soil should stay constant. Initial metal concentrations were estimated according to a procedure described by Reinds *et al.* (2001) in which present heavy metal concentrations in Europe derived from Van Mechelen *et al.* (1997) are related to various environmental factors such as soil type, soil pH and heavy metal deposition.

It has to be stressed that the regression analysis yielded quite low percentages of explained variance (about 40 – 50 %) which means that the estimates of the initial metal concentrations are very uncertain. This definitely needs to be improved in the future, preferably by using measured data obtained with standardised methods.

When stand-still loads are computed, the present metal content should remain constant which means that the critical metal concentration is the concentration that is in equilibrium with the present metal content. In De Vries *et al.* (2002), several options are given to compute this concentration from the total metal content in the soil solid phase. In this study we used the approach in which a reactive metal content is derived from the total metal content using a transfer functions with soil characteristics. Then the critical metal concentration can be derived from the reactive metal content using a Freundlich equation:

$$[M]_{ss} = (M_{re} / K_f)^{1/n} \qquad (2)$$

where:
$M_{re}$ = reactive metal concentration (mol $kg^{-1}$)
$[M]_{ss}$ = total metal concentration in soil solution (mol $m^{-3}$)
$K_f$ = Freundlich coefficient ($mol^{1-n}$ $m^{3n}$ $kg^{-1}$)
n = Freundlich exponent (-)

The Freundlich constant was computed from soil characteristics clay content, organic carbon content and pH (De Vries *et al.*, 2001). Clay content (derived from texture class) is an attribute to the soil map. Organic matter content, amount of organic layer and present pH values were estimated for each soil type separately from existing databases (De Vries *et al.*, 1993, Van Mechelen *et al.*, 1997).

The transfer equation for the Freundlich constant can be extended with the DOC concentration but since this hardly improves the prediction of the metal concentration and DOC data on a European scale can only be estimated with a high uncertainty (Reinds *et al.*, 2001) it was decided not to include DOC. In Reinds *et al.* (2001) a transfer function was including both DOC and Ca concentration which gives comparable results.

## 3. Results

Critical loads for cadmium and lead for the mineral layer using both the effect-based and the stand-still approach are given in Table 3-1. This table shows that the critical loads from both approaches are in the same order of magnitude; in the previous study (Reinds *et al.*, 2001) critical loads for the effect-based approach were higher than stand-still load due the higher critical limits that were used then.

Table 3-1 shows that ranges in stand-still loads are broader that in effect-based critical loads, due to the strong variety in present metal contents over Europe that lead to a wide range in critical soil solution concentrations.

**Table 3-1 Calculated ranges in critical loads of cadmium and lead**

| Metal | Approach | Critical load (g.$ha^{-1}$.$yr^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | 5% | 25% | 50% | 75% | 95% |
| Cadmium | Effect-based | 1.5 | 2 | 2.5 | 3.2 | 6.4 |
| | Stand-still | 0.9 | 2.9 | 4.5 | 6.7 | 15.0 |
| Lead | Effect-based | 15 | 20 | 25 | 32 | 65 |
| | Stand-still | 9 | 22 | 32 | 48 | 104 |

The maps in fig. 3-1 show the 5th percentile effect-based critical loads for Cd and Pb for each 0.5*0.5 degree grid cell. Highest critical loads are found in areas with high precipitation excess (due to a dilution effect) such as the UK and Ireland, south-western Norway and north-western Spain. Lowest critical loads are found in regions with low precipitation excess such as southern and (parts of) central and eastern Europe. Critical loads follow the pattern of precipitation excess because metal leaching dominates over weathering and uptake, especially for cadmium.

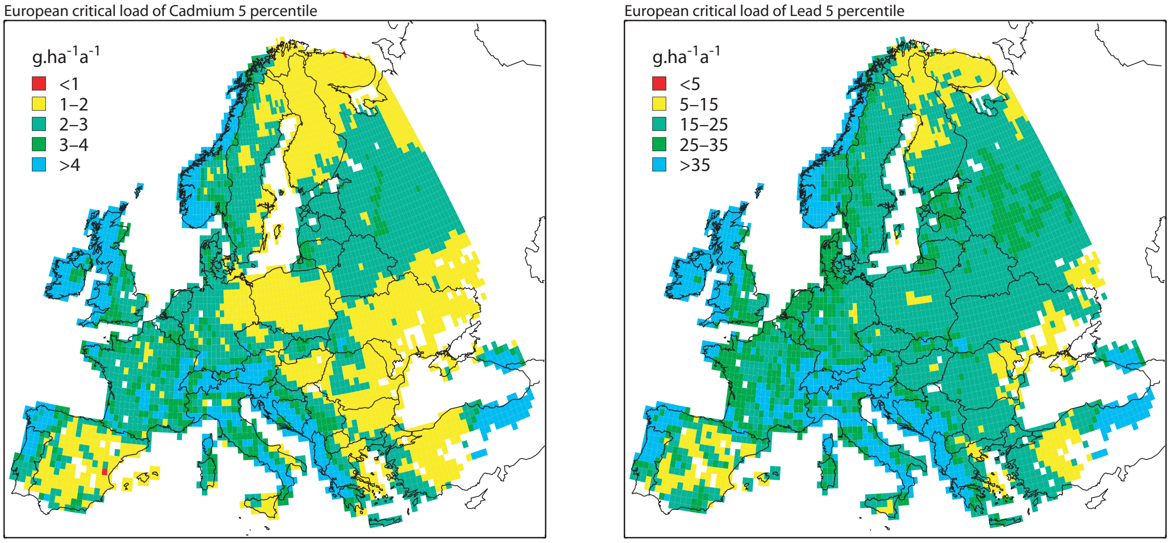

*Figure 3-1 Critical loads (5th percentile) of cadmium(left) and lead(right) computed from an European database.*

## 4. Discussion and conclusions

To assess critical loads for Cd and Pb and their exceedances, the methods described in the guidance document (De Vries *et al.*, 2001) were successfully applied to European forest soils. Both stand-still and effect-based critical loads for the mineral topsoil were computed for Cd and Pb using existing available European data bases and maps on soil, vegetation and climate. Results show that with the present critical limits, critical loads from both approaches are in the same order of magnitude. Spatial patterns in effect-based critical loads follow patterns in precipitation excess over Europe, as metal leaching is the dominating term in the critical load equation.

It should be stressed that the results from this study are uncertain. Main sources of uncertainty for the critical loads calculated by the stand-still principle are the adsorption function, the initial metal concentrations and the complexation constants (Groenenberg *et al.*, 2001). Specifically the uncertainty in present metal concentrations in the soil solid phase is large. Results of a regression analysis, relating these concentrations to environmental variables such as soil type, climate and heavy metal deposition, were consistent with what could be expected, but the percentage of explained variance was low (< 50 %). As a consequence, the estimates of initial metal concentrations in soil and in soil solution, and in turn the estimated critical loads, have a high uncertainty. Estimates of initial metal concentrations can probably only be improved by using European wide measurements. Initiatives in this direction should thus be encouraged. Furthermore there is a high uncertainty in metal adsorption functions as they are mainly based on experiments with Dutch soils. Main sources of uncertainty for the critical loads calculated by the effect-based approach are the maximum allowable metal concentration in the soil water and the estimated precipitation excess (Groenenberg *et al.*, 2001).

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