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Critical Loads of Cadmium, Lead and Mercury in Europe

J. Slootweg, J.-P. Hettelingh, M. Posch (eds.)
S. Dutchak, I. Ilyin (EMEP/MSC-E)

Contact:
J. Slootweg
European Air Quality & Sustainability
jaap.slootweg@mnp.nl

Collaborative report by:

ICP M&M Coordination Center for Effects

EMEP – Meteorological Synthesizing Centre - East

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Netherlands Environmental Assessment Agency
(MNP associated with the RIVM), PO Box 303,
3720 AH Bilthoven, The Netherlands, telephone +31 30 2742745,
website: www.mnp.nl

Contents

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Abstract

Critical Loads of Cadmium, Lead and Mercury in Europe

This progress report describes the critical loads of cadmium, lead and mercury derived for European ecosystems using human and environmental endpoints in the framework of activities of MNP-Coordination Center for Effects (CCE) under the Convention on Long-range Transboundary Air Pollution (LRTAP). Critical loads are compared to atmospheric deposition of these heavy metals in 1990 and 2000 to assess the risk to human health and the environment. Depositions of heavy metals are computed by the EMEP-Meteorological Synthesizing Centre East using national emissions recorded in official inventories. A tentative comparison is also made between critical loads and the input of cadmium and lead from agricultural practices. Finally, computed ambient concentrations of lead and cadmium in 2000 are viewed in the context of the first and fourth daughter directives of the European Commission Framework Directive 96/62/EC on ambient air quality assessment and management.
Seventeen Parties to the Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe participated in the computation and mapping of critical loads. Critical loads of cadmium, lead and mercury were computed by 16, 16 and 9 countries, respectively. Results showed exceedances to diminish between 1990 and 2000, especially for cadmium and lead. In 2000, the exceedance of critical loads of cadmium only occurs in a few European ecosystem areas. Depositions of lead, however, continue to exceed critical loads in many areas in most of the European countries. The distribution of the risk of mercury does not significantly change over time in the countries that submitted data. A preliminary assessment of fertilisation practices in Europe in 2000 suggests that the resulting lead-input will lead to a further exceedance of critical loads. Accumulation of the agricultural and atmospheric input of cadmium seems to increase the risk of cadmium in a few areas only. Finally, European guideline and limit values for yearly average ambient concentrations of lead and cadmium respectively, turn out not to be exceeded by computed ambient concentration in EMEP 50×50 km^2 grid cells in Europe in 2000. Since atmospheric ambient concentrations and deposition are related (with critical loads of lead and cadmium being exceeded in many areas of Europe), these results suggest that the European guideline and limit values may be less adequate than critical loads for the assessment of the risk of lead and cadmium in the context of long-range transboundary air pollution.

Keywords: air quality guidelines, atmospheric deposition, cadmium, critical loads, exceedances, lead, mercury.

Rapport in het kort

Kritische Waarden voor Cadmium, Lood en Kwik.

Dit rapport beschrijft de kritische waarden voor lood, cadmium en kwik voor ecosystemen in Europa, gebaseerd op menselijke en ecologische gezondheid. Kritische waarden zijn drempels voor atmosferische deposities of concentraties waarboven mens of natuur bloot staat aan schaderisico. Hierbij worden limieten voor concentraties in grondwater en voedsel uit WHO en EU documenten, en bekende ecotoxicologische effecten gehanteerd. Deze kritische waarden worden vervolgens vergeleken met de atmosferische depositie van de zware metalen in 1990 en 2000. Omdat depositie niet op zich staat worden ook de kritische waarden voor lood en cadmium tentatief vergeleken met de toevoer op landbouwgebieden van deze metalen door bemestingspraktijken in Europa. Tot slot is gekeken hoe de kritische waarden zich verhouden tot de door de Europese Commissie gehanteerde jaargemiddelde grenswaarden voor atmosferische concentraties.

Zeventien landen onder de Conventie voor grootschalige grensoverschrijdende luchtverontreiniging namen deel aan het onderzoek.

Overschrijdingen van kritische waarden van vooral lood en cadmium blijken sinds 1990 af te nemen. Toch is in 2000 de atmosferische depositie van cadmium op beperkte schaal in oost Europa nog te hoog, en blijft de depositie van lood te hoog in vele gebieden verspreid over de meeste Europese landen. Het risico van kwik blijft aanwezig in de 9 landen die hierover gegevens aanleverden.

Bemestingspraktijken leiden tot overschrijdingen van kritische waarden voor lood, met name in Nederland. Voor cadmium neemt het risico door depositie toe door de toevoer van (kunst)mest in een enkele Oost-Europese regio.

Tenslotte wordt geconstateerd dat de door de Europese Commissie gehanteerde richtlijnen voor gemiddelde jaarlijkse atmosferische *concentraties* van lood en cadmium nergens in Europa worden overschreden door de voor 2000 berekende concentraties in EMEP 50×50 km^2 gridcellen. Aangezien atmosferische concentraties en deposities samenhangen moet op basis van de gegevens van het hier gerapporteerde onderzoek voorlopig worden geconstateerd dat de Europese richtlijnen voor met name lood niet voldoende zijn om risico's van te hoge looddepositie in vele Europese regio, inclusief vrijwel geheel Nederland, te voorkomen.

Trefwoorden: atmosferische depositie, cadmium, kwik, lood, kritische drempels, luchtkwaliteit, overschrijdingen.

Preface

At its twenty-third session (Geneva, 1-3 September 2004), the Working Group on Effects requested the Coordination Center for Effects (CCE) of the International Co-operative Programme on the Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP M&M) to issue a call for data on critical loads of Cadmium (Cd), Lead (Pb) and Mercury (Hg) (see EB.AIR/WG.1/2004/2). In response to this invitation the CCE issued a call for data on these critical loads in October 2004 requesting its 25 National Focal Centres (NFCs) to respond not later than 31 December 2004.

This report summarises results based on the response of 17 parties received by the CCE before the 15th CCE workshop (Berlin, 25-27 April 2005). Results received after the 21st meeting of the Task Force of the ICP M&M (Berlin, 28-29 April 2005) have not been incorporated in this report. Critical loads of cadmium, lead and mercury were computed by 16, 16 and 9 countries respectively. The report is produced in collaboration with EMEP/MSC-E to enable the preliminary comparison of critical load maps to atmospheric deposition of lead, cadmium and mercury in 1990 and 2000.

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. The manuals and other background documents 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.

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. A preliminary application of the methodology resulted in first European maps of critical loads, published by the CCE in 2002. Work was continued by the Expert Panel on Heavy Metals, which held a meeting on the methodology (Potsdam 4-5 March 2004). Finally, the methodology was documented in the Mapping Manual (chapter 5) of the ICP M&M which was made available to the NFCs as basis for their response to the call for data.

Chapter 1 serves as an executive summary including critical load and exceedance maps. Chapter 2 provides a detailed overview of the national submissions regarding ecosystems, and input data including an inter-country comparison of data statistics. Chapter 3 describes the CCE background database for calculating critical loads of cadmium and lead for forest soils in Europe. This database could be used to provide critical loads in countries that did not submit any data. Chapter 4 describes the methodology and data involved in the modelling of atmospheric dispersion of cadmium, lead and mercury, which have been used in this study to compute critical load exceedances. Chapter 5 assesses the risk caused by atmospheric deposition by identifying European areas where critical loads of cadmium, lead and mercury are exceeded. It also provides information resulting from a preliminary assessment of the additional risk of heavy metals in fertiliser applications to agricultural areas.

Detailed NFC reports are provided in Part II. The report is completed with three appendices. Appendix A is a reprint of the "instructions" provided to the NFCs to assist in their response to the call for data. Appendix B lists the ecosystem types and their underlying EUNIS codes. Appendix C describes the methodology to derive tentative inputs of cadmium and lead from fertilisation practices in Europe.

Part I. Status of Maps and Methods

1. Critical Loads of Cd, Pb and Hg in Europe - Executive Summary

Jean-Paul Hettelingh, Maximilian Posch, Jaap Slootweg, Sergey Dutchak, Ilia Ilyin**

*EMEP Meteorological Synthesizing Centre – East, Moscow.

1.1 Introduction

At its twenty-third session (Geneva, 1-3 September 2004), the Working Group on Effects under the Convention on Long-range Transboundary Air Pollution requested the Coordination Center for Effects (CCE) of the International Co-operative Programme on Modelling and Mapping to issue a call for data on critical loads of cadmium (Cd), lead (Pb) and mercury (Hg) (see EB.AIR/WG.1/2004/2).

This call is a follow-up on preliminary results regarding critical loads of lead and cadmium which were obtained in 2002 (Hettelingh et al., 2002). Since then, significant progress has been made by many experts guided by the Expert Panel on Critical Loads of Heavy Metals under the ICP-M&M. A revised methodology for the modelling of critical loads of cadmium, lead and mercury has then been published in chapter 5.5 of the Mapping Manual, which is available (via www.icpmapping.org) to the National Focal Centres.

The call, which was sent out in October 2004 (with a deadline of 31 December 2004), requested National Focal Centres (NFCs) to provide data on the 50×50 km^2 EMEP grid system (EMEP50 grid). Parties received instructions on the format of the critical load database for submitting critical loads of cadmium, lead and mercury (see Appendix A): Respondents were encouraged to provide ecosystem information using the European Nature Information System (EUNIS; see http://eunis.eea.eu.int/habitats.jsp) to enhance cross-border comparison of ecosystems (see also Hall 2001). Responses and adjustments of submissions were received by the CCE until the beginning of February.

Following recommendations from a joint meeting of the bureaux of the EMEP Steering Body and the Working Group on Effects, the collaboration between the EMEP/MSC-E and the CCE focused on establishing results of modelled depositions of cadmium, lead and mercury for 1990 and 2000 for the computation of exceedance maps (see also Chapter 4).

This chapter summarises the NFC response, resulting European critical load maps of cadmium, lead and mercury as well as their exceedances. The chapter uses material based on the response of 17 parties received by the CCE before the 15th CCE workshop (Berlin, 25-27 April 2005). Results received after the 21st meeting of the Task Force of the ICP M&M (Berlin, 28-29 April 2005) could not be incorporated anymore in this report.

1.2 Receptors for which critical loads are calculated

Critical loads of cadmium, lead and mercury are computed to establish maximum heavy metal depositions on different receptors at which eco-toxicological or human health effects do not occur. Critical limits for indicators of effects on the functioning of ecosystems and human health have been established for use in the computation of critical thresholds. Table 1-1 lists these indicators.

Table 1-1. Overview of indicators used in the computation of critical thresholds. (Adapted from UBA, 2004, Table 5.17).

Receptor Ecosystem	*Endpoints*	*Heavy metals of concern***	*Land cover types to be considered*	*Indicator/critical limit*	*Effect number* used in Table 1-2*
Terrestrial	*Human health effects*	Cd, Pb, Hg	All ecosystems	Total concentration in soil water below the rooting zone(to protect ground water)	1
		Cd, *Pb, Hg*	Arable	Content in food, fodder and crops	2
		Cd, Pb, Hg	Grassland	Content in grass and animal products (cows, sheep)	
	Ecosystem functions	Cd, Pb	Arable land, grassland, non-agricultural	Free ion concentration in view of effects on soil micro-organisms, plants and invertebrates	3
		Hg	Forest soils	Total concentration in humus layer in view of effects on soil micro organisms and invertebrates	
Aquatic	*Ecosystem functions*	Cd, Pb, *Hg*	Freshwaters	Total concentration in view of effects on algae, crustacea, worms, fish, top predators	4
	Human health	Hg	Freshwaters	Concentration in fish	5

* 1= human health effect (drinking water) via terrestrial ecosystem; 2= human health effect (food quality) via terrestrial ecosystems; 3= Ecotoxicological effect on terrestrial ecosystems; 4= Ecotoxicological effect on aquatic ecosystems; 5= human health effect (food quality) via aquatic ecosystems.

** *Metals in italics* indicate that critical loads can be submitted on a voluntary basis

Table 1-1 shows that five effects are distinguished (last column). Critical limits were derived for human health effects of drinking water via terrestrial ecosystems (effect 1), for human health effects of food via terrestrial ecosystems (effect 2), for eco-toxicological effects via terrestrial ecosystems (effect 3) and via aquatic ecosystems (effect 4), and finally for human health of food via aquatic ecosystems (effect 5).

Internal metal cycling within an ecosystem is ignored, to keep the approach compatible with the steady-state mass balance method used for the computation of critical loads of nitrogen and acidity. Weathering inputs of metals are also neglected due to (i) low relevance of such inputs and (ii) high uncertainties of calculation methods. In consequence, critical loads were calculated as the sum of tolerable outputs from the considered systems (see chapter 5.5 in UBA, 2004).

1.3 Critical load results

Altogether, seventeen countries submitted critical loads of heavy metals. Critical loads of cadmium, lead and mercury were computed by 16, 16 and 9 countries, respectively. However not all countries addressed all effects, as is shown in Table 1-2.

Table 1-2. Overview of the country response on the call for critical loads of cadmium, lead and mercury and the 5 effects.

Country	Country code	Effect number (see Table 1-1)									
		Cd				**Pb**			**Hg**		
		1	2	3	4	1	3	4	1	3	5
Austria	AT	x	x	x		x	x		x	x	
Belarus	BY			x			x				
Belgium	BE	x		x	x	x	x	x	x	x	x
Bulgaria	BG	x				x					
Cyprus	CY	x	x	x		x	x		x		
Finland	FI										x
France	FR			x			x				
Germany	DE	x	x	x		x	x		x	x	
Italy	IT			x			x				
Netherlands	NL	x	x	x		x	x				
Poland	PL			x			x			x	
Russia	RU	x		x		x	x				
Slovakia	SK			x			x			x	
Sweden	SE		x	x			x			x	x
Switzerland	CH	x		x		x	x			x	
Ukraine[1]	UA		x								
United Kingdom	GB			x			x				
Total	17	8	6	14	1	8	14	1	4	7	3

[1]Ukraine voluntarily submitted critical loads of lead for effect number 2.

Most National Focal Centres computed critical loads for terrestrial ecosystems of all metals addressing eco-toxicological effects (effect 3) and health effects (effect 1). The European synthesis of the country submissions was done as follows. For each ecosystem in an EMEP50 grid cell the minimum critical load of effects 1 to 4 was taken to identify the effect to which an ecosystem is most sensitive. Then for each EMEP50 grid cell the 5th percentile of the distribution of minimum critical loads is calculated implying a critical load at which 95 percent of the ecosystems are protected in that grid cell against any of the four effects. Effect 5 is treated separately because it is not associated with a critical deposition but with a critical concentration in precipitation (CC). For this effect the 5th percentile critical concentration is mapped in each EMEP50 grid cell, implying a value at which 95 percent of aquatic ecosystems will be protected from a health effect caused by the consumption of fish. The results of this procedure is shown in Figure 1-1, displaying the 5th percentile of the minimum critical loads of cadmium (top left), lead (top right) and mercury (bottom left). Finally, the 5th percentile critical concentration of mercury in precipitation is mapped (bottom right).

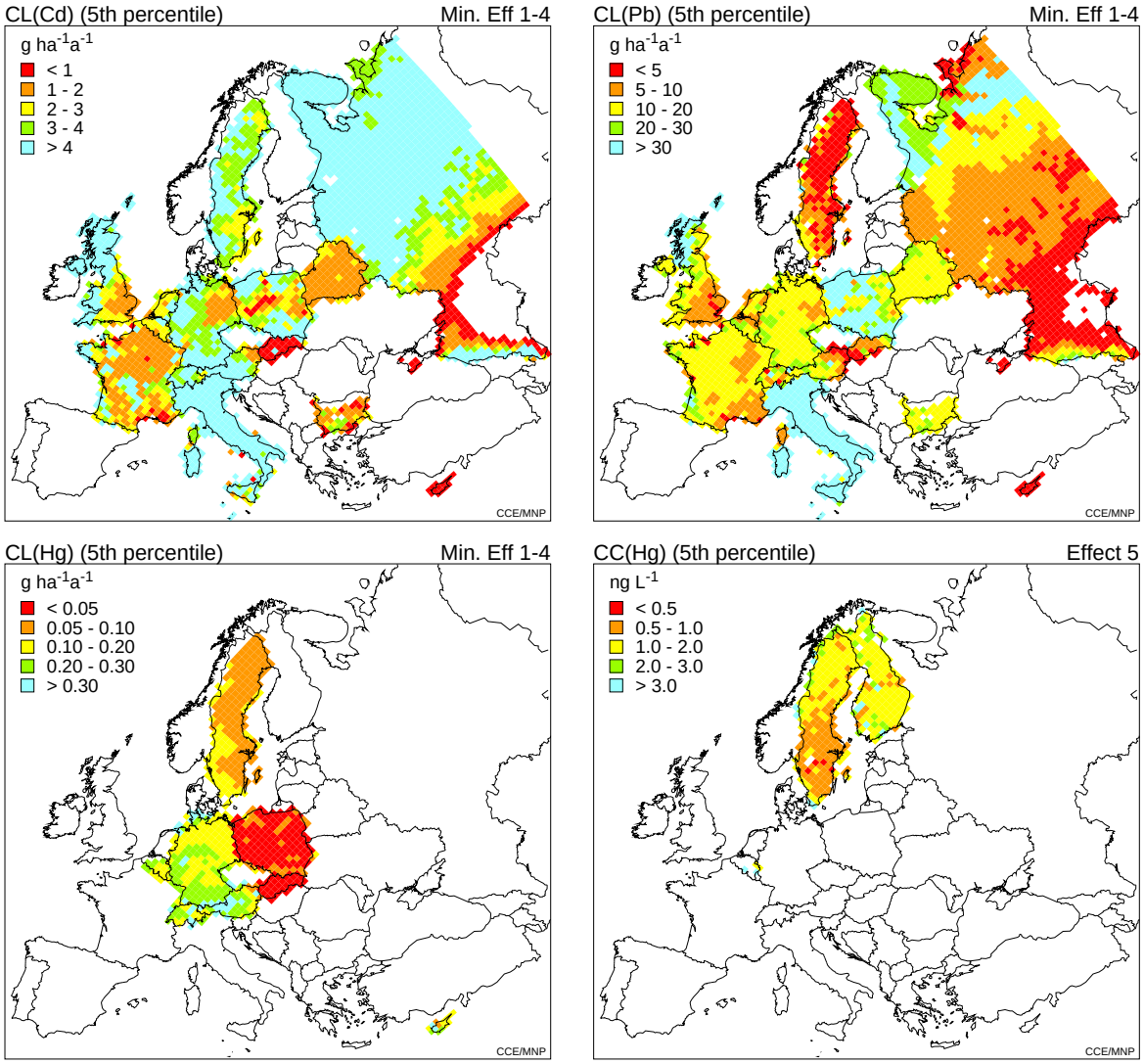

Figure 1-1. Critical loads (5th percentile) for cadmium (top left), lead (top right) and mercury (bottom left) to protect against effects 1 to 4, and the 5th percentile critical concentration of Hg for protecting against effect 5.

The areas which are most sensitive to atmospheric deposition of cadmium are in Belarus, eastern Bulgaria, Cyprus, the north-east of France, the north-east of Germany, the south-east of the United Kingdom, central Poland, Slovakia, and south-eastern Russia. With respect to lead the map of critical loads shows more sensitive areas to occur more in the east and north of Europe. Very low critical loads of mercury occur especially in Poland; and finally the lowest critical concentrations of mercury occur in the southern part of Sweden.

1.4 Preliminary exceedances

Exceedances are computed by comparing critical loads and levels with depositions and concentrations. However, the robustness of the computed depositions and concentrations of Cd, Pb and Hg can not well be established due to the uncertainty of underlying reported emissions in 1990 and 2000 (see Chapter 4). Therefore, the results described in this section are to be considered as preliminary.

The meteorology of the year 2000 deviates significantly from the average, whereas 1990 is much closer. Therefore the depositions used to calculate the exceedances for 2000 are modelled using the 1990 meteorological data.

Accumulated Average Exceedances (AAE) have been computed to identify areas where atmospheric metal depositions are higher than critical loads. An AAE is the ecosystem area-weighted sum of the exceedances (deposition of a metal minus its critical load, with zero for non-exceedance) of all ecosystems in a grid cell. The AAE with respect to acidification and eutrophication was used in

support of the LRTAP protocol to "Abate Acidification, Eutrophication and Ground-level Ozone" (Gothenburg, 1999; see Posch et al. 2001) and the National Emission Ceiling Directive of the Economic Commission in 2001. Figure 1-2 shows the AAE of Cd (left) and Pb (right) for 1990 and 2000. As for nitrogen and sulphur, the CCE has also computed critical loads of Cd, Pb and Hg for forest ecosystems (effect 3) using the European background data base (see Chapter 3). These background data could be used to 'fill-in' the European map with critical loads when national data are missing. However, the CCE did not apply the 'fill-in' procedure this time, since some countries expressed reservations about using the background data base for this purpose.

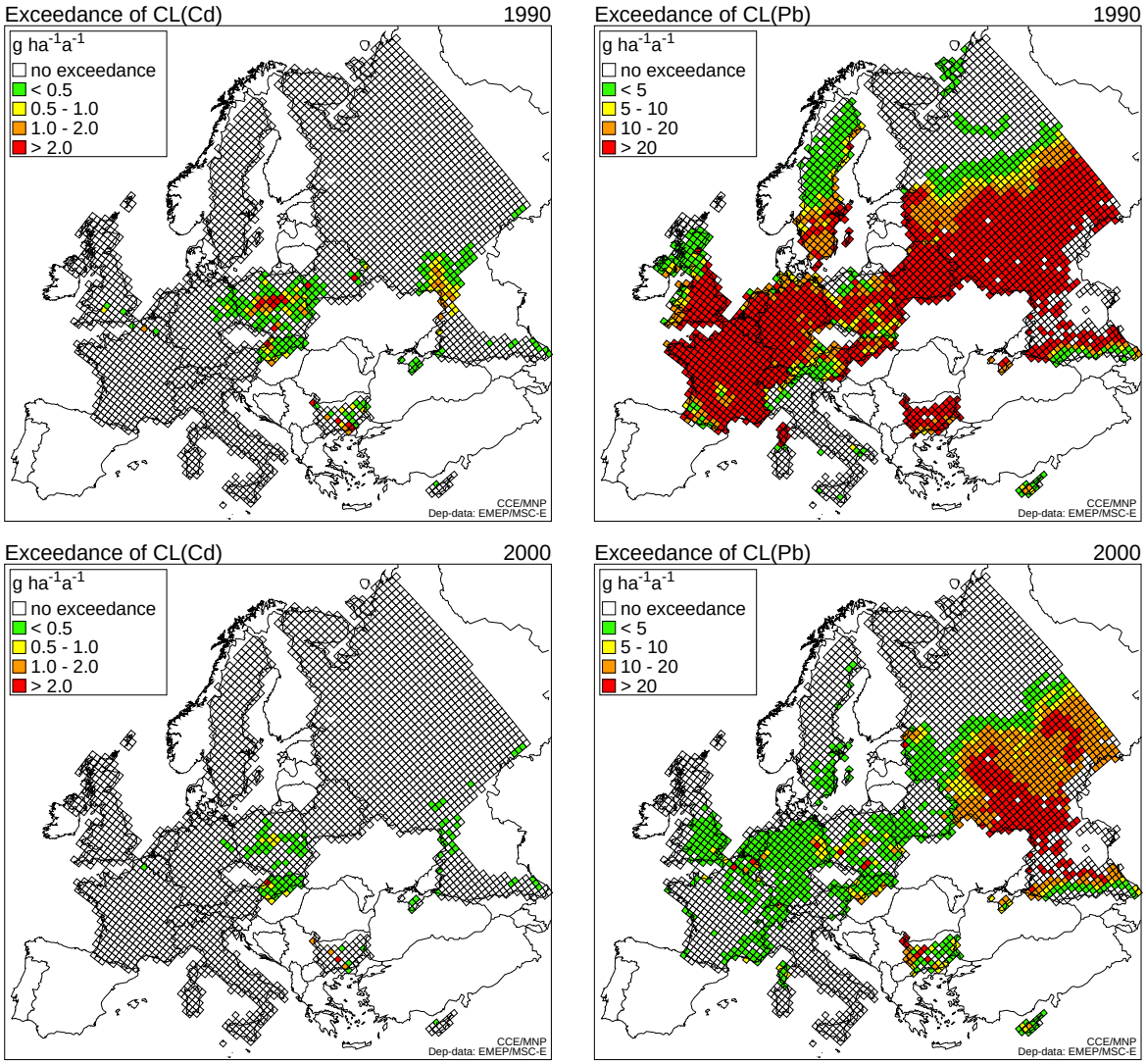

Figure 1-2. Average Accumulated Exceedances of critical loads of cadmium (left) and lead (right) in 1990 (top) and 2000 (bottom). White grid cells indicate non-exceedance, whereas white areas without grid indicate no data.

It is obvious from Figure 1-2 that exceedances of critical loads of both cadmium (left) and lead (right) have significantly decreased between 1990 (top) and 2000 (bottom). Areas which are exceeded by cadmium deposition in 2000 are found in eastern Germany, Poland and Slovakia. Lead exceedances in 2000 are more wide-spread but the magnitude has dramatically decreased since 1990.

Figure 1-3 shows Average Accumulated Exceedances (left; minimum of effects 1-4)) and Average Accumulated Concentration Exceedance (right; effect 5) of mercury from 1990 (top) to 2000 (bottom). The AAE time trend shows a decrease in Germany in 2000 in comparison to 1990. The Average Accumulated Concentration in 1990 is very similar (except for a few grid cells) to that in 2000. More can be found in chapter 5, where exceedances are discussed in relation to effects, fertilisation and deposition modelling.

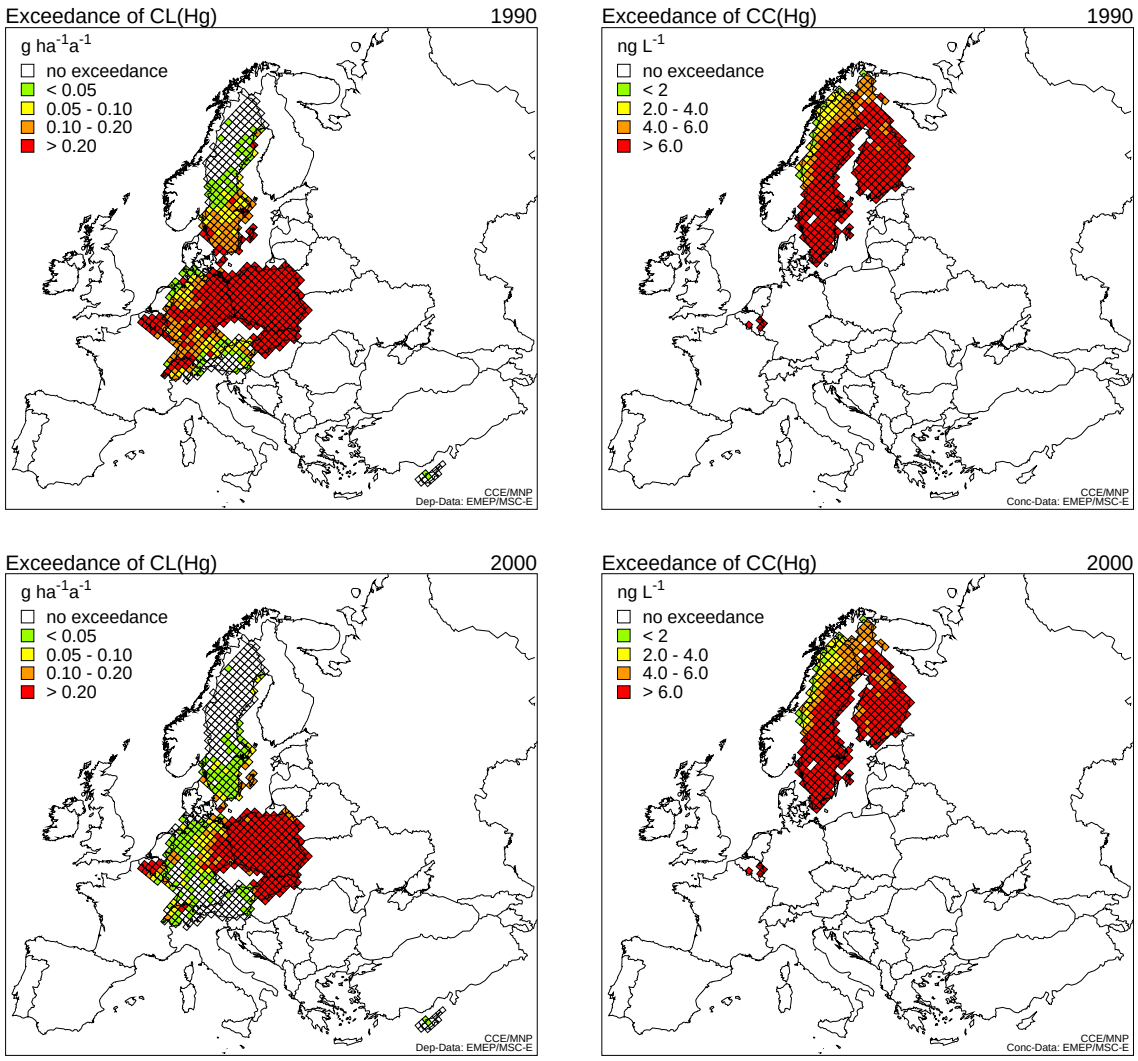

Figure 1-3. Average Accumulated Exceedances (left; minimum of effects 1-4)) and Average Accumulated Concentrations (right; effect 5) of mercury in 1990 (top) and 2000 (bottom). White grid cells indicate non-exceedance, whereas white areas without grid indicate no data.

1.5 Preliminary exceedances on agricultural areas including fertilisation

Atmospheric deposition of cadmium and lead is not the only cause for exceedance of critical loads. Fertilisation of agricultural areas also causes cadmium and lead to enter soil systems. In collaboration with other RIVM specialists (see Appendix C) a preliminary estimate of the agricultural input of these metals in 2000 was made and added to the atmospheric input. Results are shown in Figure 1-4 for cadmium (left) and lead (right).

Figure 1-4 illustrates that the inclusion of fertilisation hardly leads to an exceedance of critical loads of cadmium in countries that submitted critical loads for agricultural areas (areas marked with grid cells). However, with respect to lead Figure 1-4 shows that inputs from agricultural practices moderately change the magnitude and distribution of the AAE computed with atmospheric deposition alone (Figure 1-2). Our preliminary results on heavy metal inputs from agricultural practices suggest that fertilisation alone (excluding atmospheric deposition) causes critical loads of cadmium to be exceeded in a limited number of grid cells in countries that submitted critical loads for agricultural areas, whereas for lead exceedances occur more broadly (see Chapter 5, Figure 5-5).

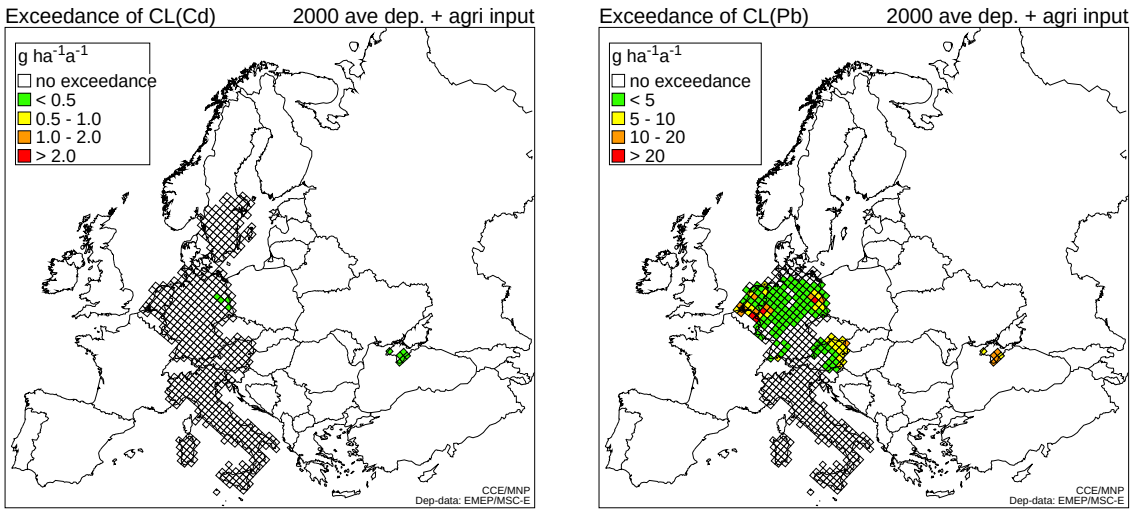

Figure 1-4. The Accumulated Average Exceedance of critical loads of cadmium (left) and lead (right) caused by the sum of atmospheric deposition and inputs from fertilisation practices on agricultural areas for which critical loads were submitted. White grid cells indicate non-exceedance, whereas white areas without grid indicate no data.

1.6 Exceedances in view of an EC limit value for Cd and an EC guideline value for Pb

In 1996 the EC Environmental Council adopted Framework Directive 96/62/EC on ambient air quality assessment and management[1]. This directive also set a timetable for the development of daughter directives on a range of pollutants including lead (first daughter directive) and cadmium (fourth daughter directive). These daughter directives include guideline and limit values for (average annual) ambient concentrations on urban and other areas, generally established on the basis of WHO recommendations. For lead the WHO recommended an annual average concentration of 0.5 µg m^{-3} as guideline value. The WHO was unable to recommend a deposition guideline value (European Commission, 1997, pp. 33). For cadmium, an average annual concentration of 5 ng m^{-3} is proposed as limit value (European Commission, 2001).

These levels were compared to average ambient concentrations computed by MSC-E for 2000 in each of the EMEP50 grid cells. These comparisons reveal that limit (Cd) and guideline (Pb) values are *not* exceeded anywhere in Europe. However, an ambient concentration is associated with a deposition in each EMEP50 grid cell. And Figure 1-2 (bottom) shows the grid cells where limit and guideline values are *not* violated, whereas critical loads of cadmium (left) and lead (right) *are* exceeded (in the year 2000).

The position paper on mercury (European Commission 2001b) states that sufficient information lacks to relate mercury levels in the air to accumulated body burden. This prevents a similar analysis to be conducted for mercury.

1.7 Conclusions

Critical loads of cadmium, lead and mercury were successfully computed and mapped by 17 Parties of the LRTAP Convention. Critical loads of cadmium, lead and mercury were computed by 16, 16 and 9 countries, respectively.

The methodology that was recommended in the call for data was carefully reviewed and documented in the Mapping Manual of the ICP on Modelling and Mapping. The methodology enabled the assessment of ecosystem specific critical loads to protect human or environmental health.

[1] http://europe.eu.int/comm/environment/air/ambient.htm

These critical loads were compared to preliminary computations of ecosystem specific deposition of the respective metals in 1990 and 2000. The robustness of deposition results can not yet well be established due to the uncertainty of reported emissions. Bearing these uncertainties in mind, it is shown that atmospheric deposition of cadmium does not cause widespread risk in 2000, that the risk of lead deposition decreases since 1990 but is still widespread in 2000 and, finally, that the risk caused by mercury does not change much throughout the years in most of the countries that provided data on mercury.

In addition to an analysis of the risk of effects caused by atmospheric deposition, two additional analyses were conducted:

The first concerns the input of cadmium and lead from agricultural practices in addition to atmospheric deposition. This analysis revealed that fertilisation alone (excluding atmospheric deposition) causes critical loads of cadmium to be exceeded in a limited number of grid cells in countries that submitted critical loads for agricultural areas, whereas for lead exceedances are higher and occur more broadly. This should be taken into consideration when assessing the exceedance of critical loads of these heavy metals.

The second analysis compares European limit values for cadmium and guideline values for lead to computed annual average air concentrations. These limit and guideline values for cadmium and lead turn out to be not exceeded by annual average concentrations computed for 2000 in EMEP 50×50 km^2 grid cells. This suggests that the European limit and guideline values are less adequate than critical loads for the assessment of the large-scale risk of lead and cadmium in the context of long-range transboundary air pollution.

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2. Summary of National Data

Maarten van 't Zelfde, Jaap Slootweg*

* Institute of Environmental Sciences (CML), Leiden University, the Netherlands

2.1 Introduction

The Working Groups on Effects (WGE) asked the Coordination Center for Effects (CCE) to issue a call for data for the heavy metals cadmium (Cd), lead (Pb) and mercury (Hg) in relation to the forthcoming review of the 1998 Heavy Metals protocol. This call was issued in October 2004 with the deadline of 31 December 2004. All the data of the Parties (National Focal Centres) that responded to the call have been merged into a European dataset, and are displayed and discussed in this chapter. Prior to this reporting the countries received a preview of the European compilation of their data, to enable feedback in an early stage.

2.2 Requested variables

The underlying methodology for calculating critical loads of heavy metals has changed significantly since the preliminary call for critical loads data (cadmium and lead) in 2001 (see De Vries et al., 2005; Hettelingh et al., 2002).
This led to the following changes to the call:
New pollutants, effects-based methodologies for mercury (Hg) are available for:

- ecotoxicological effects in forest humus layers
- human health effects: indicator is Hg in fish (surface waters)

New endpoints: Inclusion of human health aspects of Pb, Cd, Hg:

- Cd in wheat
- Hg in fish
- Pb, Cd, Hg in drinking water (protection of groundwater)

New critical limits (ecotoxicological) for Cd and Pb (application of the free ion approach for effects of Cd and Pb on biota in terrestrial systems.
Only effects based approach. The so-called "stand still", allowing no accumulation of the metals in the soil, has no longer been applied.

A description of the methodology can be found in chapter 5.5 of the recent update of the Mapping Manual (UBA, 2004). The instructions for submitting data, including the requested data structure, variable names and units, as send to all National Focal Centres, can be found in Appendix A.

2.3 National responses

The CCE has requested the 25 National Focal Centres (NFCs) for (an update of) the critical load data of heavy metals. A total of 17 NFCs have responded to the request and delivered data for one or more metals and for one or more effects (see Table 1-1). An overview of the national submissions is given in Table 2-1.

Table 2-1. Overview of the number of ecosystems per country submitted for critical loads of cadmium, lead and mercury and the 5 endpoint.

Country (Country Code)	Effect number (see Table 1-1)										
	Cadmium (Cd)				Lead (Pb)				Mercury (Hg)		
	1	2	3	4	1	2	3	4	1	3	5
Austria(AT)	2,953	1,154	2,953		2,953		2,953		2,953	455	
Belarus(BY)			9,503				9,503				
Belgium(BE)	1,833		1,833	10	1,833		1,833	10	1,833	1,833	10
Bulgaria(BG)	84				84						
Cyprus(CY)	31,893	8,274	31,893		31,893		31,893		31,893		
Finland(FI)											820
France(FR)			3,840				3,840				
Italy(IT)			881				881				
Germany(DE)	290,003	144,211	290,003		290,003		290,003		290,003	99,866	
Netherlands(NL)	12,627	10,180	30,484		12,627		30,484				
Poland(PL)			88,383				88,383			88,383	
Russia(RU)	6,616		22,828		9,992		20,206				
Slovakia(SK)			320,891				320,891			320,891	
Sweden(SE)		2450	2,070				2,070			5,396	2,977
Switzerland(CH)	57		220		56		221			277	
Ukraine(UA)		46				46					
United-Kingdom(GB)			234,654				234,654				
Total	**346,066**	**157,153**	**1,040,436**	**10**	**349,441**	**46**	**1,035,952**	**10**	**326,682**	**517,101**	**3,807**

Figure 2-1 shows the percentage of the total country area for which critical loads have been submitted of cadmium, lead and mercury by ecosystem type and by effect (see Table 1-1). Mostly critical loads of cadmium and lead, and for ecotoxicological effects for terrestrial ecosystems (effect 3) have been submitted. Finland, Sweden and Belgium have submitted data for the human health effects for aquatic ecosystems (food quality, effect 5). Belgium has also submitted the ecotoxicological effects for aquatic ecosystems (effect 4). Forest is the dominant ecosystem considered in most of Europe for submitting critical loads. Critical loads for agricultural areas were submitted by 6 countries.

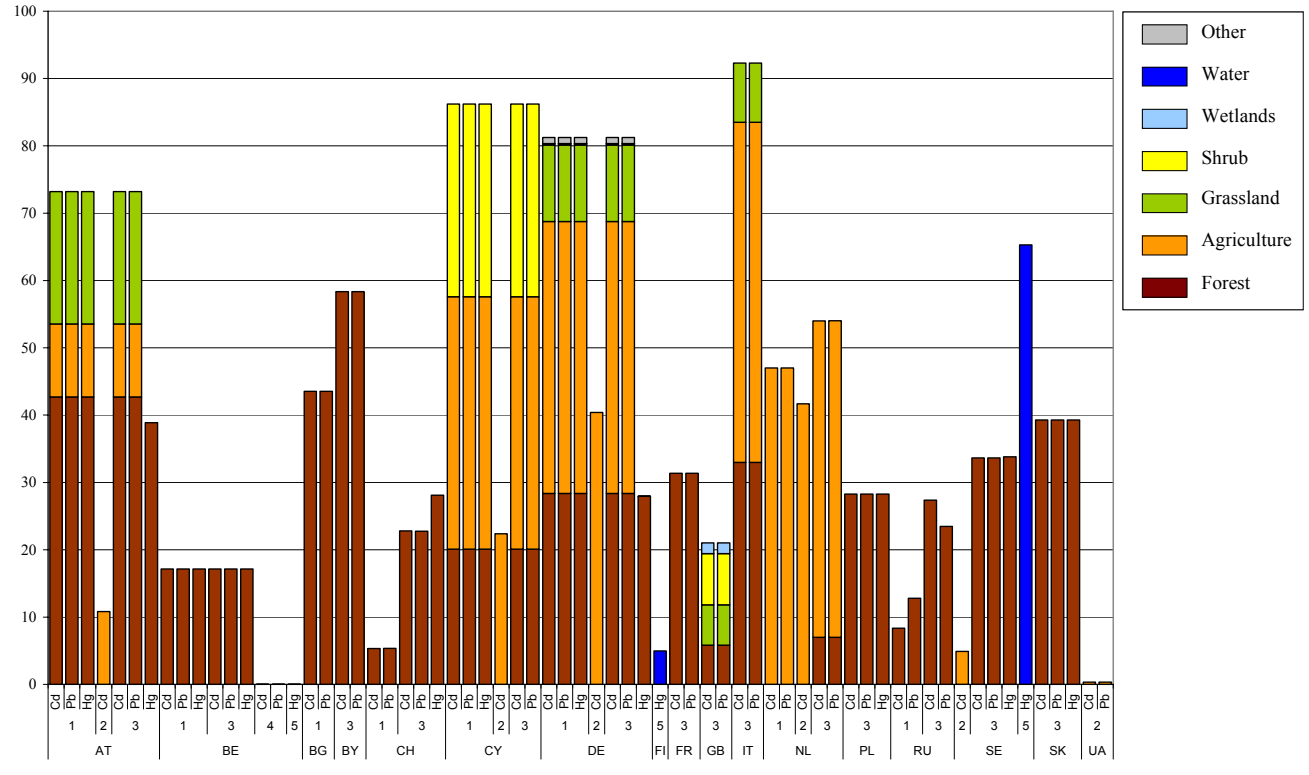

Figure 2-1. National distribution of ecosystem types (% of total country area) by effect (see Table 1-1) for critical loads of cadmium, lead and mercury.

All 17 submissions used the EUropean Nature Information System (EUNIS) to classify the ecosystem types, up to a very detailed level. These levels are truncated to a maximum of 2 characters.
Table 2-2 lists the areas (in km^2) and the number of submitted ecosystems by heavy metal, indicating the resolution each country uses for its calculations.

Table 2-2. Number of ecosystems and areas per national contribution.

Country	Country area (km^2)	EUNIS lev. 1	Cd		Pb		Hg	
			#ecosyst	Area (km^2)	#ecosyst	Area (km^2)	#ecosyst	Area(km^2)
Austria	83,858	Forest	503	35,822	503	35,822	503	35,822
		Agriculture	1,154	9,073	1,154	9,073	1,154	9,073
		Grassland	1,296	16,491	1,296	16,491	1,296	16,491
		total	2,953	61,386	2,953	61,386	2,953	61,386
Belarus	207,595	Forest	9,503	121,128	9,503	121,128		
Belgium	30,528	Forest	1,833	5,237	1,833	5,237	1,833	5,237
		Water	10	9	10	9	10	9
		total	1,843	5,246	1,843	5,246	1,843	5,246
Bulgaria	110,994	Forest	84	48,330	84	48,330		
Cyprus	9,251	Forest	7,438	1,860	7,438	1,860	7,438	1,860
		Agriculture	13,869	3,467	13,869	3,467	13,869	3,467
		Shrub	10,586	2,647	10,586	2,647	10,586	2,647
		total	31,893	7,973	31,893	7,973	31,893	7,973
Finland	338,144	Water					820	16,856
France	543,965	Forest	3,840	170,657	3,840	170,657		
Germany	357,022	Forest	101,306	101,306	101,306	101,306	101,306	101,306
		Agriculture	144,211	144,211	144,211	144,211	144,211	144,211
		Grassland	40,529	40,529	40,529	40,529	40,529	40,529
		Shrub	3,205	3,205	3,205	3,205	3,205	3,205
		Wetlands	659	659	659	659	659	93
		Other	93	93	93	93	93	93
		total	290,003	290,003	290,003	290,003	290,003	290,003
Italy	301,336	Forest	436	99,327	436	99,327		
		Agriculture	230	152,285	230	152,285		
		Grassland	215	26,551	215	26,551		
		total	881	278,163	881	278,163		
Netherlands	41,526	Forest	17,857	2,900	17,857	2,907		
		Agriculture	12,627	19,522	12,627	19,522		
		total	30,484	22,422	30,484	22,429		
Poland	312,685	Forest	88,383	88,383	88,383	88,383	88,383	88,383
Russia*	5,090,400	Forest	29,444	1,818,725	30,198	1,844,700		
Slovakia	49,034	Forest	320,891	19,253	320,891	19,253	320,891	19,253
Sweden	449,964	Forest	2,070	151,441	2,070	151,441	5,396	152,098
		Agriculture	2,450	22,050				
		Water					2,977	293,749
		total	4,520	173,491	2,070	151,441	8,379	446,177
Switzerland	41,285	Forest	277	11,612	277	11,612	277	11,612
Ukraine	603,700	Agriculture	46	1,925	46	1,925		
United Kingdom	243,307	Forest	98,827	14,134	98,827	14,134		
		Grassland	73,816	14,637	73,816	14,637		
		Shrub	49,517	18,488	49,517	18,488		
		Wetlands	12,494	3,892	12,494	3,892		
		total	234,654	51,151	234,654	51,151		
All Countries	**8,814,594**	**Grand Total**	**1,049,699**	**3,169,849**	**1,048,003**	**3,173,780**	**745,442**	**946,889**

***** European part.

All figures in this chapter show aggregated ecosystem types to EUNIS level 1, or grouped further into the main categories *forest, (other semi-natural) vegetation, agriculture* and *water*, as listed in Table 1 in Appendix B.

2.4 Critical loads

A critical load has been defined as *a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge*. In this call different endpoints, and pathways towards these endpoints, have been considered, referred to as *effects*, see Table 1-1).

This section shows critical load maps and critical load distributions by country. Characteristic national features can often be explained by studying the national reports in Part II of this report.

Maps of the 5th percentile of the critical loads and critical concentrations are presented in Chapter 1 (Figure 1-1). Figure 2-2 shows median (50th percentile) values of these minimum critical loads for countries that submitted data. Percentiles have been calculated as follows. For each ecosystem the minimum critical load of effects 1 to 4 was taken. Then for each EMEP50 grid cell the 5th and 50th percentile of the distribution of minimum critical loads is calculated implying a critical load at which 95 and 50 percent of the ecosystems are protected respectively in that grid cell against any of the four effects. Effect 5 is treated separately because it is not associated with a critical deposition but with a critical concentration in precipitation (CC). For this effect the 50th percentile critical concentration is mapped in each EMEP50 grid cell, implying a value at which 50 percent of aquatic ecosystems will be protected from a health effect caused by the consumption of fish.

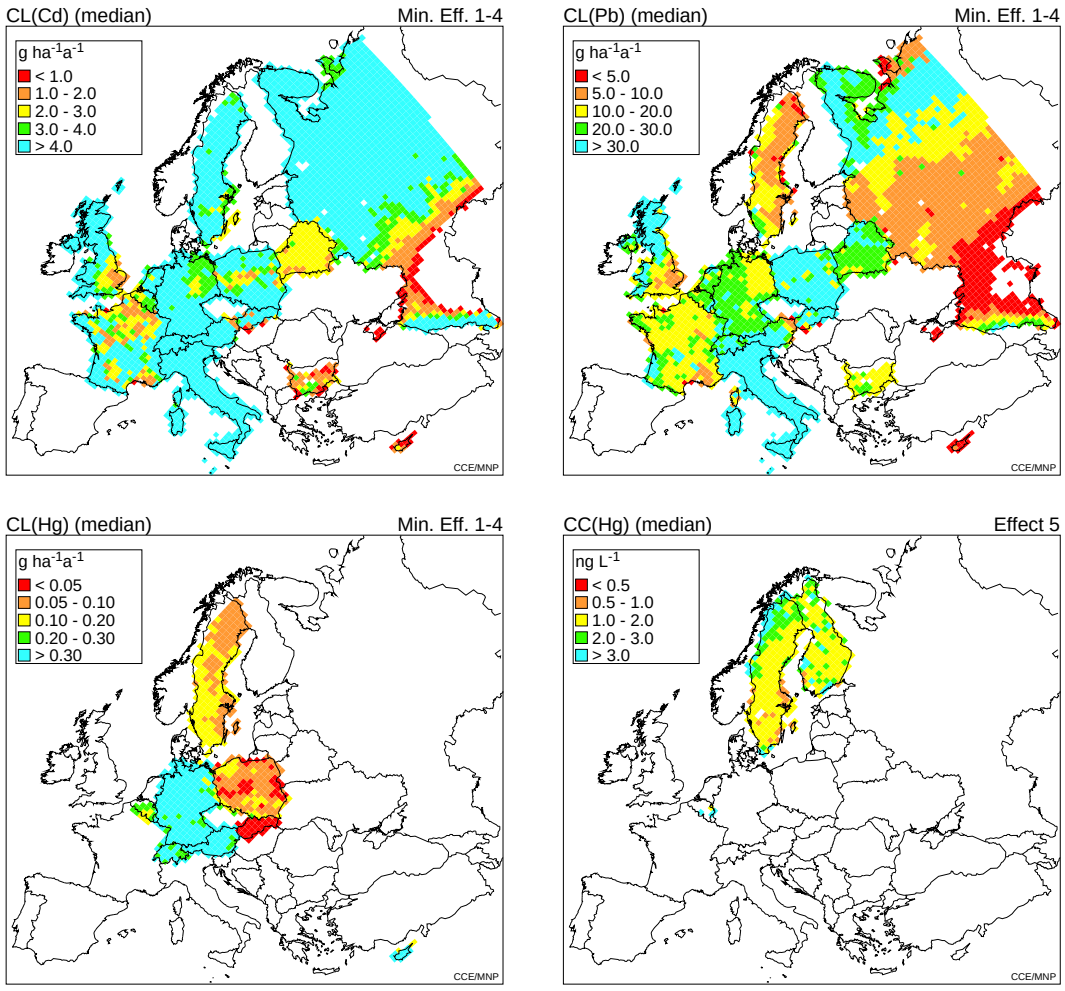

Figure 2-2. Median values of the critical loads of Cd (top left) Pb (top right) and Hg (bottom left), and the critical concentration of Hg in precipitation(bottom right) of countries that submitted data.

Critical load maps

Cadmium

Figure 2-3 shows the 5th percentile values of the critical loads of cadmium for each effect separately on the EMEP50 grid in countries that submitted data.
Most countries have submitted critical loads for effect 3 (ecotoxicological effects on terrestrial ecosystems). This map shows that the most sensitive areas are in Belarus, Cyprus, France, Poland, Slovakia and South-Russia. Comparison of the maps of the different effects shows that the effect with the lowest critical loads differs by country. For example, for the Netherlands effect 2 (human health

effects – food quality) is the most sensitive, whereas effect 1 (human health effect – drinking water) turns out to be the most sensitive for Germany.

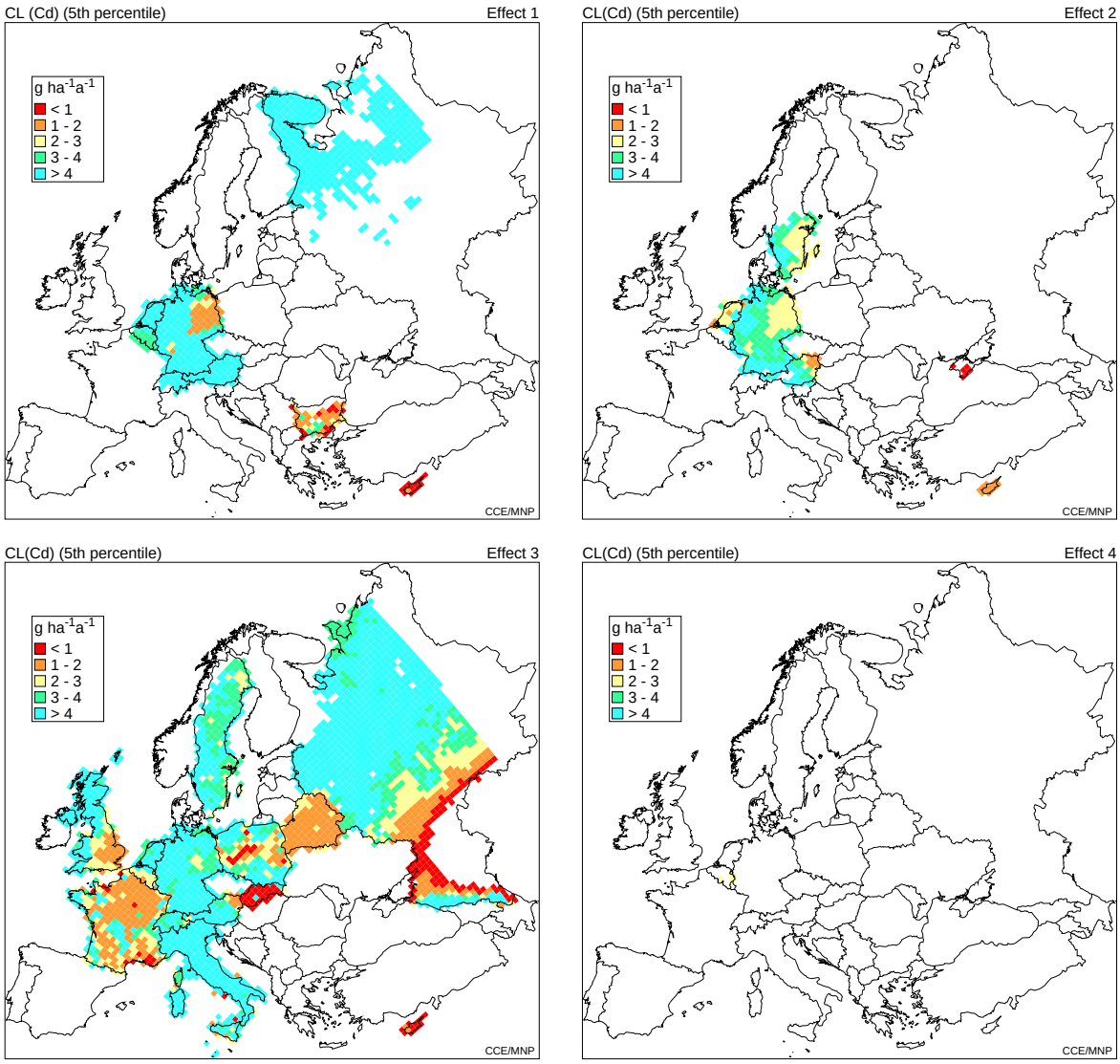

Figure 2-3. The 5th percentile EMEP50 grid values of the critical loads of cadmium for the different effects (1: human health effects – drinking water; 2: human health effects – food quality; 3: ecotoxicological effects on terrestrial ecosystems; 4: ecotoxicological effects on aquatic ecosystems).

Lead

Figure 2-4 shows the 5th percentile values for the critical loads of lead for effect 1 and 3 on the EMEP50 grid in countries that submitted data.

Ukraine has submitted critical loads for effect, which was mentioned in the Mapping Manual as a voluntary option. Belgium is the only country which also submitted critical loads for effect 4 (ecotoxicological effects on aquatic ecosystems). These two effects are not mapped here, since they show information for only three or four EMEP50 grid cells with 5th percentile values above 30 g ha^{-1} a^{-1}. For effect 3 (ecotoxicological effects on terrestrial ecosystems) the majority of countries has submitted critical loads. According to Figure 2-4 that the most sensitive areas are in Cyprus, Slovakia, Sweden, Russia and the United Kingdom.

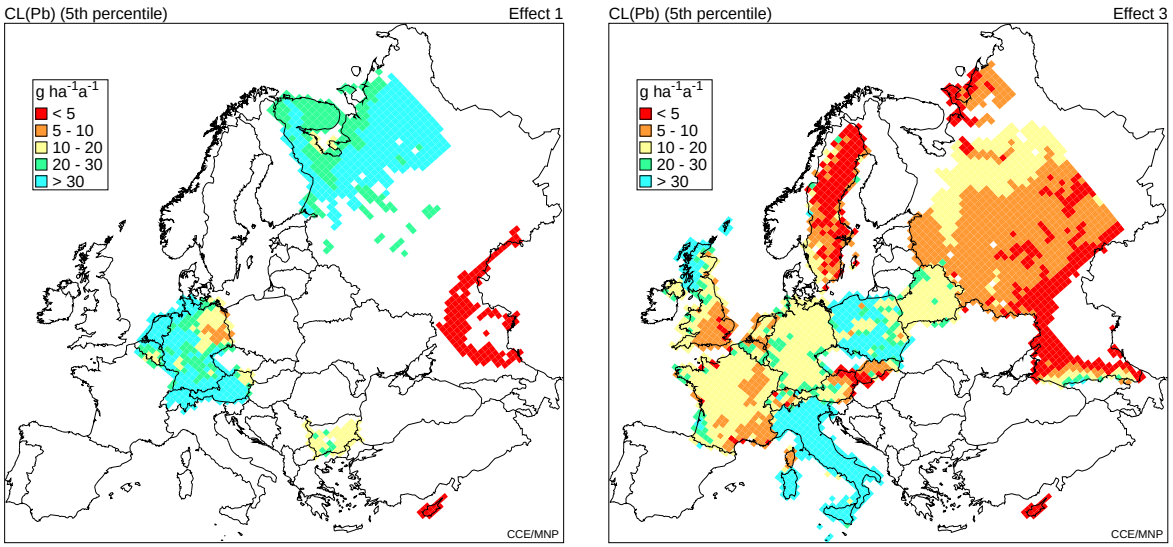

Figure 2-4. The 5th percentile EMEP50 grid values of the critical loads of lead for effect 1 and 3 (1: human health effects – drinking water; 3: ecotoxicological effects on terrestrial ecosystems).

Mercury

Figure 2-5 shows the 5th percentile values for the critical loads of mercury for effect 1 and 3. For effect 3 (ecotoxicological effects on terrestrial ecosystems) the most sensitive areas are in Poland, Slovakia and Sweden.

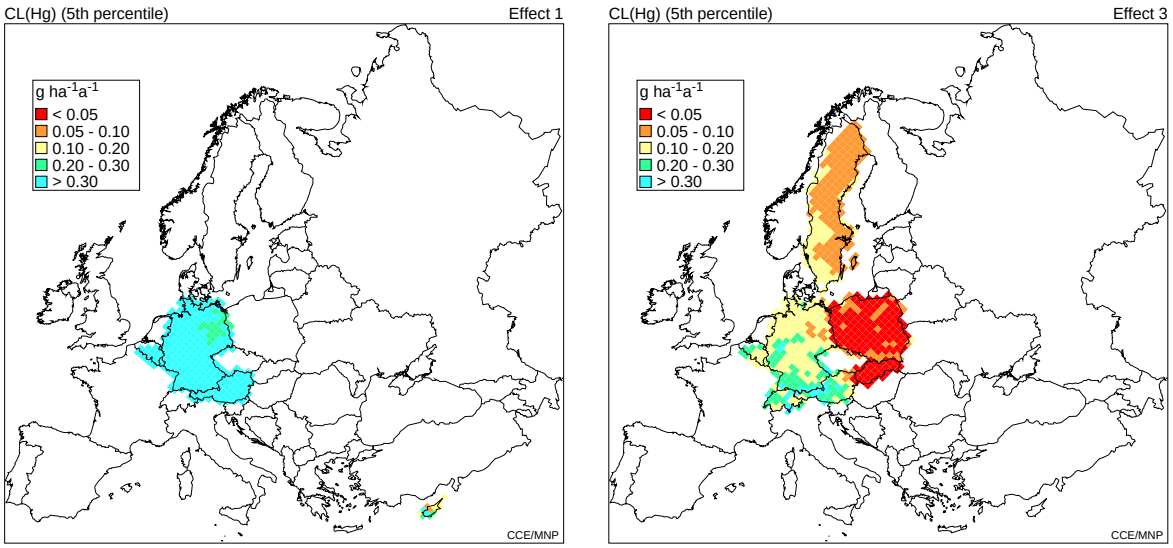

Figure 2-5. The 5th percentile EMEP50 grid values of the critical loads of mercury for effect 1 and 3 (1: human health effects – drinking water; 3: Ecotoxicological effects on terrestrial ecosystems).

Figure 2-6 shows the 5th percentile values for the critical concentration in rainfall of mercury for effect 5 on the EMEP50 grid. For effect 5 (human health effects on aquatic ecosystems) Belgium (Walloon), Sweden and Finland have submitted data. The most sensitive area is in the southern part of Sweden.

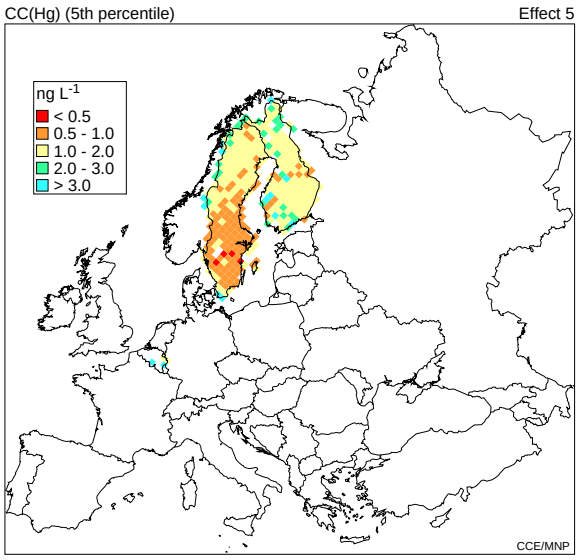

Figure 2-6. The 5th percentile EMEP50 grid values of the critical rainfall concentration of mercury for effect 5 (human health effects on aquatic ecosystems).

Critical load distributions

This section describes the cumulative distribution function (CDFs) of critical loads for each country that submitted data. A CDF of critical loads gives information on the percent of the ecosystem area (on the Y-axis) which has a critical load below or equal to specific values (on the X-axis). For reasons of graphical layout, no scale has been marked on the Y-axis of the CDFs shown in this section. Two kinds of distributions are inspected. The first focuses (plots on the left) on the distribution of critical load values for each of 4 ecosystems and the European background database (EU-DB; thin black dotted line) which only contains information on forest soils (see Chapter 3). There are no data (yet) for Cyprus in the background database. The ecosystem types which have been distinguished in the plots reflect the aggregation of classes given in the first column of Table 1 in Appendix B.

The second set of CDFs (plots on the right) looks distribution for each of the following 4 effects (except for Hg):

Drink	Effect 1	Human health effects – drinking water;
Food	Effect 2	Human health effects – food quality;
Eco-Terr	Effect 3	Ecotoxicological effects on Terrestrial ecosystems;
Eco-Aqua	Effect 4	Ecotoxicological effects on Aquatic ecosystems.

Cadmium

The CDFs of critical loads of cadmium are plotted in Figure 2-7. The submitted critical loads of cadmium are lower then those in the background database for the majority of the countries. The critical loads for agriculture ecosystems generally turn out to be lower than those for forests. Also note that 50th percentile critical loads of cadmium for forests (left plots) are between 4 and 6 g ha^{-1} yr^{-1} in France, the United Kingdom, Poland, Russia and Sweden, lower than 4 g ha^{-1} yr^{-1} in Belgium, Bulgaria and Belarus, and higher than 6 g ha^{-1} yr^{-1} in Austria, Germany, Italy, the Netherlands, Slovakia and Switzerland. Similarly we can see in the right-hand plots that the 50th percentile critical loads for effect 3 (*Eco-Terr;* Ecotoxicological effects on Terrestrial ecosystems) are between 4 and 6 g ha^{-1} yr^{-1} in the same countries.

Lead

The distributions of the national critical loads of lead are plotted in Figure 2-8. The CDF of submitted critical loads of lead for forest ecosystems are approximately comparable to the CDF of critical loads computed with the background database in e.g. Bulgaria and Switzerland. The minimum critical load for agriculture ecosystems is generally lower than that for forests in e.g. Austria and the Netherlands . The critical loads for effect 3 (Eco-Terr) are generally lower than for effect 1 (Drink).

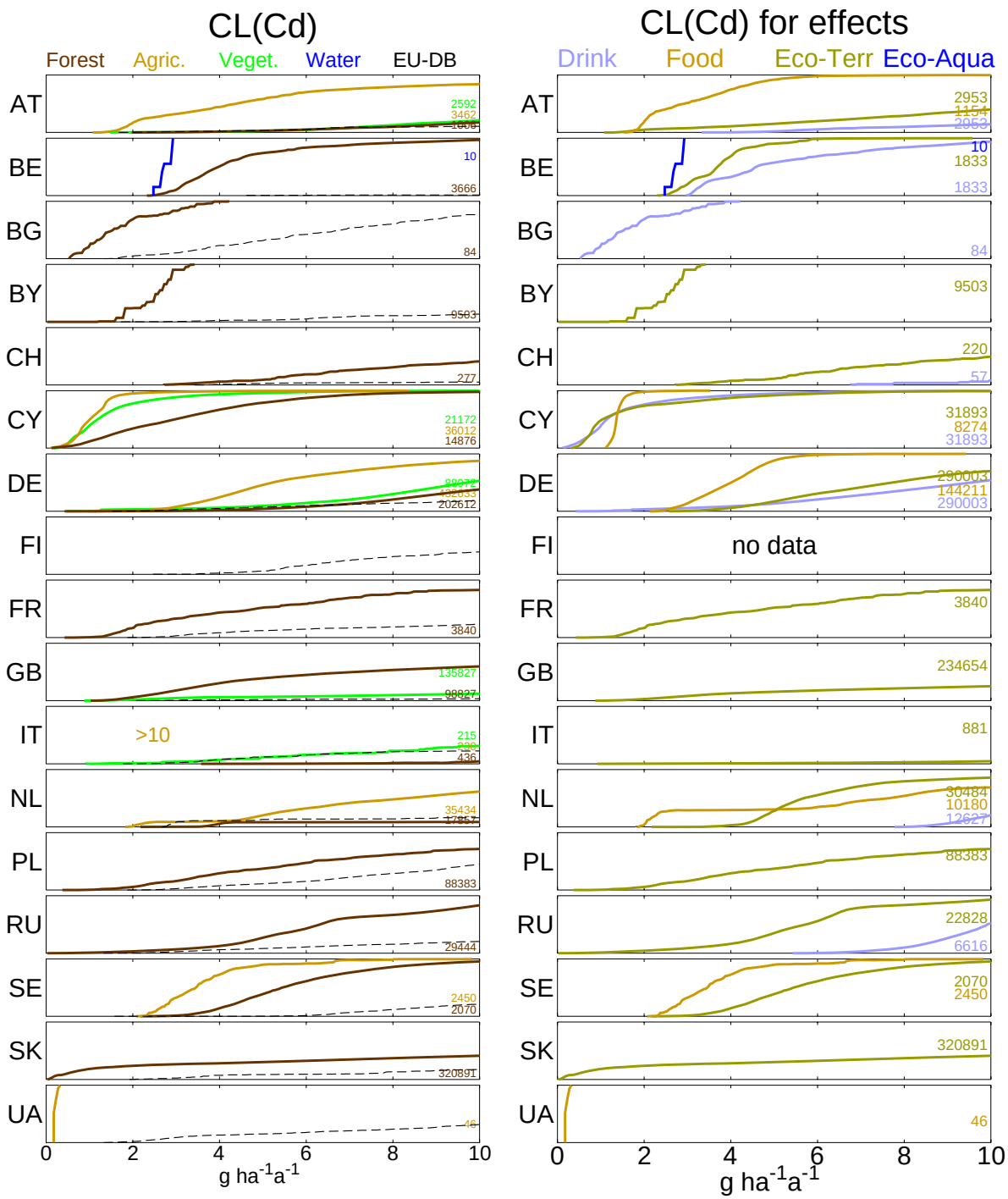

Figure 2-7. The cumulative distribution functions (CDFs) of critical load of cadmium for the different ecosystems and for the European background database ('EU-DB') (left) and for the different effects (right).

Mercury

The distributions of the national critical loads of mercury are plotted in Figure 2-9. The critical loads for Poland, Slovakia and Sweden are much lower than those for the other countries. The critical loads for effect 3 (Eco-Terr) are lower than for effect 1 (Drink).

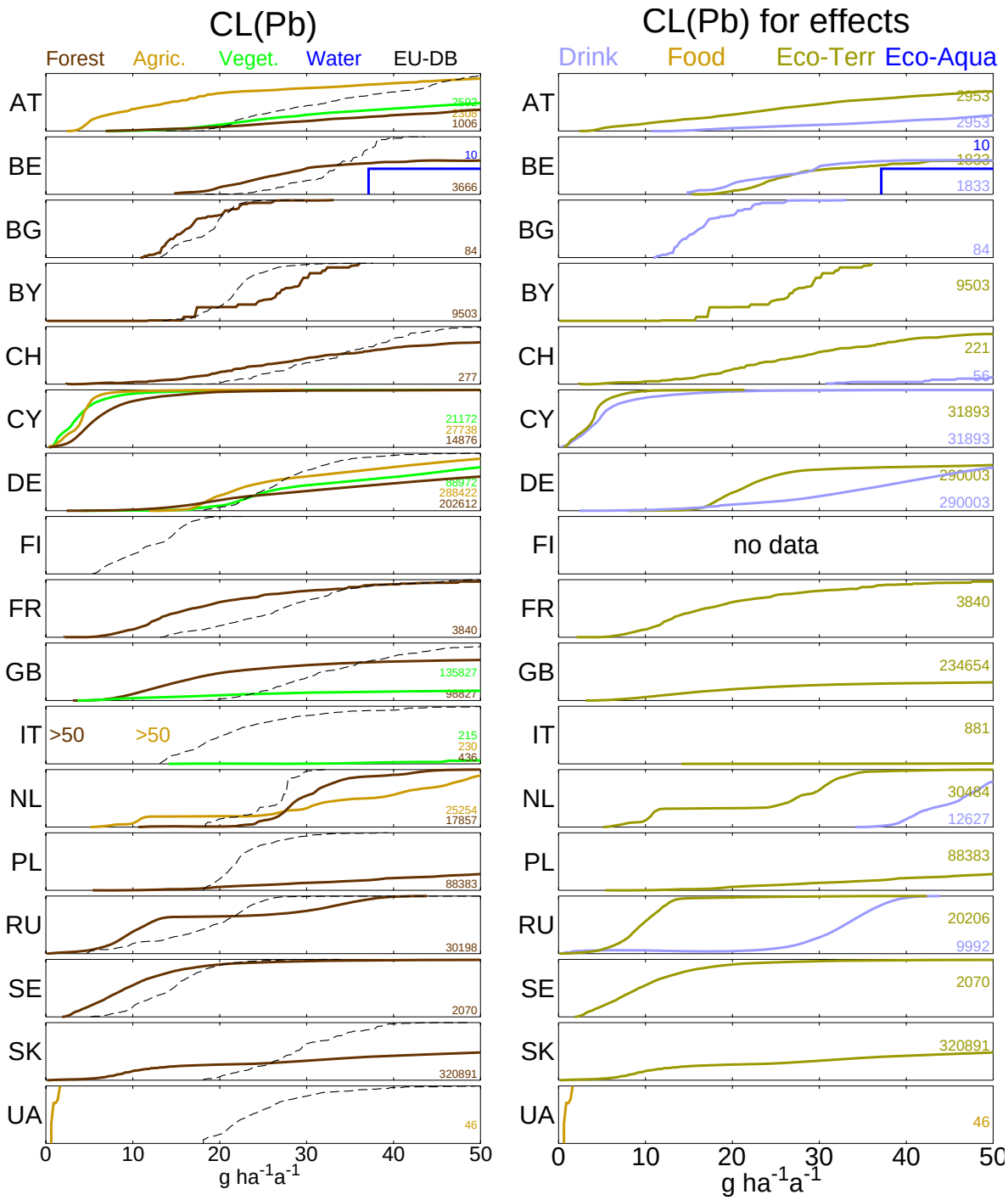

Figure 2-8. The cumulative distribution functions (CDFs) of critical load of lead for the different ecosystems (left) and for the different effects (right).

Figure 2-10 shows the critical concentrations for mercury for effect 5 (human Health effects through aquatic ecosystems). The CDF contains the cumulative area of the critical concentration by chosen fish species indicator.

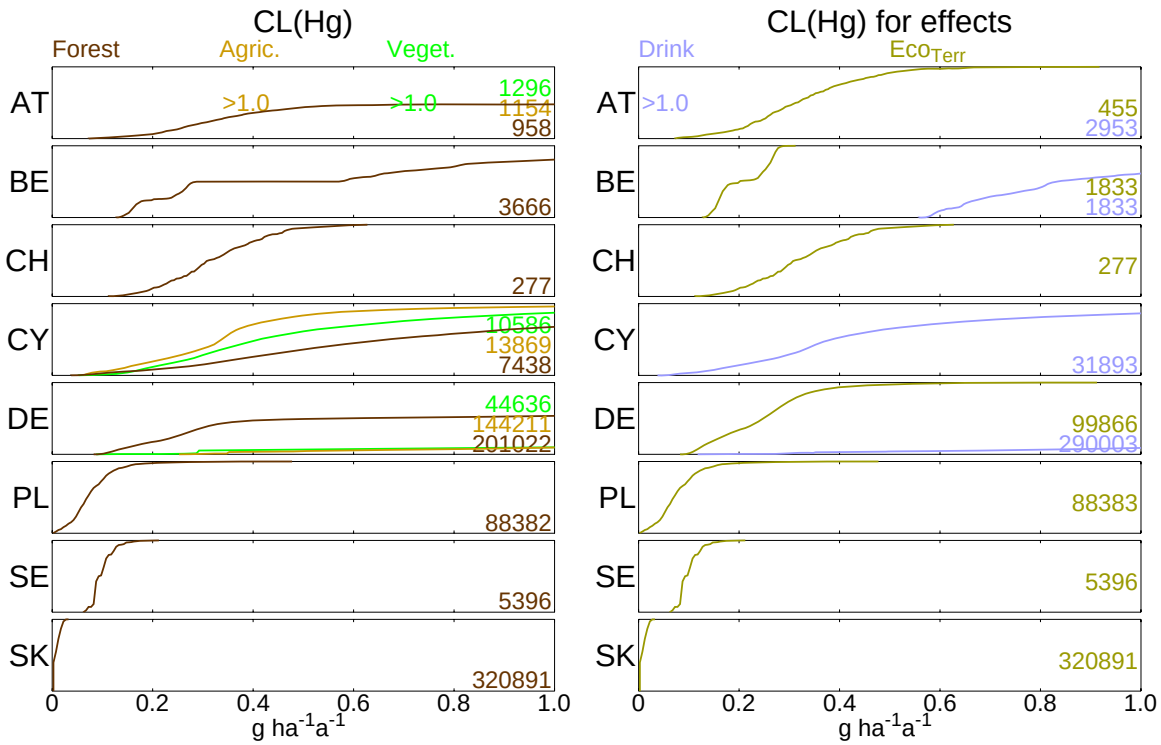

Figure 2-9. The cumulative distribution functions (CDFs) of critical load of mercury for the different ecosystems (left) and for the different effects (right).

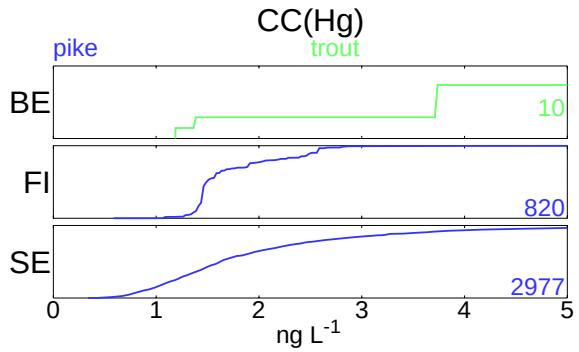

Figure 2-10. The cumulative distribution functions of critical concentration of mercury in rainfall for the different fish species.

2.5 Input variables

The CCE requested also the input variables needed to calculate the critical loads. These variables depend on the effect and receptor considered. A selection of the CDFs of these variables is plotted in the next graphs, to enable a comparison of national submissions. Details on the national data can be found in the national reports in Part II.

Cadmium

Figure 2-11 shows for cadmium the CDFs of the net uptake (Cd_u) the annual yield of biomass as dry weight (Y_{ha}), the content of Cd in the harvested part of the plant ($[Cd]_{ha}$), the critical leaching flux of Cd from the topsoil ($Cd_{le(crit)}$), critical limit ($[Cd]_{ss(crit)}$) and the flux of leaching water from the considered soil layer (Q_{le}). From these CDFs it can be observed that:

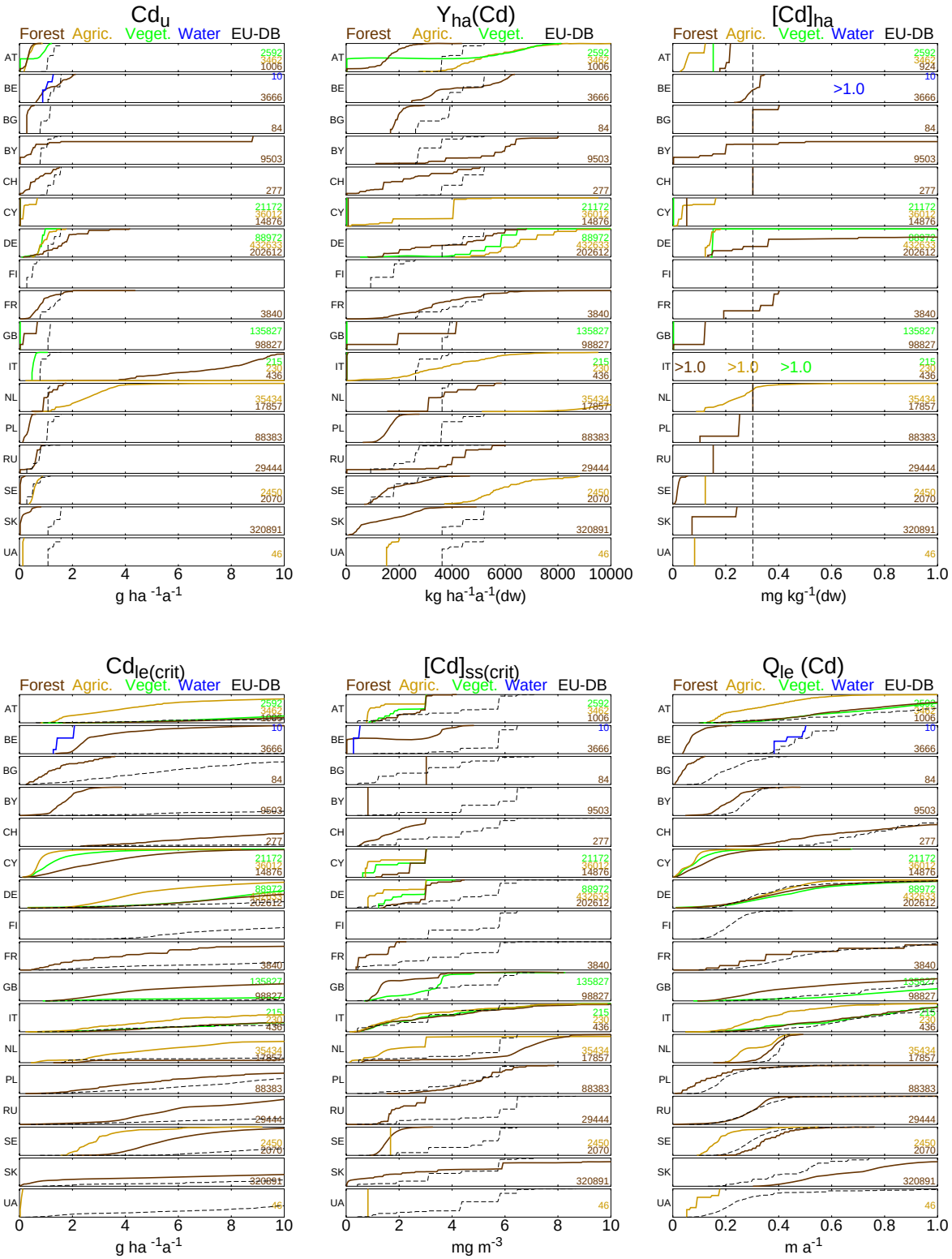

Figure 2-11. CDFs of the net uptake of cadmium (Cd_{u}), the annual yield of biomass, as dry weight (Y_{ha}), the content of cadmium in the harvested part of the plant ($[Cd]_{ha}$), the critical leaching flux of Cd from the topsoil ($Cd_{le(crit)}$), the critical limit ($[Cd]_{ss(crit)}$) and the flux of leaching water from the considered soil layer (Q_{le}).

- Italy, Belarus and the Netherlands (agriculture) have broader ranges of net uptake values for cadmium than the other countries.
- National submissions of the annual yield of biomass cover a broader range than the values of the EU-background database.
- The submitted values for the content of cadmium in the harvested part of the plant turn out to vary while the EU-database applies a standard value of 0.3 mg/kg. The submitted values for Italy are higher than those for the other countries.
- Belarus has a fixed critical leaching concentration which is close to the minimum of the ranges used by many other countries. Bulgaria used the recommendation from the Mapping Manual for drinking water, 3 mg m^3. Ranges depend on the effects addressed by NFCs
- Agriculture ecosystems have lower critical leaching fluxes than forests.
- Values for the flux of leaching water in forest soils are approximately similar to the values from the EU-background database in many of the countries.

Figure 2-12 shows for each country a scatter plot of submitted soil-pH (X-axis) versus submitted uptake (Y-axis) within the considered soil depth (Cd_u) for forest, agriculture and vegetation. There does not seem to be an apparent correlation between pH and metal uptake. Uptake quantities for Italy and the Netherlands are much higher than those of the other countries.

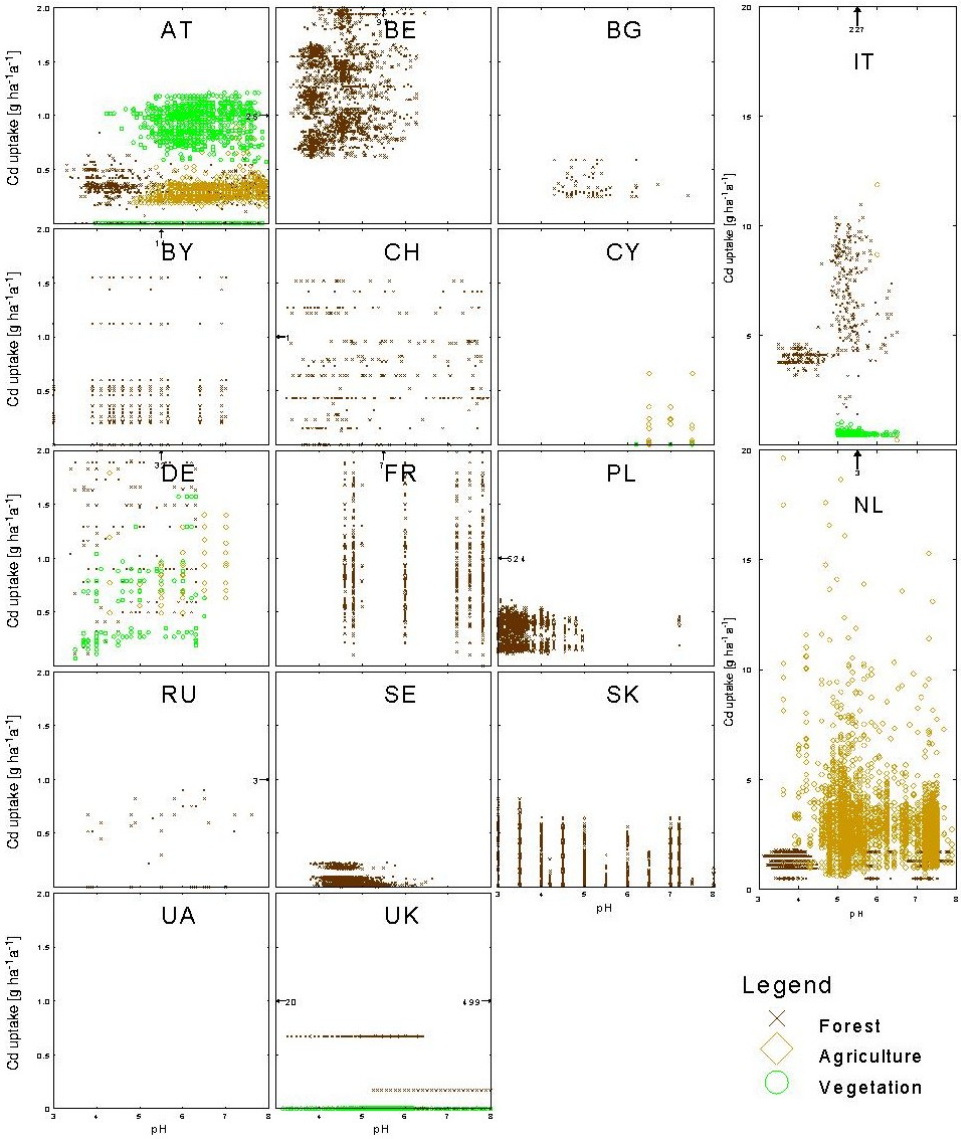

Figure 2-12. Soil-pH vs. metal uptake (Cd_u) for different ecosystem types.

The correlation between metal leaching and pH has been explored as well (see Figure 2-13). In some countries a lower leaching flux turns out to occur with higher pH values. However, for most countries no such correlation seems straightforward.

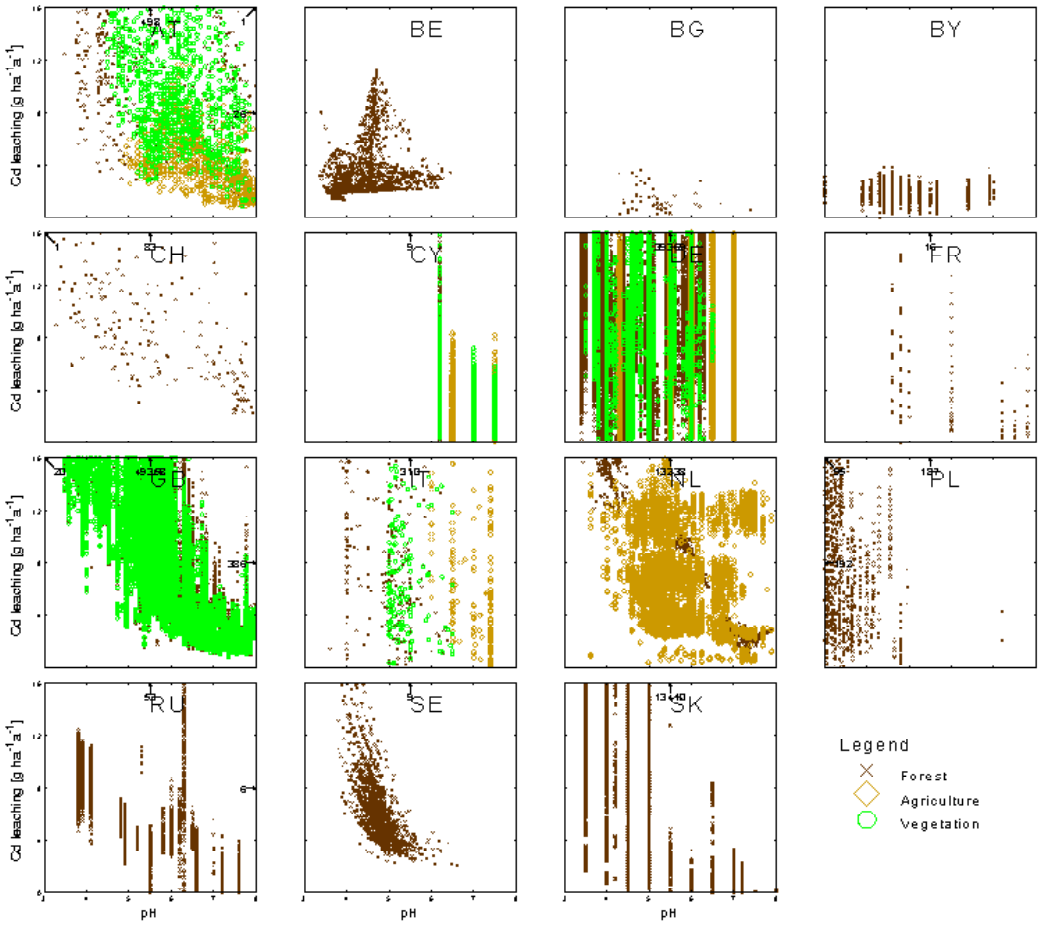

Figure 2-13. Soil-pH vs. metal leaching (Cd_{le}) for different ecosystem types.

Table 2-3 shows the used soil layer codes in the different countries. In the EU-database the critical loads have been calculated for the mineral layer. The submitted data shows that some of the NFCs have used different soil layers.

Table 2-3. The used layer codes (1 = humus layer only, 2 = mineral layer (A-horizon) only, 3 = humus layer + mineral layer, 4 = entire rooting depth).

	Humus layer		Mineral layer (A-horizon)			Humus + mineral layer		Entire rooting zone			Unknown	
Country	effect		effect			effect		effect			effect	
code	1	3	1	2	3	1	3	1	2	3	2	4
AT		85	2,450	1,154	2,868	503						
BE		1,833						1,833				10
BG	84											
BY		9,503										
CH							220	57				
CY				8,274	24,455		7,438	31,893				
DE				144,211	188,547		101,456	290,003				
FR					3,840							
GB							234,654					
IT		881										
NL					17,857			12,627	10,180	12,627		
PL							88,383					
RU						6,616	22,828					
SE							2,070				2,450	
SK					320,891							
UA											46	

Lead

The net uptake of lead (Pb_u) , the annual yield of biomass as dry weight (Y_{ha}), the content of Pb in the harvested part of the plant ($[Pb]_{ha}$), the critical leaching flux of Pb from the topsoil ($Pb_{le(crit)}$), and the critical limit ($[Pb]_{ss(crit)}$) are displayed in CDFs of Figure 2-14.

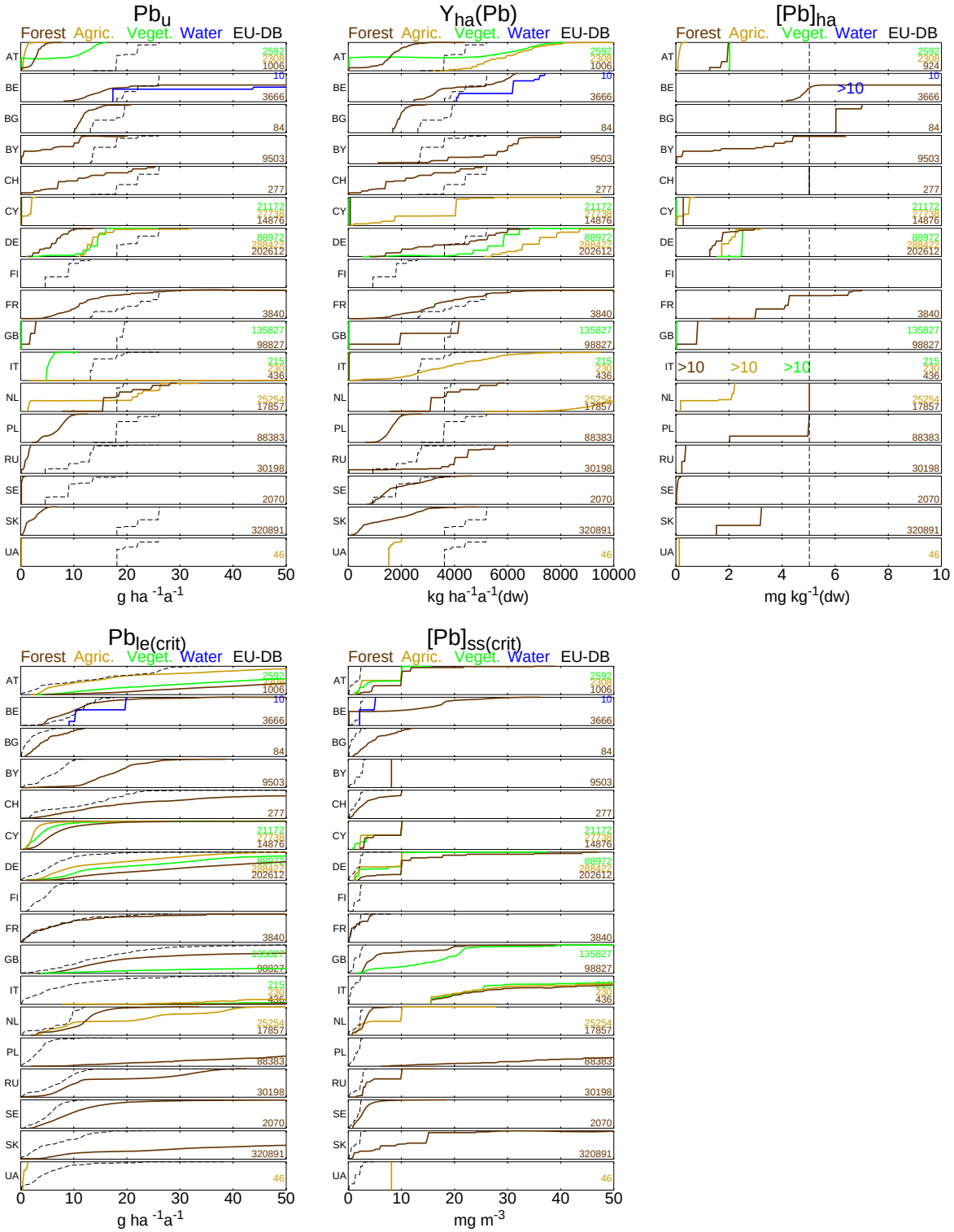

Figure 2-14. The CDFs of the net uptake of lead ($Pb_{u)}$, the annual yield of biomass as dry weight (Y_{ha}), the content of Pb in the harvested part of the plant ($[Pb]_{ha}$) , the critical leaching flux of Pb from the topsoil ($Pb_{le(crit)}$) and the critical limit ($[Pb]_{ss(crit)}$).

Inspection of the plots in Figure 2-14 can lead to the following remarks:

- The net uptake according to the background database is higher than the data submitted by NFCs. The net uptake for forests is generally lower than for other ecosystems.

- The range of values for the annual yield is broader for the submitted data than in the background database.
- Italy has very high values for the content of lead in the harvested part of the plant.
- The range of values covering the critical leaching flux in the background database is similar to the range of data submitted by many countries. For Austria the CDF of critical leaching in agricultural areas seems similar to the CDF in the background database between 5 and 25 g ha^{-1} a^{-1}.
- The CDF of the critical limit shows high values for Italy. The background database has lower values than the submitted data.

Mercury

Figure 2-15 shows the CDFs of the net uptake of mercury (Hg_u), the critical leaching flow of Hg from the topsoil ($Hg_{le(crit)}$), the critical limit ($[Hg]_{ss(crit)}$), the annual yield of biomass, as dry weight (Y_{ha}), the content of Hg in the harvested part of the plant ($[Hg]_{ha}$) and the concentration of dissolved organic matter in the soil solution ([*DOM*]).

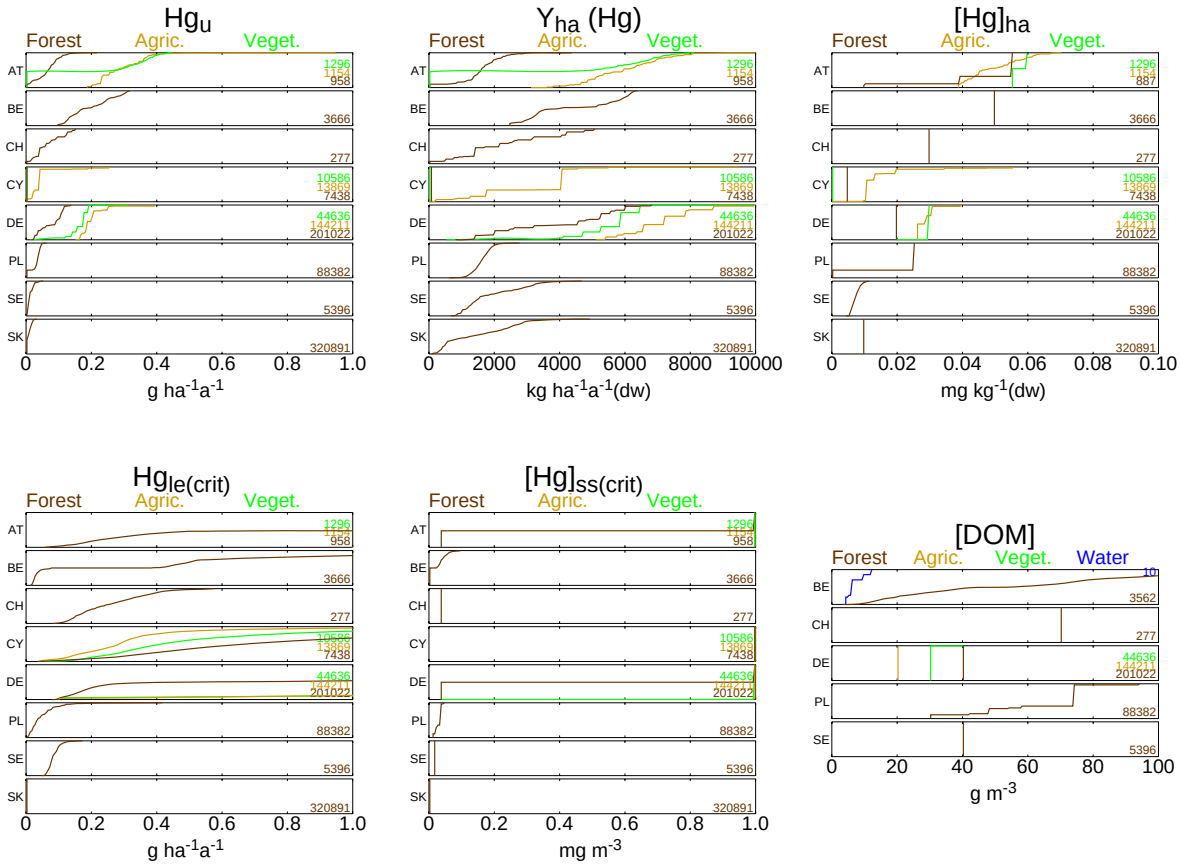

Figure 2-15. The CDFs of the net uptake of mercury (Hg_u), critical leaching flux of Hg from the topsoil ($Hg_{le(crit)}$), the critical limit ($[Hg]_{ss(crit)}$), the annual yield of biomass, as dry weight (Y_{ha}), the content of Hg in the harvested part of the plant ($[Hg]_{ha}$) and concentration of dissolved organic matter in the soil solution ([DOM]).

From Figure 2-15 we can mention:

- The net uptake by forests is lower than for other ecosystems.
- The critical leaching flux of mercury from the topsoil for Poland, Sweden and Slovakia are lower than for the other countries.
- The CDF of the critical limit shows that some countries have a fixed value for the forest ecosystems and other countries have a broader range of values.
- The annual yield of biomass in Cyprus for forests and vegetation is much lower than for agriculture. In general the values for this variable for forests are lower than for other ecosystems.
- The content of mercury in the harvested part of the plant has fixed values for some countries, although other counties have a broader range.
- The CDF of dissolved organic matter in the solution show the same characteristics.

Figure 2-16 shows for aquatic ecosystems the total organic carbon concentration in the water ([TOC]), the concentration of total phosphorus in the surface water ([*TP*]), the site specific transfer function (TF_{HgSite}) and the deviation from a standard fish (TF_{HgBio}). The concentration of total phosphorus in the water in Belgium is higher than in Sweden and Finland. Belgium uses the transfer function for trout while Sweden and Finland use pike.

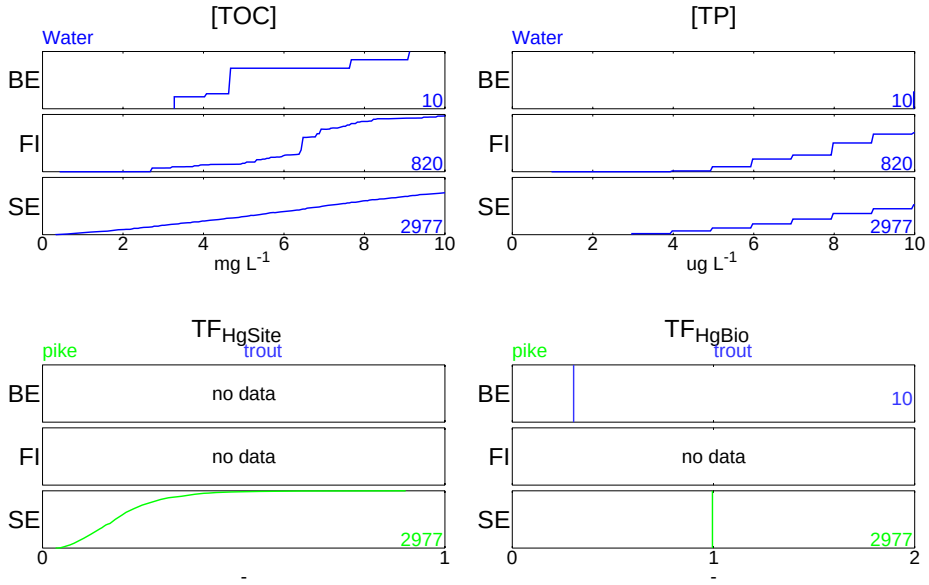

Figure 2-16. The CDFs of the total organic carbon in the water ([TOC]), the concentration of total phosphorus in the surface water ([TP]), the site specific transfer function (TF_{HgSite}) and the deviation from a standard fish (TF_{HgBio}).

2.6 Conclusions

Following the 2004 call for data, 17 National Focus Centres have submitted (updated) critical loads of heavy metals. Most countries have submitted data for cadmium and lead. Nine countries have submitted data for mercury. Most countries have submitted data for effects on terrestrial ecosystems (mainly ecotoxicological effects, effect 3). Sweden, Finland and Belgium have also submitted data for aquatic ecosystems.

The magnitude of the effects for the metals differs between the effects. The ecotoxicological effect on terrestrial ecosystems is the most sensitive effect for most of the countries which submitted more than one effect. A preliminary visual comparison of the submitted data with the calculated data in the EU-database shows that these datasets are more similar for lead than for cadmium.

Finally, the necessity to analyze different effects has emphasized the requirements of NFCs to use appropriate site identifications. The identification through site-IDs made it possible to correctly determine a minimum critical load over different effects for the same site.

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3. The European Background Database for Heavy Metals

Maximilian Posch, Gert Jan Reinds[*]

[*]Alterra, Wageningen University and Research Centre (WUR), Netherlands

3.1 Introduction

A main task of the Coordination Center for Effects (CCE) is to collect and collate national data on critical loads and to provide European maps and other databases to the relevant bodies under the LRTAP Convention to assist in the review and possible revision of protocols. Ideally all those data are based on national data submissions, provided by National Focal Centres (NFCs) upon a call for data. In addition, the CCE maintains a so-called European background database (EU-DB), which could be used to fill potential gaps on the European map.

The most recent version of the European background database used for calculating critical loads and dynamic modelling of S and N has been described in the 2003 CCE Status Report (Posch et al., 2003). Only forests (forest soils) are considered in the European background database. Individual tree species are not identified, but a distinction is made between coniferous, broad-leaved (deciduous) and mixed forests. When variables were not found in existing databases, the recommendations and transfer functions in the Mapping Manual (UBA, 2004) were followed as closely as possible. Here we describe the variables in EU-DB needed for calculating critical loads of cadmium (Cd) and lead (Pb) related to ecotoxicological effects in forests ('effect 3' in Table 1-1 in Chapter 1).

3.2 Map Overlays

Input data for critical load calculations vary as a function of location and receptor (the combination of forest type and soil type). Thus an overlay of the following base maps was constructed:

(a) A map with soil types at scale 1:1,000,000 for all European countries (Eurosoil, 1999); except for Russia, Belarus, Ukraine and Moldova, for which the FAO 1:5,000,000 soil map (FAO, 1981) was used.
(b) A map of forest types, distinguishing coniferous, broad-leaved and mixed forests, taken from the harmonised European land cover map (Slootweg et al., 2005). This map is derived from the Corine and SEI (Stockholm Environmental Institute) land cover maps.
(c) A map with climate zones for Europe, derived from EC/UNECE (1996).
(d) A global map of detailed elevation data (on a 30"×30" grid) from NOAA/NGDC (Hastings and Dunbar, 1998).
(e) A map with EMEP 50×50 grid cells, in which deposition data are provided.

Overlaying these maps, merging polygons within every EMEP50 grid cell differing only in altitude, and discarding units smaller than 0.1 km^2 results in about 90,000 different forest-soil combinations.

The soil maps are composed of so-called soil associations, each polygon on the map representing one association. Every association, in turn, consists of several soil typological units (soil types) that each covers a known percentage of the soil association. The soil typological units on the maps are classified into more than 200 soil types (Eurosoil 1999).
For every soil typological unit information is available, of which soil texture classes are used here to derive other input data. Texture classes are defined in Table 6-2 of the Mapping Manual (UBA, 2004).

3.3 Input data for critical loads of Cd and Pb

Precipitation surplus and soil water content
To compute the concentration and leaching of compounds in the soil, the annual water flux through the soil has to be known. It was derived from meteorological data available on a 0.5°×0.5° grid described by Leemans and Cramer (1991), who interpolated selected records of monthly meteorological data from 1678 European meteorological stations for the period 1931–1960.

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

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

Heavy metal uptake
Net uptake of Cd and Pb was computed by multiplying the estimated annual average growth of stems and branches with the element contents of the metals in these compartments. It was assumed that all metal uptake takes place in the considered top layer.

Forest growth was estimated according to a procedure described by Klap et al. (1997; see also Reinds et al. 2001), that calculates forest growth from yield tables as a function of forest type, forest age and climate zone (combination of climate and altitude). Since forest age is not known, the average growth of a rotation period from the yield tables was used.

Contents of Cd and Pb in all trees were taken as average of the ranges listed in Table 3 of De Vries et al. (2005): 0.3 mg kg^{-1} for Cd and 5.0 mg kg^{-1} for Pb.

Critical concentration of Cd and Pb
The critical concentration of Cd and Pb in drainage water were obtained by linearly interpolating the values in the look-up tables A9.2 and A9.3 in De Vries et al. (2005) that provide those concentrations as a function of, *inter alia*, organic matter content, DOC and pH.

Organic carbon content and pH for each soil type were derived from a pan-European data base on forest soils (Vanmechelen et al. 1997). Organic matter content was assumed to by twice the organic content.

The dissolved organic carbon (DOC) concentration was computed from a linear regression between DOC and pH and soil texture, using data from intensively monitored forest sites in Europe.

3.4 Results

The EU-DB obtained from the data described above has been used to compute critical loads of Cd and Pb. In Figure 3-1 the 5^{th} and 50^{th} percentiles of the critical loads of Cd and Pb are displayed on the EMEP50 grid.

The maps in Figure 3-1 can be compared with the maps in Chapter 1 to see the similarities and differences between critical loads computed from the EU-DB and national critical loads. The cumulative distribution functions (CDFs) of these critical loads on a national scale can be found in Chapter 2 in comparison with national submissions.

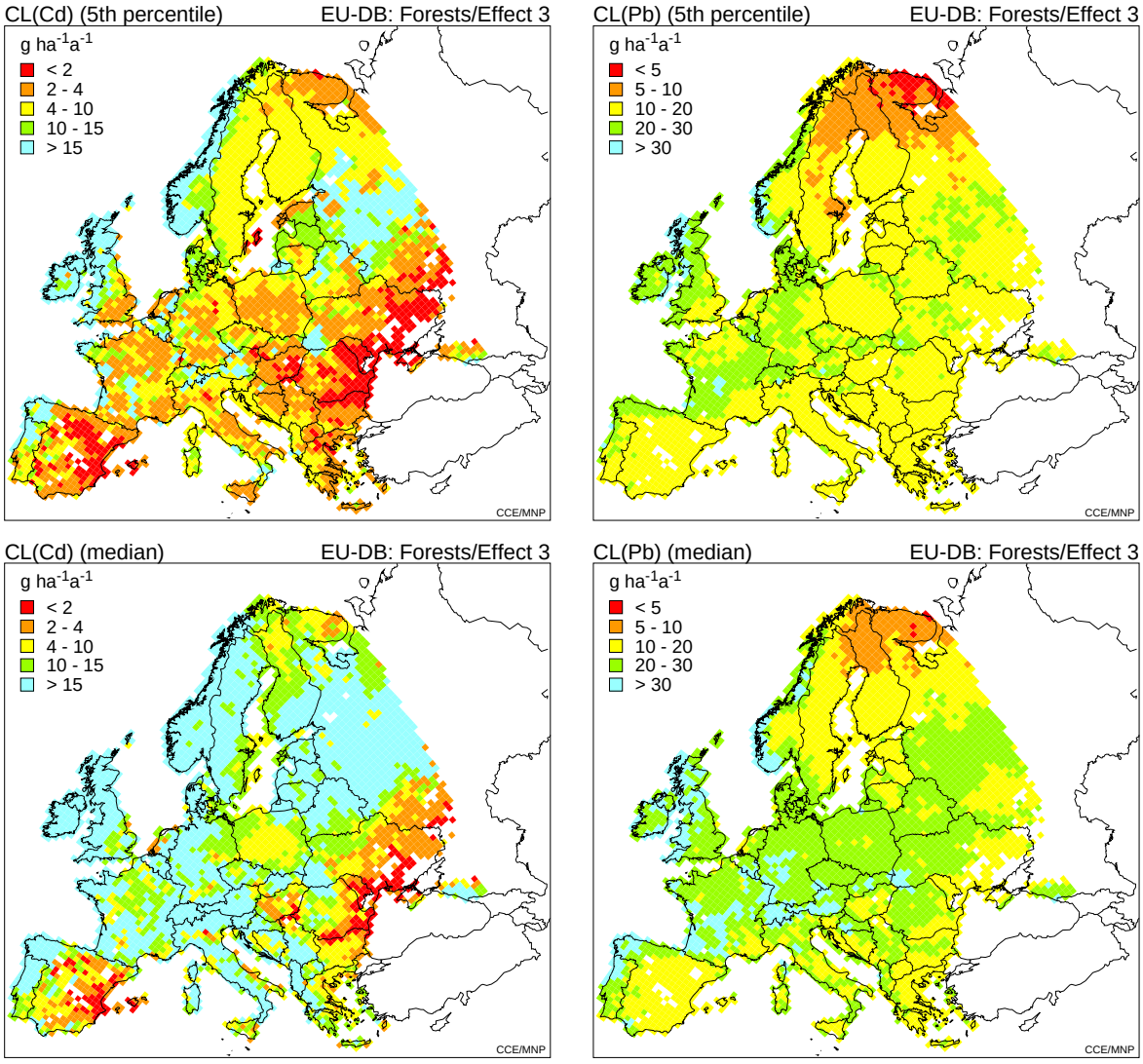

Figure 3-1. 5th and 50th percentile of the critical loads of cadmium and lead for ecotoxicological effects in forests on the EMEP50 grid, computed from the European background database.

The maps in Figure 3-2 show the exceedances of those critical loads for the years 1990 and 2000. Note, that the 2000 deposition used has been derived not with the 2000 meteorology but a reference meteorology better reflecting the long-term climate (see Chapter 4 for more details). Thus the reductions in exceedances between 1990 and 2000 reflect only the reductions in emissions. The maps shown can be compared with Figure 1-2 in Chapter 1 and especially with the exceedance maps for effect 3 in Chapter 5.

3.5 Concluding remarks

The European background database (EU-DB) has been updated with variables needed to calculate critical load of cadmium and lead. It is used by the CCE to fill in gaps left by countries which do not deliver data as well as for possible studies on a European scale. The database is not a final product; it will be checked and updated, whenever new data become available or methodological changes make it necessary.

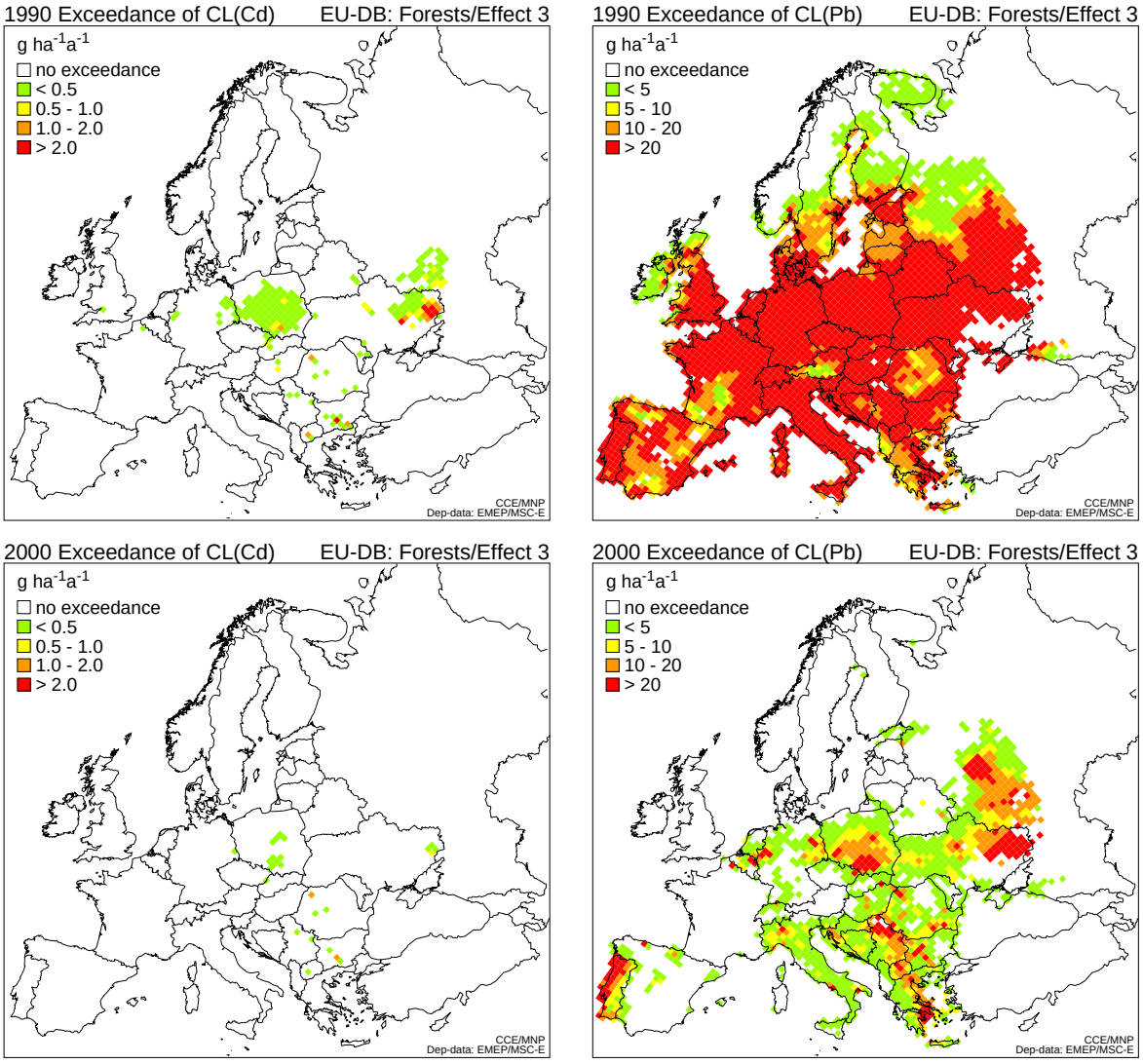

Figure 3-2. Exceedances of the EU-DB critical loads of cadmium (left) and lead (right) for ecotoxicological effects in forests on the EMEP50 grid in the year 1990 (top) and 2000 (bottom).

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4. Deposition Modelling for Heavy Metals

Ilia Ilyin, Sergey Dutchak

EMEP Meteorological Synthesizing Centre – East, Moscow

Modelling of atmospheric transport and depositions of lead, cadmium and mercury in Europe is the responsibility of the Meteorological Synthesizing Centre-East (MSC-E) of EMEP. This chapter gives a brief description of MSCE-HM model, a summary of emission data used, the selection of meteorological data for the evaluation of long-term changes in pollution levels, air concentrations, ecosystem-dependent depositions and mercury concentrations in precipitation, and experimental calculations of lead pollution based on expert-estimated emission. Besides, results of the analysis of the model uncertainties are summarized. Pollution levels were simulated for the years 1990 and 2000. Information on the emission and deposition fluxes is presented in units of g $ha^{-1}a^{-1}$, although normally in EMEP reports devoted to heavy metals g $km^{-2}a^{-1}$ or kg $km^{-2}a^{-1}$ are used.

4.1 Brief description of the MSCE-HM model

Fields of depositions of heavy metals over all EMEP grid cells can be obtained only by means of dispersion modelling. Simulation of depositions of the considered metals was performed with the MSCE-HM model. It is an Eulerian-type three-dimensional model with terrain-following vertical co-ordinate. The principle scheme of the model functioning is shown in Figure 4-1. The model accounts for atmospheric transport and turbulent diffusion, wet and dry ecosystem-dependent deposition, chemical transformations of mercury and inflow of the pollutants outside model boundaries. The spatial resolution of the model is 50x50 km. More details about the description of the physical processes in the model can be found in Travnikov and Ilyin (2005).

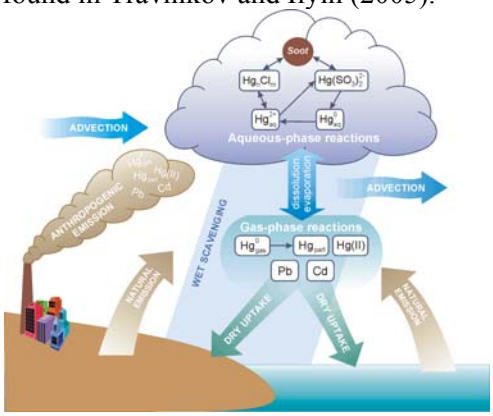

Figure 4-1. Model scheme of heavy metal behaviour in the atmosphere.

Input needed by the model includes emissions, meteorological information and geophysical data (land-cover, orography, land-sea mask etc). Emission data are represented by two components: (a) anthropogenic emission, and (b) natural emission and re-emission. Meteorological information is based on the NCEP/NCAR re-analysis project data and is processed by the MM5 system (Grell et al., 1995). Land-cover data are prepared by the Coordination Center for Effects (CCE) and described in Slootweg et al. (2005).

The main output of the model are monthly mean and annual mean fields of concentrations in air and in precipitation, wet and dry ecosystem-dependent depositions, source-receptor matrices, and depositions to sea surfaces surrounding Europe. For critical load exceedance calculations the relevant data are mean annual deposition fluxes to different types of land-use/land-cover and mercury concentrations in precipitation.

4.2 Emission data

Calculations of depositions of lead, cadmium and mercury were carried out with the emission data officially submitted by EMEP Parties (so-called official emissions). If a Party did not provide emission data, expert estimates were used (Berdowski et al., 1997, 1998). Total emissions for each European country in 1990 and 2000 are presented in Table 4-1.

Table 4-1. Total emissions of lead (Pb), cadmium (Cd) and mercury (Hg) in 1990 and 2000. Shaded boxes indicate officially reported values.

Country/Year	Pb t a^{-1}		Cd t a^{-1}		Hg t a^{-1}	
	1990	2000	1990	2000	1990	2000
Albania	33	24	0.7	0.6	0.5	0.5
Armenia	16	8	0.3	0.1	0.3	0.2
Austria	204	12	1.5	0.9	2.2	0.9
Azerbaijan	38	12	7.2	2.3	3.1	1.0
Belarus	798	46	7.6	1.4	0.5	0.4
Belgium	566	114	7.8	2.4	6.7	2.5
Bosnia and Herzegovina	97	97	1.7	1.7	2.0	2.0
Bulgaria	436	213	28.3	11.0	13.2	4.2
Croatia	466	147	1.6	1.0	1.2	0.4
Cyprus	81	74	0.2	0.2	0.3	0.3
Czech Republic	269	108	4.3	2.9	7.5	3.8
Denmark	123	7	1.2	0.6	3.5	1.2
Estonia	233	41	1.6	0.7	1.3	0.6
Finland	326	38	6.3	1.4	1.1	0.6
France	4264	247	15.8	10.4	25.3	13.4
Georgia	36	7	1.1	0.2	1.3	0.3
Germany	2323	519	31.0	11.0	113.0	28.7
Greece	470	470	3.0	3.0	13.0	13.0
Hungary	680	37	5.5	2.7	6.3	4.2
Iceland	12	0.4	0.2	0.2	0.0	0.0
Ireland	130	33	1.6	0.5	1.5	1.5
Italy	4371	943	10.0	8.9	10.8	9.9
Kazakhstan	31	18	0.7	0.4	0.1	0.1
Latvia	108	8	1.8	0.6	0.7	0.2
Lithuania	47	16	3.8	1.4	0.2	0.3
Luxembourg	77	2	0.6	0.1	0.3	0.3
Monaco	4	0	0.1	0.0	0.1	0.1
Netherlands	335	44	1.9	1.2	3.0	0.6
Norway	186	6	1.6	0.7	1.7	1.0
Poland	1372	647	91.6	50.4	33.3	25.6
Portugal	1305	1023	2.5	2.4	3.8	4.6
Republic of Moldova	253	3	3.1	0.2	4.3	0.3
Romania	580	510	22.0	20.5	7.5	6.6
Russian Federation	3591	2352	79.4	50.5	15.6	10.0
Serbia and Montenegro	600	331	8.3	6.1	3.9	3.3
Slovakia	152	74	9.5	7.2	12.5	4.4
Slovenia	460	41	1.7	1.5	0.8	0.6
Spain	2727	634	13.8	18.1	20.3	21.8
Sweden	474	15	2.5	0.5	4.7	0.8
Switzerland	520	114	4.2	2.2	6.8	2.6
The FYR of Macedonia	210	109	9.1	4.8	1.5	1.0
Turkey	774	774	14.0	14.0	4.3	4.3
Ukraine	3900	957	54.0	14.4	36.0	26.0
United Kingdom	2809	184	20.2	5.9	36.7	9.0
Total:	**36487**	**11058**	**485**	**267**	**413**	**213**

Maps of the spatial distribution of the emissions can help identifying regions with elevated pollution levels. In 1990 regions with high emission density of lead were the United Kingdom, Belgium, Italy,

Portugal, Slovenia and other countries (Figure 4-2, left). By 2000 the emissions of lead went down all over Europe (Figure 4-2, right). Relatively low lead emission reduction took place in Portugal. Reductions of cadmium and mercury emissions are also accompanied by changes of the spatial distribution. For example, the emission density of cadmium in Poland in 1990 was more than 1.5 g $ha^{-1}a^{-1}$ in almost the whole country (Figure 4-3, left). In 2000 the emissions varied from 0.5 to 1.5 g $ha^{-1}a^{-1}$ over most of the country (Figure 4-3, right). Mercury emissions were larger than 1.5 g $ha^{-1}a^{-1}$ over most of Germany, but in 2000 the emissions exceed 1.5 g $ha^{-1}a^{-1}$ only in few grid cells in the western, northern and eastern parts of the country (Figure 4-4). Some increase in the emissions of cadmium and mercury in Spain can also be seen in Figures 4-2 to 4-4.

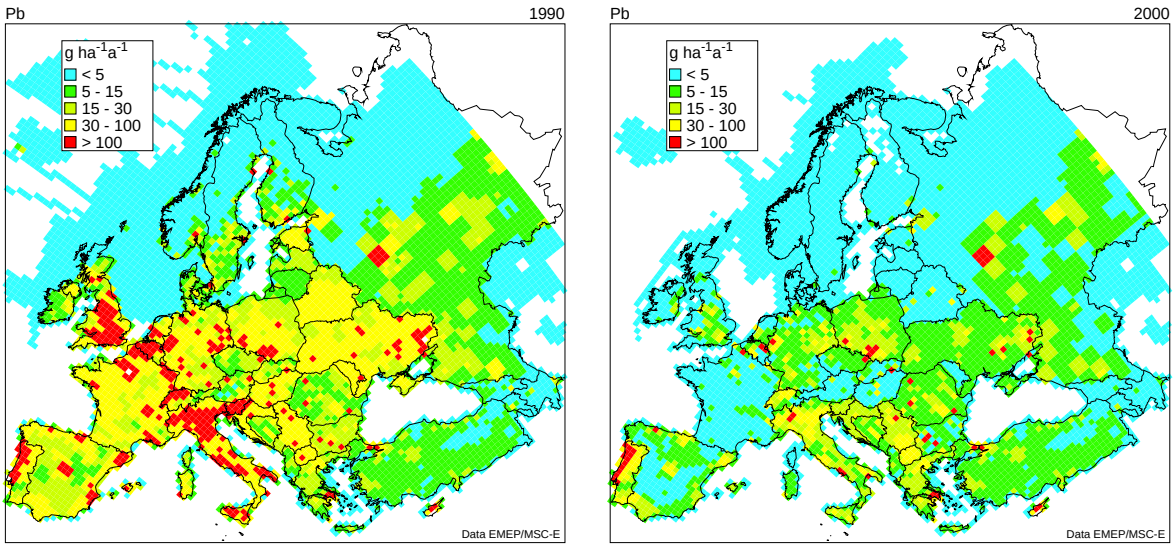

Figure 4-2. Spatial distribution of lead emissions in 1990 (left) and 2000 (right).

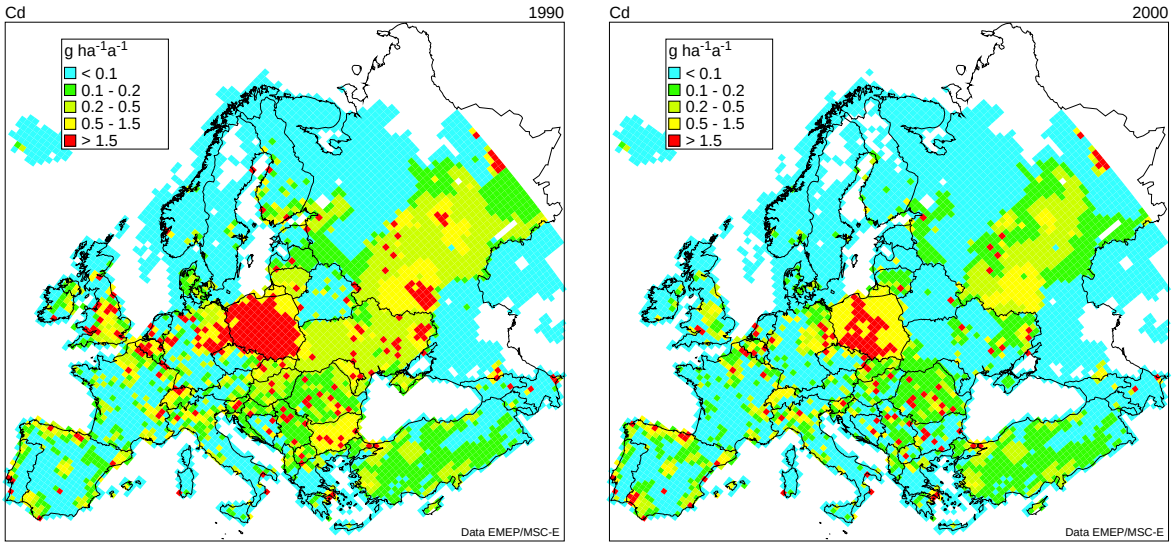

Figure 4-3. Spatial distribution of cadmium emissions in 1990 (left) and 2000 (right).

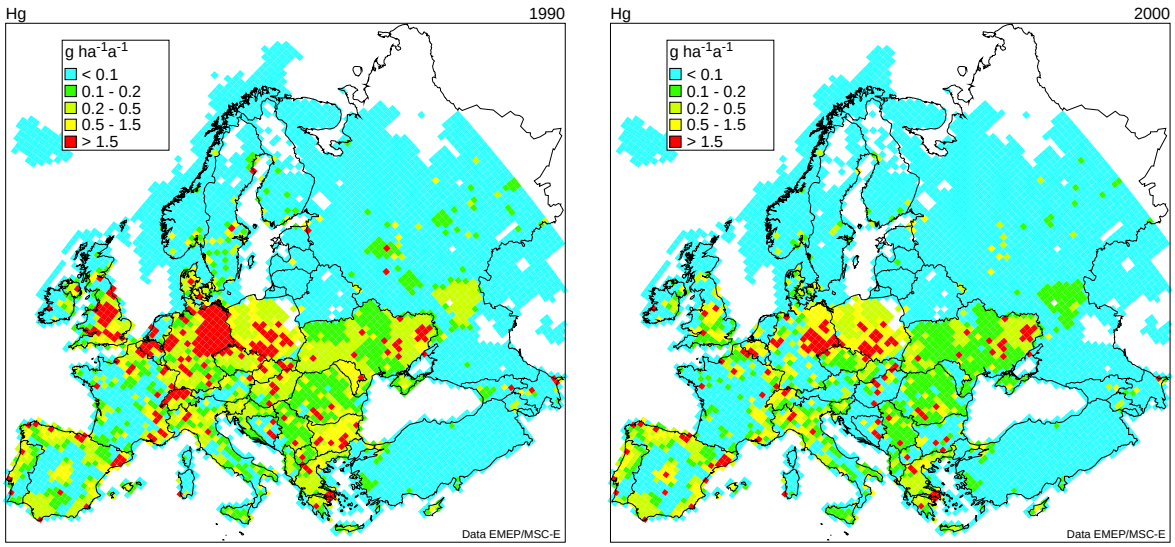

Figure 4-4. Spatial distribution of mercury emissions in 1990 (left) and 2000 (right).

4.3 Selection of reference year

Long-range transport modelling is a widely used tools for the evaluation of the efficiency of emission control strategies for long periods (decades) of time. In general, the greater the reduction of emissions, the more significant the decrease in atmospheric deposition. However, depositions of heavy metals are governed not only by emissions, but also by meteorological conditions. Therefore, the resulting trend of deposition includes both the influence of the emission changes and multi-annual variability of meteorological parameters. This variability can significantly affect the trend, especially if the emission changes are relatively small. For example, in some regions the trend can be magnified or hidden due to variability in precipitation amounts or changes in wind patterns. Therefore, if the influence of multi-annual meteorological variability were excluded, the assessment of the efficiency of emission reduction measures would be more reliable. The influence of meteorological variability can be reduced by the use of meteorological data for one year when long-term changes in emissions and pollution levels are simulated. The use of meteorological data for one year could be very helpful when pollution levels are calculated for base years (e.g. 1990 and 2000), and scenarios of future emissions are evaluated. Certainly, the pollution levels obtained in this way are somewhat artificial, but relationships between emission reduction measures and the pollution response are more distinct.

The main task for a meaningful application of this approach is the selection of the meteorological year. The key meteorological factors influencing depositions are precipitation amounts, wind fields and atmospheric stability. Theoretically, we need a set of meteorological data, in which wind fields, precipitation and stability are similar to those averaged over a long period of time (decades). Such a set of meteorological data we will call reference set, and the year the reference year.

The idea to select this reference year is as follows. We suggest simulating deposition fields for a long period of time, using the same emission data but the meteorology recorded for each year. From that an average deposition field is computed from the depositions for each year. Then the deposition field for every year is compared with the average deposition field. The reference year is the year for which the deposition field is most similar to the averaged field.

In order to select this reference year depositions of lead were calculated for each year from 1990 to 2002. Emission data were chosen for 2000, and meteorological data were specific for each year. Depositions over European countries in each year were compared with average depositions for this period over land surfaces. In the comparison the following statistical parameters were used:

Normalized Mean Square Error:

$$NMSE = \frac{1}{N \cdot \overline{O} \cdot \overline{P}} \cdot \sum_{i,j} \left(O_{i,j} - P_{i,j}\right)^2 \quad [4.1]$$

where:

$P_{i,j}$ - depositions in grid point (i,j) in a separate year in 1990–2002 period
$O_{i,j}$ - depositions in grid point (i,j) averaged over 1990–2002
$\overline{P}$ - spatially averaged deposition for individual year
$\overline{O}$ - spatially averaged value of multi-annual mean depositions
N - number of grid cells

This parameter characterises the difference between two fields. In the ideal case, $P_{i,j} = O_{i,j}$ in every grid cell (i,j) and NMSE should be equal to zero. In fact, in each grid cell $P_{i,j}$ differs from $O_{i,j}$. As NMSE characterises the sum of differences between two fields in each grid cell, it can be considered as the main parameter when selecting the reference year.

Fractional Bias:

$$FB = 2 \cdot \frac{\overline{P} - \overline{O}}{\overline{P} + \overline{O}} \quad [4.2]$$

This parameter indicates if spatially averaged depositions in an individual year are higher or lower than multi-annual mean depositions. In the ideal situation, FB is zero.

Fractional Standard Deviation

$$FSD = 2 \cdot \frac{\sigma_P^2 - \sigma_O^2}{\sigma_P^2 + \sigma_O^2} \quad [4.3]$$

σ_O - standard deviation of multi-annual mean depositions
σ_P - standard deviation of depositions in an individual year.

FSD shows how close the spatial variabilities of two different fields are. In the ideal case, FSD=0.

Correlation Coefficient

$$R = \frac{\sum_{i,j} \left(O_{i,j} - \overline{O}\right) \cdot \left(P_{i,j} - \overline{P}\right)}{\sqrt{\sum_{i,j} \left(O_{i,j} - \overline{O}\right)^2 \cdot \sum_{i,j} \left(P_{i,j} - \overline{P}\right)^2}} \quad [4.4]$$

Linear regression coefficients

If a linear relationship is assumed between multi-annual mean depositions and depositions in an individual year, the following equation for each grid cell can be written:

$$O_{i,j} = \alpha \cdot P_{i,j} + \beta + \omega \quad [4.5]$$

Here α, β and ω are unknown parameters of the equation [4.5]. Parameter α characterizes slope of regression line, β is systematic error and ω is estimate of residual dispersion, which is calculated as:

$$\omega^2 = \chi^2[\alpha, \beta] = \frac{1}{N} \sum_{i,j} (O_{i,j} - P_{i,j} - \beta)^2 \quad [4.6]$$

In the case of ideal coincidence of the two deposition fields, α should be equal to unity, and β and ω equal to zero. Minimizing χ^2, we take partial derivatives of equation [4.6] with respect to α and by β. This results in a set of two equations with two unknowns, α and β.

These statistical parameters are summarised in Table 4-2. The main parameter, NMSE, is the lowest in 1990. Fractional bias for this year is 0.02, which means 2% overestimation of the multi-annual mean depositions. FSD for 1990 is closest to zero. This implies that variability of depositions in 1990 is most similar to that of multi-annual mean deposition field. Correlation coefficients turned out to be not indicative in this test, because for each year they are quite high (0.96–0.99). As for coefficients of liner regression, α for 1990 is one of the closest to unity, β lies in the middle of the range for other years and ω is the lowest for 1990. Therefore, we can conclude that depositions in 1990 best resemble the multi-annual mean depositions; and thus we take 1990 as reference year.

Table 4-2. Statistical parameters used for selection of reference year (on the basis of lead).

Year	FB	FSD	NMSE	CC	α	β	ω
1990	0.020	0.09	0.017	0.99	0.94	54	108
1991	0.027	-0.22	0.046	0.96	1.08	-33	152
1992	0.011	0.21	0.038	0.98	0.88	94	165
1993	0.013	0.20	0.032	0.98	0.89	88	154
1994	-0.024	0.35	0.049	0.98	0.82	115	181
1995	-0.044	0.31	0.046	0.98	0.84	90	160
1996	-0.038	0.39	0.066	0.97	0.80	123	201
1997	0.017	0.28	0.044	0.98	0.85	119	187
1998	0.015	-0.28	0.046	0.96	1.11	-67	166
1999	-0.005	-0.18	0.035	0.97	1.06	-47	143
2000	0.005	-0.27	0.041	0.97	1.11	-76	164
2001	-0.003	-0.21	0.048	0.96	1.06	-47	165
2002	0.010	-0.16	0.042	0.96	1.04	-23	148

Over most of European countries deposition fluxes in grid cells in 1990 do not differ more than ±10% from the multi-annual mean values (Figure 4-5, left). Absolute difference in the deposition fluxes is mainly ±1 g $ha^{-1}a^{-1}$ (Figure 4-5, right). Depositions in 1990 are higher than the multi-annual mean in the south-eastern regions of European Russia, eastern Spain, eastern Ukraine, south-western Norway and Sicily. Relatively low depositions in 1990 (compared to the multi-annual mean) can be found in Scandinavia. The highest absolute differences between these two fields are found in the central part of European Russia, eastern Ukraine, northern Italy, and some other areas. As a rule, this high absolute difference is associated with location of significant pollution sources. Underestimated absolute values of depositions in 1990 are found in northern Italy, Romania and Serbia and Montenegro.

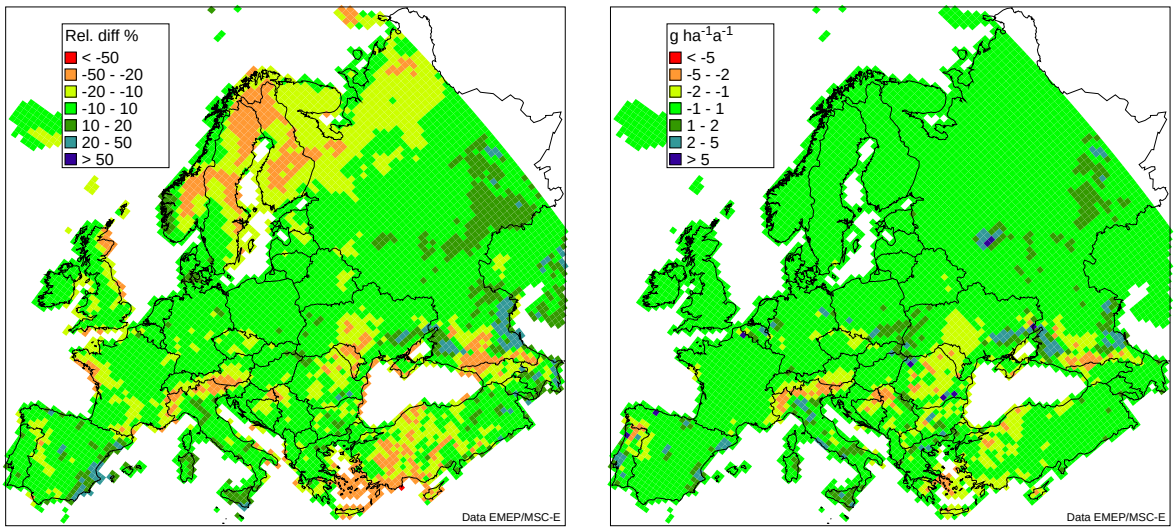

Figure 4-5. Relative (left) and absolute (right) difference between lead depositions in 1990 and multi-annual mean depositions.

Based on these results, we choose 1990 as reference year. It is important to emphasize that this reference year was selected from the viewpoint of most interesting model outcome (depositions), and not from viewpoint of meteorological data. If we were more interested in other parameters, e.g., concentrations in air, the reference year could be different. In this approach it is believed that the overall effect of meteorological factors influencing the model result is implicitly accounted for when depositions are calculated.

Depositions of lead for 1990–2002 computed on the base of the same emissions for each year were used to evaluate variability of depositions, caused by variability of meteorological conditions. Two parameters were estimated: maximum relative difference (MRD) and average relative difference (ARD) of depositions. MRD is calculated as ratio of maximum absolute magnitude of deposition flux to multi-annual mean deposition flux (Figure 4-6, left). ARD is ratio of average absolute magnitude to multi-annual mean deposition (Figure 4-6, right).

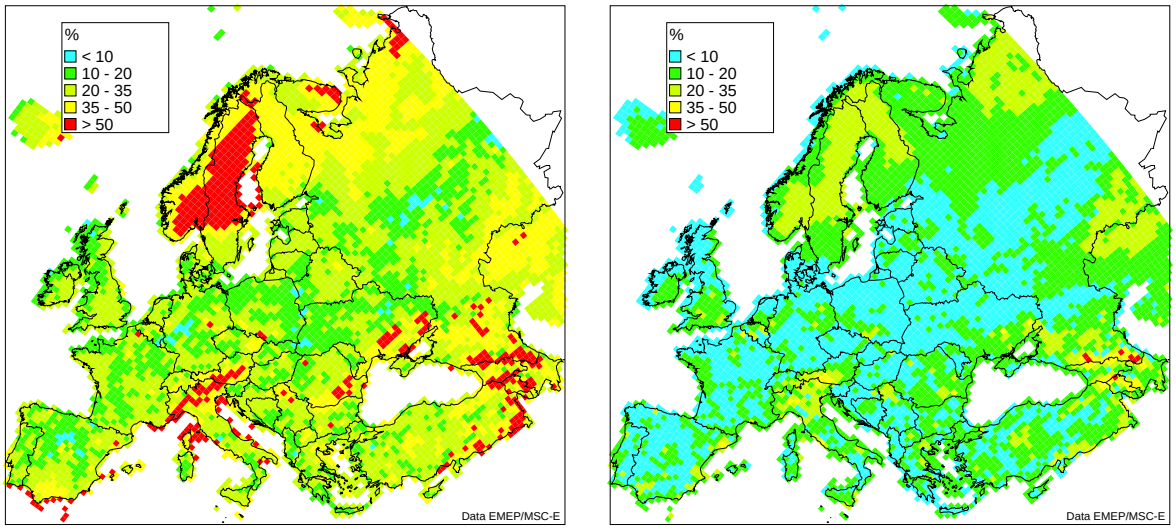

Figure 4-6. Spatial distribution of maximum relative difference (left) and average relative difference (right) of deposition fluxes.

MRD shows maximum possible difference in depositions caused by variability of meteorological data. For example, over Scandinavia the variability of depositions in some years can exceed 50%, even if the emissions are unchanged. Similar can be said about mountainous regions of the Alps and the Caucasus. Only in few grid cells is MRD less than 10%. ARD shows what difference in depositions is caused by meteorological variability on average. Similar to the MRD map, areas with the highest variability are Scandinavia, the Caucasus and the Alps. However, MRD in Scandinavia does not exceed 35%, and in the Alps and Caucasus it exceeds 35% only in a few grid cells. Over most of Europe, this variability on average does not exceed 20%. More details about effects of meteorological variability on modelled results are available in section 4.6.1 of this report, devoted to the sensitivity studies and the model uncertainty analysis, and in MSC-E report (Travnikov and Ilyin, 2005).

4.4 Depositions of lead, cadmium and mercury in the EMEP region

Calculation of critical load exceedances requires knowledge of ecosystem-dependent atmospheric depositions of lead, cadmium and mercury, and concentrations of mercury in precipitation. The required parameters were calculated for 1990 and 2000. Pollution levels for 2000 were calculated using two sets of meteorological data. In the first case the year of meteorological data of 2000 was used, in the second case the reference meteorological year (1990) was used. The following analysis is made mainly for the examples of coniferous forests and cropland depositions. However, the depositions were evaluated for all ecosystem categories given in the land cover map.

Lead:

Deposition fluxes of lead to coniferous forests in 1990 exceed 15 g $ha^{-1}a^{-1}$ over must of Europe (Figure 4-7, left). In central and eastern parts of Europe the fluxes even exceed 100 g $ha^{-1}a^{-1}$. The regions with the highest depositions are the north-west of France, Belgium, the Netherlands, United Kingdom, Hungary, eastern Ukraine and Germany. The north of Scandinavia is characterized by relatively low depositions due to its remoteness from major emission sources.

The pattern of deposition fluxes to croplands is similar to that of forests, although the magnitude of the fluxes is lower (Figure 4-7, right). Only in Italy, the Netherlands, Belgium and Luxemburg deposition fluxes greater than 100 g $ha^{-1}a^{-1}$ are modelled over most of the cropland area.

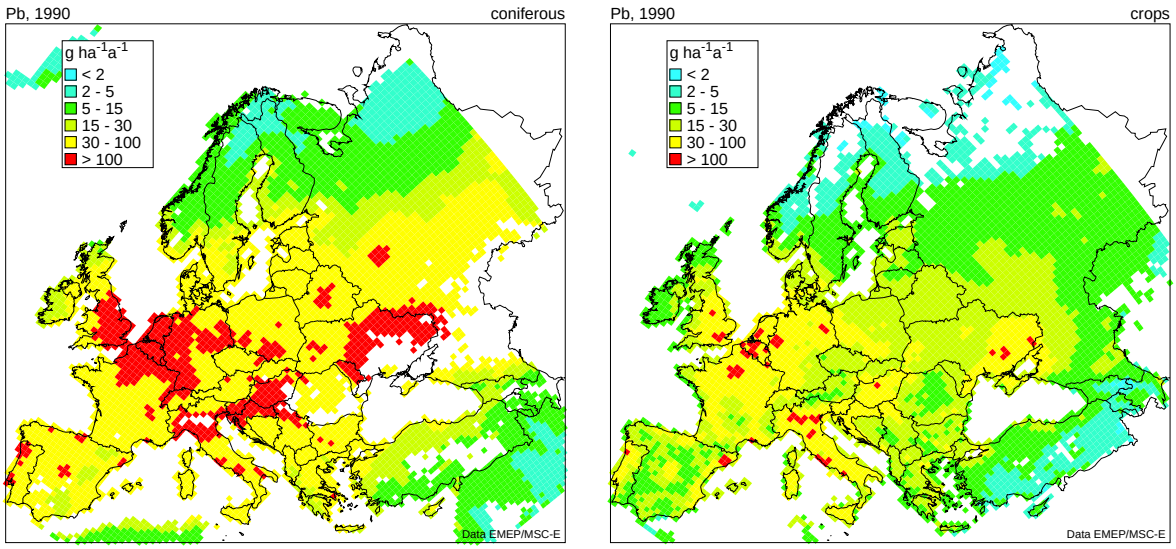

Figure 4-7. Deposition flux of lead in 1990 to coniferous forests (left), and crops (right).

The maps in Figure 4-7 demonstrate the spatial pattern of deposition flux to a specific ecosystem type. However, it is not possible to derive from this maps accurate information about the area where deposition flux falls within a certain range. This information can be obtained by analysing area distribution functions and cumulative distribution functions of the deposition fields. Area distribution function allows us to determine area where depositions fall in specific range. The maximum (mode) of the area distribution function of depositions to coniferous forests is in the range 5–10 g $ha^{-1}a^{-1}$ and for croplands for 10–15 g $ha^{-1}a^{-1}$. The size of the areas with these deposition ranges is about $0.5 \cdot 10^6$ and $0.9 \cdot 10^6$ km^2, respectively (Figure 4-8, left). Cumulative distribution functions (Figure 4-8, right) depict the area over which depositions are less than a certain value. For instance, in 2000 the deposition flux is less than 90 g $ha^{-1}a^{-1}$ over $2 \cdot 10^6$ km^2 (94%) of coniferous forests and $3.8 \cdot 10^6$ km^2 (98%) of croplands.

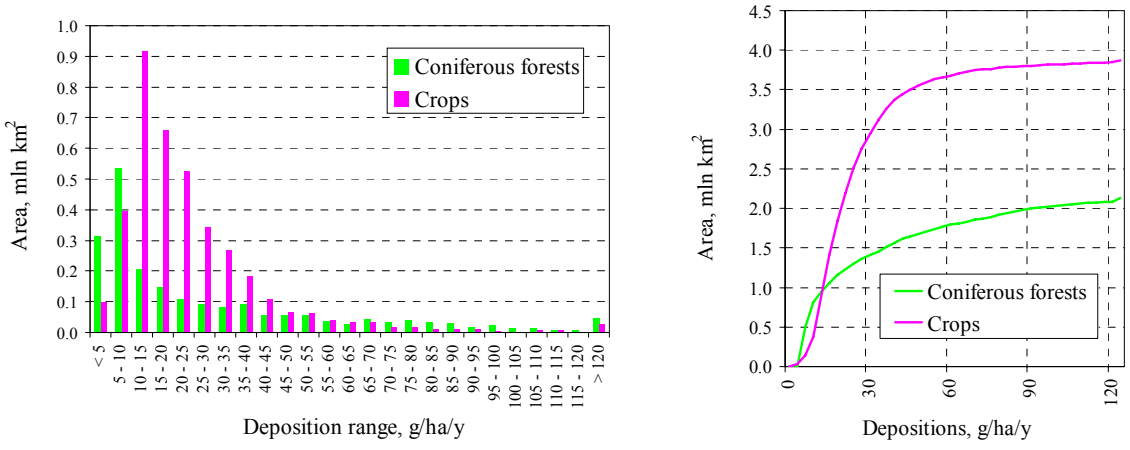

Figure 4-8. Area distribution function (left) and cumulative distribution function (right) of total deposition of lead in 1990.

In 2000 atmospheric deposition fluxes to all ecosystems were significantly lower than in 1990 (Figure 4-9). Deposition fluxes to coniferous forests mainly range from 5 to 30 g $ha^{-1}a^{-1}$ and to croplands from 5 to 15 g $ha^{-1}a^{-1}$. Areas with relatively high deposition fluxes were mostly located in eastern and south-eastern Europe, Italy and Portugal.

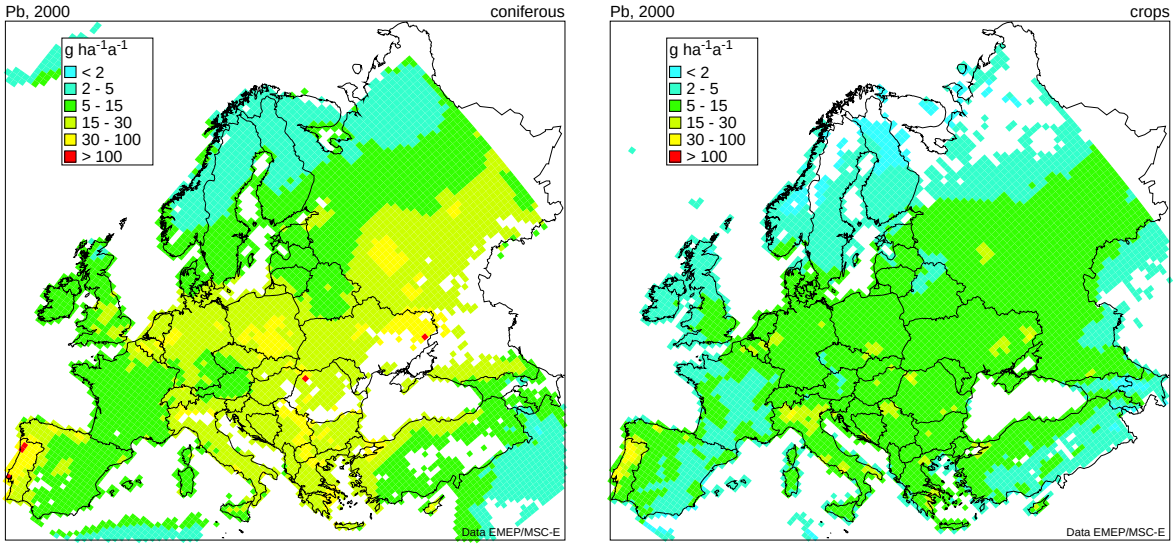

Figure 4-9. Deposition flux of lead in 2000 to coniferous forests (left), and croplands (right).

The decrease of lead pollution levels for the period 1990–2000 is also well reproduced by the area distribution functions of deposition fluxes (Figure 4-10). Over most of the area of coniferous forests and croplands the deposition flux varies from 2 to 8 g $ha^{-1}a^{-1}$ and from 4 to 10 g $ha^{-1}a^{-1}$, respectively (Figure 4-10, left). About 90% of area covered with coniferous forests gets depositions less than 20 g $ha^{-1}a^{-1}$. Depositions over almost 90% of croplands are lower than 12 g $ha^{-1}a^{-1}$ (Figure 4-10, right).

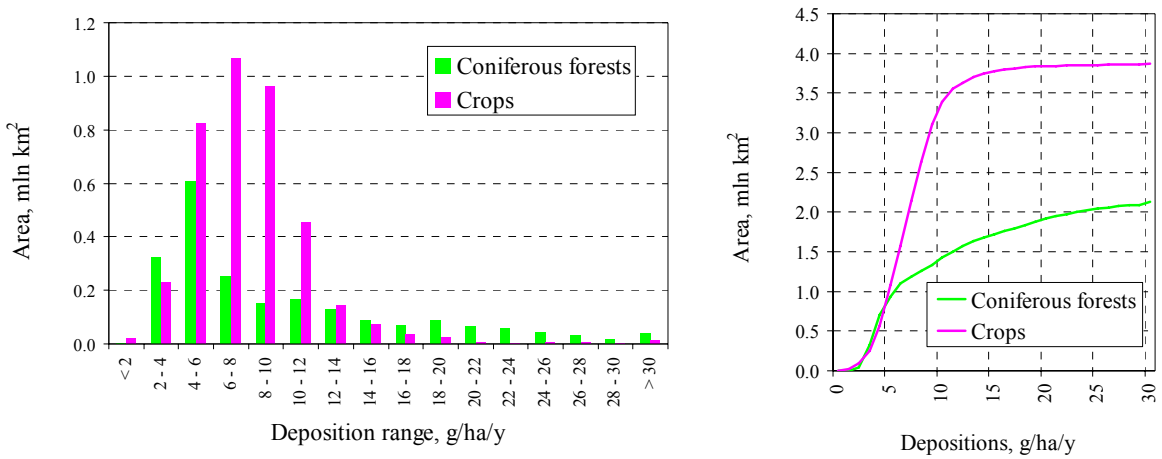

Figure 4-10. Area distribution function (left) and cumulative distribution function (right) of total deposition of lead in 2000.

Depositions in 1990 and 2000, described above, were computed with the use of meteorological data specific for each year. For policy-oriented tasks uncertainty connected with multi-annual variability of meteorological parameters should be excluded. That is why changes in deposition between 1990 and 2000 were analyzed on the base of unified meteorological data. In other words, all changes in deposition fields are fully explained by changes in the emissions.

The deposition of lead between 1990 and 2000 decreased in all countries. On average, depositions to European countries decreased by a factor of 2.7 during this decade. However, this ratio significantly differs between countries and ecosystems. For example, the maximum reduction of depositions to coniferous forests between 1990 and 2000 took place in Luxemburg (factor 8.5; see Figure 4-11). For

croplands for the same period the reduction factor is 9.5 (in the United Kingdom). Reductions in Portugal were by a factor of 1.5 and 1.3 for coniferous forests and croplands, respectively.

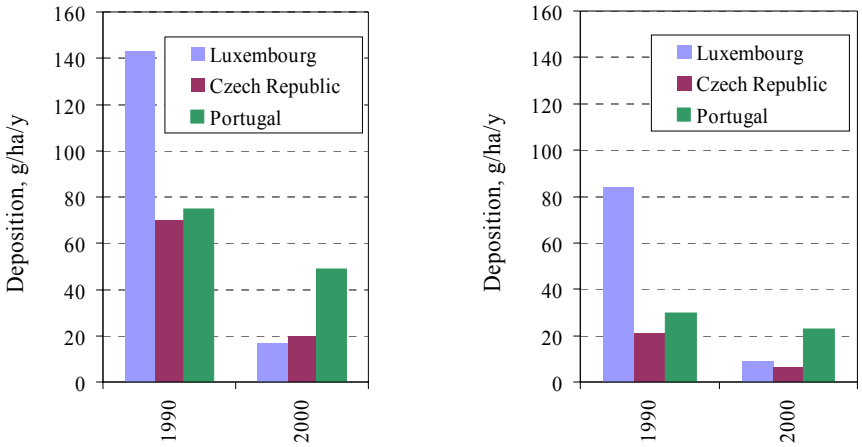

Figure 4-11. Deposition fluxes of lead to coniferous forests (left) and croplands (right) in 1990 and 2000. Luxembourg, Czech Republic and Portugal are examples of countries with high, middle and low rate of deposition reduction, respectively.

Cadmium:

The deposition flux of cadmium in 1990 is highly non-uniform over Europe (Figure 4-12). The most polluted areas were Belgium, the Netherlands, Poland, eastern Ukraine and the Balkans. In these regions the deposition to coniferous forests and croplands can exceed 1.5 g $ha^{-1}a^{-1}$. Northern Scandinavia and the Pyrenees are characterized by relatively low depositions, which range from 0.1 to 0.3 g $ha^{-1}a^{-1}$ over coniferous forests and croplands.

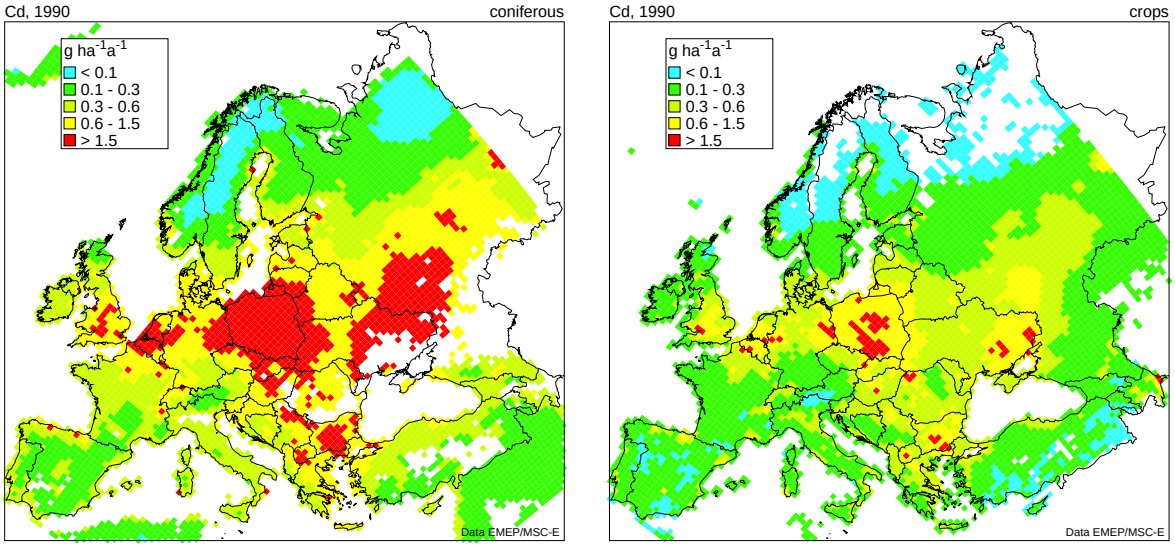

Figure 4-12. Deposition flux of cadmium in 1990 to coniferous forests (left), and crops (right).

The largest area of the distribution of cadmium depositions to coniferous forests and croplands lies in the range from 0.1 to 0.3 g $ha^{-1}a^{-1}$. Depositions in this range an area of almost $0.8 \cdot 10^6$ km^2 (Figure 4-13, left). Over 90% of coniferous forests and 98 % of croplands deposition fluxes do not exceed 1.5 g $ha^{-1}a^{-1}$ (Figure 4-13, right).

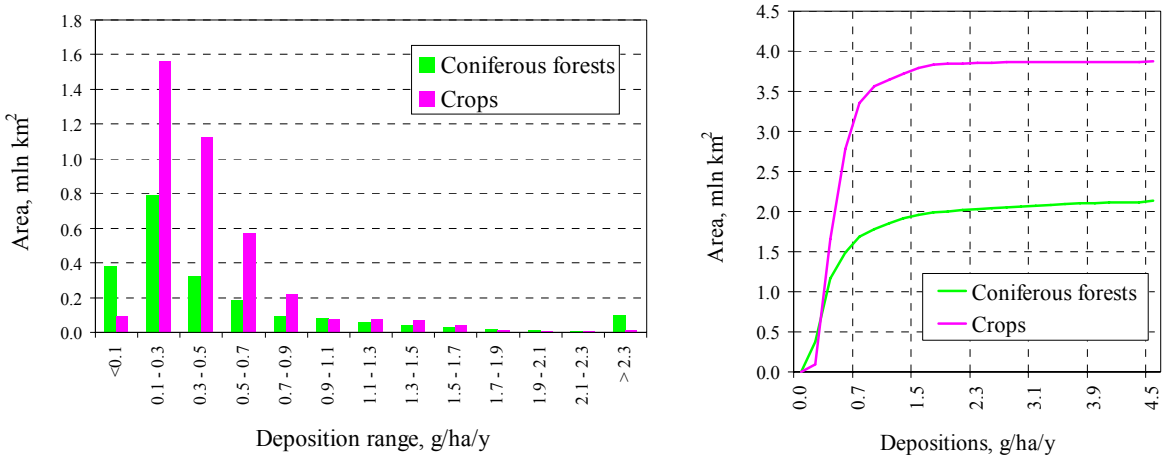

Figure 4-13. Area distribution function (left) and cumulative distribution function (right) of total deposition flux of cadmium in 1990.

In 2000 deposition fluxes of cadmium over coniferous forests were 0.3–1.5 g $ha^{-1}a^{-1}$ and over croplands 0.1–0.6 g $ha^{-1}a^{-1}$ (Figure 4-14). Relatively high deposition fluxes of cadmium over most of its area were identified for Poland. Over coniferous forests the deposition fluxes mostly exceed 1.5 g $ha^{-1}a^{-1}$ and 0.6 g $ha^{-1}a^{-1}$ over croplands.

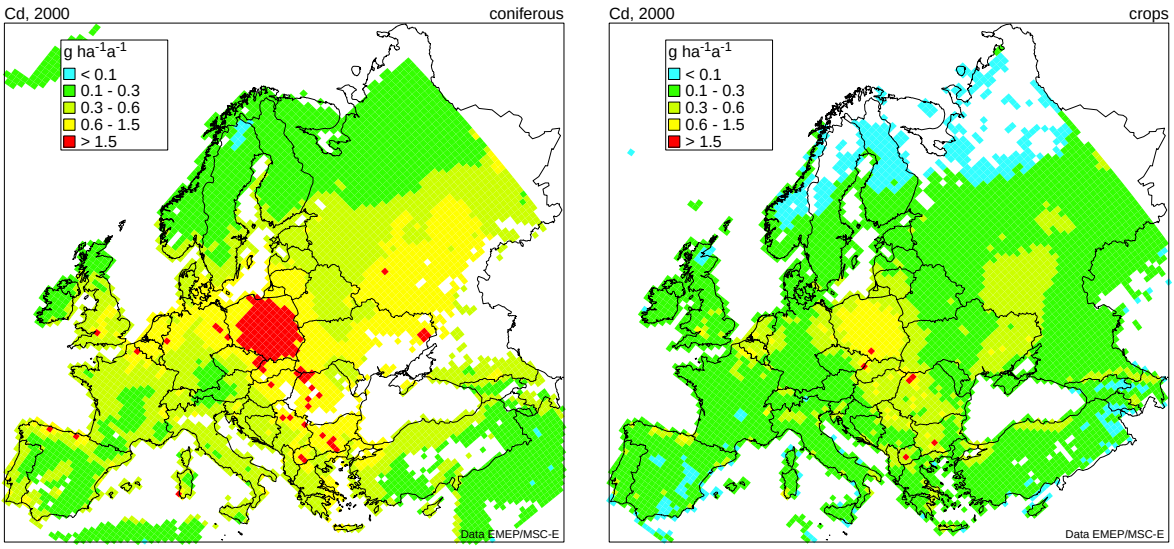

Figure 4-14. Deposition flux of cadmium in 2000 to coniferous forests (left), and crops (right).

The largest area of deposition fluxes in 2000 is in the range of 0.1–0.2 g $ha^{-1}a^{-1}$ for coniferous forests and 0.2–0.3 g $ha^{-1}a^{-1}$ for croplands (Figure 4-15, left). More than 80% ($1.7 \cdot 10^6$ km^2) of the coniferous forests area and 90% ($3.6 \cdot 10^6$ km^2) of croplands receive depositions below 0.5 g $ha^{-1}a^{-1}$ (Figure 4-15, right).

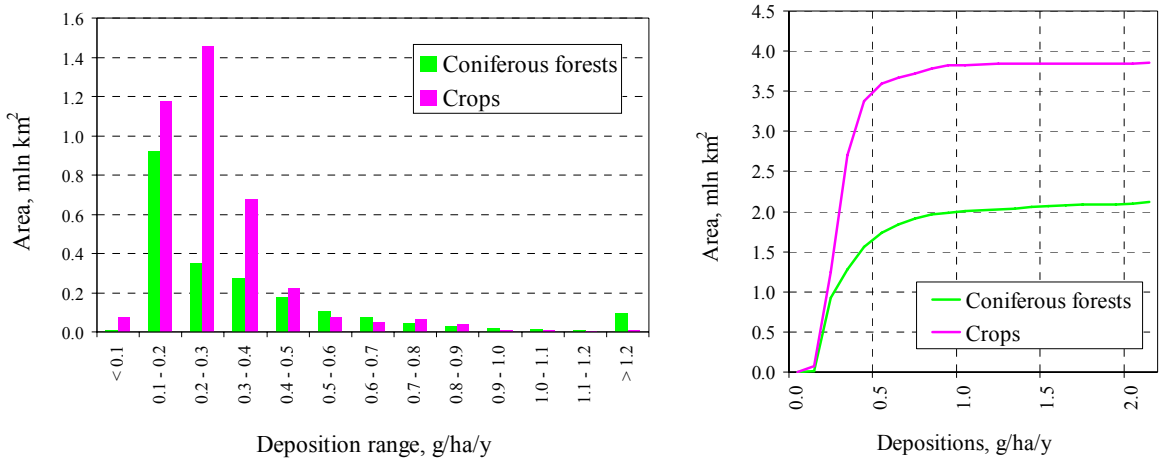

Figure 4-15. Area distribution function (left) and cumulative distribution function (right) of total deposition flux of cadmium in 2000.

Similar to lead, ecosystem-dependent depositions of cadmium were calculated for 1990 and 2000 on the base of the reference year (1990) meteorology. The highest decrease of depositions to coniferous forests occurs over Republic of Moldova and made up around 2.5 times (Figure 4-16). In 75% of countries depositions of cadmium to croplands reduced 1.4 times or more, to coniferous forests – in 1.3 times or more. In Spain and Portugal some increase (up 10 per cent) of depositions took place, caused by cadmium emission increase in Spain.

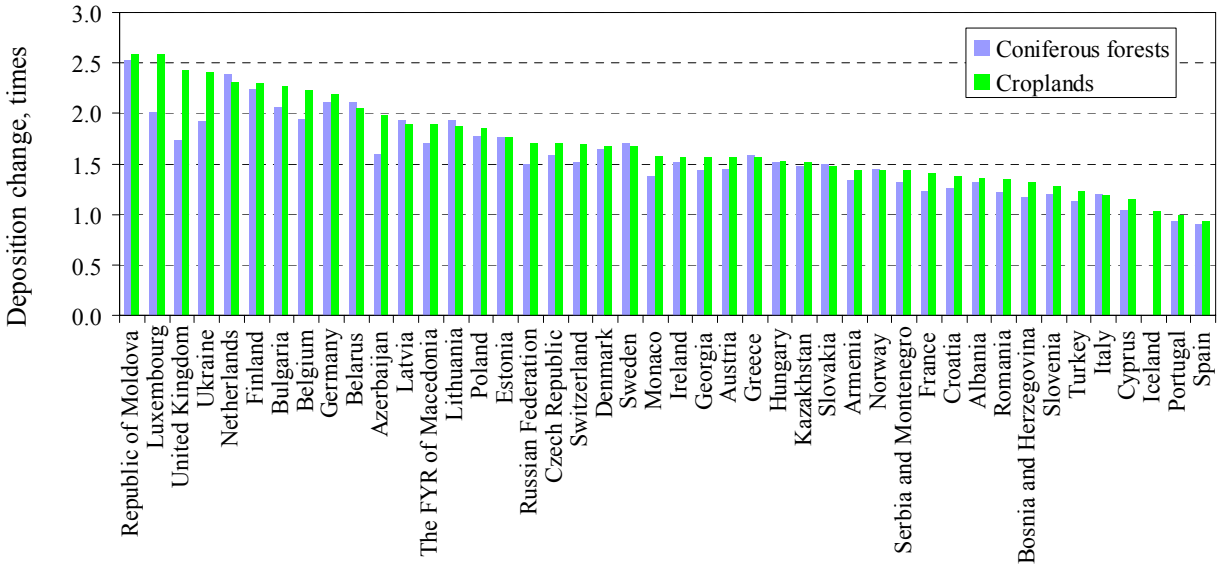

Figure 4-16. Changes of cadmium depositions to coniferous forests and croplands in the decades 1990–2000.

A similar decrease was obtained for other ecosystems. Compared to lead, the decrease of depositions of cadmium was less pronounced. This is a consequence of the lower rate of the emission decrease in Europe (see Table 4-1).

Mercury:

Calculation of exceedances for mercury differs from that for lead and cadmium. In case of mercury the key parameter defining critical limits and loads is not only deposition, but also concentration in precipitation. Mercury concentrations in precipitation in central Europe were typically 20–40 ng L^{-1} in 1990 and 10–20 ng L^{-1} in 2000 (Figure 4-17). Over Scandinavia the concentrations are around 6–10 ng L^{-1} both in 1990 and 2000.

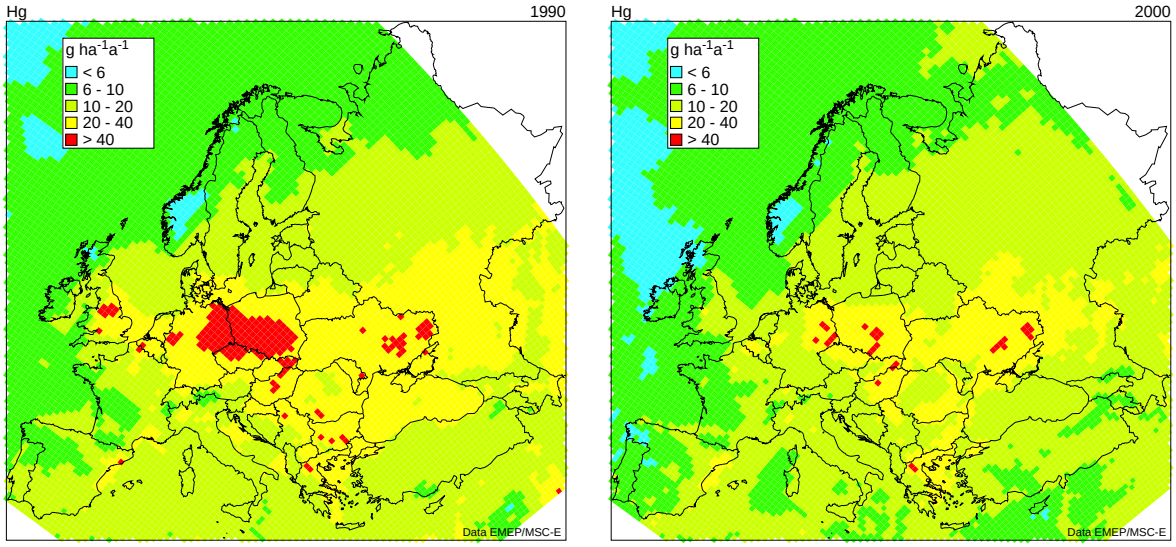

Figure 4-17. Concentrations of mercury in precipitation in 1990 (left) and 2000 (right).

One of the main pathways of mercury into the human body is consumption of fish, where mercury is bio-accumulated. Mercury can enter water bodies mainly because of runoff from catchment areas and because of atmospheric depositions directly to water surfaces. Concentrations of mercury in atmospheric precipitation over inland water bodies in 1990 most frequently fall into the range 8–12 ng L^{-1} (Figure 4-18). For over $0.28 \cdot 10^6$ km^2 (80%) of the water bodies the concentrations do not exceed 20 ng L^{-1} and in over $0.33 \cdot 10^6$ km^2 (95% of the area) do not exceed 30 ng L^{-1}.

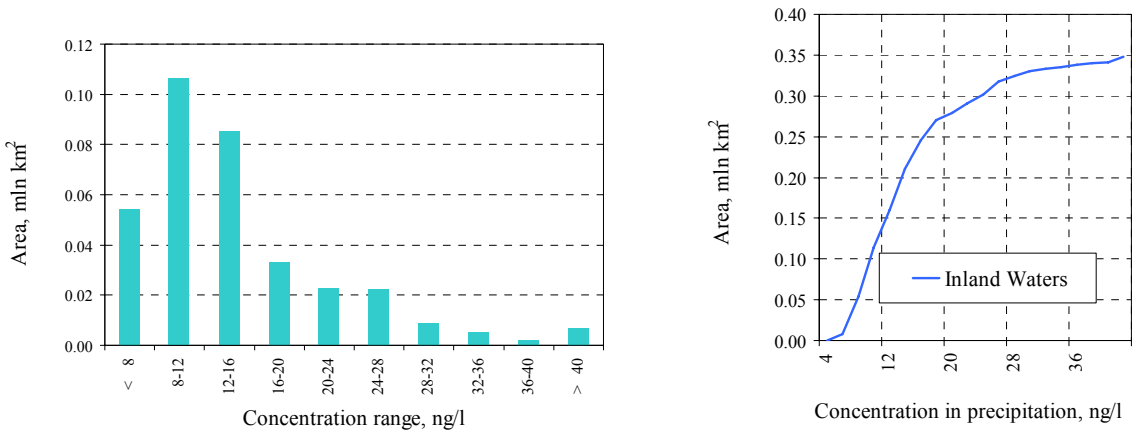

Figure 4-18. Area distribution function (left) and cumulative distribution function (right) of mean annual concentrations in precipitation of mercury over inland waters in 1990.

In 2000 the distribution of concentrations in precipitation was similar to that in 1990. The main difference is smaller areas with relatively high concentrations (Figure 4-19).

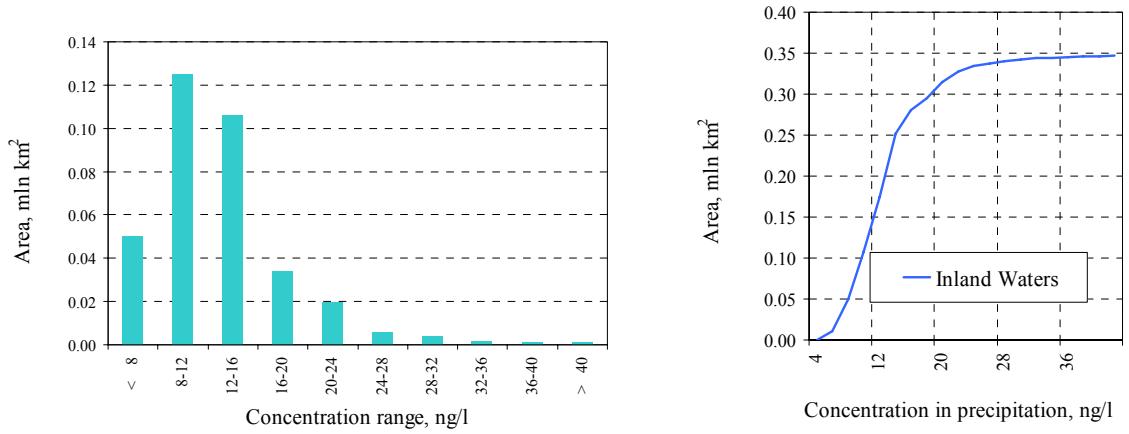

Figure 4-19. Area distribution function (left) and cumulative distribution function (right) of mean annual concentrations in precipitation of mercury over inland waters in 2000.

In order to analyse changes of mercury pollution levels in response of emission changes between 1990 and 2000 special model runs were performed on the base of reference meteorology (1990). For this period the highest reduction of mercury depositions to inland waters was obtained for Germany (2.8 times, Figure 4-20). Compared to lead and cadmium the reduction of mercury depositions over most countries is relatively small. For example, depositions to inland waters reduced by 40% or less in 60% of European countries. The main reason for this is significant influence of mercury sources (both natural and anthropogenic) located outside EMEP domain. In Portugal we can note increase of mercury depositions followed by increase of its emissions between 1990 and 2000.

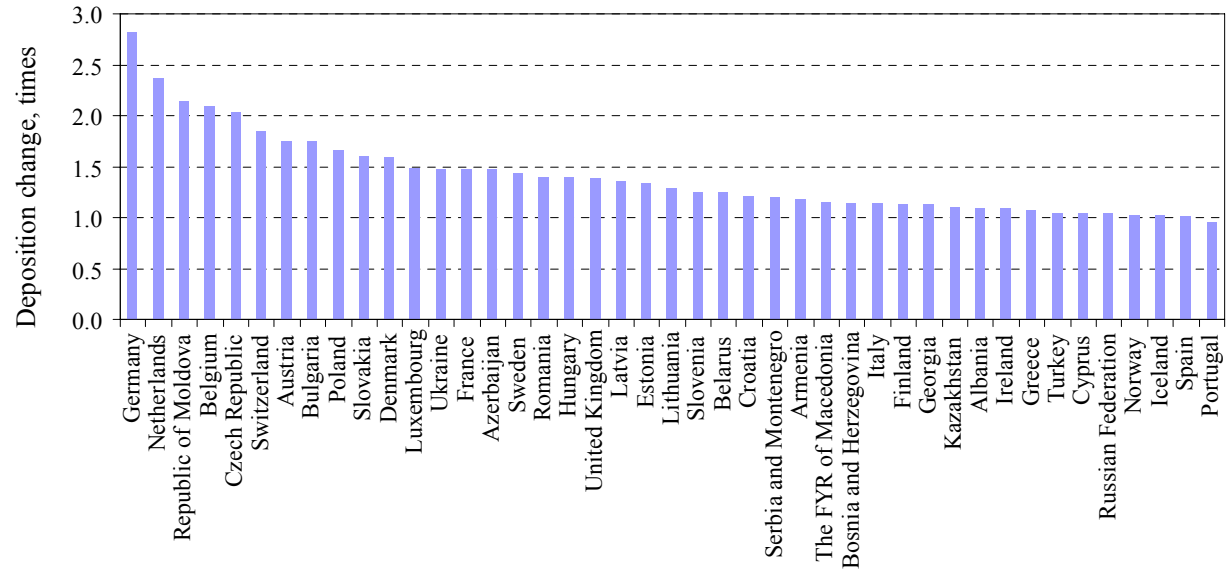

Figure 4-20. Changes of mercury depositions to inland waters in 1990–2000.

4.5 Concentrations of lead and cadmium in air

The European Parliament has established target values of air concentrations heavy metals, in particular, lead and cadmium, in Europe (European Commission, 1997). For lead the value is equal to 0.5 μg m^{-3} and for cadmium 5 ng m^{-3}. According to (European Commission, 2001), EU member states shall take necessary measures to hold the concentrations of carcinogenic air pollutants, in particular, cadmium, below their target values.

Annual mean concentrations in air of these metals were simulated by MSC-E for 1990, 2000 and 2010. In Figure 4-21 (left) concentrations of lead concentrations in air in 2000 are presented. The maximum lead concentration in Europe equals 70 ng m^{-3} and is found in Portugal. Other regions with

relatively high air concentrations of lead are eastern Ukraine (up to 32 ng m^{-3}), north (up to 35 ng/m^{-3}) and south (up to 43 ng m^{-3}) of Italy and north-western Romania (up to 34 ng m^{-3}).

Over most of Europe cadmium concentrations in air lie in the range 0.03–0.3 ng m^{-3} (Figure 4-21, right). Over most part of Poland the concentrations typically exceeded 0.3 ng m^{-3}. The highest concentrations in 2000 occurred in north-western Romania (2.6 ng m^{-3}). Other regions with comparatively high pollution are Bulgaria which maximum air concentrations 1.5 ng m^{-3}, Slovakia (1.2 ng m^{-3}), Macedonia (1.1 ng m^{-3}) and Poland (0.9 ng m^{-3}). Similar to lead, the Scandinavian peninsula is characterised by the lowest concentrations in air in Europe. They are typically below 0.03 ng m^{-3} and rarely exceed 0.05 ng m^{-3}.

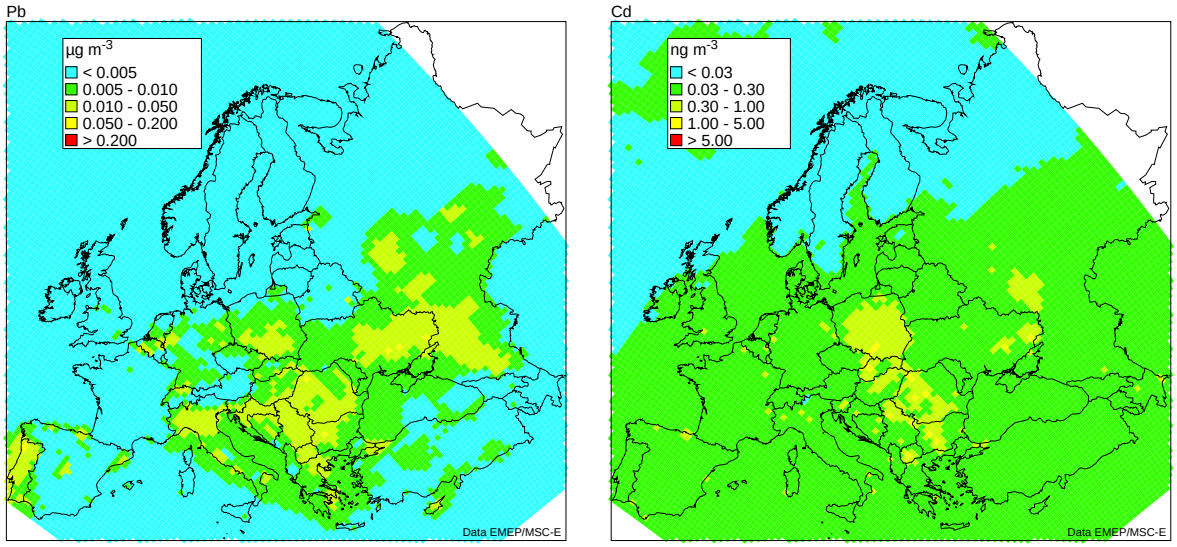

Figure 4-21. Concentrations of lead (left) and cadmium (right) in 2000

4.6 Uncertainties of modelling results

An important characteristic of any numerical model is its sensitivity to the uncertainties of input parameters. Travnikov and Ilyin (2005) performed a sensitivity study and analysis of the uncertainties of MSCE-HM model. The analysis focused on lead and mercury. The former exemplifies characteristics of particle-bound pollutants, whereas the latter on properties of a pollutant occurring in various chemical forms and capable of many chemical transformations. More details concerning this study are presented in Travnikov and Ilyin (2005), whereas in this section the main results are summarized.

Meteorological variability:

The model sensitivity to the variability of meteorological parameters (wind speed, surface pressure, cloudiness, precipitation etc.) was analysed as a separate case since these parameters are adjusted by the meteorological pre-processor and cannot be considered independently. To assess the model uncertainty due to the variability of meteorological parameters a multi-year (1990–2002) calculation was performed with the same emissions data, initial and boundary concentrations. The obtained mean annual fields of the output parameters were compared between each other and with the average value. To evaluate the inter-annual variation of the model results distribution of the relative deviation was calculated:

$$\varepsilon_{ij}^{met} = \frac{Y_{ij}^{\max} - Y_{ij}^{\min}}{2\overline{Y}_{ij}} 100\%, \qquad [4.7]$$

where Y_{ij} is a mean annual value of one of the model output parameters in a grid cell (i,j); and $\overline{Y}_{ij}$ is the parameter average over the whole calculation period. The relative deviation of lead output parameters varies from 10% to 60% in different parts of the model domain. The same range of variation characterises mercury concentration in precipitation and total deposition. However, the variability of total gaseous mercury is noticeably lower and does not exceed 20%. To quantify the

average uncertainty of the model outputs due to meteorological variability the Mean-Square Relative Error (MSRE) was calculated:

$$\varepsilon^{met} = \sqrt{\frac{1}{N}\sum_{i,j}\left(\varepsilon_{ij}^{met}\right)^2}\ , \qquad [4.8]$$

where N is the number of grid cells and summing is performed over all cells of the target area. The MSRE of concentration in the ambient air, concentration in precipitation and total deposition flux for lead and mercury are presented in Table 4-3 along with the range of the relative deviation variation corresponding to 90% confidence interval.

Table 4-3. Characteristics of the model output uncertainty due to the variability of meteorological parameters.

Output parameter	MSRE, %	Range, %
Lead		
Air concentration	28	12 - 44
Concentration in precipitation	26	15 - 37
Total deposition	29	15 - 41
Mercury		
Total Gaseous Mercury (TGM) concentration	7	3 - 11
Concentration in precipitation	28	14 - 42
Total deposition	23	12 - 34

Model sensitivity to parameters and processes:

The model sensitivity to different input parameters and to the model processes formulation was estimated by variation of the parameter or switching off the appropriate process. The obtained mean annual fields of the pollutant concentration in air and in precipitation as well as total deposition flux were compared with the base case. The main model parameters included into the sensitivity analysis are listed in Table 4-4. The table also includes expert estimates of the parameters uncertainty (half interval of the relative error) used in Section 4.6.4 for evaluation of the model uncertainty due to individual parameters. It should be noted that these estimates have rather qualitative character.

Table 4-4. Parameters and processes considered in the sensitivity analysis.

Parameter and processes	Notation	Uncertainty
Lead		
Anthropogenic emissions	E_{ant}	50% *)
Natural emissions and re-emission	E_{nat}	90%
Wet deposition coefficient	L_{wet}	75%
Dry deposition velocity	V_d	75%
Boundary concentration	C_{bound}	90%
Eddy diffusion coefficient	K_z	50%
Liquid water content	LWC	50%
Mercury		
Anthropogenic emissions	E_{ant}	50% *)
Speciation of anthropogenic emission **)	E_{spec}	40%
Natural emissions and re-emission	E_{nat}	90%
Wet deposition coefficient	L_{wet}	75%
Dry deposition velocity (all species)	V_d	75%
Dry deposition of Gaseous Elemental Mercury (GEM)	$V_d\ (GEM)$	90%
Dry deposition of fog	$V_d\ (fog)$	90%
Lateral boundary concentration of GEM	$C_{bound}\ (GEM)$	20%
Lateral boundary concentration of Total Particulate Mercury (TPM)	$C_{bound}\ (TPM)$	90%
Upper boundary concentration	C_{upp}	50%
Oxidation by O_3 in gas phase	$k\_O3(gas)$	50%
Oxidation by O_3 in aqueous phase	$k\_O3(aq)$	50%
Oxidation by OH in gas phase	$k\_OH(gas)$	75%
Oxidation by OH in aqueous phase	$k\_OH(aq)$	75%
Oxidation by Cl_2 in gas phase	$k\_Cl2(gas)$	90%
Oxidation by Cl_2 in aqueous phase	$k\_Cl2(aq)$	90%
Reduction through sulphite complexes	$k\_red(ag)$	50%
Hg ion-chloride equilibrium constant	K_Hg2+	50%

Solution-adsorption equilibrium constant	*K_sorb*	50%
pH of cloud water	*pH*	20%
Chloride ion concentration	[Cl^-]	90%
Aerosol solubility	*K_part*	50%
Liquid water content	*LWC*	50%
Henry's constant for Hg^0	*H_Hg0*	20%
Henry's constant for $HgCl_2$	*H_HgCl2*	75%

*) Only stochastic component of anthropogenic emissions uncertainty is considered. The systematic component (underestimation) is behind the scope of the current research.
**) Fraction of oxidized Hg forms (TPM and Reactive Gaseous Mercury -RGM) in anthropogenic emissions

The change of a model output variable is quantified in each grid cell of the target area by the relative deviation:

$$\varepsilon_{ij}^{Y} = \frac{Y_{ij} - Y_{ij}^{base}}{Y_{ij}^{base}}. \qquad [4.9]$$

To characterize sensitivity of the model output variable Y to variation of input parameter X the sensitivity coefficient is calculated as follows:

$$\frac{\delta Y}{\delta X} = \frac{\sqrt{\frac{1}{N}\sum_{i,j}\left(\varepsilon_{ij}^{Y}\right)^2}}{X / X_{base} - 1}. \qquad [4.10]$$

The presented below analysis of the model sensitivity does not include consideration of separate meteorological parameters by reasons discussed above. Instead, the contribution of these parameters to the model uncertainty is considered in aggregate in Section 4.6.3.

Lead:

The sensitivity coefficients of the main model outputs to uncertainty of input parameters for lead are illustrated in Figure 4-22. The error bars at the figure shows the 90% confidence interval of the sensitivity coefficient variation over the target area. As seen from the figure the model is the most sensitive to anthropogenic, natural emissions and re-emission (at current calculations natural emission and re-emission make up roughly a half of anthropogenic ones). Among other important parameters are the dry deposition velocity and the wet deposition coefficient. On the other hand, the model is only weakly sensitive to such parameters as boundary concentrations and the liquid water content.

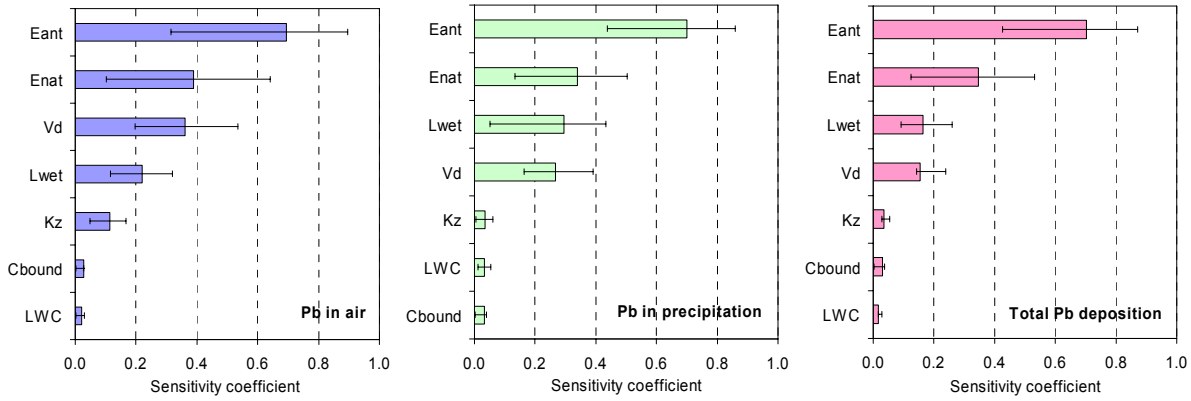

Figure 4-22. Coefficients of the model sensitivity to the main input parameters for Pb concentration in air (left), in precipitation (middle) and for total Pb deposition flux (right). The error bars show 90% confidence intervals.

Mercury:

The character of the mercury model sensitivity is principally different form that described above. The main reason for that is long residence time of the bulk mercury form in the atmosphere – gaseous elemental mercury (GEM) – and chemical transformations in gaseous and aqueous phases governing mercury removal from the atmosphere. The mercury model sensitivity coefficients to uncertainty of the main input parameters are shown in Figure 4-23.

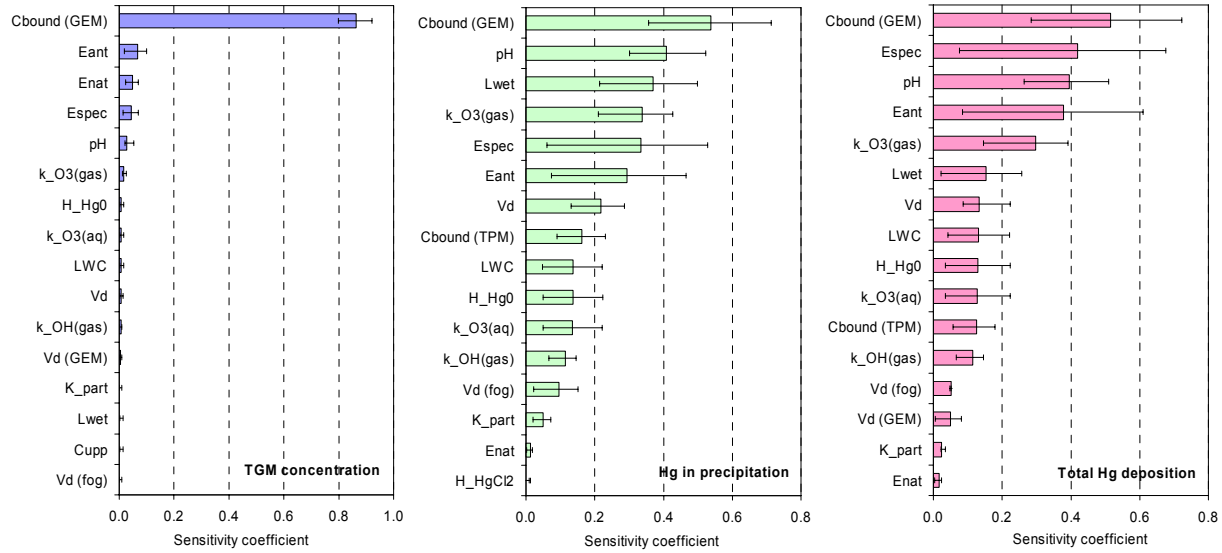

Figure 4-23. Coefficients of the model sensitivity to the main input parameters for TGM concentration (left), Hg concentration in precipitation (middle) and for total Hg deposition flux (right). The error bars show 90% confidence intervals.

The sensitivity of Total Gaseous Mercury (TGM) concentration is dominated by boundary concentration of GEM. The contribution of GEM in total gaseous mercury makes up to 99%. Taking into account very long residence time of GEM in the free troposphere (an order of year) it is obvious that this bulk mercury form can easily reach the centre of Europe or even cross the model domain. Sensitivity of TGM concentration to other parameters is significantly lower. The GEM concentration is the most important parameter for Hg concentration in precipitation and total deposition flux as well. However, since these output variables are mostly defined by oxidized mercury forms, they are also quite sensitive to other parameters responsible for emissions oxidation and removal processes. Among them are anthropogenic emissions and their speciation characteristics, oxidation by ozone in gaseous phase, wet deposition coefficient etc. Besides, as seen a very important parameter is pH of cloud water. It should be noted that at the base values of the model parameters the sulphite channel of Hg reduction in aqueous phase is practically inactive due to suppressing reaction with chloride ion available in excess leading to formation of stable chloride complexes. But situation changes considerably if pH increased because of activation of the reduction channel. It leads to significant decrease of Hg concentration in precipitation. Another specific feature of mercury removal is very low sensitivity to natural emission and re-emission within the model domain. It is expected that mercury emitted from natural sources as well as re-emitted in elemental form. As a result the most part of these emissions flow out the model domain not being oxidized and removed.

Uncertainty due to individual parameters:

The uncertainty of different input parameters can differ significantly. Therefore the contribution of an input parameter to the overall model uncertainty depends not only on the model sensitivity but also on inaccuracy of the parameter itself. To evaluate the uncertainty of a model output Y due to contribution of an input parameter X we multiplies the appropriate sensitivity coefficient by the uncertainty of the parameter ε_x:

$$\mathrm{E}_X^Y = \frac{\delta Y}{\delta X}\varepsilon_X . \qquad [4.11]$$

Estimates of the input parameters uncertainties are presented in Table 4-4. The aggregate contribution of meteorological parameters is based on the results presented in Section 4.6.1. It should be noted that the following analysis results to significant extent depend on the uncertainties of input parameters and should be considered as tentative because of rough character of the input uncertainties estimates.

Lead:

Uncertainties of the main output variables for lead caused by inaccuracies of input parameters are illustrated in Figure 4-24. The most significant uncertainties are introduced by anthropogenic and natural emissions along with re-emission and exceed 30% on average. High uncertainty of natural

emission and re-emission leads to their contribution to the overall uncertainty at least comparable with the anthropogenic one. Meteorological parameters and characteristics of removal processes also cause considerable model uncertainty.

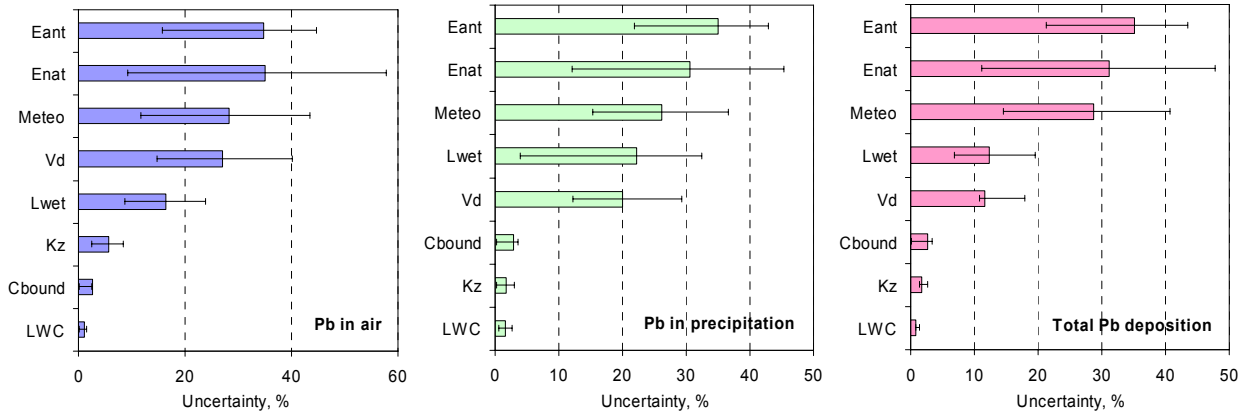

Figure 4-24. Uncertainty of Pb concentration in air (left), in precipitation (middle) and of total Pb deposition flux (right) due to inaccuracy of main input parameters. The error bars show 90% confidence intervals.

Mercury:

The most important parameters determined uncertainties of mercury concentration in air, in precipitation as well as total deposition flux are ranged in Figure 4-25. The highest uncertainty of total gaseous mercury (TGM) concentration is due to the boundary concentration of GEM and do not exceed 20%. On the other hand, this parameter is not so important for two other output variables. The uncertainty of Hg concentration in precipitation is mostly determined by uncertainty of meteorological parameters, removal characteristics and oxidation by ozone in gas phase. Besides, anthropogenic emissions and boundary conditions for TPM are also important. Meteorological variability and anthropogenic emission along with its speciation introduced the most significant uncertainty to total Hg deposition flux.

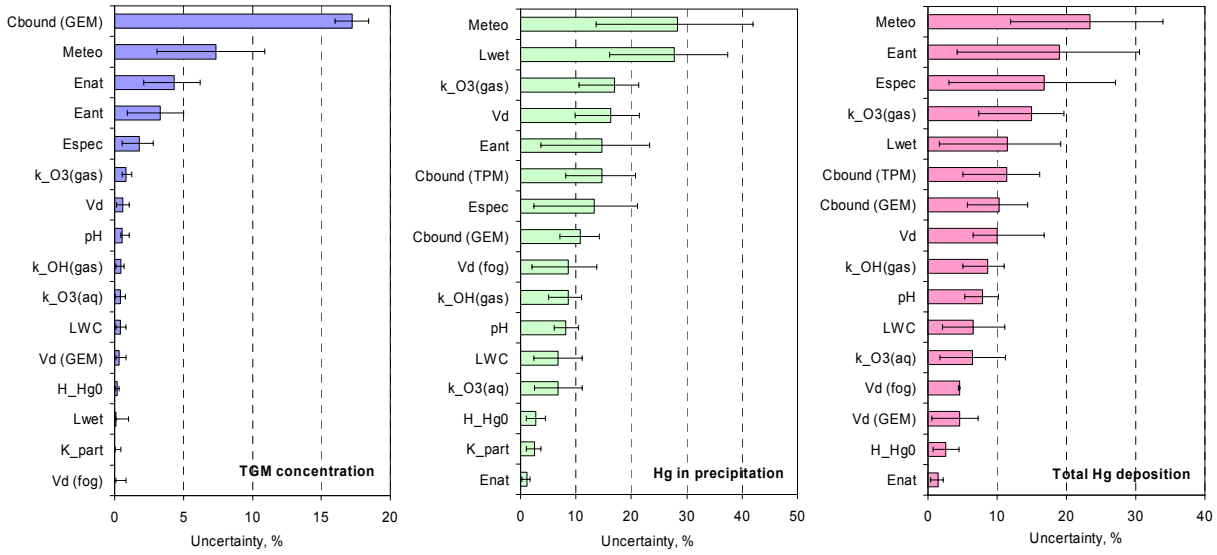

Figure 4-25. Uncertainty of TGM concentration (left), Hg concentration in precipitation (middle) and of total Hg deposition flux (right) due to inaccuracy of main input parameters. The error bars show 90% confidence intervals.

Overall uncertainty:

The overall model uncertainty can be roughly estimated from the uncertainties due to individual parameters using the following equation:

$$E^Y = \sqrt{\sum_X \left(E_X^Y\right)^2} \,. \qquad [4.12]$$

Estimated uncertainties of the main model parameters for lead and mercury are presented in Table 4-5. As it was mentioned above results of this analysis to significant extent depend on the uncertainties of input parameters and should be considered as tentative.

The intrinsic model uncertainty includes contributions of all model parameters except anthropogenic, natural emissions and re-emission. The overall model uncertainty along with other parameters includes uncertainty due to anthropogenic, natural emissions and re-emission. However, only the stochastic component of anthropogenic emissions uncertainty is considered. A possible influence of the systematic error (underestimation) is not included. The range indicates 90% confidence interval of the uncertainty variation over the model domain. The intrinsic model uncertainty of lead concentration in air, concentration in precipitation and total deposition varies from 20% to 65% over the domain with average values 43%, 40% and 33% respectively. The overall uncertainties reach 60% on average (the range 30–97%). The intrinsic model uncertainty of mercury differs for different outputs. It does not exceed 20% on average for TGM concentration (the range 16–22%) but reaches 40% for total deposition and 50% for concentration in precipitation (the ranges 20–57% and 29–74%, respectively). The overall uncertainty for mercury only slightly exceeds the intrinsic one indicating limited effect of emissions uncertainty on the model results.

Table 4-5. Model intrinsic and the overall uncertainties of the main model output parameters.

Output parameter	Intrinsic Uncertainty,%	Range, %	Overall *) Uncertainty, %	Range, %
		Lead		
Air concentration	43	22 - 64	65	39 – 97
Concentration in precipitation	40	20 - 57	61	32 – 85
Total deposition	33	19 - 49	58	31 – 81
		Mercury		
TGM concentration	19	16 - 22	20	16 – 23
Concentration in precipitation	53	29 - 74	56	29 – 80
Total deposition	39	20 - 57	46	20 – 70

*) Only stochastic component of anthropogenic emissions uncertainty is considered. The systematic component (underestimation) is not included.

4.7 Additional model runs with higher emissions of heavy metals

Results of the modelling were checked by a comparison with available measurements. Measurement data used are prepared by the Chemical Coordinating Centre (CCC) and include concentrations in air and concentrations in precipitation (Berg et al., 2002, 1996). The comparison demonstrates that modelled concentrations of lead significantly underestimate measurements (Figure 4-26). A similar degree of underestimation was obtained for cadmium. Reasons can be an underestimation of the emission data, uncertainties of the model parameterisations and inaccuracies in the measurement data. Relatively high correlation coefficients imply that the model captured the spatial distribution of the pollution levels. The magnitude of the underestimation is similar both for concentrations in air and in precipitation. This implies that the physical processes in the model are described reasonably well. Although measured values could be doubtful at a few sites, it is difficult to believe that the entire set of measurements is inaccurate. That is why we think, that the most probable reason for the underestimation of depositions is too low emission data.

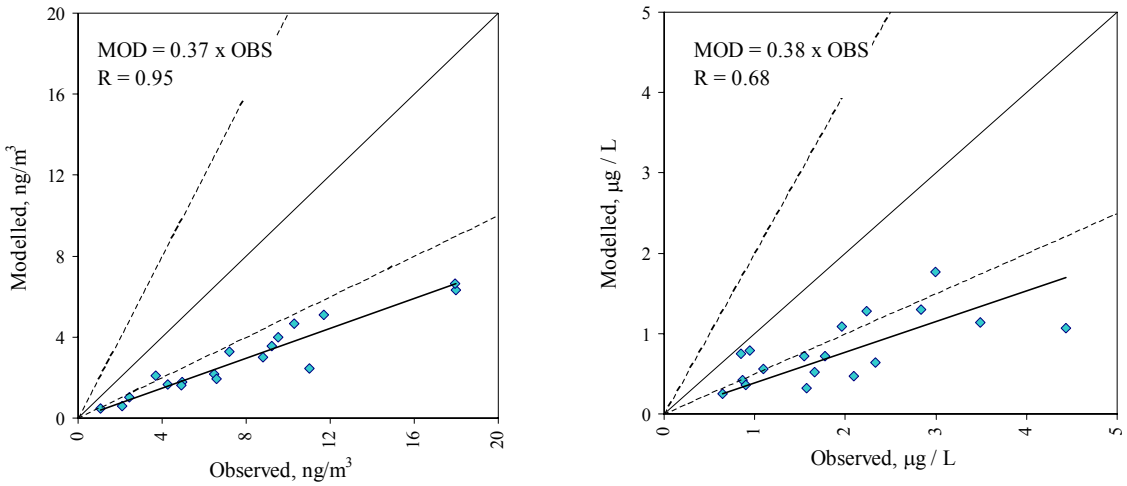

Figure 4-26. Comparison of modelled and measured air concentrations (left) and concentrations in precipitation (right) of lead. R = correlation coefficient. Dashed lines indicate the factor-of-2-range.

In order to simulate concentration and deposition fields, which better agree with measurement data, MSC-E performed additional model runs of lead pollution levels, using higher emission. An additional emission was added (called 'unaccounted emissions'), assumed to include natural emission, re-emission and possible missing anthropogenic emission. The total value of this unaccounted emission within EMEP region is 28 kt a^{-1}. The comparison of modelled and measured concentrations shows that the correlation coefficients are significant (0.93 for air and 0.66 for concentration in precipitation) (Figure 4-27). Mass of the pollutant in air and in precipitation is reproduced reasonably, because regression coefficients are around unity both for concentrations in air and in precipitation (Figure 4-22). Thus, the increase of overall atmospheric emissions in the European region results in much more realistic pollution levels.

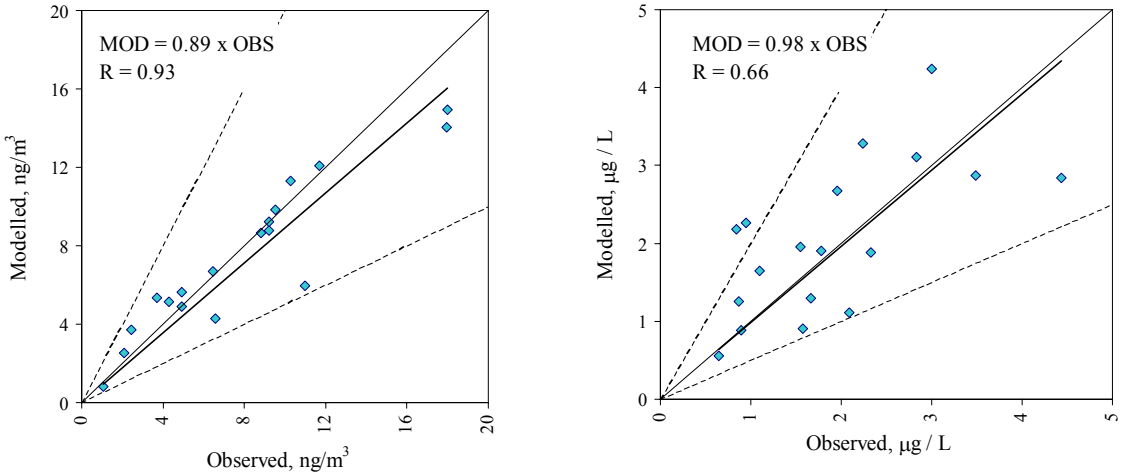

Figure 4-27. Comparison of modelled and measured air concentrations (left) and concentrations in precipitation (right) of lead for simulations with the higher emissions. R = correlation coefficient. Dashed lines indicate the factor-of-2-range.

Maps of the spatial distribution of lead depositions to coniferous forests, computed with the reported and elevated emissions indicate a significant increase in deposition fluxes everywhere (Figure 4-28). For example, deposition fluxes over most of Poland, the Netherlands and Belgium in case of elevated emission exceed 50 g $ha^{-1}a^{-1}$, whereas for reported emissions they ranged mainly from 15 to 50 g $ha^{-1}a^{-1}$.

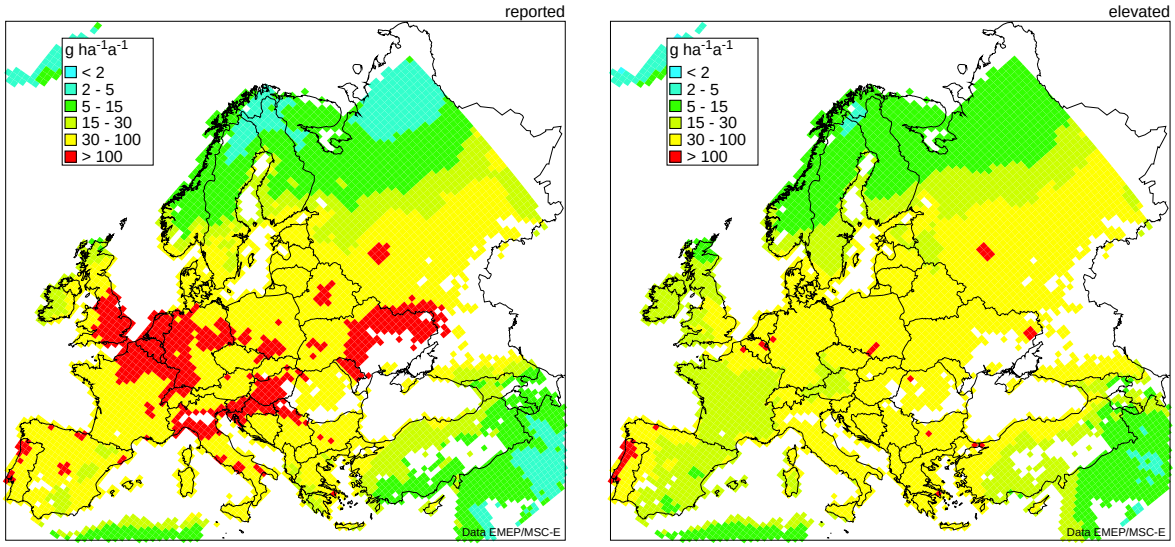

Figure 4-28. Deposition fluxes of lead to coniferous forests in 2000 computed on the base of reported (left) and elevated emission (right).

Although we believe, that too low emission data is the main reason for a substantial underestimation of observational results, other uncertainties also deserve attention. The main task of MSC-E is to carry out investigation of the most important factors controlling model performance. This investigation includes the review of the model parameterisations, input data and quality of measurements.

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5. More on Exceedances of Critical Loads

Jaap Slootweg, Jean-Paul Hettelingh, Maximilian Posch

Introduction

Exceedances are computed by comparing critical loads and levels with atmospheric depositions and concentrations, for each of the effects 1 to 5 described in Chapter 2. In addition also a preliminary assessment of non-atmospheric contributions of heavy metals from applying manure and fertilisation is provided. Throughout this chapter only depositions for the year 2000 are used, computed by EMEP MSC-East using the 1990 meteorological data.

5.1 Average Accumulated Exceedance

Accumulated Average Exceedances (AAE) have been computed to identify and map areas (grid cells) where atmospheric metal depositions are higher than critical loads. An AAE is the ecosystem area-weighted sum of the individual exceedances (deposition minus critical load, with zero for non-exceedance) of all ecosystems in a grid cell. The AAE is defined as:

$$AAE = (A_1Ex_1 + \ldots + A_nEx_n)/(A_1 + \ldots + A_n)$$

where A_i is the area of the i-th ecosystem in a grid cell and Ex_i its exceedance (i=1,…,n). In Figure 5-1 the AAE for a given deposition (D_a) is given by the grey area. (See also Posch et al., 2001, Mapping Manual, Chapters 7 and 8).

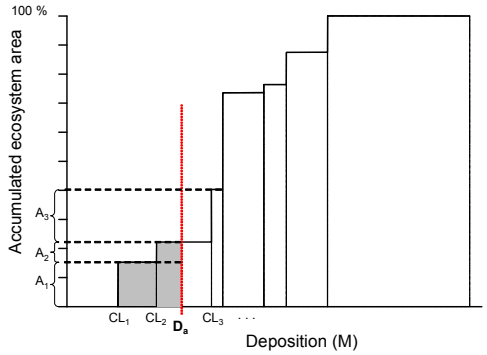


Figure 5-1. Accumulated Average Exceedance (AAE).

5.2 Exceedances for ecotoxicological effects and groundwater protection

The methodology used to compute the critical loads of Cd, Pb and Hg distinguishes between receptors and pathways towards the endpoints. The combinations of receptors, pathways and endpoints considered in the call are translated to combinations of ecosystem types and the effects listed in Table 5-1 (see also Chapter 1)

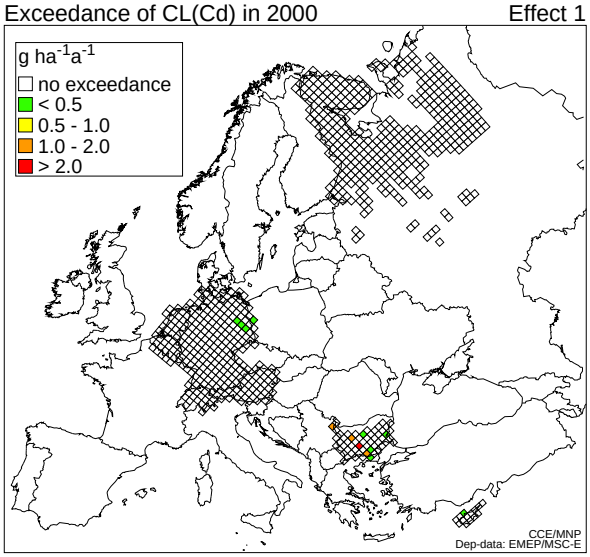
Table 5-1. Effects and heavy metals for which the critical loads are calculated (see also Table 1-1).

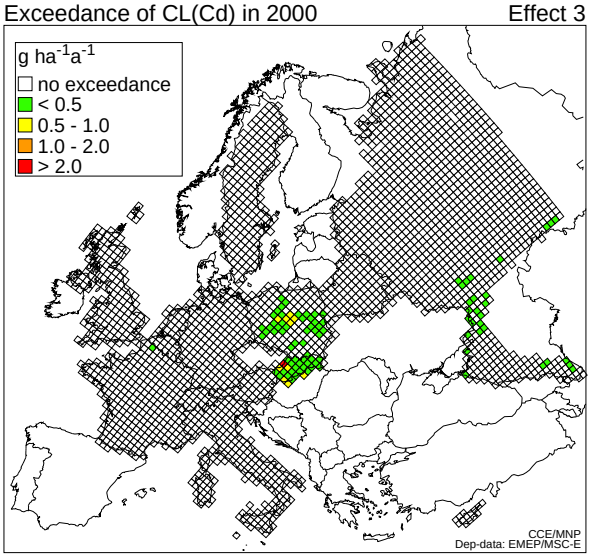
Effect_nr	Effect	Ecosystems	Metals
1	Human health effects (drinking water)	Terrestrial ecosystems	Pb, Cd, Hg
2	Human health effects (food quality)	Terrestrial ecosystems	Cd
3	Ecotoxicological effects	Terrestrial ecosystems	Pb, Cd, Hg
4	Ecotoxicological effects	Aquatic ecosystems	Pb, Cd
5	Human health effects (food quality)	Aquatic ecosystems	Hg

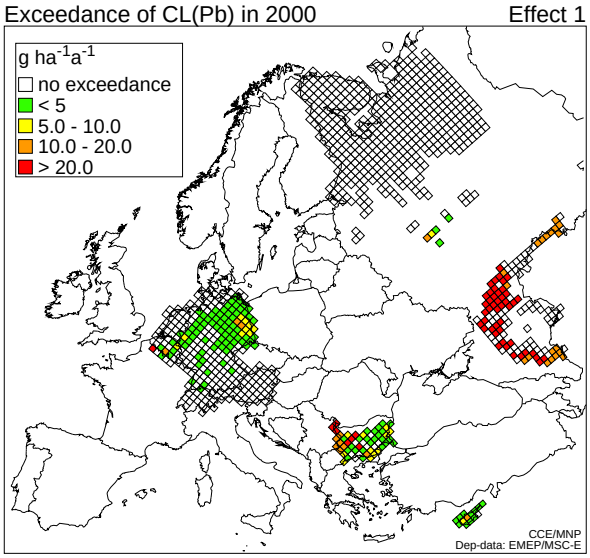
Figure 5-2 shows the AAE for effect 1 (drinking water) and effect 3 (ecotoxicological) for all three metals. It illustrates that exceedances of the three heavy metals occur both for effects 1 and 3 but with varying magnitude and geographic distribution; The AAE of the critical load of Cd prevails for effect 3 in a limited area of Poland and Slovakia. The critical loads of Pb and Hg are exceeded especially with respect to effect 3 in most of the countries that submitted data for the effect. The methodology for effect 3 leads generally to lower critical loads. Grid cells which are not shaded indicate the availability of submitted critical loads that are, however, not exceeded. Blank areas without plotted grid cells indicate the lack of submitted data for effect 1 or 3.

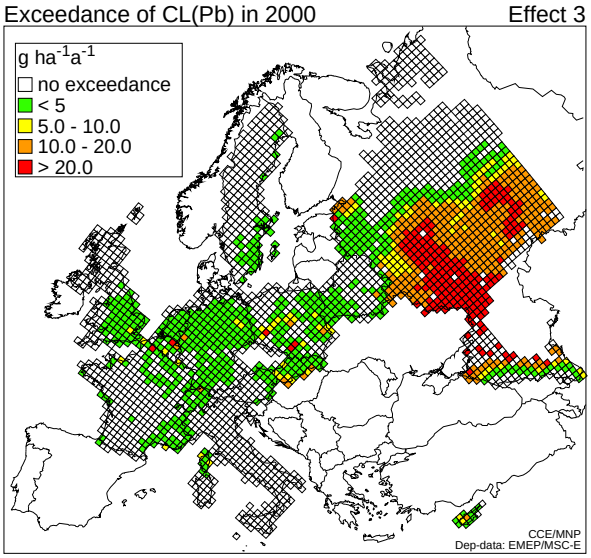
As described in chapter 2, only Walloon (Belgium) has submitted critical loads for effect 4 (Ecotoxicological effects in aquatic ecosystems. *The critical loads for effect 4 are not exceeded.* Critical loads based for effect are only exceeded in the Crimea (Ukraine). Effect 5 is only relevant for mercury for which also a threshold is defined that is related to the concentration in precipitation, The exceedance of a concentration is defined as Average Concentration Exceedance (ACE) and calculated similar to the AAE. This effect is treated separately from other effects, and the ACE is given in Chapter 1 (Figure 1-3).

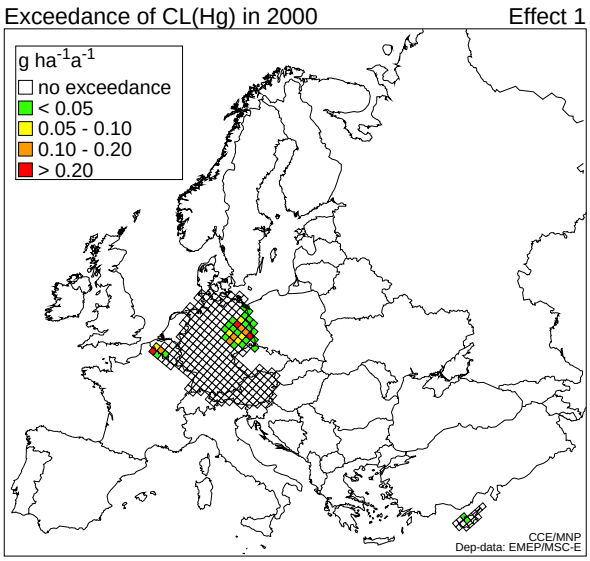
Figure 5-2. Average Accumulated Exceedance for effect 1 (left) and effect 3 (right) for Cd (top), Pb (centre) and Hg (bottom).

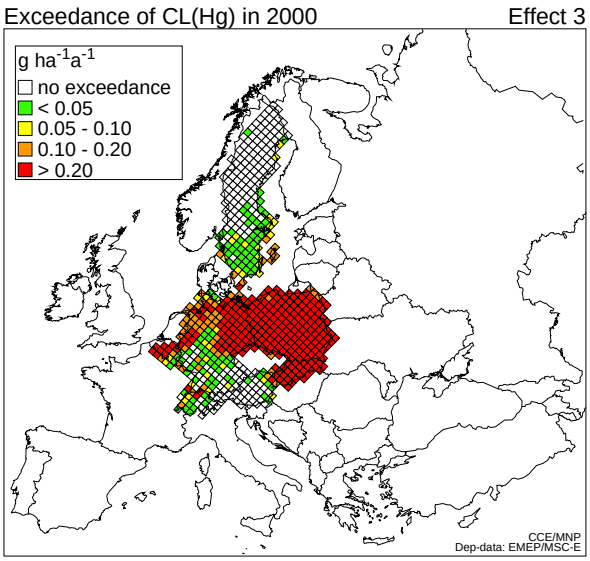












5.3 Exceedances including agricultural inputs

For agricultural areas the application of manure and fertilisers are part of the heavy metals load to the system. Figure 5-3 shows the distribution over Europe of Cd and Pb inputs for the sum of manure and fertiliser as estimated by Van der Hoek and Bouwman (2005, see Appendix C). Cadmium enters the agricultural system mostly through manure, in particular in the west of Europe. Lead turns out to be a compound both of manure, with a rather broad application distribution over Europe, but also of fertilizers with an application focus in western Europe.

Exceedances caused by agricultural inputs alone are shown in Figure 5-4. The resulting cadmium input does not cause exceedances anywhere in Europe, whereas lead leads to low exceedances, especially in the Netherlands and in the eastern part of Austria. Empty grid cells indicate the availability of both critical loads for agricultural areas and agricultural inputs but no exceedance.

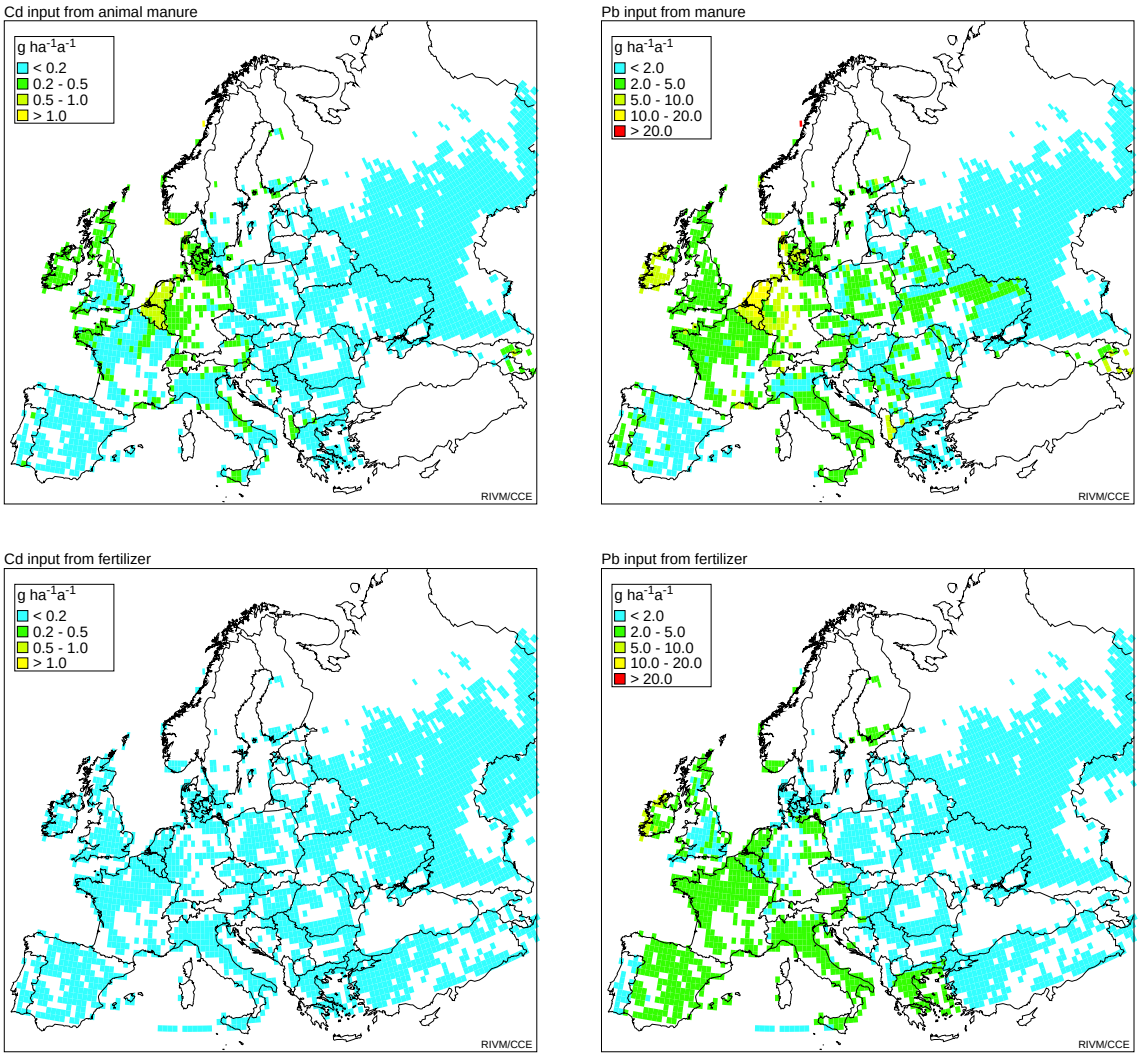


Figure 5-3. Inputs to agricultural areas of cadmium (left) and lead (right) by manure (top) and fertilisers (bottom).

Agricultural inputs should be added to atmospheric deposition to assess total exceedance. Only agricultural areas are considered. (As a consequence total exceedance in grid cells containing agricultural areas can be lower than exceedances shown for the same grid cell in Figure 5-2 or in chapter 1, where all ecosystems are considered.) Total exceedance caused by agricultural and atmospheric inputs are shown in Figure 5-4. It illustrates that the total exceedance for lead turns out to be particularly important.

This raises the question of the importance of agricultural inputs relative to atmospheric deposition. This is illustrated in Figure 5-5. In this figure the source that causes exceedance is plotted. There are

five cases. If the total input is below the critical load (CL) there is no exceedance (white grid cells). Either one of the sources (deposition or agricultural input) alone can exceed the critical load (light blue and orange cells, respectively). In some areas only the sum of the two inputs exceeds the CL (yellow; mostly in central Germany), but the Netherlands and the eastern part of Austria are exceeded by both sources (dark blue). The cases and the colours in the legend are graphically explained by Figure 5-6.

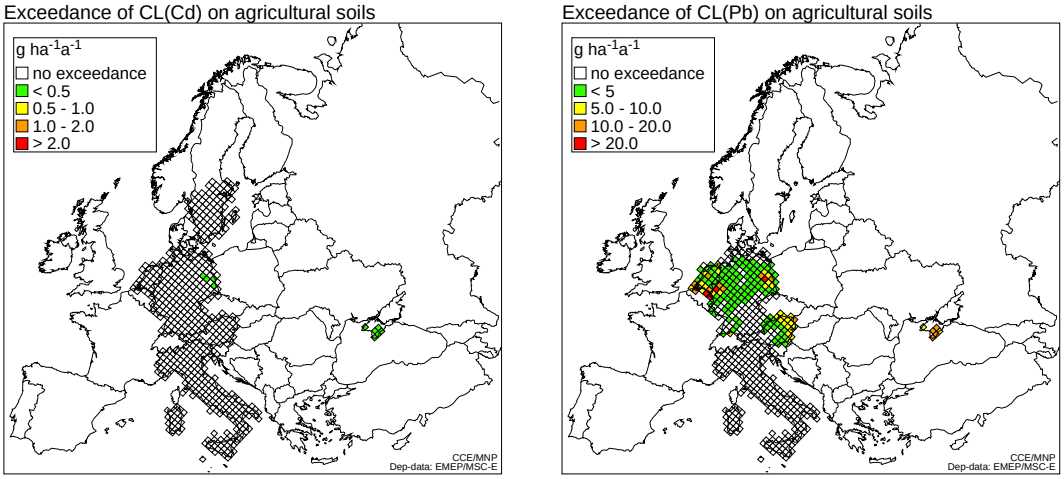


Figure 5-4. Exceedance of critical loads of Cd (left) and Pb (right) by deposition and application of manure and fertilisers.

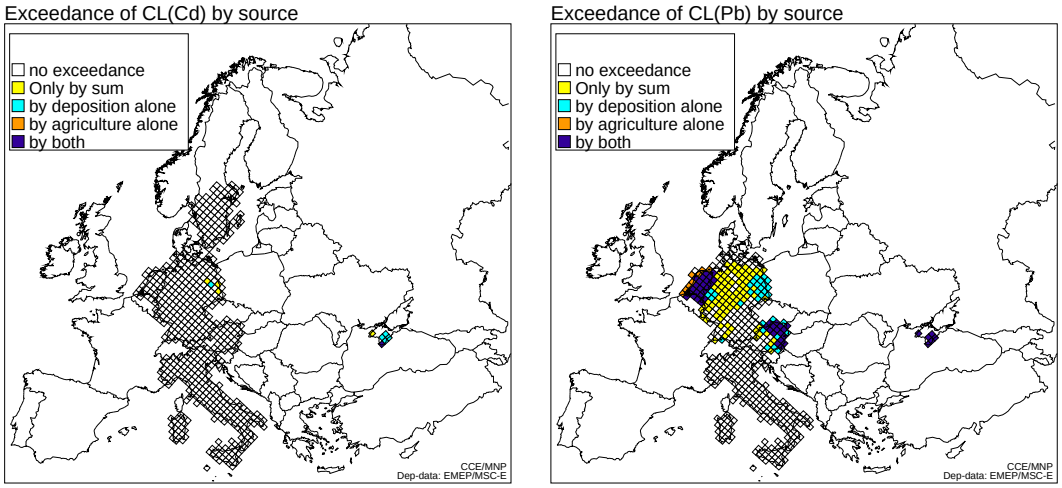


Figure 5-5. Source(s) of the exceedance of Cd (left) and Pb (right).

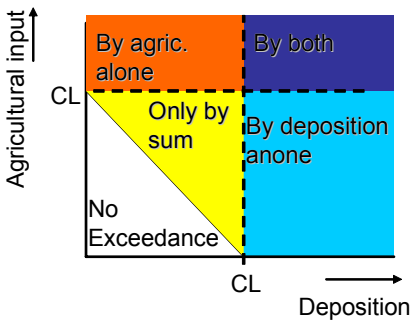


Figure 5-6. Possible cases for the exceedance of critical loads when considering both deposition and agricultural inputs.

5.4 Influence of meteorology on exceedances

For a comparison with measurements, depositions should, of course, be calculated with the meteorological input of the period (year) under consideration. For the illustration of the longer-term development, but especially for scenario analyses, it is more illustrative to use long-term (climatic) averages; or in the absence of such, a so-called representative meteorology (see Chapter 4 for more details on depositions). Here, as a sensitivity analysis, we compare the exceedances of Cd and Pb for the year 2000 obtained when (a) using 2000 meteorology, and (b) using 1990 meteorology, which is identified as more 'representative' (see Chapter 4). The resulting maps are shown in Figure 5-7. They show comparable patterns, but also quite some differences: E.g., CL(Pb) in 2000 is exceeded in most of Sweden using 2000 meteorology, whereas with 1990 meteorology (and same emissions!) it is only exceeded in parts of southern Sweden. Also in some other areas the magnitude of exceedance can be quite different. This shows that not only good emission data are important, but also care has to be exercised when comparing exceedance maps over a longer time period.

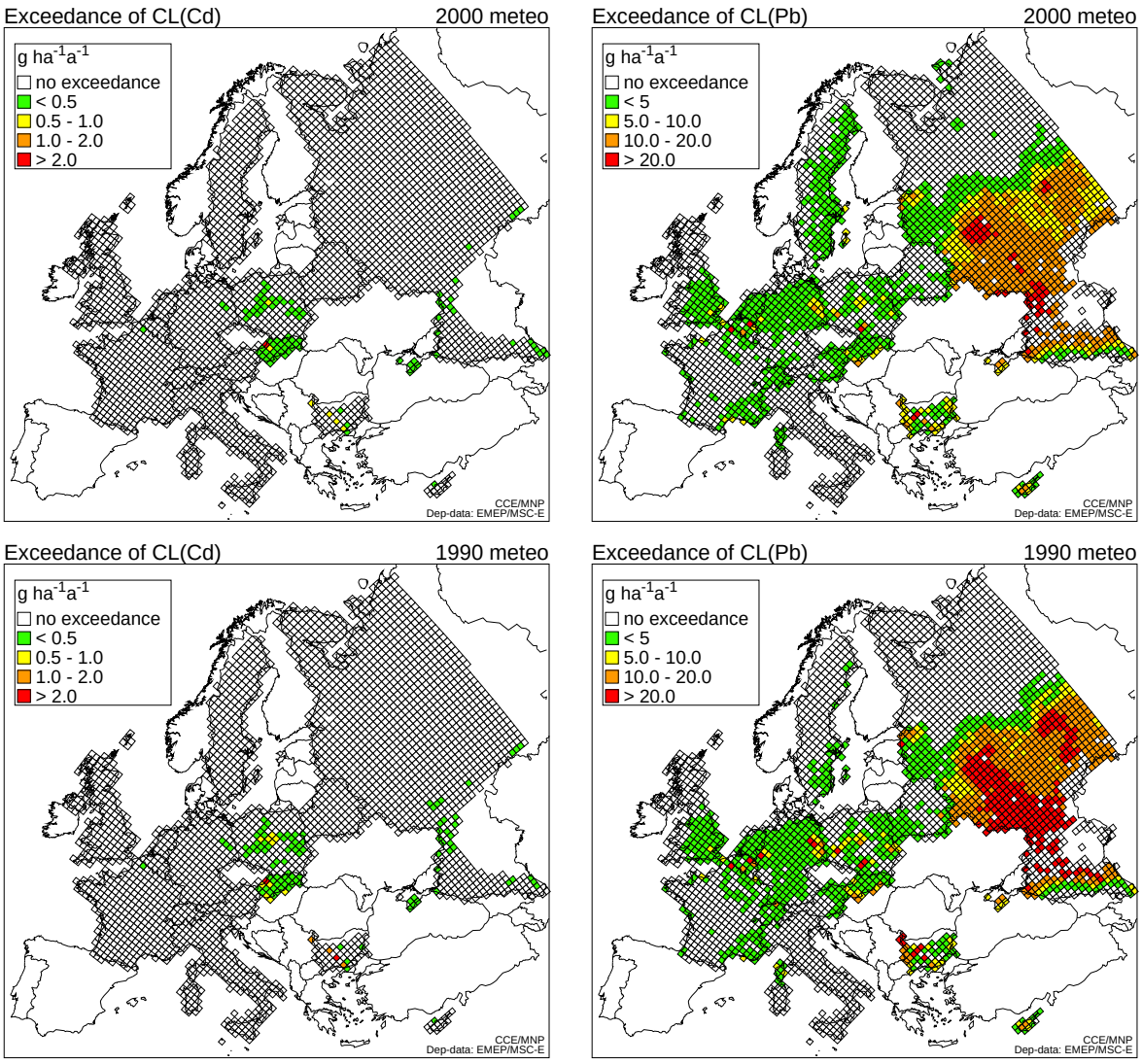


Figure 5-7. Exceedance of CL(Cd) (left) and CL(Pb) (right) with the actual depositions in 2000 (top) and the 2000 depositions calculated with 1990 meteorological data (bottom).

Part II. National Focal Centre Reports

This part consists of the national reports describing and documenting the submitted data as send to the Coordination Center for Effects (CCE) by the National Focal Centres (NFCs). The NFC reports were formatted, but were neither reviewed nor edited.

AUSTRIA

National Focal Centre

Christian Nagl
Umweltbundesamt GmbH
Department of Air Quality Control
Spittelauer Lände 5
1090 Vienna
tel: +43-1-313 04 5866
fax: +43-1-313 04 5400
christian.nagl@umweltbundesamt.at
www.umweltbundesamt.at

Collaborating institution

Erik Obersteiner
Umweltbundesamt Gmbh
Department of Terrestrial Ecology
Spittelauer Lände 5
1090 Vienna
tel: +43-1-31 304-3690
fax: +43-1-31 304-3700
erik.obersteiner@umweltbundesamt.at
www.umweltbundesamt.at

Introduction

In response to the call for data of October 2004 a new dataset of critical loads of cadmium (Cd), lead (Pb) and mercury (Hg) is provided. Calculations, assumptions and default values are generally in accordance with the Mapping Manual (UBA, 2004), Chapter 5.5 from 30.09.2004.
Critical loads are calculated for terrestrial ecosystems (arable land, grassland, forests) only, addressing human health effects and ecotoxicological ecosystem effects. The calculations are based on the sample plots of the Austrian forest soil inventory of the *Austrian Federal Office and Research Centre for Forests* (FBVA 1992; 503 sample plots) and the soil inventories for agricultural land of the Austrian federal provinces (2450 sample plots).
A detailed description of the data and the methods used for their derivation is given in the next section.

Calculation methods and data sources

Ecosystems (EUNIS)
Four forest ecosystem types are distinguished according to the EUNIS classification: G1 (Fagus sylvatica, Quercus robur), G3 (Picea abies, Pinus sylvestris, Larix decidua), G4 (mixed forests) and G5.6, which includes unmanaged mountain forests, where no biomass uptake takes place. Grassland splits into E2 (intensive grassland, meadows) and E4 (alpine grassland, pastures), arable land is set to I1.1.

Ecosystem Area
The forest ecosystem area for each dataset was identified by dividing the known ecosystem area per EMEP grid cell (information from forest inventory) by the number of soil inventory points falling into this ecosystem type. The agricultural ecosystem area (arable land, grassland) is known for each district only. After intersecting the district polygons with the EMEP grid, ecosystem area information was provided by dividing the ecosystem area per split polygon by the number of soil inventory points falling into this ecosystem type (in the same way as it is done for forest ecosystems). Due to the limitations of this system (there can be ecosystem areas, which are not represented by sample plots), not the whole ecosystem area is captured. So summing up all records will not result in total Austrian agricultural/forest area.

Topsoil depth and uptake fraction (fMu)
For forests and grassland topsoil depth of 0.1 m was taken; for arable land a 0.2 m topsoil depth was taken, contrary to the Mapping Manual suggestions. This was necessary to match with the horizon depth of most of the Austrian soil inventories. This change could lead to slightly higher values for OM and pH used for WHAM model calculations.
According to the Mapping Manual f_{Mu}=1 was taken for all effects and all ecosystems, except for the critical concentration of Hg in the forest humus layer related to ecotoxicological effects, where f_{Mu}=0.8 was used.

Biomass uptake

Information on forest biomass uptake comes from the Austrian forest inventory (Schieler & Schadauer, 2001), sampled by the *Austrian Federal Office and Research Centre for Forests*. Mean harvesting rates (separated by ecosystem type) for the years 1986 to 1996 were aggregated on the EMEP-grid cell basis. Ecosystem type G5.6 (unmanaged mountain forests) has no biomass uptake. Grid cells with too few sample points for statistical purposes were combined with neighbouring cells. Information on biomass uptake from arable land (I1.1) was taken from the *Statistics Austria* crop statistics. A mean annual harvesting rate and crop area of the main crops per district was calculated for the years 1998 to 2003. Then an area-weighted mean biomass uptake of the main crop species was calculated. Due to this approach, heavy metal content in the biomass of each district is also an area-weighted mean of the HM contents in the main crop species. Information on biomass uptake from intensive grassland and meadows (E2) was taken from the *Statistics Austria* crop statistics. Biomass uptake from alpine grassland and pastures (E4) was set to zero.
For the calculation of human health effects through intake of plant products (effect number 2; Cd in wheat), it was assumed, that the whole arable land is covered by wheat only, taking the mean wheat biomass uptake into account. In this special case a critical Cd content in wheat of 0.12 mg kg^{-1} dw was used instead of the mean value of 0.05 mg kg^{-1}, according to the suggestions in the Mapping Manual.

Heavy metal content: Heavy metal contents of the harvested parts of the plants are mean values based on a literature review. Literature can be provided upon request.

Table AT-1: Heavy metal contents in plants used for uptake calculations.

[mg kg^{-1} dw]	Pb	Cd	Hg
coniferous wood – stem	1,20	0,20	0,05
coniferous wood – bark	11,30	0,40	0,12
deciduous wood – stem	0,77	0,12	0,01
deciduous wood – bark	8,35	1,00	0,01
Wheat	0,07	0,05	0,04
other cereals	0,10	0,04	0,07
Potato	0,05	0,07	0,04
Maize	0,09	0,03	0,04
silage maize	0,40	0,07	0,07
sugar beet	0,10	0,09	0,02
mixed grassland species	2,00	0,15	0,06

Drainage water flux

Drainage water flux was calculated according to equitation 4b (chapter 5.5.2.1.3) of the Mapping Manual. Precipitation data were taken from the Hydrological Atlas of Austria (BMLFUW, 2003), mean air temperature was calculated using altitude and a relationship to temperature found by Baumgartner et al., 1983. $E_{m,pot}$ (annual mean potential evapotranspiration in humid areas at T_m = 0°C) was taken as 0.35 m a^{-1} for forests, as 0.30 m a^{-1} for grassland and as 0.25 m a^{-1} for arable land. $f_{E,zb}$ (fraction of total annual mean evapotranspiration from the investigated topsoil) was taken as 0.8 for forests and as 1 for grassland and arable land.

Critical total metal concentration in soil solution

Critical total metal concentrations in soil solution (critical limits) are in accordance to the suggestions made in the Mapping Manual for each effect.

1. Human health effects through intake of plant products (only Cd in wheat grains):
   $[Cd]_{ss(crit)}$ = 0.8 mg m^{-3}
2. Human health effects through intake of drinking water (WHO 2004 quality criteria):
   $[Pb]_{ss(crit)}$ = 10 mg m^{-3}
   $[Cd]_{ss(crit)}$ = 3 mg m^{-3}

$[Hg]_{ss(crit)}$ = 1 mg m^{-3}

3. Ecotoxicological effects on soil micro-organisms, plants and invertebrates, considering free Cd and Pb ions in soil solution:
   Tables 4 and 5 of chapter 5.5.2.2.3 of the Mapping Manual were used to interpolate critical limits, using measured pH and OM values as input parameters. Default values for DOC and CO_2 pressure were used according to the suggestions made in this chapter.
   For forest ecosystems, calculations were made for both organic layer and upper mineral horizon separately and then the most sensitive layer (lower critical limits; mostly the mineral layer) was included into the dataset.
4. Ecotoxicological effects on soil micro-organisms and invertebrates, considering Hg contents in forest humus layer:
   $[Hg]_{ss(crit)}$ = 0.035 mg m^{-3}

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BELARUS

National Focal Centre

Oleg Bely, Natallia Lysukha
Belorussian Researche Centre ”Ecology”
31A, Horuzhaya st.,
220002, Minsk
tel: +375-17-234-7064
Fax: +375-17-234-7818

Collaborating institution

Institute of Nature Resources Use Issues and Ecology of the National Academy of Sciences of the Republic of Belarus
Staroborisovsky trakt, 10,
220014, Minsk

Calculation method

Critical loads calculation of lead on the natural ecosystems of Belarus varies from 0.8 to 4.2 mg m^{-2} a^{-1} (effect-guided method), and from 0.01 to 4.37 mg m^{-2} a^{-1} (keeping method). The average values of threshold loads of lead on the ecosystems are 2.57 and 1.41 mg m^{-2} a^{-1} according to these methods. Critical loads of cadmium for different types of natural ecosystems change from 0.08 to 0.38 mg $m^{-2}a^{-1}$(effect - guided method) and from $3.3 \cdot 10^{-4}$ to 0.4 mg m^{-2} a^{-1} (the keeping method). Average values are 0.24 and 0.07 mg m^{-2} a^{-1}, respectively.
Woodland and forest habitats are more resistant to high loads of lead and cadmium then meadow and peat land. However coniferous woods, first of all fir, have the greatest absorption capacity and stability. Average values of critical loads of lead for fir forests in 1.3–1.5 times are higher, then for woods of Belarus on the whole. Threshold loads of cadmium are higher in 1.2–2 times. Pinewoods differs a wide spectrum of allowable volumes of lead and cadmium. The results received with the keeping method, are essentially lower then results received on effect - guided method, on the average they differ in 1.5–2.2 times on lead and 2.1–4.9 times on cadmium. Values of critical loads depend on soil type of ecosystem. Ecosystems on easy sandy soil resist to pollution of lead and cadmium, and ecosystems on peaty and heavy clay soil are most sensitive critical loads of lead are 35.9 mg m^{-2} a^{-1} for woodland, 21.8 mg m^{-2} a^{-1} for meadow, 26.6 mg m^{-2} a^{-1} for peat land (effect-guided method), according to the keeping method for woodland 29.9 mg m^{-2} a^{-1}, for meadow 20.8 mg m^{-2} a^{-1}, for peat land 16.1 mg m^{-2} a^{-1} at the protection of 95 % sensitive ecosystem.

BELGIUM

Flanders

National Focal Centre

S. Overloop, M. Van Steertegem
Flemish Environment Agency
Van Benedenlaan 34
B-2800 Mechelen
tel: +32-15-451471
fax: +32-15-433280
s.overloop@vmm.be
www.vmm.be

Wallonia

National Focal Centre

A. Fourmeaux, M. Loutsch
Ministry of Walloon Region, DGRNE
Avenue Prince de Liège 15
B-5100 Namur
tel: +32 -81-325784
fax: +32-81-325784
m.loutsch@mrw.wallonie.be

Collaborating institutions

V. Vanderheyden, J-F. Kreit
SITEREM S.A.
Cour de la Taillette, 4
B-1348 Louvain-la-Neuve
info@siterem.be

S. Eloy
Scientific Institute for Public Services (ISSEP)
Rue du Chera, 200
B-4000 Liège
s.eloy@issep.be

University of Liège :
E. Everbecq, J. Smitz, JF. Deliège
Environmental center, Sart Tilman B5
cenv@ulg.ac.be
V. Gennotte, A Bertrand, JP Thomé, A. Goffart
Aquapôle, Quai Van Beneden,22
a.goffart@ulg.ac.be

Catholic University of Louvain :
B. Delvaux, F. Ducarme, M. Goffin
Dept. of Soil Science
delvaux@pedo.ucl.ac.be

National Maps Produced

National maps were generally generated by combining contributions of Flanders (northern Belgium) and Wallonia (southern Belgium). However, no data have been submitted for Flanders. Maps have been produced for coniferous, deciduous and mixed forests and for lakes in Wallonia.

Mapping procedure Wallonia

Numerical maps with a total of 45000 ecosystems were overlaid by a 5 x 5 km^2 grid to produce the resulting maps. 47 Soil types were distinguished according to the soil associations map of the Walloon territory, established by Maréchal and Tavernier (1970). Each ecosystem is characterized by a soil type and a forest type.

In Wallonia, the critical value given for a grid cell represents the average of the critical values weighted by their respective ecosystem area (forest or lake).

Calculation methods for forest

Critical loads of heavy metals (Cd, Pb and Hg) for forest soils were calculated according to the method related to ecotoxicological effects or in view of groundwater protection as described in Mapping Manual Revision (30.09.2004):

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

where:

M_u = metal net uptake in harvestable part of plants

$M_{le}(crit) = Q_{le}\ M_{ss}(crit)$

The net metal uptake M_u (equal to the removal in harvested biomass) was calculated using the average growth rates measured in 25 Walloon ecological territories and the chemical composition of coniferous and deciduous trees. The chemical composition of the trees appears to be linked to the soil content.

Table BE-1. Means values of contents of Pb, Cd and Hg in biomass.

Species	Pb (1)	Cd (1)	Hg (2)
	mg kg^{-1} dw		
Beech	6.02	0.19	0.05
Oak	3.79	0.38	0.05
Spruce	30.23	0.33	0.05

(1) measured values, (2) default value proposed in the manual

The flux of drainage water leaching, Q_{le} , from the soil layer (humus layer or entire rooting depth) were estimated from lysimetric measurement on 10 different representative soil types (Table BE-2) (Catholic University of Louvain, 2005).

Table BE-2. Flux of drainage water through humus or entire root layer in Walloon soils.

Sites	Soil types	Q_{le} (m a^{-1}) 0 to 0.1m	Q_{le} (m a^{-1}) 0 to 0.5m
Bande (1-2)	Podzol	0.173	0.138
Chimay (1)	Cambisol	0.122	0.046
Eupen (1)	Cambisol	0.068	0.045
Eupen (2)	Cambisol	0.052	0.045
Hotton (1)	Cambisol	0.050	0.108
Louvain-la-Neuve (1)	Luvisol	0.039	0.039
Meix-dvt-Virton (1)	Cambisol	0.049	0.049
Ruette (1)	Cambisol	0.105	0.045
Transinne (1)	Cambisol	0.072	0.053
Willerzie (2)	Cambisol	0.067	0.044
Bailleux (1)	Cambisol	0.078	0.225

(1) deciduous, (2) coniferous forest

Critical limits for total concentration of the heavy metals Cd, Pb, and Hg in soil solution, $[M]_{ss}(crit)$, depend on the target to be protected.

Critical metal concentrations in ground water in view of human health effects through intake of drinking water are based on quality criteria for drinking water (WHO, 2004) ; $[M]_{ss}(crit) = 5\mu g\ Cd\ l^{-1}$, 10 µg Pb l^{-1} or 1 µg Hg l^{-1}.
The flux of drainage water through the entire root zone (0.0 -0.5 m) are considered to calculate the critical leaching $M_{le}(crit)$.

Critical metal (Cd, Pb) concentrations in soil solution in view of ecotoxicological effects on soil micro-organisms, plants and invertebrates are derived from critical limit functions giving free metal ion concentration in soil solution and from chemical speciation model (WHAM) giving the total concentration of metal in soil drainage water that corresponds to the free ion critical limit.

$$\text{Log } [Cd]_{free}(crit) = -0.32\ pH_{ss} - 6.34$$
$$\text{Log } [Pb]_{free}(crit) = -0.91\ pH_{ss} - 3.80$$

where:

pH_{ss} = pH in lixiviated water from lysimetric equipments

The measured values of pH_{ss}, soil organic matter content and concentration of dissolved organic carbon are submitted to CEH Lancaster, Ed Tipping (UK) to use the WHAM model. The calculated values $[Cd]_{ss}(crit)$ (ranging from 2.5 to 4.8 µg Cd l^{-1}) are higher than measured concentrations (Table BE-3). However for Pb, in some soils (Eupen, Hotton and Bailleux), the concentrations in excess compared with critical limits are measured.

Table BE-3. Measured pH and total concentration of Cd in soil solution (O layer). Comparison with calculated values.

Sites	pH_{ss} measured	$[Cd]_{ss}$ measured	$[Cd]_{ss}(crit)$ WHAM
Bande (1-2)	3.40	0.587	4.652
Chimay (1)	3.78	0.960	4.263
Eupen (1)	3.98	2.540	3.333
Eupen (2)	3.45	3.240	4.624
Hotton (1)	6.50	0.120	4.265
Louvain-la-Neuve (1)	3.67	1,159	3.760
Meix-dvt-Virton (1)	4.24	0.873	2.504
Ruette (1)	6.26	0.027	2.871
Transinne (1)	3.81	0.267	3.635
Willerzie (2)	3.35	0.480	4.844
Bailleux (1)	4.19	0.997	2.555

(1) deciduous; (2) coniferous forest

Critical total Hg concentration in soil solution in view of ecotoxicological effects on soil micro-organisms and invertebrates are derived from transfer functions based on Hg limit of 0.5 mg kg OM^{-1} as follow :

$$[Hg]_{ss}(crit) = [Hg]_{SOM}(crit)\ [DOM]_{ss}$$

where:

$[Hg]_{SOM}(crit)$ = critical limit for Hg in solid organic matter (0.5 mg kg OM^{-1})
$[DOM]_{ss}$ = concentration of dissolved organic matter in soil solution, usually equal to twice the DOC.

In Walloon organic layers, the DOC values are ranging from 26 to 99 g m^{-3}.

Results for forest soils

The mapping of critical loads of cadmium, lead and mercury related to ecotoxicological effects for forest humus layer are presented in Figures BE-1, BE-2 and BE-3 below (mapping realised by ISSEP).

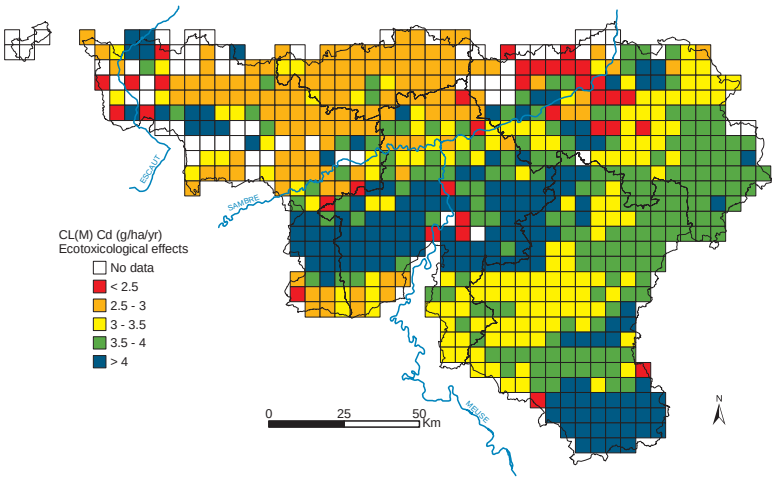

Figure BE-1. Critical loads of Cadmium for forest humus layer in Walloon region.

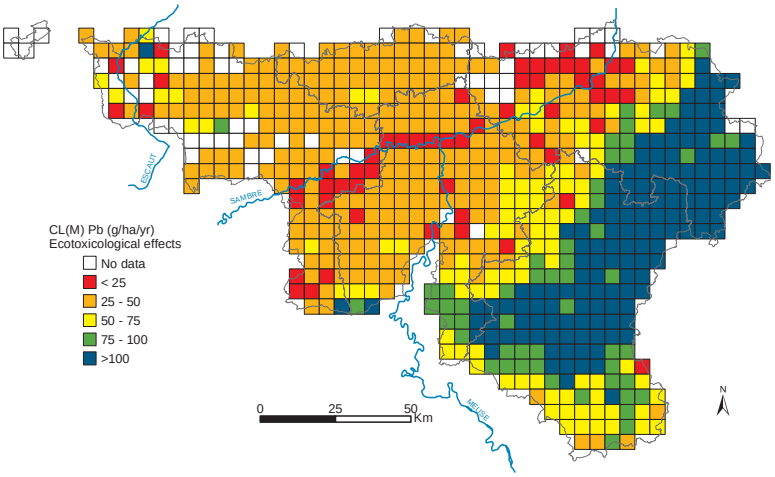

Figure BE-2. Critical loads of Lead for forest humus layer in Walloon region.

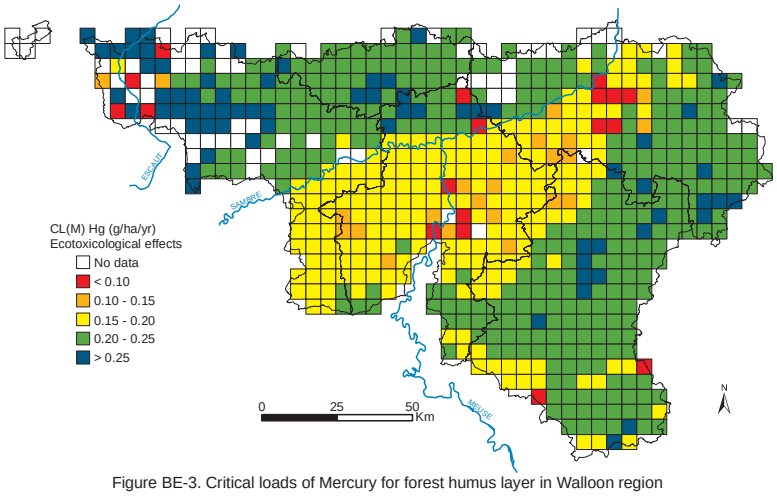

Figure BE-3. Critical loads of Mercury for forest humus layer in Walloon region

Calculation methods for lakes

Critical loads of Cd, Pb and Hg for surface waters were calculated according to the Mapping Manual Revision (30.09.2004). For Cd and Pb, the method is related to ecotoxicological effects and critical loads are calculated as follows:

$$CL(M)_{tot} = M_u + M_{lo}(crit)$$

where:

M_u = removal of heavy metal by biomass harvesting or net uptake in the catchment.

$M_{lo}(crit)$ = critical lateral outflow of heavy metals from the aquatic system (= $Q_{lo} \cdot [M]_{tot,sw}(crit)$)

In the manual, Q_{lo} (lateral outflow flux of water from the aquatic system) is defined as the flow from the aquatic system divided by the lake area. Here, we have chosen to use the catchment area instead of the lake area.

For mercury, the critical level of atmospheric pollution ($[Hg]_{PrecCrit}$) in view of human health effects through intake of fish can be calculated as follows:

$$[Hg]_{PrecCrit} = [Hg]_{fishCrit} / TF_{HgSite}$$

where:

$[Hg]_{fishCrit}$ = critical Hg concentration in the flesh of 1-kg Salmo trutta.

TF_{HgSite} = TF_{Hgrun} ([TOC] + 1) / ([TP] + 15) / 0.4

where: TOC = total organic carbon,
TP = concentration of total phosphorus

Data sources

The values of the parameters Q_{lo}, TOC, TP were derived from monitoring data.

The assessment of heavy metal removal by net uptake or release refers to the complete catchment. For aquatic ecosystems, the parameter M_u is derived from a comparable method to that used for terrestrial ecosystems (see forest soils).

For grassland and arable land, the recommended values proposed in the manual are used for yields and biomass concentrations exception made for cadmium concentration for which a value of 59.85 µg kg^{-1} dw was applied to arable land (SITEREM, 1997).

Critical limits used for the calculation of critical loads in surface waters depend on the effects to be considered. For Cd and Pb, critical limits ($[M]_{tot,sw}(crit)$) related to ecotoxicological effects are expressed as a total concentration (dissolved and in suspended particles) in water. For Hg, the critical limit ($[Hg]_{fishCrit}$) refers to human health effects and is expressed as a concentration in fish.

Critical limits of Cd are based on the latest values given in the manual. These values are critical dissolved concentrations and take the influence of hardness on the toxicity into account. To derive total concentrations, they have been multiplied by the average ratio of total Cd concentration to dissolved Cd concentration measured in Walloon surface waters ($[Cd]_{tot} / [Cd]_{diss} = 1.81$) (Table BE-4).

For Pb, the critical limits used are the green class values for the biological aptitudes of the water given by the French SEQ-Eau (2003). These values are expressed as total concentrations and are dependent on water hardness.

Table BE-4. Critical limits for total Cd and Pb concentrations (µg l^{-1}) in Walloon surface waters in function of water hardness (mg $CaCO_3$ l^{-1}).

Hardness	Cd	Hardness	Pb
< 100	0.29	< 50	2.1

100 – 200	0.54	50 – 200	5.2
> 200	0.91	> 200	10

The critical limit for Hg is the concentration referred in the manual and recommended by the USEPA (2002): 0.3 mg kg^{-1} fw in a 1-kg pike. To convert this value for the trout, the target species used here, the manual gives a method using a transfer function.

Results for lakes

In Walloon region, the critical loads (Pb, Cd) and the critical concentration in precipitation (Hg) have been calculated for 7 lakes characterised as follows (Table BE-5, Université de Liège, 2004) :
Gileppe and Eupen lakes are located in Belgian High Ardennes. The catchments of these two lakes are for 74% and 79% of areas, respectively covered by forest, while the rest of the areas is covered by agricultural land (±3%) and fens. The catchment of Ry de Rome lakes is 99% forested, while Nisramont and Eau d'Heure catchments consist of ±40% forested and ±50% of agricultural land. Bütgenbach and Robertville are ±25% forested and the rest of the area consists of urban or agricultural zones (±60%).

Table BE-5. Critical loads of Pb and Cd, and critical concentrations in precipitation for Hg.

Lakes	CL	CL	CCM
	g ha^{-1} yr^{-1}		ng l^{-1}
	Pb	Cd	Hg
Eupen	110	2.67	1.18
Gileppe	110	2.48	1.38
Ry de Rome	118	2.81	5.87
Robertville	54	2.69	5.02
Bütgenbach	64	2.74	5.92
Nisramont	69	2.68	5.23
Eau d'Heure	37	2.93	3.74

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BULGARIA

National Focal Centre

Yavor Yordanov
Executive Environment Agency
Tzar Boris III Str. 136
BG-1618 Sofia
tel: 359 2 9406473
fax: 359 2 9559015
landmon@nfp-bg.eionet.eu.int

Collaborating institutions

Nadka Ignatova
University of Forestry
Department of Chemistry and Biochemistry
Prof. Dr. Kitka Jorova
University of Forestry
Department of Soil Science
Kliment Ochridsky Street 10
1756 Sofia
tel: +359 2 91907 (351) (N I)
+359 2 91907 (360) (K J)
fax: +359 2 862 28 30
nadia_ignatova@hotmail.com
castproject@abv.bg

Emilia Velizarova
Department of Soil Science
Forest Research Institute
Kliment Ochridsky Street 136
1756 Sofia
tel: +359 2 962 29 61

Radka Fikova
Central Laboratory of Total Ecology
Bulgarian Academy of Sciences
Gagarin Street 2
1300 Sofia
tel: +359 2 719195

National maps produced

Critical loads of lead and cadmium for deciduous and coniferous forests were calculated in separate records and mapped on 50×50 km^2 EMEP grid. The total critical loads of lead and cadmium and their exceedances were calculated and integrated for each EMEP grid cell and mapped also.
The following maps were produced:
Critical loads of lead for broadleaved forest ecosystems;
Critical loads of lead for coniferous forest ecosystems;
Total Critical loads of lead for both broadleaved and coniferous forest ecosystems in each grid cell;
Critical loads of cadmium for broadleaved forest ecosystems;
Critical loads of cadmium for coniferous forest ecosystems;
Total Critical loads of lead for both broadleaved and coniferous forest ecosystems in each grid cell;
Exceedances of critical loads of lead by present dry and wet depositions;
Exceedances of critical loads of cadmium by present wet depositions.

Calculation methods

Critical loads of lead and cadmium as an acceptable total load of their anthropogenic inputs were calculated with respect to recommendations mentioned in the last version of the Manual on Methodologies and Criteria for Modelling and Mapping Critical loads and Levels and Air Pollution Effects, Risks and Trends (UBA, 2004). It corresponds to the sum of tolerable outputs from the

ecosystem by harvest and leaching, while assuming a steady state situation. The effect based Steady-state mass balance model was used to calculate the critical loads of lead and cadmium. Comparing with previous preliminary calculation of heavy metals critical loads (Ignatova 2001, Ignatova et al. 2002), the model was simplified by neglecting the release of Pb and Cd from the weathering in the mineral topsoil because of very low values. The model implies that the critical load equals the net uptake by forest growth plus an acceptable metal leaching rate, according to the follow equation:

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

where:

$CL(M)$ = critical load of a heavy metal M (Pb or Cd) (g ha^{-1} a^{-1});
M_u = Metal net uptake in harvestable parts of plants under critical load conditions (g ha^{-1} a^{-1});
$M_{le(crit)}$ = critical leaching flux of heavy metal M (Pb or Cd) from the considered soil layer (g ha^{-1} a^{-1}).

The metal net uptake by harvestable parts of plants was calculated by multiplying of annual yield with fraction of metal net uptake within the considered soil depth and metal content of the harvestable parts of the plants as follow:

$$M_u = f_{Mu}\ Y_{ha}\ [M]_{ha}$$

where:

f_{Mu} = fraction of metal net uptake within the considered soil depth, accounting also for metal uptake due to deposition on vegetation surfaces (–);
Y_{ha} = yield of harvestable biomass (dry weight) (kg ha^{-1} a^{-1});
$[M]_{ha}$ = metal content of the harvestable parts of the plants (g kg^{-1} dw).

Since critical loads of heavy metals for forest ecosystems are calculated for the mineral topsoil, the fraction of metal net uptake within the considered soil depth have been taken equal to 0.1.

The critical leaching flux of a heavy metals from the topsoil was calculated according to the follow equation:

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

where:

$M_{le(crit)}$ = critical leaching flux of heavy metal from the topsoil (g ha^{-1} a^{-1});
Q_{le} = flux of drainage water leaching from the regarded soil layer (m a^{-1});
$[M]_{ss(crit)}$ = critical limit for the total concentration of heavy metal in the soil solution (10 mg m^{-3} for Pb and 3 mg m^{-3} for Cd) (UBA, 2004);
c_{le} = 10, factor for conversion of flux units from mg m^{-2} a^{-1} to g $ha^{-1}a^{-1}$.

Exceedances of critical loads of lead and cadmium by present atmospheric loads were defined by following equation:

$$CL(M)ex = PL_{dry}(M) + PL_{wet}(M) - CL(M)$$
$$PL_{dry}(M) = C_{dry}(M)\ Vd\ f$$
$$PL_{wet}(M) = 10\ Sum[C_{wet}(M)\ P]$$

where:

$CL(M)ex$ = exceedance of critical load of a heavy metal M (Pb and Cd);
$PL_{wet}(M)$ = annual deposition of heavy metal with throughfall (g ha^{-1} a^{-1});
$CL(M)$ = critical load of a heavy metal M (g ha^{-1} a^{-1});
$PL_{dry}(M)$ = dry deposition of heavy metal from atmosphere (g ha^{-1} a^{-1});
$Cdry(M)$ = heavy metal concentration in atmosphere (µg m^{-3});
$Cwet(M)$ = heavy metal concentration in throughfall (mg dm^{-3});
V = deposition velocity (mm s^{-1});
P = amount of throughfall (mm);
f = factor for conversion of deposition velocity and concentration.

Data sources

National monitoring data:

i. Data on annual biomass removal for all forest species have been derived from the National Forests Survey Agency;
ii. For estimating of metal content of the biomass an information for main tree species and their parts (stems and branches) in Bulgarian part of EMEP grid have been used (Jorova, 1992; Ignatova, 2001; De Vries and Bakker, 1998; De Vries et al., 2001).

Table BG-1. Mean metal content in harvested part of forest biomass at relatively unpolluted sites (mg kg^{-1}).

Forest ecosystem	Metal content in harvested part (mg kg^{-1})	
	Pb	Cd
Coniferous forest	0.007	0.0004
Broadleaved forest	0.006	0.0003

iii. Runoff of water under root zone has been measured in grid cells of 10x10 km for the entire country;
iv. A total of 208 forest soil profiles have measured values for the Pb and Cd total soil concentration, the content of the organic mater (%) and the pH of the soil;
v. Annual wet throughfall deposition of Pb and Cd has been defined by means of 50 permanently opened collectors under the crowns of main forest species and then interpolated for all forested areas using Kriging geostatistical method;
vi. Mean annual atmospheric concentrations of Pb and Cd have been measured at 42 monitoring stations integrated in National Ambient Air Quality Monitoring System (NAAQMS), supported by Bulgarian Executive Environmental Agency and then interpolated for all forested areas using Kriging geostatistical method;

National maps:

i. Soil type information from the FAO soil map of Bulgaria;
ii. Geographical maps of Bulgaria with mean annual precipitation and air humidity data;
iii. Geographical maps of Bulgaria with altitudes above sea level data;
iv. Vegetation map – CORINE land cover data map for Bulgaria

Results and comments

Broad leaved and coniferous forest species have been selected as receptors in view of the different effects of heavy metals on forests. All data needed to calculate critical loads of Pb and Cd in accordance with the resolution and standards were collected and archived. Software for calculating critical loads of Pb and Cd with a spatial resolution of 50×50 km in EMEP grid cells was produced to facilitate further calculating procedure. Calculated critical loads of Pb and Cd for broad leaved and coniferous forest units 50/50 km have been mapped using GIS systems and Arcview Programme. All critical loads of heavy metals and their compartments were computed for both broad leaved and coniferous forests in separate records for each EMEP grid cell 50×50 km.
The maximum lose of Pb by runoff from forested catchments was estimated as 12.05 g $ha^{-1}a^{-1}$ with a minimum of 0.90 g $ha^{-1}a^{-1}$. The Cd lose by runoff was between 0.27 and 3.62 g $ha^{-1}a^{-1}$ respectively. Biomass uptake of Pb by the stem of broadleaved forests was relatively homogenous and obtained values ranged from 10.05 to 14.95 g $ha^{-1}a^{-1}$. Concerning coniferous forest catchments the diversity of biomass uptake of Pb was higher than for broadleaved ones and the values were situated between 11.58 and 20.97 g $ha^{-1}a^{-1}$. The Cd biomass uptake was very low and the calculated values were

between 0.33 and 0.60 g $ha^{-1}a^{-1}$ for coniferous forests and between 0.25 and 0.37 g $ha^{-1}a^{-1}$ for broadleaved ones.
On the base of the sum of biomass uptake and lose by runoff, computed values for critical loads of Pb using effect based approach ranged from 11.00 to 23.27 g $ha^{-1}a^{-1}$ for broadleaved forests (Figure BG-1 top) and from 14.83 to 33.02 g $ha^{-1}a^{-1}$ for coniferous forested units (Figure BG-1 bottom).
Critical loads of Cd were lower than the values of Pb and they were situated between 0.54 and 3.74 g $ha^{-1}a^{-1}$ for broadleaved forests (Figure BG-2 top) and between 0.47 and 1.33 g $ha^{-1}a^{-1}$ for coniferous ones (Figure BG-2 bottom).
Comparing the average values of critical loads of lead and cadmium 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 (Figure BG-3). The average critical leaching of lead was about 4.84 g ha^{-1} a^{-1} against 1.39 g ha^{-1} a^{-1} for cadmium.
Biomass uptake of lead by harvestable part of coniferous as average annual value ranged 16.62 g ha^{-1} a^{-1} when for deciduous forested catchments this value was 11.38 g ha^{-1} a^{-1}. For Cd corresponding values were 0.49 g ha^{-1} a^{-1} for coniferous and 0.28 g ha^{-1} a^{-1} for broadleaved forests.
As shown on Fig. BG-3 the metal leaching of lead was the dominating term in the critical loads calculations of lead whereas the uptake of cadmium by the biomass was much higher than Cd leaching by the percolating soil solution for both types of receptors.
Finally the average critical load of both lead and cadmium for all over the country were higher for coniferous forested areas (for Pb 22.69 g ha^{-1} $a^{-1}$and for Cd 2.16 g ha^{-1} a^{-1}) than for broadleaved ones (for Pb 15.82 g ha^{-1} a^{-1} and for Cd 1.66 g ha^{-1} a^{-1}) (Figure BG-3).

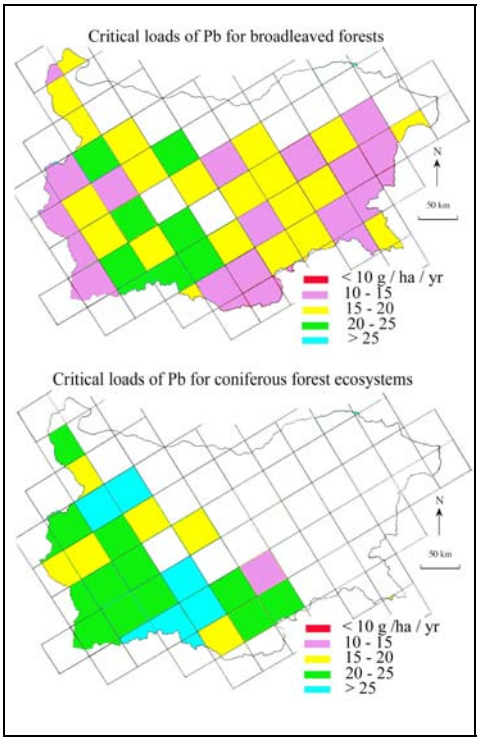

Figure BG-1. Critical loads of Pb for broad-leaved (top) and coniferous (bottom) forests in Bulgaria for 2003 (g ha^{-1} a^{-1}).

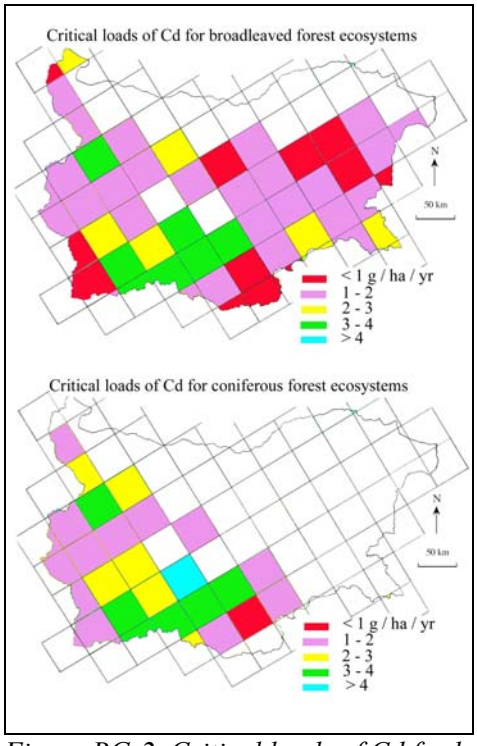

Figure BG-2. Critical loads of Cd for broad-leaved (top) and coniferous (bottom) forests in Bulgaria for 2003 (g ha^{-1} a^{-1}).

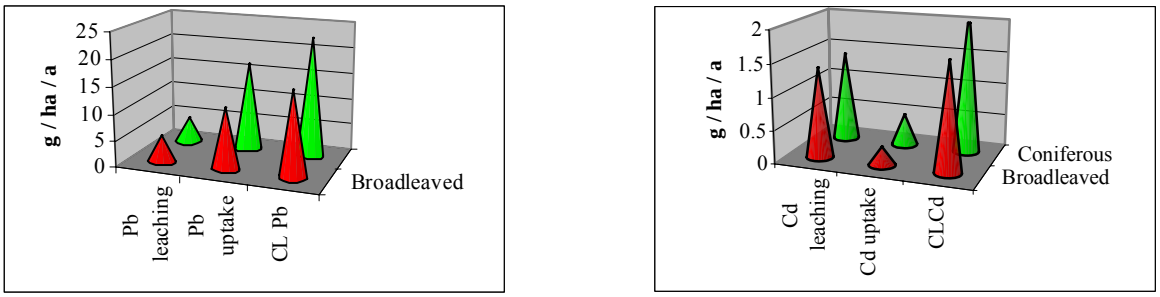

Figure BG-3. Leaching, uptake by the biomass and critical loads of Pb (left) and Cd (right) for broad-leaved (red) and coniferous (green) forests in Bulgaria for 2003 (g ha^{-1} a^{-1}).

Conclusion

To assess critical loads of Pb and Cd and their exceedances, the effect based steady state mass balance method was successfully applied to Bulgarian forest ecosystems.
The critical loads of both Pb and Cd for broadleaved forested catchments were lower than those for the coniferous at similar ecological and climatic parameters due mainly to the lower growth uptake by the biomass of broadleaved forest species which demonstrates the higher sensitivity of deciduous forest ecosystems to the heavy metals pollution than the coniferous ones.
All critical loads of Pb and Cd obtained by means of effect based approach were higher than the previous preliminary calculation for 2001 because of higher values of critical metal concentrations in soil solution recommended by the Coordination Center of Effects.
With respect to results of critical loads of lead and cadmium, there is a trend, that possibility of forest ecosystem to assume the heavy metals depositions without risk are not very big. According to observed receptors, the stability of coniferous ecosystems is much bigger than broadleaved ones. The critical loads of both lead and cadmium for coniferous receptors are bigger in cases of mixed ecosystems in observed EMEP grid cells.

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CYPRUS

National Focal Centre

Christos Malikkides
Senior Labour Inspection Officer
Head, Industrial Pollution Control Section
Department of Labour Inspection
Ministry of Labour and Social Insurance
12, Apellis Street
1493 Nicosia
Tel: +357 22 405631
Fax: +357 22 663788
cmalikkides@dli.mlsi.gov.cy

Databases and calculation methods

Cyprus has submitted national data on critical loads of three heavy metals CL(Cd, Pb, Hg) for terrestrial ecosystems using the steady-state mass balance approach as it is described in the Modelling and Mapping Manual (UBA, 2004), chapter 5.5, status of September 2004. These critical loads address human health effects (protection of drinking water and food quality) as well as effects on ecosystem functioning. Forests, semi-natural vegetation as well as agricultural land have been included in the calculation. These ecosystems together cover 89 % of the total area of Cyprus. The Cyprus database consists of

- 31895 records of CL(Pb, Cd, Hg) with respect to protection of ground water (drinking water) quality, and CL(Pb, Cd) aiming at protection of ecosystems
- 8274 records for CL(Cd) with respect to protection of food quality

CL (Hg) related to effects on microbiota and invertebrates in forest humus layers were calculated for 15 ICP Forests Monitoring sites (level 1), only. These data were not part of the data submission to CCE, but the results are mentioned in this short report. A detailed description of the data and the methods for derivation is given in Table CY-1. Main databases for the calculation of the critical loads of heavy metals (CL(M)) were provided by the Ministry of Agriculture, Natural Resources and Environment of Republic of Cyprus:

- the Vegetation Map of Cyprus 1 : 250 000 containing 31 different units and, among these, 28 types of vegetation,
- Agricultural Statistics providing information on crop ratios and agricultural yields
- the Cyprus Soil Map 1 : 250 000 in combination with description of FAO soil types
- data from the Meteorological Service of Cyprus 1991 - 2000

Information on how the ecosystem types of forests and semi-natural vegetation have been arranged to EUNIS habitat classification as well as an overview on the soil types of Cyprus were already provided in the national contribution of Cyprus in the CCE Status Report 2004. In addition to the EUNIS classes for forests and semi-natural vegetation for all classes of agricultural use including permanent crops as olive, carob, vine and citrus, the EUNIS -Code I was applied without further classification. For the calculation of net uptake of heavy metals, detailed information was available on agricultural structure and yields as well as on metal contents in a series of plant species. For other plants, information from Table 2 of the Manual was used as well as from further literature, providing ranges of contents of the three metals in plants, the latter in particular to estimate metal contents in harvested parts of permanent crops. In general, if information from Cyprus databases was missing, the lowest values from ranges were used considering the high binding capacity for metals of Cyprus soils. In high forests only Pinus brutia was assumed to be harvested, suggesting a coverage of this tree species of 60 %. Semi-natural vegetation as well as reforestation were assumed to have no net-uptake.

Table CY-1. National critical load of heavy metals database and calculation methods/approaches.

Parameter	Name (header)	Symbol in the Manual (Sept. 2004)	Unit	Description
critical load of the metal M	CLM	CL(M)	g ha^{-1} a^{-1}	eq. (1) in the Manual (UBA, 2004)
net uptake of the metal M	Mu	M_u	g ha^{-1} a^{-1}	according to eq. (2) in the Manual and related instructions.
annual yield/increment of biomass	Yha	Y_{ha}	kg ha^{-1} a^{-1} (dw)	based on Statistical Service (2002), Markides (1999b), and data from ICP Forest Monitoring plots (Christou 2004)
metal content in the harvested parts of plant	Mha	$[M]_{ha}$	g kg^{-1} (dw)	data from the Cyprus Dept. of Human Health protection; Manual, Table 2; literature data
critical leaching flux of heavy metal from the topsoil	Mlecrit	$M_{le(crit)}$	g ha^{-1} a^{-1}	according to eq. (3) in the Manual and related instructions
Q_{le} = flux of leaching water from the considered soil layer	Qle	Q_{le}	m a^{-1}	derived using eq. 4b in the Manual, based on data from the Meteorological Service of Cyprus
thickness of the soil layer considered z = entire rooting depth z_b the biological active upper soil layer	thick	z z_b	m	information from Cyprus Dept. of Agriculture and from ICP Forests Monitoring plots
critical total dissolved metal concentration in the soil solution	Mcrit	$[M]_{ss(crit)}$	mg m^{-3}	human health effects: WHO limits for drinking water, or (Cd in wheat) based on table 3 in the Manual ecotoxicological effects (Pb, Cd): using Model W6-MTC2 (Tipping 2004) ecotoxicological effects (Hg): based on eq. 9 in the Manual
soil characteristics	pH OM pCO_2	pH $[OM]_s$ pCO_2	- % (dw) * air	information from Cyprus Dept. of Agriculture (Markides 1999a) default: 15
	DOC	$[DOC]_{ss}$	g m^{-3}	defaults: 5 - 20, depending on land use

The leaching water flux and the critical metal leaching was calculated based on equation 4b and equation 3 in the Manual, respectively. With respect to human health effects (drinking water) the WHO critical limits were applied and, with respect to human health effects via food uptake a critical concentration of 0.8 mg m^{-3} (related to the critical limit for Cd in wheat of 0.12 mg kg-1 (dm)). The critical concentration in soil drainage water related to ecotoxicological effects was derived using the chemical speciation model WHAM W6S-MTC2, kindly provided for use by E. Tipping (CEH Lancaster, UK).

One of the most important soil parameters in the calculation, strongly influencing the results of CL(Pb, Cd) related to ecosystem effects, is the pH value of the soil solution. The available information on measured pH values of Cyprus soils were used to derive pH values in undisturbed soil solution, adapted to the suggested partial pressure of CO_2 (15 x pCO_2 atmosphere), thus avoiding calculatory over-saturation of CO_2 in the soil layers in focus. These pH values ranged between 7 and 7.5 for calcareous soils and 6.2 to 6.5 for all other soils. They represent the upper values of the related buffer range for acidity.

Critical load results

The results of the critical loads calculation are presented here in Table CY2 enabling the comparison of the different types of CL(M. Maps are only provided for CL(Cd, Pb) related to ecotoxicological effects, and CL(Cd) as well as CL(Hg) related to protection of human health. The maps of CL(M) related to drinking water quality look very similar for all three metals. Therefore only the CL(Hg) map is presented.

Table CY-2. Statistical classification of receptor sensitivity for critical loads critical loads of cadmium, lead, and mercury in Cyprus

CL(M) class [g ha^{-1} a^{-1}]	protection of drinking water quality, area per class in [%]	protection of food quality related to the total receptor area (in brackets: related to the cereals area) area per class in [%]	protection of ecosystem functioning area per class in [%]
Cadmium			
< 0.5	10.1	0	3.5
0.5 – 1	26.5	0	43.5
1 - 1.5	28.7	20.5 (79.1)	17.4
1.5 – 2	10.5	4.9 (19.0)	9.2
2 – 3	10.7	0.5 (1.9)	6.8
3 – 4	5.2	0	7.0
4 – 5	3.3	0	4.4
5 – 6	2.2	0	3.1
> 6	2.8	0	5.0
Lead			
< 2	13.5	-	16.5
2 – 4	23.8	-	28.6
4 – 6	30.6	-	40.0
6 – 8	12.2	-	9.2
8 – 10	6.1	-	3.7
10 – 12	3.6	-	1.3
12 – 14	2.5	-	0.3
> 14	7.7	-	0.4
Mercury			
< 0.25	20.5	-	15 ICP Forests plots: 0.1 - 0.25
0,25 – 0.5	44.3	-	
0.5 - 1.0	21.6	-	
1.0 - 1.5	7.0	-	
1.5 - 2.0	3.8	-	
2.0 - 3.0	2.1	-	
>3.0	0.7	-	

Critical loads of cadmium

In general the critical loads related to protection of ecosystems and protection of drinking water quality both were strongly driven by the critical leaching flux. This is caused by the in general low uptake of cadmium by plants under the conditions of Cyprus (high binding of metals in the calcareous soils, low atmospheric deposition). In consequence the highest critical loads can be found in the mountain areas receiving high amounts of rain. In regions where the critical leaching is relatively equal, the patterns of Cd uptake are partly visible, in particular areas without Cd uptake show lower values (e.g. the east of the Larnaca bay). With respect to critical loads related to ecotoxicological effects there is an overlap of high leaching flux and high critical concentrations in the region of Troodos mountains up to the west coast (to a smaller extend also in the Pentadactylos mountains and other parts of the country) causing extra high critical loads of Cd (see Figure CY-1). However, in

comparison to the critical loads related to ground water protection the ecotoxicological based critical loads are slightly more sensitive.
The critical loads aiming at protection of the quality of human food are only covering the agricultural areas where the production of cereals is considered in the map of vegetation types. The distribution of this type of critical loads is shown in Figure CY-2. In principle two classes of critical loads of cadmium (food quality) are relevant for consideration with the leaching flux being the only parameter responsible for these small differences.

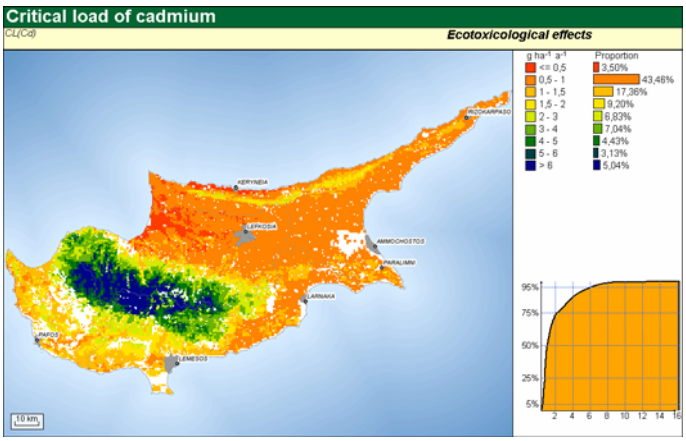

Figure CY-1. Regional distribution of critical loads of cadmium related to ecotoxicological effects.

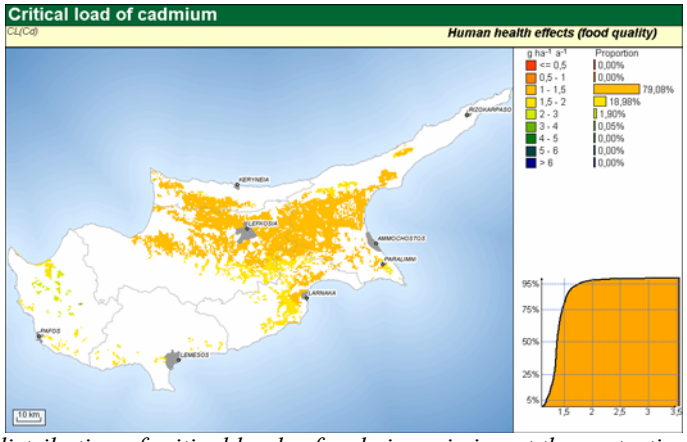

Figure CY-2. Regional distribution of critical loads of cadmium aiming at the protection of food quality.

Although the critical concentration in the soil drainage water aiming at non exceedance of the critical limit of Cd in wheat is clearly lower (0.8 mg m^{-3}) than the critical limit in order to protect ground water (3 mg m^{-3}), the critical loads values to protect food quality are equal or in some areas even higher than the critical loads to protect ground water. This occurs, because the critical uptake of Cd by wheat is higher than the actual uptake of mixed cultures calculated for the other types of critical loads of Cd. Also the leaching flux considered here (Qle,zb) is higher than the leaching flux below the rooting zone (Qle) considered in the critical loads calculation aiming at ground water protection.

Critical loads of lead

Small differences in the distribution of CL(Pb) aiming at ground water protection compared to the other metals can be caused by the variation of the Pb uptake. The reason for this is that metal contents in the harvested parts of plants are specific for each plant species. CL(Pb) based on ecotoxicological critical limits are clearly more sensitive than those for drinking water protection. Also for this CL type the regional distribution is determined by the leaching, but not only the water flux drives the CL(Pb), but also the critical concentration in the soil solution. Belts of high CL(Pb) can be found along the tops of the Pentadactylos mountains in the North as well as belts of very low critical loads along the Southern border of these mountains and along the Northern to central lowland part (Figure CY-3).

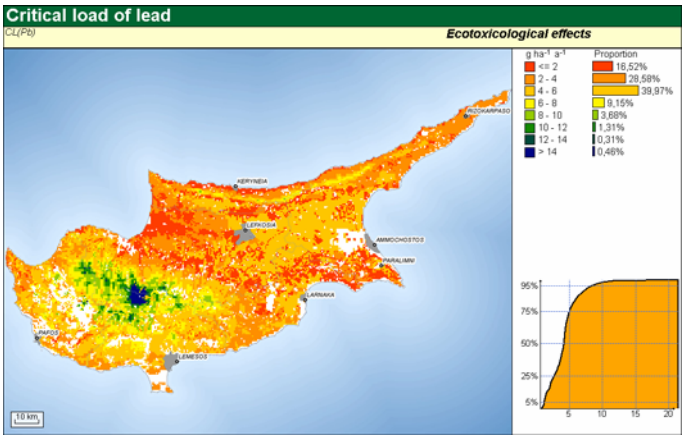

Figure CY-3. Regional distribution of critical loads of lead related to ecotoxicological effects.

Critical loads of mercury

Critical loads of mercury were calculated with respect to protection of drinking water quality (see Figure CY-4). A map of critical loads related to protect ecosystem functioning (the humus layer of forests) could not be produced, since the occurrence of an humus layer is limited in Cyprus forests and in many places the layer consists mainly of litter. The litter layer should, however, excluded from the critical loads calculation. CL(Hg) calculations focusing on ecosystem protection were conducted for 15 monitoring plots of ICP Forests in Cyprus. Although a comparison with a critical loads map related to ecotoxicological based CL(Hg) is not possible, it can be stated that the human health related CL(Hg) are in general clearly higher. The certain explanation for this is the much lower critical concentration, if ecosystem effects (forest humus layer) are addressed.

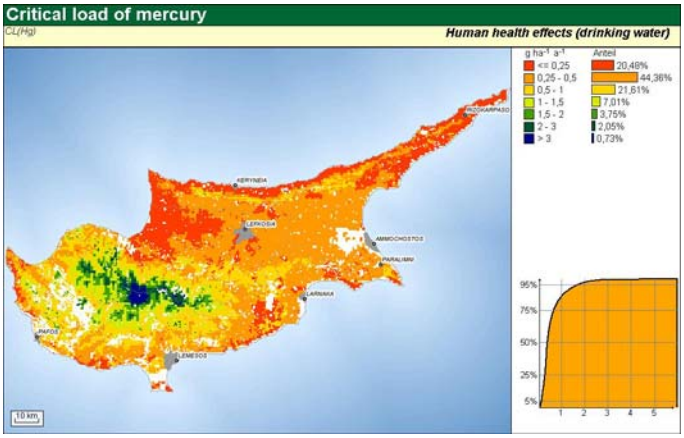

Figure CY-4. Regional distribution of critical loads of mercury aiming at ground water protection.

Comments and conclusions

In the interpretation of the critical loads of Cyprus and their exceedances it has to be taken into account that there is at present no steady state between inputs and outputs of heavy metals and it may take hundreds of years before the critical limit is reached in soil solution. First preliminary estimates of such time scales for Cyprus resulted in 635 up to more than thousand years. This means, that, although several types of CL(M) may be exceeded currently in certain areas of Cyprus, there is not necessarily a risk at present. However if sustainability is aimed at, the critical loads should not be exceeded in the long term.

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GERMANY

National Focal Centre

OEKO-DATA
Hans-Dieter Nagel
Gudrun Schuetze
Hegermuehlenstr. 58
D-15344 Strausberg
tel.: +49-3341-3901921
fax: +49-3341-3901926
hans.dieter.nagel@oekodata.com
gudrun.schuetze@oekodata.com

National data set

The German NFC provides its response to the CCE call for data on critical loads of heavy metals (CL(M)) of October 2004 with:

- 290.003 records on CL(Cd, Pb, Hg) aiming at protection of drinking water quality, or CL(Pb, Cd) related to ecotoxicological effects;
- 144.211 records on CL(Cd) with respect to the protection of food quality;
- 99.866 records on CL(Hg) aiming at the protection of microbiota and invertebrates living in the humus layer of forest soils.

The calculations were done following the methodology for calculation of CL(M) provided in Chapter 5.5 of the Modelling and Mapping Manual (UBA, 2004), status September 2004. Different types of ecosystems (arable land, intensive used grassland, semi-natural ecosystems and forest) are covered. Swamps and bogs have been excluded from the database, because for these types of ecosystems the soils can be considered as water logged. This refers to about 0.4 % of the total area of Germany. The CL(Cd) related to protection of food quality and CL(Hg) related to ecotoxicological effects cover smaller parts of the total area of Germany than the other datasets, because they refer to specific land use classes or depend on the occurrence of a humus layer, respectively. No data were excluded due to high geological metal contents or high natural metal weathering rates.

Databases and methods

The calculation of the net uptake of heavy metals has been conducted according to equation (2) in the Manual 5.5. Annual dry mass yields have been derived taking into account the geographical patterns of soil quality, climatic conditions, tree species or crop ratio, respectively, and information from agricultural statistics. The crop ratio in agricultural areas has been arranged in agreement with the soil quality. This approach is new compared to earlier deliveries of CL(M) data from Germany. The metal contents in the plants were obtained from literature and surveys in relatively unpolluted areas. High uncertainties are still included with respect to Hg contents in plants. It was assumed that metal net uptake from the upper biologically active soil layers equals the uptake from the entire rooting zone in all ecosystem types. Thus there is no difference between the net uptake in CL(M) calculations for ecosystem protection and drinking water protection. The critical Cd uptake into wheat grains is, however, higher than the net Cd uptake on arable land if a mixture of crops and median metal contents are considered.
To calculate the critical leaching according to equation (3) in the Manual 5.5, information on the flux of soil drainage water is needed. A map of $Q_{le,z}$ was provided by the Federal Institute on Geological Sciences and Natural Resources (BGR, 2002; Duijnisveld et al., 2003). In order to account for the water flux below the upper biological active soil layer $Q_{z,b}$, the share of transpiration drawing water

from the layers between depths z_b and z was considered to be 50 % or 25 %, the latter with respect to the flux of leaching water below the humus layer in the calculation of CL(Hg) related to ecotoxicological effects. The transpiration flux could be calculated from the long-term average of the yearly precipitation amount, the leaching flux $Q_{le,z}$, and literature data on the proportion of interception transpiration and soil evaporation (both dependent on land use).

Table DE-1. National critical load of heavy metals database and calculation methods/approaches.

Parameter	Name (header)	Symbol in the Manual (09 / 2004)	Unit	Description
critical load of the metal M	CLM	CL(M)	g ha^{-1} a^{-1}	equation (1) in Manual 5.5
net uptake of the metal M	Mu	M_u	g ha^{-1} a^{-1}	according to eq. (2) in the Manual and related instructions.
annual yield/increment of biomass	Yha	Y_{ha}	kg ha^{-1} a^{-1} (dw)	OEKO-DATA model for yields in agriculture and forests, based on data from agricultural statistics (Statistik regional 2003) and depending on soil and climate conditions of the site (Nagel et al. 2004)
metal content in the harvested parts of plant	Mha	$[M]_{ha}$	g kg^{-1} (dw)	data from unpolluted areas (Jacobsen et al. 2002, Nagel et al. 2004)
critical leaching flux of heavy metal from the topsoil	Mlecrit	$M_{le(crit)}$	g ha^{-1} a^{-1}	according to eq. 3 in the Manual and related instructions
Q_{le} = flux of leaching water from the considered soil layer	Qle	Q_{le}	m a^{-1}	based on data from Hydrological Atlas of Germany (BGR 2002, Duijnisveld et al. 2003), DWD Offenbach,
thickness of the soil layer considered	thick	z z_b	m	information from the General Soil Map of Germany (BÜK 1000, Hartwich et al. 1995)
critical total dissolved metal concentration in the soil solution	Mcrit	$[M]_{ss(crit)}$	mg m^{-3}	human health effects: WHO limits for drinking water, or (Cd in wheat) based on table 3 in the Manual ecotoxicological effects (Pb, Cd): using Model W6S-MTC2 ecotoxicological effects (Hg): based on eq. 9 in the Manual
soil characteristics	pH OM pCO_2	pH $[OM]_s$ pCO_2	- % (dw) * air	data from BÜK 1000 (see above) default: 15
	DOC	$[DOC]_{ss}$	g m^{-3}	defaults: 10 - 20, depending on land use

The critical total concentrations of Cd, Pb, and Hg in the leaching flux have been applied according to the recommendations in the Manual 5.5. Aiming at human health protection that means the application of the WHO limits Cd, Pb, Hg for drinking water, or the critical Cd concentration related to the protection of food quality of 0.8 mg m^{-3}, respectively. The critical total concentrations of Cd and Pb related to ecotoxicological effects were derived using the W6S-MTC2 model, kindly provided by Ed Tipping, CEH Lancaster, UK (Tipping 2004). The critical concentration of Hg in the leaching flux below the humus layer of forest soils was calculated according to equation (9) in Manual 5.5 assuming a uniform DOM concentration in the forests humus layers of 70 mg l^{-1}.
The ecosystem code compares to main classes of the EUNIS habitat classification. The geographical basis for the arrangement of the data records to the EUNIS classes was done by combination of information from CORINE Land Cover and the General Soil Map of Germany (Hartwich et al. 1995).

Critical load results

An overview on results of CL(M) calculation is provided in Table DE-2 enabling the comparison of the different types of CL(M). Maps and statistical evaluations are provided for CL(Cd, Pb, Hg) related

to ecotoxicological effects (Figures DE-1 - DE-3). The maps of CL(M) related to drinking water quality look very similar for all three metals. Therefore only the CL(Pb) map for this CL type is presented (Figure DE-4).

Table DE-2. Statistical classification of receptor sensitivity for critical loads of cadmium, lead, and mercury in Germany.

CL(M) class [g ha^{-1} a^{-1}]	protection of drinking water quality, area per class in [%]	protection of food quality related area per class in [%]	protection of ecosystem functioning area per class in [%]
Cadmium			
≤ 2.5	4.5	2.1	0
2.5 – 5.0	8.9	85.6	16.6
5.0 – 7.5	18.6	12.1	30.0
7.5 - 10	22.4	0.2	23.2
10 - 15	30.5	0	15.2
15 - 20	8.0	0	7.1
20 - 25	3.4	0	3.4
25 - 30	1.4	0	2.0
30 - 35	0.8	0	1.3
> 35	1.5	0	1.2
Lead			
≤ 5	0.1	-	0
5 – 10	1.0	-	0.1
10 – 20	9.3	-	30.4
20 – 30	14.4	-	40.7
30 – 40	25.5	-	4.5
40 – 50	25.0	-	3.4
50 – 75	18.4	-	8.1
75 – 100	3.6	-	3.4
100 – 150	2.0	-	3.0
> 150	0.7	-	6.4
Mercury			
≤ 0.25	0.4	-	49.4
0.25 – 0.5	3.5	-	47.7
0.5 – 1	5.0	-	2.9
1 – 2	17.1	-	0
2 – 3	25.4	-	0
3 – 4	24.9	-	0
4 – 5	10.8	-	0
5 – 7.5	8.5	-	0
7.5 – 10	2.4	-	0
> 10	2.2	-	0

In general the CL(M) are mainly determined by the critical leaching of metals and less by the net uptake. Therefore high critical loads concentrate in the mountains, while low values can be found especially in the more continental eastern lowland part of Germany. This holds in particular for the CL(M) aiming at protection of drinking water, specifically Cd and Hg, because for these CL(M) the critical concentrations in soil water are often higher than critical concentrations aiming at protection of ecosystem functions.

Also for the CL(Pb), both related to protection of ground water and of ecosystems, the critical leaching flux has high influence on the results. The CL(Pb) related to ecosystem effects concentrate in the lower CL classes, i.e. ecosystems are slightly more sensitive receptors with respect to inputs of Pb than the use of groundwater for drinking water purposes. The ecotoxicological based critical limits (and related total concentrations in soil water) considerably increase with decreasing pH. Therefore there is a strong overlap of areas with high leaching water flux and high ecotoxicological based critical Pb concentrations resulting in very high critical loads in mountain areas with mainly acidic forest soils (see Figure DE-2).

Also the CL(Cd) related to ecotoxicological effects are slightly lower than those for drinking water protection. Here in particular the loess areas with mostly arable land as well as other regions with high soil pH show very low critical loads, if combined with low leaching rates. The CL(Cd) aiming at protection of human food are distributed with considerable proportions in only two classes of relatively low CL values. The differentiation within this type of CL(Cd) is caused to the largest part on the different leaching water flux, while differences in the yields play a minor role.
The CL(Hg) related to drinking water protection are much less sensitive than ecotoxicological based CL(Hg). This is caused by much higher critical concentrations in the leaching water. The ecotoxicological CL(Hg) are differentiated by both Hg uptake and the water leaching flux, the latter having stronger influence.

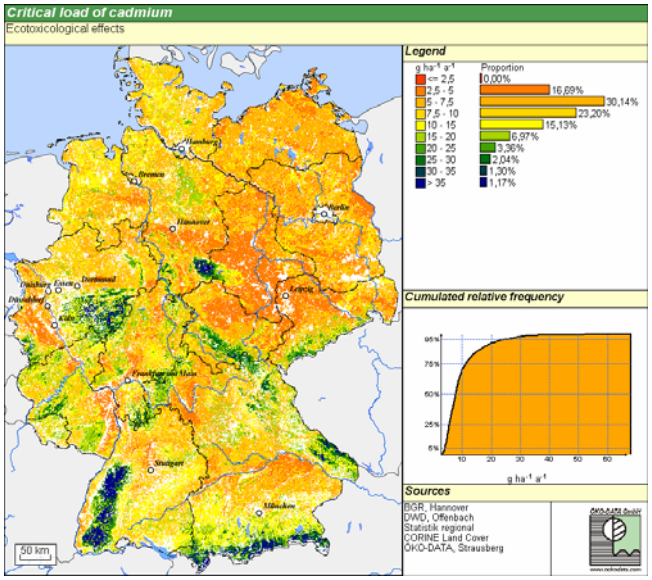

Figure DE-1. Regional distribution of critical loads of cadmium for terrestrial ecosystems related to ecotoxicological effects.

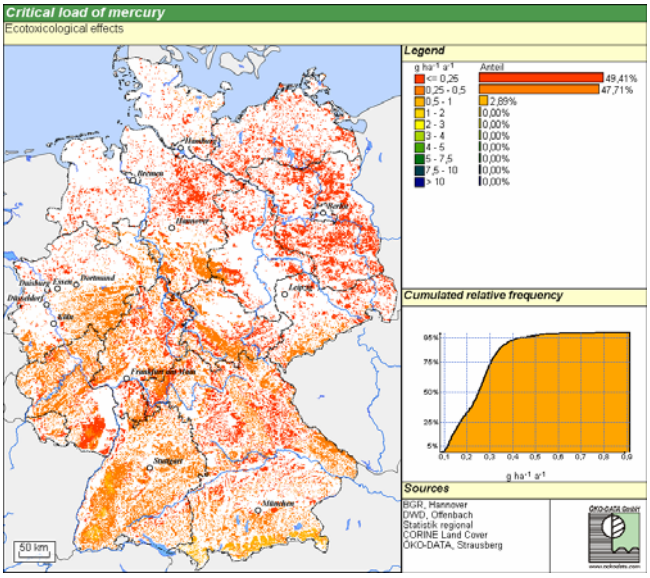

Figure DE-3. Regional distribution of critical loads of mercury for forest humus layers related to ecotoxicological effects.

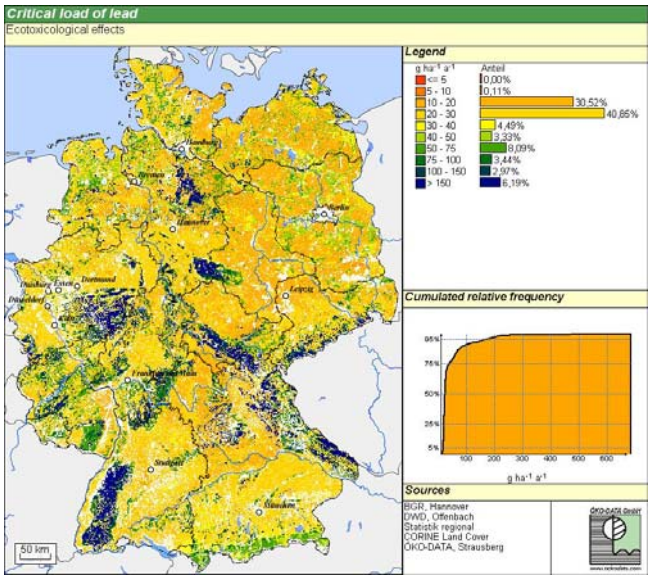

Figure DE-2. Regional distribution of critical loads of lead for terrestrial ecosystems related to ecotoxicological effects.

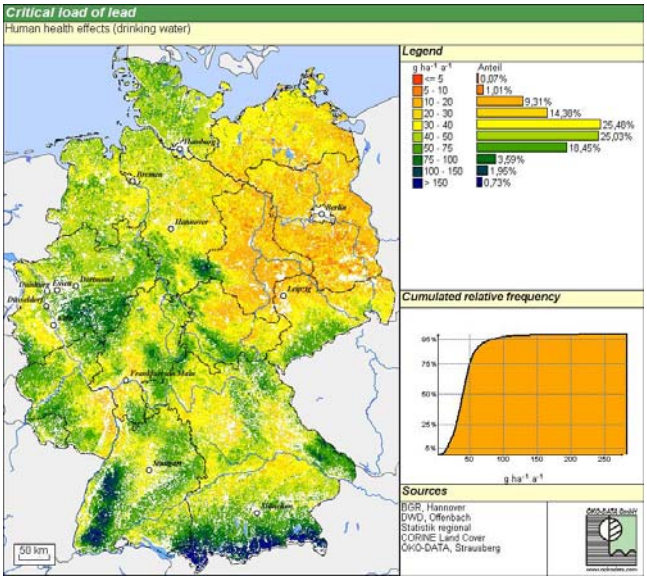

Figure DE-4. Regional distribution of critical loads of lead for terrestrial ecosystems aiming at the protection of groundwater (drinking water use).

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FINLAND

National Focal Centre

Maria Holmberg, Martin Forsius, Petri Porvari, Matti Verta, Jussi Vuorenmaa
Finnish Environment Institute (SYKE)
P.O. Box 140
FI-00251 Helsinki
tel: +358-9-403000
fax: +358-9-4030 0390
maria.holmberg@ymparisto.fi
www.environment.fi/syke

Collaborating institutions

Markus Meili
Institute of Applied Environmental Research
Stockholm University
SE-10691 Stockholm, Sweden
www.itm.su.se

Ilia Ilyin
MSC-E of EMEP
Leningradsky prospekt 16/2
RU-125040, Moscow, Russia
www.msceast.org

Birgitta Backman, Timo Tarvainen
Geological Survey of Finland
P.O. Box 96, FI-02151 Espoo
www.gsf.fi

Ritva Mäkelä-Kurtto, Markku Yli-Halla
MTT Agrifood Research Finland
Environmental Research
FI-31600 Jokioinen
www.mtt.fi/english/

Antti-Jussi Lindroos, Michael Starr,
Liisa Ukonmaanaho
Finnish Forest Research Institute
P.O. Box 18, FI-01301 Vantaa
www.metla.fi

Critical levels of mercury in precipitation

We have calculated the critical levels of mercury in precipitation in order to provide an estimate of the tolerable input to freshwaters considering human health effects in relation to mercury concentration in fish. Critical levels of mercury in precipitation were calculated from the surface water concentrations of total organic carbon $[TOC]_{sw}$ and total phosphorus $[TP]_{sw}$, with Equations 14, 15 and 16a in Chapter 5.5 of the Mapping Manual (2004). The critical concentration of mercury in the flesh of 1-kg pike was set to 0.3 mg kg^{-1}fw, and the value 250 000 L kg^{-1}fw was used for the transfer of atmospheric mercury to fish flesh via runoff (Mapping Manual, 2004).

The surface water concentrations of $[TOC]_{sw}$ and $[TP]_{sw}$, as well as lake and catchment area, stem from the survey conducted in 1995 (Henriksen et al., 1997; Henriksen et al., 1998; Rantakari et al., 2004). Here we report the critical levels of mercury in precipitation $[Hg]_{PrecCrit}$ for 820 lakes for which the catchment area was available. In the smallest size class, 0.04 to 0.1 km^2, we calculated $[Hg]_{PrecCrit}$ for 304 lakes (Table FI-2).

Calculated from the values of $[TOC]_{sw}$ and $[TP]_{sw}$, the critical level of mercury in precipitation reaches its lowest values for the smallest lakes (Table FI-2, Fig. FI-1). This is in accordance with the purpose of the formulae in the Mapping Manual, designed to reflect that Hg concentration in fish are generally highest in nutrient-poor lakes in acidic catchments (e.g. Verta et al., 1986; Meili 1997).

Although the highest calculated value of $[Hg]_{PrecCrit}$ (10 ng L^{-1}) was obtained for a small lake (area 0.04 km^2), the critical level of mercury in precipitation exceeded 5 ng L^{-1} for only 3 lakes smaller than 0.1 km^2, that is 1 % of the lakes in that size class (Table FI-3).

Conclusions and future work

Comparisons with local observations of mercury concentrations in atmospheric precipitation: 5–6 ng L^{-1}, at most 8 ng L^{-1} reported by Porvari (2003), leads to the conclusion that the critical levels of mercury in precipitation are exceeded for most Finnish lakes, at least in the case that these deposition levels are regionally representative.

So far, we have only addressed human health effects related to metal concentrations in fish. With our collaborating institutes, we have started formulating routines for addressing also human health effects in relation to metal contend in food, as well as ecosystem functioning in relation to free metal ion concentration in soil solution. The concrete work has not begun because funding has not yet been clarified.

Table FI-1. Summary of Finnish critical levels of mercury in precipitation.

Critical loads parameter (units)	EUNIS code	Min. value	Max. value	Data/ Method	Reference
[Hg]*PrecCrit* (ng L^{-1})	C1	0.6	10.0	[Hg]*PikeCrit*/ TF*HgSite*	Mapping Manual 30.09.2004
TF*HgSite* (L kg^{-1}fw)	C1	30068	505952	TF*HgRun*([TOC]*sw*+1)/ (0.4 ([TP]*sw*+15))	Mapping Manual 30.09.2004
[TOC]*sw* (mg L^{-1})	C1	0.4	33.8	Northern European Lake Survey 1995	Henriksen et al. 1997 Rantakari et al. 2004
[TP]*sw* (µg L^{-1})	C1	1	200	Northern European Lake Survey 1995	Henriksen et al. 1997 Rantakari et al. 2004
A*catchment*/A*lake*	C1	1	6750	Northern European Lake Survey 1995	Henriksen et al. 1997 Rantakari et al. 2004

Table FI-2. Critical levels of mercury in precipitation $[Hg]_{PrecCrit}$ (ng L^{-1}) for each lake size class.

Lake size	N	Min	Max	Median	Mean	Standard Deviation
0.04–0.1 km^2	304	0.6	10.0	1.5	1.7	0.89
0.1–1 km^2	268	0.7	5.4	1.6	1.8	0.86
1–10 km^2	159	0.9	6.6	1.8	2.0	0.85
10–100 km^2	44	1.1	5.3	1.7	2.0	0.92
> 100 km^2	45	1.1	2.9	1.6	1.8	0.46
All sizes	820	0.6	10.0	1.6	1.8	0.86

Table FI-3. Percent distribution of number of lakes for three levels of calculated values of $[Hg]_{PrecCrit}$ and five lake size classes.

Lake size	N	[Hg]*PrecCrit* < 1 ng L^{-1}	[Hg]*PrecCrit* 1 – 5 ng L^{-1}	[Hg]*PrecCrit* > 5 ng L^{-1}
0.04 – 0.1 km^2	304	13 %	86 %	1 %
0.1 – 1 km^2	268	6 %	93%	1%
1-10 km^2	159	1%	97%	2%
10-100 km^2	44	0%	95%	5%
> 100 km^2	45	0%	100%	0%
All sizes	820	7%	92%	1%

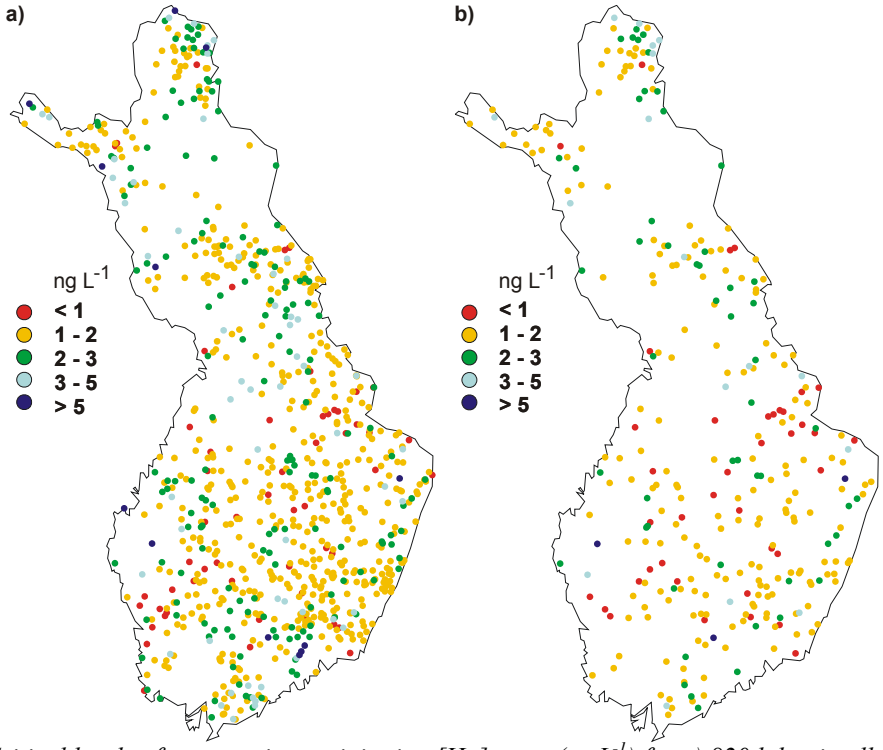

Figure FI-1: Critical levels of mercury in precipitation $[Hg]_{PrecCrit}$ (ng L^{-1}) for a) 820 lakes in all size classes; and b) 304 small lakes (area 0.04 to 0.10 km^2).

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FRANCE

National Focal Centre

Anne Probst, David Moncoulon
Laboratoire des Mécanismes de Transferts en Géologie
LMTG/OMP
UMR 5563 CNRS/UPS/IRD
14, avenue Edouard Belin
F-31400 Toulouse
aprobst@lmtg.obs-mip.fr
dmoncou@lmtg.obs-mip.fr

Jean-Paul Party
Sol-Conseil
251 rte La Wantzenau - Robertsau
F-67000 Strasbourg

Collaborating institutions

Laurence Galsomiès, Christian Elichegaray
ADEME
Centre de Paris - Vanves
Département Air
27, rue Louis Vicat
F-75737 Paris cedex 15

Erwin Ulrich, Luc Croisé
Office National des Forêts
Direction Technique
Département Recherche et Développement
Réseau RENECOFOR
Boulevard de Constance
F-77300 Fontainebleau

Philippe Cambier
Science du Sol
INRA
F-78026 Versailles Cedex

Louis-Michel Nageleisen
Ministère de l'Agriculture, de l'Alimentation, de la Pêche et des Affaires Rurales (DGFAR)
Département de la Santé des Forêts Antenne Spécialisée
Cenre INRA de Nancy
F-54280 Champenoux

Anne-Christine Le Gall
Direction des Risques Chroniques
Unité MECO
INERIS BP N°2
F-60550 Verneuil en Hallatte

Marc Rico, Monique Allaux
Ministère de l'Ecologie et du Développement Durable
Bureau de la pollution atmosphérique, des équipements énergétiques et des transports
Direction de la Pollution et de la Prévention des Risques
20, avenue de Ségur
F-75007 Paris

Introduction

In 2002 the French National Focal Centre (NFC) did not send the data for critical loads of lead and cadmium, since the methodology was still evolving. Following two years of expert meetings to

improve the calculation method, the French NFC has decided to send preliminary data on critical loads of heavy metals.

The French ecosystem classification was updated in 2003 for calculation and mapping the critical loads of acidity and nutrient nitrogen (Moncoulon et al., 2004; Probst et al., 2003). To ensure consistency with acid critical load database, critical loads of heavy metals have been calculated on the same ecosystem database.

Methodological choices

Studied area
The studied area, representing French forest ecosystems, consists of 170,657 km², i.e. 30% of France's total area. Following instructions for this call for data, critical load calculations are not carried out on soils with reductive conditions: wetlands are not included in the map.

Fluxes of heavy metals in the agricultural ecosystem are still difficult to model at the national scale. Further investigations on fertilizer inputs, on pesticide inputs, on uptake by crops and on the impact of winter nude soil period are necessary because of very wide range of variations and lacking data. When data will be more calibrated and improved, critical loads could be calculated and sent to the European database. Advances in recent investigations will allow their calculation for the next call for data for heavy metals and present map will be updated. Thus critical loads are restricted for forest ecosystems.

Studied metals
For similar reasons, the French NFC has decided to calculate critical loads of lead and cadmium since further advances on mercury research are still awaited in France.

Chosen receptor
Some uncertainties remain in the critical load calculation method for protection of groundwater for human consumption. In this method, soil characteristics are not taken into account to determine metal leached critical concentration. Metal content in drainage water is considered equivalent to metal concentration in soil solution. However, relationships between these two concentrations should be strongly dependant on soil binding capacities. For this reason, critical loads for groundwater protection were not calculated.

Consequently the data sent in 2005 concern critical loads of lead and cadmium for terrestrial ecosystems with the objective to protect micro-organisms in soil.

Calculation method

The manual methodology as defined by the expert group has been applied for forest ecosystems (UBA, 2004):

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

where CL(M) is the critical load of heavy metal. M_u is the net uptake in harvestable parts of plants under critical load conditions. $M_{le}(crit)$ is the critical leaching of heavy metal from the considered soil layer.

$$Mu = f_{mu} \; Y_{ha} \; [M]_{ha} \qquad (2)$$

where f_{mu} is the fraction of metal net uptake within the considered soil depth. Y_{ha} is the yield of harvestable biomass (dry weight). $[M]_{ha}$ is the metal content of the harvestable parts of plants.

$$M_{le}(crit) = Q_{le} \; [M]_{ss}(crit) \qquad (3)$$

where Q_{le} is the flux of drainage water leaching from the regarded soil layer. $[M]_{ss}(crit)$ is the critical total concentration of heavy metals in the soil solution.

Data sources

Annual increment of biomass was determined using IFN (Forest National Inventory 2002) productivity data for French forest ecosystems for tree species and forested areas. The same data were used to calculate the base cation uptake in case of critical loads of acidity.

Content of metal in the harvested part of the plant was determined for the 18 potential vegetation types of the ecosystem classification using literature data (Freitas et al., 2004; Soltz and Greger, 2002; Bechtel Jacobs Compagny LLC, 1998). A lot of references have been found on oak trees and coniferous trees for lead content. Less data are available for cadmium content. Manual guidelines data (UBA, 1996) were taken into account for these less studied vegetation types.

The Fraction of uptake in the considered soil depth (0.2 m) is simplified to 1 for coniferous forest and 0.8 for deciduous forest.

The flux of leaching water from the considered soil depth is taken from the acidity critical load database on efficient rain (Moncoulon et al., 2004; Probst et al., 2003).

Critical concentration of heavy metal in soil solution

$[M]_{crit}$ has been calculated using the WHAM model and manual look-up tables (Tipping, 1998; Tipping et al., 2003; UBA, 2004) on the 31 soil types of the ecosystem database. The critical dissolved metal in soil solution was estimated from soil characteristics (pH, DOC, OM and pCO_2). The concentration in soil solution was considered equivalent to the concentration in leaching water. Data for pH, OM, pCO_2, DOC are from the acidity critical load database (Moncoulon et al., 2004; Probst et al., 2003), which is the synthesis of the RENECOFOR network data (Brethes and Ulrich, 1997), and the European soil database (Badeau and Peiffer, 2001).

Results

The following maps (Figures FR-1 and FR-2) present results of calculation of critical loads for forest ecosystems. The most sensitive areas for lead and cadmium deposition in case of soil protection are located in the calcareous ecosystems where soil present high binding capacities: Southern Alps and Mediterranean area, north-eastern part of France (primary limestones), volcanic ecosystems in Massif Central.

Following the increased precision of the ecosystem map, sensitive ecosystems like river alluvium appear in each EMEP grid cell. Thus, the fifth percentile of the EMEP grid appears more sensitive than the complete ecosystem map. This reflects the complexity and the diversity of the ecosystems in France.

Acid soils are less sensitive to metal deposition with the objective of soil protection: indeed, with poor binding capacities, these types of soils do not retain metallic pollutants. Nevertheless, on these types of soils, the highest risk stands for ground water protection.

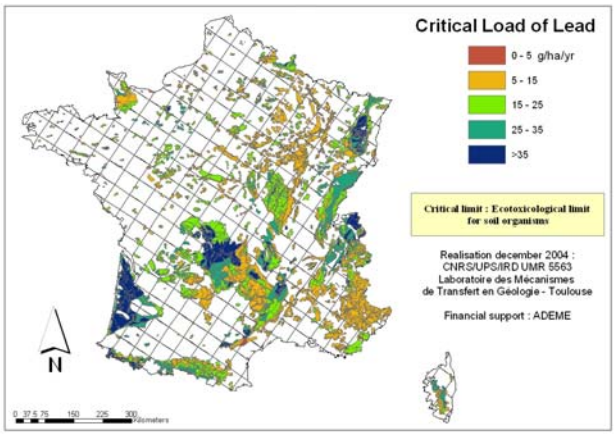

Figure FR-1. Map of critical loads of lead for French ecosystems: protection of soil micro-organisms.

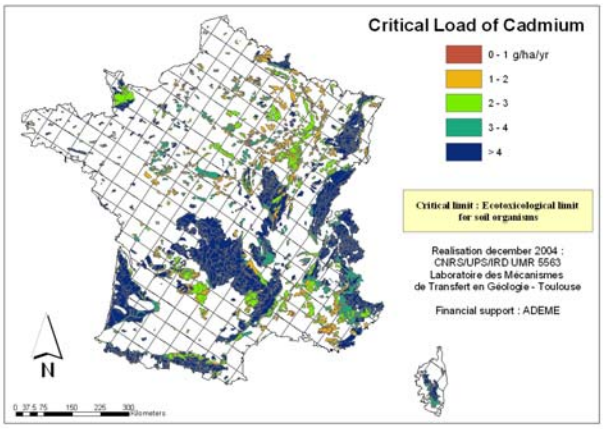

Figure FR-2. Map of critical loads of cadmium for French ecosystems: protection of soil micro-organisms.

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ITALY

National Focal Centre

Mara Angeloni
Ministry for the Environment
Via Cristoforo Colombo
I- 00147 Rome
tel: + 39-6-5722 8113
angeloni.mara@minambiente.it

Collaborating institutions

Valerio Silli
Patrizia Bonanni
APAT (National Agency for the Environmental Protection and Technical Services)
Via Vitaliano Brancati, 48
I- 00144 Rome
tel: +39-6-5007 2800
+39-6-5007 2801
fax: +39-6-5007 2986
silli@apat.it, bonanni@apat.it

Roberto Daffinà
APAT Consultant
Via Vitaliano Brancati, 48
I- 00144 Rome
tel: +39-6-5007 2962
fax: +39-6-5007 2986
daffina@apat.it

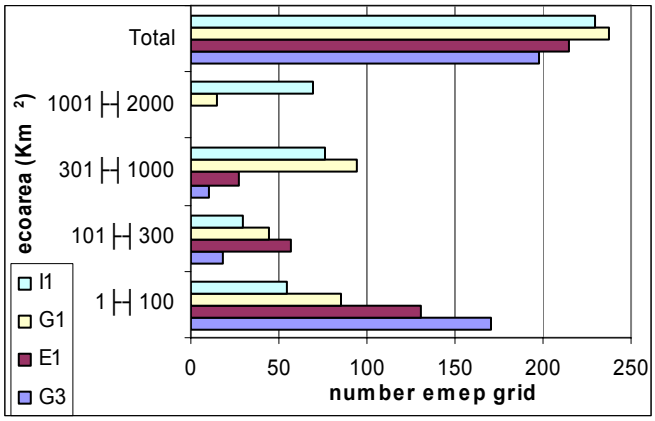
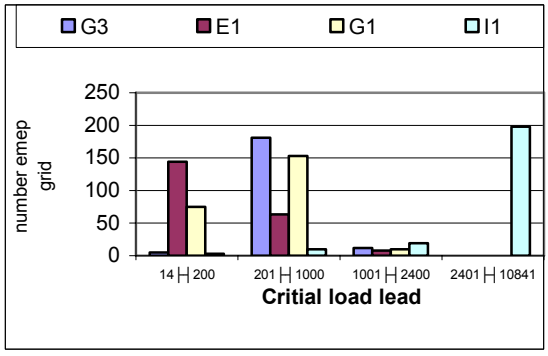
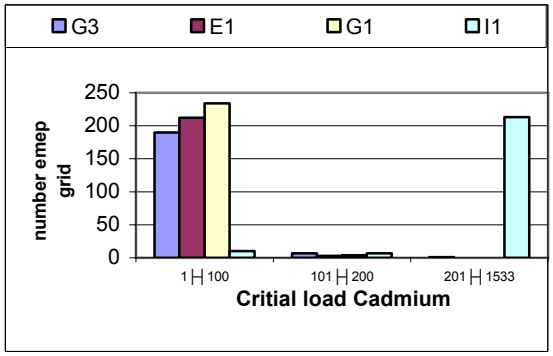
Armando Buffoni
APAT Consultant
Via Pergolesi 2
20124 Milano
tel/fax: 02 66713184
ab-mi@libero.it

Introduction

The heavy metal critical loads calculation follows the methodology described in the Mapping Manual (UBA, 2004).
Data have been extracted from national databases or have been derived by appropriate equations.
Land use data were derived from Image & Corine Land Cover 2000 (APAT, 2004).
Land use data have been reclassified under the EUNIS Habitat classification. This result represent a preliminary level I classification.

Data sources and methodology

Table IT-1. Overview of the Italian data sources, methodologies and statistics for the submitted variables.

Variable	Method/Source	Statistics
Ecosystem area [km^2]	Calculated from Italian soil inventory database	
Critical Load of Metal (CLM) [$g*ha^{-1}*a^{-1}$]	Mapping Manual 2005 chap. 5.5.2.1 eq. 1	
	lead	
	Cadmium	
Critical concentration of metal in precipitation (CCM) [km^2]		Not determined yet
Effect	Effect_nr=3 Ecotoxicological effect Terrestrial ecosystems	

<table>
<tr>
<td>Net uptake of metal (Mu) [g*ha^{-1}*a^{-1}]</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.2; eq. 2</td>
<td>
<table>
<tr><td>Lead</td><td>MIN</td><td>MED</td><td>MAX</td></tr>
<tr><td>G3</td><td>144,9</td><td>182,6</td><td>209,9</td></tr>
<tr><td>E3</td><td>4,8</td><td>5,3</td><td>10,6</td></tr>
<tr><td>G1</td><td>28,3</td><td>135,0</td><td>219,2</td></tr>
<tr><td>I1</td><td>1,7</td><td>4236,1</td><td>10661</td></tr>
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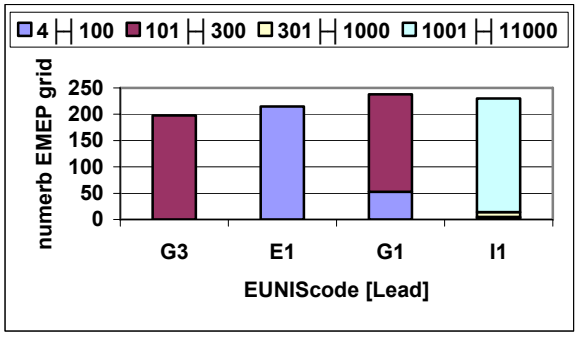

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<tr><td>Cd</td><td>MIN</td><td>MED</td><td>MAX</td></tr>
<tr><td>G3</td><td>3,2</td><td>4,0</td><td>4,6</td></tr>
<tr><td>E3</td><td>0,5</td><td>0,5</td><td>1,1</td></tr>
<tr><td>G1</td><td>1,4</td><td>6,8</td><td>11,0</td></tr>
<tr><td>I1</td><td>0,2</td><td>607,0</td><td>1527,0</td></tr>
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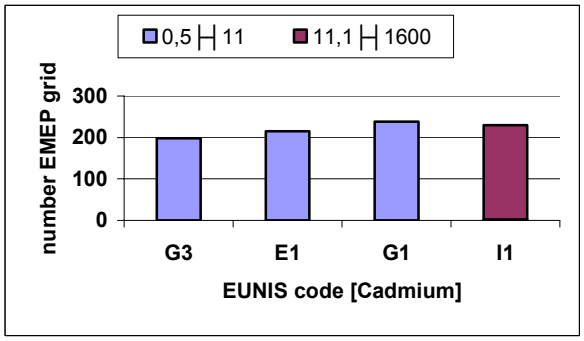

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</tr>
<tr>
<td>Annual yield/increment of biomass (Yha) [g*ha^{-1}*a^{-1}]</td>
<td>Calculated from Italian agricultural inventory database (ISTAT)</td>
<td>
<table>
<tr><td></td><td>MIN</td><td>MED</td><td>MAX</td></tr>
<tr><td>G3</td><td>36,21</td><td>45,7</td><td>52,47</td></tr>
<tr><td>E3</td><td>3,20</td><td>3,5</td><td>7,08</td></tr>
<tr><td>G1</td><td>7,08</td><td>33,8</td><td>54,80</td></tr>
<tr><td>I1</td><td>1,52</td><td>3903,1</td><td>17429,6</td></tr>
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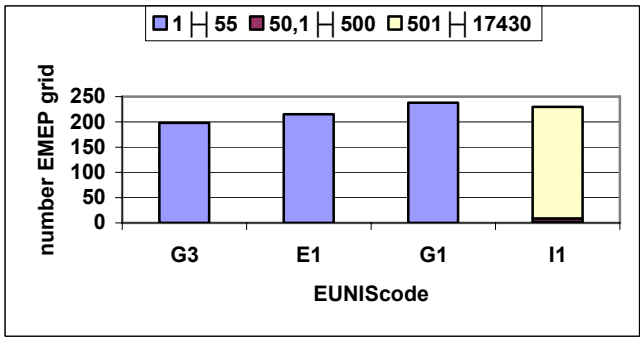

</td>
</tr>
<tr>
<td>Content of metal in the harvested part of plant (Mha) [g*ha^{-1}*a^{-1}]</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.2 table 2</td>
<td>
<table>
<tr><td>EUNIScode</td><td>Pb</td><td>Cd</td></tr>
<tr><td>G3</td><td>5,00</td><td>0,11</td></tr>
<tr><td>E3</td><td>1,50</td><td>0,15</td></tr>
<tr><td>G1</td><td>5,00</td><td>0,25</td></tr>
<tr><td>I1</td><td>1,12</td><td>0,16</td></tr>
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</td>
</tr>
<tr>
<td>Fraction of the uptake with the considered soil depth (fMu)</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.2</td>
<td>fMu (forest)=0,8 other fMu=1,0</td>
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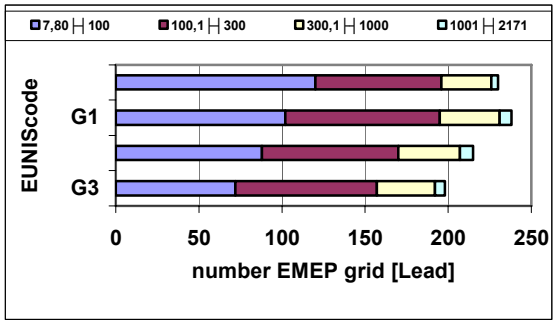
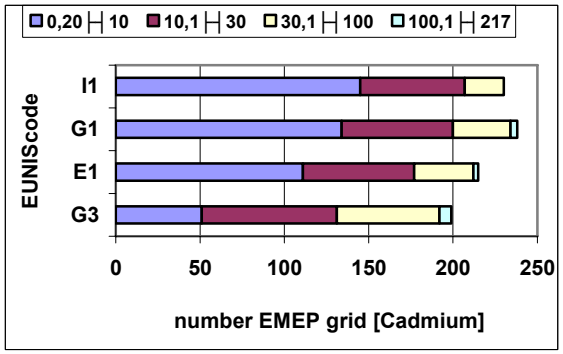
</table>

<table>
<tr>
<td>Critical leaching flux of heavy metal from the topsoil (Mlecrit) [g*ha-1*a-1]</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.3 eq. 3</td>
<td> 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<tr>
<td>Flux of leaching water (Qle) [m*a^{-1}]</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.3 eq. 4b</td>
<td>
<table>
<tr><th></th><th>MIN</th><th>MED</th><th>MAX</th></tr>
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<tr><td>E3</td><td>0,0</td><td>0,6</td><td>2,0</td></tr>
<tr><td>G1</td><td>0,0</td><td>0,5</td><td>1,7</td></tr>
<tr><td>I1</td><td>0,0</td><td>0,4</td><td>1,5</td></tr>
</table>
</td>
</tr>
<tr>
<td>Soil thickness (thick) [m]</td>
<td></td>
<td>thick=0,1m forest and grassland;
thick=0,3m arable</td>
</tr>
<tr>
<td>Type of soil layer (layercode)</td>
<td></td>
<td>layercode=1 humus layer only</td>
</tr>
<tr>
<td>Critical concentration of dissolved metal in the soil (Mcrit) [mg*m^{-3}]</td>
<td>Mapping Manual 2005 chap. 5.5.2.1.3 eq. 5</td>
<td>
<table>
<tr><th>Lead</th><th>MIN</th><th>MED</th><th>MAX</th></tr>
<tr><td>G3</td><td>15,7</td><td>39,5</td><td>195,89</td></tr>
<tr><td>E3</td><td>15,6</td><td>36,4</td><td>185,61</td></tr>
<tr><td>G1</td><td>15,6</td><td>37,0</td><td>185,64</td></tr>
<tr><td>I1</td><td>15,6</td><td>36,8</td><td>185,26</td></tr>
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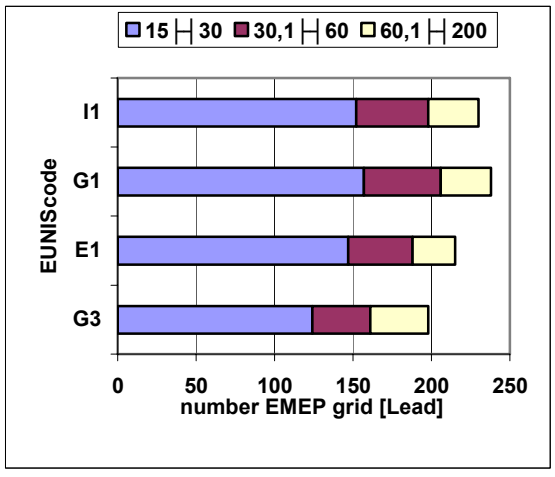
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<table>
<tr>
<td></td>
<td></td>
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<table>
<tr><th>Cadmium</th><th>MIN</th><th>MED</th><th>MAX</th></tr>
<tr><td>G3</td><td>0,20</td><td>5,0</td><td>16,55</td></tr>
<tr><td>E3</td><td>0,48</td><td>2,9</td><td>10,04</td></tr>
<tr><td>G1</td><td>0,35</td><td>2,8</td><td>10,01</td></tr>
<tr><td>I1</td><td>0,10</td><td>2,6</td><td>9,89</td></tr>
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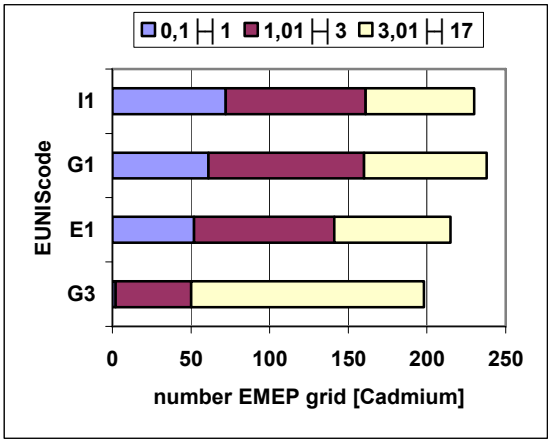

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</tr>
<tr>
<td>pH</td>
<td>derived from Italian soil inventory database</td>
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<tr><td>G3</td><td>3,5</td><td>4,1</td><td>5,0</td></tr>
<tr><td>E3</td><td>5,0</td><td>5,4</td><td>6,5</td></tr>
<tr><td>G1</td><td>4,5</td><td>5,3</td><td>6,5</td></tr>
<tr><td>I1</td><td>6,0</td><td>6,9</td><td>7,4</td></tr>
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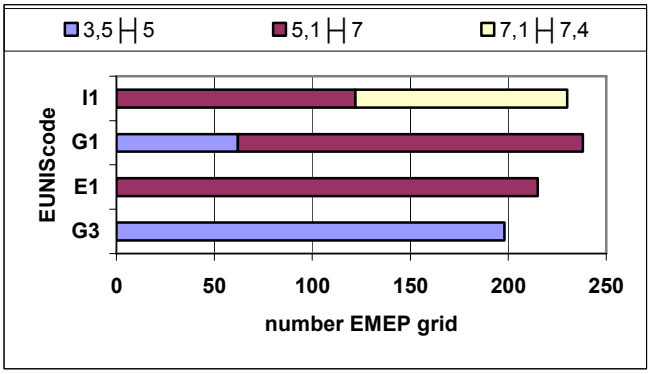

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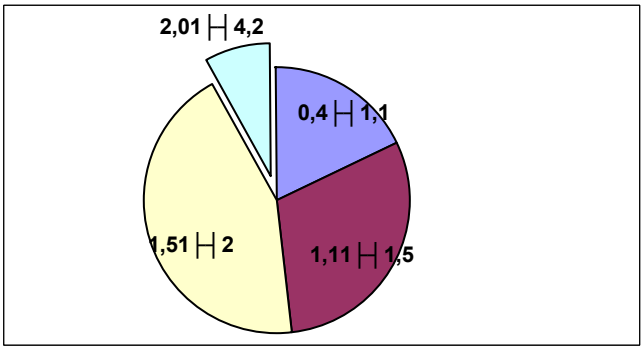
<tr>
<td>Organic matter content of the soil (OM) [%]</td>
<td>derived from Italian soil inventory database</td>
<td>


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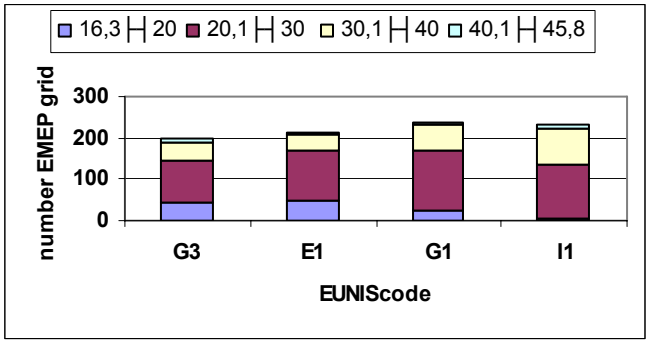
<tr><td>Partial pressure of CO_2 (pCO_2) [*air]</td><td>Calculated from Italian soil inventory database by Mapping Manual 2005 chap. 5 eq. 5.44</td><td> 
</td></tr>
<tr><td colspan="2">Concentration of suspended particulate matter in the soil (SPM) [g*m^{-3}]</td><td>Not determined</td></tr>
<tr><td>Concentration of dissolved organic carbon in the soil (DOC) [g*m^{-3}]</td><td>Manual Mapping 2005 chap. 5.5.2.2.3 after table 6</td><td><table>
<tr><td>Ecosystem</td><td>DOC</td></tr>
<tr><td>Forest (0-10cm)</td><td>20</td></tr>
<tr><td>Grassland</td><td>15</td></tr>
<tr><td>Arable land</td><td>10</td></tr>
</table></td></tr>
<tr><td>Concentration of dissolved organic matter in the soil (DOM) [g*m^{-3}]</td><td>Manual Mapping 2005 chap. 5.5.2.2.3 after table 6</td><td><table>
<tr><td>Ecosystem</td><td>DOM</td></tr>
<tr><td>Forest (0-10cm)</td><td>40</td></tr>
<tr><td>Grassland</td><td>30</td></tr>
<tr><td>Arable land</td><td>20</td></tr>
</table></td></tr>
</table>

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NETHERLANDS

National Focal Centre

Arjen van Hinsberg
Netherlands Environmental Assessment Agency (MNP)
P.O. Box 303
3720 AH Bilthoven
tel: +31-30-274 3062
fax: +31-30-274 4419
arjen.hinsberg@mnp.nl

Collaborating institution

Gert Jan Reinds
Wim de Vries
J.E. Groenenberg
Alterra, Wageningen UR
P.O. Box 47
6700 AA Wageningen
tel: +31-317 474697
fax: + 31- 317 419000
gertjan.reinds@wur.nl
wim.devries@wur.nl

National Maps Produced

Critical loads for cadmium and lead were computed in view of their ecotoxicological effects for both agricultural and non-agricultural soils and with respect to different human-toxicological effects for agricultural soils only, as shown in Table NL-1. The critical loads for Cd were computed as loads that in a steady-state situation (effect-based approach) will not lead to concentrations of Cd above critical limits in: (i) soil solution, (ii) drinking water, (iii) crop contents (wheat) and (iv) animal organs (kidney). For Pb the calculations were limited to soil solution (agricultural and non-agricultural soils) and drinking water (agricultural soils only), as shown in Table NL-1. The methods and results of the derived critical loads are discussed below.

Table NL-1 Effects and limitsand land cover types for which critical loads for the given metal are calculated.

Metal	Type of effect	Limit	Grassland	Arable land	Forest
Cd and Pb	Ecotoxicological	Critical value soil solution	x	x	x
Cd and Pb	Human – toxicological	Drinking water value	x	x	-
Cd	Human – toxicological	Food quality criterion wheat	-	x	-
Cd	Human – toxicological	Food quality criterion kidney	x	-	-

Calculation Methods

Critical loads of lead and cadmium for Dutch soils related to critical limits for: (i) soil solution and (ii) drinking water were calculated according to the chapter 5.5 of the Mapping Manual (UBA, 2004). For crop contents in wheat, the use of a fixed concentration, based on a direct relationship between plant and soil was not used. Instead we used a critical Cd content in wheat of 0.1 $mg.kg^{-1}$ and calculated the related soil concentration by the inverse application of the soil-plant relationship, followed by the soil-solution relationships (from total metal to reactive metal to dissolved metal concentration). The various relationships used are presented in the background to the mapping manual (De Vries et al., 2004). The critical load of Cd for grassland in view of a critical limit in the kidney of cows was calculated according to Annex 3 of the background to the mapping manual (De Vries et al., 2004). In forest soils, the calculations are limited to the organic layer and the upper part of the mineral soil layer (with a considered depth of 10 cm). In agricultural soils, the calculations ate limited to the upper soil (plough) layer of 10-20 cm for grassland and 20-30 cm for arable land.

Data derivation for forest soils

Vegetation and soil types: Similar to the derivation of Dutch critical loads of nitrogen and acidity (Van Hinsberg et al., 2001), critical loads were calculated at a 250x250m grid scale. Table NL-2 describes the distinguished soil (16 types) and vegetation types (3 types). For each individual 250x250

grid cell, critical loads were calculated, based on soil and vegetation/forest type specific parameters. The used soil and vegetation maps are described in Van Hinsberg et al. (2001).

Table NL-2.Forest-soil type combinations for which critical loads were calculated.

Soil type[1]	Sand poor (Carbic Podzols, Arenosols)
	Sand rich (Gleyic Podzols, Gleysols)
	Sand calcareous (Arenosols)
	Peat (Histosols); 4 texture classes
	Loess (Luvisols); 3 texture classes
	Clay non-calcareous (Fluvisols); 4 texture classes
	Clay calcareous (Fluvisols)
Vegetation/forest type	Deciduous forest (broadleaved)
	Spruce forest (coniferous)
	Pine forest (coniferous)

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

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 according to Chapter 5.5 of the Mapping Manual (UBA, 2004).

It was assumed that 80% of the uptake takes place in the organic layer already, and that at 10 cm depth in the mineral soil, uptake is complete. Yields are soil and forest type specific (Table NL-3). 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 computed are given in Table NL-4.

Table NL-3. Estimated yields ($kg.ha^{-1}.a^{-1}$) for the considered forest type-soil type combinations.

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-4. Calculated uptake rates for the mineral soil for Cd and Pb ($g\ ha^{-1}a^{-1}$) for the considered forest type-soil type combinations.

Soil type	Cd uptake			Pb uptake		
	Deciduous	Pine	Spruce	Deciduous	Pine	Spruce
Clay calcareous	1.47	0.47	1.05	24.5	7.9	17.5
Clay non-calcareous	1.05	0.47	1.05	17.5	7.9	17.5
Loess	1.47	1.09	1.76	24.5	18.1	29.4
Peat	1.05	0.47	1.05	17.5	7.9	17.5
Sand calcareous	1.47	0.47	1.05	24.5	7.9	17.5
Sand rich	1.47	1.09	1.76	24.5	18.1	29.4
Sand poor	0.63	0.84	1.05	10.5	14.0	17.5

Leaching rates: The critical leaching flux and the water flux leaching from the mineral topsoil were calculated according to Chapter 5.5 of Mapping Manual (UBA, 2004). 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 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. Data for forest transpiration have been calculated for all combinations of forests types and soil types with a hydrological model (De Vries, 1996).

Transpiration values for the organic layer were multiplied by a root uptake factor of 0.35 and 0.2 for conifers and deciduous forest respectively, being the ratio of fine roots up to the mineral soil divided by the fine root biomass in the complete root zone. For the uppermost 10 cm of mineral soil, cumulative uptake fractions were set at 0.65 and 0.5 for conifers and deciduous forest, respectively. 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 values) in leaching rates for the considered forest type-soil type combinations.

Soil type	Forest type	Q_{le} (m a^{-1})		
		Min	Avg	Max
Clay calcareous	Deciduous	0.32	0.36	0.42
	Pine	0.28	0.29	0.32
	Spruce	0.19	0.19	0.19
Clay non-calcareous	Deciduous	0.33	0.39	0.49
	Pine	0.27	0.31	0.35
	Spruce	0.21	0.24	0.27
Loess	Deciduous	0.34	0.4	0.49
	Pine	0.3	0.33	0.38
	Spruce	0.17	0.21	0.28
Peat	Deciduous	0.3	0.36	0.44
	Pine	0.25	0.29	0.35
	Spruce	0.15	0.2	0.23
Sand calcareous	Deciduous	0.36	0.39	0.43
	Pine	0.32	0.34	0.37
	Spruce	0.24	0.25	0.26
Sand poor	Deciduous	0.35	0.41	0.49
	Pine	0.31	0.36	0.44
	Spruce	0.23	0.28	0.34
Sand rich	Deciduous	0.34	0.41	0.49
	Pine	0.3	0.35	0.43
	Spruce	0.23	0.28	0.33

Critical dissolved metal concentrations: The critical limits used for dissolved metal concentrations were derived from the mapping manual by interpolating in the table that gives critical concentrations as a function of pH and DOC, using actual pH and DOC concentrations of the soil/forest combination. Values for the pH were estimated from environmental factors, such as 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). For pH the percentage of explained variance of the regression model was about 54%. DOC concentrations were estimated as a function of layer (organic, mineral), soil type and vegetation type.

Data derivation for agricultural soils

Vegetation and soil types: For agricultural soils, critical loads were calculated for 4647 so-called STONE plots, consisting of one or more 500x500m^2 grid cells with a unique combination of land use, soil type and ground water table class A distinction is made between grassland and arable land (maize and various rotations with potatoes, sugar beet, cereals, and vegetables) whereas soils are divided in sand, loess, clay and peat. Furthermore, a distinction is made in different hydrological regimes (wetness classes), using ground water table classes (Gt) from the 1: 50 000 soil map used in the plots, according to:

- wet (poorly drained): Gt I, II, II*, III, III*, V, V*; mean highest water level <40cm;
- moist (moderately drained): Gt IV, VI; mean highest water level 40-80cm;
- dry (well drained): Gt VII, VII*; mean highest water level >80cm.

Critical loads were calculated for each STONE plot, based on soil and vegetation specific parameters.

Uptake rates: Geo-referenced data on net annual Cd and Pb uptake were estimated by multiplying yields and Cd and Pb concentrations as a function of land use and soil type (and in case of yield also ground water table class), thus allocating them to combinations occurring in distinct plots. For arable land, data were used of the area of each considered crop within each STONE plot to assess the yield and metal content (and thus the uptake) by those crops. The resulting uptake from arable land was calculated by an area averaged uptake of all the considered crops in the STONE plot. In the situation where wheat is used as the critical indicator, the calculation is made as if all arable land consists of wheat.

The used average yields in ton dry matter per hectare are presented in Table NL-6. Apart from grass and maize all yield data were derived by multiplication of available data on the average yield in fresh weight with the dry matter percentage as presented in Table NL-7. The data for potatoes, wheat and sugar beet were taken from Schröder et al. (2004) Yields for vegetables "category other" and "other cereals" were based on data in CBS stat line.

Table NL-6. Yield data in ton dry matter per hectare for the considered crops in the calculation.

Soil	Drainage	Yield (ton dry matter ha-1)						
		Grass	Maize	Potato	Wheat	Sugar beet	Other cereals	Other crops
Sand	Dry	10	13	10	6.4	12.2	5.1	7.5
	Moist	12	16	10	6.4	12.2	5.1	7.5
	Wet	12	16	10	6.4	12.2	5.1	7.5
Loess /	Dry/Moist	12	16	11.5	7.4	13.8	5.5	7.5
Clay	Wet	10	13	11.5	7.4	13.8	5.5	7.5
Peat	Dry/Moist	11	11	10	6.4	12.2	5.1	7.5
	Wet	10	10	10	6.4	12.2	5.1	7.5

Table NL-7. Yield data in ton fresh weight per hectare and the dry matter percentage of arable crops.

Soil	Drainage	Yield (ton fresh weight/ha)				
		Potato	Wheat	Sugar beet	Other cereals	Other crops
Sand	Dry	43.6	7.5	53	6	15
	Moist	43.6	7.5	53	6	15
	Wet	43.6	7.5	53	6	15
Loess /	Dry/Moist	50	8.7	60	6.5	15
Clay	Wet	50	8.7	60	6.5	15
Peat	Dry/Moist	43.6	7.5	53	6	15
	Wet	43.6	7.5	53	6	15
		Dry matter percentage				
		23	85	23	85	50

For Cd, the content in each crop was calculated by the soil to plant transfer relationships using soil properties from each plot, with the exception of potatoes for which the relationship was not reliable. For Pb (and Cd in potatoes), for which no reliable soil-plant relationships exists, median Pb (and Cd) concentrations for the various combinations of land use and soil type were used in the simulation.

Leaching rates: As with forest soils, the critical leaching flux and the water flux leaching from the mineral soil were calculated according to chapter 5.5 of the Mapping Manual (UBA, 2004) and precipitation estimates have been derived from 280 weather stations in the Netherlands, using interpolation techniques to obtain values for 10x10 km^2 grids. Interception fractions were considered to vary with land use type only, independent of soil type and water table class. Values were set at 0.10 for grassland, 0.03 for maize land and heath land and 0.02 for arable land based on a run with the hydrological model SWATRE for the Netherlands (Groenendijk, *pers. comm.*). Data used for soil evaporation are 90 mm a^{-1} for grassland and 165 mm a^{-1} for arable land. Reference transpiration data are given in Table NL-8 based on a run with the hydrological model SWATRE for the Netherlands (Groenendijk, *pers. comm.*). Transpiration values for the mineral topsoil were multiplied by 1,

assuming that all root uptake takes place in the topsoil. In general, the sum of soil evaporation and transpiration was about half the precipitation.

Table NL-8. Average transpiration as a function of land use and soil type.

Soil type	Water table class	Transpiration (mm a^{-1})		
		Grassland	Maize land	Arable land
Sand	Dry	347	217	194
	Moist	372	217	199
	Wet	374	184	182
Loess	Dry	362	222	205
	Moist	388	227	205
	Wet	373	232	205
Clay	Dry	367	212	198
	Moist	362	189	184
	Wet	353	154	171
Peat	Dry	359	199	192
	Moist	365	196	182
	Wet	347	144	154

1) Dry is related to a MHW level of >80 cm
2) Moist is related to a MHW level between 40 and 80 cm
3) Wet is related to a MHW level below 40 cm

Critical dissolved metal concentrations: Unlike forest soils, the critical dissolved Cd and Pb concentrations in soil drainage water were not interpolated from a table that gives critical concentrations as a function of pH and DOC, but calculated as a function of pH and DOC with the WHAM model, using the critical limit functions for free metal ion concentrations of Cd and Pb given in the manual. For grassland a constant DOC level of 15 mg l^{-1} was assumed and for arable land 10 mg l^{-1} (De Vries et al., 2004). A distinction was made between mineral soils (with an OM below 20%) and organic soils (with an OM above 20%). The pCO_2 was set at 15 times the atmospheric pressure and SPM was set =0 (values thus equal the total concentration in soil solution). The results for a set of pH values are given in Table NL-9.

Table NL-9. Values used for the total critical Cd and Pb, Cu and Zn concentrations in soil drainage water [M]tot,sdw(crit) in mineral soils and peat soils below arable land (DOC = 10 mg l^{-1}) and grassland (DOC = 15 mg l^{-1}) at various pH levels.

Soil	DOC[1]	[M]tot,SDW(crit) ($mg.m^{-3}$)									
	mg.l-1	pH 3.5	pH 4.0	pH 4.5	PH 5.0	PH 5.5	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
		Cd									
mineral	10	4.04	2.81	1.95	1.42	1.11	1.13	0.93	0.74	0.65	0.83
	15	4.05	2.82	1.97	1.46	1.19	1.35	1.14	0.90	0.74	0.87
organic	10	4.07	2.87	2.11	1.65	1.38	1.14	0.93	0.74	0.65	0.83
	15	4.11	2.93	2.21	1.80	1.59	1.36	1.14	0.90	0.74	0.87
		Pb									
mineral	10	34.97	11.72	4.22	1.82	1.05	1.39	2.02	2.30	2.38	2.47
	15	35.05	11.86	4.42	2.08	1.34	1.97	2.97	3.40	3.46	3.35
organic	10	35.99	14.08	6.72	3.97	2.53	1.43	2.02	2.30	2.38	2.47
	15	37.49	15.58	8.18	5.24	3.51	2.03	2.97	3.40	3.46	3.35

[1] DOC values of 10 and 15 $mg.l^{-1}$ are used as an average value for arable land and grassland.

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POLAND

National Focal Centre

Wojciech A. Mill, Adrian Schlama
Institute of Environmental Protection
Section of Integrated Modelling
Grunwaldzka Str. 7B/2
PL-41-106 Siemianowice Śl.
tel/fax: +48 32 2281482
mill@silesia.top.pl

Collaborating institutions

Anna Pasieczna, Jozef Lis
Polish Geological Institute
Environmetal Geology Department
Rakowiecka Str. 4
PL-00-975 Warszawa
tel: +48 22 8495351
apas@pgi.waw.pl
jlis@pgi.waw.pl

Krzysztof Okła, Jolanta Starzycka
General Directorate of the State Forests
Spatial Information System
Wawelska Str. 52/54
PL-00-922 Warszawa
okla@lasypanstwowe.gov.pl,
j.starzycka@lasypanstwowe.gov.pl

Introduction

In reaction to the second call for national critical loads data of heavy metals the Polish NFC responds with input and output databases as well as relevant maps for cadmium, lead and mercury addressed to broadleaved (EUNIS class G1) and coniferous (EUNIS class G3) woodlands. Calculations were based on the revised methodology described in chapter 5.5 of the recent version of the Mapping Manual.

Input and output data specification

Table PL-1. Minimum, maximum and mean values for site-specific input parameters.

Parameter		Minimum	Maximum	Mean	Data source
Yha	G1	1108	2761	1854	Office of Forest Management and Geodesy,
(kg $ha^{-1}a^{-1}$)	G3	636	2508	1567	Warszawa
Qle (m a^{-1})		0.005	1.37	0.16	Hydrological Atlas of Poland
pH		2.6	7.2	3.3	II-level forest monitoring by the Forest Research Institute under a contract of the State Inspectorate of Environmental Protection
OM (% dw)		4.6	7.9	5.3	II-level forest monitoring by the Forest Research Institute under a contract of the State Inspectorate of Environmental Protection
DOC (g m^{-3})		15	47	3.2	Estimates based on the data from literature review and Intensive Monitoring Plots in Europe given in the Background Document – Annex 11 of the Mapping Manual

Table PL-2. Minimum, maximum and mean values for selected input variables and critical loads of cadmium, lead and mercury.

Parameter	EUNIS code	Cd			Pb			Hg		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
CLM	G1	0.38	65.7	8.03	5.4	1080.5	106.6	0.0012	0.289	0.038
($g\ ha^{-1}\ a^{-1}$)	G3	0.62	66.9	8.23	10.2	1189.6	126.0	0.033	0.476	0.093
$M_{le(crit)}$	G1	0.21	65.6	7.85	2.0	1077.2	102.9	0.0012	0.289	0.038
($g\ ha^{-1}\ a^{-1}$)	G3	0.23	66.4	7.84	1.89	1177.2	118.1	0.0185	0.416	0.054
$[M]_{ss(crit)}$	G1	0.0015	0.0079	0.0047	0.0061	0247	0.065	0,015	0.027	0.023
($mg\ m^{-3}$)	G3	0.0023	0.0079	0.0051	0.0078	0.249	0.079	0.015	0.047	0.034
Mu	G1	0.11	0.28	0.19	2.22	5.52	3.71	0.0	0.0	0.0
($g\ ha^{-1}a^{-1}$)	G3	0.16	0.63	0.39	3.18	12.54	7.84	0.016	0.063	0.039

Critical total dissolved metal concentrations $[M]_{ss(crit)}$ for cadmium and lead were calculated by use of the chemical speciation model W6S-MTC2 developed by Professor Ed Tipping and made available to the Polish NFC.
Values for contents of Cd, Pb and Hg in biomass of harvestable parts of coniferous and deciduous trees were adopted from Mapping Manual, chapter 5.5 Table PL-2.

Further work

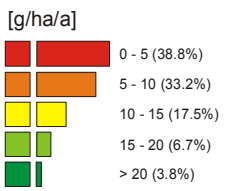
In the next step of calculation of critical loads of heavy metals the Polish NFC considers to address human health and ecosystem effects for arable land, grassland and non-agricultural land.

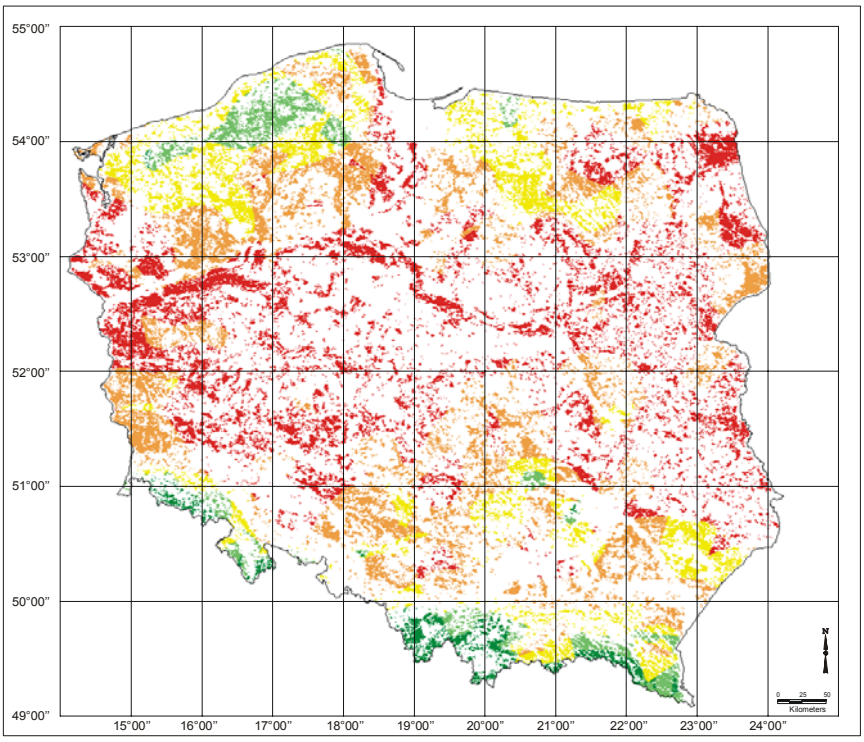
Figure PL-1. Effect-based critical loads.

Institute of Environmental Protection
Department of Environmental Policy - Section of Integrated Modelling
Grunwaldzka Str. 7b/2, 41-106 Siemianowice Sl., Poland

Effect-based critical loads of Cd

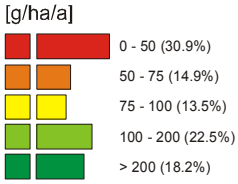
2004





Effect-based critical loads of Pb

2004



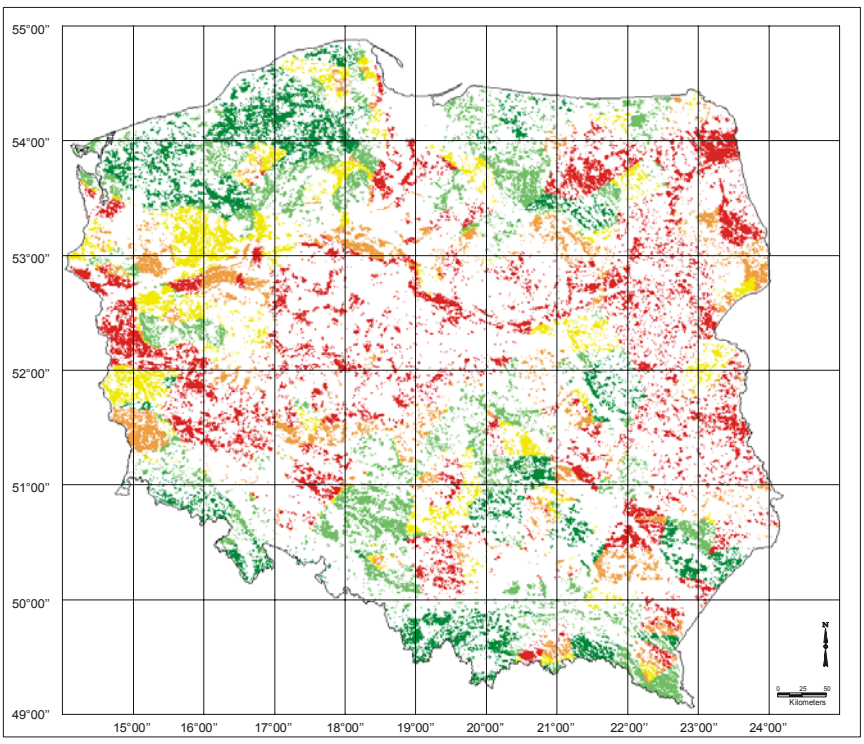


Figure PL-2. Effect-based critical loads.

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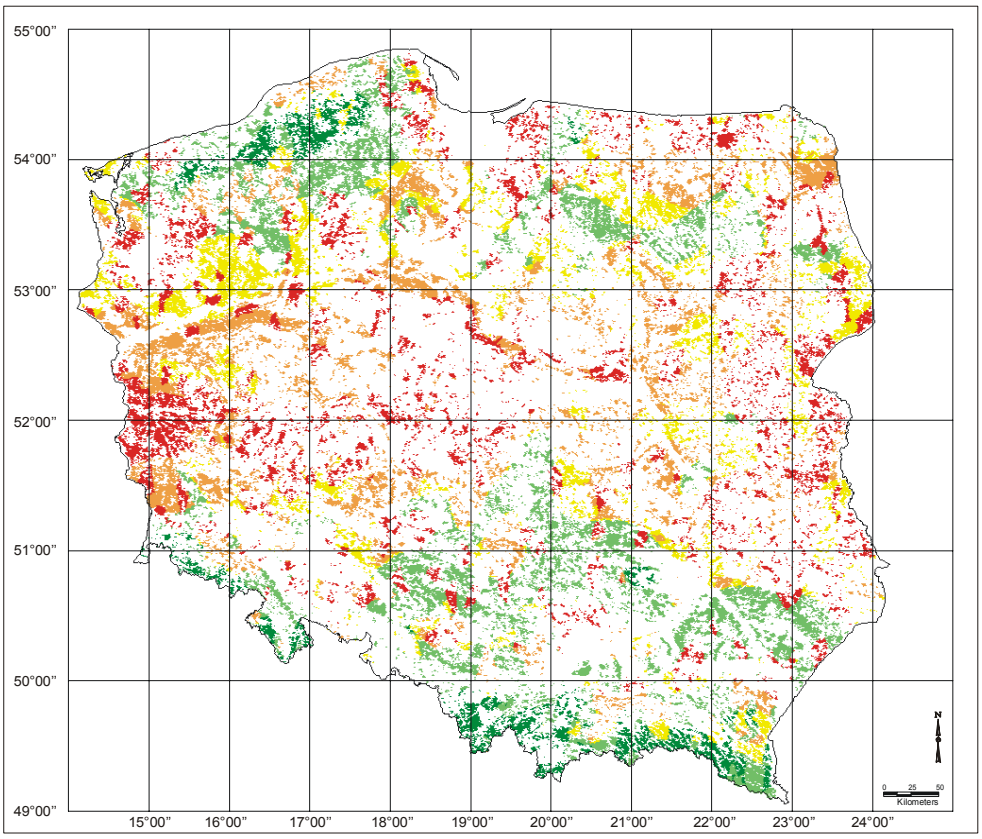
Department of Environmental Policy - Section of Integrated Modelling
Grunwaldzka Str. 7b/2, 41-106 Siemianowice Sl., Poland

Effect-based critical loads of Hg

2004



[g/ha/a]

- 0 - 0.05 (23.1%)
- 0.05 - 0.07 (24.3%)
- 0.07 - 0.09 (18.6%)
- 0.09 - 0.15 (26.5%)
- > 0.15 (7.5%)

RUSSIAN FEDERATION

National Focal Centre

Vladimir N. Bashkin
Geography Department
Moscow State University
Vorobyovy Gory
Moscow 119 189
tel./fax: +7-095-939 2284
bashkin@fadr.msu.ru

Collaborating institution

Irina Priputina, Alex Abramychev
Institute of Physicochemical and Biological Problems in Soil Science of RAS
Pushchino, Moscow region, 142 290
tel: +7-0967-730755
fax: +7-0967-330595
v_35_6@rambler.ru

Calculation methods

The calculation of critical loads for the ecosystems of the European part of Russia follows the methods recommended in the Mapping Manual (UBA, 2004; Chapter 5.5). The receptor types considered are *coniferous* and *mixed woodlands* (EUNIS classification codes G3 and G4, correspondingly). *Two types of the effects* for two metals (*Pb and Cd*) have been considered. The first is *human health effects* aiming to ground (drinking) water protecting. The second is *ecotoxicological effects* aiming to forest soils biota protecting. The simplified version of steady-state mass balance model (Eq.1) has been applied for calculating both types of critical loads. The minimal value of two critical loads has been included into dataset submitted to CCE.

Tolerable removal of HM from the biological active topsoil, z_b, by net growth of wood biomass has been estimated using Eq.2. Fraction of metal net uptake, f_{Mu}, equals 1 in all calculations. Yields of wood biomass, Y_{ha}, have been computed as a sum of branches and stem (trunk) annual growth estimated on the base of simulating biomass production in the main forest types and taking into account the climatic and soil-geochemical factors. Data on Pb and Cd accumulation in the wood has been varied depending on forest types.

Critical leaching flux of heavy metals has been estimated according to the equation 3. In calculations of critical loads in view of ground waters protection, the recommended values of critical limits of Pb and Cd (10 mg/m^3 and 3 mg/m^3, correspondingly) have been applied. Critical metal leaching concerned with ecotoxicological effects has been computed using the critical limits estimated on the base of look-up tables. Data on water leaching flux, $Q_{le,zb}$, have been calculated using annual mean precipitation and air temperature data (Michalzik et al., 2001).

Data sources

The values of critical loads vary as a function of spatial distributed parameters including soil and forest type data as well as climate indexes. As a basis for computing critical loads, overlay of three maps was made:

- FAO soil map (FAO, 1992);
- Forest types map generalized from Land use map (IGBP Map of EDC DAAC 1997);
- Water percolation map created using the data from IWMI World Water and Climate Atlas (2002).

The minimal size of grid cell is 5x5 km^2. Total number of the ecosystems is more than 30,000.
Soil information needed for calculating metal critical limits in drainage waters is based on literature data correlated with twenty six soil types. Soils characteristics are published in (Priputina et al., 2003). The ranges of Pb critical limits related to ecotoxicological effects are 1.7–21 mg m^{-3}. The values

higher than 10 mg m^{-3} have been estimated for dystric Histosols, gleyic and orthic Podzols. The ranges of critical limits of Cd are 1–3.3 mg m^{-3}.

Information on metal uptake has been derived from monitoring and simulating data. Net yield of wood biomass has been estimated using simulation procedures and forest inventory data from key plots (Table RU-1). Metal contents in the wood have been obtained from sampling of the trees in the background areas of European Russia (Table RU-2).

Table RU-1. Parameters of wood biomass growth for main tree types in the forests of European Russia; results of simulating based on EFIMOD (Chertov and Komarov 1997, Priputina et al. 2004).

Type	Location	Wood biomass growth, kg m-2 (dw)		
		Stem	Branches	Total
Pine	Northern regions	0.35-0.38	0.06-0.08	0.4-0.45
(Pinus silvestris)	Central regions	0.35-0.4	0.08-0.1	0.45-0.5
Spruce	Northern regions	0.15-0.16	0.03-0.04	0.18-0.2
(Picea abies)	Central regions	0.5-0.52	0.08-0.1	0.6-0.62
Birch	Northern regions	0.1-0.12	0.01-0.02	0.11-0.15
(Betula pendula)	Central regions	0.3-0.35	0.03-0.04	0.35-0.4
Oak	Central regions	0.25-0.26	0.05-0.06	0.3-0.32
(Quercus robur)	Southern regions	0.25-0.3	0.05-0.8	0.3-0.4

Table RU-2. Pb and Cd content in stem wood of main tree types. Overview of the data from relatively unpolluted areas of European Russia (Priputina et al. 2004).

Tree type	Pb, mg kg^{-1}(dw)	Cd, mg kg^{-1}(dw)
Spruce (*Picea abies*)	0.35 (0.10-1.6)*	0.20 (0.07-0.70)
Pine (*Pinus silvestris*)	0.10 (0.01-1.1)	0.13 (0.01-0.42)
Oak (*Quercus robur* L.)	0.45 (0.03-1.3)	0.05 (0.01-0.40)
Lime (*Tilia cordata*)	0.65 (0.15-1.7)	0.10 (0.03-0.30)
Birch (*Betula pendula*)	0.35 (0.01-1.0)	0.10 (0.01-0.65)
Aspen (*Populus tremula*)	0.60 (0.25-1.8)	0.35 (0.15-0.65)

* Median values (minimum-maximum values in parentheses).

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SLOVAKIA

National Focal Centre

Dusan Závodský
Slovak Hydrometeorological Institute
Jeséniova 17
SK-833 15 Bratislava
tel.: +421 7 5941 5377
fax: +421 7 5477 5670
zavodsky@mail.shmu.sk

Collaborating institution

Jozef Mindas
Forest Research Institute
T.G.Masaryka 22
SK-960 92 Zvolen
tel.: +421 855 5314 206
fax: +421 855 5321 833
mindas@fris.sk

Data sources and comments

Variable	Comments
Mha	HM uptake has been calculated by using of the data of HM content in wood and bark from ICP forest monitoring sites as weighted means (except Hg), for Hg the default value of 0.01 mg kg^{-1} dw has been used
Yha	Data for coniferous and broadleaved tree species have been used from the national yield tables
Qle	Data have been taken from the previous calculations
Msscrit	Data have been taken from the previous calculations (Pb, Cd), for Hg default value of 0.035 ug l^{-1}
Ecosystem	Only two categories: coniferous forests (CONIF) and broadleaved forests (BROAD)

SWEDEN

National Focal Centre

Håkan Staaf
Swedish Environmental Protection Agency
SE-106 48 Stockholm
tel: +46 8 698 1442
fax: + 46 8 698 1402
hakan.staaf@naturvardsverket.se

Ulla Bertills
Swedish Environmental Protection Agency
SE-106 48 Stockholm
tel: +46 8 698 1502
fax: + 46 8 698 1584
ulla.bertills@naturvardsverket.se

Collaborating institutions

Nicholas Jarvis
Swedish University of Agricultural Sciences
Dept. of Soil Sciences, P.O Box 7014
SE-750 07 Uppsala
nick.jarvis@mv.slu.se

Kjell Johansson
Swedish University of Agricultural Sciences
Dept. of Environmental Assessment
P.O. Box 7050
750 07 Uppsala
kjell.johansson@ma.slu.se

Markus Meili
Institute of Applied Environmental Research (ITM)
Stockholm University
SE-106 91 Stockholm
markus.meili@itm.su.se

Lars Rapp
Swedish University of Agricultural Sciences
SLU Environmental Data Center
P.O. Box 7062
SE-750 07 Uppsala
lars.rapp@md.slu.se

Introduction

This report provides a brief overview of the methods and data sources used for the first Swedish delivery of results on critical loads on metals. We have mapped the following land cover types:

- arable land; human health effects of cadmium
- forests, ecotoxicological effects of cadmium, lead and mercury
- freshwaters; human health effects of mercury.

Arable land

Calculation methods:
Calculations have been performed according to the mapping manual using cadmium content in wheat as the critical limit indicator. A critical limit value of 0.1 mg Cd kg^{-1} fw in harvested grain was used. The critical concentration of Cd in soil solution and removal by harvest was estimated using national data.

Data sources:
The critical loads calculations have been based on data from a national survey of the chemical composition of agricultural topsoils (N=3100) and cereal grain (N=606 for winter wheat) carried out during 1992–1995, with sampling sites evenly distributed over arable land (Eriksson et al., 2000). Winter wheat is not cultivated at many of the sites included in the national survey, mainly in the

inland highland regions of south Sweden and the north of Sweden. These sites were therefore excluded from the calculations due to lack of crop yield data (see below). The total number of observation sites for which critical load calculations were made was therefore reduced to 2450.

The calculation of critical loads of Cd in wheat grain requires estimates of harvest yields of wheat, water percolation from the plough layer, and an estimate of the critical Cd concentration in soil water. The sources of these data are described below.

Harvest yields
Swedish arable land is divided into 104 'yield survey districts' that exhibit similar conditions for cropping. In these areas, typical harvest yields ('standard yields') are estimated by SCB ('Statistics Sweden') from measurements made on selected areas during a period of five years. The standard yields reported in 2003 were used to calculate Cd removal for the 68 districts in Sweden where standard yields for winter wheat were reported.

Percolation
The long-term annual percolation flux was estimated at each sampling site in the wheat-growing districts from calculations made for 266 catchment areas in Sweden using the HBV hydrological model calibrated against measured discharges for the period 1961–1990. In order to ensure a reasonably conservative estimate of the critical load, the percolation out of the plough layer q was estimated as 70% of the estimated catchment-scale annual discharge. An implicit assumption in this method is that stream discharge equals the sum of surface runoff and water flow percolating out of the topsoil (i.e. that all root water uptake takes place in the topsoil, and none from the subsoil.

Critical concentration in soil solution
National data was available that allowed the calculation of a critical Cd concentration in soil water leading to critical Cd concentrations in wheat grain. Soil solution Cd concentrations were measured in batch equilibrations in 0.01 M $Ca(NO_3)_2$ for 50 stored topsoil samples originating from the national soil and grain survey, where data on wheat grain Cd content was available. The soils were also selected to cover a wide range of values for those properties considered most important in controlling Cd solution concentrations, namely pH, total Cd content and organic carbon content.
The following regression equation (forced through the origin) for the concentration of Cd in wheat grain (mg Cd kg^{-1}) as a function of topsoil Cd concentration was obtained:

$Cd(grain) = 0.0521\ Cd(s)$ $(r^2 = 0.56, N = 42)$

95% confidence intervals gave estimates of the slope ranging from 0.044 to 0.06. With a maximum allowable grain Cd concentration of 0.1 mg Cd kg^{-1}, a slope of 0.06 would imply a critical plough layer soil solution Cd concentration of 1.66 μg L^{-1}. Given the significant uncertainties in accurately estimating the loss pathways, and bearing in mind the 'precautionary principle', we calculated critical Cd loads assuming C_{crit} = 1.66 μg L^{-1} . This critical concentration is somewhat larger than the value of 1.05 μg L^{-1} suggested in the mapping manual, based on Dutch data.

Forests

Calculation methods:
Critical loads of cadmium, lead and mercury were calculated with the simple steady-state model for the soil described in the mapping manual: CL(M) = Mu + Mle(crit). For Hg the calculations were carried out for the organic horizon (O-horizon) of 5396 forest sites, while for Pb and Cd the model was applied to two horizons (N= 2070); the organic soil horizon and the upper part of the mineral soil (A/upper B-horizon). For Pb and Cd the lowest critical loads were consistently found in the mineral soil horizon and thus used for mapping. It was assumed that 80% of the uptake occurred in the O horizon.

The critical leaching of Cd and Pb from the topsoil was calculated from the look-up tables in the mapping manual. For the organic soil horizon the following parameter values was assumed for all sites; organic matter (OM) = 50%, SMP = 0 and DOC = 20 mg L^{-1}, and for the mineral soil horizon OM = 10%, SMP = 0 and DOC = 5 mg L^{-1}. Percolation was calculated according to Eq 4b in the mapping manual and the parameter $f_{E,zb}$ was set to 0.8 and 1.0 for the O- and A/B-horizon, respectively. Measured pH(H2O)-values from each site was applied in the look-up tables and the corresponding concentrations in soil drainage water was derived after interpolation between the default values. For mercury the critical concentration in the soil solution is based a critical concentration = 0,5 mg kg^{-1} OM, DOC = 20 mg L^{-1} and a fractionation ratio (ff) = 1 between Hg on solid OM and DOC.
Data sources:
Data on soil and tree stand characteristics used in the calculations were taken from the Swedish Survey of Forest Soils and Vegetation and the Swedish National Forest Inventory (www.slu.se). Only sites with humus type mor or moder were used. Annual long term average of precipitation and temperature were taken from the Swedish Meteorological and Hydrological Institute (www.smhi.se). The long-term uptake of metals, Mu, was calculated as net removal with biomass during a forest rotation. Biomass data for each site was combined with metal concentrations in different biomass components, derived from five forest sites in a north/south gradient over Sweden (A. Alriksson, unpublished). Besides stem harvesting the extraction of forest residues for energy was considered; at present slash harvesting takes place on approximately 20% of the clear-cut area in the country; mainly in the southern part (National Board of Forestry 2001). About 70% of the branches, 25% of the needles are harvested on site level in coniferous forest.
DOC values used in the calculations are based on field measurements. Twelve recorded sites had site-specific values between 6-60 mg/L, with no clear geographical differences (Fölster et al., 2003; Fröberg et al., 2004). In soil solutions of the upper part of the B-horizon, the range of DOC values was 2-8 mg L^{-1} with 5 mg L^{-1} as an overall mean.

Freshwaters

Calculations were done for mercury and aimed at protecting fish consumers (humans and wildlife) by keeping the ecosystem mean of Hg concentrations in a standard fish (1-kg pike, *Esox lucius*) below the critical limit of 0.3 mg kg^{-1} fw.

Calculation methods:
Calculations were made for 2977 Swedish lakes according to eqs. 15 and 16a in Chapter 5.5 of the Mapping Manual (UBA, 2004).

Data sources:
Data were taken from the 1995 Swedish Lake Survey (Wilander et al., 1998), which was part of a Nordic Lake Survey (Henriksen et al., 1998). The lakes are identical with those for which the acidification status is reported.

Some lakes were deemed unsuitable for the calculations because of either unreliable data or significant pollution with nutrients. This is indicated by an excess of unused phosphorus (TP >200 µg L^{-1}, TOC/TP <50 g g^{-1}) which may be the result of nitrogen limitation. In such lakes, phosphorus is not an indicator of bioproduction, which makes Eq. 16a invalid, as indicated also by unrealistically low values of TF_{HgSite} <0.05 L kg^{-1}. However, only the six most extreme sites were excluded. Also lakes with an extremely high TOC/TP >2000 g g^{-1} (TF_{HgSite} >0.5 L kg^{-1}) may indicate unreliable data, but were not excluded because such values probably originate from the polyhumic water of pristine bog lakes without direct pollution.

Comments and conclusions

We consider that there are three main uncertainties in the calculation of critical loads of cadmium on arable land:
the estimation of the critical soil solution concentration is based on limited data, in our case measured in only one year, when it is known that grain Cd concentrations can vary significantly from year to year. The Cd removal from arable land is calculated assuming that wheat is grown in monoculture. Other crops in the rotation may have smaller yields and/or Cd concentrations in harvested plant parts than wheat (e.g. barley). Estimates of leaching losses from the topsoil are critical, since under Swedish conditions, this loss pathway appears more important than crop removal. Leaching predictions are highly uncertain, partly because little is known about the influence of non-equilibrium processes such as preferential flow on long-term leaching.

In forest, the mineral soil horizon had lower critical loads of Cd and Pb than the organic layer, which is due to higher pH, lower DOC and somewhat smaller water flow in the upper B horizon. Since the results are based on relatively few measurements of DOC concentrations in soil, improved knowledge on the local and regional variation of this parameter could give rise to a different picture. Also the question of how biological effects are related to different soil horizons should be considered further.

In Sweden, present Hg concentrations in fish exceed the critical limit in far more than half of the lakes. Since further increases of fish Hg levels are expected before steady state is reached with the current level of atmospheric Hg pollution, the critical level of atmospheric Hg pollution is currently exceeded in >95% of the Swedish lakes.

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SWITZERLAND

National Focal Centre

Swiss Agency for the Environment, Forests
and Landscape (SAEFL)
Air Pollution Control Division
Beat Achermann
CH-3003 Bern
tel: +41-31-322 9978
fax: +41-31-324 0137
beat.achermann@buwal.admin.ch

Collaborating institutions

METEOTEST
Beat Rihm
Fabrikstrasse 14
CH - 3012 Bern
tel: +41-31-307 2626
fax: +41-31-307 2610
office@meteotest.ch

EKG Geo-Science
Daniel Kurz
Ralligweg 10
CH – 3012 Bern
tel: +41-31-302 6867
fax: +41-31-302 6825
geoscience@swissonline.ch

Ecosystems and Effects

Only terrestrial ecosystems (forests) are considered, including

- coniferous forests (EUNIS-code G3)
- deciduous forests (EUNIS-code G1)
- mixed/undetermined forests (EUNIS-code G4)

Critical loads are calculated with respect to

- ecotoxicological effects
- human health effects (drinking water, groundwater protection)

For each site, the minimum critical load of the two criteria is chosen. For Cd, the drinking water criterion was lower on 57 (out of 277) sites. For Pb, there were 56 such sites. For Hg, the ecotoxicological criterion was always lower.
The 277 sampling sites are not equally distributed over Switzerland. Therefore, the area of the ecosystem within the EMEP grid cell, for which the critical load is computed (EcoArea), is calculated separately for each EMEP grid cell by dividing the total forested area by the number of sampling sites.

Methods

The calculation methods follow strictly the proposals in the Mapping Manual (UBA, 2004).
For Cd and Pb, the critical total dissolved metal concentration in the soil solution $[M]_{ss(crit)}$ was calculated by Tipping (2004) using the WHAM6-MTC21 speciation model, based on suitably formatted input files according to Annex 2 of the Mapping Manual. For Hg, a constant $[M]_{ss(crit)}$ of 0.035 $\mu g\ l^{-1}$ is used.
The calculation was made separately for humus layers (O-horizons, also labelled as L-, H-, and F-horizons) and the top mineral layers (A-horizons). Finally, the minimum critical load was chosen for each site.
If the soil-profile records do not explicitly list O-horizons or Ah-horizons for a certain site, all soil samples at depths of less than 0.1m were used. This can be the case, if no Ah-horizon was identified but for instance an AE-horizon.

The thickness of the soil layer (THICK) is the depth of the lower boundary of the horizon with the minimum critical load. For the groundwater criteria, thickness was set to the main rooting zone (HWR).
For several parameters default or constant values are used, see Table CH-1.

Table CH-1: Constant and default input parameters.

Name	Value	Description
f_{Ezb} "ecotox"	0.8	fraction of evapotranspiration within the considered soil depth for ecotoxicological effects. Default value.
f_{Ezb} "groundwater"	1.0	fraction of evapotranspiration within the considered soil depth for groundwater protection.
f_{Mu}	1.0	fraction of uptake within the considered soil depth. Default value.
$[Cd]_{ss(crit)}$ "groundwater"	3.0 µg/l	critical total dissolved metal concentration in the soil solution. Default value for groundwater protection.
$[Pb]_{ss(crit)}$ "groundwater"	10.0 µg/l	critical total dissolved metal concentration in the soil solution. Default value for groundwater protection.
$[Hg]_{ss(crit)}$ "groundwater"	1.0 µg/l	critical total dissolved metal concentration in the soil solution. Default value for groundwater protection.
$[Hg]_{ss(crit)}$ "ecotox"	0.035 µg/l	critical total dissolved metal concentration in the soil solution. Default value for ecotoxicological effects.
$[Cd]_{ha}$	0.3 mg/kg	content of the metal in the harvested part of the plant[1)]. Average from Mapping Manual, Table 2.
$[Pb]_{ha}$	5.0 mg/kg	content of the metal in the harvested part of the plant[1)]. Average from Mapping Manual, Table 2.
$[Hg]_{ha}$	0.03 mg/kg	content of the metal in the harvested part of the plant[1)]. Average from Mapping Manual, Table 2.
SPM	0.0 g/m^3	concentration of suspended particulate matter in the soil solution. Default value.
$[DOM]_{ss}$ (only CL(Hg))	70 g/m^3	concentration of dissolved organic matter in the soil solution. Default assumption for ecotoxicological effects of Hg.

[1)] For $[M]_{ha}$ the same values are used for coniferous and deciduous forests.

Input data

Soil data
The data for the 277 soil-profiles is taken from the database compiled for dynamic modelling (Kurz 2004). For each site, between 3 and 8 soil layers are described by type of horizon, thickness of the horizons, thickness of the rooting zone (HWR) as well as by measurements of pH and Corg. Corg was transformed to OM by a factor of 1.724.
DOC and pCO_2 were calculated as a function of depth (z_b) with empirical relationships (Kurz, 2004).

Harvesting Rate (Yha)
Uptake is calculated on the basis of long-term harvesting rates as it was done for calculating critical loads of nutrient nitrogen with the SMB method (FOEFL 1996). The harvesting rates are regional average values for five regions (Jura mountains, Plateau, Lower Alps, Alps, Southern Alps) differentiating between deciduous and coniferous woodland. In unmanaged forests the net uptake is zero.

Hydrology
The flux of leaching Water (Qle) was calculated by Zierl (2000) by applying a physically-based hydrological model to 11 000 sites of the national forest inventory (LFI). These results were spatially interpolated to those CLM-sites, which do not coincide with the LFI.

Acknowledgements

We are very grateful to Ed Tipping for calculating metal concentrations in soil solution with the WHAM6-model and for his help in producing consistent input files. We also thank Stefan Zimmermann (WSL) and Sabine Braun (IAP) for the preparation of the soil-profile data.

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Annex: Results

The following figures show maps and cumulative frequency distributions of the resulting critical loads for Pb, Cd and Hg.

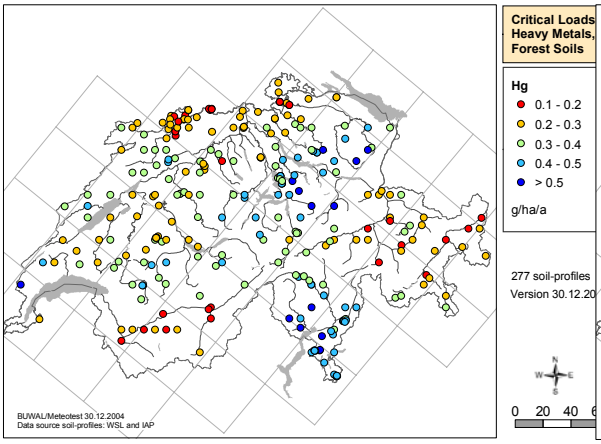

Figure CH-1. Critical loads of mercury.

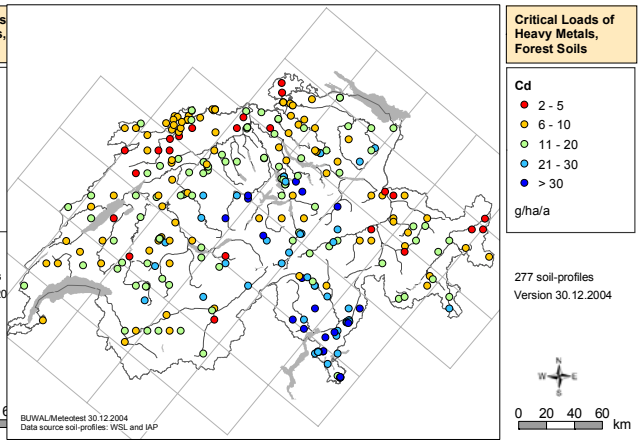

Figure CH-2. Critical loads of cadmium.

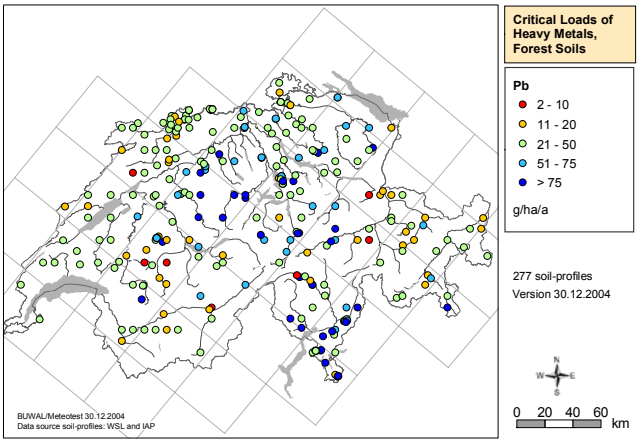

Figure CH-3. Critical loads of lead.

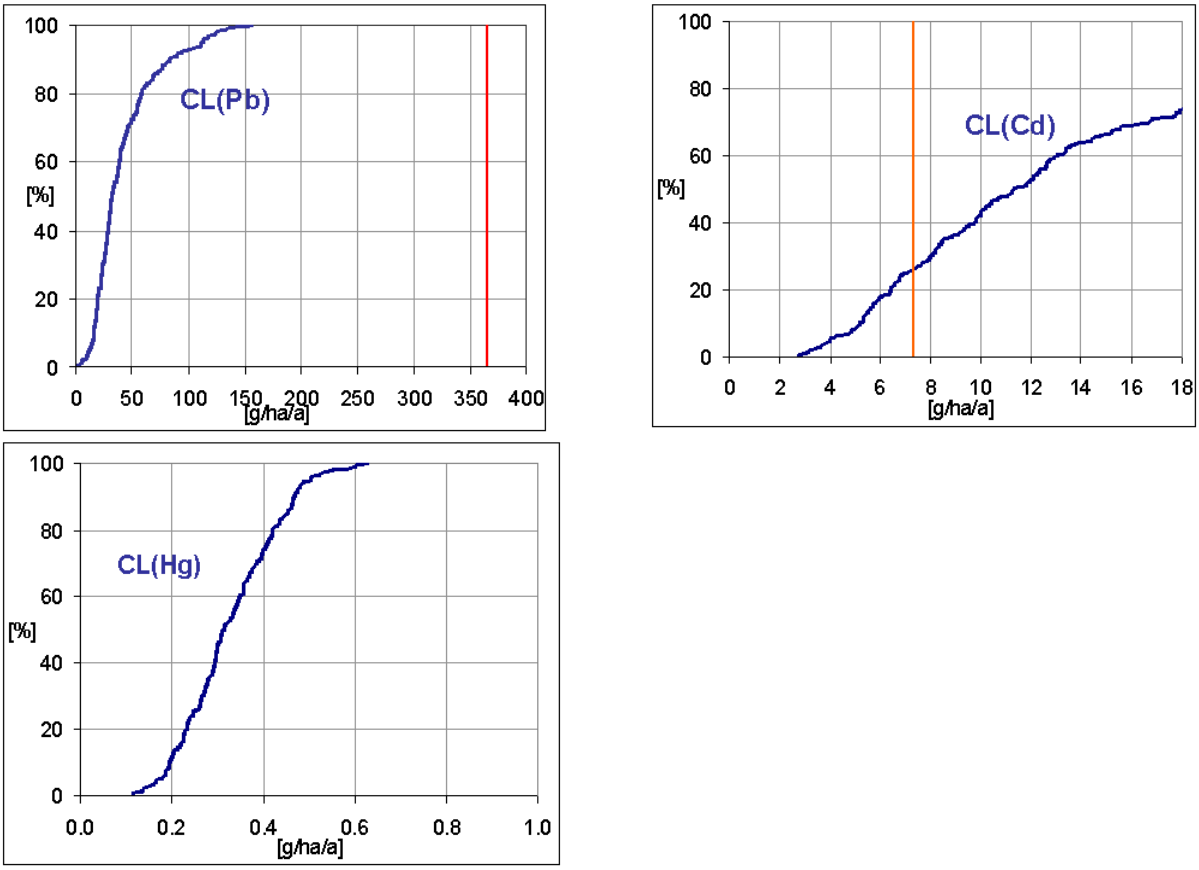

Figure CH-4. Frequency distributions of the critical loads of Pb, Cd and Hg. The red lines indicate maximum deposition values according to Swiss legislation for Pb and Cd.

UKRAINE[2]

National Focal Centre

Evstafyeva Helene,
Ovsyannikova Natalia
Crimean State Medical University
Blvd.Lenine 5/7
Simferopol, 95006
helene@csmu.strace.net

Collaborating institution

Karpenko Sergey,
Gluschenko Irina
Taurida National University
Av.Vernadsky, 4
Simferopol
turr@tnu.crimea.ua

Description of the sources of the data

All calculations were based on the manual 5.5. Critical loads of cadmium, lead and mercury.

1. $M_{[ha]}$ metal content of the harvestable parts of the plants was taken from Table 2. (Mapping Manual chapter 5.5) for wheat.
2. Y_{ha} yield of harvestable biomass 1500-2000 kg/ha/a
3. Q_{le} flux of drainage water leaching from the regarded soil layer was taken from database Bdb.ua (Workshop on dynamic modelling, Prague 2003).
4. M_{crit} metal content in soil solution (De Vries et al., 2002)

[2]The official status of the Ukrainian contribution is unknown at the time of print.

UNITED KINGDOM

National Focal Centre

Jane Hall
Joseph Fawehinmi
Centre for Ecology and Hydrology
Monks Wood
Abbots Ripton
Huntingdon PE28 2LS
tel: +44 1487 772429
fax: +44 1487 773467
jrha@ceh.ac.uk, ojf@ceh.ac.uk
http://critloads.ceh.ac.uk

Collaborating institutions

Michael Ashmore
Laura Shotbolt
Environment Department
University of York
Heslington
York YO10 5DD
tel: +44 1904 434070
ma512@york.ac.uk, l.shotbolt@leeds.ac.uk

Ed Tipping
Steve Lofts
Centre for Ecology and Hydrology
Lancaster Environment Centre
Bailrigg
Lancaster LA1 4AP
tel: +44 1524 595800
fax: +44 1524 61536
et@ceh.ac.uk, stlo@ceh.ac.uk

Introduction

In response to this call for data the UK NFC has submitted critical loads of cadmium and lead for ecotoxicological effects to terrestrial ecosystems; effects to aquatic ecosystems and to human health have not currently been considered nationally. Since the last call for data in 2002 the following updates have been made:

- Critical loads have been calculated for five metals in the UK: lead, cadmium, zinc, nickel and copper; although data are only submitted for cadmium and lead as requested in this call.
- Habitat masks have been extended to include upland and lowland areas of managed coniferous woodland, managed broadleaved woodland, unmanaged woodland and semi-natural habitats, comprising acid grassland, calcareous grassland, dwarf shrub heath, bog and montane habitats. The habitat masks used are consistent with those used for national mapping of acidity and nutrient nitrogen critical loads.
- 1km national data sets for soil properties have been derived from values assigned to individual soil series throughout the UK, enabling 1km resolution critical loads maps to be generated for the different habitats being considered.
- National transfer functions have been further developed which can be applied to a wide range of forest and semi-natural habitats.
- The WHAM model version 6 (Tipping et al., 2003) has been used to calculate critical loads based on pH dependent free-ion critical limit values for the UK. The methods are consistent with the latest version of the Mapping Manual.
- New methods have been developed for mapping DOC concentration as a function of land-cover and runoff

Relating UK habitats to EUNIS habitat classes

The UK maps critical loads for selected Biodiversity Action Plan (BAP) Broad Habitats, sensitive to acidification and eutrophication. The same habitats, with the exception of supra-littoral sediments and freshwaters, have been considered for heavy metals. At the UK scale critical loads maps have been

presented for all woodlands (managed and unmanaged) and for semi-natural vegetation (acid grassland, calcareous grassland, dwarf shrub heath, bog, montane). However, critical loads have been calculated for individual habitat types within these classes and data are submitted by EUNIS habitat class as listed in Table UK-1 below.

Table UK-1. Relating UK Broad Habitats to EUNIS habitat classes.

UK Broad Habitat	EUNIS class	EUNIS description*
Broadleaved, mixed & yew woodland	G1	Broadleaved woodland (managed)
	G1&G3	Broadleaved & coniferous woodland (unmanaged)
Coniferous woodland	G3	Coniferous woodland (managed)
Calcareous grassland	E1.26	Sub-Atlantic semi-dry calcareous grassland
Acid grassland	E1.7	Non-Mediterranean dry acid grassland
	E3.5	Moist or wet oligotrophic grassland
Dwarf shrub heath	F4.11	Northern wet heaths
	F4.2	Dry heaths
Bogs	D1	Raised and blanket bogs
Montane	E4.2	Moss & lichen dominated summits (*Racomitrium* heath)

* Additional UK specification in brackets.

Parameterisation of critical limits and critical load models

This section summarises the national data used in the calculation of pH dependent critical limits and critical loads.

Data on soil properties (soil type, pH, organic carbon) are available from the national soil surveys for England and Wales (National Soils Resources Institute; McGrath and Loveland, 1992), Scotland (Macaulay Institute) and Northern Ireland (Department of Agriculture and Rural Development; Jordan et al., 2000). Representative values of soil pH and organic carbon (OC) for each soil series or map unit were combined with a 1km database of the dominant soil series in each grid square to give 1km resolution maps of these soil properties. The pH data are derived from measurements in soil solution and were converted to the Mapping Manual definition of soil pH (UBA, 2004) with the function: pH = 1.0462 * pH–0.2847.

Loss-on-ignition (LOI) data were not directly available but were instead derived from percentage OC values using the following relationship suggested by Broadbent (1965): LOI = 1.8 * OC.

Dissolved organic carbon (DOC) data were also not directly available. An analysis of a data set of UK lysimeter-based studies of DOC for 71 individual sites indicated that:

- DOC concentrations in the UK are generally lower than global averages
- UK concentrations of DOC are highly variable
- DOC flux increases with runoff, although it tends towards a maximum flux
- DOC flux varies between different habitats

Empirical relationships between DOC flux, runoff and habitat type were derived, where the DOC concentration in soils may be envisaged as a function of both the generation and accumulation of DOC in soil, and the removal by runoff. Therefore higher DOC flux relative to runoff is found in soils with low runoff but higher total DOC flux where runoff is high. The following equations were applied to derive DOC values for the different habitats:

(i) Acid grassland (also applied to calcareous grassland and montane)
DOC (mg l^{-1}) = 257.23 * runoff (mm a^{-1})$^{-0.4554}$

(ii) Heathland (applied to dwarf shrub heath and bog)

DOC (mg l^{-1}) = 113.48 * runoff (mm a^{-1})$^{-0.2309}$

(iii) Woodland (applied to managed and unmanaged woodlands)
DOC (mg l^{-1}) = 112.91 * runoff (mm a^{-1})$^{-0.2867}$

The relationships between DOC concentration and runoff are not strong and may introduce significant uncertainty. Nevertheless, they provide a more realistic estimation for the UK of DOC than the default value of 20 mg l^{-1} in the Mapping Manual (UBA, 2004), which is high in comparison to the UK median and does not account for the influence of runoff. The runoff data are at 1km resolution and based on 30 year (1941–1970) mean rainfall data.

National data sets for the partial pressure of carbon dioxide (pCO_2) and the concentration of suspended particulate matter (SPM) were not available and could not be derived with any measure of confidence. For the UK critical load calculations pCO_2 was set to 30 times atmospheric pressure and SPM was set to 5 mg l^{-1}, both based on expert advice. These values differ from the default values in the Mapping Manual.

The net uptake and removal of metals by harvesting is taken into account in the critical load calculations for managed woodlands. Metal uptake values were calculated from estimates of annual biomass increment, forest rotation data and the content of the metals in the trees (Broadmeadow et al., 2004). The data are from the 20 UK Level II plots studied under the ICP Intensive Forest Health Monitoring Survey. The sites comprise four oak, six beech, four Scots Pine, four Sitka spruce and two Norway spruce sites distributed across the UK. Mean uptake values for all conifer species (0.67 g $ha^{-1}a^{-1}$ for Cd, 2.98 g $ha^{-1}a^{-1}$ for Pb) and all broadleaved species (0.17 g $ha^{-1}a^{-1}$ for Cd, 1.81 g $ha^{-1}a^{-1}$ for Pb) were applied to all 1km grid squares of the corresponding woodland type. For unmanaged woodland and semi-natural habitats the growth uptake is assumed to be zero, ie, no net removal of metals.

Development of UK transfer functions

Transfer functions required for the conversion of total metal concentrations to free-ion concentrations (or vice versa) have previously been developed in the UK for non-forested upland soils. Recent work has included the collection of additional soil samples from five land cover types (acid grassland, heathland, upland and lowland coniferous and broadleaved woodland) from "background" sites, largely National Nature Reserves and Forestry Commission sites. Data from the analysis of all the UK sites have been combined to produce a set of transfer functions suitable for the range of habitat and soil types being considered for UK critical loads. These equations are used for UK mapping in preference to the transfer functions in the Mapping Manual. The transfer functions were recalculated as Freundlich partitioning coefficients (K_f). This type of transfer function is preferred as it enables us to use the same partitioning equation to calculate either free-ion or reactive soil metal (Römkens et al., 2004). Furthermore, the non-linear Freundlich model allows us to take into account, if necessary, the tendency of binding strength to decrease as the amount of metal sorbed increases. K_f is related to soil properties such that:

$\log K_f = a + b\ pH + c \log LOI$ [where $K_f = Q_{total} / Q_{free}^{n}$]

The regression coefficients for determining K_f for Cd and Pb are given in Table UK-2 below.

*Table UK-2. Regression coefficients for determining partitioning (*Kf*) between total soil metal concentration and free-ion activity. Derived from soils data for all UK sampled sites.*

	a	*b*	*C*	*n*	r^2	s.e.
log K_f Cd	-5.712	0.399	0.727	0.63	0.665	0.372
log K_f Pb	-4.191	1.175	0.762	1	0.919	0.483

Deriving pH dependent free-ion critical limits

The pH dependent free-ion critical limits are based on ecotoxicological data for soils which have been collated and critically screened. Toxic endpoints, expressed as lowest observed effect concentrations (LOECs), no observed effect concentrations (NOECs) and EC_{10} values, were related to soil pH and organic matter content. Through the use of transfer functions (see above), relating free metal ion concentrations (Cd^{2+} and Pb^{2+}) to soil pH, organic matter content and metal content, the toxic end-points were expressed in terms of free-ion concentrations and pH. Species sensitivity has also been taken into account, and critical limit functions have been derived that protect 95% of species. The critical limit functions take the form:

$$\text{Log } M_{free,crit} \text{ (mol } l^{-1}) = \alpha \cdot pH + \gamma$$

where $M_{free,crit}$ is the critical limit expressed as the concentration of metal free-ion, and α and γ are constants.
Expression of the critical limits in this way establishes a direct link between chemical speciation and toxicity, and simplifies the calculation of the critical load. The same calculation methodology also provides critical limit functions expressed in terms of total soil metal, and taking into account variations in pH and organic matter content (Lofts et al., 2004). The soil toxicological databases have been harmonised as far as possible with those being used under EU Risk Assessment processes. The values of the coefficients of the critical limit functions that were used are those in the Mapping Manual, ie: for Cd: $\alpha = -0.32$ and $\gamma = -6.34$; for Pb: $\alpha = -0.91$ and $\gamma = -3.80$.

Calculating critical loads

Critical loads are calculated via the following mass balance equation:

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

where:

- $CL(M)$ = critical load of a heavy metal M (g $ha^{-1}a^{-1}$)
- M_u = net uptake of metal in harvestable parts of plants under critical load conditions (g $ha^{-1}a^{-1}$)
- M_{we} = weathering rate of the metal (g $ha^{-1}a^{-1}$)
- $M_{le(crit)}$ = critical leaching flux of heavy metal M from the considered soil layer(g $ha^{-1}a^{-1}$)

The weathering rate is set to zero and the uptake rate is calculated for managed forests only.

The critical leaching flux is calculated as:

$$M_{le(crit)} = Q_{le} * [M]_{crit}$$

where:

- Q_{le} = flux of drainage water leaching from the soil, ie, runoff (m a^{-1})
- $[M]_{crit}$ = total concentration of metal in the soil drainage water at the critical limit, comprising total dissolved metal, together with metal bound to suspended particulate matter (SPM).

The total dissolved metal concentration is calculated from the critical free-ion concentrations using the WHAM speciation model (see below), and the SPM-associated metal is calculated from the critical free-ion concentration using the appropriate transfer function (see above), assuming that the SPM has the same metal-binding properties as the soil.

The WHAM chemical speciation model

The chemical speciation of metals in solution was calculated using WHAM / Model VI (Tipping, 1994, 1998). Model VI describes the competitive interactions of protons and metal ions with dissolved organic matter (DOM), using parameters derived from laboratory experimental data with isolated humic substances (Tipping, 2002). In WHAM, Model VI is combined with an inorganic speciation model, the species list and constants for which were given by Tipping (1994).

Critical load values
The minimum and maximum values of the data submitted, including the critical load values, are given in Table UK-3. Although the range of critical load values differs for the metals, all display the same general trends across the country, with generally the lowest critical loads across lowland areas of England and the highest critical loads in upland areas of Wales, northern England and Scotland.

Critical loads represent acceptable levels of deposition that, under steady state conditions would result in soil metal concentrations at the critical limit. As a result, the range in critical loads varies between metals in response to differences in the critical limit and metal speciation within the soil system.

For each metal, the critical loads vary by a factor of at least two orders of magnitude between grid squares. This large degree of variation demonstrates the large effect that variation in factors such as soil organic matter, pH, land cover and runoff can have on critical limits and critical loads. One reason for the large degree of variation is the bimodal distribution shown when the frequency distribution of critical loads is plotted. This reflects a high spatial co-variance of a set of factors, i.e. low pH, high soil organic matter, and high runoff, that are all associated with high values of critical loads.

Table UK-3. Summary of input parameters and critical load values by EUNIS habitat class.

Critical loads parameter	EUNIS code	UK Habitat	Minimum value	Maximum value	Comment
CL(Cd) (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	1.17	40.46	
	G1&G3	Unmanaged woodland	1.04	35.06	
	G3	Coniferous woodland (managed)	2.25	137.37	
	E1.26	Calcareous grassland	0.87	24.83	
	E1.7	Dry acid grassland	1.72	115.68	
	E3.5	Wet acid grassland	1.74	171.15	
	F4.11	Wet dwarf shrub heath	2.31	174.14	
	F4.2	Dry dwarf shrub heath	3.15	119.91	
	D1	Bog	4.22	174.28	
	E4.2	Montane	7.84	133.35	
CL(Pb) (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	5.10	160.72	
	G1&G3	Unmanaged woodland	3.08	159.42	
	G3	Coniferous woodland (managed)	7.21	1660.01	
	E1.26	Calcareous grassland	3.65	142.38	
	E1.7	Dry acid grassland	4.02	691.45	
	E3.5	Wet acid grassland	4.21	1974.37	
	F4.11	Wet dwarf shrub heath	5.68	1965.87	
	F4.2	Dry dwarf shrub heath	4.99	733.65	
	D1	Bog	13.99	2011.52	
	E4.2	Montane	18.50	1011.39	
Cd uptake (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	0.17	0.17	
	G3	Coniferous woodland (managed)	0.67	0.67	
Pb uptake (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	1.81	1.81	
	G3	Coniferous woodland (managed)	2.98	2.98	
Yha (kg $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	1967	1967	
	G3	Coniferous woodland (managed)	4169	4169	
$[Cd]_{ha}$ (g kg^{-1})	G1	Broadleaved woodland (managed)	0.00012	0.00012	
	G3	Coniferous woodland (managed)	0.00012	0.00012	
$[Pb]_{ha}$ (g kg^{-1})	G1	Broadleaved woodland (managed)	0.000815	0.000815	
	G3	Coniferous woodland (managed)	0.000815	0.000815	
f_{Mu}	G1, G3	Managed woodlands	1	1	Data not available, default applied
$Cd_{le(crit)}$ (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	0.998	40.29	
	G1&G3	Unmanaged woodland	1.04	35.06	
	G3	Coniferous woodland (managed)	1.58	136.70	

	E1.26	Calcareous grassland	0.87	24.83	
	E1.7	Dry acid grassland	1.72	115.68	
	E3.5	Wet acid grassland	1.74	171.15	
	F4.11	Wet dwarf shrub heath	2.31	174.14	
	F4.2	Dry dwarf shrub heath	3.15	119.91	
	D1	Bog	4.22	174.28	
	E4.2	Montane	7.84	133.35	
$Pb_{le(crit)}$ (g $ha^{-1}a^{-1}$)	G1	Broadleaved woodland (managed)	3.29	158.91	
	G1&G3	Unmanaged woodland	3.08	159.42	
	G3	Coniferous woodland (managed)	4.23	1657.03	
	E1.26	Calcareous grassland	3.65	142.38	
	E1.7	Dry acid grassland	4.02	691.45	
	E3.5	Wet acid grassland	4.21	1974.37	
	F4.11	Wet dwarf shrub heath	5.68	1965.87	
	F4.2	Dry dwarf shrub heath	4.99	733.65	
	D1	Bog	13.99	2011.52	
	E4.2	Montane	18.50	1011.39	
Q_{le} (m a^{-1})	All		0.0566	3.8760	Same data for all habitat types
thickness z (m)	All		0.15	0.15	Topsoil depth assumed to be 0.15 metres
$[Cd]_{ss(crit)}$ (mg m^{-3})	G1	Broadleaved woodland (managed)	0.75	1.86	
	G1&G3	Unmanaged woodland	0.75	1.78	
	G3	Coniferous woodland (managed)	0.99	8.24	
	E1.26	Calcareous grassland	0.67	1.76	
	E1.7	Dry acid grassland	1.02	5.46	
	E3.5	Wet acid grassland	1.02	8.24	
	F4.11	Wet dwarf shrub heath	1.27	8.26	
	F4.2	Dry dwarf shrub heath	1.28	5.54	
	D1	Bog	1.43	8.25	
	E4.2	Montane	0.73	5.46	
$[Pb]_{ss(crit)}$ (mg m^{-3})	G1	Broadleaved woodland (managed)	1.79	24.89	
	G1&G3	Unmanaged woodland	1.67	23.76	
	G3	Coniferous woodland (managed)	1.58	162.94	
	E1.26	Calcareous grassland	1.50	24.06	
	E1.7	Dry acid grassland	1.60	52.82	
	E3.5	Wet acid grassland	1.61	162.73	
	F4.11	Wet dwarf shrub heath	1.87	163.91	

	F4.2	Dry dwarf shrub heath	2.13	55.20	
	D1	Bog	2.28	163.60	
	E4.2	Montane	2.39	52.83	
pH	G1	Broadleaved woodland (managed)	5.16	8.19	
	G1&G3	Unmanaged woodland	5.27	8.19	
	G3	Coniferous woodland (managed)	2.64	6.51	
	E1.26	Calcareous grassland	5.69	8.19	
	E1.7	Dry acid grassland	3.17	5.88	
	E3.5	Wet acid grassland	2.64	5.88	
	F4.11	Wet dwarf shrub heath	2.64	6.18	
	F4.2	Dry dwarf shrub heath	3.17	6.18	
	D1	Bog	2.64	5.25	
	E4.2	Montane	3.17	7.51	
$[OM]_s$ (%)	G1	Broadleaved woodland (managed)	1.52	60.99	
	G1&G3	Unmanaged woodland	1.46	99.75	
	G3	Coniferous woodland (managed)	0.57	99.90	
	E1.26	Calcareous grassland	1.52	85.69	
	E1.7	Dry acid grassland	0.57	99.90	
	E3.5	Wet acid grassland	1.90	99.90	
	F4.11	Wet dwarf shrub heath	1.46	99.90	
	F4.2	Dry dwarf shrub heath	0.57	99.90	
	D1	Bog	2.47	99.90	
	E4.2	Montane	5.32	99.90	
pCO_2	All		30	30	Default of 30 x atmosphere assumed
SPM (g m^{-3})	All		5	5	Default assumed
DOC (g m^{-3})	G1	Broadleaved woodland (managed)	11.29	30.83	Based on woodland DOC equation
	G1&G3	Unmanaged woodland	11.29	30.24	
	G3	Coniferous woodland (managed)	10.98	29.76	
	E1.26	Calcareous grassland	6.73	35.15	Based on acid grassland DOC equation
	E1.7	Dry acid grassland	6.22	29.33	Based on acid grassland DOC equation
	E3.5	Wet acid grassland	5.98	29.17	
	F4.11	Wet dwarf shrub heath	16.84	35.73	Based on heathland DOC equation
	F4.2	Dry dwarf shrub heath	17.19	33.76	
	D1	Bog	17.12	34.93	Based on heathland DOC equation
	E4.2	Montane	5.97	13.85	Based on acid grassland DOC equation

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Appendix A. Instructions for the Call for Data

Instructions for submitting critical loads data for lead, cadmium and mercury

This Appendix is a reprint of the instructions as it was sent to the National Focal Centres with the call for data

Introduction

This document is a guide for the submission of data to the CCE on critical loads of lead (Pb), cadmium (Cd) and mercury (Hg).
The data submission should be accompanied by a document describing the sources and the methods used to produce data.

Your submission should contain the following key outputs (see Table 2):

1. **Critical loads of Pb, Cd and Hg**
2. **Input variable values (including critical limits)**
3. **Documentation**

Please note

- The deadline for the submission is **31 December 2004. Note:** Because of the double call this year the CCE has to be very strict; submissions after the deadline cannot be accepted.

- The preferred file format of the data is an Access database file (mob), but also files with formats of DBase, Excess, or comma separated ASCII files are accepted. The easiest way to comply with the requested format is the use of the prepared Access database that is made available by the CCE. The file with this database 'HM_2004.mdb' contains the tables for each metal, named 'HM_Cd', HM_Pb' and 'HM_Hg'. The fieldnames within the tables are nearly identical and are listed in Table 2. A full explanation of the variables and methods can be found in chapter 5.5 of the manual.
- Please email your submission to jaap.slootweg@rivm.nl . The data can be attached to this email, but large data files may also be uploaded using ftp to ftp://ftp.mnp.rivm.nl/cce/incoming/ . If you intend to use ftp, please inform J. Slootweg of this by email.
- Note that the latest version of the Mapping manual is available on the website of the ICP M&M (www.icpmapping.org) an on www.rivm.nl/cce. Concerning critical loads of heavy metals the Mapping Manual includes an update of chapter 5.5.
- For questions regarding methodology or data to use, please send your questions to Gudrun Schütze (email: gudrun.schuetze@oekodata.com), for questions concerning submitting of data don't hesitate to mail to J. Slootweg (email address is given above)
- In the instructions of last call for data on heavy metals (Sept. 2002) there was a reference to the wrong version of the EMEP50 grid. Please verify the coordinates with your country borders of figure A-1 of the CCE Status Report 2003 (p. 127)

Most important changes since the 2001 call for critical loads of heavy metals

A significant number of changes have been since the call for preliminary critical loads of cadmium and lead was conducted in 2001. In summary:

- **New Pollutants:**

Effects-based methodologies for Hg are available:

  - ecotoxicological effects in forest humus layers

- human health effects: indicator is Hg in fish (surface waters)

- **New end points :**

Inclusion of human health aspects of Pb, Cd, Hg:

- Cd in wheat
- Hg in fish
- Pb, Cd, Hg in drinking water (protection of groundwater)

- **New Critical limits (ecotox) for Cd and Pb:**

Application of new approach for effects of Cd and Pb on biota in terrestrial systems.

- **New Receptors**

Critical loads of Cd and Pb on arable land

A more detailed overview of the changes are described in chapter 5.5 of the Mapping Manual.

Data structure

Distinct effects on receptors can be utilised in the calculation of critical loads. Effects considered for the metals with the relevant ecosystems are listed below.

Table 1. Effects leading to critical loads considered in this call.

Effect_no	Effects	Ecosystems	Metals
1	Human health effects (drinking water)	Terrestrial ecosystems	Pb, Cd, Hg
2	Human health effects (food quality)	Terrestrial ecosystems	Cd
3	Ecotoxicological effects	Terrestrial ecosystems	Pb, Cd, Hg
4	Ecotoxicological effects	Aquatic ecosystems	Pb, Cd
5	Human health effects (food quality)	Aquatic ecosystems	Hg

For any one ecosystem more then one effect and/or receptor can be considered and submitted. To identify a distinct ecosystem, please use unique integers for '*SiteID*'.

The variables needed to calculate the critical loads depend on the effect and receptor considered. Please provide the variables you used, and leave the others empty (*null*). The full list of variables is given in Table 2. Table 2, using the prepared ACCESS database (see above) should be used for each metal separately. See chapter 5.5 of the recent update of the Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends. (www.icpmapping.org under *manual*; www.rivm.nl/cce under *news*)

Table 2. List of attributes of each of the tables in the call

name (header)	symbol in the Manual	unit	Description
SiteID			identifies the ecosystem, use unique integers
Lon / Lat		dec. °	The geographical co-ordinates of the site or a reference point of the polygon (sub-grid) of the receptor under consideration (in decimal degrees, ie. 48.5 for 48°30', etc.)
I50 / J50			Indices (integers) of the 50kmX50km EMEP-grid cell in which the receptor is located. See "Appendix A" of the CCE Status Report 2003

			or chapter 8 of the mapping manual for details on this grid.
EcoArea		km^2	area of the ecosystem within the EMEP grid cell, for which the critical loads are computated
CLM	CL(M)	g ha^{-1} a^{-1}	critical load of the metal
Mprec	$[M]_{prec(crit)}$	ng L^{-1}	critical metal concentration in precipitation.
effect_no			number of the effect, according to table 1
Mu	M_u	g ha^{-1} a^{-1}	net uptake of M, according to eq. (2) in the manual and related instructions. In calculations of CLM for effect_no 2 only the Cd uptake in wheat on arable land has to be calculated on the basis of the critical limit of 0.12 mg kg^{-1}(dw), assuming that the arable land is covered by wheat only.
Yha	Y_{ha}	kg ha^{-1} a^{-1} (dw)	annual yield/increment of biomass (dry weight)
Mha	$[M]_{ha}$	g kg^{-1} (dw)	content of the metal in the harvested part of the plant
fMu	f_{Mu}	-	fraction of the uptake within the considered soil depth
Mlecrit	$M_{le(crit)}$ $M_{lo(crit)}$	g ha^{-1} a^{-1}	$M_{le(crit)}$ = critical leaching flux of heavy metal from the topsoil (in calculations for effects_no 1,2,3), according to eq. 3 in the manual and related instructions $M_{lo(crit)}$ = critical lateral outflow of heavy metal from the aquatic system (in calculations for effects_no 4) according to eq. 12 in the manual and related instructions
Qle	Q_{le} Q_{lo}	m a^{-1}	Q_{le} = flux of leaching water from the considered soil layer (thick z or z_b, depending on effects_no 1,2,3) Q_{lo} = lateral outflow flux of water from the aquatic system (in calculations for effects_no 4)
thick	Z z_b	m	thickness of the soil layer considered, with z = entire rooting depth and z_b the biological active upper soil layer (including humus layer and upper most mineral horizon)
layercode			type of soil layer, please use following codes: 1 = humus layer only; 2 = mineral layer (A-horizon) only; 3 = humus layer + A-horizon; 4 = entire rooting depth
Mcrit	$[M]_{ss(crit)}$ $[M]_{tot,sw(crit)}$	mg m^{-3}	$[M]_{ss(crit)}$ = critical total dissolved metal concentration in the soil solution (dissolved metals only) $[M]_{tot,sw(crit)}$ = critical total metal concentration in the surface water (including dissolved metals and metals bound to suspended particles)
pH	pH	-	For terrestrial ecosystems, please take table 6 as well as explaining text in the Manual into account
OM	$[OM]_s$	% (dw)	organic matter content of the soil or, in case of surface waters, organic matter content of the suspended particles (eq. A1.5 in Annex

			1 of the manual), respectively
pCO2	pCO_2	* air	partial pressure of CO_2, expressed as the multiple of the atmospheric value of pCO_2; the default is 15 with a range of 3 - 30
SPM	$[SPM]_{ss}$, $[SPM]_{sw}$	g m^{-3}	concentration of suspended particulate matter in the soil solution ($[SPM]_{ss}$) or in the surface water ($[SPM]_{sw}$)
DOC	$[DOC]_{ss}$, $[DOC]_{sw}$	g m^{-3}	concentration of dissolved organic carbon in the soil solution ($[DOC]_{ss}$) or in the surface water ($[DOC]_{sw}$)
DOM	$[DOM]_{ss}$, $[DOM]_{sw}$	g m^{-3}	concentration of dissolved organic matter in the soil solution ($[DOM]_{ss}$) or in the surface water ($[DOM]_{sw}$)
TOC	[TOC]	mg L^{-1}	total organic carbon in the surface water
AlAcRatio	A_l / A_c	ha	Ratio of area of the lake and the catchment for which the CL is calculated
Psw	[TP]	µg L^{-1}	concentration of total phosphorus in the surface water
TFHgSite	TF_{HgSite}	L kg^{-1} (fw)	site (watershed) specific transfer function
TFHgBio	TF_{HgBio}	-	describing the deviation from a standard fish
fish_spec			the fish species/fish taxa addressed in the calculation, please use following codes: 1=pike, 2=pike-perch, 3=perch, 4=trout, 5=arctic char, 6=whitefish, 7=burbot, 8=bream, 9=roach
EUNIScode			EUNIS code, up to 5 characters

Although only a single table format is used all four effects and all requested metals, not all variables are relevant for each effect. Table 3 indicates the relevance of a variable for each method.

Table 3. Relevance of the variables for each method.

Method / Variable	Human health effects (drinking water)	Human health effects (food quality) on terrestrial ecosystems	Ecotoxico-logical effects on Terrestrial ecosystems	Ecotoxico-logical effects on Aquatic ecosystems	Human health effects (food quality) for aquatic ecosystems
For metal	Pb,Cd,Hg	Cd	(see below)	Pb,Cd	Hg
CLM	X	X	Pb,Cd,Hg	X	
Mprec					X
Mu	X	X	Pb,Cd,Hg	X	
Yha	X	X	Pb,Cd,Hg	X	
Mha	X		Pb,Cd,Hg	X	
fMu	1	X	Pb,Cd,Hg		
Mlecrit	X	X	Pb,Cd,Hg	=Qlocrit	
Qle	X	X	Pb,Cd,Hg	=Qlo	
thick	X	X	Pb,Cd,Hg		
layercode			Pb,Cd,Hg		
Mcrit	WHO limit		Pb,Cd,Hg	X	
pH			Pb,Cd	X	
OM			Pb,Cd	X	
pCO2			Pb,Cd		
SPM			Pb,Cd	X	
DOC			Pb,Cd	X	
DOM			Hg		
TOC					X
AlAcRatio				X	
Psw					X
TFHgSite					X
TFHgBio					X
fish_spec					X

Documentation

Please send with the data a document containing a description of the sources of the data, the methods used, and the personal particulars of the NFC and the collaborators. Use the usual setup regarding paragraphs, table numbering etc., but refrain from more complicated layout features like double columns (see CCE Status Report 2003 or the CCE Progress report 2004). Regarding the methodology you are strongly requested to follow agreed methods (Mapping Manual) and list the choices and/or adaptations that you made.

Appendix B Ecosystem types and EUNIS codes

Table B-1. Types of ecosystems for different levels as used in this report

Main categories	EUNIS Level 1	EUNIS code	EUNIS description
Forest	Forest	G	Woodland and forest habitats and other wooded land
		G1	Broadleaved deciduous woodland
		G2	Broadleaved evergreen woodland
		G3	Coniferous woodland
		G4	Mixed deciduous and coniferous woodland
		G5	Lines of trees, small anthropogenic woodlands, recently felled woodland, early-stage woodland and coppice
Vegetation	Grassland	E	Grassland and tall forb habitats
		E1	Dry grasslands
		E2	Mesic grasslands
		E3	Seasonally wet and wet grasslands
		E4	Alpine and sub alpine grasslands
	Shrubs	F	Heath land, scrub and tundra habitats
		F1	Tundra
		F2	Arctic, alpine and sub alpine scrub habitats
		F4	Temperate shrub heath land
		F5	Maquis, matorral and thermo-Mediterranean brushes
		F7	Spiny Mediterranean heaths
		F9	Riverine and fen scrubs
	Wetlands	D	Mire, bog and fen habitats
		D1	Raised and blanket bogs
		D2	Valley mires, poor fens and transition mires
		D4	Base-rich fens
		D5	Sedge and reed beds, normally without free-standing water
		D6	Inland saline and brackish marshes and reed beds
	Other	A2	Littoral sediments
		B1	Coastal dune and sand habitats
		B2	Coastal shingle habitats
		C3	Littoral zone of inland surface water bodies
		Y	Undefined
Agriculture	Agriculture	I	Regularly or recently cultivated agricultural, horticultural and domestic habitats
		I1	Arable land and market gardens
Water	Water	C	Inland surface water habitats
		C1	Surface standing waters
		C2	Surface running waters

Appendix C First Estimate of Cadmium and Lead Input by Fertilizers and Animal Manure to Agricultural Soils

K.W. van der Hoek and A.F. Bouwman*

*National Institute for Public Health and the Environment (RIVM), the Netherlands

The cadmium and lead content of fertilizers and animal manure is expressed as gram per kg P. Multiplying these values with the amounts of P fertilizer and P in animal manure loadings to agricultural soils, the corresponding input of cadmium and lead is estimated.

Cadmium and lead content of fertilizers

The cadmium and lead input by fertilizers is based on a survey which comprised all sources of cadmium and lead inputs to agricultural soils in the Netherlands in the year 2000 (Delahaye et al. 2003).

The N, P, K, and lime fertilizers contributed in total 1960 kg of cadmium. The P fertilizers were responsible for 85% of the cadmium input, so the P fertilizers can be used as tracer. In the year 2000 the P fertilizer use was 27,000,000 kg, so the average content is calculated as 1,960,000/27,000,000 = 0.073 g Cd per kg P fertilizer.

The N, P, K, and lime fertilizers contributed in total 4890 kg of lead. The contribution of P fertilizers was 46% and lime fertilizers contributed 35%. As no data were available for lime use in Europe, it was decided to use P fertilizers as tracer and the average content is calculated as 4,890,000/27,000,000 = 0.181 g Pb per kg P fertilizer.

Cadmium and lead content of animal manure

The Dutch survey gives only a total input of cadmium and lead by animal manure but does not give a specification for the various animal categories. Therefore we used data from a Swiss survey where about 1100 manure samples were analysed (Menzi and Kessler, 1998).

Table C-1 Content of heavy metals in manure relative to phosphor

Animal category	Type of manure	g Cd/kg P	g Pb/kg P
Dairy cattle	Liquid manure	0.019	0.40
	Slurry	0.022	0.42
	Solid manure	0.025	0.49
Beef cattle	Liquid manure	0.016	0.31
	Solid manure	0.033	0.50
Cattle, average		0.023	0.42
Fattening pigs	Liquid manure	0.008	0.07
Dry sows	Liquid manure	0.009	0.11
Sows + piglets	Liquid manure	0.013	0.13
Pigs, average		0.010	0.10
Laying hens	Litter from belts	0.014	0.10
	Litter from deep pits	0.008	0.08
Broilers	Litter	0.024	0.24
Poultry, average		0.015	0.14

In 1998 cattle represented 75% of the total P excretion by animals in the 15 member states of the European Union, pigs and poultry contributed 15% respectively 10%. Based on this partition the average contents of animal manure are 0.020 g Cd/kg P and 0.35 g Pb/kg P.

Regional inputs by fertilizers and animal manure

The IMAGE-database provided detailed information on use of P fertilizers and P loadings with animal manure on agricultural soils. The used grid scale was 0.5 by 0.5 degree and it was taken into account that extensive used agricultural soils did not receive fertilizer or animal manure. This explains that for some countries the used Cd and Pb input per hectare is higher than the national average input per hectare using the total agricultural area in these countries.

Additional information from some countries

A short literature search revealed for the following countries more information on Cd and Pb inputs to agricultural soils:
Denmark: Bak et al. (1997) Moolenaar (1999)
Finland: Moolenaar (1999)
France: Mench (1998)
Germany: Wilcke and Döhler (1995)
The Netherlands: Moolenaar (1999), De Vries et al. (2002), Delahaye et al. (2003)
Sweden: Moolenaar (1999), Berndes et al. (2004)
Switzerland: Menzi and Kessler (1998), Keller et al. (2001), Keller and Schulin (2003)
United Kingdom: Nicholson et al. (2003)

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