Texte
47
03

ISSN
0722-186X

Proceedings

Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application

Berlin, 2.-4. Dezember 2002

UMWELTBUNDESAMT

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14191 Berlin
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Telefax: 030/8903 2285
Internet: http://www.umweltbundesamt.de

Redaktion: Gudrun Schütze, Fa. Ökodata

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Berlin, Juli 2003

FOREWORD

The Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application was held 2 – 4 December 2003 in Berlin. It was the follow-up of the first Meeting of the Ad-hoc International Expert Group on Effect-based Critical Limits for Heavy Metals (11 – 13 October 2000 in Bratislava), continuing international scientific discussion, the first steps of which were UNECE workshops 1997 in Bad Harzburg and 1999 in Schwerin.

The derivation of an effects-based approach for heavy metals aiming at emission abatements has been continuously developed since the mid of the 1990's. It started even before the Protocol on Heavy Metals of the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) was signed by 36 parties, 1998, in Århus (Denmark). The process was induced by the results of the Dutch project "European Soil & Sea Quality due to Atmospheric Deposition (ESQUAD, 1994) as well as by the elaboration of first draft manuals (De Vries and Bakker 1996, De Vries et al. 1996) on behalf of the Air and Energy Directorate of the Dutch Ministry of Housing, Spatial Planning and the Environment, providing methods to calculate critical loads for heavy metals in terrestrial and aquatic ecosystems. The methods proposed there have been amended in several steps according to the most current status of knowledge. While the main principles of such calculations nowadays are widely agreed within the UNECE International Cooperative Programme on Modelling and Mapping of Critical Loads & Levels and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping), within the last three years most emphasis was laid on strengthening the scientific basis of critical limits (concentrations) and transfer functions (necessary to describe heavy metal partitioning in soils and surface waters) as well as their harmonisation between countries. A first European exercise on mapping critical loads of lead and cadmium and their exceedances could already be conducted in 2002 in cooperation between ICP Modelling and Mapping and EMEP Meteorological Synthesizing Centre East (MSC-E) (Hettelingh et al. 2002, see also http://www.unece.org/env/documents/2002/eb/wg1/eb.air.wg.1.2002.13.e.pdf). The results of this study helped to identify the most crucial items for completing the effects oriented methods for heavy metals

The expert meeting in Berlin was another important step on this successful way. It was held according to the work plan of ICP Modelling and Mapping and considered the recommendations drawn from the first European mapping exercise. The German Ministry for the Environment, Nature Conservation and Nuclear Safety sponsored the meeting, which was organised by the Federal Environmental Agency in cooperation with OEKO-DATA Strausberg. Relevant scientific input was provided by the international expert groups on critical limits and transfer functions of heavy metals in the framework of ICP Modelling and Mapping.

Presently the UNECE Protocol on Heavy Metals, which was mainly based on the principle of best available technology (BAT), has been ratified by 13 countries and the EU, and is expected to enter into force soon. According to Article 6 (g) of the Protocol the effects-based approach, which should aim at protection of human health and the environment, was intended to be developed "for the purpose of formulating future optimized control strategies ...". To be prepared for scientific support of eventual deliberations toward a future effects based Protocol on Heavy Metals, it will be necessary to finish the methodological developments temporarily and to produce advanced European maps on critical loads of heavy metals in 2005 as demanded in the Medium-term Work Plan of the Working Group on Effects (WGE) under the CLRTAP.

The conclusions and recommendations of the workshop in Berlin will guide the further challenging work of the international expert groups on heavy metals and the Modelling and Mapping Programme. These results will be reported to the Task Force of the ICP Modelling and Mapping and to the WGE. The proceedings presented here will be distributed to all participants of the expert meeting as well as to those, who are interested in such issues. It is planned to make an electronic version available on the ICP website (www.icpmapping.org).

Strausberg/Berlin, April 2003

Gudrun Schütze,	workshop chairwoman
Till Spranger,	Chairman of the UNECE ICP Modelling and Mapping

ACKNOWLEDGEMENTS

The „Expert meeting on Critical Limits for Heavy Metals and Methods for their Application", was organized under the UNECE International Cooperative Programme on Modelling and Mapping of Critical Loads & Levels and Air Pollution Effects, Risks and Trends and sponsored by the German Ministry for the Environment, Nature Conservation and Nuclear Safety.

We are grateful for the support by the Chairman of the UNECE Working Group on Effects (WGE), Mr. Heinz-Detlef Gregor, and other members of the WGE Secretariat. Our specific thank goes to Mr. Marek Jakubowski, who represented the Joint Task Force on Health Aspects of Air Pollution at the meeting.

The organisers wish to thank the members of the international expert groups on critical limits and transfer functions of heavy metals in the framework of ICP Modelling and Mapping. In particular the authors of draft background documents and main speeches, the chairpersons and rapporteurs of working groups, participants who provided special contributions to the workshop and to this book, as well as all those who participated actively in the discussions, thus enabling a constructive approach of the expert meeting, are gratefully acknowledged.

Also, we thank the Dietrich-Bonhoeffer Haus, Ziegelstraße 30, in Berlin, for providing pleasant atmosphere and excellent conference facilities.

Methods and criteria for calculating critical loads for heavy metals have been further developed after the meeting. Contributions to the continuing work have been sent by experts from several countries, including The Netherlands, Russian Federation, Sweden, and United Kingdom. We explicitly emphasize our gratitude for this further support of the tasks of ICP Modelling and Mapping related to effects-based approaches for heavy metals. Since this book is designed to be a background document for the December 2002 Expert meeting, these contributions have not been documented here. However, they will contribute greatly to the development of a chapter on critical loads of heavy metals of the ICP Modelling and Mapping Manual. This chapter will be finalized in spring 2004.

EXPERT MEETING

ON

CRITICAL LIMITS FOR HEAVY METALS AND METHODS FOR THEIR APPLICATION

BERLIN, GERMANY
2 – 4 DECEMBER 2002

PROCEEDINGS

UNECE CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
ICP MODELLING AND MAPPING

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1. INTRODUCTION

Gudrun Schuetze, Régis Farret, Jean-Paul Hettelingh, Till Spranger

The UN/ ECE Convention on Long-range Transboundary Air Pollution (CLRTAP) has over the years substantially contributed to the development of international environmental law and has created the essential framework for controlling and reducing the damage to human health and the environment caused by transboundary air pollution. In the years from its entering into force (1983) until today problems of acidification and eutrophication due to anthropogenic emissions of sulphur and nitrogen compounds as well as damage to individual receptors like human health, surface waters, vegetation, materials and cultural heritage by air pollutants were in the main focus of the effects oriented work under the Convention.

In the 1990s the problems related to heavy metals (HM), their accumulation in ecosystems and their impact on the environment and human health became increasingly important. Specific attention was devoted to deriving effect-based abatement strategies. Already in 1991, just after the first meetings of the Task Forces on Heavy Metals and Persistent Organic Pollutants under the Working Group on Abatement Techniques, ideas were launched to see whether a critical load approach as devised for acidification and eutrophication could work for these substances as well. These ideas led to the Dutch project "The Impact of Atmospheric Deposition of Non-Acidifying Pollutants on the Quality of European Forest Soils and the North Sea" (ESQUAD project, Van den Hout 1994) where a first systematic assessment of critical loads and excess loads of three HM and two persistent organic pollutants (POPs) for European forest soils and the North Sea was made.

Since the first workshop on effects based approaches for heavy metals and POPs under the umbrella of CLRTAP, 1997, in Bad Harzburg (Gregor et al. 1998), the principle methodology for deriving critical values for HM was discussed at a row of meetings, a number of research projects in several countries have been performed and numerous scientific papers were produced (in particular the „Manuals for Calculating Critical Loads for Heavy Metals in Aquatic and Terrestrial Ecosystems" by De Vries and Bakker 1998 a, b). In the UNECE Protocol on Heavy Metals (ECE/EB.AIR/61), which was signed in Århus (Denmark) by 36 parties, lead, cadmium and mercury were named as the first priority metals (Annex I). Abatement strategies for these metals as described in the Annexes III – VII are based on best available technologies (BAT). In Article 6 (g) the parties were encouraged to support the development of an effects-based approach for possible future optimised control strategies. The ICP Modelling and Mapping played an important role in further developing the effects-based approaches for heavy metals, including mapping of critical loads, in the framework of the WGE.

At the workshop on Effects-based Approaches for Heavy Metals, 1999, in Schwerin (Gregor et al. 1999), international experts agreed that for lead and cadmium the mass balance approach is most appropriate to calculate critical loads, while for mercury the basic principles of methodology are still in discussion. Independent of the model chosen, in an effects-based approach critical limits are needed, but methods for their derivation were not finally agreed in Schwerin. It was decided to establish an ad-hoc expert group on effects-based critical limits for heavy metals. Another recommendation was to calculate a "stand-still load", aiming at no further accumulation of the heavy metal in the ecosystems, in parallel to the effects based critical loads and use the minimum of both for abatement strategies.

The ad-hoc expert group on effects-based critical limits for heavy metals held its first meeting in October 2000 in Bratislava, the present meeting in Berlin is the second one, and the next and probably final meeting is foreseen in spring 2004. A first set of critical limits was chosen in Bratislava by the participating experts and recommended for use to National Focal Centres (NFCs). To enable NFCs to start immediately with mapping exercises of critical loads on the basis of the suggested critical limits a "Short Guidance" (Gregor et al. (2000) was produced immediately after the workshop and published in the proceedings (Čurlík et al. 2000). It summarized all necessary steps of calculation in terrestrial ecosystems as well as guidelines for the derivation of input data.

At the 11th Workshop of the Coordination Center for Effects (CCE), 2001 in Bilthoven and the 17th Task Force on ICP Modelling and Mapping, 2001 in Bratislava, a number of countries stated their readiness to participate in first mapping exercises for heavy metals on European level. The experiences with use of the “Short Guidance” and the set of critical limits lead to the conclusion that further harmonisation of both, the limits as well as transfer functions for heavy metals, is urgently necessary and a precondition to make a possible first European mapping exercise for lead and cadmium successful. One small international ad-hoc expert group was established, which has been working from that time until now on these tasks on behalf of the Task Force on ICP Modelling and Mapping. Confirming the overall objective to “further develop and test” the overall methodology, the Working Group on Effects (WGE) decided during its 20th session to invite ICP Modelling and Mapping and the CCE to issue, by the end of 2001, a call for relevant data on critical loads of Cd and Pb on a voluntary basis.

Based on their first results, the international ad-hoc working group in cooperation with the CCE elaborated a revised “Guidance for the calculation of critical loads for cadmium and lead in terrestrial and aquatic ecosystems” (De Vries et al. 2001), which was the methodological basis for the call for data by CCE. A set of harmonised critical limits was provided after statistical evaluations of updated effects data bases from several countries and the EU and in depth scientific discussions. Also as a set of transfer functions, derived mainly from Dutch databases, was recommended for use. The scientific background for both, critical limits and transfer functions, was comprehensively described in De Vries et al. (2002).

Seventeen countries responded to the call of the CCE, of which eleven provided data.. The results of the first European mapping exercise were introduced at the 12th CCE workshop and (back to back) the 18th Task Force on ICP Modelling and Mapping, 2002 in Sorrento. They can also be found in the common report of CCE and EMEP MSC-E (Hettelingh et al. 2002, see also website of the CCE, www.rivm.nl/cce). Both the critical load maps and first exceedance maps, as well as all results presented within the report have a preliminary status. After broad discussion in both meetings, a list of conclusions and recommendations for further work was agreed. This list served as the guideline for the work of the expert group until the follow-up expert meeting.

The “Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application” was held 2 – 4 December 2003, in Berlin, as a follow-up of the Bratislava expert meeting in October 2000. Taking into account the Medium-term Work Plan of WGE (EB.AIR/WG.1/2002/4), the main objectives of this meeting were to agree on operational approaches and to provide the scientific basis for an effect-based revision of the UNECE Protocol on Heavy Metals by 2004. In this respect, the meeting welcomed not only experts in chemistry or modelling, but also experts in biology or toxicology.

The Berlin meeting was structured according to its most important tasks (according to the recommendations of Sorrento 2002):

- **Review of the harmonised set of Critical Limits for heavy metals for soils and waters**, whereby inclusion of limits for Hg and of human health effects was most important;
- **Further development of transfer functions of Pb, Cd and Hg** for soils and sediments, with emphasis on their applicability to the broad spectrum of European soils;
- **General methodological aspects**, including the
    - choice of approaches (critical loads model versus stand-still model) according to the "decision tree", proposed in Sorrento (2002),
    - identification and European-wide mapping of present heavy metals pollution (Pb, Cd, Hg) of soils and their sources,
    - methods to consider other heavy metal inputs to soils and surface waters than atmospheric pollution,
    - peculiarities and applicability of an effect-based approach for Hg

These headings were at the same time the themes of three draft background documents provided before the expert meeting and the names and the scope of three working groups during the workshop. For each of the items a list of most relevant questions was prepared.

The proceedings of the expert meeting in Berlin, provided for the benefit of a wider number of interested scientists, advisors and decision makers, contain a short reflection on future work to be done, the workshop report (Minutes), including the conclusions and recommendations of the three working groups and six annexes, as well as the abstracts of short presentations and posters presented at the meeting. In line with a decision of Berlin, the draft background documents have been revised before inclusion into the proceedings, thus already mentioning the proposals for methodological improvements, which were agreed upon. However, in order to keep the proceedings as a document of the status of work at the end of the year 2002, it was not possible to reflect in detail all the comprehensive new information, which was sent to the editorial group, e.g. by experts from Netherlands, Russian Federation, Sweden and UK, in the months after the meeting. The Expert Panel on Critical Loads of Heavy Metals, established as one working unit from experts of the former international working groups on critical limits and transfer functions for heavy metals, will make a full use of the new knowledge in its further activities. Contributions to the continuing development of effects based methods for heavy metals received already as well as those to be come will be documented on the website of ICP Modelling and Mapping, www.icpmapping.org.

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2. WAYS AHEAD TO THE REVIEW OF THE HEAVY METALS PROTOCOL

Heinz-Detlef Gregor, Chairman of the Working Group on Effects

In December 2002 14 parties to the Convention on Long-range Transboundary Air Pollution had ratified the Protocol on Heavy Metals. Thus the Protocol is approaching entry into force and, after this, the review process will be starting.

In Article 6 (g) of the Protocol Parties are encouraged to support the development of an effects based approach for heavy metals. In line with this the Updated Medium-term Work plan of the Working Group on Effects (WGE) (EB.AIR/WG.1/2002/4, heavy metals issues see table 1) considers the requirements for scientific support of a possible effects based review by 2004/5. Following decisions taken by the WGE at its twentieth session and the EMEP Steering Body (SB) at its twenty-fifth session, both programmes coordinated their work plans (see table), taking note of planning activities already carried out by the CAFE programme, at a joint meeting of the bureaux of EMEP SB and WGE in February 2002. At this meeting the need for increasing awareness of national experts regarding the importance of the work on heavy metals was noted.

All ICPs and the Joint Task Force on Health Aspects of Air Pollution (TF Health) under the WGE participate in the work on heavy metals. An ICP Waters workshop on heavy metals, Lillehammer, March 2002, contributed considerably to progress in knowledge as well as investigations and evaluations performed by the ICPs on Forests, Integrated Monitoring, Vegetation and the Task Force on Health Aspects, which were reported to the WGE and documented in the programmes' reports. ICP Materials is starting its work on release of heavy metals by corrosion. Another important step in providing scientific input to the review process of the heavy metals protocol was the first mapping exercise within the ICP on Modelling and Mapping dealing with critical loads for cadmium and lead, based on a call for data to the National Focal Centres by the CCE, to be responded on a voluntary base. Sets of harmonised critical limits and transfer functions had been developed in advance of this call. The WGE at its 21st session, August 2002 in Geneva, noted with appreciation the progress achieved in deriving critical limits and effects based methods for heavy metals, but noted also the need for further development of methods.

As reported to the 12th CCE Workshop and the 18th Task Force on ICP Modelling and Mapping, the European mapping exercise showed that producing maps of critical loads and stand-still loads of Cd and Pb, based on a mass balance model, as well as mapping of exceedances is possible and leads predominantly to plausible results. Open questions, uncertainties and necessary methodological improvements could be identified and described more precisely, inter alia questions related to the use of critical limits and critical loads. The WGE confirmed at its 21st session, that, if present deposition was below critical loads, increasing deposition and filling the gap up to the critical load was not in line with the accepted critical loads approach and would be against the spirit of the Convention, aiming, inter alia, to control and, if possible, decrease air pollution and its effects and avoid any deterioration of the environment. Other open questions identified are subject of discussions during this international expert meeting on "Critical Limits for Heavy Metals" in Berlin, which will also mean a large step forward in the development of methods and strengthening their credibility.

The Working Group on Strategies and Review (WGSR) under the Convention decided at its thirty-fourth session, 18 – 20 September 2002 in Geneva, to recommend to the Executive Body to set up an expert group on heavy metals to start work in 2003. The Working Group agreed that the experts should, inter alia,

- collect information within and outside the framework of the Convention on the effects of heavy metals,
- review information on abatement options and their costs, taking into account the synergies with the abatement of PM and
- review the information on heavy metals not yet included in the Protocol.

In particular the first point, listed above, demands the WGE to give all necessary support to the further effects based work on heavy metals and to comply to the Medium-term Work Plan. One important task following the Berlin meeting will be the edition of a draft new chapter on heavy metals for the Mapping Manual, which is currently being generally updated. After the revision of critical limits and transfer functions, as proposed during the discussions of this meeting, these have to be tested in national studies. The experiences made in these exercises will then be reported to ICP Modelling and Mapping and will be reviewed by another international workshop on effects-based approaches for heavy metals, which could possibly be held at the beginning of 2004. The recommendations of this upcoming meeting, as far as approved by the WGE, would then be the basis for a preliminary last update of the Mapping Manual chapter on heavy metals and for the advanced mapping of critical loads for heavy metals as a scientific input to the review process of the CLRTAP heavy metals protocol.

Joint Meeting of the Bureaux of the EMEP Steering Body and the Working Group on Effects, Geneva, 27 February 2002: Activities under the Convention on Long-range Transboundary Air Pollution concerning heavy metals

YEAR	EMEP Steering Body (EMEP SB)		Working Group on Effects (WGE)		REMARKS
	DELIVERABLES	INPUTS FROM WGE	DELIVERABLES	INPUTS FROM EMEP	
2002		Maps of land-use categories from CCE	Surface water pollution assessment (Cd, Hg and Pb) Methodology to map exceedances of Cd and Pb CLs (with MSC-E)	Preliminary deposition maps	Raise profile to encourage Parties to contribute
2003	Transfer matrices for Cd, Hg and Pb Deposition maps by land use category for Cd, Hg and Pb	Preliminary map of CL for Cd and Pb Validation in cooperation relevant ICPs	Preliminary CL maps for Cd and Pb Health effect assessment Moss survey results Release of HMs due to corrosion	Deposition maps	Risk assessment for other HMs?
2004	First report (with CCE) on CL exceedances for Cd and Pb Hemispheric scale modelling for Hg IAM scenarios linking to Cd and Pb effects	Revised map of CL	Risk assessment for forests Advanced CL maps for Cd and Pb*) First report (with MSC-E) on CL exceedances for Cd and Pb		
2005	Material for Protocol review (emissions, transfer)		Material for Protocol review (CL maps, risk assessment of other HMs)		

*) The postponing of the second call for data on critical loads for heavy metals will lead to a delay of the production of advanced maps until 2005.

3. MINUTES

The minutes were prepared by the chairperson of the workshop, Gudrun Schuetze, in consultation with the chairman of the International Cooperative Programme on Modelling and Mapping.

Introduction

1. Following the conclusions and recommendations of the First Meeting of the Ad hoc International Expert Group on Effect-based Critical Limits for Heavy Metals, held on 11 –13 October 2000, Bratislava, Slovak Republic, a follow-up meeting was organised in 2002. This responds also to the decisions of the 20th Session of the Working Group on Effects, noting that methodologies have to be further developed.

   The meeting held from 2 - 4 December 2002 in Berlin, Germany, was hosted by the German Federal Environmental Agency and sponsored by the German Ministry of the Environment, Nature Conservation and Nuclear Safety. The meeting was chaired by Ms. Gudrun Schuetze, organiser of the international working group on critical limits for heavy metals of the International Cooperative Program (ICP) on Modelling and Mapping. It was attended by 39 experts from 16 countries (Austria, Belgium, Czech Republic, Finland, France, Germany, Italy, Netherlands, Poland, Russian Federation, Slovakia, Spain, Sweden, Switzerland, Ukraine, and the United Kingdom). The Bureau of the Working Group on Effects (WGE) (Chairman and Vice-Chairman) and the Task Force on Health Effects of Air Pollution (TF Health) were represented. The chairman of the ICP Modelling and Mapping was present as well as contact persons from ICP Waters (Mr. Ed Tipping) and ICP Forests (Mr. Wim de Vries). A list of participants is attached as Annex I.

2. Ms. Gudrun Schuetze (Germany) welcomed the participants and wished the meeting a constructive and successful approach.

3. The meeting was opened by Mr. Régis Farret (France), vice-chairman of the WGE, who introduced the recent development of the effect oriented activities with respect to heavy metals in different ICPs. The aim is to provide the scientific basis for an effect-based revision of the UNECE Protocol on Heavy Metals by 2004. He suggested that this work should be done in contact with other studies in the organisations outside the Convention. He stressed the need, according to the decision of WGE, to refine the methodologies to derive critical limits and to calculate critical loads for cadmium, lead and mercury. Some significant results have been achieved in year 2002 within the expert group on heavy metals and the preliminary call for data led by the CCE, but this meeting is a crucial step to improve the credibility of the work. He especially wished a fruitful interaction between on one hand experts in chemistry or modelling, on the other hand experts in biology or toxicology.

4. Mr. Till Spranger, chairman of ICP Modelling and Mapping explained the aim and structure of the meeting. He emphasised the need to comply with the Medium-term Work Plan of WGE (EB.AIR/WG.1/2002/4) and to provide the scientific basis for the Manual revision. Hence the assessment of critical limits and transfer functions for heavy metals as well as the general methodology to derive critical loads should be finished in 2003 and preliminary maps of critical loads of heavy metals for all EMEP grid cells should be produced for use by TFIAM. In addition to this task, a secondary, long-term aim is to interpret present heavy metal concentrations as a consequence of natural site characteristics and/or anthropogenic inputs (historical, present; atmospheric, non-atmospheric). He summarized the main expectations from the meeting, i. e. to

   - gain agreement at this Expert Meeting on the methods to derive critical limits for lead (Pb), cadmium (Cd) and mercury (Hg) including the consideration of human health aspects
   - agree on operational approaches (easy to communicate to politicians and the public; scientifically sound; relevant for IAM results; available in time) to calculate tolerable atmospheric inputs.

   He also summarized the products expected from this meeting: 1) a new chapter of the Mapping Manual; 2) a report to the WGE via the TF M&M; 3) Proceedings from the meeting.

5. The workshop participants agreed to the agenda of the meeting.

Structure of the meeting

6. The programme of the meeting has been broken up into three separate sessions:

Session I **Plenary presentations**

Session II **Working group discussions**

II.1 **Derivation of critical limits for Pb, Cd and Hg for soils and waters**, whereby inclusion of limits for Hg and of human health effects is most important

II.2 **Transfer functions Pb, Cd and Hg** for soils and sediments with emphasis on applicability of the transfer functions to European soils

II.3 **General methodological aspects**, including the

- choice of approaches according to the "decision tree", proposed earlier
- identification and European-wide mapping of present heavy metals pollution (Pb, Cd, Hg) of soils and their sources (is there a sufficient and consistent data basis?),
- methods to consider other heavy metal inputs to soils and surface waters than atmospheric pollution,
- peculiarities and applicability of an effect-based approach for Hg

Session III **Plenary presentations and discussions**

7. Mr. Jean-Paul Hettelingh (head of the Coordination Centre for Effects, CCE, in Bilthoven) explained the results of a call for data on Pb, Cd and introduced preliminary results of modelling and mapping of critical loads for cadmium and lead in Europe and first exceedance estimations for 1990 and 2010 (Protocol). Following the presentation of the results in the WGE and WGSR the CCE notes that the further development of a credible methodology and databases of European critical loads for Cd and Pb should be given priority. Improved knowledge of cause-effect relations of Mercury is important, even if a critical load approach may turn out ambitious at this stage. Recommendations of the WGSR draws our attention for the need to also address non atmospheric loads.

8. Ms. Gudrun Schuetze explained a possible outline of the a new chapter on heavy metals to the revision of the Mapping Manual. She reviewed the status of the methodology for the particular metals of concern as well as recent and future tasks.

9. Mr. Régis Farret provided an overview on general methodological aspects with respect to the calculation of critical loads for cadmium, lead and mercury. He explained time dependent consequences in several cases, where present concentrations in the soil are higher than critical limits or the opposite. Moreover he mentioned some of the open questions to be solved during the workshop (e.g. methods to identify sources of heavy metals pollution in soils and surface waters, and the relation between critical limits and endpoints).

10. Mr. Markus Meili explained in general the concentration and effects based methodology for mercury, the situation in Sweden at present and at steady state, and possibilities for considering the history and the dynamics of Hg pollution in simple models for calculation critical levels of atmospheric pollution. For aquatic systems, the critical limits for 1 kg pike can be the starting point of calculation. For Hg in soils the forest soil microflora might be the most important receptor.

11. Mr. Wim de Vries introduced the background paper on critical limits for heavy metals (Pb, Cd and Hg) including aspects of direct ecotoxicological effects, secondary poisoning and human health. He

stressed that the methodological basis for the derivation of critical limits for direct ecotoxicological effects is the OECD approach. He also pointed to the relation between exposure criteria for human health effects and food quality criteria, which are used in the derivation of soil critical limits.

12. Mr. Bert-Jan Groenenberg spoke on the background paper on transfer functions for heavy metals. He explained the need for transfer functions, mentioned the problem of different extraction methods used in the particular countries, and options for use of transfer functions. Data from 6 countries were included in a method comparison.

13. Within in depth discussion points for debate within the working groups have been identified and added to an already existing list of questions.

14. Seven selected short speeches, dealing with critical limits and general methodological aspects, were presented during the plenary. The announced short presentations dealing with heavy metal partitioning in soils and surface waters were held at the beginning of the working group discussion on transfer functions (Tuesday, 3 December). For a list of short presentations see Agenda (Annex II).

15. Nine Posters, reflecting the current stage of knowledge with respect to effects of heavy metals, partitioning in soils and waters and the critical load methodology in several countries were available and have been discussed during the meeting. A list of the posters is provided in Annex IV.

16. The participants split into three working groups (Annex V). A list of relevant questions was prepared before and completed during the first plenary meeting (Annex VI).

17. At the beginning of the final plenary meeting, Mr. Heinz-Detlef Gregor, chairman of the WGE, reviewed the history of the effects-based approaches for heavy metals, explained the needs for action with respect to the compliance to the Medium-term Work Plan of the WGE and counted the necessary steps ahead to an effects-based revision of the Convention's Protocol on heavy metals.

Conclusions and recommendations of the working groups

18. Each conclusion or recommendation was discussed during the plenary meeting. The wording of the related paragraphs of the draft minutes was amended in parallel, if necessary. As far as the following conclusions and recommendations are referring to the questions of the list (Annex VI), this is marked as e. g. Q1 (= question 1).

19. Concerning the **general questions, which were addressed to all groups**, the following answers and proposals were agreed :

    a) (Q1) As soon as they are approved here in the group and validated by ICP Mapping, the methods are designed to be scientifically sound, while producing a result which can be used in Integrated Assessment Modelling (IAM).
    The methods developed to derive critical limits for soil, soil solution and surface water are scientifically sound and the data requirements to apply them are limited to pH, alkalinity (for surface waters) and DOC (this refers to the methods agreed upon during this meeting).

    b) (Q2) The decision tree (see Annex III) indicates the different tasks which are to be undertaken in a continuum : NFC → CCE → IAM. At least the upper part is fully within the scope of this expert group.
    Concerning critical limits, only those that do influence the final result of IAM have been discussed in detail.

    c) (Q3, Q4) About time plan and further responsibility for the tasks to be solved, methodology should be ready by the end of 2003 (for review by WGE in 2004), and available to NFCs to support a call for data in 2004.

    The plans and improvements suggested here concerning limits can be solved by spring 2003 :

    - Derivation of critical limits (direct effects, see also point a and b related to Q6 and Q7) for free and total metal (Cd, Pb and Hg) concentration in soil solution and surface water as a function of pH and DOC: UK (Spurgeon) and NL (de

Vries), specifically for Cd and Pb, and Sweden (Meili and Bringmark), specifically for Hg.

- Derivation of relationship between deposition and uptake by crops for Hg by D (Schuetze) and for Pb by B (De Temmerman).
- Inclusion of critical limits related to human health (ADIs, limits for drinking water) by WHO (Jakubowski) and relation to food quality criteria by D and NL (Schuetze and de Vries).
- Further description of relationships of Hg in soil and solution by SE (Meili), and of Cd in wheat and soil by B (De Temmerman)
- Critical limits for soil solution based on direct measurements in relation to effects (see also point c related to Q8) will be sent for Hg by SE (Sverdrup), for Cd by F (Cambier) and for both, Cd and Pb by NL (De Vries).

Concerning methodological aspects, suggestions for future work are :

- European map of agricultural inputs (farm inputs), e.g. in contact with EU Concerted Action (AROMIS, results by end 2003). In the framework of AROMIS national information will be delivered to EU, it is, however, not planned to produce maps.
- Check possibilities for a preliminary European map of zones with high geogenic input/concentration
- Check and, if possible, decide on critical limits and an appropriate model design to take humus layer into account, see recommendations of WG II.1, II.2, II.3

d) (Q5) Ready for the inclusion into a revised Mapping Manual are:

- The critical loads mass balance equations for Pb and Cd
- The decision tree

Still in discussion during a few months after the meeting, but should be ready soon :

- A table of critical limits with indication of the most stringent ones, corresponding to the most sensitive routes
- A table of transfer functions

e) It was agreed that a complete model on human exposure pathways is not needed in the critical load methodology, since use of food quality criteria is a good alternative for this aspect. In this way human exposure will be considered in the expert group on critical limits and the possibilities to convert those limits to soil critical limits will be checked in order to allow critical load calculations.

In case it would afterwards considered necessary to develop an accurate way of integrating several pathways towards the human endpoint, this specific task could be undertaken within the expert group on critical limits.

20. The **working group II.1 on derivation of critical limits for Pb, Cd and Hg for soils and waters, chaired by Mr. W. De Vries (Rapporteur: Ms. G. Schuetze)** agreed on the following points:

Direct ecotoxicological effects

a) (Q6) There are clear and aimed suggestions to improve critical limits related to ecotoxicological effects, which can be easily applied (see time frame above). Critical limits for free and total metal (Cd, Pb and Hg) concentration in soil solution and surface water have to be derived as a function of pH and DOC (+ alkalinity for surface waters). For soils this implies application of transfer functions on NOEC soil data (see below).

b) (Q7) It can be assumed that most or nearly all eco-toxicological data are related to soil solution effects. Therefore, the group will test use of pH and DOC dependent free and total metal ion concentrations, to set critical limits for soil solution only, based on NOEC-Data on soil. Derivation will be based on plants, microbiota and soil fauna (except the hard bodied) using one common database. If it works, the critical loads modelling will become easier. For comparison an analogous evaluation of critical limits for the reactive soil content will also be included.

c) (Q8) Results on effects of Hg, measured for soil solution, on tree roots are available, but they only relate to seedlings, not to mature trees. There are also a limited number of data giving soil solution data in relation to sub-lethal effects for Cd from France. Furthermore, there is a Dutch literature review including data for Cd and Pb on phytotoxic effects on plants, mainly from laboratory studies. These data will be provided to the critical limits group.

d) (Q9) There are critical limits for Hg for humus layers, that can be harmonized to the organic matter content in these layers. Furthermore, for Cd and Pb there are effects data of both mineral layers and humus layers, derived in the seventies and eighties in Scandinavia (Bååth data), which should be tested for possible use.

e) (Q10) In general the relevant soil depth is depending on the receptor. Is has to be considered that soil - plant relationships are derived for top soils. According to the guidance document it is suggested to consider 25 - 30 cm for arable land and 10 - 20 cm for the grassland (major zone of metal uptake and of biotic activity) and 10 cm for forests (major zone of biotic activity).

f) (Q11) Surface waters: Work is already done by OECD for Pb, Cd, Hg (Report ”1992”). However, it is questionable to relate (total) concentrations in surface waters to effects on aquatic organisms without accounting for the environmental chemistry. An applicable approach could be to look for pH, alkalinity and DOC to improve the relationships. The Swedish classification (report “Environmental quality criteria for lakes and water courses”), which has lower values than OECD (perhaps due to low calcium in these waters, should be also considered. Work will be done in contact with M. Meili, K. Johansson.

Mercury

g) (Q12) Surface waters: The endpoint is human health with content in fish as indicator. Functions to relate levels in waters to levels in fish are available for Sweden. They should be tested in other countries.

Arable soils:	Crops are not so important for Hg intake by humans.
Forest soil:	Endpoint is microbial processes. Preliminary transfer functions for Hg in forest soil are available relating solution concentration to soil concentration and DOM. Further elaboration, including possible impacts of Fe/Al hydroxides and clay content, may be needed. The transfer functions will be further elaborated (Meili, Bringmark) and be used to derive critical limits for soil solution concentration of Hg.

Food chain models

h) (Q13) We agree to use of the food quality criteria for Cd, Pb, Hg in food crops and for Hg in fish (EU, WHO) as an alternative to using exposure limits (e.g., ADIs) and deriving critical soil limits based on a comprehensive model on human exposure pathways. Information will be included to show how exposure limits do relate to food quality criteria, including scientific background of EU data. In this context information will be given of the most recent exposure limits from TF Health.

Food quality criteria can be back-calculated to critical limits in soils from Cd content in crops, and to waters for Hg in fish. For Pb and Hg in food crops, back calculation to soil content is not possible (see also point i). The pathway of Cd via wheat is most important for human health and a special critical soil Cd limit for arable soils is relevant. The critical limit wheat - arable soil should be used including the formula to calculate soil - plant transfer.

Indirect effects on soil eating animals (including those, which take up soil by grazing as cows) are possible for Cd, Pb, Hg but give much higher results than critical limits for direct effects. Critical soil Cd limits are also low in view of impacts on worm-eating birds, but yet considered too uncertain to apply in the critical load calculation.

Information on uncertainties can be given but requires information on standard error of all parameters in soil plant relation and residual error. This will be included in the background document.

i) (Q14) Because there are no relationships between content of soil and contents in plants for Pb and Hg, direct uptake from atmosphere to plant has to be considered. It is assumed that uptake of Hg is completely due to direct uptake from atmosphere. We will contact colleagues at EMEP, using those models (Schuetze). For Pb, direct uptake is relevant for e.g lettuce and spinach. Data on relation Pb and Hg inputs (from monitoring atmosphere) and plant contents will be provided by B (de Temmerman).

j) (Q15) The critical limits (soil), related to human and animal health, provided in the background document results refer to aqua regia (so-called total metal contents). In NL, there are also data to relate (measured) reactive soil metal content and plant content.

k) (Q16) Drinking water limits are available, i.e. 3 $\mu g\ l^{-1}$ for Cd, 10 $\mu g\ l^{-1}$ for Pb and 1 $\mu g\ l^{-1}$ for Hg (WHO). These limits will be included as limits for ground water as it might be of importance (specifically for Pb) to reduce (cut) the critical concentrations which were derived by transfer calculations for acid soils.

Summarizing tables

l) (Q17, 18) A table can be prepared which synthesizes the tables on critical limits for different endpoints that can be found in the background papers to this workshop. However, the critical limits will be still improved within the next months after the meeting, and will then be sent to NFCs. An intermediate result is already available.

m) (Q19) Methods to establish the original (natural) concentrations of heavy metals in soils are independent from the setting of critical limits. It might be very difficult to derive those pedo-geogenic contents, in particular pedo-geogenic concentrations in soil solution.

21. **Working Group II.2, "transfer functions", chaired by Mr. Bert-Jan Groenenberg (Rapporteur: Laura Shotbold)**, arrived at the following conclusions:

a) (Q20), according to open questions in the background document Groenenberg et al. (2002), with related numbers, e. g. (1.), (2.), etc., see Annex V a, and (Q21)

   There are no Hg transfer functions at present in Europe, but potential data sets could be derived from German, Slovakian, Swedish data. Strong relationship between Hg and DOC in Swedish river data have been shown. The binding of Hg to organic and sulfidic ligands has been studied in the US. There is potential to use archived soil samples where they have been stored properly. Transfer functions for Hg analogous to those for other metals will be derived from the data from Sweden.

   (2.) For Cd and Pb there are at present 3 data sets used from which transfer functions are derived (Germany, Netherlands, UK). An overview will be included in a table. There are differences in the extractions used to derive these transfer functions (Germany NH_4NO_3, UK and Netherlands HNO_3). Differences in extraction techniques occur due to different ideas about what the reactive content represents. UK and Netherlands see it as total, potentially available content that can react with the solution, whereas Germany sees it as a more weakly bound fraction that is readily exchanged with the solution, and is better correlated to soil solution metal concentration.

   Recommendation is to continue with both methods (NH_4NO_3 / HNO_3) but for the manual to put forward a scheme, maybe highlighting strengths and weaknesses of each extraction, which can be used to decide which method to use. It is advised to combine as much as possible data bases in the future work on transfer functions.
   We have also to keep in mind that there is also difference in the extraction technique for soil solution. We should check possible extractions (reactive) for calcareous soils.

   (3.) DOC measurements have been sometimes found to be very high particularly in CaCl extractions but also from rhizon samplers (often 100 - 1000 mg l^{-1}). This is not a problem for the derivation of transfer functions expressed as free ion concentrations, but would be for total soil solution. However, this would affect calculation of metal leaching from soil profiles. Recommended is not to use these high values but to estimate from field data (lysimeters, or stream concentrations).

   (4.) Considering the type of transfer function to use, it is recommended to relate adsorption constants to soil properties which can be used to calculate soluble metal concentration from solid metal concentration or vice versa. However, for critical load calculations the amount in solution is usually derived from the soil concentration for which the CQ (aQ) approach is appropriate. Transfer functions that take into account solution speciation are preferred and this will be included as options in the above scheme concerning the different transfer functions.

   (5.) The Dutch transfer function data set demonstrated uncertainties of up to an order of magnitude. Further uncertainty is added from input parameters. These uncertainties will not be improved with further data input.

   (5. / 7.) One possible way of decreasing uncertainty would be to derive transfer functions for groups of soils, rather than forcing one transfer function through the whole data set. From the large data set the optimum number of groups will be derived statistically.

   (8.) For calcareous soils, there is not, at present, enough data to derive transfer functions. We need to know how many data are needed to derive the transfer functions, which can be determined from statistical analysis of existing data sets.

b) (Q22 and Q7) There is progress on determination of transfer functions for organic soils, though existing data is for upland grassland sites and this needs to be extended into forest soils. Some small data sets exist that could be combined to provide these data.

c) (Q23) It is possible to take account of future changes in soil properties in determining steady state critical loads (such as increasing pH). Whether the present value or a future expected value (at steady state) should be used must be considered.

d) A table with existing and missing transfer functions should be provided after the meeting to be inserted in the final background document.

22. **Working group II.3 on General Methodological Aspects, chaired by Mr. Régis Farret, (Rapporteur: Jean-Paul Hettelingh)** provided the following conclusions and recommendations:

a) (Q24) Policy may ultimately require knowledge of temporal scales involved for protection or damage. Currently, science is being improved to enable the assessment of critical loads on a European scale. Maps of critical loads can be used in a next stage as a basis for assessing exceedances, i.e. quantifying damage and recovery time delays using dynamic modelling.

b) (Q25 / Q27) The decision tree provides information, how to deal with the differentiation between pedo-geogenic and anthropogenic share of heavy metals contents in soils.

c) (Q26) Historical inputs affect future recovery and damage time delays. They complete the understanding of the origin of the problem in particular to the public, industry and policy analysts. They are also important as input to dynamic modelling.

d) (Q28) Soils do NOT distinguish heavy metals on the basis of their origin.

e) (Q29) As far as necessary in the future, more countries are willing to test the use of the critical reactive soil metal concentration limit, and critically review it (this approach might become obsolete in most cases according to recommendation g) of working group II.1 on critical limits)

f) (Q30) The critical loads methodology should take into account humus layers/humic soils. In principle this can be included in the methodology, but more knowledge is needed on transfer functions and critical limits.

g) (Q31) A critical load for human health is feasible. Separate critical limits are required for the following pathways (a) fish (i.e. Hg) , (b) agricultural crops (i.e. Cd), and (c) drinking water (i.e. Pb). The relevance of consideration of Pb concentrations in air will be checked by the critical limits group.

h) (Q32) Separate critical load calculations are made for each receptor. Integrated Assessment Modellers should be able to differentiate between human health and environmental endpoints for policy support.

i) (Q33) The endpoints to assess Hg impacts are human health, top predators in (water-) ecosystems, and decomposers in top forest soils. The Simple Mass Balance method can be applied. Also models with an increasing level of complexity (see e.g Sverdrup *et al.*, Nov. 26, 2002 and Meili et al., July 2002) can be explored.

j) (Q34) The current work plan focuses on the assessment of critical loads for use in IAM. Stand still loads can become part of a next stage involving dynamic modelling. See decision tree (Annex VI).

k) (Q35) Methods to quantify non-atmospheric inputs are required. Non-atmospheric inputs to ecosystems, leading to an exposure of biota including humans, include at least fertilizers and geological releases.

Reporting the outcome of the meeting

23. After adoption, the Minutes of the meeting will be circulated to the participants to enable slight editorial changes (in particular with respect to the description of presentations) with a close deadline.

24. The participants agreed to delay the edition of the Proceedings of this meeting until spring of 2003. This allows the background documents to be amended and completed following the recommendations for short term future work of this meeting.

25. The results of the expert meeting will be reported to the 19th Task Force on ICP Modelling and Mapping (May 2003) and, with possible amendments, to the 22nd Session of the WGE (August 2003).

Future work

26. The draft chapter of the Mapping Manual should only be produced after the revision of the background documents is finished. However, the draft should be available by March 2003 to be circulated before the 19th Task Force on ICP Modelling and Mapping, showing also clearly the gaps in knowledge and methodology, which have to be filled until the end of 2003

27. A (last) follow-up meeting of the hoc expert group could be planned in 2004.

28. Potentially applicable products for the work under the Convention, in the form of maps of critical loads for heavy metals should be available by 2004, national results achieved earlier should be circulated and made widely available including documentation of methods and data bases.

Concluding remarks

29. The meeting adopted the Minutes.

30. On behalf of the chairman of ICP Modelling and Mapping Gudrun Schuetze thanked participants for their valuable contributions (posters, presentations and contributions to the discussion), the chairmen and rapporteurs of the working groups for their comprehensive support and in particular the authors of the background papers for providing the scientific basis for the discussions during the meeting.

Expert meeting on Critical Limits for heavy metals and methods for their application, Berlin, 2 – 4 December 2002

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Annex II

Expert meeting on Critical Limits for heavy metals and methods for their application

2 – 4 December 2002, in Berlin

Agenda

2 December:	**Plenary**
12.00	Registration
13.00	Welcome *(Gudrun Schuetze)*
13.10	Opening *(Regis Farrét, vice chairman of WGE)*
13.20	Aims and structure of the workshop *(Till Spranger, chairman of ICP Modelling and Mapping)*
13.30	Preliminary modelling and mapping of critical loads for cadmium and lead in Europe *(Jean-Paul Hettelingh et al.)*
13.40	Introduction of a draft chapter on heavy metals for the new Mapping Manual (*Gudrun Schuetze*)
13.50	Introduction of a background paper on general methodological aspects, including methods to identify sources of heavy metals pollution in soils and surface waters (*Regis Farrét*)
14.10	General methodology applied for operational modelling of mercury *(Markus Meili)*
14.30	Introduction of a background paper on critical limits for heavy metals (Pb, Cd and Hg) including human health aspects (*Wim de Vries et al.*)
14.55	Coffee
15.25	Introduction of a background paper on transfer functions for heavy metals (Pb, Cd and Hg) (*Bert-Jan Groenenberg et al.*)
15.50	Discussion and identification of (further) points for debate within the working groups
16.20	Health based critical limits for cadmium *(Marek Jakubowski)*
16.30	Critical Limits used in legislation and problems of their use in calculations of critical loads

(Milan Sanka)

16.40 Zinc titration as a means of distinguishing uptake routes
(Willie Peijnenburg)

16.50 Combining ecotoxicological data and speciation modeling for critical limit calculation
(David Spurgeon)

17.00 Are humus layers different? Critical Limits for Pb, Cd, Hg
(Lage Bringmark)

17.10 Preliminary dynamic modelling of heavy metals in soils
(Ed Tipping)

17.20 Swedish approaches on mercury
(Harald Sverdrup)

17.30 Poster session

18.30 End of sessions

Proposals for working groups (WGs) for Tuesday, 3 Dec. 2002:

1. WG Critical limits Pb, Cd and Hg for soils and waters,
2. WG Transfer functions Pb, Cd and Hg for soils and sediments
3. WG General methodological aspects

Presentations on heavy metal partitioning to be held at the beginning of the discussions in WG 3. on 3 December:

- The influence of soil properties on distribution and mobility of airborne contaminants in high mountains
  (Jan Čurlík)

- Comparison of transfer functions for Cd and Pb partitioning between soil and solution based on field and laboratory data
  (Tatiana Pampoura)

- Chemical speciation in organic soils of the UK uplands
  (Edward Tipping)

- Applicability of transfer functions in humus to determine toxicity of heavy metals
  (Staffan Akerblom)

3 December: - Working group discussions

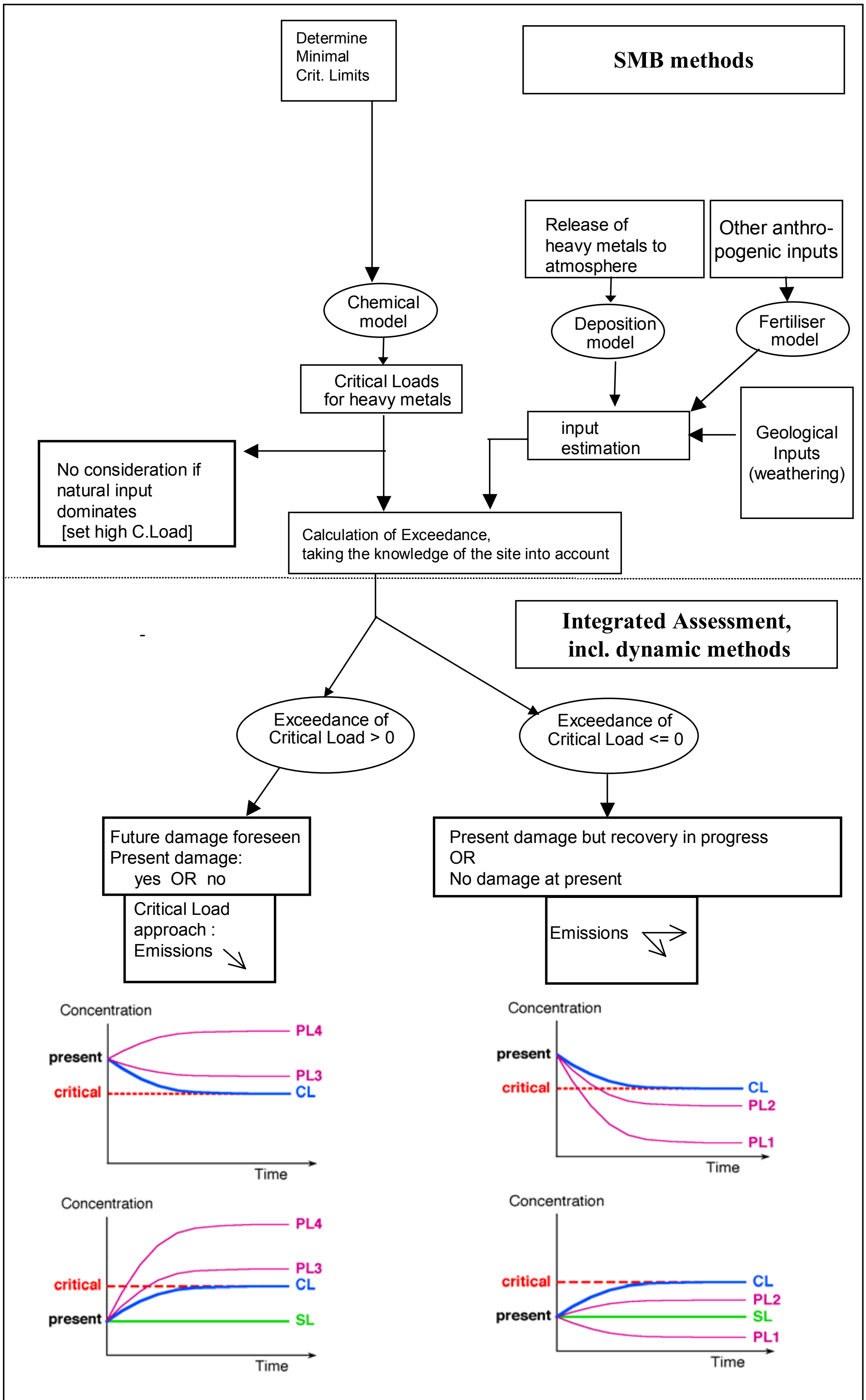
8.45	Setting up of working groups
9.00	WG discussions
10.30	Coffee
11.00	WG discussions
12.30	Lunch and walk around
14.30	Short plenary meeting to exchange results and open questions to other WGs
15.30	WG discussions
16.00	Coffee
16.30	WG discussions
18.00	End of sessions
19.00	Workshop dinner

4 December: Plenary

9.00	Ways ahead to the review of the heavy metals protocol *(Heinz-D. Gregor, chairman of WGE)*
9.15	Conclusions and recommendations from the working groups WG Critical limits /discussion WG Transfer functions /discussion WG General aspects / discussion
	In parallel revision of the draft minutes of the Meeting
10.30	Coffee
11.00	General discussion, recommendations for elaboration of the new draft Manual Chapter on heavy metals
12.00	Time plan of work in 2003
12.15	Agreement on the draft Minutes
12.16	
12.30	Finish of the Expert Meeting

Critical Loads for heavy metals – decision tree

(slightly revised by the editorial group after the Berlin meeting)



Legend for the graphs: PL: Present load; CL: Critical load; SL: Stand-still load;

Expert meeting on Critical Limits for heavy metals and methods for their application, 2 – 4 December 2002, in Berlin

List of poster presentations

Ashmore, Michael et al.	Further development of an effects-based approach for determining metal critical loads in the United Kingdom
De Marco, Alessandra et al.	Heavy metals critical loads for Italian soils
Evstafyeva, Helene	Human health aspects and physiological approaches in the critical loads work on heavy metals
Hernandez Laura, Probst Anne et al.	Heavy metals in some French forests. Distribution , origin and controlling factors
Probst, Anne, Moncoulon, David et al.	Mapping critical loads for Lead in France: First results for forest soils. Comparative investigations on transfer functions and weathering fluxes.
Rabago, Isaura	Behaviour of heavy metals in Spanish soils
Gudrun Schuetze, Hans-Dieter Nagel	German experiences with proposed critical limits for lead and cadmium and their application in first critical loads calculations
Shotbold, Laura	Mapping critical loads and their exceedence in the UK
Skořepová, Irena et al.	Effects of Cd and Pb in soils on microbial biomass - Assessing critical Loads
Zappa G., Letardi A., et al.	Analytical data survey carryied out by ENEA monitoring projects in different italian areas
Zappa G., Letardi A., et al.	Determination of Pb and Cd in soils and vegetables: reference materials availability and evaluation of uncertainty of results

Expert meeting on Critical Limits for heavy metals and methods for their application, 2 – 4 December 2002, in Berlin

Participation in Working group discussions

WG II.1 **Critical Limits**	**WG II.2** **Transfer Functions**	**WG II.3** **General Aspects**
Chairmen: **Wim de Vries**	**Bert-Jan Groenenberg**	**RÉGIS FARRET**
Rapporteurs: **Gudrun Schütze**	**Laura Shotbolt**	**Jean-Paul Hettelingh**
Lage Bringmark	Staffan Akerblom	Alan Irving
Philippe Cambier	Peter Blaser	Kjell Johansson
Helene Evstafyeva	Ján Čurlík	David Moncoulon
Beat Frey	Sigbert Huber	Milan Sanka
Marek Jakubowski	Agostino Letardi	Valerio Silli
Alessandra de Marco	Markus Meili	Till Spranger
Willie Peijnenburg	Tatiana Pampura	Harald Sverdrup
David Spurgeon	Anne Probst	Vincent Vanderheyden
Ludwig de Temmerman	Isaura Rabago	Matti Verta
	Katrin-Nanette Scholz	
	Laura Shotbold	
	Irena Skorepová	
	Edvard Tipping	
	Konstantin Terytze	

Annex VI

Expert meeting on Critical Limits for heavy metals and methods for their application, 2 – 4 December 2002, in Berlin

List of relevant questions to the Working groups

All groups

Q1 Do methods and data allow a scientifically sound assessment of environmental improvement options (e.g. Integrated Assessment Modelling)?

Q2 Are the decisions on methodological aspects relevant for the final results of IAM (if no, do not discuss them!)

Q3 Which open questions can be solved until spring of 2003 (to be ready for a decision of the Task Force on ICP Modelling and Mapping) or end of 2003 (to be ready for a possible next call for data on critical loads for heavy metals)

Q4 Time plan and further responsibility for the tasks to be solved

Q5 Which items are ready to be included into the draft chapter on heavy metals of the revised Mapping Manual

Critical Limits

Q6 Are there clear and aimed suggestions to improve critical limits related to ecotoxicological effects, which can be easily applied (see time frame above).

Q7 Is the choice of endpoints (species) within the ecosystem agreed ? (for both soil Clim and soil solution Clim)

Q8 Are there results of laboratory or open field ecotoxicological tests relating directly *soil solution* concentrations of Pb, Cd, Hg to effects?

Q9 Is there progress with critical limits for humus layers and organic soils? With different limits for different soil categories ?

Q10 Relevant Depth of Soil layers…

Q11 Critical limits for surface waters

Q12 For Hg, which method and for which endpoint can be best applied by all interested NFCs of ICP Modelling and Mapping (availability of data)?

Q13 Is a Clim/CLO for indirect exposition (food chain) feasible ? (both for animals and for humans). If yes, with which level of uncertainty ?

Q14 Derivation of a critical limit (soil) for health aspects of Pb and Hg seems to be impossible on the basis of calculation of soil-plant transfer (see background paper). Is it necessary and do we have other possibilities to consider human health effects of these two metals (cross tabulation like German approach, direct uptake atmosphere-plant, ...) ?

Q15 The critical limits (soil), related to human and animal health, provided in the background document refer to which kind of extraction method (aqua regia, 0.43 HNO3 or others?)

Q16 Is harmonisation with drinking water limits necessary and possible?

Q17 Can a Table be prepared which synthesizes the Tables on critical limits for different endpoints, that can be found in the background papers (De Vries et al., Sverdrup et al.…) to this workshop

Q18 How is a table of critical limits best tailored to NFCs requirements`?

Q19 (Can a Table be prepared which synthesizes methods to establish the original present concentrations? How is this Table best tailored to NFC requirements?

Transfer functions

Q20 Please add the List of questions in the background paper

Q21 Do other countries confirm the German experience that the transfer functions might overestimate concentrations of Cd and Pb in soils with low binding capacity? If yes, can the transfer functions be improved anyhow in the time available (see above)?

Q22 Is there progress with transfer functions for humus layers and organic soils?

Q23 Should, and can the CLO modelling take into account the possible changes in soil properties ? (e.g. acidification !)

General aspects

Q24 Are the methods and results easy enough to communicate to be accepted by policy makers and the public?

Q25 How do we deal with the differentiation between pedo-geogenic and anthropogenic share of the HM contents in soil (surely the use of critical loads will be more restrictive than use of stand-still approach in the case of contents/concentrations higher than critical limit).

Q26 Among anthropogenic historical inputs, is it necessary (feasible?) to distinguish atmospheric and non-atmospheric inputs?

Q27 Which kind of content/concentration should be used for the comparison of present and critical contents/concentrations – reactive or soil solution? For both in most countries data are not available and can therefore only be calculated by using transfer functions. These functions bear some uncertainties.

Q28 Are anthropogenic HM inputs to soils more bio-available than geogenic contents?

Q29 Are other countries than D and NL willing to use the critical limit „reactive“ for critical load calculations?)

Q30 Should, and can, the CLO modelling take into account the humus layer/humic soils ?

Q31 Is CLO for human health feasible ? If yes, under which assumptions/simplifications ? (e.g. select only one pathway of contamination ?)

Q32 In case the answer to the previous question is yes: Should all CLO concerning human health (including Hg in fish) be carried out independently from CLO concerning ecosystems, for future Integrated Assessment Modelling ?

Q33 For Hg, which method and for which endpoint can be best applied by all interested NFCs of ICP Modelling and Mapping (availability of data)?

Q34 How can possibly necessary decisions between models (critical load and stand-still load, see „decision tree“ of Sorrento, see Background paper) be adapted to the requirements of Integrated Assessment Modelling ?

Q35 Methods to quantify non-atmospheric inputs of Cd, Pb, Hg to soils (mainly fertilizers on agricultural land

4. BACKGROUND DOKUMENTS

4.1 CRITICAL LIMITS FOR CADMIUM, LEAD AND MERCURY RELATED TO ECOTOXICOLOGICAL EFFECTS ON SOIL ORGANISMS, AQUATIC ORGANISMS, PLANTS, ANIMALS AND HUMANS

Wim de Vries[1], Gudrun Schütze [2], Steve Lofts[3], Markus Meili[4], Paul Römkens[1], Regis Farret[5], Ludwig de Temmerman[6] and Marek Jakubowski[7]

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5 Direction de Risques Chroniques – Unitè Meco, Ineris BP No 2, F-60550 Verneuil en Halatte, France.
6 Centrum voor onderzoek in diergeneeskunde en agrochemie C.O.D.A. Leuvensesteenweg 17, 3080 Tervuren, Belgium.
7 Institute of Occupational Medicine, 8 sw. Terezy str., PL-90-950 Lodz, Poland.

With contributions by:
Bert Jan Groenenberg and Ed Tipping : transfer functions
Lage Bringmark and Kjell Johannson: critical limits
Harald Sverdrup: relation acceptable intake for humans and food quality criteria
Konstantin Terytze[2], Katrin Scholz[2]: discussion aspects.

BACKGROUND DOCUMENT
FOR THE

EXPERT MEETING ON CRITICAL LIMITS FOR HEAVY METALS AND METHODS FOR THEIR APPLICATION

BERLIN, 2-4 DECEMBER 2002

held under the
UN-ECE Convention on Long range Transboundary Air Pollution

4.1.1 INTRODUCTION

Available methodologies to derive critical loads and critical limits

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

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

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

Approach of the expert group on critical limits

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

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

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

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

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

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

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

Agreements and assumptions related to critical limits methodologies

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

- The methods for derivation of critical limits (Cd, Pb, and Hg) should be in line with the EU/OECD methodologies.
- HC_5 values (protecting 95 % of the population, with a confidence level of 50 %) derived from statistical analysis of effects data (plants, microbiological processes, invertebrates) are recommended to be the scientific basis of critical limits for both soil and soil solution.
- The major route of exposure on plants and micro-organisms is pore water (apart from rock-eating fungi and mycorrhizae), while for hard bodied invertebrates the adsorbed ("reactive") content is most important, due to exposure through ingestion. Following this assumption, critical limits for heavy metals in soil solution and for the reactive heavy metal content can preliminary be considered without further distinction to soil type and soil properties.
- The effect data from laboratory investigations can best be related to reactive metal content. The comparability of extraction methods, used in different countries to describe the reactive pool, should however be provided.

A critical evaluation of those assumptions is given in Section 4.1.6.

Aim and contents of this background document

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

First the receptors and related critical limits that are considered relevant are described (Section 4.1.2). Section 4.1.3 focuses on critical limits related to direct ecotoxicological effects on soil organisms and plants. This includes: (i) an overview of main methodological aspects, (ii) a summary of critical limits for Cd and Pb suggested in the first call for data and (iii) a preliminary overview of possible critical limits for Hg. The effects of bioaccumulation have been considered in deriving critical limits for soil, by the use of food chain models. Methods and results thus obtained in view of human health effects are described in Section 4.1.4, while distinguishing between (i) impacts on food quality of crops and (ii) impacts on food quality of animal products, concentrated on grazing cows and sheep. Section 4.1.5 focuses on critical limits related to impacts on animal health, while distinguishing between (i) simple food chain models on birds and mammals feeding on worms and/or plants and (ii) elaborated food chain models including birds and mammals of prey. The document ends with a critical evaluation of the assumptions related to the derivation and use of the critical limits and recommendations (Section 4.1.6).

4.1.2 RELEVANT RECEPTORS AND RELATED CRITICAL LIMITS

4.1.2.1 Relevant receptors

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

The receptors that are considered in this background document in terrestrial ecosystems, distinguishing arable land, grassland and non-agricultural land, and in aquatic ecosystems are presented in Table 1. Possible effects on soil life and plants (phytotoxicity) and terrestrial fauna are of concern in all types of ecosystems. Food quality criteria are, however, of relevance for arable land and grassland (limits for animal food), whereas possible secondary poisoning effects on cattle are relevant in grassland and non-agricultural land. A final critical limit can be based on the most sensitive receptor.

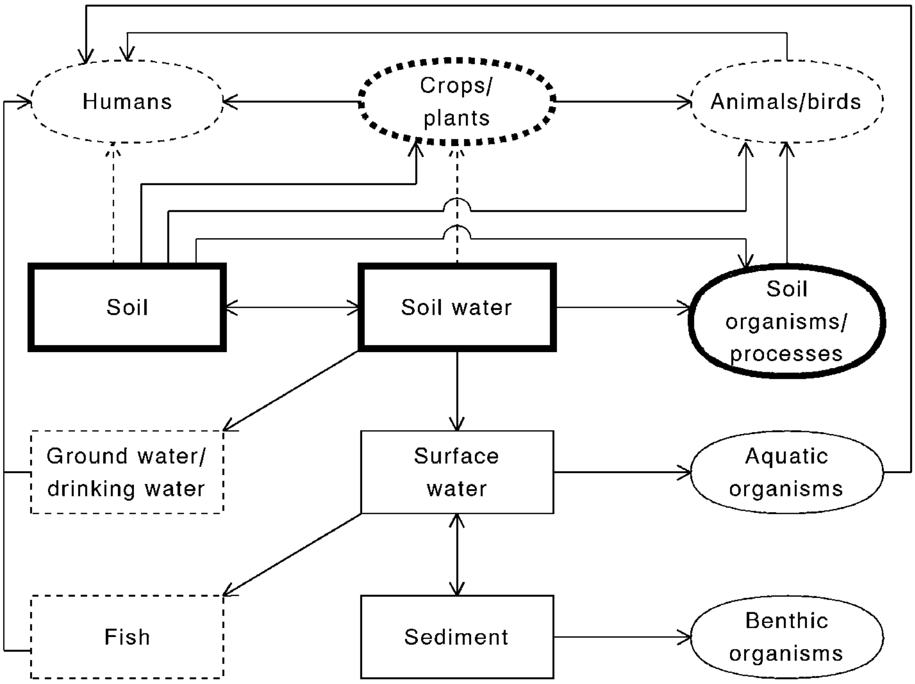


Figure 1 Overview of the relationships and fluxes of metals from the soil to other compartments. Compartments in black are related to direct impacts on the terrestrial ecosystem, normal compartments relate to direct impacts on the aquatic ecosystem and dotted compartments refer to indirect impacts on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

Critical limits for soil are limited to direct ecotoxicological effects on soil organisms and plants and indirect effects on food crops, terrestrial fauna and humans (see Section 4.1.2.2). The effect on humans is assumed to be accounted for by food quality criteria for metals in food crops, animal products (cows/sheep), fish and drinking water (ground water) consumed by them (see Section 4.1.2.3).

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

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

[1] This refers specifically to ground water used as drinking water

4.1.2.2 Ecotoxicological and human toxicological effects

Ecotoxicological effects

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

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

Health effects

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

Cadmium: The kidney, and to a lesser extent the lungs, are the critical organs in a long-term occupational or environmental exposure to cadmium. Cd affects the functioning of kidneys and bones and may cause cancer (Jakubowski, 2003). Järup (1998) mentions reports of a higher prevalence of kidney stones among cadmium-exposed workers. Painful bone disorders, including spontaneous bone fracture, have been observed in humans chronically exposed to cadmium in food (IPCS, 1992). In its latest evaluation of the carcinogenic risk from cadmium exposure (IARC, 1993), concluded that there was sufficient evidence to classify cadmium and cadmium compounds as human carcinogens. This assessment was, to a great extent, dependent on the significant relations between the risk of lung cancer and estimated cumulative exposure to cadmium reported by Thun et al. (1985) and Stayner et al. (1992) in their analyses of mortality among a cohort of workers from a single cadmium recovery plant in the United States. The existing evidence is inadequate to evaluate an association between inhalation exposure to cadmium and reproductive effects (Jakubowski, 2003). The half-life time of cadmium in human tissue is long due to the near incapability of the body to excrete the metal. In the liver it is 7 years, in the kidney it is approximately 15 years, in muscle tissue and the brain probably more than 30 years. In bone it could probably be more than 100 years (Kjellström and Nordberg., 1978)

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

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

4.1.2.3 Related critical limits

Type of limits

For most of the receptors or compartments indicated in Table 1, critical limits have been defined related to ecotoxicological or human-toxicological risks, such as:

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

- Humans: acceptable daily intake or ADI ($\mu g.kg^{-1}.d^{-1}$). This dose is the quantity of a compound to which man can be orally exposed, on the basis of body weight, without experiencing adverse effects on health.

The aim of this background document is to present or derive critical limits for soil, soil solution, ground water or surface water, to be used in critical load models, distinguishing between:
- Soil and soil solution related to direct effects on soil organisms and plants
- Soil and ground water drinking water) related to indirect effects on terrestrial fauna and/or humans.
- Surface water related to direct effects on aquatic organisms and indirect effects on human health.

Critical limits related to human-toxicological effects

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

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

4.1.3 CRITICAL LIMITS RELATED TO DIRECT ECOTOXICOLOGICAL EFFECTS ON TERRESTRIAL AND AQUATIC ORGANISMS

There are two possible types of critical limits for soil and for surface water:
- A critical reactive metal concentration in the solid phase (soil or sediment)
- A critical dissolved metal concentration (soil solution or surface water)

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

In this chapter we first describe the methodological approaches to derive critical soil and surface water limits from laboratory data and the possibility to derive critical soil solution limits including the limitations of the approaches (Section 4.1.3.1). We then present critical limits for reactive metal concentrations in soil and dissolved metal concentrations in soil solution and surface water (Section 4.1.3.2). Finally, a proposal is made for the critical limits for Cd, Pb and Hg to be used in soils, soil solution and surface water, based on those results (Section 4.1.3.3).

4.1.3.1 Methodological approach

Below we describe the:

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

The methodology to derive critical limits for soil and surface water

Relevant toxicity data

An international framework, in which much work has been done on the subject of critical limits, is the Organisation for Economic Co-operation and Development (OECD). Within this framework a methodology has been developed for the calculation of Maximum Permissible Concentrations (MPC's) or critical limits of substances in the soil (OECD, 1989) and the aquatic environment (OECD, 1992). In this context, a distinction is made in acute toxicity data based on short-term ecotoxicological experiments (< 1 day) and chronic toxicity data, based on long-term ecotoxicological experiments (1 day - 1 month). Acute toxicity is defined by the EC_{50} or LC_{50} value which is equal to the concentration at which 50% of the considered organism is either affected (EC_{50} with EC = effect concentration) or even dead (LC_{50} with LC = lethal concentration). Chronic toxicity is defined by No Observed Effect Concentrations (NOEC's), sometimes referred to as No Observed Effect Levels (NOEL's), of several species in an ecosystem. From a range of NOEC data an HC_p can be derived, being the hazardous concentration at which p% of the species in an ecosystem is potentially affected, or 100-p % is protected.

Organisms considered in the effect assessments

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

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

The protection of the soil community requires protection of all these organisms playing a leading role in the structure and the functioning of the ecosystem. Consequently, the organisms or taxonomic groups that are considered in deriving $L(E)C_{50}$ or NOEC data for terrestrial ecosystems are micro-organisms or microbe-mediated soil processes (e. g. enzymatic activity), invertebrates (earthworms and arthropods) and plants.

The organisms or taxonomic groups that are considered in deriving $L(E)C_{50}$ or NOEC data for surface water include algae, crustacea and fish.

Calculation of critical limits using statistical extrapolation techniques

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

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

A concentration of a certain compound is considered hazardous when the probability of selecting a species with a NOEC below this concentration equals 5 %. This implies that theoretically 95 % of the species within an ecosystem are protected. Using this method, the 95% protection level calculated with 50% confidence is regarded as the MPC (MPC =HC_5). Pragmatically, it has thus been decided that the 5% of the SSD using a 50% confidence (this means that there is 50% chance that the true value is below this estimated value and 50% chance that it is above it) equals the MPC or critical limit. The confidence interval of this value should also be estimated

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

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

where:

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

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

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

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

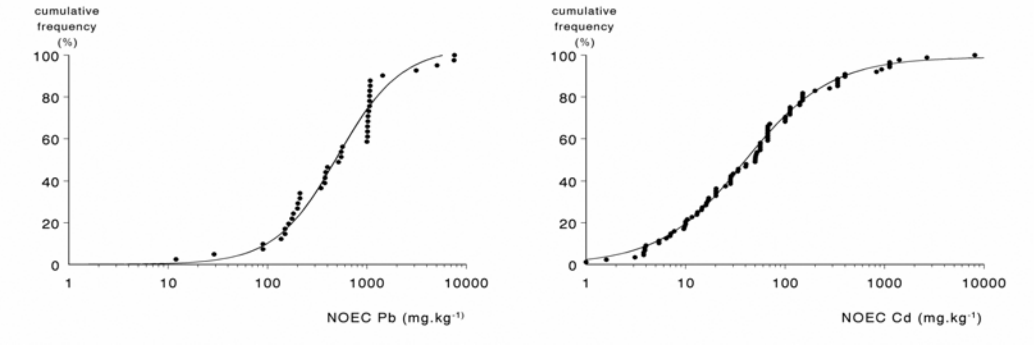


Figure 2 Fitted log-logistic distribution functions through NOEC data for Cd and Pb in soil.

The methodology used to derive critical soil solution limits

General approach

Apart from using NOEC data for Cd and Pb in soil solution, critical soil solution limits can also be based on literature information on NOEC soil data of organisms that are affected through the soil solution (plants and micro-organisms). This can be done by the application of transfer functions, relating dissolved and solid phase metal concentrations while accounting for the impact of soil properties, on the NOEC solid phase data. This requires the availability of data on those soil properties (at least pH and organic matter content and preferably also clay content) in laboratory experiments. Data sets including both NOEC soil data and soil properties thus allow calculation of NOEC soil solution data that can again be evaluated by a statistical approach deriving limits based on a 95% protection level, as described in Section 4.1.3.1.

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

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

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

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

and in the case of activities as:

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

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

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

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

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

Table 3 values for the regression coefficients for the activity– reactive metal content relationship (Eq.3) and statistical measures R^2 and se(Y) based on results of studies carried out in the Netherlands and the UK (after Groenenberg et al., 2003).

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

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

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

K_f can thus be calculated according to:

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

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

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

Uncertainties in the calculation of critical soil and soil solution limits

The function of risk assessment is the overall protection of the environment. Certain assumptions are made to allow extrapolation from single-species toxicity data to ecosystem effects, such as: (i) ecosystem sensitivity depends on the most sensitive species, and (ii) protecting ecosystem structure protects community function. It is thus assumed that protection of the most sensitive species protects ecosystem structure and function.

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

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

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

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

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

Due to these uncertainties, arbitrary safety (or assessment) factors have been suggested to extrapolate from single-species laboratory data to a multi-species ecosystem. The size of the safety factor depends on the confidence with which a critical limit can be derived from the available data. This confidence increases if data are available on the toxicity to organisms at a number of trophic levels, taxonomic groups and with lifestyles representing various feeding strategies. Thus lower safety factors can be used with larger and more relevant long-term data sets. In this study no use has been made of safety factors when sufficient NOEC data were available form major taxonomic groups to avoid the derivation of unrealistically low critical limits. Furthermore, comparison of field and laboratory data do not show a consistently lower result for the field data (..).

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

Critical limits on the basis of NOEC soil data

It is assumed that effects data from ecotoxicological tests are related to the reactive fraction, because in those tests the metals are added in a well available form. Besides, the reactive fraction is better related to the concentration in soil solution than total contents (Römkens et al., 2003). As reactive fraction, the adsorbed fraction of metals can be regarded. This share of the total content may be determined by extraction using weak acids like e.g. 0.43N HNO_3 or complexing agents like EDTA, DTPA.

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

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

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

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

Metal	N[1]	μ	B	R^2_{adj}	Critical limit HC_5 (mg.kg^{-1})	Data source
Cd	13	1.10	0.41	93	0.78	Crommentuijn et al. (1997)
	30	1.82	-0.35	93	6.0	Schütze and Throl (2000)
	12	1.64	-0.41	90	2.7	(Farret and Magaud, pers. comm.)
	67	1.57	-0.46	91	**0.9**	All
Pb	13	2.71	0.30	93	66	Crommentuijn et al., (1997)
	10	2.94	-0.48	87	34	Schütze and Throl (2000)
	12	2.48	-0.37	93	33	(Farret and Magaud, pers. comm.)
	52	2.64	-0.41	90	**30**	All
Hg	5	0.109	-0.8223	92	**0.03**	Schütze and Throl (2000)

[1] N is the number of experiments

Normalisation of critical limits to organic matter content

Most forest soils, at least in Northern and Central Europe, are covered by an organic Organic layer (mor) in which many deposited pollutants are efficiently retained. Since plant root systems and fungi are located in this layer, there is an immediate risk of biological disturbance. Reduced decomposition of organic matter may have direct consequences for the mineralisation of nutrients in forest soils and ultimately for forest growth.

The critical limits derived in Table 4 above are all related to mineral soil. There is, however, a difference between the sensitivity of organism, in the Organic layer and the mineral soil. To illustrate this difference, the NOEC data for micro-organisms exposed to metals in both Organic layer and mineral soil compiled by Bååth (1989) were evaluated with a log-logistic fit to calculate the critical limits. Results refer to effects on enzyme synthesis and activity, litter decomposition and soil respiration. Results for Cd and Pb are presented in Table 5. For the sake of comparison, results for Cu and Zn were also added.

Table 5. Fitted parameter values and resulting critical limits for reactive metal contents in organic layers and mineral soil, based on a compilation of NOEC data for micro-organisms by Bååth (1989)

Metal	Layer	N[1]	M	B	R^2_{adj}	Critical limit (mg.kg^{-1})		
						5%	20%	50%
Cd	Organic layer	17	2.070	-0.8715	92	**0.3**	7.3	118
	Mineral soil	53	1.510	-0.6152	97	**0.5**	4.5	32
Pb	Organic layer	16	2.989	-0.2914	76	**135**	385	976
	Mineral soil	56	2.839	-0.4511	96	**32**	164	690
Cu	Organic layer	42	2.678	-0.4032	98	31	132	477
	Mineral soil	62	2.296	-0.5205	98	5.8	38	198
Zn	Organic layer	30	2.994	-0.4387	97	50	243	986
	Mineral soil	49	2.652	-0.4706	94	19	100	449

The results show that the HC5 values for mineral soil for Pb are comparable to those given in Table 4 (30 and 32), but the results for the organic layer are 4 times as high mineral soil in case of the HC_5. This is comparable to results from Sweden, reporting a critical value of 34 mg.kg^{-1} in the mineral soil and a range of 50-144 mg.kg^{-1} for the organic layer (Bringmark, pers. comm.). The HC_{20} and HC_{50} is approximately 2 and 1.5 times as high. The results for Cd are quite opposite. Here the HC_5 is comparable for the organic layer and mineral soil but the HC_{20} and HC_{50} are is approximately 1.5 and

4 times as high. For Cu and Zn, the results for the organic layer are consistently a factor 2-4 higher than for the mineral soil. The different results for the ratio of critical limits in organic layer and mineral soil for the various metals imply that it is not simply possible to normalise the results of the mineral soil to the organic matter content. Instead, it seems reasonable to use comparable values for Cd in both organic layer and mineral soil, while for Pb, one can best use a four times higher value for the organic layer than for the mineral soil.

Unlike the other metals, mercury concentrations in soils and sediments, river and lake waters, and in biota are recommended to be normalised to organic matter, being the dominating carrier of this metal (Meili, 1991, 1997; Meili et al., 2003). This applies in particular to the biologically active layers of forest soils, which are considered as critical receptor systems to Hg pollution (Meili et al., 2003), which are typically rich in organic matter. In soils with appreciable organic matter content (tentatively >10% dw), organic matter dominates the Hg cycling (transport, dilution, and toxicity). Even conceptually the Hg content of total organic matter is quite directly related (although not equal) to the Hg content in living organic matter (Meili, 1997), and thus to the toxicity of soil Hg. If the organic content is very low, other matrices are likely to control the cycling of Hg, and in particular the soil content of iron and aluminium (oxyhydroxides, reactive) and clay should be taken into account to set the critical limit.

Recent field studies show some observational and experimental indications of a reduced respiration in forest soils at Hg concentrations close to those encountered in rural areas of south Sweden (Bringmark and Bringmark, 2001a, b). These findings suggest a lowering of effect levels for Hg (as well as Pb) in soils considerably below known values. A tentative critical limit is that the Hg concentration in the Organic layer (O-horizon) of podzolic forest soils should not exceed the present mean level in the most contaminated regions of south Sweden, where further increase should be avoided. This level is about 0.4 mg.(kg dw)$^{-1}$, which after normalisation with respect to organi c matter content corresponds to a more robust value of 0.5 mg.(kg org)$^{-1}$ in these highly organic soils (see also Meili et al., 2003 and references therein).

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

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

Critical limits for cadmium and lead concentrations in soil solution

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

The recommended critical limits for Cd and Pb in soil solution are based on literature information on NOEC soil data that are: (i) limited to organisms from which you can be sure that the effect is only through the soil solution (certainly plants and micro-organisms), (ii) accompanied by data on soil properties (pH, clay and organic matter content) to allow calculation of NOEC soil solution data using harmonised transfer functions and (iii) evaluated by a statistical approach deriving limits based on a 95% protection level, as described in Section 4.1.3.1.

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

- Combining available data by Schütze and Throl (2000), Farret and Magaud, pers.comm.) and Klepper and Van de Meent (1997), who mainly included data from Crommentuijn et al. (1997).
- Separating them in NOECs for soil for plants and micro-organisms.
- Applying harmonised general transfer functions for Cd and Pb (Römkens et al., 2003) to calculate related NOECs for soil solution.
- Applying a log-logistic fit to derive the HC_5, being the critical limit.

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

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

Metal	Receptor	N[1]	μ	B	R^2_{adj}	Critical limit HC_5 (ug.l^{-1})
Cd	Micro-organisms	83	2.802	-0.9893	95	0.78
	Plants	86	1.869	-0.8143	86	0.30
	All	169				0.6 (0.3-0.8)
Pb	Micro-organisms	31	1.369	-0.8270	91	1.7[2] (0.09)
	Plants	10	2.739	-0.5280	90	15[2] (1.5)
	All	41				8 (2-15)

[1] N is the number of experiments

[2] Values presented for Pb are HC_{20} values. HC_5 values (given in brackets) are likely to be too low, especially for micro-organisms and plants since the transfer function for lead is unreliable at low concentrations.

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

Current work on soil critical limits for heavy metals (Cu, Zn, Cd, Pb) in the UK has focused on deriving limits expressed as the free metal ion concentration, following the recommendations of the Bratislava workshop (Curlík et al., 2000). The principle of expressing the critical limit as the free ion concentration is that this form of metal is believed to be available for interactions with organisms (Lanno et al., 1999). However, it has been shown that the acute toxicity of metals to freshwater organisms is not a function of the free ion concentration alone, but also of the concentrations of other cations present (e.g. H+, Ca^{2+}, Mg^{2+}) (Meyer et al., 1999). This approach has been used in formulating the Biotic Ligand Model (BLM), which postulates uptake of metal at a receptor site on an organism, in competition with other cations. The BLM has been used to explain variability in acute toxic endpoints for several freshwater species, as a function of water chemistry (Santore et al., 2001; De Schamphelaere and Janssen, 2002).

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

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

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

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

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

In this report we do not yet present final results obtained for free metal ion concentrations as a function of pH. In Section 4.1.6, we discuss, however, the possibility to derive such pH dependent critical limits for the free metal ion concentrations, including some illustrating material for Cd and Pb.

Critical limits for mercury concentrations in soil solution

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

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

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

Critical total mercury concentrations in soil solution can be calculated by assuming a similar critical Hg/org ratio in the solid phase and in the liquid phase, at least in oxic environments where binding to sulphides is negligible. The following reasoning supports this:

- As with soil, the Hg concentration in solution can (should) be expressed on an organic matter basis, since virtually all dissolved Hg is bound to dissolved organic carbon (DOC) in a concentration range between 10-60 $mg.l^{-1}$ (e.g. Meili, 1997). The distribution coefficient suggests that 95-99% of all Hg in soil solutions is bound by organic substances if considering dissolved species alone, and far more if considering the whole soil (99.999%).
- If the binding properties of particulate and dissolved organic matter are similar, we would expect a similar Hg/org ratio in soils and stream waters, which is indeed supported by field data (Meili, 1991, 1997).
- Organic carbon concentrations in boreal stream runoff typically peaks at DOC = 15-20 $mg.l^{-1}$. This is well within the range found in soil solutions, which supports the assumption that there are no fundamental differences between the two waters.

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

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

The concentration of "bioreactive" Hg (analog to "free ion" concentration) can be calculated by dividing the critical cocentration of "organically sorbed" Hg by the distribution coefficient for Hg on (dissolved) organic matter. Field and laboratory studies using biota to determine the bioreactive ("free") species, and involving different types of soil and lake organic matter, suggest that the value for this distribution coefficient is around 10^6 (one million) $l.kg^{-1}$. This value seems to be fairly independent of the soil or water from which the organic matter originates (Meili, 1997). Note that this distribution coefficient is operationally defined for ecotoxicological purposes by using biota to determine the "free" Hg, and that chemical Hg binding considered here may involve any constituent associated with natural organic matter.

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

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

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

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

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

[1] N is the number of experiments

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

The data refer to various taxonomic groups (including algae, crustacea, macrophyta and oligochaeta). In an EC Technical Guidance document on risk assessment 2002 in prep; (Farret and Magaud, pers. comm.), an HC$_5$ of 0.31 ug.l^{-1} was derived. Consequently, a value of 0.3 ug.l^{-1} is suggested for Cd, 11 ug.l^{-1} for Pb and 0.23 ug.l^{-1} for Hg. Comparison with the limits for soil solution, shows that the critical limit for Cd in surface water is lower, whereas the critical limit for Pb is higher.

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

4.1.4 CRITICAL LIMITS FOR SOIL RELATED TO IMPACTS ON HUMAN HEALTH

4.1.4.1 Methodological approach

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

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

Health risks and dominant exposure pathways

The major routes for human exposure are consumption of food, drinking of water and inhalation of air and to a lesser extent soil (children). An overview of “Health risks of heavy metals from long range transboundary air pollution” was presented to the Executive body at the nineteenth session of the working group of effects in august 2000 (EB.AIR/WG.1/2000/12). In this document it was concluded that food is the dominant route of exposure of Cd and Pb of non-smokers (tobacco smoking can at least double the Cd intake), while the intake of fish is an important route of Hg intake. The most sensitive (and therefore important) target organism to protect is the kidney in case of Cd and inorganic Hg. The target site for Pb toxicity is cognitive impairment associated with Pb levels in blood above 100 $\mu g.l^{-1}$.

In principle, critical limits for soil related to human-toxicological can be derived from critical limits for humans (ADI values) with an integrated model in which all relevant exposure pathways, but in this background document human-toxicological effects are considered to be adequately covered by food quality criteria (see also section 4.1.2). Considering the important role of food intake, this document follows the recommendations of the document on "Health risks of heavy metals from long range transboundary air pollution" (EB.AIR/WG.1/2000/12) by focusing on the relationships between metal (Cd, Pb and Hg) contents in food crops and soil.

Derivation of food quality criteria from acceptable daily intakes

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

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

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

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

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

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

To perform the calculations for Cd and Hg, it is assumed that the diffuse background exposure due to other exposure pathways is approximately equal to the exposure caused by eating grain (bread) or fish. For Cd, another important pathway is drinking water. For Hg another significant source has historically been dental fillings, but this problem is rapidly decreasing with the increased use of polymer and silicate based materials in dentistry. In performing the calculations to derive a critical Cd content in grain, the daily intake of grain is taken at 400 g and the body uptake efficiency, defined as the ratio between the total amount taken up by the body to the total administered dose, is assumed to equal 15%. Actually, the uncertainty in this range is large and can vary from 5-20% (Friberg et al., 1979). To derive a critical Hg content in fish, a weekly intake of 200 g of fish is assumed.

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

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

The major routes for human exposure are consumption of food, drinking of water and inhalation of air. In Table 9, an overview is given of relevant critical limits for Cd, Pb and Hg in this context, focusing on wheat in the case of food. Food is the main source of cadmium exposure in the general population (about 94 -99 % of the total intake in non-smokers). In this context, wheat is an important food product and furthermore, wheat is one of the most strongly accumulating crops, thus leading to the most sensitive critcal limit for soil (see Section 4.1.4.2).

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

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

[1] All critical limits for food and fish are in mg.kg^{-1} fresh weight

[2] Examples are endive, spinach, lettuce etc.

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

The critical limit adopted for fish is based on recommendations by the WHO/FAO and is the same as in many other countries (Lindqvist et al., 1991); it should be noted, however, that the US Environmental Protection Agency now recommends a lower fish Hg limit of 0.3 mg.(kg fw)$^{-1}$ referring to methyl-Hg alone, which constitutes virtually all Hg in fish-eating freshwater fish (US-EPA, 2001). The Swedish Food and Health Administration is at present evaluating the relevance of a new limit at 0.3 mg.kg^{-1}. Japan has already adopted a 0.3 mg.kg^{-1} guideline (Dickman and Leung, 1998). These limits are largely based on the potential exposure of fish consumers, but recent studies suggest behavioural effects of low-level methyl-Hg exposure also in fish (Matta et al., 2001; Hammerschmidt et al., 2002). Critical Limits for Hg have also been discussed at the Workshop on Heavy Metals in Surface Waters in Lillehammer, Norway (Skjelkvåle and Ulstein, 2002). At this workshop the above mentioned Hg limits were adopted (0.3 - 0.5 mg.kg^{-1} according to EPA or WHO, respectively). Models for estimating critical loads of Hg for aquatic ecosystems should thus address the basic question: What is the maximum load that will keep the mercury level in fish below 0.3 or 0.5 mg Hg.kg^{-1}.

General approach to critical soil limits from food quality criteria

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

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

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

In the following sections, target values in crops have been back calculated to the soil using soil-plant relations, while accounting for the possible impacts of organic matter and clay content and of soil pH on these relationships (Section 4.1.4.2). Furthermore, target values for metals in animal products are used and back calculated to the soil using soil-plant and plant-animal relations, including the effects of soil properties on these relationships (Section 4.1.4.3).

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

Approach

Figure 3 shows how critical limits for the soil have been derived from critical limits in crops, distinguishing between food quality criteria in view of human health, fodder quality criteria in view of animal health and phytotoxic level in view of toxic effects on the crop itself. The latter aspect is not related to human health but was included to be sure that the food quality criteria do not lead to situations where food crops are adversely affected. Since the kind of crop influences the soil limit, it is necessary to derive relationships for the most sensitive crops to assess critical soil limits. In this document a distinction has been made between the food crops wheat, potato, lettuce and endive (use of food quality criteria), the fodder crops grass, maize and sugarbeet (fodder criteria). Furthermore, critical limits for all those crops were derived from the literature in view of phytotoxic effects on the crop itself. The mathematical approach to calculate critical soil limits, the used critical metal contents in plants and the results obtained are described separately below. More information on the approach is given in De Vries et al. (2003).

Calculation of critical limits in soil from critical limits in crops

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

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

where:

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

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

$\mathrm{BCF}_{\mathrm{sp}}$ = bioconcentration factor from soil to plant, being the ratio of metal concentration in plant to metal concentration in soil (-)

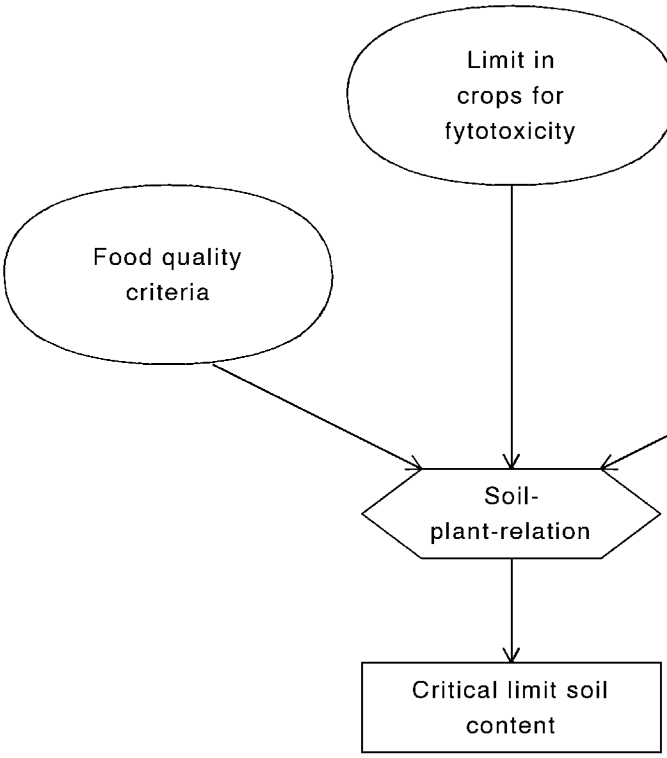


Figure 3 Procedure that has been applied to derive critical limits for heavy metals in the soil from quality criteria in food crops in view of effects on humans (arable land) and in fodder in view of effects on animals (grassland) and from critical limits in crops in view of phytotoxic effects (grassland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

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

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

$$[\mathrm{Me}]_p = K_{sp} \cdot [\mathrm{Me}]_s^{\,n} \qquad (9)$$

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

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

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

where:
SOM = soil organic matter content (%)
Clay = clay content (%)

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

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

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

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

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

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

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

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

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

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

Soil-plant relationships

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

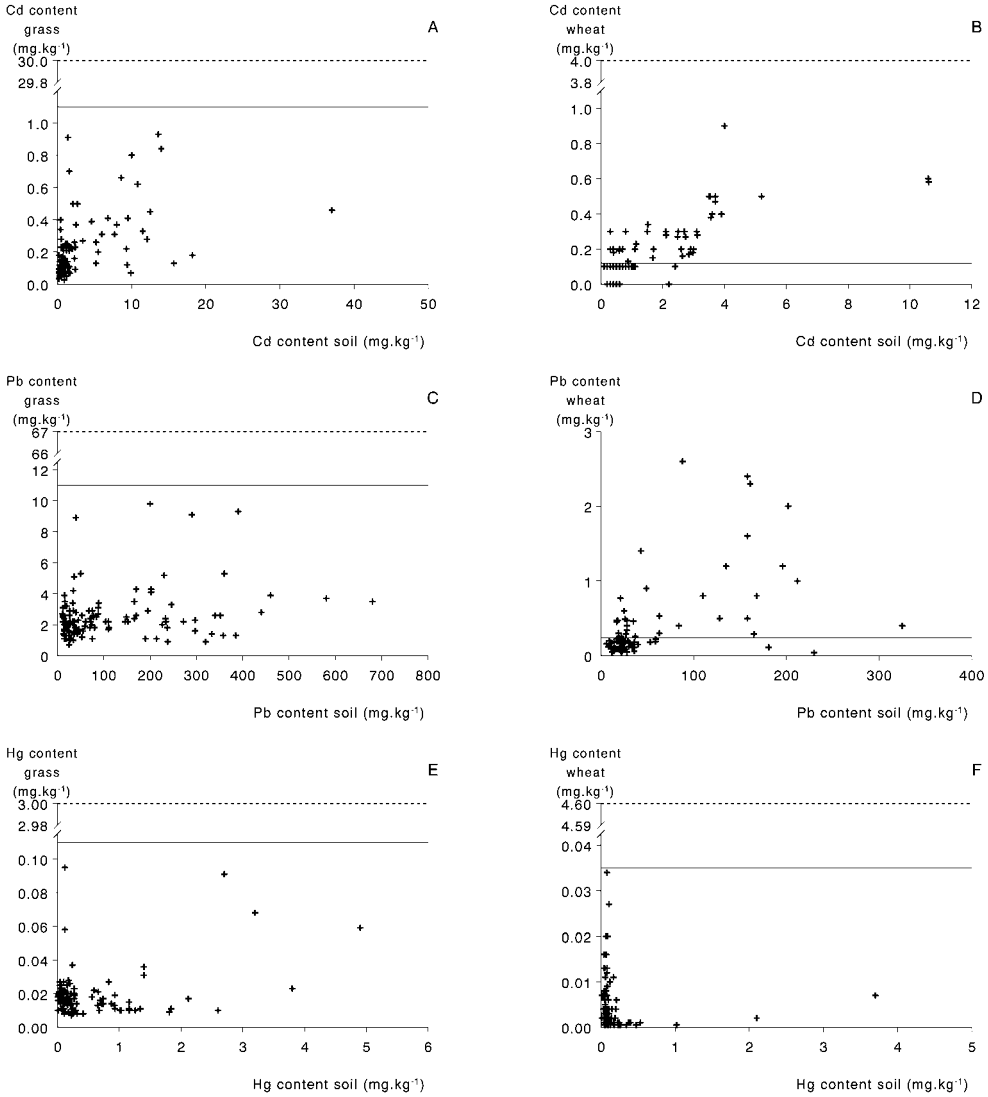


Figure 4 Relationships between Cd, Pb and Hg contents in grass and soil (A, C and E) and in wheat and soil (B,,D,F). The solid line represents the fodder or food quality criteria and the dashed line represents limits in view of phytotoxic effects on crops.

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

$$\log[\mathrm{Me}_{\mathrm{plant}}] = \mathrm{a} + \mathrm{b} \cdot \mathrm{pH} + \mathrm{c} \cdot \log(\mathrm{clay}) + \mathrm{d} \cdot \log(\mathrm{OM}) + \mathrm{n} \cdot \log[\mathrm{Me}_{\mathrm{soil}}] \qquad (12)$$

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

When one requires a minimum R^2 value of 0.5, the relationships derived for Pb in wheat and lettuce are also not acceptable for application. This implies that only for Cd significant relationships are available. Furthermore, the maximum plant contents in the data set used for the derivation do approach or exceed the critical limit, thus allowing to convert food quality criteria to soil criteria for this metal alone.

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

Crop	Soil– Plant relationship[1]	R^2
Grass		
Cd	$\log(Cd_{plant}) = 0.17–0.12*pH – 0.28*\log(OM) + 0.49*\log(Cd_b)$	0.53
Pb	No relationship found	-
Maize		
Cd	$\log(Cd_{plant}) = 0.9– 0.21*pH^2 – 0.32*\log(clay) + 1.08*\log(Cd_{soil})$	0.62
Pb	No relationship found	-
Wheat		
Cd	$\log(Cd_{plant}) = 0.35– 0.15*pH – 0.39*\log(OM) + 0.76*\log(Cd_{soil})$	0.72
Pb	$\log(Pb_{plant}) = – 0.25*pH – 1.42*\log(OM) + 1.14*\log(Pb_{soil})$	0.24
Lettuce		
Cd	$\log(Cd_p) = 2.55 – 0.33*pH – 0.19*\log(clay) – 0.39*\log(OM) + 0.85*\log(Cd_{soil})$	0.71
Pb	$\log(Pb_p) = -0.65 +0.59*pH – 0.30*\log(OM) + 0.59*\log(Pb_{soil})$	0.40

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

Critical limits for cadmium

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

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

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

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

- Sandy soil with an organic matter content of 3%, a clay content of 3% and a pH-KCl of 5.5.
- Clay soil with an organic matter content of 3%, a clay content of 25% and a pH-KCl of 6.5.
- Peat soil with an organic matter content of 30%, a clay content of 15% and a pH-KCl of 6.0.

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

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

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

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

Approach

Figure 5 shows how critical limits for the soil have been derived from food quality criteria in animal products/organs related to human health and from acceptable daily intake by animals related to animal health. The latter aspect was included to be sure that the food quality criteria for humans do not lead to situations where animal health is adversely affected. The derivation was limited to grazing animals (cows and sheep), which are most sensitive due to ingestion of soil in addition to grass intake. The figure shows that such a derivation thus derives information on grass and soil intake and on soil-plant and plant-animal product relationships.

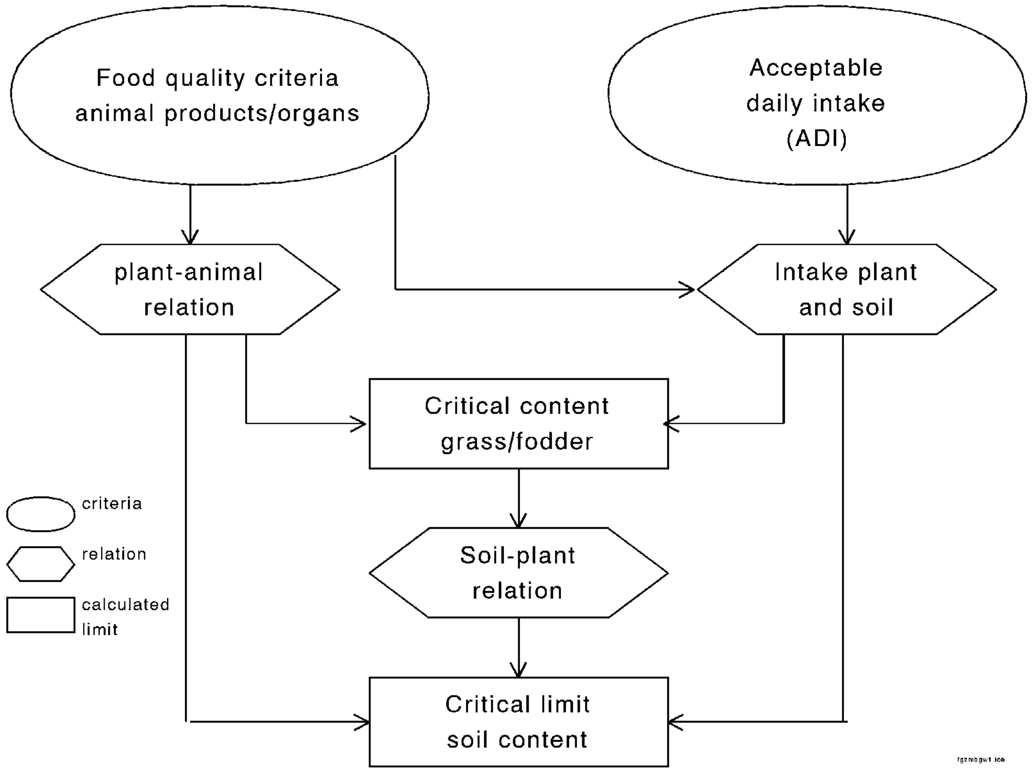


Figure 5 Procedure that has been applied to derive critical limits for heavy metals in the soil (on grassland) from food quality criteria in animal products/organs in view of effects on humans and from acceptable daily intakes in view of toxic effects on animals.

The presentation in the figure is based on the implicit assumption that the transfer of metal in (mixed) plant and soil to animal products is equal. The mathematical approach to calculate critical soil limits, the used critical metal contents in animal products and organs and the results obtained are described below. More information on the approach is given in De Vries et al. (2003).

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

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

$$[\mathrm{Me}]_{\mathrm{p(crit)}} \cdot \mathrm{Ip} + [\mathrm{Me}]_{\mathrm{s(crit)}} \cdot \mathrm{Is} = \mathrm{ADI} \qquad (13)$$

where:
ADI = Acceptable daily intakes of metals (mg.dag^{-1})
Ip = Intake of plants (fodder) (kg.dag^{-1})
Is = Intake of soil (kg.dag^{-1})

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

$$\mathrm{K}_{\mathrm{sp}} \cdot [\mathrm{Me}]_{\mathrm{s(crit)}}{}^{\mathrm{n}} \cdot \mathrm{Ip} + [\mathrm{Me}]_{\mathrm{s(crit)}} \cdot \mathrm{Is} = \mathrm{ADI} \qquad (14)$$

From Eq. (14), the value of $[\mathrm{Me}]_{\mathrm{s(crit)}}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp}, Ip and Is. When a significant soil-plant relationship does not exist, e.g. due to strong buffering on metal contents in plants, a plant metal content that is not related to the soil content (by using the median value in available data sets) and calculating the soil content, according to:

$$[\mathrm{Me}]_{\mathrm{s(crit)}} = (\mathrm{ADI} - [\mathrm{Me}]_{\mathrm{p}} \cdot \mathrm{Ip})/\mathrm{Is} \qquad (15)$$

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

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

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

$$[\mathrm{Me}]_{\mathrm{ao(crit)}} = \left(\frac{[\mathrm{Me}]_{\mathrm{p(crit)}} \cdot \mathrm{Ip} + [\mathrm{Me}]_{\mathrm{s(crit)}} \cdot \mathrm{Is}}{\mathrm{Ip} + \mathrm{Is}} \right) \cdot \mathrm{BCF}_{\mathrm{pa}} \qquad (16)$$

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

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

$$\mathrm{ADI} = [\mathrm{Me}]_{\mathrm{ao(crit)}} \cdot (\mathrm{Ip} + \mathrm{Is}) / \mathrm{BCF}_{\mathrm{pa}} \qquad (17)$$

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

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

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

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

Animal	Organ	Critical limit ($\mathrm{mg.kg^{-1}}$)					
		Food safety			Animal health		
		Cd	Pb	Hg[1]	Cd	Pb	Hg
Cow	Kidney	1.0	0.5	0.05	5	3	14
	Liver	0.5	0.5	0.05	1.4	2	2
	Meat	0.05	0.1	0.05	0.02	-	-
Sheep	Kidney	1.0	0.5	0.05	4	5	1
	Liver	0.5	0.5	0.05	2	5	4
	Meat	0.05	0.1	0.05	-	0.1	-

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

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

Animal	Organ	$\mathrm{BCF_{pa}}$[1,2]			ADI food safety ($\mathrm{mg.d^{-1}}$)			ADI animal health ($\mathrm{mg.d^{-1}}$)		
		Cd	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Hg
Cow[1]	Un-specific	-	-	-	-	-	-	63	2380	28
	Kidney	2.99	0.086	0.638	5.8	101	1.4	29	604	380
	Liver	0.554	0.0404	0.158	16	214	5.5	44	857	219
	Meat	3.3. 10^{-3}	1.3. 10^{-3}	9.2. 10^{-4}	262	1332	941	105	-	-
	Min.	-	-	-	5.8	101	1.4	29	604	28
Sheep[2]	Kidney	2.08	-	0.468	1.25	-	0.28	5	-	5.6
	Liver	1.85	-	0.0572	0.70	-	2.3	2.8	-	182
	Meat	2.9. 10^{-3}	-	9.4. 10^{-4}	45	-	138	-	-	-
	Min.				1.25		0.28	2.8		5.6

[1] Estimates for $\mathrm{BCF_{pa}}$ for cows are based on Van Hooft (1995).

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

Results

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

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

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

4.1.5 CRITICAL LIMITS RELATED TO IMPACTS ON ANIMAL HEALTH

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

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

Approach

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

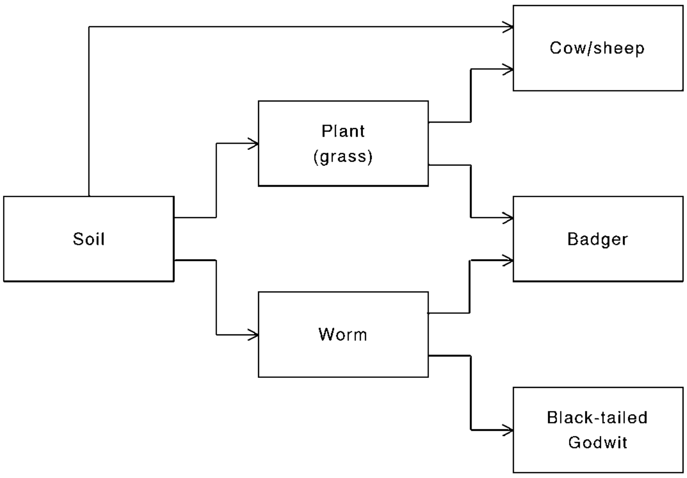


Figure 6 Indicator and target organism and procedure that has been applied to derive critical limits for heavy metals in the soil from criteria in animal organs in view of toxic effects on animals.

The food chain: soil ---> plant (grass) ---> cattle has been described in the previous chapter for agricultural soils. This food chain is also relevant for cows and sheep grazing in nature. In this case the parameterisation of the model described in Section 4.1.4.2 (e.g. the intake of grass and soil and the body weight of the cow) is slightly different, but the overall result is comparable to that presented in Table 16. In this section we do thus focus on the food chain: soil ---> soil invertebrate ---> mammal/bird. Assuming that the mammal or bird only feeds on soil invertebrates (e.g. worm-eating birds or mammals) the simplest model to calculate a critical metal content in the soil, $[\mathrm{Me}]_{\mathrm{s(crit)}}$, based on this food chain is (Romijn et al., 1991a, b):

$$[\mathrm{Me}]_{\mathrm{s(crit)}} = [\mathrm{Me}]_{\mathrm{in(crit)}} / \mathrm{BCF}_{\mathrm{sin}} \tag{18}$$

in which:

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

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

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

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

$$\ln \mathrm{BCF}_{\mathrm{Cd}} = b_0 + b_1 \cdot \mathrm{pH} + b_2 \cdot \mathrm{SOM} + b_1 \cdot \ln \mathrm{Cd}_{\mathrm{soil}} \tag{19}$$

where:

$\mathrm{BCF}_{\mathrm{Cd}}$ = the ratio of Cd in the earthworm (dry weight) and Cd in the soil (dry weight) ($\mathrm{kg.kg^{-1}}$)

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

Below we first describe the approach to calculate critical metal contents in soil from critical metal contents in target organs and acceptable daily intakes, distinguishing between the black-tailed godwit, feeding on worms only, and the badger feeding on both plants and worms. We then describe the results based on this approach using data for soil-plant and soil-worm relations and available target values for the kidney of the godwit and badger.

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

Black-tailed godwit: vermivores

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

$$[\mathrm{Me}]_{\mathrm{w(crit)}} = \mathrm{ADI}/\mathrm{I}_{\mathrm{w}} \qquad (20)$$

where:

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

$\mathrm{I_w}$ = Daily intake of earthworms ($\mathrm{kg.d^{-1}}$)

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

$$[\mathrm{Me}]_{\mathrm{w(crit)}} = \mathrm{K}_{\mathrm{sw}} \cdot [\mathrm{Me}]_{\mathrm{s(crit)}}{}^{\mathrm{m}} \qquad (21)$$

where:

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

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

$$\mathrm{Log\ K_{sw}} = \mathrm{a_o} + \mathrm{a_1} \cdot \log(\mathrm{CEC}) + \mathrm{a_2} \cdot \log(\mathrm{OM}) + \mathrm{a_3} \cdot \mathrm{pH} \qquad (22)$$

where:

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

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

$$[\mathrm{Me}]_{\mathrm{s(crit)}} = (\mathrm{ADI}/\mathrm{I_w})/\mathrm{K_{sw}})^{1/\mathrm{m}} \qquad (23)$$

Direct information on the acceptable daily metal intake is generally not available, but this information can be derived from a critical metal content in the kidney of the vermivore and the critical time period in which this critical content is reached. The kidney is used since this is the most sensitive organ for the intake of Cd, Pb and Hg. The critical time period is set equal to the reproductive phase of the species. For both Cd and Pb, there is enough information available to derive an ADI according to (De Vries et al., 2003):

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

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

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

where

$[\mathrm{Me}]_{\mathrm{org\,(crit)}}$ = critical limit for metal content in target organ (kidney) ($\mathrm{mg.\ kg^{-1}}$)

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

Badger: Omnivores

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

$$[\mathrm{Me}]_{p(crit)} \cdot \mathrm{Ip} + [\mathrm{Me}]_{w(crit)} \cdot \mathrm{Iw} = \mathrm{ADI} \qquad (26)$$

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

$$\mathrm{Ip} \cdot \mathrm{K}_{sp} \cdot [\mathrm{Me}]_{s(crit)}^{\ n} + \mathrm{Iw} \cdot \mathrm{K}_{sw} \cdot [\mathrm{Me}]_{s(crit)}^{\ m} = \mathrm{ADI} \qquad (27)$$

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

$$[\mathrm{Me}]_{s(crit)} = ((\mathrm{ADI} - \mathrm{Ip} \cdot [\mathrm{Me}]_{p}) / (\mathrm{Iw} \cdot \mathrm{K}_{bw}))^{1/m} \qquad (28)$$

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

Critical metal contents in target organs and acceptable daily intakes

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

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

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

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

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

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

[4] This critical limit is based on Ma (1996)

Soil-worm relationships

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

$$\log[\mathrm{Me}_w] = a_o + a_1 \cdot \log(\mathrm{CEC}) + a_2 \cdot \log(\mathrm{OM}) + a_3 \cdot \mathrm{pH} + n \cdot \log[\mathrm{Me}_s] \qquad (29)$$

where:

$[\mathrm{Me}]_w$ = metal content in earthworm ($\mathrm{mg.kg^{-1}}$)
$[\mathrm{Me}]_s$ = metal content in soil ($\mathrm{mg.kg^{-1}}$)

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

$$\mathrm{CEC} = ((3.0 + 0.44 \cdot \mathrm{pH}) \cdot \mathrm{clay} + (5.1 \cdot \mathrm{pH} - 5.9) \cdot \mathrm{OM}/2)/10 \qquad (30)$$

The results of this analysis for Cd and Pb, based on data for six soils with different levels of metal pollution, are given in Table 18, while including and excluding the organic matter content. Despite its lower value of R^2, the latter relationship was used to avoid unwanted effects of increased organic matter contents. Results with soil metal content and pH and CEC alone still show a reasonable to good fit of the relationship, implying that the metal content in worms can reasonably to well described by soil metal contents and these soil properties

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

Metal	Parameters					
	a_0 -	a_1 (CEC) $\mathrm{mmol_c.100\ gr^{-1}}$	a_2 (OM) %	a_3 (pH) -	n $\mathrm{mg\ kg^{-1}}$	R^2
Cd	2.28	-0.70	0.61	-0.09	0.25	0.80
Pb	1.88	-1.49	1.21	-0.09	0.62	0.72
Cd	2.69	-0.38	-	-0.14	0.51	0.72
Pb	1.92	-0.99	-	-0.22	1.16	0.61

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

Results of the critical limits for Cd and Pb in soil based on acceptable daily intakes of those metals by the godwit and badger (determined by the target values for those metals in the kidney) are given in Table 19. A distinction has been made in agricultural and non-agricultural soil based on the expected difference in pH. With respect to clay and organic matter content, use was made of the values presented before in Section 4.1.4.2. The pH values used are:

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

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

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

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

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

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

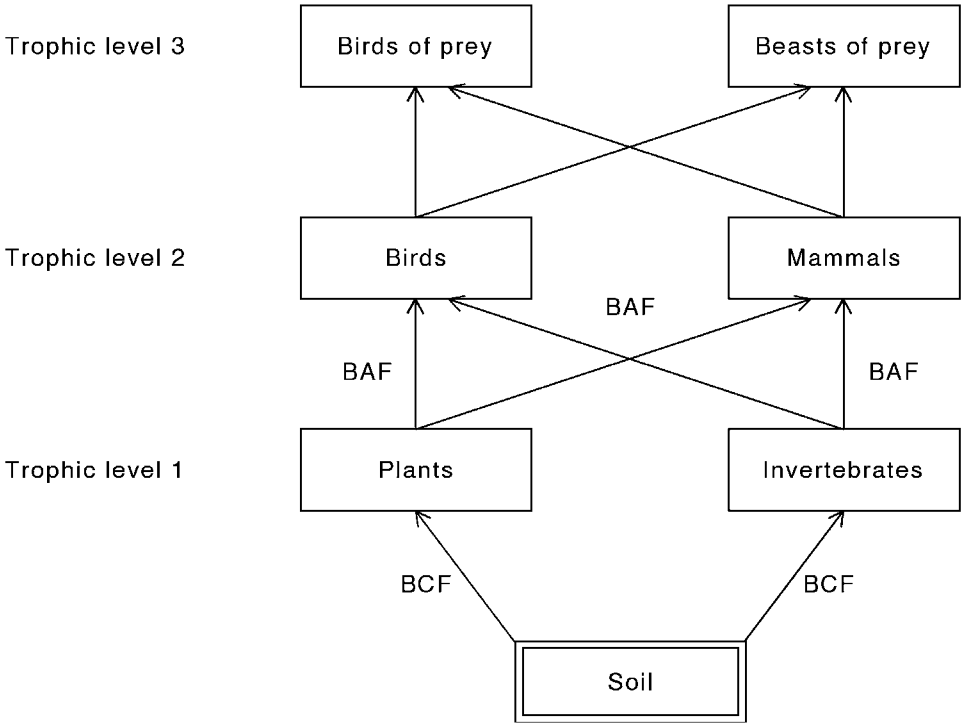


Figure 7 Scheme of a terrestrial food web used for modelling bioaccumulation. The compartments plants and invertebrates can be split up in several groups, depending on the availability and variation among bioaccumulation data.

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

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

To illustrate the results of such an approach, the results obtained for Cd are presented in Table 20. Results show that for Cd (i) birds of prey are always more sensitive than beasts of prey and (ii) bioaccumulation is lowest in the food chain soil --> leaf --> bird/mammal and highest in the food chain soil --> worm --> bird/mammal. The latter food chain to birds of prey is by far the most critical pathway for Cd exposure, leading to very low critical limits for soil (approximately 0.1 mg.kg^{-1}). When one aims to protect the most sensitive species, the latter limit seems appropriate.

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

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

4.1.6 DISCUSSION AND CONCLUSIONS

Recommended set of critical limits and discussion

A recommended set of critical limits for Cd, Pb and Hg for the assessment of critical loads, including ranges for uncertainty assessment, is given in Table 21. More information on the derivation of those limits has been given before (see also De Vries et al., 2002). For the sake of comparison, the drinking water limits are also included (see also Section 4.1.4.1). Those data can be use as an upper limit for groundwater. Apart from Pb, those data are much higher than the results obtained form ecotoxicological tests for soil organism and aquatic organisms (see Table 21).

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

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

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

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

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

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

Discussion aspects

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

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

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

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

Use of critical reactive metal concentrations in soil

In De Vries et al. (2002) the expert group agreed preliminarily on the assumption that effects data from ecotoxicological investigations in laboratory can be best related to a “reactive” heavy metal concentration in the soil, since the heavy metal applied in such tests is in a well available form. Furthermore, it was assumed that the effects on soil invertebrates can best be related to the “reactive” metal content of the soil, because these organisms partly eat soil, whereas the soil solution is relevant as pathway for effects of heavy metals for plants and micro-organisms. In view of those considerations only one critical limit (soil solution) as well as one critical limit (“reactive”) have been set for each of the two metals, Cd and Pb. Those critical limits were directly or indirectly (by using transfer functions) derived from ecotoxicological databases as described in Section 4.1.3.2.

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

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

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

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

In Germany, the effects based critical limits for soil have been compared to background values in order to consider the different ability of soils to accumulate pollutants like heavy metals. The latter is an important argument. It means that e.g. soils with low binding capacity for metals, which are exposed only to a relatively low (ubiquitous) input rate of Cd will probably never reach the critical limit for Cd “reactive” (found in laboratory) because the metal is permanently washed out. On the other hand the critical limit for Pb “reactive” is exceeded in soils with higher binding capacity because most of the Pb input is bound, but effects have not been proved under natural conditions.

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

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

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

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

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

The precautionary values are based on evaluation of ecotoxicological effects data. However, neither factor method nor statistical distribution method was used to set these values (Terytze, 2001). The precautionary values are set in a more empirically way, using literature data on the ranges of NOECs and LOECs, assuming that in sandy soils effects occur at lower thresholds as in well binding soils like e.g. clay soils.

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

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

Possible improvement of critical limits for soil solution and surface water

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

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

Use of critical limits expressed as free metal ion

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

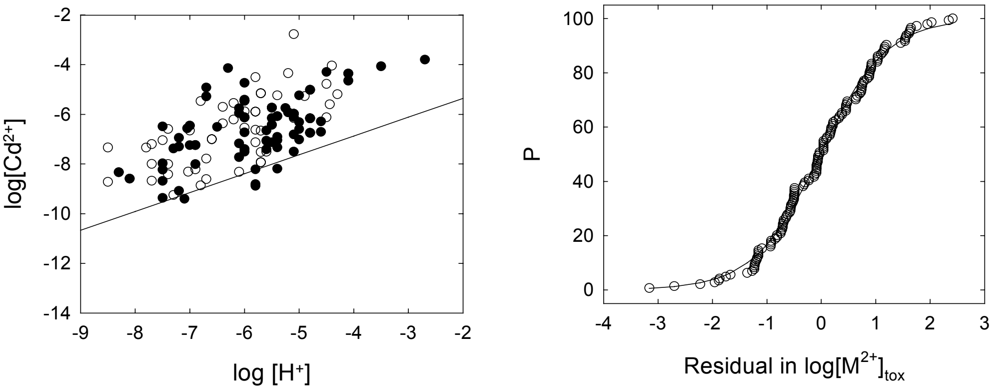


Figure 8 Left: $\log[Cd^{2+}]tox$ plotted against $\log[H^+]$, showing the critical limit function (solid line) derived from weighted regression and the distribution of residuals in $\log[Cd^{2+}]_{tox}$ (right). Solid points in the left hand pane are for effects on plants and animals, open points are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

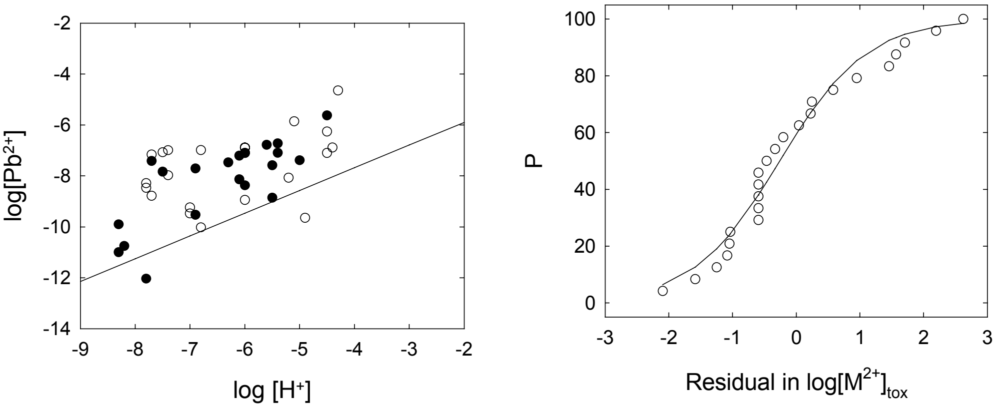


Figure 9 Left: $\log[Pb^{2+}]tox$ plotted against $\log[H^+]$, showing the critical limit function (solid line) derived from weighted regression and the distribution of residuals in $\log[Pb^{2+}]_{tox}$ (right). Solid points in the left hand pane are for effects on plants and animals, open points are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

For each metal, considering all species and effects endpoints together in a database compiled in the UK, a significant ($P < 0.001$) correlation between $\log[M^{2+}]_{tox}$ and $\log[H^+]$ was seen. It was not possible with the current data to determine any independent effects of Ca^{2+} or Mg^{2+} on $[M^{2+}]_{tox}$. Therefore critical limits for the free metal ion were expressed as functions of $\log[H^+]$ only. This was done using a method which is intended to combine the species sensitivity distribution approach of Aldenberg and Slob (1991) with a description of the dependence of the critical limit, $[M^{2+}]_{crit}$, upon $\log[H^+]$.

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

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

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

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

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

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

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

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

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

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

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

The resulting linear regression relationships that were derived are:
Cd deposition = -15 + 456 Cd content endive R^2= 0.81
Cd deposition = -1.8 + 139 Cd content lettuce R^2= 0.92
Pb deposition = 39 + 240 Pb content endive R^2= 0.58
Pb deposition = 42 + 50 Pb content lettuce R^2= 0.52

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

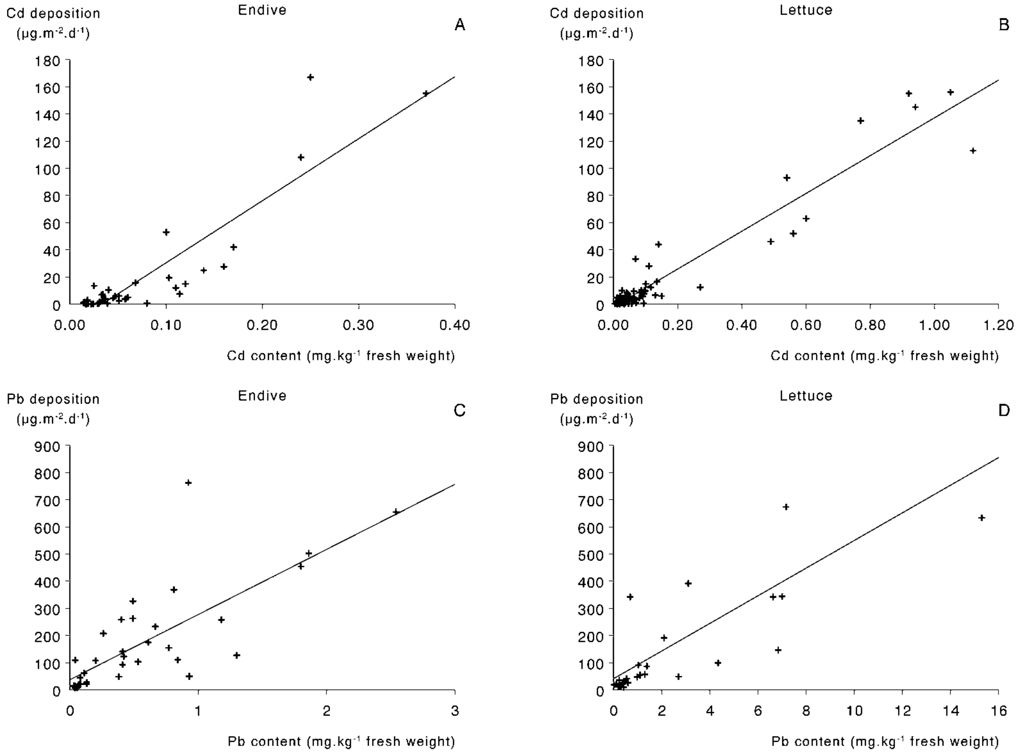


Figure 10 Relationships between inputs from the atmosphere in $ug.m^{-2}.d^{-1}$ and plant contents in $mg.kg^{-1}$for Cd in endive (A) and lettuce (B), Pb in endive (C) and lettuce (D).

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

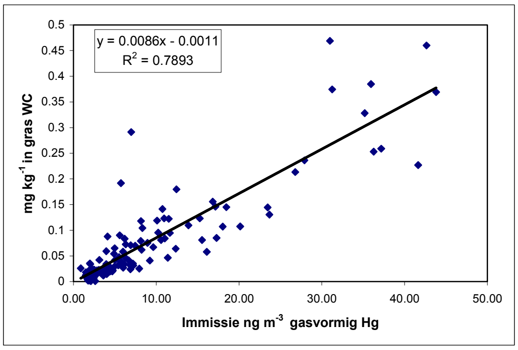


Figure 11 Relationships between inputs from the atmosphere and plant contents for Hg in grass.

Consequences and options for the further approach

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

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

Aspects of human health have to be considered in future for the agricultural types of land use and again the most sensitive critical load should be the measure for emission reduction strategies. In the future, in view of dynamic modelling, it is also relevant to calculate a stand-still critical load. The uncertainties of the transfer functions have the same influence on the calculations of a stand-still critical load as in the effects based approach using critical reactive metal contents. The difference is that the calculations are based on measured values for the heavy metal content in the soil. When dynamic models are applied it might become also relevant to calculate a target load for a finite period with a (simple) dynamic approach. A target load includes an acceptable net accumulation in the soil (based on the difference from background values of total contents to Critical Limits for total contents) as presented in De Vries and Bakker (1998) and de Vries et al. (2001). Such a load implies that the soils with high binding capacity would be presented as the least sensitive ones. This is according to the imagination of a soil, being insensitive against heavy metal input.

Acknowledgements

This work was funded by the Dutch Ministry of Agriculture and the Dutch Ministry of Environment and the UK Department of the Environment, Food and Rural Affairs under grant EPG /1/3/188.

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

Crommentuijn et al. (1997) determined LC_{50}, EC_{50} (weight) and EC_{50} (individuals) of cadmium for *F. candida* in 12 artificial soils (pH 3.12-7.29, % O.M. 2.0-10.0). The LC_{50} was determined for eight soils only. Endpoint free ion concentrations were calculated using the transfer function:

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

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

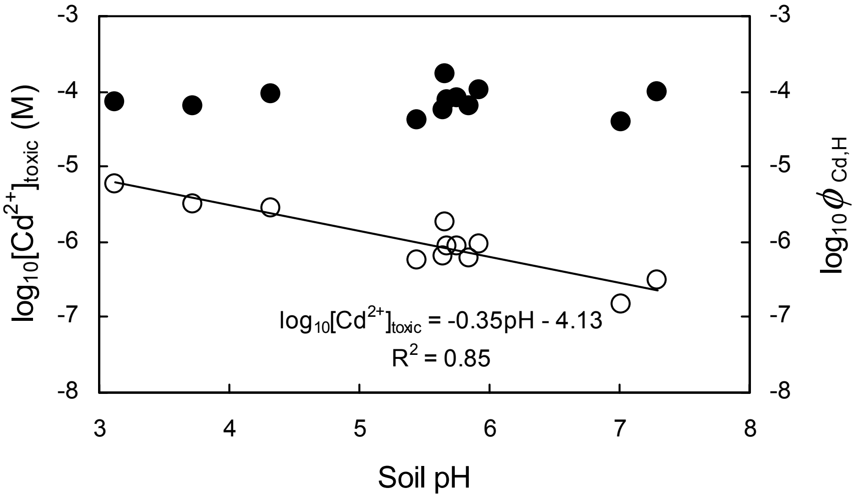
LC_{50}: $\log_{10}[Cd^{2+}\ LC_{50}]_{toxic} = -0.38pH - 3.12\ r^2 = 0.97$ (36)
EC_{50}-weight: $\log_{10}[Cd^{2+}\ EC_{50}\text{-weight}]_{toxic} = -0.34pH - 3.63\ r^2 = 0.94$ (37)
EC_{50}-individuals: $\log_{10}[Cd^{2+}\ EC_{50}\text{-individuals}]_{toxic} = -0.35pH - 4.13\ r^2 = 0.85$ (38)

Variances in the endpoints, expressed as $\log_{10}$[total added Cd], $\log_{10}[Cd^{2+}]_{toxic}$ and $\log_{10} \phi_{Cd,H}$, are given in Table 1. $\log_{10} \phi_{Cd,H}$ consistently gives the lowest variance of the three endpoints. Free ion endpoints (EC_{50} individuals), unadjusted and adjusted for pH, are shown in Figure 2.

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

	LC_{50}	EC_{50}-weight	EC_{50}-individuals
$\log_{10}$[total added Cd]	0.04	0.03	0.05
$\log_{10}[Cd^{2+}]$	0.17	0.18	0.20
$\log_{10} \phi_{Cd,H}$	0.01	0.01	0.03

Figure A1. Cadmium toxicity to *F. candida*. EC_{10} values expressed as the free ion (open symbols), and as the index of free ion toxicity (closed symbols).



Annex 2 **Impact of pH on copper toxicity to alfalfa**

González (1991) determined EC_{10} (relative yield) concentrations of copper for alfalfa in ten Chilean soils (pH 5.3-7.5, %O.M. 0.3-14.5). The endpoint concentrations ranged from 32 mg Cu.(kg soil)$^{-1}$ to 1253 mg Cu.(kg soil)$^{-1}$, expressed as the reactive (added) Cu concentrations. Endpoint free ion concentrations were calculated using the transfer function

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

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

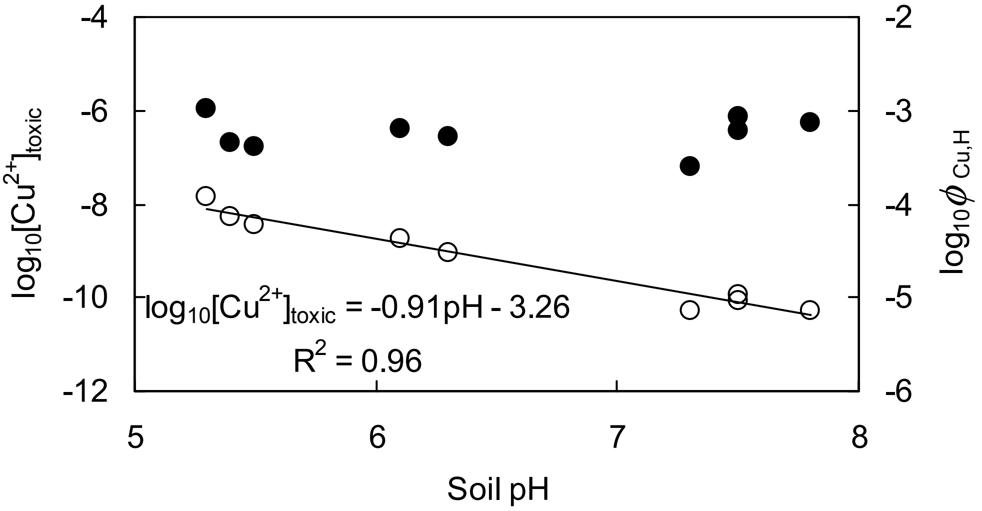
$$\log_{10}[Cu^{2+}]_{toxic} = -0.91pH - 3.25 \quad r^2 = 0.96 \qquad (40)$$

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

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

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

Figure A2. Copper toxicity to Alfalfa. EC_{10} values expressed as the free ion (open symbols), and as the index of free ion toxicity (closed symbols).



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4.2 TRANSFER FUNCTIONS FOR THE CALCULATION OF CRITICAL LOADS FOR LEAD AND CADMIUM

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BACKGROUND DOCUMENT
FOR THE

EXPERT MEETING ON CRITICAL LIMITS FOR HEAVY METALS AND METHODS FOR THEIR APPLICATION

BERLIN, 2-4 DECEMBER 2002

held under the
UN-ECE Convention on Long range Transboundary Air Pollution

4.2.1 INTRODUCTION

Aim of transferfunctions

Transfer functions for the partitioning of heavy metals between the solid and the solution phase in soils are crucial to calculate critical loads for terrestrial systems. To calculate a critical load for a terrestrial system, a critical leaching rate has to be calculated by multiplying the precipitation excess with a critical limit expressed in a critical concentration in the soil solution. Depending on the methodology this critical limit is related to (i) an effect based critical limit or (ii) the present metal content in the soil (stand still principle).

For the effect based approach it is assumed that the major route of exposure for the soil ecosystem is the dissolved metal concentration (see expert group on Critical limits). Because NOEC data on metal contents in soil from ecotoxicological tests are almost exclusive available (reactive), one has to calculate a critical dissolved metal concentration from this critical reactive metal concentration in soil, using a transfer function for heavy metal partitioning.

Alternatively to the effect-based approach, a stand still approach may be used, which aims to avoid any accumulation of the heavy metals in the soil. The present metal concentration in the soil is then the critical limit, which has to be related to a dissolved metal concentration.

In the future besides steady state models also dynamic models will be used to evaluate the effects of (changes in) metal inputs to soils. An essential part of such a model would be the calculation of metal partitioning for which transfer functions can be used.

Setting up of the working group on transferfunctions

At the 17th Task Force on ICP Modelling and Mapping the setting up of a specific expert group on transfer functions was decided, which should elaborate harmonised transfer functions for common use in European mapping exercises of critical loads of heavy metals. The working group consists of a group of people active in the derivation of transfer functions for metal partitioning. The working group consists of Bert-Jan Groenenberg, Paul Römkens, Wim de Vries (NL), Gudrun Schuetze (D), Tatiana Pampura (R) and Ed Tipping (UK). The group did not meet until now. The present background document is a compilation and evaluation of the work done by the different groups and will serve as a document for discussion.

The basis for the working group are the conclusions from earlier workshops in Schwerin and Bratislava. At the workshop in Schwerin in 1999, the working group on key processes and models in terrestrial systems concluded that transfer functions should be developed between the reactive metal content and total soil solution concentration, based on clay content, organic matter content and pH, which can be applied across Europe. A similar conclusion was drawn at the workshop in Bratislava (Curlik et al., 2000). Furthermore the need to derive relationships between different extraction methods, as used in different countries, to quantify the reactive metal concentration in soil was expressed. It should be noted that also for total or pseudo total metal contents, different methods for extraction are used.

In the first period, transferfunctions for the partitioning of Cd and Pb were derived on the basis of a Dutch dataset (Römkens et al., 2002). These transferfunctions also served as the basis for the first call for calculations of critical loads for Cd and Pb in Europe and were part of a short guidance to calculate critical loads (De Vries et al. 2001) Furthermore also regression functions were developed for the calculation of reactive metal contents from ‘so called ‘total metal contents (Aqua Regia) and to calculate Aqua Regia extractable metal contents from total contents as extracted with concentrated HF.

From this basis the work should develop towards a set of transferfunctions which can be used international for the calculation of critical loads. Therefore the following topics/questions should be addressed.

1. What kind of partition relation should be used? A linear function (K_d) or non linear function (e.g. Freundlich)?
2. What are the relations between total and reactive metal contents and between different extraction techniques for total and reactive metal contents? Which extractions can be used to determine reactive metal contents in soil?
3. Should partition relations be derived for activities or for total concentrations in soil solution or for both? If so, what kind of relation for what kind of application?
4. What kind of mathematical/statistical methods are to be used for the derivation of transfer functions? Are direct assessments of total or free metal concentrations in soil solution from reactive metal contents acceptable or should you only use transfer functions with the adsorption constant? In short: what is the choice of response and predictor variables and consequences of these choices?
5. How large are the uncertainties associated with the use of transfer functions and what are the implications of these uncertainties for their use?
6. How good are the present transfer functions, as derived from data on Dutch soils, to calculate metal partitioning for soils from other countries and how can metal partition studies from other countries than NL be included in the derivation? Should we try to establish a common dataset from a variety of countries, as we did for Critical Limits?
7. Are there any transfer functions for the organic horizon of forest soils or for peat soils, and if so what is their quality? Is there any research going on related to this aspect?
8. Can the use of country specific transfer functions lead to more accurate results, by considering specific properties for country/region typical soils or can transfer functions be improved by the inclusion of geological and climatic regions (Different properties of clay and organic matter due to differences in geological origin, clay mineralogy and climate)?.
9. Are transfer functions applicable to calcareous soils as found in central and southern Europe?
10. According to Tatiana Pampura (in Curlik et al. 2000, and a report on more current results obtained in a study with German soils is in preparation), the Freundlich equation is not well appropriate to describe the binding of some metals in the soil in the lower concentration range (near background). Are there alternative approaches and which of them could be more appropriate?

In this document the topics 1-7 will be addressed. Information for points 8-10 is still lacking.

Annex 1 gives a list of used symbols with explanation.

4.2.2 METHODOLOGICAL ASPECTS

4.2.2.1 Relevant transferfunctions

As pointed out in the introduction transferfunctions for metal partitioning are needed to calculate (free) metal concentrations in solution from metal contents in the soil solid phase.

There are several possibilities with respect to the availability of present metal concentration data. The data might be total concentrations based on a HF destruction or “so-called” total concentrations, based on an aqua regia destruction a concentrated nitric acid destruction or a destruction with a mixture of concentrated nitric and perchloric acids, etc... It is also possible that countries do have data sets on reactive metal concentrations based on mild acid extractions (e.g. 0.43 $Mol.L^{-1}$ HNO_3, extractions with complexing agents (e.g. EDTA, DTPA) and extractions with salt solutions (e.g. NH_4NO_3, $CaCl_2$). Relations between concentrations in the solid phase with concentrations in solutions are derived for different measures of the solution concentrations. These can be solution sampling with solution samplers (e.g. rhizon sampler), centrifugation of the soil or extractions with diluted salt solutions.

Possibilities for the calculation of a solution concentration from solid phase data are presented in Figure 1.

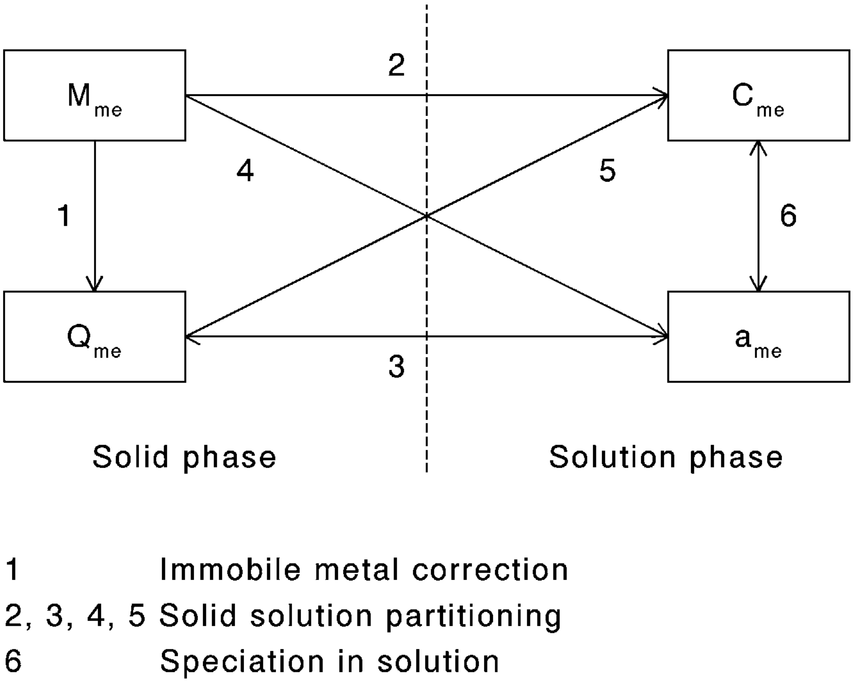

Figure 1 Overview of relations between solid and solution concentrations in soils

The direct calculation of a total concentration of metals in solution (C_{Me}) from a total concentration in the solid phase (M_{Me}) (relation 2 Fig 1.) and the calculation of a free metal (a_{Me}) activity direct from a total metal content in the solid phase (relation 4) are not described in this document, because it was agreed earlier to derive partition relations from reactive metal contents. Depending on the available data, the soil concentration has to be translated to a dissolved concentration using the following sequence of possible transfer functions:

1. Relations between different extractable contents in the solid phase(see Chapter 3)
   - From total (HF) to "so-called" total (e.g. aqua regia) metal concentration (not in the figure)
   - From "so-called" total (e.g. aqua regia, $M_{Me,\ AR}$) to reactive (e.g. 0.43N HNO_3 or EDTA extraction, $Q_{Me,\ HNO3/EDTA}$) metal concentration (relation 1). This relation possibly involves soil characteristics (e.g. clay and organic matter content).
2. Partition relations between solid phase and soil solution (see Chapter 4)

- From a reactive metal content (Q_{Me}) to a free metal ion concentration (a_{Me}) in soil solution (relation 3)
   - From reactive (e.g. 0.43N HNO_3 or EDTA extraction) to a total dissolved metal concentration Directly via relation 5 in figure 1, or via relation 3 and 6.

To calculate the total dissolved metal concentration from the uncomplexed metal concentration, chemical speciation models can be used which include the complexation of metals with DOC (relation 6). For calculations at larger scales the data needed to be able to use a speciation model are not available. Therefore it is needed to have also direct relations between the reactive metal content and total concentrations in solution.

Central in this document are relations 3 and 5 for the partitioning of heavy metals between the reactive pool in the solid phase and the concentration or activity in soil solution.

4.2.2.2 Overview of approaches

Different types of transferfunctions

Transferfunctions which relate heavy metal partitioning with soil properties can be roughly divided into two main categories. First there is a group with transfer functions which either directly relates the concentration in the solution phase with the concentration in the solid phase and soil properties (further referred as the C-Q approach, see Eq. 1) or the concentration in the solid phase with the concentration in the solution phase and soil properties (further referred as the Q-C approach, see Eq. 4).

$$\log C_{Me} = F(\log Q_{Me}, pH, \log(A_{.1}...A_j) \text{ or } \log a_{Me} = F(\log Q_{Me}, pH, \log(A_{.1}...A_j) \qquad (1)$$

$$\log Q_{Me} = F(\log C_{Me}, pH, \log(A_{.1}...A_j) \text{ or } \log Q_{Me} = F(\log a_{Me}, pH, \log(A_{.1}...A_j) \qquad (2)$$

where:
Q_{Me} = reactive metal concentration
C_{Me} = total metal concentration in soil solution
a_{Me} = activity of free metal ion in solution
with $A_1..A_j$ being various soil properties like the organic matter content, the clay content, oxalate extractable iron, the CEC etcetera.

The transferfunction derived should be applicable on a large scale. This restricts the choice of explaining variables in the derived regression analysis because of data limitation at larger scales. Here we have chosen for a basic set of soil data to be used in the regression functions. These are: pH, organic matter content and the clay content

The second group is based on the derivation of an adsorption constant which is related to soil properties. This can either be based on a linear model (further referred as the K_D approach, see equation 3 and 4) or on a nonlinear model such as the Freundlich model (further referred as the K_F-approach, see equation 5 and 6).

$$\log Q_{Me} = \log K_{D,C} + \log C_{Me} \text{ or } \log Q_{Me} = \log K_{D,a} + \log a_{Me} \qquad (3)$$

$$\log K_{D,C/a} = F(pH, \log(A_{.1}...A_j) \qquad (4)$$

$$\log Q_{Me} = \log K_{F,C} + n \log C_{Me} \text{ or } \log Q_{Me} = \log K_{F,a} + n \log a_{Me} \qquad (5)$$

$$\log K_{F,C/a} = F(pH, \log(A_{.1}...A_j) \qquad (6)$$

where:
$K_{D,C}$ and $K_{D,a}$ = linear partition constants
$K_{f,C}$ and $K_{f,a}$ = Freundlich constants
n = Freundlich exponent (-)

Transferfunctions can either be based on total concentrations of the metal ions in solution (C_{Me}) or solution speciation can be taken into account calculating free metal ion activities (a_{Me}). Complexation of metal ions with DOC is of importance, especially for Pb. To distinguish between regression functions based on activities (thus including chemical speciation) and those based on concentrations these are referred to as Q-a, a-Q, $K_{D,a}$, $K_{F,a}$. For concentrations the adsorption constants are denoted as $K_{D,C}$ and $K_{F,C}$. Reasons for using different approaches are elaborated below.

Direct approaches (C-Q and a-Q)

The direct approach has an analogy with the Freundlich isotherm. The logarithmic form of the direct approach is equal to the logarithmized form of the Freundlich isotherm. A pitfall in the use of direct methods can be the mistake that a Q-C relation is used the inverse way to calculate the concentration in solution from the metal content in the soil and soil properties or inversely that a C-Q relation is used to calculate the content in the soil from the solution concentration and soil properties. Q-C and C-Q relations are not equal to each other and linear regression will give different estimates for the regression coefficients. In the case of a C-Q approach the sum of squares of $C_{regression}$-$C_{measured}$ is minimized whereas the sum of squares for $Q_{regression}$-$Q_{measured}$ is minimized for the Q-C approach. Incorrect use of these direct methods can lead to large errors. Figure 2 shows the effect of the incorrect use of these relations i.e. the calculation of the concentration in solution with the use of a Q-a relation (Fig. 2 B) and the calculation of the reactive metal content with an a-Q relation (Fig. 2D). Figures 2A and 2C show that in case of correct use of these relations the error in the predicted values is considerable smaller.

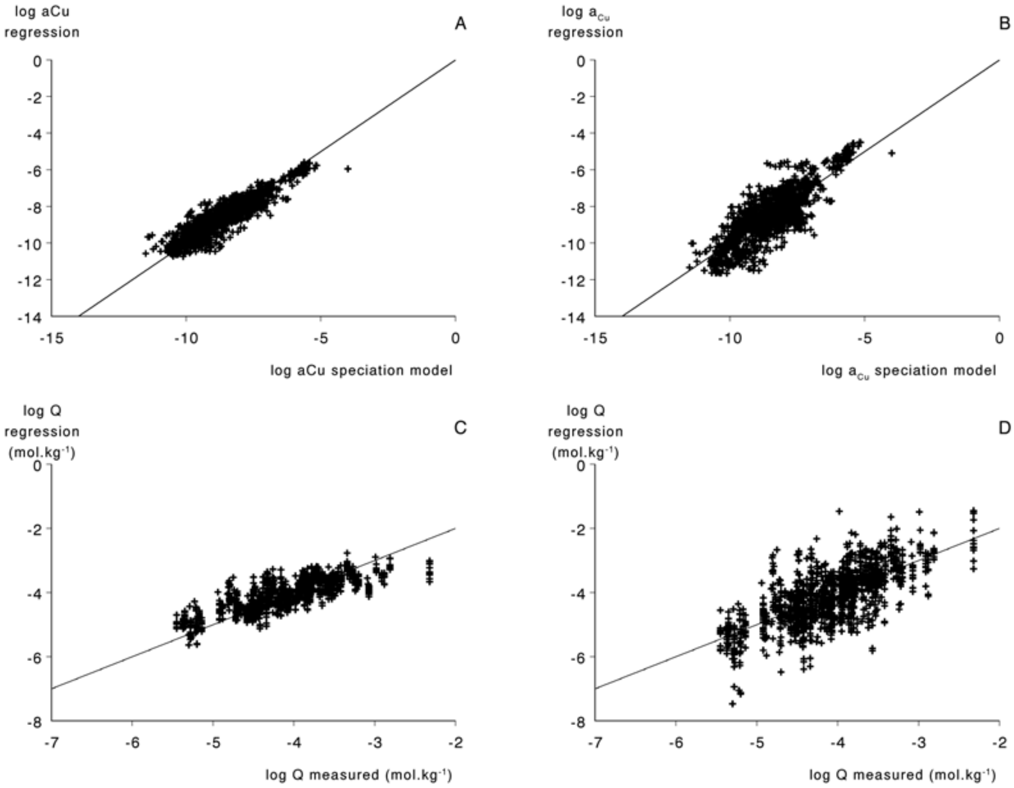

Figure 2 Comparison of measured and calculated dissolved (A, B) and solid phase (C, D) Cu concentrations using transferfunctions in a correct (A, C) and incorrect way (B, D).

Because in the case of critical loads a solution concentration or ion activity has to be calculated from a metal content in soil, C-Q or a-Q relations have to be derived when a direct approach is used. The derivation of Q-C and Q-a relations is therefore not further discussed in this document.

Indirect approaches: K_D and K_F

As pointed out direct methods have the disadvantage that they can only be used to calculate Q from C in the case of a Q-C relation or to calculate C from Q with a C-Q relation. Preferably one should have only one relation which can be used in both directions. Especially in the case of dynamic models, in which the partitioning of metals is calculated, this is a prerequisite. A possibility is to derive relations in which adsorption/partition constants are fitted to soil parameters instead of deriving relations in which Q or C are the explained variables.

Freundlich isotherms that relate the reactive metal content (Q) to the concentration in soil solution (C) can be expressed as:

$$Q_{Me} = K_{f,C} \cdot C_{Me}{}^{n} \text{ or } \quad Q_{Me} = K_{f,a} \cdot a_{Me}{}^{n} \qquad (7)$$

K_f can thus be calculated according to:

$$K_{f,C} = \frac{Q_{Me}}{C_{Me}^{n}} \text{ or } K_{f,a} = \frac{Q_{Me}}{a_{Me}^{n}} \qquad (8)$$

In case the Freundlich exponent n equals 1 the K_F is equal to K_D. In case of a K_D relation non linearity, as general observed, is not accounted for. Calculated values of KD and K_F can be related to soil properties to obtain a transferfunction that is applicable to a range of soils according to equations 4 and 6.
The derivation of a transferfunction for KD is straightforward because all variables needed are known. For the calculation of K_F however the value of the Freundlich exponent is not a priori known. Römkens et al (2002) developed a methodology in two steps to derive transferfunctions for Kf. Kf-values are calculated for a range of preset n-values according to equation 8. These Kf values are then regressed with soil properties. For all these regressions the F-value (a measure for the significance of the model) is calculated and n is optimized by maximizing the F-value.

Another possibility is to optimise all explaining variables simultaneously (Q, C and soil properties), taking into account that all variables have variance, with an advanced statistical procedure, the total least squares method.

4.2.2.3 Selection of available partitioning studies

Several relations to relate metal partitioning to soil properties have been derived. Table 1 summarises available transferfunctions classified according to the relations as described in Figure 1. It was decided during the workshop in Schwerin to use only partition relations based on reactive metal contents. This excludes a large part of the partition relations listed in Table 1. Studies with Q-C and Q-a relations are not useful within the context of the work of critical loads and critical limits. Furthermore preference is given to studies with measured partitioning from field soils without adding additional metal. Adsorption studies are therefore omitted by now but can be used later for comparison with results from partitioning of field soils. The present evaluation of transferfunctions is therefore constrained to the partitioning studies of Tipping et al. (2003), Römkens et al. (2003) and Pampura et al. (2002).

Table 1 Overview of available transferfunctions for solid solution partitioning of Cd and Pb

Type of relation	metals	Type of study	Additional information	Reference
Q-C and Q-a	Cd, Cu, Pb, Zn	Derived from literature data on adsorption studies	Q is added metal	Elzinga et al. (1999)
a-M	Cd	Measured partitioning of contaminated soils	M_{Me} measured with concentrated HNO_3	Sauve et al. (1998)
a-M	Pb	Measured partitioning of contaminated soils	M_{Me} measured with concentrated HNO_3	Sauve et al. (2000)
K_d (M-C)	Cd, Cu, Pb, Zn, Cr	Measured partitioning of soils	M is aqua regia extracted metal	Janssen et al. (1996)
$K_{f,a}$	Cd, Cu,Pb	Derived from literature data on adsorption studies	Q is added metal	Bril (1995)
K_f	Cd	Adsorption studies	Q is added metal	Springob and Böttcher (1998)
$K_{d,a}$, C-Q and a-Q	Cd, Cu, Pb, Zn	Measured partitioning of soils. Estimation of free ion concentration with speciation model	Q is 0.43 mol.L^{-1} HNO_3 extraction. Solution extracted with rhizon samplers	Tipping et al. (2003)
$K_{F,a}$, $K_{F,C}$, C-Q and a-Q	Cd, Cu, Ni, Pb, Zn	Measured partitioning of soils. Estimation of free ion concentration with speciation model	Q is 0.43 mol.L^{-1} HNO_3 extraction. Solution extracted with diluted salt extractions	Römkens et al. (2003)
Q-C, Q-a, C-Q, a-Q, K_{fa} , K_{fC}	Cd, Pb	(a) Measured partitioning, (b) adsorption experiments	(a) Q is 1M NH_4NO_3 extractable pool, a (b) Q is added metal	Pampura et al. (2002)

4.2.3 REGRESSION FUNCTIONS FOR RELATIONS BETWEEN DIFFERENT EXTRACTION TECHNIQUES

Different extraction techniques are used to determine the metal contents in the soil solid phase. A differentiation can be made between extractions which are used to determine the total metal concentration in the soil and extractions to determine the reactive metal content in the soil. The latter is the metal content available for exchange with the soil solution. Preferably reactive metal contents are to be used when calculating metal concentrations in soil solution. However most geographic databases on heavy metal contents and databases used to determine toxicity relationships are based on total metal contents. Unfortunately different extraction techniques are used to determine these total metal contents and this is the same for the reactive metal contents. Regression functions which relate different extraction techniques may help to overcome some of these problems. In this chapter regression relations are presented between different extraction techniques for the total metal content (HF-Aqua Regia), the reactive metal content (0.43 Mol.L^{-1} HNO_3 and EDTA) and between the total content and the reactive content (Aqua Regia - 0.43 Mol.L^{-1} HNO_3/EDTA, and concentrated nitric and perchloric acids - 0.43 Mol.L^{-1} HNO_3/EDTA)

4.2.3.1 Transfer functions from total to "so-called" total metal concentrations

Different extraction techniques are used as a measure for the total metal concentration in soil. A complete destruction of the soil extracts all metals including metals from the lattice structure of clay minerals. Aqua regia extracts nearly all metals from soil except metals in the lattice structure. Another strong extractant widely used as a measure for the total metal contents in soil is a 2 mol.L^{-1} HNO_3 extraction and the extraction with a mixture of nitric and perchloric acids.

Utermann et al. (2000) provided transfer functions to calculate "so-called" total contents of heavy metals (M_{AR} the amount of metal extracted with aqua regia from total contents (M_{HF}; the HF extractable amount), according to:

$$\log \mathrm{M}_{\mathrm{Me,AR}} = \beta_0 + \beta_1 \cdot \log \mathrm{M}_{\mathrm{Me,HF}} \qquad (9)$$

where:

M_{HF} = total concentration of heavy metal M in soil extracted with HF(mg.kg^{-1})

M_{AR} = "so-called" total concentration of heavy metal M in soil extracted with Aqua Regia (mg.kg^{-1})

The parameters β_0 and β_1 for different types of soils are listed in Table 2 for Cd and Table 3 for Pb

Table 2: Relation between cadmium (Cd) content in soils extractable by aqua regia (AR) and total contents extractable by HF in dependence on the parent material.

parent material	β_0	β_1	n	r^2 $\alpha \leq 0.05$	range of validity Cd (HF) (mg.kg^{-1})	
Basic and intermediate igneous rock	0.13	1.41	25	0,94	0,25	1,12
Boulder clay	0.09	1.38	26	0.91	0.07	0.39
Limestone	-0.15	1.24	25	0.91	0.26	1.86
Loess or loessic loam	-0.15	1.26	25	0.91	0.07	0.88
Marl stone	-0.05	1.24	25	0.93	0.10	0.98
Sand	-0.02	1.26	37	0.89	0.04	0.65
Sandy loess	0.29	1.78	36	0.82	0.06	0.29
Acid igneous and metamorphic rock	-0.09	1.08	25	0.80	0.09	0.63
Quartzitic arnd stones and conglomerates	-0.11	1.23	25	0.81	0.07	0.60
Clay stone, hard argillaceous and silty slates	-0.05	1.33	25	0.96	0.14	1.88
General	-0.12	1.19	274	0.91	-	-

Table 3: Relation between lead (Pb) content in soils extractable by aqua regia (AR) and total contents extractable by HF in dependence on the parent material.

Parent material	β_0	β_1	n	r^2 $\alpha \leq 0.05$	range of validity Pb (HF) (mg.kg^{-1})	
Basic and intermediate igneous rock	-0.20	1.11	25	0.97	5.6	113.6
Boulder clay	-054	1.32	26	0.95	8.3	49.5
Limestone	-0.02	0.99	22	0.88	24.8	132.7
Loess or loessic loam	-0.42	1.22	24	0.91	15.1	91.8
Marl stone	-0.03	0.95	25	0.94	5.5	124.0
Sand	-0.54	1.31	49	0.91	2.7	76.7
Sandy loess	0.72	1.46	43	0.97	6.0	75.9
Acid igneous and metamorphic rock	-0.84	1.44	25	0.84	14.6	106.1
Quartzitic arnd stones and conglomerates	-0.55	1.28	25	0.88	12.6	109.2
Clay stone, hard argillaceous and silty slates	-0.11	1.05	25	0.98	13.9	270.3
General	-0.45	1.24	289	0.95	-	-

4.2.3.2 Relations between different extractions for the reactive metal content

Different extraction techniques are developed to determine the reactive metal pool in soil. All these extraction techniques result in an operationally defined metal pool. A division can be made between extraction techniques which suck the heavy metals from soil like EDTA and other complexing agents by complexing almost all free metal ions in soil solution and extractions which push the metals from soil like mild acid extractions (e.g. 0.43 Mol.L^{-1} HNO_3) and the stronger salt extractions (1 Mol.L^{-1} NH_4NO_3). De Vries et al. (2003, in prep.) and Tipping et al. (2003) derived regression relations between the reactive metal pool as extracted with 0.43 Mol.L^{-1} HNO_3 and EDTA for respectively a dataset with Slovakian and Hungarian soils and a dataset with upland soils from England and Wales (UK dataset) according to:

$$\text{Log}(Q_{\text{Me,HNO3}}) = \beta_0 + \beta_1.\log(Q_{\text{Me,EDTA}}) \qquad (10)$$

Figure 2 shows the relation between both extraction techniques for the Slovakian/Hungarian dataset.

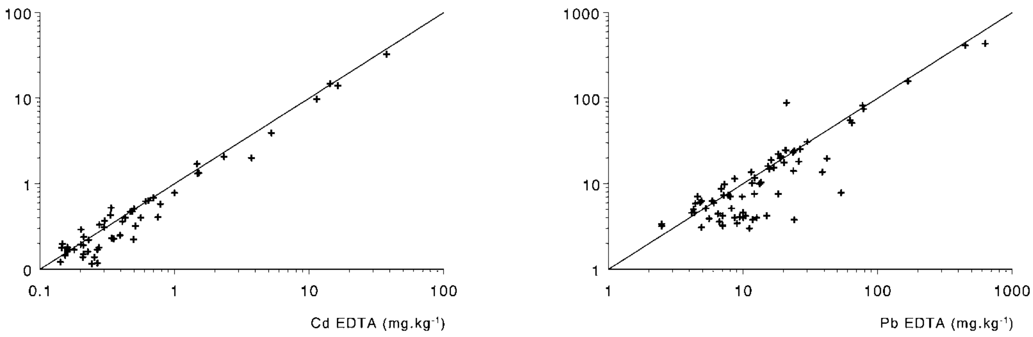

Fig.2 Comparison of measured reactive concentrations of Cd, and Pb with a mild (0.43 N) HNO_3 extraction and an EDTA extraction.

Regression relations between both extractions using the log-transformed data from the Slovakian/Hungarian dataset and from the UK dataset are given in table 4

Table 4 Values for the regression coefficients in the logarithmic relationship (Eq. 10) between reactive concentrations of Cd and Pb extracted by 0.43N HNO_3 and by EDTA for the Hungarian/Slovakian dataset (De Vries et al., 2003) and the UK dataset (Tipping et al., 2003).

Metal	Hungarian/Slovakian data			UK data		
	β_0	β_1	R^2	β_0	β_1	R^2
Cd	-0.09	1.07	91	-0.10	0.99	85
Pb	-0.03	0.93	75	-0.09	0.97	83

Both studies show a considerable agreement between the HNO_3 and EDTA extraction. For both metals the slope of the regression is almost equal to 1 and the intercepts are not significant. From the figures it can be seen that the variation for Cd is less than for Pb. It should be preferable to give besides the explained variance (R^2) also the standard error of the regression. This gives an impression of the uncertainty of the predictions with the use of these regressions.

This paragraph will be extended in a later version with relations between 0.43 $Mol.L^{-1}$ HNO_3 and 1 $Mol.L^{-1}$ NH_4NO_3 extractions based on a dataset from Pampura for soils from Russia when available .

4.2.3.3 Relations between 'so called total' and reactive metal extractions

The reactive metal concentration (Q_{Me}) can be related to the so-called total concentration extracted with Aqua Regia ($M_{Me,AR}$) according to:

$$\log Q_{Me} = \beta_0 + \beta_1 \cdot \log\ M_{Me,AR} + \beta_2 \cdot \log(\%OM) + \beta_3 \cdot \log(\%clay) \qquad (11)$$

where:

Q_{Me} = reactive concentration of heavy metal Me in soil ($mol.kg^{-1}$)

Dutch dataset

Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 $Mol.L^{-1}$ HNO_3 and Aqua Regia. The dataset consists of large variety of soil types with a wide variety in soil properties as the organic matter and clay content. The dataset comprises both polluted and unpolluted soils. Results are shown in Table 5. More information on the data set is given in Annex 2

Table 5 Values for the coefficients β_0-β_3 in the relationship (Eq. 11) between relating reactive, Q_{Me} (0.43N HNO_3), and "so-called" total soil concentrations, $M_{Me,AR}$ of Cd and Pb, using a Dutch dataset (Römkens et al., 2003).

Metal	β_0	β_1	β_2	β_3	R^2	se-yest[1)]
Cd	0.225	1.075	0.006	-0.020	0.82	0.26
Pb	0.063	1.042	0.024	-0.122	0.88	0.17

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

Slovakian/Hungarian dataset

Values for the various coefficients relating reactive and total soil concentrations of Cd and Pb (Eq. 11) derived for the 72 soils investigated in Slovakia and Hungary are shown in Table 6 and 7, while distinguishing between HNO_3 and EDTA, respectively.

Table 6 Values for the coefficients β0-β3 in the relationship relating reactive (0.43N HNO_3) and "so called" total soil concentrations (Aqua Regia) of Cd and Pb according to Eq. (2) derived for 72 soils in Slovakia and Hungary (De Vries et al., 2003).

Metal	β0	β1	β2	β3	R^2	se y-est
Cd	-0.302	1.037	-	-	85.1	0.264
Pb	-0.245	0.939	-	-0.192	75.4	0.238

Table 7 Values for the coefficients β0-β3 in the relationship relating reactive (EDTA) and 'so called ' total soil concentrations (Aqua Regia) of Cd and Pb, according to Eq. (2) derived for 72 soils in Slovakia and Hungary (De Vries et al., 2003).

EDTA	β0	β1	β2	β3	R^2	se y-est
Cd	-0.440	0.926	-	0.176	86.1	0.224
Pb	-0.237	0.856	-	-	67.0	0.259

A comparison of the reactive metal concentrations thus estimated and the measured metal concentrations do also give an indication of the reliability of the estimates. Results thus obtained for the metals considered are presented in Figure 3.

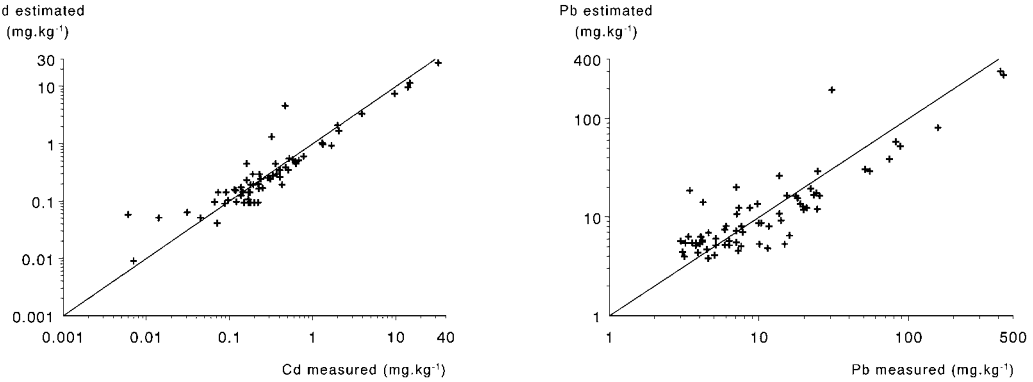

Fig.3 Comparison of measured reactive concentrations of Cd and Pb and estimated concentrations, using the logarithmic relationship between reactive ($Q_{Me,HNO3}$) and 'so called' total ($M_{Me,AR}$) metal concentrations (Eq.11) and the model parameters derived in this study (Table 7)

Validation of 'Dutch' regression relations on the Slovakian/Hungarian dataset.

To get an idea of the applicability of the derived regression functions for the relation between Q_{Me} and M_{Me} the regression functions derived from the Dutch dataset were applied to the soils of the Slovakian/Hungarian dataset. A comparison of the reactive metal concentrations thus estimated and the measured reactive metal concentrations is presented in Figure 4. The figure shows a good resemblance for calculated with measured concentrations of Cd whereas Pb concentrations are somewhat overestimated.

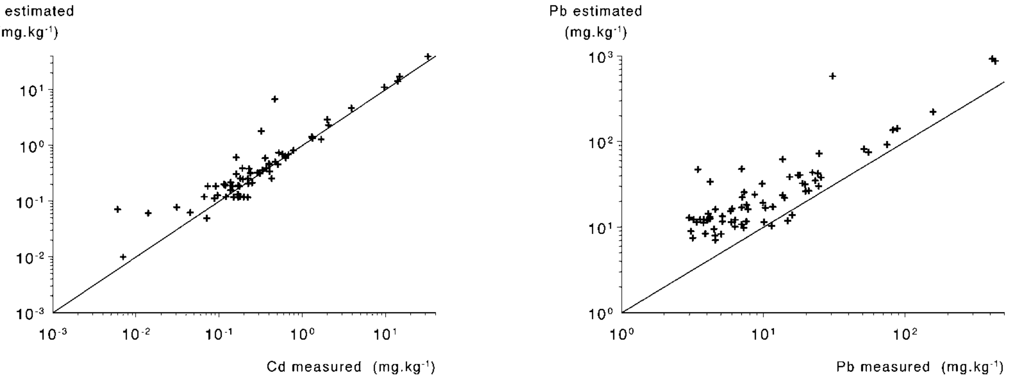

Fig.4 Comparison of measured reactive concentrations of Cd, Pb and estimated concentrations, using the logarithmic relationship between reactive and total metal concentrations (Eq.11) and the model parameters derived by Römkens et al. (Table 6)

UK-dataset

Tipping et al. (2003) derived regressions between the total metal content as measured with a mixture of concentrated nitric and perchloric acids and the reactive metal content measured either with EDTA or HNO_3. Soil properties were not taken into account. The logarithm of the reactive metal concentrations was regressed with the logarithm of the total metal concentration. Table 8 gives the regression parameters for these regressions. The slopes are almost equal to 1 which means that the reactive metal contents are linearly related to the total metal content (as determined with the mixture of nitric and perchloric acids) for the metals Cd and Pb. For Cd the reactive metal content is about 40% of the total metal content, for Pb this is 91%.

Table 8 Relations between the reactive metal contents as determined with EDTA or HNO3 with total contents as determined with a mixture of nitric and perchloric acids.

Metal	extractant	intercept	slope	R^2	se y-est
Cd	EDTA	-0.37	0.99	0.63	-
	HNO_3	-0.40	0.99	0.71	-
Pb	EDTA	-0.03	1.02	0.82	-
	HNO_3	-0.05	1.03	0.95	-

4.2.4 TRANSFER FUNCTIONS FOR HEAVY METAL PARTITIONING BETWEEN THE SOIL SOLID AND SOLUTION PHASE

This chapter summarises the results obtained from the selected studies to derive transferfunctions for heavy metal partitioning. The study of Tipping et al. (2003) is based on a dataset containing organic rich upland soils from England and Wales, further referred to as the UK-dataset. Transferfunctions derived by Römkens et al. (2003) are based on a dataset containing different types of soils (sand, clay and peat) from the Netherlands, further referred to as the Dutch dataset. The study of Pampura et al. (2002) contains mainly sandy and organic rich soils from Germany, further referred to as the German dataset. Appendices 2,3 and 4 give a more detailed description of the studies involved.

For the UK-dataset complexation of Cd and Pb were calculated with WHAM (Tipping et al. 1992) and WHAM/Model VI (Tipping, 1998). Both speciation models gave similar results. Here only the results based on calculations with WHAM/Model VI are presented. Speciation calculations for the Dutch and German dataset were calculated with CHARON (de Rooij and Kroot, 1991) and EPIDIM respectively. For the complexation of Cd and PB with DOC a simple diprotic model was used (Bril, 1995 and Römkens, 1998).

4.2.4.1 Results direct approach (C-Q and a-Q)

To be able to compare the derived relations from the different datasets as described by Tipping et al. (2002) and Römkens et al. (2003), all regression results are presented in accordance with the regression functions given below (Eq. 12 and 13). Furthermore constants were back calculated to the same units i.e. concentrations and activities in soil solution in mol.L^{-1}, reactive metal contents in the solid phase in mol.kg^{-1} , DOC in mg.L^{-1}, SOM and clay in weight percentages.

$$\log[C_{Me}] = a + b\cdot\log[\%OM] + c\cdot\log[\%clay] + d\cdot pH + e\cdot\log[DOC] + m\cdot\log[Q_{Me}] \quad (12)$$

and in the case of activities as:

$$\log[a_{Me}] = a + b\cdot\cdot\log[\%OM] + c\cdot\cdot\log[\%clay] + d\cdot pH + m\cdot\log[Q_{Me}] \quad (13)$$

UK-dataset

Table 9 values for the regression coefficients for a C-Q relationship and statistical measures R² and se(Y)

	a	b	c	d	e	m		
Metal		*%OM*	*clay*	*pH*	DOC	$Q_{Me,HNO3}$	se(Y)	R^2
Cd	-2.65	-0.61	-	-0.20	0.28	0.78	-	0.55
Pb	-3.90	-0.47	-	-0.20	0.79	0.89	-	0.81

Table 10 values for the regression coefficients for an a-Q relationship and statistical measures R² and se(Y) using model VI

	a	b	c	d	m		
Metal		*%OM*	*%clay*	*pH*	$Q_{Me, HNO3}$	se(Y)	R^2
Cd	-0.28	-0.69	-	-0.42	0.97	0.36	0.76
Pb	0.90	-0.53	-	-1.14	0.87	0.45	0.95

Dutch data set

Table 11 values for the regression coefficients for a C-Q relationship and statistical measures R² and se(Y)

	a	b	c	d	e	m		
Metal		*(SOM)*	*(clay)*	*(pH)*	DOC	(Q)	se(Y)	R^2
Cd	1.91	-0.73	-0.48	-0.39	0.08	1.27	0.53	0.67
	2.05	-0.69	-0.48	-0.40	-	1.26	0.54	0.67
Pb	*	-0.75	-0.33	-0.21	0.33	0.72	0.63	0.50
	-2.49	-0.54	-0.30	-0.26	-	0.70	0.65	0.48

* not significant

Table 12 values for the regression coefficients for an a-Q relationship and statistical measures R² and se(Y)

	a	b	c	d	m		
Metal		*(SOM)*	*(clay)*	*(pH)*	(Q)	se(Y)	R^2
Cd	2.27	-0.87	-0.42	-0.46	1.31	0.53	0.70
Pb	-1.33	-0.90	-0.23	-0.70	0.68	0.62	0.78

*Note: It is crucial to use proper units in the above given equations. First the molar reactive concentration has to be derived from concentrations that are generally given in mg.kg^{-1}, by first dividing them by 1000 and then dividing them by the molar weight of Cd (112.4) or Pb (207.2). The resulting metal concentration in solution in mol.L^{-1} has to be multiplied by 10^6 and then by the molar weight of Cd or Pb to get the concentration in mg.m-3 used in the critical load calculations.

German dataset

Q in $mol.kg^{-1}$, C and a_{Me} in $mol.L^{-1}$,DOC in $mol.L^{-1}$, SOM and clay in weight %

Table 13 values for the regression coefficients for a C-Q relationship and statistical measures R^2 and se(Y)

	a	*b*	*c*	*d*	e	m		
Metal		*(SOM)*	*(clay)*	*(pH)*	DOC	(Q)	se(Y)	R^2
Cd	-6.59	-	-	-	-	0.19	0.30	0.17
	-11.36	0.46	0.05	-0.38	-	-0.72	0.18	0.75
	-14.82	0.42	-0.15	-0.39	-0.99	-0.86	0.13	0.86
Pb	-3.46	-	-	-	-	0.67		0.86
	-5.19	0.42	-	-0.30	-	0.19	0.21	0.94
	-1.54	0.21	-	-0.15	1.20	0.29	0.13	0.98

Table 14 values for the regression coefficients for an a-Q relationship and statistical measures R^2 and se(Y)

	a	*b*	*c*	*d*	m		
Metal		*(SOM)*	*(clay)*	*(pH)*	(Q)	se(Y)	R^2
Cd	-5.13	-	-	-	0.52	0.65	0.26
	-13.31	0.54	-	-0.74	-1.14	0.48	0.64
Pb	-0.81	-	-	-	1.57	1.02	0.76
	-6.55	1.03	-	-1.40	-0.43	0.31	0.98

The results for the Q-C and Q-a approach for the UK and Dutch dataset are consistent with each other. Of the three datasets these are the most similar. Reactive metal is extracted in both cases with 0.43 $Mol.L^{-1}$ HNO_3 and the explaining variables pH and organic matter (as determined by loss on ignition) and DOC in the case of Q-C are the same. The Dutch regression functions have 1 explaining variable extra, the clay content. For all derived functions there are positive correlations between C and Q and C and DOC (for C-Q) and negative correlations between C and SOM and C and pH. These results are also consistent with expectations.

The coefficients for DOC are larger for the UK dataset than for the Dutch dataset especially for Cd. Coefficients for SOM are in the same order. The Dutch C-Q relations show a stronger relation between C and pH. The coefficients for Q are clearly different especially for Cd. For both datasets the explained variance (R^2) increases when accounting for solution speciation as is the case in the derivation of a-Q relations. Both sets of transferfunctions will be validated on data from each other. If possible the datasets will be combined to derive a general transferfunction for the combined dataset. A possible problem is that for the UK dataset no clay contents are available which may be needed to describe partitioning in mineral soils.

The results of the German dataset show a positive correlation between concentrations in soil solution and the NH_4NO_3-extractable metal content if $Q_{Me,NH4}$ is the only variable considered. For Pb this gives meaningful relations, for Cd the relation is not significant (see Tables 13 and 14). When soil properties like organic matter content and pH are included in the relation unexpected coefficients were found. For both Cd and Pb the concentration is negatively correlated with Q_{NH4} and positively with OM, as one would expect it just the other way around. This ‘unexpected’ behaviour is the result of the fact that NH_4NO_3 is a weak extractant which only extracts part of the reactive metal content. Soil properties like organic matter content and pH together with the magnitude of the extracted content itself influence the fraction of the metal content extracted ranging from a minimum of 0.1% for Pb and 2% for Cd to a maximum of 20% for Pb and 80% for Cd (Pampura, data presented at expert meeting Berlin Dec. 2002). The negative correlation of C with pH is consistent with the other results and as expected. Transferfunctions based on weak extractions like NH_4NO_3 can be used well to calculate solution concentrations from available data on NH_4NO_3 extracted metal contents. Although inclusion of soil properties like organic matter content and pH improves the explained variance it also brings about danger for erroneous use. Use of these relations in combination with regression relations for the relation between aqua regia and NH_4NO_3 extractable contents such as those derived by Prinz and

Bachmann (1999) gives a negative correlation between concentrations in soil solution and aqua regia extracted metal contents. Such a negative correlation is physically impossible.

4.2.4.2 Results indirect approach (K_F and K_D)

For the UK and Dutch dataset also relations between adsorption constants and soil properties were derived. Tipping et al. (2003) derived relations using the K_D approach for solution data including speciation. Römkens et al. (2003) derived relations using the K_f approach for both total concentrations in solution and free metal ion activities.

UK-dataset

Table 15 values for the regression coefficients for a Kd relationship and statistical measures R^2 and se(Y), speciation calculated with model VI

	a	*b*	*c*	*d*		
Metal		*(SOM)*	*(clay)*	*(pH)*	se(Y)	R^2
Cd	-5.93	0.71	-	0.43	-	0.73
Pb	-7.36	0.60	-	1.13	-	0.94

The $K_{D,a}$ relations for the different speciation models show some differences between the derived regression coefficients between SOM and pH.

Dutch dataset

Table 16 values for the regression coefficients for a $K_{F,C}$ relationship and statistical measures R^2 and se(Y)

	a	*b*	*c*	*d*	e	n_{opy}		
Metal		*(SOM)*	*(clay)*	*(pH)*	DOC	(Q)	se(Y)	R^2
Cd	-6.37	0.61	0.29	0.26	-0.05	0.54	0.33	0.80
	-6.47	0.58	0.28	0.27	-	0.54	0.33	0.79
Pb	-4.57	0.95	0.07	0.22	-0.23	0.73	0.55	0.59
	-5.00	0.83	0.02	0.25	-	0.68	0.55	0.57

Table 17 values for the regression coefficients for a $K_{F,a}$ relationship and statistical measures R^2 and se(Y)

	a	*b*	*c*	*d*	n_{opy}		
Metal		*(SOM)*	*(clay)*	*(pH)*	(Q)	se(Y)	R^2
Cd	-4.76	0.66	0.25	0.29	0.55	0.32	0.83
Pb	-3.28	1.19	0.12	0.74	1.00	0.65	0.82

The explained variance of the transferfunctions increases when accounting for solution speciation especially for Pb as was the case for the c-Q and a-Q relation. The role of the pH increases clearly when using solution speciation. The use of DOC in the $K_{F,C}$ relation does not improve the explained variance largely.

The regression functions of $K_{F,a}$ for Cd and Pb have about the same explained variance (R^2). The standard error of the estimate (se(Y)) is however two times as high for Pb as it is for Cd. This shows that estimates for Pb will be much more uncertain than those for Cd. It is therefore recommended to include the standard error of the Y-estimate when presenting the results of regression analysis to make it possible to evaluate the uncertainty.

The results for Pb for the $K_{F,a}$ transferfunctions from the Dutch dataset can be compared with the $K_{D,a}$ transferfunctions for the UK-dataset since the Freundlich constant equals 1. The regression coefficients show a stronger response for pH for the UK-dataset. Solution speciation is calculated with different models for the complexation of metals with DOC. It would be interesting to evaluate the influence of the used speciation model.

4.2.5 DISCUSSION AND CONCLUSIONS

Extraction techniques

The extractions with 0.43 Mol.L^{-1} HNO_3 and EDTA compare reasonably well. Regression functions can be used to calculate the extracted amounts from one to another. The extraction with 0.43 Mol.L^{-1} HNO_3 as a measure for the reactive metal content gives consistent and meaningful results when used in the derivation of transferfunctions, both for the direct approach (C-Q and a-Q) as well for the K_F-approach.
Regression functions are available to calculate the reactive metal content from total (perchloric acids) and 'so called total' metal contents (aqua regia) if needed. In case only total contents are available from total destruction with HF, regression functions can be used to calculate first the 'so called' total metal content (aqua regia) and secondly the reactive metal content. The introduction of additional uncertainty with the use of one ore more of these relations should be evaluated.

Transferfunctions for the partitioning of heavy metals should preferably be based on partitioning studies in which the metal content in the solid phase is a measure for the total reactive metal content in soil. Total and 'so called total' metal contents include a pool of metals that is not available for exchange with the soil solution. When transferfunctions for partitioning are used to derive critical limits based on (free ion) concentrations of metals in solution from existing ecotoxicological data, the reactive metal content in the transferfunction should reflect the added metal content. To be able to perform dynamic calculations the metal content in the transferfunction should be based on a total reactive metal content to allow proper mass balance calculations. Unpublished results (Pampura and Groenenberg) show a good recovery (>80%) of added Cu by EDTA in adsorption experiments. The extraction with NH_4NO_3 seems too weak as a measure for the total reactive metal content. Only a small fraction (could be less than 1%) of adsorbed Pb could be recovered with this extraction (Pampura et al., 2002). The use of relations with extractions which extract only a part of the reactive metal pool is restricted. Such relations may however be useful in case large (geographical) databases based on such extractions exist to compare calculated critical loads with the present situation.

Type of partition relation to be used

Because Kf-and K-d relations can be used in both directions to calculate C from Q and Q from C these relations are preferred compared to C-Q relations. K_F relations are preferred above K_D relations as the partitioning of metals is not expected to be linear. However if the Freundlich coefficient is 1 ore close to 1 (such is the case for Pb) there is no difference between both approaches.

The derived partition relations which take into account solution speciation (a-Q , $K_{F,a}$ and $K_{D,a}$ relations) have a higher explained variance than relations based on total solution concentrations, therefore relations which account for solution speciation are preferred. Furthermore relations based on total concentration in solution seem to be highly dependent on the extraction technique used to sample soil solution. This was shown by Pampura et al (2002) in which data from diluted salt extractions at high water to soil ratios where compared with extracts from saturated soils both in terms of concentrations and free metal activities. Total concentrations were clearly different for both methods whereas activities calculated from total concentrations and solution speciation showed much better agreement.
In case one is interested in the total concentration in solution, e.g. when calculating leaching, there are two possibilities. Total concentrations are calculated direct from transferfunctions based on total concentrations or first free metal ion concentrations are calculated and from these free metal ion concentrations and solution speciation total metal concentrations in soil solution are calculated (pathways using relations 3 and 6 in Figure 1). The first approach can only be used if the solution extraction used in the derivation of the transferfunction resembles solution concentrations one is interested in. The second approach depends on the availability or on the reliability of estimates on data needed in speciation calculations (especially data on DOC concentrations).

Uncertainties

For the Dutch dataset an initial excercition was carried out to determine the uncertainty of the regression functions determined. To be able to calculate the confidence interval for the predicted solution concentrations and the contribution of the derived regression coefficients to this uncertainty and the contribution of the unexplained variance both the unexplained variance and the standard error in the regressed parameters and the correlation between those parameters were determined.

Analysis with a Monte Carlo method revealed that the unexplained variance of the regression accounts (almost) completely for the variance of the prediction. This means that results for predictions can not be improved by better estimates of the regression coefficients and it will not help to extend this dataset with more observations to get more reliable results.
The uncertainty can now be easily presented by the 95% confidence interval as calculated from the unexplained variance (Se_Y)

Figures 6 and 7 shows the confidence intervals for predictions with a Dutch C-Q relations an UK a-Q relation respectively.

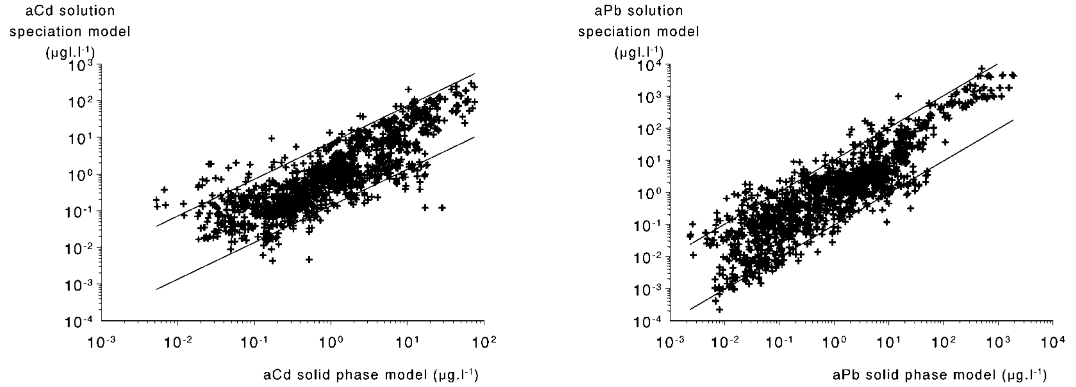

Figure 6 Comparison of metal concentrations of Cd an Pb calculated with the Dutch C-Q transferfunctions and measured concentrations

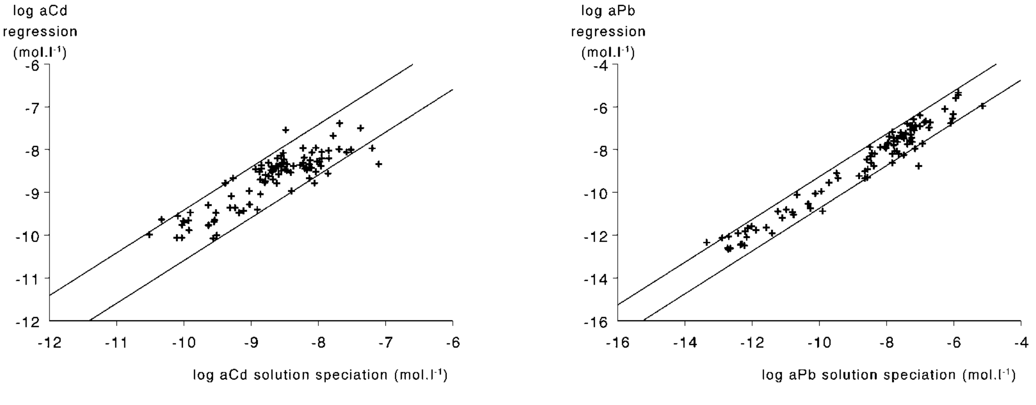

Figure 7 Comparison of metal activities of Cd an Pb calculated with the UK a-Q transferfunctions (table ..)and activities calculated from soil solution speciation (Model VI)

Comparison of the results of the datasets can give information on how well these regression functions work. Validation of the 'Dutch' transferfunctions on data from UK (and later Russia) can give information on how this very general transferfunction applies to soils from different countries. Validation of the 'UK transferfunction' on the Dutch dataset or a subset with only organic rich soils can give info on the use of separate transferfunctions derived for a special group of soil types.

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Annex 1 Explanation of used symbols

symbol	explanation
$M_{Me,HF}$	Total concentration of metal Me in solid phase extracted with HF
$M_{Me, AR}$	"so called total" metal concentration in the solid phase extracted with Aqua Regia
$Q_{Me,HNO3/EDTA}$	Total chemical reactive metal concentration in the solid phase extracted with HNO3 or EDTA
$Q_{Me,NH4}$	Exchangeable metal content extracted with NH_4NO_3
C_{Me}	Total concentration of metal Me in soil solution
a_{Me}	Activity of free metal ion Me in soil solution
$K_{f,C}$	Freundlich constant for total solution concentrations
$K_{f,a}$	Freundlich constant for speciated metal concentrations
$K_{D,a}$	Linear partition constant for speciated metal concentrations

Annex 2 Dutch dataset (Römkens et al., 2003)

Data used to derive partition relations

Two data-sets that contained respectively 49 and 65 different soil samples were used. The first data-set of 49 samples contains samples form both unpolluted and polluted (top)soils and have been described in detail previously (e.g. De Groot et al., 1998). From each soil sample, 1:2 soil solution extracts were obtained using different extractants (like 0.01 M and 0.002 M $CaCl_2$, 0.1 M $NaNO_3$). The 1:2 soil:solution ratio was chosen to obtain conditions that are somewhat closer to reality compared to extracts obtained at 1:10 ratios or more.

The second data-set contains 65 different samples that originate from 11 distinctly different soil profiles. This database contains soils samples from the topsoil down the parent material. The reason for doing so is that information on the behaviour of metals in soil layers other that the topsoil are still scarce. From each of the 65 samples, both a 0.01 M and a 0.002 M $CaCl_2$ extract was made a ratio of 1:2. This was done at three pH levels, the natural soil pH and two more acid levels obtaining a range in pH that occurs in reality as well (between 3 and 7 to 8). When referring to the pH, the pH measured in the final extract is used, not pH soil.

In this study the 0.43 N HNO_3 extractable metal content was used as an estimate of the total reactive metal content. In many cases the Aqua Regia or even HF extractable metal content is used to derive partition relationships but this is incorrect since a part of the metal present in the strong acid destruction is not available but included in clay or mineral crystal structures. Especially in soil with a low metal content, a substantial part of the metals is not chemically reactive and therefore does not contribute to the dissolved metal concentration.

The final database containing all extracts from the two data-sets mentioned here contains a total of 1466 complete records (both solid phase and solution composition)

Data used to derive relations between so called total and reactive metal contents

A database has been used that contains approx. 630 records where both the Aqua Regia and 0.43 N HNO_3 extractable metal content was determined aside from soil properties like organic matter, clay and pH-KCl. In table 1 a short overview of the main soil characteristics are given as well as the range in the Aqua Regia and 0.43 N HNO_3 metal content. The data originate from different inventories and studies:

1. a national inventory on the quality of non-polluted arable soil (312 records);
2. an inventory on floodplain soils (200 records, both contaminated and non-contaminated soils);
3. two smaller studies (resp. 49 and 69 records) on Dutch soils where both samples from the top soil as well as deeper soil layers were included from arable soils and samples taken in natural areas (forest, grassland).

Table 1. Soil properties in database used to derive total - reactive partition relationships

	pH-KCl	SOM %	Clay %	Cdst1 mg.kg^{-1}	Cdre2 mg.kg^{-1}	Cust1 mg.kg^{-1}	Cure2 mg.kg^{-1}
min	2.4	0.4	0.2	0.08	<0.02	0.63	0.25
max	7.8	73.4	55.0	37.0	19.9	326.0	309.8
median	6.5	4.0	12.2	0.60	0.47	24.0	12.1
	pH-KCl	SOM %	Clay %	Pbst1 mg.kg^{-1}	Pbre2 mg.kg^{-1}	Znst1 mg.kg^{-1}	Znre2 mg.kg^{-1}
min	2.4	0.3	0.2	3.96	1.21	1.56	0.34
max	7.8	73.4	55.0	1646.0	1536.2	3118	2764
median	6.1	4.2	13.7	37.0	23.9	165.1	74.2

[1]: So-called total concentration: here Aqua Regia

[2]: Reactive concentration: here 0.43 N HNO_3 extractable

Annex 3 **UK dataset (Tipping et al. 2003)**

Soil sampling

Sampling of the soils focused on organic rich soils from the uplands of England and Wales**.** These soils have accumulated heavy metals from atmospheric deposition, both long-distance and localised, and in some cases also from the weathering of soil mineral matter. Measurements were made of key soil parameters, including heavy metal contents, together with soil solution compositions. The resulting data set (98 samples) covers wide ranges of conditions, enabling speciation and regression analyses to be performed to identify the factors responsible for solid-solution partitioning, and to attempt to predict free metal ion concentrations.

Samples of surface soil (0-5 cm) were collected from upland moorland sites at Dartmoor, the English Lake District, North Wales, the Peak District, and the Yorkshire Dales (Fig. 1). They were from the following soil types: brown earth, humic brown podzol, humic ranker, peat, peaty gley, podzol, shallow loam, stagnohumic gley, stagnopodzol. In each case, a block of intact soil, of approximate area 14 cm^2, was encased in an air-tight container and placed immediately into cold storage in preparation for extraction of soil porewater. . A separate quantity (100-200 g) of soil was collected in preparation for analysis of total and extractable metals and soil properties.

Soil analysis

Determinations were made of soil water content, by oven drying, and of loss-on-ignition (LOI). "Total" soil metal contents were determined by digestion with a mixture of concentrated nitric and perchloric acids, followed by leaching of the residues with 5 mol L^{-1} HCl, and analysis by ICP-AES. Extractions with 0.43 mol L^{-1} HNO_3 were performed at a ratio of 1 g air dried soil (2 mm sieved) to 10 cm^3 of extractant. After extraction for 2 h, the samples were centrifuged, 5 cm^3 of the supernatant were removed to separate tubes and 0.5 cm^3 of 5 mol L^{-1} HCl was added prior to analysis by ICP-AES. Extractions with 0.1 mol L^{-1} Na_2EDTA (ethylenedinitrolotetraacetate) were also made at a ratio of 1 g to 10 cm^3. The supernatants after centrifugation were digested with concentrated nitric and perchloric acids, as for the "total" soil metal determinations, prior to ICP-AES analysis, in order to remove the EDTA.

Solution extraction and analysis

Water was added to soil samples to bring them to field capacity. After about one week of equilibration the soil solution was sampled with rhizon moisture samplers. The soil solution was analysed for pH, DOC and metal concentrations (after passing a 0.2 um filter with ICP-MS).

Annex 4 **German dataset (Pampura et al. 2002)**

Soil sampling

Eleven soil samples with different properties were collected from 4 sampling sites in Germany (Hessen)

Gley Braunerde (Of/Oh, Aeh, Bhv, Bv), Mörfelden;
Niedermoor (0-10 cm, 10 –30 cm), Gernsheim;
Pararendzina from Loess (0-10cm, 30-60cm), Heppenheim;
Braunerde (Of/Oh, Ah, Bv), Königstein;

Soil analyses

The main soil characteristics as cation exchange capacity (CEC), organic carbon (C_{org}), clay, Fe and Mn oxides content, pH were determined by standard methods. The set of samples provides very big variability in soil characteristics responsible for metal binding and retention by soil

SOM (%)	1.61	-	76.6
PH	3.6	-	7.8
Clay (%)	0	-	12.4
CEC effct. (mmol/100g)	16.4	-	110.4
CEC potent.(mmol/100g)	23.2	-	317.6
WHC (g/100g air dry soil)	24.95	-	172.7

Field partitioning (DC)

Cadmium and lead field partitioning as a function of main soil characteristics (for 11 soil samples, all triplicate) was studied. The experimental procedure involved the following steps:

Water holding capacity (WHC) was determined for triplicate samples in plastic tubes as described in (Referenzmethoden, 1998).

Soil samples were kept at 100 % WHC overnight.

After staying overnight, soil and solution were separated by centrifuging at 5000 rpm in the special double bottom centrifuge tubes. The pH in supernatant was measured immediately after centrifuging. After that, solutions were filtered via 0.45 µm cellulose-nitrate membrane filters.

Filtrates were analyzed for Pb, Cd and main cations and anions including dissolved organic carbon (DOC) (see below).

The reactive metal content in soil after separation of supernatant was determined using 1M NH_4NO_3 extraction (DIN 19730).

Data on soil solution composition were used for metal activity calculation using geochemical speciation program EPIDIM (Groenendijk, 1995)

Analytical methods

Metal (Pb and Cd) concentrations in the initial and final solutions were analyzed by Atomic Absorption Spectrometer with graphite furnace system GFAAS (Perkin Elmer 2100 AAS). Concentration of Ca, Mg, Fe, Mn, K, Na, Al, S, P in solutions were determined by ICP-OES (Perkin Elmer, Optima-3200DV). Dissolved organic carbon (DOC), inorganic carbon and total N content in solutions was determined using TOC/TN analyzer (Analyticjena AG multi N/C 3000), SO_4, NO_3 and Cl concentrations were determined by ion chromatography (Dionex DX 100).

The “reactive” pool of metal adsorbed by soil samples during adsorption experiments was determined with 1M NH_4NO_3 extraction (DIN 19730). As a result not only adsorption, but also “desorption” (‘reactive” metal content in soil vs. concentrations (activity) in soil solution) isotherms were obtained.

Multiple linear regression analysis were used to derive transfer function connecting amount of metal adsorbed (or “reactive” metal content in soil) and metal concentration in soil solution, pH of soil solution, and main soil characteristics as CEC effective, organic matter, clay, oxides content.

4.3 GENERAL METHODOLOGY

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BACKGROUND DOCUMENT
FOR THE

EXPERT MEETING ON CRITICAL LIMITS FOR HEAVY METALS AND METHODS FOR THEIR APPLICATION

BERLIN, 2-4 DECEMBER 2002

held under the
UN-ECE Convention on Long range Transboundary Air Pollution

4.3.1 INTRODUCTION

The elaboration and harmonisation of Critical Limits for heavy metals is the main mandate of the international *ad hoc* expert group under the UNECE Task Force on ICP Modelling and Mapping. However a more in-depth discussion about the methodologies for using those Critical Limits turned out to be necessary, too : How should we use the effect-based critical limits and their related critical loads ? Should we consider geogenic inputs and other inputs than atmospheric ones ? Indeed we have to design the methodology itself more precisely, keeping in mind the conclusions of the 2001 and 2002 session of the Working Group of Effects. The present background paper makes suggestions in this respect, which are to be completed by the full conclusions of the Berlin meeting of the *ad hoc* expert group in December 2002. Some conclusions are illustrated through a "decision tree" –here annexed– which is inspired from the document that was adopted by the ICP Modelling and Mapping in 2002. It shows that the effect-based critical load should be considered as a part of a continuum and that its calculation by National Focal Centres is not independent from its possible later use within Integrated Assessment Modelling.

4.3.2 DEFINITIONS :

Biocenosis :
It is the complex of all organisms connected with a determined biotope (= habitat), with functional links.

Ecosystem :
It is the association of a biotope and the corresponding biocenosis.

Adverse Effect :
Any biochemical change, functional impairment, or pathologic lesion which impairs performance and reduces the ability of an organism to respond to additional challenge. An adverse effect may have different degrees of severity. In the present context we consider chronic effects due to a long-time exposure to one pollutant (metal).

Endpoint :
Endpoint is the parameter that is measured in a toxicity test and that characterises an effect (i.e. reproduction, shoot growth, survival, mobility…)

Target :
In this context, the living element of the environment that is subject to an adverse effect (we could also call it receptor). The target can be a given species of interest (e.g. Scott pine; *E.Coli*, etc), or it can cover several species considered representative of a larger group (e.g. plants, soil invertebrates, fish, algae, etc). The whole ecosystem is typically the subject of interest in the Critical Load approach and may therefore also be considered as a target (see part 4.1).

Exposure route :
It is the route of entry of a pollutant to the organism (e.g. ingestion, inhalation, diffusion via skin,…). It therefore corresponds to a given compartment of the environment (e.g. air, soil solution,…). Several exposure routes may contribute to the same effect for the same target.

In the present context we will call indirect effect an effect which entails a food chain before the pollutant enters the organism. In this case, we can also specify a pathway (e.g; soil-worm-bird, or soil solution - plant - cattle)

Critical Limit (Clim) *= Critical Concentration :*
To avoid confusion, only limits that are based on effects should be called "critical limits", as a short expression of "effect-based critical limit".

A critical limit is a concentration threshold within the ecosystem, based on adverse effects : below this Clim significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge.

Before a more detailed discussion in paragraph 4 here-after, it is useful to specify here that :
- the underlying assumption is that these "sensitive elements of the environment" (or target) have been specified before – which means that a critical limit somehow reflects a biological model.
- in principle a Clim may be given for any of the compartments of the ecosystem.

Critical level :
It is an atmospheric concentration, defined in the 1999 Multi-effect Protocol as follows : "mean concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as human beings, plants, ecosystems or materials, may occur, according to present knowledge";

This definition does not apply to metals, but it is interesting to note that the effects on human beings are added in this definition. This is of importance for the work of the *ad hoc* expert group on heavy metals, which was asked by the ICP Modelling and Mapping to include human health in its work.

Critical Load (CLO) :
It represents the deposition rate below which harmful effects will not occur at the site of interest in a long-term perspective. In this context, it is the total metal input which causes the concentration within the ecosystem to be equal to the Clim, when the ecosystem is at equilibrium – which is a theoretical situation in an undetermined future. The CLO is usually derived from the Clim through a flux model applied to this location, assuming steady-state for the fluxes as well as chemical equilibrium.

The Critical Load is an indicator for the level of sensitivity of the ecosystem. The lower the CLO, the more sensitive the ecosystem at the site of interest.
In principle, only the atmospheric deposition is the goal of the management strategy given by the Critical Load approach.

In principle, a Critical Load may also be derived empirically, directly from measurements of deposition combined with observations of the extent of impacts. However such an approach has not been proposed for metals.

Present Load (PL) :
It is the present total input, either measured or calculated by an model. For forest and natural ecosystems the present load is generally equal to the atmospheric load.

***Exceedance** :*
It is the difference between the Present Load and the Critical Load. There is no Exceedance if the Present Load is inferior to the Critical Load. The Exceedance is therefore assumed to be null or positive. If it is positive, it means that future damage is foreseen at the site of interest.

The Exceedance is an indicator of the probability of harmful effect. There is no direct proportionality between the extent of damages and the value of the Exceedance (nor the value of the CLO). However, in order to carry out Integrated Assessment strategies, the RAINS model needs a quantitative estimate and therefore uses the "Accumulated Exceedance" as a surrogate for quantifying the effects : this "accumulated Exceedance" is calculated in an EMEP grid cell (50km x 50 km) by summing the individual Exceedances of each ecosystem, weighted by the surface of the ecosystem.

Stand-still Load (SL) :
It is the atmospheric deposition flux corresponding to the stand-still principle, which means that no further increase of metal concentration in the ecosystem is accepted. The present total metal concentration in the soil is considered the limit. One should note that :
1°) the Stand-still load SL has nothing in common with the Present Load PL.
2°) Stand-still is a very particular case of steady-state at present concentration. The calculation of the Critical Load CLO assumes steady-state (in the future) but not stand-still.

Dynamic or semi-dynamic approaches were also suggested. They require generally more calculations and inputs. They differ fundamentally from the concept of Critical Load and from the approaches here above because they do not assume steady-state. They are not considered here, only their principles are reminded for clarification : For instance in the case when the system is already damaged (present concentration superior to Clim), a Target Time TT for recovery may be chosen, and the corresponding Target Load (TL) is then calculated, corresponding to a decrease of the concentration towards the Clim by this Target Time.[1]

4.3.3 NATURAL CONCENTRATION AND HISTORICAL HM INPUT

4.3.3.1 Concepts

Pedo-geogenic natural level :
What we usually call "natural concentration" is more accurately defined by the concept of pedo-geogenic natural level. This is the concentration of metal in the soil which is inherited from the parent material above which the soil has developed. Several processes have concurrently contributed in the past to the present " natural" distribution of HM in soils :

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

Background values :
In Germany background values are defined as follows: "background values are representative values for common background contents of a substance or a substance group in top soils. The background content of a topsoil is composed of the naturally caused (geogenic/pedogenic) content and the ubiquitous substance distribution as consequence of diffuse man-made substance inputs in soils."

Hence background values are in general superior to the natural concentration. This definition is similar to the ISO/11074 proposal for a norm on soil quality. Some French experts prefer the denomination of "usual concentration" (in order to avoid any confusion with the background noise used for an signal analysis) but with a similar meaning.

Necessity to determine the natural concentration :
Let us take the example of a location where present concentration is superior to Clim. This may reflect either a cumulative deposition of anthropogenic sources (agriculture, atmospheric deposition), or natural (pedo-geogenic) high levels. In the latter situation, it would be irrelevant to impose a decrease. The more logical management option in such a case is probably a strategy similar to Stand-still Load, not the Critical Load. Hence, to distinguish between natural and anthropogenic HM pools in the soil is a crucial point.

French and German data show that cases like (b) happen rather often for Pb, like in other countries probably : in “unpolluted” zones, we know that a large part of high background values are due to geogenic sources (e.g. for France around Massif Central - Baize 1997).

One should note that what is natural is not necessarily good : it has not been demonstrated that the metal part which is natural is less bio-available or toxic than anthropogenic inputs. However the biocenosis in those soils may be different and adapted (see “Different soil types”, above).

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[1] Theoretically it is also possible to define a Target Load when the present concentration is under the Clim (the Target Time will be when the present increasing concentration will reach the Clim). Yet, such an approach was already excluded by the 2002 session of the ICP Modelling and Mapping because it entails "filling up to the limit", and even going beyond it, in a certain time.

4.3.3.2 How to determine the natural level in soils

Isotopy :
There are 4 isotopes of Lead, only one being non radiogenic (^{204}Pb). Due to different formation of rocks each region has a proper signature, as well as each lead deposit which is exploited as a raw material. Diagrams of ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb or ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb enable to define different typical profiles : radiogenic natural lead, non-radiogenic lead from gasoline, industrial lead, etc. It is for example possible to determine the signature of Pb coming from leaded gasoline anywhere in the environment, due to a predominance of a few sources of raw material used as additives by the petroleum industry.

Till now Pb isotopes have been more employed for determining the origin of Pb contamination in Oceans, in the Arctic or Greenland, or for determining the origin of a water ressource (Kendall and McDonnell, 1998). Some studies are aiming at soils and soil catchments, especially at determining the natural/anthropogenic ratio at a local scale, but generally a limited number of samples is considered.

Emmanuel and Erel (2002) studied together with T.Paces and A.Veron soils from Czech Republic and France. Given that Czech atmospheric Pb signatures typically possess lower values for 206Pb/207Pb ratio, they showed that the Pb content in the soil was of predominantly natural origin but that a mixing clearly occurs towards the top of the profiles. They also showed that exchange of natural Pb by anthropogenic Pb is likely to have occurred in the French Mediterranean soils, even in the non-labile silicate fraction (but not in Czech soils).

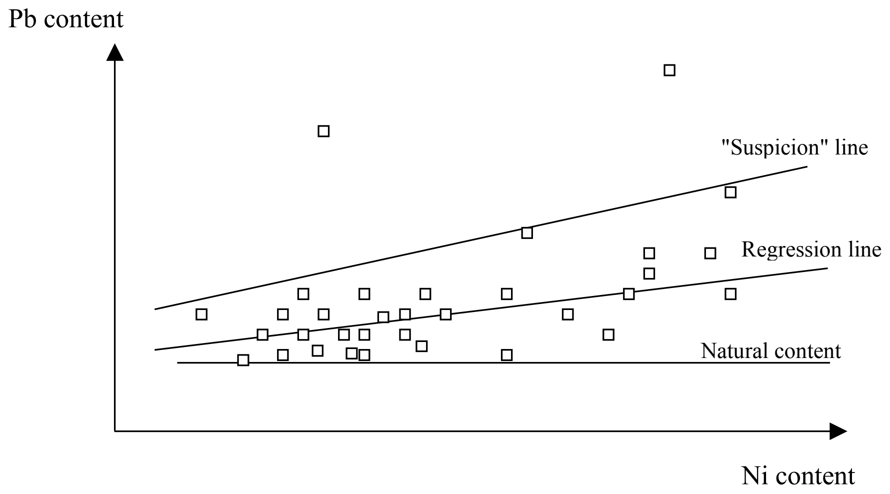
L.Hernandez, A.Probst and E.Ulrich studied several sites of the RENECOFOR network in France. The Pb isotopes allowed them to determine the anthropogenic share and they could show a significant enrichment in surface horizons for all the forested soils. They confirmed these data by the analysis of the Scandium element, as a tracer of the natural content.

Study of a family of soils :
The basic principle, exposed by Baize and Sterckeman, consists in analysing different sites with a similar land use and belonging to the same "family" of soils -i.e. same parent material, same morphology, etc. Then the analysis of diagrams (clouds of points) of HM content against Ni content or against granulometry can give a lot of information (see fig.1) :

1- Determine the "outlets" or suspicious points with higher content. These will most probably be sites with anthropogenic (local) contamination.
2- Determine a regression line from the plots (outlets excluded), hence giving a prediction of the background value for this family of soils.
3- Determine a baseline for the cloud : The weaker values are most probably very close to the (initial) natural pedo-geogenic level for this family of soils.

This method is valid for metals like Pb, Zn, Cu. However results obtained so far with Cd are more difficult to analyse, probably because of the higher mobility of this metal. The method is very applicable, although it requires a number of field measurements and of course a good knowledge of the region studied and its geology. Such data is now available for a French region (Nord-Pas-de-Calais), with mainly agricultural sites.

Fig. 1 Illustration of Pb vs Ni analysis in a series of soils. Inspired from Baize, 1997.



Weathering rates :
Various options have been suggested to calculate weathering rates, generally by scaling them to the base cation weathering, using the molar ratio of the total metal content and the total base cation content in parent material. The Mapping Manual (De Vries and Bakker, 1998), presents the model PROFILE from Sverdrup and Warfringe, 1992 and the equation from Vrubel and Paces, 1996. It also gives a brief overview of total content in the parent material for several soil types. However these models are designed to calculate a flux (weathering rate) but not the background content in soil, which derives from the integration of this weathering rate for ages -among others. For this purpose the models have to be completed by a mass-balance modelling using all fluxes with the assumption of background conditions -including atmospheric deposition, leaching, etc. This necessitates a similar calculation than a Critical Load modelling, hence the global level of knowledge is not really improved and depends mainly on the reliability of the mass-balance model.

Go back in the past :
The idea here is to sample a matrix which is likely to represent the concentration some hundreds or thousands of years ago. The best examples in the environment are probably 1°) sediments, the content of which is supposed to be linked with the concentration in water, and 2°) gases in the arctic snow, which can show the level of air contamination.

M. Meili suggests a method for estimating natural (historical) concentrations of mercury in soils, waters, and fish from present concentrations by means of compartment-specific and site-specific scaling factors accounting for the slow and non-linear response to changes in atmospheric pollution. Such scaling factors can be derived from concentration changes in lake sediments and their relationship with ecosystem properties (Meili et al. 2002).

Conclusions
The methods suggested here to determine the natural level may be not yet readily applicable for mapping at a large scale – the concepts of going back in the Past lead, and of studying of a family of soils (both under 4.3.3.2) are perhaps the more applicable but they are data-demanding. However, it is not in the mandate of the *ad hoc* expert group to recommend one particular method. In regions/zones where the natural levels are high the results of CLO calculation have to be handled with care (see 4.3.3.1). Therefore it is above all for such zones that it becomes necessary to know the natural level. In many cases the general location of such zones is known but the opportunity and feasibility of deriving a map at the European level has to be studied.

Generally speaking, any result/decision should be based not only on the pure CLO calculation but also on its further validation, for example by considering the knowledge of the site : geology and land use, natural concentration if possible, reliability of measurements if there are some, local history and history of anthropogenic inputs, etc. The "decision tree" (fig.3) illustrates this.

4.3.4 HOW TO USE PROPERLY THE EFFECT-BASED APPROACH

4.3.4.1. Description of various situations and management decisions

We have already described here above the particular case of a natural concentration being superior to the supposed critical concentration. Let us analyse 4 other cases, which are illustrated by the fig.2. Each case is illustrated by a diagram of the concentration against time, showing the Clim, the Present Concentration, and the evolution according to several options :

- A deposition equal to the CLO, given by the calculation at steady-state. Therefore the concentration will increase or decrease but will always become equal to Clim one day
- Two other deposition rates, assumed to be Present Loads (PL1 and PL2, or PL3 and PL4)
- A Stand-still load, allowing no increase of the concentration.

(a) If (Present Conc° > Clim) and (Present Load > CLO : Exceedance)
(bottom right diagram of fig.2)
It a rather obvious case, where present damage exists, and present load does not allow recovery. It has to be lowered to CLO.

(b) If (Present Conc° < Clim) and (Present Load > CLO : Exceedance)
(bottom left diagram of fig.2)
Future damage is foreseen even if the Clim is not reached yet. Modelling such a site is of great help for showing that emission reduction must occur, although no present damage is observed yet. Of course the CLO has to be considered as an objective.

A more stringent ("extremist" ?) option would be to consider the Stand-still Load SL as an objective, inferior to CLO, allowing no increase within the ecosystem. But this very specific option has not been considered yet in discussions, and this case is considered together with the (a) case, keeping CLO as an objective for both (see the bottom left of the final "decision tree" - fig.3)

(c) If (Present Conc° > Clim) and (Present Load < CLO)
(top right diagram of fig.2)
This case is somehow the contrary to the previous one. There is present damage (Present Conc° > Clim) but recovery is in progress because deposition is low. In this case, strictly speaking, the effect-based critical load (CLO) will not impose emission reduction, but the present load (PL1 or PL2) has to be maintained, since it is lower. This is still in line with the overall principles of the Critical Load approach.[1]

(d) If (Present Conc° < Clim) and (Present Load < CLO)
(top left diagram of fig.2)
At a first glance this case is very simple (no damage and no damage foreseen) but in fact it caused some rather fundamental discussions along 2002. Strictly speaking, the use of the Critical Load alone would lead to allowing inputs higher than today, since CLO is superior to Present Load PL1 or PL2 ! However, such a "permissive" conception means an increase of the concentration up to the Critical

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[1] We could even impose a stricter reduction by considering a Target Load as shown on the diagram (the same thing in (a) in fact), in order to reach the critical limit in a shorter time (target time) - which would be in line with the current dynamic approach for acidity. We have, however, to consider that such a constraint may result in a target load with a negative value, which is not helpful for emission reduction strategies… Moreover, it has been decided that dynamic options are still outside the scope of our activities.

Limit_("fill up to the Critical Limit"). This is not in line with the aims of the Convention on LRTAP nor the spirit of Critical Loads calculations, as the 2002 session of the Working Group on Effects confirmed, as well as the Executive Body. A first answer is therefore to consider the Present Load as the objective.

Now, let us consider the case where Present Load = PL2. In this case the Present Load causes no damage and does not fill up to the limit, but allows a slight increase all the same. A "restrictive" (or "extremist"?) conception would suggest to take the Stand-still Load SL instead as an objective, thus allowing no increase within the ecosystem. Is this desirable ? This very specific option has not been discussed yet. The diagram shows that, depending on the present status, the Stand-still Load SL may be more or less stringent than the Present Load (PL1 or PL2).

In the final decision tree (bottom right of fig.3) this case is considered together with (c), showing that the CLO itself should not be considered an objective.

4.3.4.2 Conclusions - The "decision tree"

We saw that in specific cases the effect-based approach is not feasible (e.g. in case of high natural level) and that in other cases the effect-based Critical Load is not always the right option to keep, even if it is necessary to calculate it as a first stage (see above). In some cases it is necessary to consider another option than the effect-based calculation, namely present load or stand-still load. The decision tree presented in fig.3 summarises the different situations presented here above in the form of an agreed methodology for choosing the appropriate option. Based on a proposal of Regis Farret to consider the current stage of pollution (in DeVries et al. 2002, Annex 2), it has been revised after in depth discussion during the 12th CCE Workshop, 15-17 May 2002 in Sorrento, as well as in the Expert Meeting, 2-4 December 2002 in Berlin.

At least the upper part of the decision tree is fully within the scope of the ad hoc expert group on heavy metals, and gathers what is around the simple mass-balance (SMB) method. The most upper part represents the calculation of the Critical Load CLO, starting from the Critical limit Clim. Just beside are briefly described the other models which results are also needed : deposition model (EMEP), fertiliser model, weathering model. While deposition and fertilizer model are needed for exeedance canculation, the wheathering model is part of the critical load. After getting this row of results a kind of "evaluation" is needed, before the CLO is used in the lower part of the tree : All sites where high geological (natural) contents of the heavy metal are the main reason for present concentration being higher than Critical Limit should be excluded from effect-based approaches.[2]

Similarly, the sites where other inputs than atmospheric deposition lead to present concentration being superior to the Clim, may deserve to be considered apart (the best example concerning heavy metals is inputs by fertilizers on agricultural soils). However this , but this is not a task for ICP Modelling and Mapping

Then the Exceedance is calculated and the lower part of the tree identifies two main options, the choice of which belongs primarily to Integrated Assessment activities. The relative situations are illustrated by diagrams and are briefly described here under (This description applies to soil ecosystems but its principles can be generalised).

1. If the Critical Load is exceeded by anthropogenic atmospheric inputs, these inputs should decrease until the Critical Load is reached (bottom left in the lower part of the tree). Doing so the concentration in the soil will either decrease to Critical Limit of will stay below the Critical Limit if it is already inferior.

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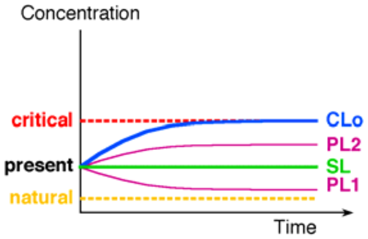
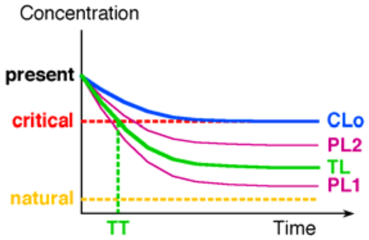
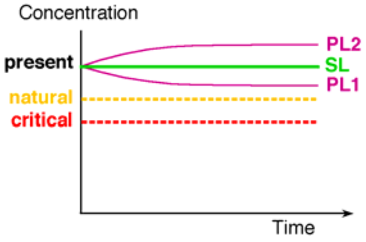
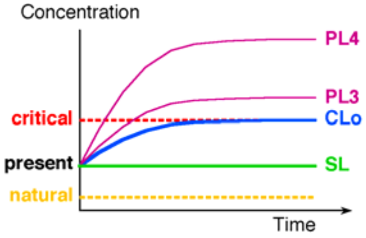
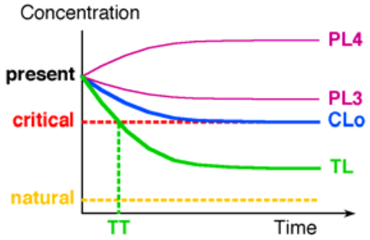
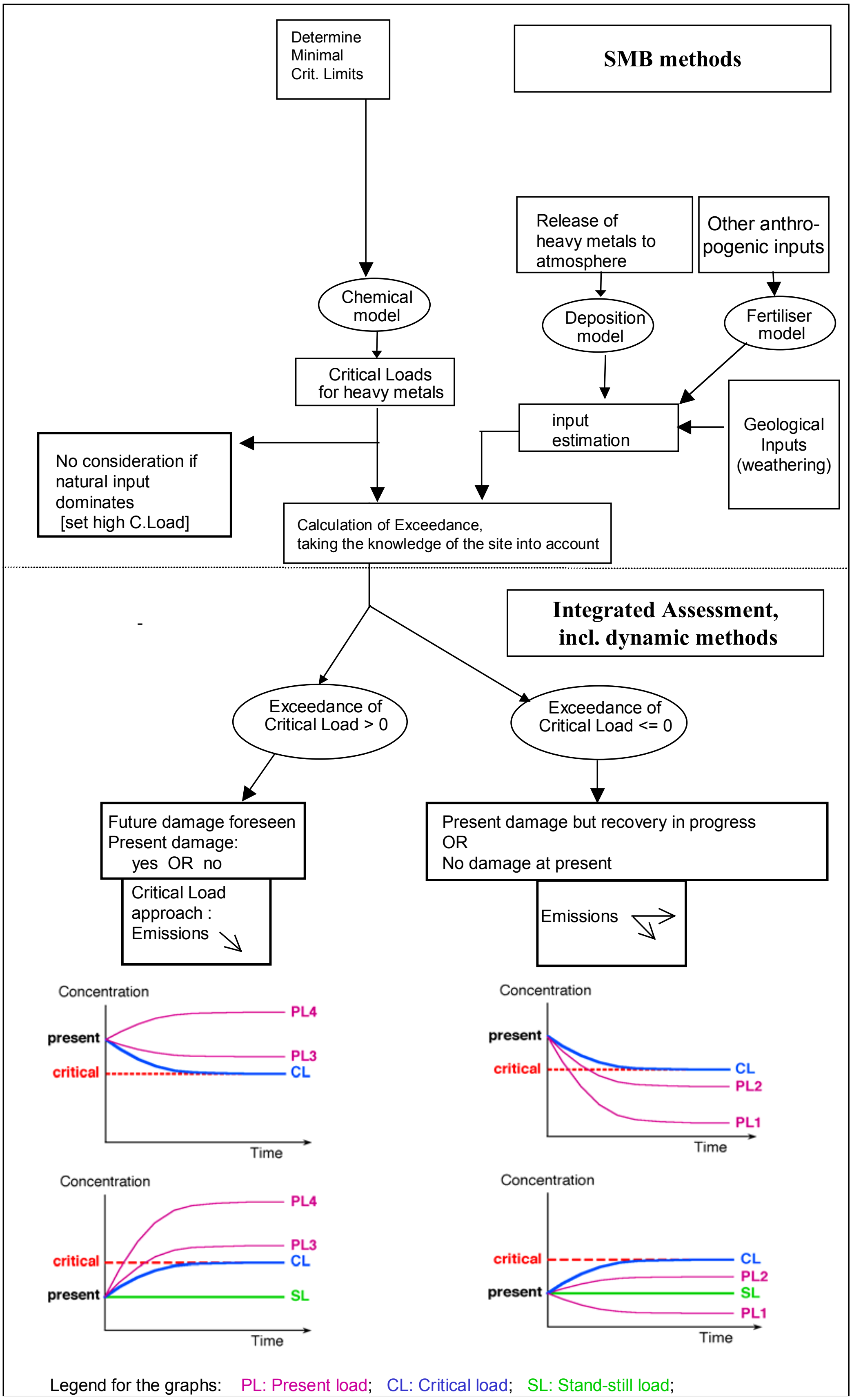
[2] A “stand still” approach is feasible, aiming at no further accumulation in the soil. However this appears to be a particular case of dynamic methods and this consideration belongs to the integrated assessment and not to the action of the NFCs.

Fig.2 DECISION TABLE considering PRESENT LOAD and PRESENT CONCENTRATION

	Present concentration < Critical limit	**Present concentration > Critical limit**	
		Anthropogenic	**Natural**
Present Load **< Critical Load** **(Exceedance < 0)**	**No damage at present or foreseen:**  ➔ Keep the Present Load (more stringent than Critical Load) or ➔ Consider Stand-still Load (i.e. an additional constraint to avoid increase of conc., more stringent than Critical Load)	**Present damage but recovery in progress:**  ➔ Keep the Present Load (more stringent than Critical Load) or ➔ Consider Target Load (more stringent than Critical Load)	 Effect-based Critical Load is not feasible ➔ Stand-still or similar
Present Load **> Critical Load** **(Exceedance > 0)**	**Future damage foreseen:**  ➔ Effect-based Critical Load (emissions must decrease, even if concentrations in the ecosystem are allowed to increase further) or ➔ Consider Stand-still Load (i.e. an additional constraint to avoid increase of conc., more stringent than Critical Load)	**Present damage, no recovery foreseen:**  ➔ Effect-based Critical Load (imposing a decrease of concentrations in the ecosystem) or ➔ Consider Target Load (more stringent than Critical Load)	

Legend for the graphs: PL: Present load; CLo: Critical load; SL: Stand-still load; TL: Target load; TT: Target time.

Fig.3 Decision Tree approved after the Berlin meeting



2. If the present inputs are lower than Critical Loads, the Critical Load should not be considered an objective (no exceedance, bottom right in the lower part of the tree). Either the Present Load or the Stand Still Load may be considered instead, depending on the integrated assessment options and the will to consider dynamic options or not. The concentration in the soil will either decrease to Critical Limit or will stay below Critical Limit, but in any case the concentration curve should be inferior to what the application CLO alone would allow.

The main conclusion is that the overall "critical load approach" appears to be wider than the calculation of the critical load itself. A continuity between the actions of the National Focal Centres, the Centre of Coordination for Effects and the Integrated Asssessment Modelling is needed.

4.3.5 HOW TO ADDRESS DIFFERENT TARGETS AND DIFFERENT PATHWAYS

4.3.5.1 The large influence of the choice of the target(s)

The different possible targets

We assume here that one effect corresponds to one given target, but may correspond to several exposure routes (see definitions in part 1). In principle, a Critical Limit (CLim) may aim at one of the following effects :

1. Ecotoxicology 1.1. direct effect on one species - or several species chosen as representative of a larger group (e.g. plants, soil invertebrates, fish, algae, etc)
    1.2. direct effect on the whole ecosystem
    1.3. indirect effect on higher consumers (food chain)
2. Human health (e.g. ground water, food chain)

Basically, the methodology of Critical Loads and Critical Limits was designed for 1.2 = direct effect for the whole ecosystem. According to ecotoxicological standards, a CLim for the whole ecosystem should be based on data from various ecotoxicological tests which have to represent the variability within the ecosystem and different trophic levels : Plants, invertebrates and microorganisms are classically chosen for soil ecosystem – at least fish, algae and crustacea for waters.

One should never forget that a Clim is always relying upon a biological model, which means 1°) (eco)toxicological data and 2°) a harmonised way of interpreting them and inter/extrapolate them through statistical analysis - both of them containing uncertainties of course -see background paper on Critical Limits. The reliability of these underlying ecotoxicological tests and their experimental conditions has to be checked carefully (see Farret, in De Vries et al, 2002)

It has been decided during year 2002 to address the other targets quoted here above, too. Concerning secondary poisoning through the food chain, the task may be more difficult and the data less reliable, both for ecosystem and human health (e.g: worm → mammal → bird, or soil → grass → meat or milk → human). Although their modelling includes more uncertainty, these effects are likely to give more stringent Clim, mainly because of biomagnification along the food chain –as it has already been demonstrated for Cd in the EU Risk Assessment report for example.

These issues are explained in more details in the background paper on critical limits.

Different compartments

Once the target is chosen, it may be contaminated by several exposure routes, which we can approximate by compartments C_j, $j \in [1;p]$ (or phases): e.g. soil matrix, soil solution, water, food (grain or plant content), etc. To take into account several routes would be a rather fundamental evolution of the concept of Critical Limits and Loads (see 4.2)

Practically, for soil ecosystems the two basic "compartments" of interest will mainly be soil matrix and soil solution, for which critical limits may be defined. All definitions and principles described in the previous chapters, including the decision tree, apply to either compartments whatever the target is.

The case of human health

The problem is more complicated for human health. Like for ecosystems, we assume that direct exposition to atmospheric concentration for humans (inhalation) is negligible - see the report on metals of the TF on Human Health. Food and drinking water are probably the two pathways to be considered. However, "food" can cover several kinds of inputs : vegetable and grain are the most direct route ; but indirect pathways like milk, meat (etc) could also be contaminated ; besides, the oral route also includes ingestion of soil (by children). So, even if neglecting inhalation, it is not obvious to link pathways to concentration in one or two compartments of the environment. The use of food quality criteria should make it unnecessary to consider a complete model on human exposure pathways within the Critical Load methodology.

Different soil types

The choice of targets to be considered is of course ecosystem/land use dependant. The number of compartments C_j of concern as well. In case of a soil ecosystem all targets quoted in “The different possible targets” (above) can be addressed, however the pathways to be modelled will depend on the land use : forest, grassland, arable land.

The study of an arable soil will focus on the top layer (mixed by ploughing). On the other hand, for a more natural ecosystem generally the mineral layer is considered, which has different properties than the top humus layer, both from the physical-chemical and from the biological points of view. Hence the case of humus layer is not taken into account in 2002 in the preliminary guidance for Critical Loads calculations.

In order to allow preliminary calculations of CLO for metals, the 2002 report of the expert group on heavy metals (De Vries et al, 2002) does not distinguish different soil categories. However this option is not excluded in the next discussions and publications on transfer functions and critical limits. Indeed it is possible that the conceptual design of future models will depend on the soil characteristics or the soil category (i.e. type of parent material for example) :

- for chemical reasons : it may prove justified to use different adsoption/absorption /equilibrium processes, different transfer functions for different types of soil ;
- for biological reasons : it is likely that the biocenosis which developed in a specific soil is different than the "average" soil and should be considered sensitive to different thresholds than the "average" Clim : For example in soils with higher natural levels of metal or higher level of organic matter This was demonstrated by L.Bringmark for humic soils in Sweden. Hence it would be a very interesting option to consider different critical limits for different types of soil, provided the adequate ecotoxicological data is available.

4.3.5.2. Towards an aggregated Critical Load

For different targets

Considering different targets, <u>the first solution is to address each target separately when calculating Critical Loads at any site</u>. The aggregation between the different targets would then be a problem of the Task Force on Integrated Assessment Modelling, e.g. by integrating the "value" of each kind of awaited effect. This integrated assessment should consider human health and ecosystems separately for policy support, even if this would lead to more complexity. The experience in risk assessment studies shows that two independent calculations are usually made.

But theoretically, by enlarging the CLO methodology, we are able to consider several targets T_i, $i \in [1;p]$ with an aggregated CLO_a. Then, for each compartment C_j of concern, several Clim(i,j) will be derived. It will be logical to consider only the most stringent of these Clim(i,j) : it will be Clim(j) = *Min (Clim(1,j)…Clim(p,j)).* From each Clim(j) will then be derived one CLO(j) for this compartment C_j. Generally, the "aggregated CLO" for the site of interest will be the minimum of these CLOs.

This approach may be appropriate for soil and soil solution for example, in case the ecotoxicological data for soil matrix consider different species than the ecotoxicological data for soil solution (this was the case in the 2002 report of the expert group, but is likely not to be the case in future guidances). Yet, we have to look more carefully at the case where for several compartments it is the same target T_i which contributes to the choice of the (minimum) Clim for these compartments. This case is similar to the study of one target only with several pathways or compartments, described below.

For one target and several pathways

Let us consider carefully the case of one single target. As it was stated during the discussions of year 2001 from the experience in health studies, to study all pathways is feasible but is a specific task, requiring a new approach which analyses the contributions of different sources in the daily intake, as well as other inputs than atmospheric deposition (e.g. agricultural), especially when considering human health (see “The case of human health”, above). This section describes a first attempt to define the basic principles of an "aggregated CLO" accounting for several pathways.

Let us consider a simplified situation where one particular target will be contaminated by 2 pathways only (j=1 or 2), each of them giving a Clim(j). In case each pathway would cause a different type of effect, the minimum of CLO(j) would be the appropriate "aggregated CLO".

Let us assume that 1°) each Clim(j) is calculated independently, assuming that it is the only pathway, from its own (eco)toxicological data, and 2°) the 2 pathways cause similar toxicological mechanisms within the target. Then the only complete and accurate method is to sum up the contributions of the two pathways.[3]

Let us define the critical exposure for the target as being equal to 100 (arbitrary unit). The concentration in compartment C_1 causes an exposure of 100 when it equals to Clim(1). The $CLO_{(1)}$ determined by pathway 1 causes the concentration in compartment C_1 to be equal to Clim(1). But this load also produces a concentration in compartment C_2 that has some additive effect on the target, through pathway 2. The cumulative exposure is then greater than 100. So the "aggregated CLO" given by pathways 1 and 2 together is lower than $CLO_{(1)}$ - similarly it is lower than $CLO_{(2)}$.

In order to have a more precise idea of what this "aggregated CLO" can look like, let us assume a simple linearity between load, concentration and exposure . This is a rough approximation of course.

- A load **LO** will cause the concentration in compartment C_1 to be equal to $Clim_{(1)}$ x ($L/CLO_{(1)}$) and causes an exposure of 100 x (**LO**/$CLO_{(1)}$) through pathway 1.
- But this load also produces a concentration in compartment C_2 equal to $Clim_{(2)}$ x (**L**/$CLO_{(2)}$) and causes an exposure of 100 x (**LO**/$CLO_{(2)}$) through pathway 2
- The cumulated exposure is 100 x (**LO**/$CLO_{(1)}$ + **LO**/$CLO_{(2)}$). We want this exposure not to be greater than 100 (defined as the critical exposure), which entails : 100 = 100 x (**L**/$CLO_{(1)}$ + **LO**/$CLO_{(2)}$), or : 1 = **LO**/$CLO_{(1)}$ + **LO**/$CLO_{(2)}$

Therefore an approximation of the aggregated critical load $\mathbf{CLO_a}$ for this target, taking into account the pathways (1) and (2) , is given by : $\mathbf{1/CLO_a = 1/CLO_{(1)} + 1/CLO_{(2)}}$

Of course this formula can be generalised for more compartments and pathways but a more detailed analysis of the different pathways and their relative importance in the daily intake would be preferable. Finally, let us remember the assumptions which led to this proposal :

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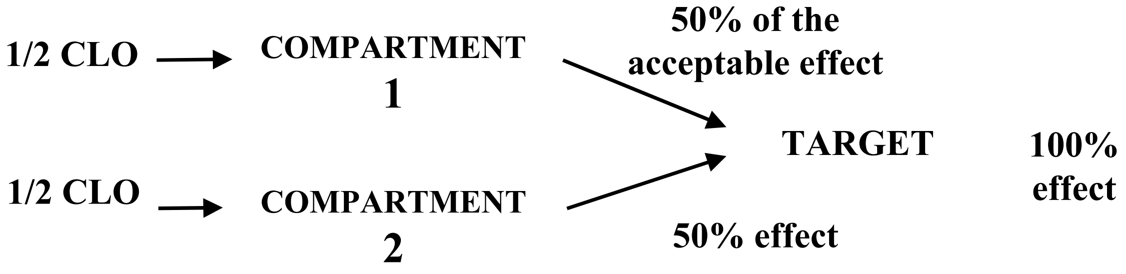
[3] A point of exception may be mentioned here : as concerns human health, some WHO recommendations giving a Clim for one particular pathway may take into account an "average background" exposition through the other pathways. This shows that a case by case analysis has to be performed together with experts in toxicology.

- The different pathways cause similar toxicological mechanisms within the target (this is always the case if the oral route is concerned several times). In case each pathway would cause a different type of effect, the minimum of CLO(j) could be kept, with no approximation.
- The different Clim are concerning the same target but are derived independently.
- For the final formula, linearity is assumed between load and effect, which obviously is not true.

Even without this assumption of linearity, we can conclude anyway that :

- Example 1 : If the 2 pathways contribute roughly to a similar extent in the effect, the aggregated CLO_a is half of the individual CLOs.



- Example 2 : If pathway 1 widely dominates pathway 2, it means that $(1/CLO_{(1)}) >> (1/CLO_{(2)})$, then it is of course appropriate to consider only this pathway and its related Clim (and CLO). To consider the minimum of the Clim is a good approximation.

This whole approach assumes that different effects and targets are considered through one single CLO – hence at the level of the National Focal Centres or the Centre of Coordination for Effects. We show here that it is feasible, yet different effects may in fact be better taken into account in the Integrated Assessment Modelling, in "downstream" interpretation of different CLOs. Anyway a continuity with the Integrated Assessment activities is needed, as already stated in part 3.

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5. SUGGESTED METHODS FOR MERCURY

5.1 CRITICAL LEVELS OF ATMOSPHERIC POLLUTION: CRITERIA AND CONCEPTS FOR OPERATIONAL MODELLING OF MERCURY IN FOREST AND LAKE ECOSYSTEMS

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ELSEVIER

The Science of the Total Environment 304 (2003) 83–106

the Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

Critical levels of atmospheric pollution: criteria and concepts for operational modelling of mercury in forest and lake ecosystems

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Received 20 February 2002; accepted 15 October 2002

Abstract

Mercury (Hg) is regarded as a major environmental concern in many regions, traditionally because of high concentrations in freshwater fish, and now also because of potential toxic effects on soil microflora. The predominant source of Hg in most watersheds is atmospheric deposition, which has increased 2- to >20-fold over the past centuries. A promising approach for supporting current European efforts to limit transboundary air pollution is the development of emission-exposure-effect relationships, with the aim of determining the critical level of atmospheric pollution (CLAP, cf. critical load) causing harm or concern in sensitive elements of the environment. This requires a quantification of slow ecosystem dynamics from short-term collections of data. Aiming at an operational tool for assessing the past and future metal contamination of terrestrial and aquatic ecosystems, we present a simple and flexible modelling concept, including ways of minimizing requirements for computation and data collection, focusing on the exposure of biota in forest soils and lakes to Hg. Issues related to the complexity of Hg biogeochemistry are addressed by (1) a model design that allows independent validation of each model unit with readily available data, (2) a process- and scale-independent model formulation based on concentration ratios and transfer factors without requiring loads and mass balance, and (3) an equilibration concept that accounts for relevant dynamics in ecosystems without long-term data collection or advanced calculations. Based on data accumulated in Sweden over the past decades, we present a model to determine the CLAP-Hg from standardized values of region- or site-specific synoptic concentrations in four key matrices of boreal watersheds: precipitation (atmospheric source), large lacustrine fish (aquatic receptor and vector), organic soil layers (terrestrial receptor proxy and temporary reservoir), as well as new and old lake sediments (archives of response dynamics). Key dynamics in watersheds are accounted for by quantifying current states of equilibration in both soils and lakes based on comparison of contamination factors in sediment cores. Future steady-state concentrations in soils and fish in single watersheds or entire regions are then determined by corresponding projection of survey data. A regional-scale application to southern Sweden suggests that the response of environmental Hg levels to changes in atmospheric Hg pollution is delayed by centuries and initially not

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PII: S0048-9697(02)00559-4

proportional among receptors (atmosphere $\gg$ soils $\neq$ sediments $>$ fish; clearwater lakes $\gg$ humic lakes). This has implications for the interpretation of common survey data as well as for the implementation of pollution control strategies. Near Hg emission sources, the pollution of organic soils and clearwater lakes deserves attention. Critical receptors, however, even in remote areas, are humic waters, in which biotic Hg levels are naturally high, most likely to increase further, and at high long-term risk of exceeding the current levels of concern: $\leqslant 0.5$ mg (kg fw)$^{-1}$ in freshwater fish, and 0.5 mg (kg dw)$^{-1}$ in soil organic matter. If environmental Hg concentrations are to be reduced and kept below these critical limits, virtually no man-made atmospheric Hg emissions can be permitted.

Keywords: Hg; Methylmercury; Critical load; Deposition; Soil runoff; Lake sediment; Fish; Pike; Humic; Model

1. Introduction

1.1. Background: European protocols to reduce atmospheric pollution

Long-range atmospheric transport of mercury (Hg) and other micropollutants has caused a widespread contamination of soils and lakes even in remote areas, including the boreal forest zone. In Sweden, attention is presently focused on alarmingly high Hg levels in fish exceeding health advisory guidelines in tens of thousands of lakes (e.g. Lindqvist et al., 1991; Johansson et al., 2001; Meili, 2001) as well as indications of toxic mercury effects on the microflora of organic soils (Bringmark and Bringmark, 2001a,b; cf. Zelles et al., 1986). Atmospheric deposition is considered to dominate the Hg input to most soils and lakes in the boreal forest zone (Lindqvist et al., 1991; Fitzgerald et al., 1998; Landers et al., 1998; Johansson et al., 2001), an area of considerable economic interest, both for forestry and sport fishing. Atmospheric Hg deposition, originating mainly from mining of Hg and combustion of fossil fuels as the dominating primary sources (e.g. Lindqvist et al., 1991; Hylander and Meili, 2002), has increased 2- to >20-fold over the past centuries due to anthropogenic emissions and subsequent dispersal on local, regional, and global scales (e.g. Lindqvist et al., 1991; Swain et al., 1992; Meili, 1995; Fitzgerald et al., 1998; Landers et al., 1998; Lockhart et al., 2000; Johansson et al., 2001; Munthe et al., 2001; Bindler et al., 2001; Lamborg et al., 2002; www.emep.int). Europe is currently seeking an approach for limiting transboundary air pollution by Hg and other persistent micropollutants, in line with existing protocols for sulfur and nitrogen emissions within the framework of the UN/ECE Geneva Convention (Gregor et al., 2001). Concern about the health of boreal and other ecosystems has called for concepts on which to base international regulations of atmospheric Hg emissions. In 1998, a protocol to reduce anthropogenic emissions of heavy metals (Hg, Cd, Pb) was signed at the all-European Fourth Ministerial Conference ‘Environment for Europe’ in Århus, within the framework of the United Nations Economic Commission for Europe’s Geneva Convention on Long-Range Transboundary Air Pollution (UN/ECE, CLRTAP, EB.AIR/1998/1, see www.unece.org/env/lrtap). This agreement also states that the parties of the convention are aware that further and more effective action to control and reduce emissions of certain heavy metals may be needed and that, for example, effects-based studies may provide a suitable basis for further actions.

1.2. Focus: critical level of atmospheric pollution

One approach to support international negotiations on the reduction of atmospheric emission and deposition of pollutants is to determine the maximum level of constant atmospheric pollution that causes no or tolerable damage to sensitive elements of the affected environment. We refer to this as the ‘critical level of atmospheric pollution’ (CLAP), a term addressing the multiple speciation modes and exposure pathways of Hg by encompassing other terms referring specifically to either deposition loads or toxic effects. Such concepts have previously provided a successful basis for controlling acidifying pollutants in Europe, in particular sulfur and nitrogen (e.g. Henriksen et al., 1992; Posch et al., 1997; Gregor et al., 2001; Spranger et al., 2001). A major advantage of this approach is that it can be used to optimize the international investment in pollution control for protection of the environment. A major difficulty is the quantification of the relationship between atmospheric emission, immission/deposition, environmental partitioning, exposure of organisms and other environmental elements, and ultimately environmental effects.

In the past years several studies have been carried out to assess critical loads (long-term acceptable inputs) for micropollutants, specifically heavy metals, on a national scale (De Vries et al., 1998a) and a European scale (Van den Hout et al., 1999). Recently, two manuals have been developed to calculate critical loads for heavy metals in terrestrial and aquatic ecosystems (De Vries and Bakker, 1998; De Vries et al., 1998b). These manuals are, however, limited to Pb, Cd, Cu, Zn and Ni, whereas Cr and Hg are only minimally addressed. The reason is that the methods involved include a steady-state mass balance approach, assuming that the metals concerned are portioned over the soil solid phase, dissolved organic matter and soil solution, while accounting for sorption and complexation processes but not for redox processes. This was regarded inadequate for Hg, the biogeochemical cycling of which includes different oxidation states and microbial transformations such as methylation/demethylation of mercuric Hg^{2+} and volatilization of elemental Hg^0. Therefore, the calculation of a critical load of Hg using a process-based approach was considered too complicated (De Vries and Bakker, 1998).

Although this may appear difficult, it is important and urgent to quantify the CLAP for Hg, considering that environmental Hg levels are alarmingly high even in remote areas (e.g. Johansson et al., 2001; Meili, 2001), and that Hg is a priority pollutant for emission reductions (Gregor et al., 2001). Apart from that, Hg may be particularly suitable as a pilot substance to start developing emission-exposure-effect concepts such as those for sulfur also for micropollutants, because much of the biogeochemical cycle of Hg is tightly coupled with that of sulfur (e.g. Meili, 1991a, 1994, 1997; Munthe et al., 2001; Tsibulsky et al., 2001; Branfireun et al., 2001). The focus of this paper is primarily on basic concepts for modelling environmental exposure and on a feasibility assessment that may serve as a basis for progressing towards a general operational tool. This entails several steps: (1) identification of critical receptors, (2) determination of critical concentrations in these receptors, (3) review of concepts for other substances or limited to a qualitative approach (e.g. Johansson et al., 1991), (4) expansion of exposure concepts to address not only lacustrine food chains but also terrestrial ecosystems as a critical receptor, (5) integration of concepts into a quantitative model of the Hg cycle in watersheds of the boreal forest zone (cf. Meili, 1991a), (6) consideration of current biogeochemical concepts and recent findings, (7) identification and quantification of relevant ecosystem dynamics, and (8) reduction of model complexity and data requirements to the essentials. Particular efforts aim at taking advantage of the strong association between Hg and organic matter, and at reducing uncertainties related to less-well understood environmental transformations of Hg (e.g. methylation/demethylation, dry deposition/volatilization).

1.3. Challenge: quantification of emission-exposure-effect relationships

A major challenge is to transform complex empirical findings and conceptual insight into operational tools. This includes the development of robust ecosystem models requiring a minimum of data, while still accounting for the most important factors controlling receptor levels and response dynamics. Further, an application of emission-exposure-effect concepts and models to particular ecosystems requires consideration of the natural variability related to source terms (e.g. load or concentration), processes (e.g. partitioning, equilibration), and receptors (e.g. body concentration). This refers to relevant spatial scales related to the variability in both load and response (nations, regions, lakes, taxa, individuals) and temporal scales related to both pollution history and environmental turnover rates (years, decades, centuries).

Our aim is to develop a flexible modelling tool for determining the CLAP for Hg, using Swedish forest and lake ecosystems as an example, but following general principles that are applicable also in other areas (e.g. Meili, 1991a, 1997, 2001). Such a model should be workable with a minimum of reliable data available at low cost from maps and from traditional surveys, and preferably without any need for flux estimates, or for time series other than those found in natural archives such as sediments. In Sweden, where Hg has been considered a serious problem for many decades, a large body of data is now available (see most references), which greatly facilitates the establishment and statistical testing of quantitative source–receptor relationships. A potential difficulty in developing such relationships for Hg is the great complexity of its biogeochemical cycle (e.g. Lindqvist et al., 1991; Porcella et al., 1995; Meili, 1997; Grigal, 2002; Lamborg et al., 2002) relative to that of many other pollutants already considered in manuals for mapping critical loads (Section 1.2). In order to keep a modelling tool simple enough to be operational at different levels of application, it should contain only the most essential components with respect to the most relevant issue: what is the maximum tolerable atmospheric Hg pollution that will keep environmental Hg levels below critical limits over the coming decades and centuries? Furthermore, the model formulation should provide flexibility for adaptation and expansion for use with different environmental data, at different spatial and temporal scales, and in complex multi-pollutant scenarios.

A CLAP usually aims at long-term protection and thus relates to steady-state conditions in a distant future. For quantification and implementation, it is therefore crucial to assess not only the present but also the natural ecosystem status in relation to critical limits, to identify and account for relevant dynamics in cases where environmental equilibria have not yet been reached, and to develop robust concepts and modelling tools adapted to cope with the natural variability and non-linearity of emission-exposure-effect relationships. The approach presented addresses these issues.

2. Environmental risk assessment, and present status in Sweden

2.1. Critical receptors

Ecotoxicity is proportional to the ratio between dose (e.g. aqueous or tissue concentration) and susceptibility (i.e. toxic effect per dose) at both the individual and the ecosystem level. In the case of Hg in biota, both dose and susceptibility depend on the form of Hg. At each trophic transfer along food chains, the tissue concentrations in animals increase several-fold for methyl-Hg, but decrease for inorganic Hg (e.g. Meili, 1997). As a result, the dose of methyl-Hg increases with the trophic level in food webs, while the dose of inorganic Hg is highest at low trophic levels as represented by all kinds of microorganisms, in particular detritivores and associated food chains (Parkman and Meili, 1993). The susceptibility to methyl-Hg is particularly high in the central nervous system of developing vertebrate and bird embryos, while the susceptibility to inorganic Hg is known to be considerable at the microbial level (cf. its use for disinfection). In ecosystems exposed to a given dose of Hg, toxic effects can thus be expected primarily in top predators and at the microbial level.

2.2. Critical limits

In the early 1990s, the Swedish Environmental Protection Agency has suggested the following environmental quality objectives: for the protection of human health and a sustainable management of natural resources the concentration of total Hg in fish must not exceed 0.5 mg (kg fw)$^{-1}$ (fresh weight); for the protection of biological diversity and a sustainable management of natural resources further large-scale accumulation of metals in the humus layer of forest soils must stop (SEPA, 1994). The critical limit adopted for fish is based on recommendations by the WHO/FAO and is the same as in many other countries (Lindqvist et al., 1991); it should be noted, however, that the US

Table 1
Stepwise quantification of source–receptor relationships for Hg in the boreal forest zone: summary matrix of input data (six standardized variables in four matrices, see Section 3.2) and derived key parameters (transfer factors and dynamics, see Section 3.5), exemplified with values representing regional means for undisturbed watersheds in the forested inland of southern Sweden (56–59°N, Fig. 3) around 1985 (t)

Watershed compartment:	Atmosphere	Soil	Runoff	Lakes		Fish	
Lake type:				$f_R=1$	$f_R=0$	$f_R=1$	$f_R=0$
Recent concentration data (model input)	Hg_{Prec} (ng kg^{-1}) 20	Hg_{Soil} (mg (kg org)$^{-1}$) 0.4	– –	Hg_{new}/Hg_{old} $q_{Lake\ (sediment)}$ 2	 10	Hg_{Fish} (mg (kg fw)$^{-1}$) 1.0	 0.4
Recent transfer ratios $k_X'=Hg_X(t)/Hg_{Prec}(t)$		20 000	–	–	–	50 000	20 000
Recent contamination factors $q_X=Hg_x(t)/Hg_x(t=0)$							
Atmospheric (P for precipitation)	q_{Prec} 10				q_{LakeP} 10		q_{FishP} 10
Terrestrial (R for runoff)		q_{Soil} 4	q_{Run} 2	q_{LakeR} 2		q_{FishR} 2	
Recent equilibration state $e_X=q_X/q_{Prec}$		e_{Soil} 0.4	e_{Run} 0.2	e_{LakeR} 0.2	e_{LakeP} ($\equiv 1$)	e_{FishR} 0.2	e_{FishP} ($\equiv 1$)
Steady-state transfer factors $k_X=Hg_X(t=0)/Hg_{Prec}(t=0)$		k_{Soil} 50 000				k_{FishR} 250 000	k_{FishP} 20 000

Note the difference between recent transfer ratios and steady-state transfer factors. Resulting concentrations are shown in Table 2 and Fig. 3.

Environmental Protection Agency now recommends a lower fish Hg limit of 0.3 mg (kg fw)$^{-1}$ referring to methyl-Hg alone, which constitutes virtually all Hg in fish-eating freshwater fish (USEPA, 2001). These limits are largely based on the potential exposure of fish consumers, but recent studies suggest behavioral effects of low-level methyl-Hg exposure also in fish (Matta et al., 2001; Hammerschmidt et al., 2002).

For soils, effects-based criteria are currently developed along the following lines. Most Swedish forest soils are covered by an organic humus layer (mor) in which many deposited pollutants are efficiently retained. Since plant root systems and fungi are located in this layer, there is an immediate risk of biological disturbance with economic dimensions: reduced decomposition of organic matter may have direct consequences for the mineralization of nutrients in forest soils and ultimately for forest growth. Indeed, recent studies show some observational and experimental indications of a reduced respiration in forest soils at Hg concentrations close to those encountered in rural areas of south Sweden (Bringmark and Bringmark, 2001a,b). These findings suggest a lowering of effect levels for Hg (as well as Pb) in soils considerably below known values. A tentative critical limit is that the Hg concentration in the humus layer (O-horizon) of podzolic forest soils should not exceed the present mean level in the most contaminated regions of south Sweden, where further increase should be avoided. This level is approximately 0.4 mg (kg dw)$^{-1}$, which after normalization with respect to organic matter content corresponds to a more robust value of 0.5 mg (kg org)$^{-1}$ in these highly organic soils (Meili, 2001; based on data from Andersson, 1991; cf. Alriksson, 2001). For soils where organic matter is not the dominating matrix and where Hg sorption to mineral matrices needs to be accounted for, an equivalent and biologically relevant but more general formulation of the critical limit for soils proposed here is that Hg concentrations in soil organic matter should not exceed 0.5 mg (kg org)$^{-1}$.

2.3. Variability and scale: standardization of data

For implementing environmental goals, receptor levels need to be defined that are spatially and temporally robust and easy to quantify. In boreal forest soils, the organic top layer of podzols (spodosols) provides a fairly uniform matrix that can be used as a proxy to assess the exposure of soil microflora to Hg and other pollutants. Given the survey data available (Andersson, 1991; Alriksson, 2001), a homogenate of the whole mor layer is considered here (Hg_{Soil}). Hg concentrations in biota, on the other hand, show a wide variability: methyl-Hg concentrations range over no less than four orders of magnitude in ‘unpolluted’ freshwaters alone, even if normalizing to whole-body organic dry weight and disregarding seasonal variations (Meili, 1997). Within a given freshwater ecosystem, the variation of methyl-Hg concentrations among organisms is approximately 200-fold, and among fish of all species and size classes approximately 30-fold (Meili, 1997). To eliminate this source of variation, cross-system comparisons need to be based on a system-specific reference value, for example on Hg in a single type of fish (Hg_{Fish}). In Sweden, the mean concentration in 1-kg pike (*Esox lucius* L.) has been used since the beginning of Hg monitoring in the 1960s and is now available for several thousand lakes in Sweden alone (e.g. Lindqvist et al., 1991; Johansson et al., 2001; Meili, 2001). This lake-specific parameter provides a suitable operational measure because it is related to human consumption habits, is easily measured, and is spatially as well as seasonally rather stable. Moreover, it is a relevant value from an ecotoxicological point of view since it is closely related to, and only approximately two-fold lower than, the highest methyl-Hg concentrations in any type of aquatic organism within the same system (usually the largest individuals of the same species, not considering birds and mammals feeding on lacustrine fish).

While the variation of Hg concentrations among biota within ecosystems can be eliminated by standardization, the variability among ecosystems is a more difficult issue. The variation among Swedish lake ecosystems alone is considerable, with mean Hg concentrations in the muscle tissue of 1-kg pike ranging from 0.04 to 2.6 mg (kg fw)$^{-1}$, and typically from 0.1 to 2.0 mg (kg fw)$^{-1}$ in properly sampled lakes (at least 5 spring individuals close to 1 kg), even when only considering samples collected and analyzed after 1980 in lakes without direct Hg discharge and at some distance from known atmospheric point sources of Hg (Lindqvist et al., 1991). While part of this variation may be explained mechanistically or statistically (Lindqvist et al., 1991), some of the variation always remains unexplained and may be enhanced by various errors. For implementation of a CLAP for Hg, we suggest the testable goal that 95% of the relevant ecosystem units (e.g. lakes) are to comply with the mentioned critical limit of 0.5 mg (kg fw)$^{-1}$ in the muscle tissue of 1-kg pike. Such a probabilistic approach may not protect all ecosystems, but is robust with respect to outliers and has earlier been applied to acidifying and eutrophying substances (Henriksen et al., 1992; Gregor et al., 2001; Spranger et al., 2001). As a first step, we focus here on mean values rather than total variability, but address variability by considering ecosystems of different type. A recent data compilation shows that even regional means of Hg in lake fish can vary 10-fold within Sweden alone, also if accounting for present and historical differences in atmospheric Hg exposure (Meili, 2001). Regional means of Hg in fish differ also among lake types (e.g. hydrography, organic and inorganic chemistry), and comparisons with other data suggest a strong link with Hg in soils (e.g. Lindqvist et al., 1991; Meili, 1991a,b, 1997; Tables 1 and 2).

For forest soils, a national survey in Sweden during 1983–1984 showed Hg concentrations ranging from 0.07 to 1.0 mg (kg dw)$^{-1}$ (Andersson, 1991; similar to another survey 10 years later, Alriksson, 2001). This survey was aiming at standardized values for the organic top soil (humus or mor layer, O-horizon, between organic litter and mineral soils) of podzols on sandy till, which is probably the most common soil type in the boreal forest zone. Due to the association of most Hg with organic matter in organic-rich environments, concentrations are suitably normalized with respect to the concentration of organic matter (Meili, 1991a, 1997, 2001), here referred to as 'org'. This standardization reduces spatial variability and yields regional means of approximately 0.4 mg (kg org)$^{-1}$ in the forested inland of southern Sweden (Fig. 3), at some distance from major point sources (Table 2; Meili, 2001; based on data from Andersson, 1991). Because of the strong association of Hg with organic matter, the turnover of Hg in these soils is largely controlled by the turnover of organic matter. Accordingly, annual export of Hg as well as methyl-Hg from soils to lakes is largely controlled by the export of organic matter with runoff water (e.g. Johansson et al., 1991; Meili, 1991a,b, 1997; Bishop and Lee, 1997). The annual mean Hg/org ratio in this exported material is probably related to the Hg/org ratio in relevant soil compartments of the area. However, the Hg/org ratio may not be the same in mor and runoff, in either present or steady-state (cf. Meili, 1991a), but may vary among areas and watershed compartments (Johansson and Iverfeldt, 1994) and even within the mor layer where the ratio increases naturally with depth (Grondin et al., 1995).

Table 2
Standardized Hg concentrations[a] in precipitation, forest soils, and lacustrine fish: estimates of past, recent, potential, and maximum tolerable (critical) mean levels in forested inland regions of southern Sweden (56–59°N, Fig. 3)

Temporal scale	Pre-industrial[b]	Recent[c]	Future[d]			
Environmental scale	Global	Regional	Continued	Reduced	Global	Tolerable?
Hg_{Prec} (ng l^{-1}, wet precipitation)	⩽2	20	20	8	4	2
Hg_{Soil} (mg (kg org)$^{-1}$)						
Whole mor (humus) layer	⩽0.1	0.4	*1.0*	0.4	0.2	0.1
Slowly equilibrating compartments	⩽0.1	0.2	*1.0*	0.4	0.2	0.1
Hg_{Fish} (mg (kg fw)$^{-1}$, 1-kg pike)						
Clearwater lakes (no terrestrial Hg)	⩽0.04	0.4	0.4	0.16	0.08	0.04
Oligohumic lakes (1/3 → 71% terr. Hg)	⩽0.37	*0.6*	*3.7*	*1.5*	*0.74*	0.37
Mesohumic lakes (2/3 → 91% terr. Hg)	⩽0.46	*0.8*	*4.6*	*1.8*	*0.92*	0.46
Polyhumic waters (only terrestrial Hg)	⩽0.50	*1.0*	*5.0*	*2.0*	*1.00*	0.50

Receptor values exceeding current levels of concern of 0.5 mg kg^{-1} are in italics.

[a] Regional and annual (decadal) means (see text for data sources and standardization); locally, Hg/org ratios in the organic top layer (mor) of forest podzols (spodosols) may vary approximately 2-fold among neighboring watersheds; lake means of Hg in 1-kg pike (*Esox lucius*, muscle tissue) may vary locally approximately 4-fold among neighboring lakes; variabilities vary among regions depending on their homogeneity.

[b] *Pre-industrial:* Based on the pre-industrial/recent ratio in short sediment cores. Natural concentrations may be lower than pre-industrial ones (Aston et al., 1973; Martínez-Cortizas et al., 1999) or not (Bindler et al., 2001).

[c] *Recent:* Observations around 1975–1995, adjusted to 1985; Hg in precipitation has declined since then to about half in south Sweden (Munthe et al., 2001; Johansson et al., 2001; Bindler et al., 2001), cf. *reduced* below. *Regional:* Areas with minimal local contamination, located >100 km from large cities and major atmospheric point sources including historical ones, thus excluding part of the elevated values in the Swedish data.

[d] *Future:* After at least 1000 years of constant atmospheric pollution (see text). *Continued* (high)*:* Atmospheric pollution is maintained at the level observed 1986–1990. *Reduced:* Atmospheric pollution is maintained at the level observed 1998–2000 (Munthe et al., 2001 and unpublished); this is required to avoid further increase of Hg in the organic layer (mor, profile mean) of forest soils in south Sweden, and to keep regional means below 0.5 mg (kg org)$^{-1}$. *Global:* Atmospheric pollution is maintained at the global background level observed 1990–2000; this is required to avoid further increase of Hg in soils, in runoff, and in 1-kg pike. *Tolerable*?*:* Maximum to keep regional means of Hg in 1-kg pike in humic lakes below 0.5 mg (kg fw)$^{-1}$.

3. Modelling

3.1. General concepts

The objective is to develop a simple and flexible model that uses available monitoring data to estimate the critical exposure of soils and lakes to atmospheric pollution, both at the regional and at the local (lake) scale. Model complexity can be minimized at several levels: structural, dynamic, and dimensional. Flexibility is obtained by using scale-independent transfer factors and relative ratios rather than absolute mass units. Ecosystem modelling can be simplified substantially by focusing on functional relationships (e.g. transfer functions) rather than an ecological mass balance requiring a complete set of data on relevant pools and fluxes.

We therefore propose the use of concentrations when assessing emission-exposure-effect relationships and critical levels of toxic pollutants. For atmospheric pollutants, this includes the interpretation of 'critical level' as 'critical concentration' in precipitation and/or air, rather than 'critical load' of deposition. The use of concentrations is conceptually preferable, both from a toxicological point of view since effects of a pollutant are related to body concentration rather than uptake rate or body burden, and from a geochemical point of view since sorption/desorption equilibria of a pollutant in soil depend on concentrations in soil and soil solution rather than on soil inventories or deposition fluxes. The consistent use of concentrations is also likely to produce more robust results, since data requirements and associated errors are reduced substantially by avoiding the need for flux measurements. Furthermore, this approach has practical advantages since the transformations needed for modelling the linkage of source and receptor can be minimized, often to simple calculations based on a few basic concentration measurements. Expressing source–receptor relationships by scale-invariant transfer functions facilitates model implementation for different ecosystems and spatial applications (mapping). This applies in particular to modelling and mapping of atmospheric exposure since mean pollutant concentrations in precipitation and air are spatially less variable than atmospheric deposition loads that are strongly influenced by local conditions (climate, vegetation).

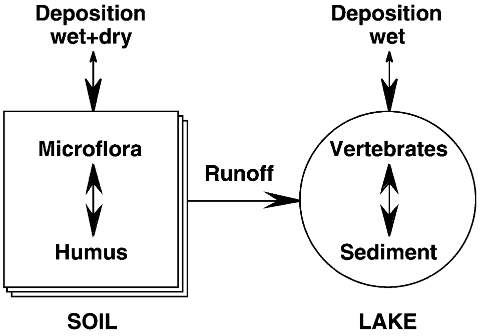

Fig. 1. Conceptual model of critical sources, receptors, and pools of Hg in the boreal forest zone. Deposition refers to recent as well as historical wet and dry deposition originating from global, regional, and local sources. For long-term predictions, slow response dynamics are considered important in soils but negligible within lakes. The partitioning of Hg within each compartment is reduced to quantitative relationships between Hg concentrations in the primary source, in the dominating matrix and in the critical receptor. This does not preclude the consideration of a complex biogeochemistry or a structuring of soils (or lakes) into subcompartments.

3.2. Model structure

For Hg in boreal ecosystems, essential structural elements and their causal links (Fig. 1) can be determined based on recent research in Sweden and elsewhere (e.g. Lindqvist et al., 1991; Bishop and Lee, 1997; Meili, 1997). The following key concentrations were identified, based on an earlier modelling approach (Meili, 1991a; see also Section 2.3):

Hg_{Prec}: Total Hg in wet deposition (Hg/water)
Hg_{Soil}: Total Hg in (forest) (top) soil, normalized to organic matter (Hg/org)
Hg_{Run}: Total Hg in soil runoff, normalized to organic matter (Hg/org)
Hg_{Lake}: Total Hg in lacustrine sediment, normalized to organic matter (Hg/org)
Hg_{Fish}: Total Hg in lacustrine fish, here in muscle of 1-kg pike (Hg/fw or Hg/org)

This set of variables includes the atmosphere as the principal Hg source (Hg_{Prec}), the critical aquatic and terrestrial receptors (Hg_{Fish} and Hg_{Soil}), the critical long-term ecosystem dynamics (reflected in Hg_{Soil} and Hg_{Run}), and the degree of pollution as it is reflected in the historical archive of lake sediment cores (Hg_{Lake}). These key variables were also chosen because they can be quantified with limited resources, and because extensive data sets of high quality already are available. Atmospheric Hg immission is here represented by the total Hg concentration in precipitation, which is the most commonly, most easily, and most reliably measured quantity that is of ecological relevance also without conversions. Other source terms can be used instead, or simultaneously in parallel twin models if proven necessary, for example accounting for gaseous Hg fluxes separately. Potential addition by dry deposition and loss by post-depositional volatilization can be substantial (Grigal, 2002), but are difficult to quantify. In the present model formulation, which is based on relative changes and ratios, unknown additions and losses are always accounted for as long as they remain proportional to the degree of pollution in any compartment (first order reactions). For example, dry deposition is linked to the atmospheric pollution represented by Hg_{Prec} (but not necessarily by wet deposition which varies temporally and spatially with the amount of precipitation), consistent with a rapid equilibrium partitioning of relevant atmospheric species such as particulate and reactive gaseous Hg (cf. Lamborg et al., 2002). All receptor concentrations are consistently expressed in a way that accounts for the close coupling of the environmental Hg cycle to the cycling of organic matter (Meili, 1991a), they can be conceived either as a concentration of Hg in organogenic matter or as a ratio of their respective fluxes. All these concentrations are commonly available from monitoring programs or may otherwise be estimated by spatial interpolation or from other empirical relationships. Volumetric Hg concentrations in surface waters are here deliberately omitted or arithmetically eliminated (Section 3.5), since wide variations in concentrations and speciation as well as limited understanding of rapid transformation processes make a biologically relevant and cost-efficient assessment unrealistic. Data requirements and uncertainty linked to spatial and temporal variability are further reduced by using ratios of covarying concentrations as a basis for modelling.

3.3. Steady-state formulation

The transfer and partitioning of Hg in a given ecosystem at steady-state can be formulated in accordance with a simple conceptual partitioning model (Fig. 1) without any need for mass balance considerations or detailed understanding of ecosystem processes. In a constant environment with steady-state Hg partitioning, this can be achieved by linking critical receptors (e.g. soil and fish) directly rather than sequentially to the main immissions and by using transfer factors (k) to describe the relationship of their Hg concentrations at steady-state:

For soils: $Hg_{Soil}/Hg_{Prec}=k_{Soil}$

For fish: $Hg_{Fish}/Hg_{Prec}=k_{FishR}f_R+k_{FishP}(1-f_R)$

where k_{Soil} refers to the transfer from the atmosphere (precipitation) to soil, k_{FishR} to the transfer from the atmosphere to fish via soil runoff, k_{FishP} to the transfer from the atmosphere to fish via deposition on the lake surface, and f_R to the fraction of Hg input to lakes contributed by runoff. The last equation describes the Hg in lacustrine animals as a mixture composed of a component controlled by terrestrial processes in the watershed and a component related to direct input. Their relative contribution is controlled by f_R ranging from 0 in precipitation-fed lakes to 1 in runoff-fed lakes and rivers. Both contributions are linked directly to the Hg concentration in precipitation by transfer factors, which may be treated as a function of any environmental variables. With this formulation, it is possible to account for terrestrial processes including Hg transformations that may influence the transfer of atmospheric Hg to fish significantly (Section 4.2).

The equations and criteria above are the basis for calculating the critical level of atmospheric mercury pollution (CLAP-Hg, for example defined as the critical concentration in precipitation, $Hg_{PrecCrit}$) referring to the critical steady-state concentrations of Hg in critical receptors (soils and their organisms, fish and their consumers):

For soils: $\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{SoilCrit}} / k_{\mathrm{Soil}}$

For fish: $\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{FishCrit}} / \left[k_{\mathrm{FishR}} f_{\mathrm{R}} + k_{\mathrm{FishP}} (1 - f_{\mathrm{R}}) \right]$

The coefficients in these equations can only be adequately quantified from steady-state information, which for most pollutants is not available. However, estimates can be made by reconstructing relevant long-term dynamics in ecosystems.

3.4. Dynamic formulation

If the response of a receptor to changes in pollution is slow (decades to centuries), environmental dynamics need to be considered for adequate quantification of the CLAP. This can be accomplished by dynamic functions accounting for the deviation from steady-state, most conveniently by introducing equilibration state coefficients (e) that describe the dynamic state at any given time (t) while approaching a steady-state value of 1. The following model formulation includes all the different compartments mentioned above and complies with an earlier synthesis (Meili, 1991a):

$$\mathrm{Hg}_{\mathrm{Soil}}(t) / \mathrm{Hg}_{\mathrm{Prec}}(t) = k_{\mathrm{Soil}} e_{\mathrm{Soil}}(t)$$

$$\mathrm{Hg}_{\mathrm{Run}}(t) / \mathrm{Hg}_{\mathrm{Prec}}(t) = k_{\mathrm{Run}} e_{\mathrm{Run}}(t)$$

$$\mathrm{Hg}_{\mathrm{Lake}}(t) / \mathrm{Hg}_{\mathrm{Prec}}(t) = k_{\mathrm{LakeR}} e_{\mathrm{Run}}(t) f_{\mathrm{R}} + k_{\mathrm{LakeP}} (1 - f_{\mathrm{R}})$$

$$\mathrm{Hg}_{\mathrm{Fish}}(t) / \mathrm{Hg}_{\mathrm{Prec}}(t) = k_{\mathrm{FishR}} e_{\mathrm{Run}}(t) f_{\mathrm{R}} + k_{\mathrm{FishP}} (1 - f_{\mathrm{R}})$$

where k_{Run} refers to the Hg transfer from the atmosphere (precipitation) to terrestrial runoff, k_{LakeR} to the Hg transfer from the atmosphere to lakes (water and sediment) via terrestrial runoff, k_{LakeP} to that via direct input, and the equilibration state coefficients $e_{\mathrm{Soil}}(t)$ and $e_{\mathrm{Run}}(t)$ to the deviation from steady-state for soil and runoff, respectively. In this way, the dynamic relationship between Hg concentrations in receptors and atmospheric pollution is described by a few scale-independent coefficients that can be adapted to local conditions. These coefficients are elaborated in more detail below (Section 3.5).

Note that with the last two equations, the relative contribution of atmospheric and terrestrial Hg is allowed to differ between fish and sediments. This formulation accounts for differences in Hg speciation (methylated/inorganic, particulate/dissolved) that may cause differences in bioavailability or settling velocity. Also note that for Hg in lakes (sediments and lacustrine animals), long-term dynamics are accounted for in the terrestrial component where the response to changes is expected to be slowest (centuries), whereas the atmospheric component is only influenced by lake-internal processes that are assumed to be sufficiently rapid (years) to be negligible in this context.

For a given ecosystem exposed to Hg pollution, the four equations further imply the following assumptions on Hg fluxes (cf. Meili, 1991a, 1997; Fitzgerald et al., 1998; Lamborg et al., 2002): (1) Atmospheric input is the only Hg source and is adequately represented by $\mathrm{Hg}_{\mathrm{Prec}}$ (Section 3.2); (2) in soils, the weathering input of Hg is negligible, and Hg volatilization and net retention are either negligible or remain proportional to $\mathrm{Hg}_{\mathrm{Prec}}$ and/or $\mathrm{Hg}_{\mathrm{Soil}}$ (Section 3.2); (3) in lakes, Hg sedimentation, volatilization and bioaccumulation in fish all consist of two components that may vary widely among systems and among each other but remain proportional to $\mathrm{Hg}_{\mathrm{Prec}}$ and $\mathrm{Hg}_{\mathrm{Run}}$, respectively. These assumptions basically imply that the long-term response of a compartment to a change in $\mathrm{Hg}_{\mathrm{Prec}}$ is little affected by the properties of the compartment, or that the system properties (e.g. the Hg partitioning) remain constant. This may not always be valid for absolute concentration changes and for specific lakes subjected to environmental changes, but appears reasonable for the relative response of regional mean values to a relative change in atmospheric Hg pollution (cf. Lamborg et al., 2002). In other words, a doubling of atmospheric Hg levels is assumed to eventually result in a doubling of Hg levels in any element of any watershed, irrespective of soil or lake type, initial Hg levels, Hg pathways and transformations, and the time it will take to reach a new steady-state. Further normalization of Hg concentrations with respect to organic matter facilitates data collection, comparisons, generalizations, and environmental understanding, but may not always be necessary.

Since $e_{\mathrm{Soil}}(t)$ and $e_{\mathrm{Run}}(t)$ can be any function of time, our model formulation accounts for relevant dynamics in the ecosystem transfer of contaminants, but is general and independent of detailed knowledge on both structure and dynamics of the system, e.g. the number, size, connection, and turnover of different compartments within soils. The concentration-based approach also circumvents many of the difficulties associated with flux-based dynamic mass balance models, including the appropriate consideration of many ecosystem processes and the quantification of all relevant pools and fluxes of Hg, water, organic matter, and other matrices. Another advantage with this modelling approach is that all critical ecosystem components are related directly to the forcing variable $\mathrm{Hg}_{\mathrm{Prec}}$ by means of a few key coefficients (Section 3.5) that can be evaluated independently, which also facilitates the formulation of a CLAP as a single equation. Finally, the state of the ecosystem is described in scale-invariant relative terms at any given time after any change in $\mathrm{Hg}_{\mathrm{Prec}}$ (cf. Lamborg et al., 2002). This facilitates applications at different scales and in different types of environments.

3.5. Fundamental model parameters

The relationship between receptor contamination and source strength is here described by a transfer ratio k_X', which describes a concentration in a receptor X *relative* to a source concentration at a given time (t) for which data are available; the corresponding steady-state transfer factor k_X is conceptually related to bioaccumulation factors and other partition coefficients:

$$k'_X \equiv \frac{\mathrm{Hg}_X(t)}{\mathrm{Hg}_{\mathrm{Prec}}(t)}, \quad k_X \equiv \frac{\mathrm{Hg}_X(t=0)}{\mathrm{Hg}_{\mathrm{Prec}}(t=0)},$$

where X = Soil, Run, Lake, or Fish.

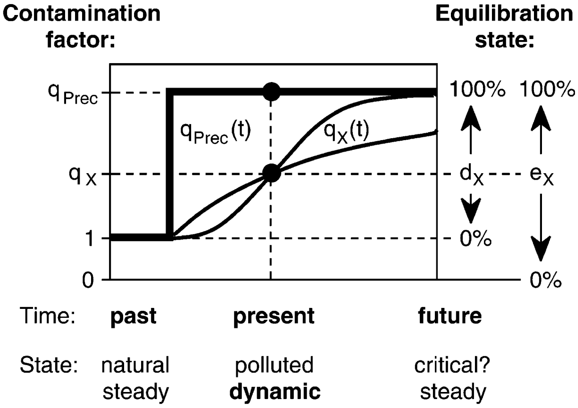

Fig. 2. General concept for semi-dynamic ecosystem modelling based on relative concentrations: illustration of various scale-independent parameters used to quantify and predict ecosystem contamination, and to account for complex pollutant partitioning and slow ecosystem dynamics (equilibration) without having to consider the actual shape of equilibration trajectories or underlying processes. The curve examples in the diagram refer to a sudden change of a concentration in precipitation as a result of atmospheric pollution. q_X, contamination factor; e_X, equilibration state coefficient; d_X, degree of equilibration (see text and Table 1 for further explanations).

Changes over time in the degree or impact of pollution can be quantified by *relative* contamination factors q_X, i.e. ratios of current values to pre-industrial, steady-state values (Fig. 2):

$$q_X \equiv \frac{\mathrm{Hg}_X(t)}{\mathrm{Hg}_X(t=0)},$$

where X = Prec, Soil, Run, Lake, or Fish.

Contamination factors have the advantage of being fairly independent of system-specific differences in Hg biogeochemistry, because these are ideally cancelled out in such ratios. In this way, response dynamics can be accounted for without specifically addressing complex issues such as turnover rates, aqueous speciation and complexation, microbial transformation (methylation, volatilization), or bioaccumulation and biomagnification.

The dynamic state of each receptor can be expressed by a scale-invariant equilibration state coefficient e_X that describes the deviation of a receptor from steady-state balance with the source in *relative* terms, irrespective of underlying processes (Fig. 2). It is defined as the ratio between the contamination factor of the receptor and the one of the source. The equilibration state coefficient can assume any positive value: 1 at steady-state, <1 after onset of pollution, >1 after remediation. Assuming that the steady-state transfer at a distant future is the same as in the pre-industrial past, the equilibration state coefficient is equivalent to the ratio between the actual value and any future steady-state value of the concentration ratio between receptor and source (Fig. 2):

$$e_X \equiv \frac{q_X}{q_{Prec}} \equiv \frac{Hg_X(t)/Hg_X(t=0)}{Hg_{Prec}(t)/Hg_{Prec}(t=0)} = \frac{Hg_X(t)/Hg_{Prec}(t)}{Hg_X(t=0)/Hg_{Prec}(t=0)} \equiv \frac{k'_X}{k_X}$$

Alternatively, the degree of equilibration between two steady-states, i.e. the accomplished fraction d_X of the way from one steady-state to another (Fig. 2), can be derived from contamination factors as follows:

$$d_X \equiv \frac{q_X - 1}{q_{Prec} - 1}$$

This coefficient varies between 0 at departure from a steady-state and 1 (or 100%) at a new steady-state. In contrast to e_X, d_X is always positive irrespective of the direction of equilibration, e.g. increasing or decreasing pollution. e_X may be more convenient for formulating and solving model equations, d_X for comparisons with environmental data.

All these ratios are scale-independent numbers, which adds to the generality of model formulations. These coefficients can be treated either as lake-specific or as regional means and can be expressed either as constants or as functions of environmental variables that are available. They can be quantified directly or indirectly from survey data, as exemplified in the following.

3.6. Quantifying the natural steady-state and the current state of equilibration

The CLAP refers to a sustainable steady-state in the future. After sufficient time of equilibration to reach balance with any constant level of pollution (e.g. Hg_{Prec}), all dynamic state functions $e_X(t)$ in the equations gradually reach the predefined steady-state value 1. The magnitude of e_X is the basis for prognostic calculations based on synoptic (snapshot) data collected at time (t). For predicting future concentrations in a dynamic system based on available data covering only a short period of time, a critical issue is the actual state of equilibration these data represent. The closer current Hg concentrations in critical receptors still are to the pre-industrial state, the longer they will continue to increase to reach a new balance with a given degree of pollution, and the higher are the levels they will reach in the future. For a relevant emission-exposure-effect assessment, it is therefore essential to determine not only the current state but also the natural state of source and receptors (Section 4). Inherent response dynamics of ecosystem compartments also need to be accounted for when defining action levels. This raises the question: how can complex ecosystem dynamics be accounted for without sacrificing operational simplicity?

The response trajectories over time of different ecosystem compartments to environmental changes are difficult to predict without a detailed understanding of the turnover dynamics within ecosystems. For the calculation of the CLAP, however, the consideration of dynamic aspects can be reduced to a minimum: the only quantitative information needed is how much current receptor levels (Hg_{Soil}, Hg_{Fish}) deviate from a steady-state balance with the current source level (Hg_{Prec}). One of the major remaining difficulties in determining the CLAP is thus to actually quantify the transfer factors (k_X) at a future steady-state ($e_X=1$) based on data representing the current state of a system that is likely dynamic ($e_X \neq 1$). For persistent pollutants with a natural background level, such as metals, this can be achieved by expanding our knowledge from the current state to the natural steady-state of the past ($e_X=1$), for example by extracting transfer factors from historical records.

A link to the past can be obtained from vertical concentration profiles in lake sediments, which have been used many times as a historical record of atmospheric Hg pollution (e.g. Aston et al., 1973; Johansson, 1985; Swain et al., 1992; Johansson et al., 1995; Fitzgerald et al., 1998; Landers et al., 1998; Lockhart et al., 2000; Bindler et al., 2001). However, lake load is not identical with atmospheric load, but controlled by the deposition both directly on the lake surface and indirectly via runoff input, the proportion of which varies widely among lake types. Since most boreal lakes are linked to a large watershed, runoff from soil usually dominates the total input of Hg except in the least humic lakes (Meili, 1991b; see also Section 5.3), whereas atmospheric deposition on the lake surface dominates the input to seepage lakes and other precipitation-fed lakes that cover a large fraction of their watershed (Swain et al., 1992; Hrabik and Watras, 2002). In lakes surrounded by a large catchment area, soils act as an efficient Hg filter responding very slowly to input changes, and therefore sediment profiles do not properly reflect the extent of Hg deposition over the past century, even in relative terms (Meili, 1995; see also Section 4.1). Sediment contamination factors may, however, adequately reflect the historical increase of the total Hg input to lakes relative to natural conditions, at least in relative terms which are fairly independent of lake-internal processes. The differential response of sediment Hg may at first glance appear to complicate the quantification of source–receptor relationships, but provides in fact a key to quantify relevant Hg dynamics in entire watersheds by comparing lakes of different type, to estimate pre-industrial Hg exposure, and to reconstruct natural balances between atmospheric exposure and environmental concentrations of Hg.

3.7. The critical level of atmospheric pollution: semi-dynamic solutions

By using sediment contamination factors as a link between dynamic and steady-state conditions, the model equations in Section 3.4 can be combined and reformulated based on Section 3.5 to expressions describing the CLAP-Hg defined in Section 3.3 for key receptors defined in Section 3.2 as simple functions of regional survey information collected at any given time:

For soils:

$$\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{SoilCrit}}/k_{\mathrm{Soil}}$$

For fish in runoff-fed lakes:

$$\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{FishCrit}}[\mathrm{Hg}_{\mathrm{Prec}}/\mathrm{Hg}_{\mathrm{FishR}}][q_{\mathrm{LakeR}}/q_{\mathrm{LakeP}}]$$

For fish in precipitation-fed lakes:

$$\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{FishCrit}}(\mathrm{Hg}_{\mathrm{Prec}}/\mathrm{Hg}_{\mathrm{FishP}})$$

which includes the following parameters from synoptic surveys:

$\mathrm{Hg}_{\mathrm{Prec}}$: total Hg in precipitation;
$\mathrm{Hg}_{\mathrm{FishR}}$: total Hg in fish from runoff-fed waters (polyhumic lakes or streams);
$\mathrm{Hg}_{\mathrm{FishP}}$: total Hg in fish from precipitation-fed lakes (clearwater lakes);
q_{LakeR}: Hg contamination factor in sediments from runoff-fed lakes;
q_{LakeP}: Hg contamination factor in sediments from precipitation-fed lakes;
k_{Soil}: Hg transfer factor for soil organic matter at steady-state (quantification see Section 4.3).

These equations demonstrate that with the access to adequate regional survey data, the potentially complex transfer functions k_{FishR} and k_{FishP} in the initial model formulation can be eliminated, as well as the need to account for biogeochemical processes in the watershed and in the lake including sorption/desorption, erosion/sedimentation, volatilization, methylation/demethylation, and bioaccumulation/biomagnification. Relevant dynamics in watersheds are, however, still accounted for. For illustrative purposes, also k_{FishR} and k_{FishP} are quantified below.

If local data for $\mathrm{Hg}_{\mathrm{Prec}}$ are not available, its magnitude can often be estimated with sufficient accuracy by means of atmospheric dispersion models (cf. Munthe et al., 2001; Meili, 2001). Such models are also useful for regulating Hg emissions by linking the CLAP-Hg at any given site to any emission source.

For a basic assessment of the CLAP-Hg, one of the three formulae in this section is sufficient,

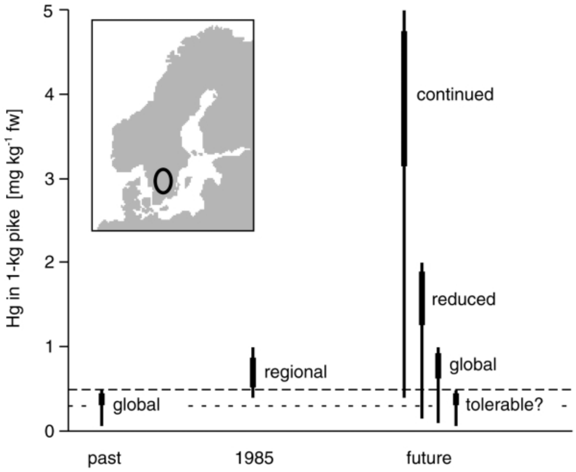

Fig. 3. Standardized Hg concentrations in lacustrine fish of the boreal forest zone at various levels of atmospheric pollution over time (see Table 2 for explanations). Estimates of pre-industrial, recent, potential, and maximum tolerable (critical) values, given as representative regional mean values for undisturbed watersheds in forested inland regions of southern Sweden (56–59°N). Thin bars show the potential range from precipitation-fed clearwater lakes (low) to runoff-fed polyhumic waters (high); bold bars show the representative range for boreal forest lakes where runoff accounts for 20–80% of the Hg input in the 1980s (Meili, 1991b) but 60–95% at steady-state (Section 5.3). All levels refer to standardized regional means and are based on observations in several hundred watersheds; ranges are larger if accounting for local variability among lakes due to other factors (∼4-fold) or among different fish within a lake (∼30-fold; Meili, 1997). The broken lines show current levels of concern (Section 2.2).

preferably the one focusing on the most sensitive environment.

4. Application to southern Sweden

In order to test our modelling approach to calculating the CLAP-Hg, it was applied at a regional scale to the inland of southern Sweden (Fig. 3) and related to the status around 1985, based on data collected around 1975–1995. This is the time when large-scale Hg monitoring was initiated, and represents the recent status that is here taken as an example of current or 'present' status, as opposed to future, critical and natural status. The stepwise derivation of source–receptor relationships is illustrated in Table 1, and resulting concentrations are summarized in Table 2 and Fig. 3.

4.1. Response dynamics in watersheds

The anthropogenic contribution of Hg to lakes can be quantified as the increase of Hg concentrations in surface sediments relative to background values in deep sediments. In lakes in southern Sweden around 1980, the mean sediment contamination factor q_{Lake} (Section 3.7) varied from $\geqslant 10$ to 2 along the whole potential range of drainage ratios from precipitation-fed clearwater lakes covering most of their watershed to runoff-fed, polyhumic waters with large watersheds (cf. Meili, 1995). The higher value is equivalent to the relative increase in atmospheric Hg pollution ($q_{\mathrm{LakeP}} = q_{\mathrm{Prec}} \approx 10$), the lower value reflects the relative increase of Hg levels in runoff from boreal forest soils ($q_{\mathrm{LakeR}} = q_{\mathrm{Run}} \approx 2$).

These numbers reveal several key aspects of the Hg cycle in the boreal forest zone. From the much lower sediment contamination factors in north Sweden (Johansson, 1985; cf. Landers et al., 1998) it is evident that lake sediments indeed reflect the steep regional gradient of atmospheric Hg concentrations and deposition over Scandinavia that is known from analysis of precipitation and other environmental samples in contact with the atmosphere (Lindqvist et al., 1991; Munthe et al., 2001; Johansson et al., 2001). On the other hand, the relative increase of Hg in lake sediments rarely reflects the full extent of atmospheric pollution because of the Hg retention in soils. This creates a risk of underestimating anthropogenic impact, either by underestimating current pollution if past levels are known, or, more commonly, by overestimating the natural background based on current values (Meili, 1995). A comparison of available sediment data (Meili, 1995; Bindler et al., 2001) suggests that by 1980, decadal means of atmospheric Hg deposition in the inland of southern Sweden had increased at least 10-fold during the past century, and probably even more along the southernmost coast and close to urban and industrial areas.

Since q_{Run} is much lower than q_{Prec}, the comparison of sediment contamination factors further suggests an extremely slow response of soils and streams to Hg pollution. This is reflected in the degree of equilibration for Hg in runoff-fed lake sediments in the 1980s:

$$e_{\mathrm{Run}} = e_{\mathrm{LakeR}} = q_{\mathrm{Run}}/q_{\mathrm{Prec}} \approx 2/10 \approx 0.2.$$

$$d_{\mathrm{Run}} = d_{\mathrm{LakeR}} = (q_{\mathrm{Run}} - 1)/(q_{\mathrm{Prec}} - 1) \approx (2-1)/(10-1) \approx 0.1.$$

These values imply that the Hg exported from soils was only at approximately 20% of the level expected from simultaneous levels of precipitation Hg, and that only approximately 10% of the increase in Hg deposition over recent decades was reflected in the soil runoff to lakes, i.e. that Hg_{Run} had passed approximately 10% of its potential change from a pre-industrial to a future steady-state relationship with Hg_{Prec}. These values can be expected to increase over time towards balance between Hg_{Run} and Hg_{Prec} ($e_{\mathrm{Run}} = d_{\mathrm{Run}} = 1$, cf. Fig. 2), following an unknown equilibration trajectory (break-through function), but to levels that can be quantified: If Hg_{Prec} was maintained at the level of the 1980s, the mean Hg_{Run} in the inland of southern Sweden could be expected to gradually increase approximately five-fold, that is from two-fold (q_{Run}) to 10-fold (q_{Prec}) the natural level. Note that this important quantification of the dynamic state of Hg in watersheds can be obtained without any information on present, past, or future levels of Hg_{Prec}, without considering pools or fluxes of Hg or organic matter, without knowing subsystem structures or process dynamics, and without any more advanced calculations than those presented above. The low value of $d_{\mathrm{Run}} \approx 10\%$ after several decades of severe pollution and a period of amelioration suggests that Hg levels in soils and drainage lakes need several centuries to reach steady-state. The value of $e_{\mathrm{Run}} \approx 20\%$ is supported by the imbalance of recent Hg fluxes to and from such watersheds (Section 5.3), but is here derived independently and without flux measurements. Since Hg_{Run} represents a level far 'downstream' along the Hg flow, Hg levels in streams and lakes may increase temporarily even after atmospheric Hg emissions have declined or ceased. The rate of change in d_{Run} is likely to vary regionally and locally with properties of the watershed, e.g. the amount and distribution of organic matter.

Natural (or rather pre-industrial) levels of Hg_{Prec} can be derived from sediment profiles and recent levels of Hg_{Prec} (Meili, 1995). Around 1986–1990, Hg_{Prec} was approximately 20 ng l^{-1} in the south Swedish inland (Lindqvist et al., 1991; Meili, 1994; Munthe et al., 2001), based on reported levels in southern Scandinavia of Hg wet deposition and rainfall at remote stations, i.e. >100 km from major urban areas and industrial emissions and further away in the case of coastal stations near foreign emission sources. Scaling with the appropriate contamination factor in sediment profiles from the same region during the same period ($q_{\mathrm{Prec}} \approx 10$, Section 4.1) yields a pre-industrial Hg_{Prec} of approximately 2 ng l^{-1}. This value is obtained also for north Sweden when applying the same approach (not shown here) and is in agreement also with previous estimates of the global background at these latitudes (Meili, 1991a, 1994, 1995). Natural values may have been even lower than pre-industrial ones, at least in some regions (Aston et al., 1973; Martínez-Cortizas et al., 1999).

4.2. Critical exposure of lacustrine fish

Steady-state transfer factors for animals in undisturbed lakes of different types may be obtained by using q_{Lake} from sediment cores for converting recent biotic levels such as Hg_{Fish} (data from Johansson et al., 2001) to natural values ($= Hg_{\mathrm{Fish}}/q_{\mathrm{Lake}}$). In most lakes, however, the contamination factor for fish may not be the same as that found in sediments (Sections 3.4, 5.4 and 5.5), unless all Hg inputs follow the same time trend (response dynamics). This is most likely in precipitation-fed clearwater lakes where the input of Hg is dominated by atmospheric input ($f_{\mathrm{R}} = 0$, $q_{\mathrm{FishP}} = q_{\mathrm{LakeP}} = q_{\mathrm{Prec}} \approx 10$), and runoff-fed, polyhumic lakes where the input of Hg is dominated by terrestrial input ($f_{\mathrm{R}} = 1$, $q_{\mathrm{FishR}} = q_{\mathrm{LakeR}} = q_{\mathrm{Run}} \approx 2$). The steady-state transfer factor k_{Fish} linking fish contamination to atmospheric pollution is thus quantifiable by scaling to the natural concentration in precipitation ($=Hg_{Prec}/q_{Prec}$, Table 2):

$$\begin{aligned} k_{FishP} &= \left[Hg_{FishP}/q_{Prec}\right]/\left[Hg_{Prec}/q_{Prec}\right] \\ &= [0.4\ \text{mg (kg fw)}^{-1}/10]/[20\ \text{ng l}^{-1}/10] \\ &\approx 20000\ \text{l (kg fw)}^{-1} \end{aligned}$$

$$\begin{aligned} k_{FishR} &= \left[Hg_{FishR}/q_{Run}\right]/\left[Hg_{Prec}/q_{Prec}\right] \\ &= [1.0\ \text{mg (kg fw)}^{-1}/2]/[20\ \text{ng l}^{-1}/10] \\ &\approx 250000\ \text{l (kg fw)}^{-1} \end{aligned}$$

Note the striking difference between k_{FishR} and k_{FishP}, which implies that at steady-state, Hg_{Fish} is typically several-fold higher in humic lakes than in precipitation-fed clearwater lakes (Table 2, Fig. 3). This difference may vary among regions in magnitude, but is consistent with independent evidence suggesting that at least in boreal forest regions, atmospheric Hg entering lakes by soil runoff is many-fold more bioavailable and/or less efficiently removed or diluted in waters and food webs than atmospheric Hg entering lakes by direct deposition (cf. Meili, 1991a, 1997). The bioavailability of Hg can change substantially along environmental pathways, depending on the abundance of inorganic and organic (biotic) ligands and the time available for abiotic and microbial transformations during transit, and is influenced notably by the abundance and proximity of environments with steep redox gradients favoring net methylation of passing Hg (Meili, 1997; Bishop and Lee, 1997; Grigal, 2002). In forested watersheds rich in wetlands, methyl-Hg in runoff waters can already reach critical levels, also outside the boreal zone, whereas methyl-Hg levels in precipitation are low (Meili, 1997; Munthe et al., 2001; Grigal, 2002). This is consistent with the transfer factors above, which also account for influences related to lake-internal Hg transformations. In combination with the dominance of terrestrial Hg input to most boreal lakes (Section 5.3), the transfer factors above suggests that fish Hg levels in boreal lakes are almost entirely controlled by processes in the watershed and will thus respond only very slowly to changes in atmospheric pollution (Section 4.1).

Such differential Hg partitioning depending on sources and pathways can be adequately described by simple transfer functions, but is a serious obstacle for the use of simple mass balance models treating all Hg equally, whereas complex models accounting for various Hg transformations are difficult to validate without considerable effort and rarely operational. Note further that the steady-state concentrations in fish are expected to be highest in humic lakes, even though the total Hg concentration in the water entering a lake may be lower in humic lakes (Hg_{Run}) than in precipitation-fed lakes (Hg_{Prec}) (e.g. Meili, 1991a,b; cf. Section 5.3). Accordingly, assessments of exposure limits for Hg in fish should be focused on humic lakes, where the transfer of atmospheric Hg to fish appears to be most efficient. Further work is needed to develop site-specific transfer functions linking Hg levels in fish to a given level of atmospheric pollution in different regions and ecotypes.

For polyhumic waters, the mean CLAP-Hg in the inland of southern Sweden for a $Hg_{FishCrit}$ of 0.5 mg (kg fw)$^{-1}$ can be obtained using the transfer factor k_{FishR}:

$$Hg_{PrecCrit} = Hg_{FishCrit}/k_{FishR} \approx 2\ \text{ng l}^{-1}.$$

This suggests that the maximum Hg concentration in precipitation to maintain the regional mean Hg concentrations in 1-kg pike in humic lakes below the critical limit of 0.5 mg (kg fw)$^{-1}$ is approximately 2 ng l^{-1}. Preliminary studies indicate that this limit may be even lower in some regions (cf. Meili, 2001), in particular if the recent USEPA (2001) recommendation of 0.3 mg (kg fw)$^{-1}$ is adopted as the critical limit for fish (Fig. 3).

4.3. Critical exposure of forest soils

Most of the current Hg content of soils is attributed to atmospheric emissions since 1880 (Lindqvist et al., 1991; cf. Munthe et al., 2001; Johansson et al., 2001; Hylander and Meili, 2002). By scaling recent measurements of Hg deposition with historical data of Hg emissions, S emissions, and S deposition (Lindqvist et al., 1991; Meili, 1991a; Munthe et al., 2001; Tsibulsky et al., 2001), the total anthropogenic Hg accumulation in soils from recent excess deposition can be estimated as roughly 2 mg m^{-2} in the inland of southern Sweden. This accounts for some net dry deposition (total dry deposition minus total volatilization) and runoff losses, but excludes local contributions close to point sources such as chlor-alkali industries and other historical emissions (Lindqvist et al., 1991). The accumulated excess deposition accounts for more than half of the total amount of Hg of approximately 2.5 mg m^{-2} in the mor layer of forest soils in the same area (based on 1984 data from Andersson, 1991; similar to another survey 10 years later, Alriksson, 2001). An anthropogenic contribution of approximately 70–80% has been suggested earlier (Andersson, 1991; Johansson et al., 1995), i.e. a contamination factor $q_{\mathrm{Soil}} \approx 4$. Distributing the Hg pools over the organic pool of approximately 3 kg m^{-2} yields a recent mean $\mathrm{Hg}_{\mathrm{Soil}}$ of approximately 0.4 mg (kg org)$^{-1}$ and a pre-industrial mean value of approximately 0.05–0.15 mg (kg org)$^{-1}$. The pre-industrial range is similar to earlier estimates of 0.075 mg (kg dw)$^{-1}$ at org/dw ≈ 60–80% (Andersson, 1991), and much lower than recent concentrations (Table 2). Corresponding background estimates for other regions are similar despite widely differing soil thickness and climate, which is consistent with a regionally or even globally uniform pre-industrial exposure to Hg, and also with simple equilibrium sorption concepts (including the consideration of a critical concentration in precipitation rather than a critical deposition load as the CLAP). Accordingly, the steady-state transfer of Hg from precipitation to soil can be described by a transfer factor (partition coefficient) derived from the pre-industrial concentration ratio:

$$\begin{aligned} k_{\mathrm{Soil}} &= \left[\mathrm{Hg}_{\mathrm{Soil}}/q_{\mathrm{Soil}}\right]/\left[\mathrm{Hg}_{\mathrm{Prec}}/q_{\mathrm{Prec}}\right] \\ &\approx \left[0.4\ \mathrm{mg\ (kg\ org)^{-1}}/4\right]/\left[20\ \mathrm{ng\ l^{-1}}/10\right] \\ &\approx 50000\ \mathrm{l\ (kg\ org)^{-1}} \end{aligned}$$

Interestingly, this soil transfer factor is similar in magnitude to the partition coefficient between Hg and humic substances in natural surface waters or in experimental aquatic systems (e.g. Meili, 1997; Sjöblom et al., 2000). This may reflect similar sorption mechanism and support CLAP concepts based on the concentration of free ions in soil solutions (cf. De Vries and Bakker, 1998), but such concepts are difficult if not impossible to implement because of analytical difficulties, notably in the case of Hg.

Apparently the relative increase in Hg deposition is not fully matched by the relative increase of Hg in soils ($e_{\mathrm{Soil}} < 1$, $d_{\mathrm{Soil}} < 1$). A recent increase of $\mathrm{Hg}_{\mathrm{Soil}}$ from approximately 0.1 to 0.4 mg (kg org)$^{-1}$ in the mor layer (Table 2) suggests that $e_{\mathrm{Soil}} = q_{\mathrm{Soil}}/q_{\mathrm{Prec}} \approx 0.4$ and $d_{\mathrm{Soil}} = (q_{\mathrm{Soil}} - 1)/(q_{\mathrm{Prec}} - 1) \approx 0.3$, implying that the soil contamination in the 1980s had only passed approximately 30% of its potential change from a pre-industrial to a future steady-state relationship with $\mathrm{Hg}_{\mathrm{Prec}}$. This value may vary between 20 and 80% depending on the pre-industrial soil Hg level in southern Sweden, which can be estimated by comparison with corresponding soils in northernmost Sweden where the impact of European pollution is minimal, by adopting either all or half of either the concentration or the pool of Hg (cf. Andersson, 1991). However, it is evident that d_{Soil} is much higher than $d_{\mathrm{Run}} \approx 0.1$, which means that the response of Hg in soil runoff to changes in Hg deposition is lagging far behind that of Hg in the organic soil layer, as proposed previously (Meili, 1991a). This implies that a forest soil is not adequately described by the simplest approach of using a single mixed compartment for modelling, but only by a series of several compartments, the stratification being vertical, horizontal, or functional (Meili, 1991a; cf. Johansson et al., 1991; Grondin et al., 1995; see also Section 2.3).

The CLAP-Hg for soils, i.e. $\mathrm{Hg}_{\mathrm{Prec}}$ meeting the criterion of not causing any further increase of $\mathrm{Hg}_{\mathrm{Soil}}$, can be estimated by scaling recent mean values of $\mathrm{Hg}_{\mathrm{Soil}}$ in southern Sweden (Table 2) using the transfer factor k_{Soil}, analogous to the procedure for fish: $\mathrm{Hg}_{\mathrm{PrecCrit}} = \mathrm{Hg}_{\mathrm{SoilCrit}}/k_{\mathrm{Soil}} = \mathrm{Hg}_{\mathrm{Soil}}/k_{\mathrm{Soil}} \approx 8$ ng l^{-1}. It should be noted, however, that this limit only applies when averaged over the entire mor layer (i.e. the Swedish soil data available), whereas increasing Hg in runoff (see above) strongly suggest that a lower limit should be applied to protect all soil compartments from an increasing contamination. For the soil compartment feeding the soil runoff, where the contamination has increased only approximately two-fold above natural ($q_{\mathrm{Run}} \approx 2$), the CLAP-Hg is given by:

$$\mathrm{Hg}_{\mathrm{PrecCrit}} = \left[\mathrm{Hg}_{\mathrm{Prec}}/q_{\mathrm{Prec}}\right] q_{\mathrm{Run}} \approx 2 \ \ \mathrm{ng\,l^{-1}} \times 2 \approx 4 \ \ \mathrm{ng\,l^{-1}}.$$

It can be noted that in the inland of southern Sweden, the CLAP-Hg for soils is higher than the CLAP-Hg for fish (2 ng l^{-1}). However, given the apparently increasing concentrations in some soil compartments as well as the uncertainties of soil estimates and potential regional differences, it appears advisable to adopt the lower limit for fish of $\mathrm{Hg}_{\mathrm{PrecCrit}} \approx 2$ ng l^{-1} also for soils. Note that with the chosen approach, the estimate of $\mathrm{Hg}_{\mathrm{PrecCrit}}$ for fish is obtained independently and is not affected by uncertainties in $\mathrm{Hg}_{\mathrm{PrecCrit}}$ for upstream soils.

5. Comparisons and implications

5.1. Dynamic watershed modelling

The CLAP of lakes and forests by Hg and other toxicants can be assessed by comparing the degree of pollution at a distant future with critical limits. Future levels can be estimated by adequate projection of source–receptor relationships based on a reconstruction of the past from data collected in the present. An important insight is that present Hg levels in forest soils and humic lakes are far from having reached steady-state balance with present Hg concentrations in precipitation. Therefore, it is essential to account for critical ecosystem dynamics, even if atmospheric Hg levels should remain constant after the recent changes. Such dynamics can be recognized and quantified from basic field data. They can then be used to estimate past and future steady-state concentrations in critical receptors without mass balance modelling of complex ecosystem processes and without dynamic quantification of non-linear trajectories. This is achieved by using process- and scale-independent concentration ratios from recent observations to extract key parameters, in particular the steady-state transfer factor and the current degree of equilibration for each receptor of interest. Simple concepts combined with a few traditional survey parameters are thus sufficient to produce reasonable estimates of past, present and future Hg concentrations in precipitation, soils, and fish in humic and clearwater lakes. Resulting values are consistent with each other and with observed data (Table 2, Fig. 3).

5.2. Differences among receptors in both levels and dynamics

Data from southern Sweden suggest that at steady-state, the Hg concentration in the organic matter of forest soils (mg (kg org)$^{-1}$) slowly approaches a mean transfer factor relative to the concentration in precipitation (ng kg^{-1}) of approximately 1/20 ppm. The same applies to the corresponding transfer factor for fish, but with important deviations related to lake type: the transfer factor for the average Hg concentration in 1-kg pike (mg (kg fw)$^{-1}$) approaches rapidly a mean value of approximately 1/50 ppm in precipitation-fed lakes, and much more slowly a mean value of approximately 1/4 ppm in runoff-fed lakes (Table 1). Accordingly, Hg levels in fish at steady-state (e.g. natural) are far higher in humic waters than in clearwater lakes, which is important for the formulation of critical receptors and critical pollution levels. Further, the difference between these lake types is much more pronounced at steady-state than at the current state of recent pollution (Table 2, Fig. 3). This highlights the importance of considering site- and compartment-specific response dynamics when assessing emission-exposure-effect relationships in ecosystems.

5.3. Comparison with Hg fluxes in watersheds

A comparison of observed Hg fluxes in boreal watersheds supports the key aspects of our modelling approach and also highlights the importance of watershed processes for the future Hg levels in fish: in the inland of southern Sweden, lakes of different type (median and range from clearwater to humic) cover typically 6% (20–2%) of their watershed, and runoff (40% of precipitation) accounts for 85% (60–95%) of the water input. In this setting, runoff supplied about half (20–

80%) of the total Hg entering lakes in the 1980s (cf. Meili, 1991b), but approximately 85% (60–95%) of the methyl-Hg (not accounting for methylation within the lakes). This is based on recent monitoring in these and other forested watersheds, showing that the mean methylated fraction of Hg accounts for 3–10% of total Hg in runoff (with high values in humic waters), but only 1–2% in precipitation (cf. Bishop and Lee, 1997; Meili, 1997; Munthe et al., 2001; Grigal, 2002). As Hg fluxes in the watershed approach steady-state ($e_{\mathrm{Run}} \rightarrow 1$), the runoff contribution to lakes is predicted to increase further and to reach natural proportions of approximately 85% (60–95%) for total Hg and 97% (90–99%) for methyl-Hg, irrespective of pollution level. This is based on the equations in Section 3.4, according to which a fraction at steady-state (f_{R}) is related to that at any given state (f_{R}') as $f_{\mathrm{R}} = 1/[1 + (1/f_{\mathrm{R}}' - 1)e_{\mathrm{Run}}]$, and confirms independently obtained transfer factors showing an overwhelming dominance of terrestrial Hg input to most Swedish lakes, in particular to their biota (Section 4.2).

Comparison of runoff to deposition shows that the mean Hg output from soils in southern Sweden is only approximately 10–15% of the input during the 1980s if not considering any net dry deposition of Hg (Meili, 1991b) and $<10\%$ if including an estimate of gross dry deposition (Meili, 1991a; cf. Johansson et al., 1991: 5–30%). This imbalance lends support to the low value of $e_{\mathrm{Run}} \approx 20\%$ which was here derived from lake sediment contamination factors, i.e. independently and without flux measurements (Section 4.1). Both the watershed imbalance and the limited increase of sediment contamination in humic lakes (only ~two-fold) indicate that at least half of the current runoff Hg may consist of Hg deposited on the watershed before the onset of pollution, and that ‘new’ Hg may be equally mobile as ‘old’ Hg or possibly less given the values above. However, long-term consequences of atmospheric Hg pollution for surface waters can be foreseen from the increasing Hg accumulation in soils (Section 4.3).

5.4. Interpretation of survey data

Among the lakes in southern Sweden, which all have been exposed to about the same history of atmospheric pollution, the response of Hg levels appears to differ widely among watersheds and ecosystem compartments. Interestingly, our evaluation suggests that in most Swedish lakes (Table 2, oligo-polyhumic), Hg levels in fish have not more than doubled thus far, even in areas where Hg levels in precipitation have increased to 10-fold or more during at least one decade. This is explained by the dominance of terrestrial influences on the fish Hg levels in these lakes, notably at steady-state (Sections 4.2 and 5.3). The historical increase of fish Hg levels may be regularly more than two-fold only in lakes where more than 90% of the present Hg load is supplied by direct input such as atmospheric deposition on the lake surface (cf. Table 2). Such lakes are rare in Sweden (Meili, 1991b), but common among seepage lakes, where Hg levels in fish indeed appear to respond very rapidly to changes in atmospheric deposition (Hrabik and Watras, 2002). The relative importance of terrestrial influences, which are here conservatively related to the fluxes of total Hg, may be altered in either direction by lake-internal processes, which can induce substantial variability among lakes (cf. Meili, 1997). However, the bioaccumulation of Hg must in one way or another depend on the supply of Hg.

Another important observation related to the non-linearity of ecosystem response is that the increase of Hg levels in sediments (typically 2–6-fold; Meili, 1995) is much more pronounced than that in fish, but usually much less than the increase in atmospheric deposition. This implies that the interpretation of sediment profiles as quantitative archives of pollution history is not straightforward and may also differ with the target (see also Section 5.5).

The slow response of environmental Hg levels to changes in atmospheric deposition (in both directions) and the strong influence of climatic factors (e.g. Grigal, 2002) have implications also for the interpretation of environmental time series. Changes in fish Hg levels during the past decades, both upward and downward, have been reported from studies in Sweden covering each about one decade (Lindqvist et al., 1991; Johansson et al., 2001). These changes were more rapid than can be explained by an equilibration of soil and runoff

Hg, are only in part consistent with simultaneous trends in various measures of atmospheric Hg pollution, and are rarely supported by more recent compilations of fish Hg levels in Sweden and Finland (unpublished) showing interannual changes but no systematic trends over longer time intervals. Changes of Hg levels in fish may be a temporary and regional phenomenon linked to for example known decadal fluctuations in climate, rather than a response to changes in atmospheric pollution. Further, local variations among different ecosystems need to be considered: while the response to climatic changes may be large and rapid in humic lakes, the response to changes in atmospheric pollution may be rapid in precipitation-fed seepage lakes (Hrabik and Watras, 2002) but difficult to quantify or even verify in humic lakes where the input of Hg and particularly methyl-Hg is largely terrestrial and affected by hydrological fluctuations (Section 5.3; Bishop and Lee, 1997; Grigal, 2002). Continuation of long-term monitoring as well as mechanistic studies will help resolving these issues.

5.5. Present, past and future Hg concentrations

Using the equations in Section 3.4, past and future Hg levels in fish can be predicted for lakes of different type (Table 2 and Fig. 3). Present levels of Hg in pike exceed current levels of concern in most lakes of southern Sweden (Table 2; Lindqvist et al., 1991; Johansson et al., 2001; Meili, 2001). However, even natural levels can be high in boreal regions, where the lake average (oligo-polyhumic) can reach at least 0.4 mg (kg fw)$^{-1}$, or at least 0.5 mg (kg fw)$^{-1}$ if considering only humic lakes (Table 2, Fig. 3; cf. Meili, 2001). Both the magnitude and the patterns of these estimates are in good agreement with estimates for Finnish lakes in less polluted areas (Verta et al., 1986).

The present situation can be regarded as a transition from the natural to a future steady-state. Atmospheric Hg deposition during the 1980s and preceding years is estimated to have exceeded natural deposition at least 10-fold in the inland of southern Sweden, and approximately four-fold in the north. The increase of Hg concentrations in fish, however, may today be less than two-fold in most boreal lakes, due to the filtering or buffering effect of surrounding soils (Sections 5.3 and 5.4). For the same reason, sediment contamination factors provide valuable information about long-term changes in watersheds, but need to be interpreted with care as a consequence of slow and non-linear response dynamics in watersheds. The maximum extent of atmospheric Hg pollution may have been higher than estimated by assuming a proportional response of sediment Hg levels; on the other hand, the historical increase of Hg levels in fish over the past century may have been less than estimated by assuming proportionality between fish and sediment Hg levels or by comparison with generic background levels for all lakes (Section 4.1; cf. Johansson et al., 1991, 2001).

Natural levels of standardized Hg concentrations in fish can vary by more than an order of magnitude among lakes within a region (Table 2). Also regional variations within the boreal zone can be substantial, as indicated by a nation-wide reassessment of Swedish data showing the lowest Hg levels in fish in the most polluted region but high levels in remote regions (Meili, 2001). Some regions appear to be particularly susceptible to atmospheric Hg pollution and may include thousands of lakes where even natural Hg levels in fish may have exceeded current critical limits. Such regional variability of natural Hg levels in biota needs to be considered when regulating regional as well as global Hg emissions.

5.6. Critical level of atmospheric pollution

Near Hg emission sources, attention should be focused on the pollution of clearwater lakes and organic soils, where critical limits may be reached most rapidly (current Hg levels of concern: $\leqslant 0.5$ mg (kg fw)$^{-1}$ in freshwater fish, and 0.5 mg (kg dw)$^{-1}$ in soil organic matter). However, critical receptors also in remote areas are boreal humic lakes, where Hg levels in biota are naturally high, most likely to increase further, and at high long-term risk of exceeding the current levels of concern. In typical Swedish lakes, concentrations in fish are predicted to increase unless virtually all regional emission sources are closed (Table 2, Fig.

3). However, this may not be sufficient, since Hg levels in 1-kg pike can reach 0.3–0.5 mg (kg fw)$^{-1}$ naturally in some regions, even in typical lakes (Table 2). The CLAP to avoid further increase of Hg in Swedish soils and to keep regional means of Hg in 1-kg pike in the most sensitive watersheds below 0.5 mg (kg fw)$^{-1}$ is estimated to be reached at a Hg concentration in precipitation of 2 ng l^{-1}. This concentration is about half of the present level in the most remote areas of the northern hemisphere, and similar to the pre-industrial background (Meili, 1995), implying that virtually all regional as well as global anthropogenic emissions need to be eliminated to achieve the goal.

It should be considered that our present assessment of future Hg levels in 1-kg pike refers to regional mean values, implying that after several centuries of equilibration, critical limits may still be exceeded in about half of the humic lakes, even without anthropogenic emissions. For individual fish, the same limit is exceeded in many more lakes. Accordingly, the formulation of environmental goals and action levels must include aspects of scale and statistics, and also take into consideration that even natural Hg levels may exceed critical limits. Further studies should address the spatial and temporal variability of transfer factors as well as transfer dynamics among and within regions and watersheds.

6. Conclusions and prospects

As indicated by our first assessment, the CLAP can be estimated based on simple models combined with traditional survey data, without need for advanced measurements or calculations. While we are aware of the complexity of Hg cycling in airsheds, watersheds and lake ecosystems (e.g. Lindqvist et al., 1991; Meili, 1997; Bishop and Lee, 1997; Bringmark and Bringmark, 2001b; Munthe et al., 2001; Sjöblom et al., 2000; Grigal, 2002), we have here chosen to focus on long-term effects of fundamental non-linearities that are characteristic of perturbed watersheds. Such non-linearities require consideration in the interpretation of common survey data as well as in the implementation of pollution control strategies. They can be addressed with a very basic approach and quantified with limited data, while uncertainties can be reduced as more information becomes available. Although practically no fluxes, processes, and turnover dynamics were considered other than implicitly, the proposed approach provides estimates that are quantitatively consistent with observed Hg levels in soils as well as in lacustrine fish in Sweden and elsewhere. A model with more sophisticated structures and dynamics may provide a tool reaching beyond the stated purpose of quantifying CLAP, but justification, validation, and application based on traditional survey data alone may be difficult.

The findings reported here may be regarded as a first approximation of the mean long-term fate of Hg in southern Sweden, a typical boreal region where podzolic soils on igneous bedrock, coniferous forests, peatlands, and poorly buffered humic lakes are common features. In other regions, the transfer factors and dynamics may be different, and within regions, variability may be considerable. However, many of the basic modelling principles and some of the specific aspects presented here may well be applicable also to other pollutants, areas and ecosystems, and at different scales, if basic survey data are available. Assessments thus far suggest that the proposed approach is applicable over a wide range of contamination scenarios, climatic gradients, and lake hydrography. By working with normalized concentration ratios and relative changes over time (cf. Lamborg et al., 2002), many of the problems related to the enormous complexity of the Hg cycle and the variability among and within ecosystems can be eliminated for operational assessments. Many confounding factors are cancelled out in ratios, or else they can be treated as unknown but constant provided that the impact of anthropogenic activities other than Hg emissions is limited. This applies to the atmospheric and aqueous Hg speciation and turnover (including dry deposition/volatilization, particle sorption/desorption, and methylation/demethylation in waters, soils and sediments), lake characteristics (such as hydrography, chemistry, and productivity), as well as ecological and physiological factors (such as bioavailability and biomagnification). Accordingly, sources and sinks of methyl-Hg may not need to be addressed specifically other than indirectly, even though the methylated fraction of Hg is known to vary substantially among ecosystems and ecosystem compartments (e.g. Meili, 1997; Grigal, 2002).

The proposed modelling approach to determine the critical level of atmospheric Hg pollution has been applied here with a regional and long-term perspective. However, it is designed to be flexible and to provide a basis for future expansions towards models with a higher spatial and temporal resolution (e.g. watershed-specific dynamic models for assessing ecosystem effects over time before or without reaching steady-state). Key requirements for application to different regions (soil types and lake types) are robust algorithms for specific transfer factors and equilibration factors. Further development may include interactions with other pollutants (e.g. sulfate and acids; Branfireun et al., 2001; Hrabik and Watras, 2002) and environmental changes (e.g. climate; Grigal, 2002). Ultimately, site-specific dynamic models for annual or even seasonal predictions may be developed based on site-specific parameters, but this requires further research into the Hg dynamics at the air–land interface and into the sources and environmental fates of methyl-Hg including its formation and stability in various terrestrial and aquatic environments.

Acknowledgments

Financial support was provided by the Swedish Environmental Protection Agency (Naturvårdsverket). The SEPA and other authorities are also acknowledged for the early initiation and continued support of environmental monitoring programs generating a wide array of unique data.

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5.2. THREE SIMPLE METHODS FOR CALCULATING CRITICAL LOADS FOR MERCURY IN FOREST AND AQUATIC ECOSYSTEMS

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November 26, 2002

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1 Introduction

The major environmental exposure of mercury in Scandinavia is from fish originating mainly in freshwater lakes. Another significant source has historically been dental fillings, but this problem is rapidly decreasing with the increased use of polymer and silicate based materials in dentistry. A significant number of Scandinavian lakes have fish with contents above the presently recommended 0.5 mg Hg/kg; the range is approximately from 0.1 to 3 mg/kg wet weight fish. It is estimated from reoccurring lake surveys and fish analyses that perhaps as many as 50% of all Swedish lakes may have fish with mercury above the limit. In Scandinavia there is a long rooted tradition with fishing in lakes, and the fish is used for domestic consumption. All lakes in Sweden (300'000), Norway (200'000) or Finland (200'000) cannot be surveyed and the fish analysed for mercury, making deposition reductions important for the long term. In the European perspective, Scandinavia is the area with a most visible mercury problem related to long range pollution. Because of the magnitude of the problem here and the low focus on these issues in Europe, the Scandinavian countries will take the initiative to develop assessment models.

2 Objectives and methods

The objective is to develop several models ranging from very simple to rather complex that can be used to estimate the critical load for mercury, using fish in lakes as the environmental endpoint and a proxy for human exposure through freshwater fish consumption. The following models were derived;

1. The simplest possible empirical model for direct deposition partitioning to fish (CLAP)
2. The simplest possible mass balance model (SMB)
3. The simplest possible dynamic model (VSD-Hg)
4. A complex multi-compartment dynamic model (DECOM-Hg/FORSAFE-Hg)

The models should be operable within the data available in the Swedish lake survey and the Swedish forest inventory databases. The different approaches have been tried to investigate how different model can be adapted to different situations. The simples model has been developed in order to make an approximate estimate possible, even when little data is available. The more complex models have been investigated in order to be able to adress the slow dynamics of the system, and in order to be able to include feedbacks from soil acidification, soil acidification recovery caused by the sulphur and nitrogen protocols, climate changes and changes in forest management. All these can potentially have a significant effect on the assessment. A complicating factor for assessing actual effects come from all the non-industrial non-environmental exposures such as materials used in dentistry, smoking of tobacco, exposure to mercury used as preservative additives in vaccines and paint and contamination from industrial processing of food. All such factors will be ignored in this study. The formal method applied for determining a critical load always starts with the definition of the objective ecosystem. It is not a technical construct of political nature as sometimes stated, but a formal exersize in natural science to connect ecosystems to maximum tolerable loads in a defined and quantitative way (Nilsson and Grennfelt 1988). The definition applied here is adapted to mercury after the Skokloster definition (Nilsson and Grennfelt 1988, Sverdrup and Warfvinge 1988): This is based on setting the higest critical limit with no documented response, "the precautionary principle":

The critical load of mercury is the maximum load of mercury to an ecosystem that will not cause long term damage to ecosystem structure nor function

The above definition does not exactly represent what was actually done for acidification, which in reality turned out to be an ”maximum acceptable damage approach”. It was based on setting limits based on a cutoff of a response function; For acidification ”damage” was defined as a 20% response in experiments. The correct definition, using the modified interpretation of Barkman (1998), is;

The critical load of mercury is the maximum load of mercury to an ecosystem that will cause the maximum long term sustainable damage to ecosystem structure or function

The definitions has been used to derive a formal sequence of steps to be taken to derive this load (Sverdrup et al 1988);

1. Define target ecosystem
2. Find ecosystem indicator(s)
3. Determine chemical ecosystem limit for every indicator
4. Calculation
   (a) Select method
   (b) Collect data to representatively sample the ecosystem
   (c) Execute calculation
5. Map critical load
6. Assess degree of excess pollutant load
7. Quantify mitigation requirements

The procedure ensures that the derived critical load is securely linked to the ecosystem. This proceedure has been successfully performed for deposition of acidity and nutrient nitrogen to terrestrial and aquatic ecosystems. The experience is that the consept is very adaptable and can principally be used for any pollutant or activity having adverse effect in ecosystems. The simplest steady state model can in principle be operated with a pencil on the back of an envelope. The present dynamic models were developed with the STELLA software, in order to facilitate development, modifications and transport between MAC and PC computer platforms.

3 Some basic principles and assumptions

3.1 Ecosystems and indicators

For mercury, the first important ecosystem is the human being, the inhabitant of Sweden. The second ecosystem applied is the forest ecosystem. A secondary specified indicator in the terrestrial ecosystem is the decomposition mechanism in the forest soil, the soil microbiological flora. This is a functional criteria. It is of relevance for the response that this indicator is also affected strongly by other pollutants, but these are not relevant for mitigation. The ecosystem must be able to withstand and tolerate every individual pollutant, or it must be reduced to such a tolerable level, the critical load. A third relevant ecosystem may be the land ecosystem, using predatory birds and birds that feed on bottom fauna in streams as ecosystem indicators.

3.2 Setting limits

A critical limit has only been defined for fish as a proxy for humans in Sweden. So far, no other limit has been proposed in quantitative terms, even if this appear to be possible for some other ecosystems (predatory birds, decomposition in soils, uptake to food crops). The recommended uptake limit has been set to approximately 30 g/day by the USEPA. From this they derived their limit for water at 1 g/day by using a safety factor of 30, corresponding to a concentration limit based on a 2 liter per day consumption. The Swedish Food Administration recommends a limit in the range of 40 g/day to derive the limit for fish. No safety limit was involved, nor was any allowance for exposure from any other source made. The recommended limit for mercury in Scandinavian has been defined for fish contents recommended not to exceed 0.5 mg Hg/kg. An alternative would be to make assumptions like allowing half the limit to be reserved for background exposure and exposure from other sources, and thus only 10-20 g/day would be allowable for mercury from fish consumption. This would lead to a fish limit in the range of 0.25 mg/kg fish. New data and such considerations may bring changes. The Swedish Food and Health Administration is at present evaluating the relevance of a new limit at 0.3 mg Hg/kg. Different considerations using mathematical modelling and historical records from sediments suggest that fish content 500 years ago was less than 0.1 mg/kg fish. Data for occurrence of symptoms versus human exposure are difficult to find. The presented data originate from different industrial pollution events in the past. Adapting the ”precautionary principle” instead of the ”prove the damage” approach, such data is very useful. The human limit is based on the view that the limit for human intake should be placed at approximately 40 g/day. This corresponds to a symptom incidence of approximately 50 per 100,000 inhabitants. Assuming a maximum intake of 20 g/day correspond to a symptom incidence of 5 per 100,000 inhabitants. Despite all the uncertainties involved, use of the diagram allow for setting a risk level and subsequently derivation of a safe level with respect to that risk incidence. A back-of-the-envelope calculation with the data yield a limit of 0.5 mg Hg/kg for fish and by assuming the same standards of risk as is accepted for medical risk levels in medication or contraceptive pills, we get a somewhat lower value, consistent with the proposed lower new limit, not yet implemented by the Swedish Food and Health Administration (0.3 mg/kg fish). There is apparently no safe limit for mercury, there is an incidence of symptom associated for every exposure, regardless how small. This makes it necessary to work with statistical methods of epidemology for establishing an acceptable symptom incidence in the population.

If we want to accept the ”maximum allowable damage approach” and define this as a 20% impact according the response function available, we get a limit of 0.6 g/l. The same approach leads to the limit set for fish, 0.5 mg/kg fish. If we adopt the ”precautionary principle”, then we set the limit before the response curve start to rise and suggest we have effect. The much lower limits must be suggested, for soil microbial function 0.2 g/l and for fish 0.1 mg/kg fish. Only very few studies are available on mercury toxicity to trees and microorganisms in the forest ecosystem. Studies on trees indicate that methylmercury has a toxic effect on tree root growth, possibly there would be a similar effect on biomass decomposition.Godbold et al (1987) did experiments on the tolerance of tree roots to methyl mercury. Effect at very low levels were reported. A Hill-type retardation model was adapted to the data (h(Hg) = 1/(1 + k·[Hg]^{m})), the parameters are k=3.2$\cdot$10^{15} and m=1.75 when the concentration is expressed as kmol/m^{3}. This implies that for no effect the limit is 0.2 g/l and for an effect of 20% it is 0.6 g/l.

3.3 Ecosystem transport of mercury

Mercury is deposited mainly as metallic metal and divalent salts to the soil, the divalent salts dominate, since they are water soluble, and are washed out of the atmosphere with the wet precipitation. In the soil divalent mercury will be absorbed to the organic matter in ion exchange

Ecosystem	Indicator for limit	No effect observed	Observed effect
Humans	Fish content (Pike)	0.1 mg/kg fish	0.5 mg/kg fish
Humans	Drinking water	0.4 g/l	5 g/l
Forest; Root growth	Solution MeHg-conc	0.2 g/l	0.6 g/l
Forest; Soil microbiology	Total content	0.1 mg/kg	0.25 mg/kg
Land fauna; Otter survival	Otter diet content	0.05 mg/kg food	0.2 mg/kg food
Land fauna; Otter survival	Otter muscle content	0.5 mg/kg	1 mg/kg food
Land fauna; Eagle survival	Eagle muscle content	1 mg/kg food	2 mg/kg food
Lake fauna; Pike survival	Pike muscle content	4 mg/kg food	8 mg/kg food

Table 1: *Suggested limits for mercury, based on observed effects.*

sites. Several biochemical processes will rapidly transform mercury in the ion exchange positions into organically bound forms of mercury (Gunneriusson and Sjöberg, 1991, Mierle and Ingram, 1990). The soil reservoir of mercury is predominantly in the organically bound form, it is readily methylated in the soil. In Scandinavia, there is a long history of mercury accumulation in animals and plants due to human activities. Analysis of feathers from large carnivorous birds like Norwegian eagle, indicate that the mercury content has increased steadily since 1840 untill present, and that the increase in rather accellerating than stagnating. More recent studies by Dr. I. Rehnberg at Umeå University on lake sediment cores, show that mercury input to Swedish lakes culminated in the late 1980's. The sediment cores also revealed that prehistoric deposition levels must have been extremely low. Mercury is contained in most types of food, but fish from the Baltic Sea and acid lakes may have substantially elevated levels. Mercury content in fish has been related to the pH of the lake (Björklund et al. 1984, Håkansson et al., 1988), based on the data from the Swedish lake mercury research programme. The fish uptake rate dependence on aqueous mercury concentration in the water or interstitial sediment concentration is suggested to be approximately first order by these authors. This has later been questioned in later literature. The dependence on the amount of mercury in the sediments, play an important role mercury content in planctivore fish in eutrophic lakes. For lakes where the fish does not feed on the sediment, sediment content is less the cause of fish content. A study by Svensson et al., (1987) indicate that the relation between human blood concentration of mercury and fish mercury content is approximately first order with respect to the mercury concentration in the substrate. The turnover of mercury inside the lake has been omitted in all the models presented here, because we have assumed that internal turnover is rapid. If all annual additions of mercury is cycled between the sediment and the lake more than once a year, then the fish may be exposed to the whole load. Then we may get away from having to deal with methylation and demethylation, volatilization. Organically bound implies that mercury is complexed to organic acids, incorporated and strongly bound to humus complexes and contained in biomass as methylmercury (Strohal and Huljev, 1971; Lodenius and Autio; 1989). Methylmercury is water soluble, can be positively charged, and take part in soil ion exchange, it is very mobile. Methylmercury is dissociated in the soil. Methylmercury complexes readily with both soil organic matter and DOC under normal soil conditions. One observation

Approach/substance	Cadmium	Mercury	Lead
Precautionary principle	9 microgram d^{-1}	15 microgram d^{-1}	120 microgram d^{-1}
Maximum allowable damage	26 microgram d^{-1}	24 microgram d^{-1}	250 microgram d^{-1}

Table 2: *Suggested uptake limits for cadmium, mercury and lead, based on epidemologically observed effects and two different risk approaches. The limits are based on a normal grown up person with 65-70 kg body weight, and the limits should be adjusted proportionally to weight for smaller individuals or children. It is important to take into account that data suggest that children tolerate significantly less than grown up persons.*

Symptom incidence, fraction	Total daily dose mcrg Hg/d^{-1}	Background daily dose fish mcrg Hg/d^{-1}	Available daily dose mcrg Hg/d^{-1}	Fish content limit mg/kg
200/100,000	40	12	28	1.00
50/100,000	26	12	16	0.56
20/100,000	19	10	9	0.31
10/100,000	15	8	7	0.25
5/100,000	10	5	5	0.18

Table 3: *Suggested limits for mercury content in fish from Swedish lakes, based on one weekly intake of 200 gram wet weight of fish as a function of epidemic population risk. The precautionary principle we define to imply a risk of 0.01% symptom incidence or less, the maximum acceptable damage principle we set at 0.1% symptom incidence. mcrg is microgram.*

from the Swedish lake surveys are that fish in clearwater lakes have less mercury than fish in lakes with high DOC concentrations, but the same deposition load. The implication of this is that an incease in lake water DOC somehow promotes fish uptake of mercury, probably by making more methyl mercury available in complexed form in the aqueous phase. In a steady state approach, methylation can be eliminated as a transient process. Because we are only looking at the final point in time, all processes that does not involve permanent sinks or sources must be eliminated. Methylation converts one form of mercury to another, and as long as we work with total mercury concentrations, it will be of no significance for the results. Fig. 2 show the causal loop diagram for the transfer of mercury from deposition to fish in lakes. A plus sign imply that an increase at the source of the arrow cause an increase at the target, a negative sign imply that an increase at the source, yield a decrease at the target. The diagram does not take any stand on the strength of the action, only its potential existence and the direction of the effect (the sign of the differential). When we research the effect of mercury on ecosystems we move from the deposition through mechanisms to the ecosystem receptor, difined as the human being. This is cause-effect based research, mapping pathways and mechanisms.

Fig. 4 and 3 shows a mass flow diagram for the transfer of mercury from deposition to fish in lakes. In the soil, mercury very rapidly adsorbs to organic matter. Some methylation and demethylation activity may take place, also causing some revolatilization of volatile forms of mercury (Metallic and methylated). The deposition rate must thus reflect the net deposition rate. In the lake a number of processes occur. Mercury is transported there mostly as bound to dissolved organic matter and organic matter particles. In the lake, fast cycles transfer organically bound to methylated and back to organically bound. A majority of the mercury remain as bound to organics. A significant amount sedimentates to the bottom where a significant fraction will remain buried. Under anoxic conditions, mercury will be precipitated as cinnabar, mercury sulfide. This is very stable and can be seen as a permanent storage. Fig. 1 show a diagram for mercury transport from a catchment to a lake in Canada related to the transport of dissolved and particulate organic matter.

3.4 Fish mercury uptake

From studies of mercury content in fish as related to the pH of the lake, Björklund et al. 1984 derived an empirical relationship between pH in the lake and mercury content in fish. Håkansson et al., (1988) give a similiar dependence on pH, but a slightly higher exponent (0.25-0.3). The correlation to lake pH may have been spurious and more of an effect of co-correlation between acid deposition and mercury deposition. But, these invenstigations went on to search for correlations between substrate mercury content and body content. The uptake rate dependence on mercury concentration in the water or lake sediment is indicated to be approximately first order. Mercury

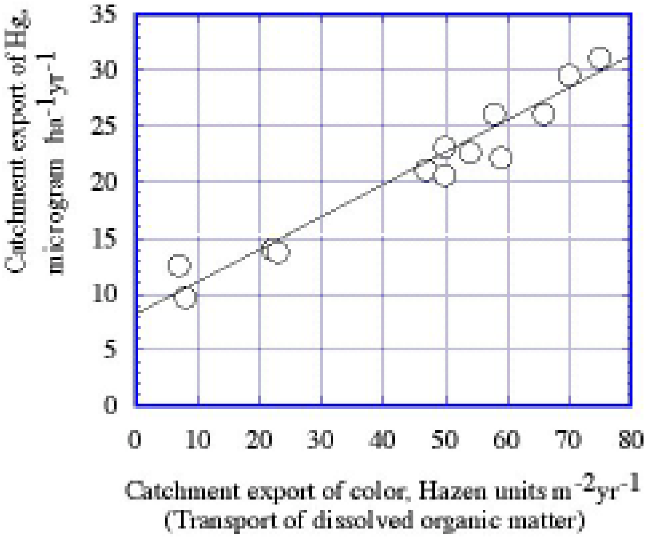

Figure 1: *The figure show an estimate of mercury export from a catchment. This situation is believed to be general for most catchments exposed to mercury deposition.*

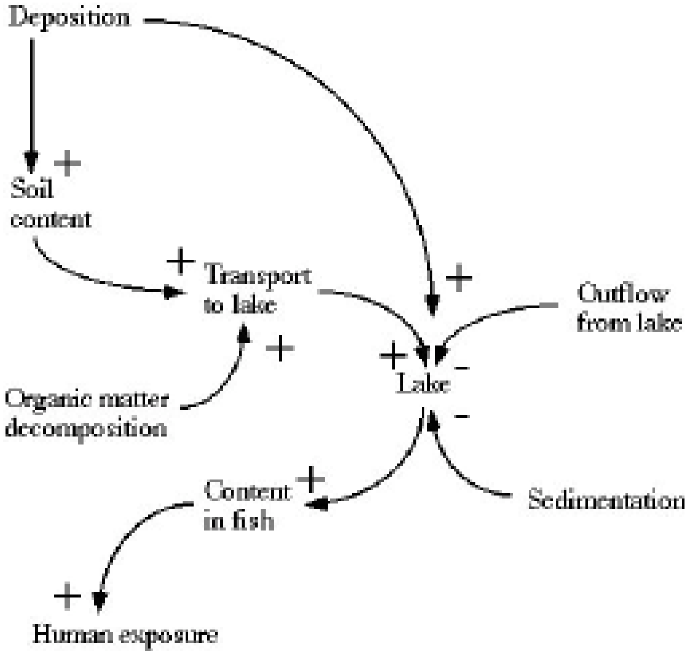

Figure 2: *Causal loop diagram for the transfer of mercury from deposition to fish in lakes. A plus sign imply that an increase at the source of the arrow cause an increase at the target, a negative sign imply that an increase at the source, yield a decrease at the target.*

is complexed strongly with organic matter. An increase in lake DOC will cause more mercury to be complexed and cause uncomplexed concentrations to decrease. Two pathways for exposure to the fish is possible (Fig. 3). Either the non-complexed mercury is most available to the fish and complexed less. Or we could have the opposite, that complexed to DOC would be more available. It is observed in Swedish lakes that in lakes with apparently equal present lake loading, fish will have lower body mercury content if the lake is a clearwater lake and higher body content of mercury if the lake is a brown water lake. The consequence of this observation is that a) the load to the lake water is really equal and then the complexed mercury must be the important pool for mercury exposure (Pathway 1). Alternatively that the lake water load is not really equal, but that at the time of observation a part of the apparently eaual load was retained iin the catchment and that more DOC simply reflects more load at present (Pathway 2). Formally, we may state the partitioning equation based on both pathways:

$$[Hg]_{fish} = k_p \cdot ([HgDOC] + \quad \cdot [Hg] \qquad (1)$$

The fish mercury partition coefficient is expressed by an affinity term and a part compensating for dilution of the load in lakes with higher biomass density:

$$K_p = K_0 \cdot z(pH) \cdot j(DOC) \cdot v(biomass) \qquad (2)$$

The pH function for affecting fish mercury uptake is matter of dispute and two expression were tested:

$$z(pH) = 0.3 + (5.7 - 0.7 \cdot pH_{lake})^{0.5} \qquad and \qquad z(pH) = 1 \qquad (3)$$

The fish content partition coefficient has the value k_{fish}=1 when fish content is in mg Hg per

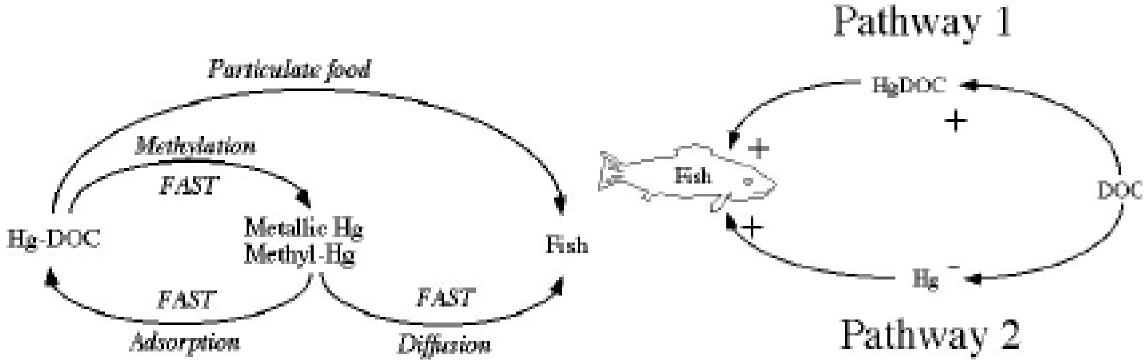

Figure 3: *The diagram show how the exposure pathways for fish in a lake are all fast processes. This allows for simplification and in the long perspective, the assumption of immediate partitioning of mercury directly from load to fish. Flow diagram for partition of mercury from lake water to fish. Mercury is complexed strongly with organic matter. An increase in lake DOC will cause more mercury to be complexed and cause uncomplexed mercury concentrations to decrease. It is observed in Swedish lakes that in lakes with equal lake loading, fish will have lower body mercury content if the lake is a clearwater lake and higher body mercury content if the lake is a brown water lake.*

kg fish and lake load is in g Hg per m^{-3}. Tab. 4 show proposed coefficients for different fishes. Proposed default partition coefficients for different fish species apply to the 2-3 year, of weight 1 kg, when the response is in mg Hg per kg fish and the cause in g Hg per m^{-3}. The coefficient was estimated straight from total mercury concentration and with no consideration for lake DOC as this was not available. These partition coefficents are preliminary and needs to be verified against field data. Data for sturgeon, zander, mal, carp, lake, and the top predator otter, and several birds are missing from the data. The partition coefficient increase with a factor of 5-10 with every trophic level. meat.

Fish species	Freshwater K_p	Saltwater Brackish water K_p
Pike, Perch, Lake, Pikeperch, Eel	1	0.4
Sole, Flounder	-	0.3
Cod	-	0.15
Herring	-	0.1
Roach, Bream	0.2	(0.08)
Trout, Brown trout, salmon	0.05	(0.02)

Table 4: *Proposed default partition coefficients (k_f) for different fish species at 2-3 year, 1 kg size, when the response is in mg Hg per kg fish and the cause in g Hg per m^{-3}. The coefficient was estimated straight from total mercury concentration and with no consideration for lake DOC*

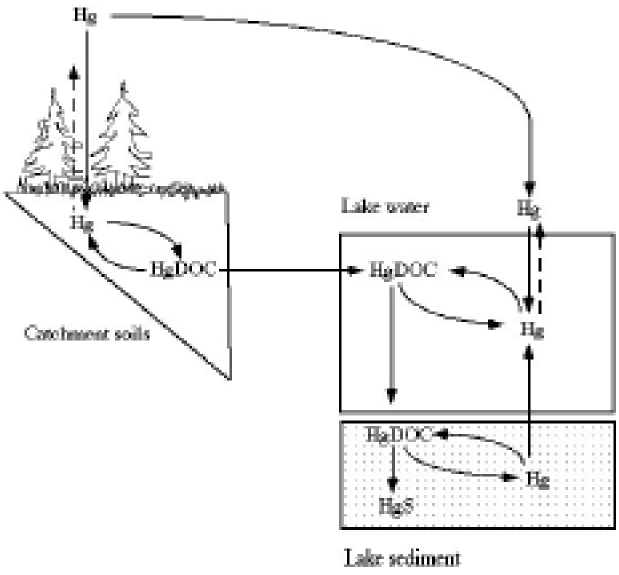

Figure 4: *Mass flow diagram for the transfer of mercury from deposition to fish in lakes. In the soil, mercury very rapidly adsorbs to organic matter. In the lake a number of processes occur. Mercury is transported there mostly as bound to dissolved organic matter and organic matter particles. In the lake, fast cycles transfer organically bound to methylated and back to organically bound. A majority of the mercury remain as bound to organics. A significant amount sedimentates to the bottom where a significant fraction will remain buried. Under anoxic conditions, mercury will be precipitated as mercury sulfide. This is very stable and can be seen as a permanent storage.*

In this study, a thorough exploration of possible modifiers to the fish partitioning expression has not been made beyond some initial trials. The effect of lake total biomass is suggested to be expressed as linear scaling function, inverse proportional to total lake biomass, where the amount of total biomass can be regionally derived from trophic classification (oligothroph 20, mesothroph 50, eutroph 100, hypereutroph 300 kg/ha m lake depth). An alternative being investigated, would be to make it directly lineraly inverse proportional to the total dissolved phosphorus in mg/l, expressed as a scaling function in relation to a reference level $[P]_{ref}$. Assuming a linear partition between free mercury and DOC (mercury saturation is far from the capacity) yields the following expression for free mercury (mostly methylated) concentration:

$$[HgDOC] = k \cdot [Hg] \cdot [DOC] \quad (4)$$

where [HgDOC] is the complexed mercury, DOC is total DOC and equal to the maximum complexing capacity, [Hg] is the dissolved uncomplexed mercury in water. More DOC leads to less free mercury in the water, thus less chemical partitioning with the fish. This expression needs parameterization from field or laboratory data. We have the condition:

$$[Hg]_{tot} = [HgDOC] + [Hg] \tag{5}$$

Inserting this gives us the HgDOC as a function of total Hg concentration. If Pathway 1 as illustrated in Fig. 3 for exposure is dominating, we get for partitioning to fish:

$$[Hg]_{fish} = k_p \cdot [Hg]_{tot} \cdot \frac{k \cdot [DOC]}{1 + k \cdot [DOC]} \tag{6}$$

It implies that if DOC increase in the lake under constant mercury loading, fish content will increase. This appears to be most consistent with present observations. Mercury is associated with the dissolved organic matter and the pariculate carbon. Zooplancton feed on plancton and these organic particulates, and mercury is thought to enter the fish population this way as zooplancton is a very important fish food. Pike and Pikeperch are top predators and accumulate the mercury with age. The lower trophic leves act as collectors for the higher trophic levels, because of the increase in numbers towards the bottom of the trophic cascade. Few at the top feed on many at the lower level. Humans come in as an additional trophic level in this ecosystem. Mercury turnover in a fish is not exactly known, but can be estimated to be more than two years and less than seven years. In Fig. 3, the exposure pathways for fish in a lake are shown. They are generally understood as fast processes. This allows for simplification and in the long perspective, the assumption of immediate partitioning of mercury directly from load to fish. Some conclusions are important to make at this point:

1. Mercury is present predominantly in two forms into which all other forms converge; complexed with in the soil with organic matter and in the aqueous solution complexed to DOC and as freely dissolved methylated mercury.
2. The major part of the mercury load to a lake is transported with dissolved organic carbon and with suspended organic carbon particles
3. Fast transformation cycles are important for fish exposure in the lake system
4. Slow transformation cycles in the carbon system is rate determining for the transport of mercury from land to waters.
5. In a steady state approach, methylation can be eliminateds.

These conclusions are important for our model formulation. This implies that methylation, demethylation and conversion between metallic and methylated can be simplified to instant conversion to the final forms; complexed and free methylated. Methylation is present, but instantly occurring. Uptake processes to fish have been substituted with direct partition to fish. It implies that the intrisic rate of methylation and vapour diffusion rates are not needed.

4 Estimation methods for critical load

4.1 Calculation method; The empirical model

4.1.1 Basic assumptions

The basic principles of the model is that fish content can be empirically related to aqueos ecosystem input, the load, and that the load is expressed in the lake concentration. We have assumed for this model:

1. Deposition load is linearly proportional to lake concentration

2. Fish content is determined by direct linear partitioning of total lake concentration
3. The system was at steady state when the data was collected
4. Lake DOC has no effect on fish mercury uptake

This implies that we assume that the delays in the catchment is of no significance when the data used for calibration was determined. It would appear as possible that a scaling function based on lake DOC could be introduced by extracting empirical expressions for it from the available Swedish datasets.

4.1.2 Key equations

Using data on background levels in fish and observations on fish content in systems exposed to different deposition loads, and investigated with the dynamic model described later in the text, we could propose the simplest possible model:

$$[Hg]_{fish} = a + b \cdot D_{Hg} \tag{7}$$

where a=0.15 and b=0.025 for 1 kg pike, if mercury content in fish mg/kg and deposition (D_{Hg}) is g/km^2. The physical significance of a is that it indicates the background mercury content in the fish. This we can estimate from semi-independent sources such as data from remote areas or historical data. b is the propotionality of fish content to deposition increase. This we can rearrange to the empirical equation for the critical load:

$$CL = \frac{Limit - a}{b} \tag{8}$$

where $Limit$ is the limit for fish meat content as defined in Tab. 3.2 and a and b are the species specific parameters given above. Important assumption here was that the water concentration was at steady state with the deposition at the time our dataset was measured. This is not certainly true, and this could cause the value of b to be underestimated by 50%.

4.1.3 Data requirements

Required minimum data for use is:

1. Target fish species
2. Fish property parameters (from the manual)

After modification, this model may require present lake DOC concentration in mg/l.

Fish	a	b
Pike	0.2	0.025
Eel	0.2	0.025
Baltic cod	0.08	0.009
Herring	0.05	0.006
Salmon	0.01	0.0014

Table 5: *Preliminary parameters a and b of the empirical model, when fish limit is expressed as mg Hg/kg fish and CL is expressed as g Hg/km^2.*

4.2 Calculation method; The simple mass balance model

4.2.1 Basic principles

The simple mass balance is based on the fundamental principle of mass conservation. The objective of the simple mass balance model beside estimating critical loads, is that it looks at the catchment and lake with the view to do the greatest simplifications possible and still have an applicable model. The system is taken to have one single compartment, all transient processes are ignored completly. At steady state, all inputs must be in balance with the inputs, making lake load equal to total catchment input:

$$\frac{dm}{dt} = in + prod - sinks - out \tag{9}$$

Steady state implies that all differential are set to zero; implying that the accumulation (dm/dt) in the system is zero (no change in the water phase equivalent to that the concentrations do not change, no change in the soil phase, implying no net accumulation in the solid phase). This implies that at this state, input to the soil equals output. This way we can calculate the final state without having to solve the differential equations involved. Setting (dm/dt)=0, we get the mass balance at steady state:

$$in + prod = sinks + out \tag{10}$$

For the system we are considering, in is the net deposition input, $prod$ is what is internally produced in the system, $sink$ is permanent removal from the system and out is the transport out with water.

4.2.2 Assumptions

In the present assessment we have assumed:

1. The boundary for the system is the catchment; thus catchment plus lake is one box for which the mass balance is made
2. All processes involving re-emission or volatilization back to the atmosphere is assumed to have been taken care of in ”net deposition”
3. Sedimentation is assumed to be permanent
4. Methylation and complexing of any deposited mercury is assumed to be rapid
5. Influx caused by weathering of soil minerals and rocks is assumed to be neglible
6. Removal by ecosystem harvesting is assumed to be neglible
7. Feedbacks between parameters are simple
8. We have two options for partitioning:
    (a) Fish content is partitioned to total mercury aqueous concentration
    (b) Fish content is partitioned to total waterbody load

4.2.3 The key equation

The steady-state approach is only interested in the final result, regardless of the time it might take to establish that final result. Time is simply another and later issue, to be dealt with by different tools. From a mass balance combined with the simples view of the system, we can derive the equation for the maximum load to the ecosystem at steady state, by setting all differentials to 0. The implication of steady state is also that there is no retention in the catchment, at steady state deposition to the soil is balanced by an equally large leaching to the lake. If the approach and assumptions are applied and spelled out for mercury to a lake, we get a mass balance. The inputs by deposition to the lake is balanced by outputs by flow and sedimentation:

$$D \cdot (A_{lake} + \quad \cdot A_{soil}) = Q_{out} \cdot [Hg]_{tot} - r_{sed} \tag{11}$$

where D is the area-specific deposition, A is the area of the lake or dry land in the catchment and r_{sed} is the sedimentation rate to the bottom. is the deposition enhancement factor of the land area as compared to the open lake surface. At steady state all deposition passes to the lake, both what falls on the catchment and what comes directly to the lake surface. For suspended organic matter the rate coefficient for first order sedimentation is assumed to be approximately 0.25 per year in a 3 meter deep lake.

4.2.4 Approach 1; Lakes

Mercury is partitioned directly to the fish by using total mercury concentration:

$$[Hg]_{fish} = k_f \cdot [Hg]_{tot} \tag{12}$$

where k_{fish} is the partition coefficient. The mass balance may be reorganized to;

$$D \cdot (A_{lake} + \quad \cdot A_{soil}) = Q \cdot \frac{Limit}{k_f} + r_{sed} \tag{13}$$

The runoff Q is a product of the specific runoff R and the total effective catchment area:

$$Q = R \cdot (A_{lake} + \quad \cdot A_{soil}) \tag{14}$$

Sedimentation as an approximation, can be set to be proportional to lake DOC concentration, lake area and water turnover:

$$r_{sed} = k_{sed} \cdot [DOC] \cdot A_{lake} \tag{15}$$

The equations can be rearranged to the expression for the deposition corresponding to the critical limit in the fish, inseting the areadependence of Q and the sedimentation expression. Set D = Critical Load when the fish content is equal to the critical limit:

$$[Hg]_{fish} = Limit \tag{16}$$

Then we get for the critical load:

$$Lake\ Critical\ Load = R \cdot \frac{Limit}{k_f} + k_{sed} \cdot [DOC] \cdot \frac{A_{lake}}{(A_{lake} + \quad \cdot A_{soil})} \tag{17}$$

4.2.5 Data requirements

Required minimum data for use is

1. Specific runoff R (m^3/km^2 yr)

2. Lake surface area (km^2)
3. Catchment surface area (km^2)
4. Sedimentation rate (g Hg/km^2 yr)
5. Target fish species with limit (in manual) and partition coefficient (in manual)

Optional and not strictly necessary are the following data;

1. Lake DOC for estimation of sedimentation and any modification of k_f (g/l)
2. Biomass density for modification of k_f (kg/ha lake surface)
3. Lake retention time for modification of sedimentation (yr$_{-1}$)

4.2.6 Approach 2; Lakes

An even simpler model may be proposed, we may partition the lake load directly to fish:

$$[Hg]_{fish} = \ _f \cdot lakeload \tag{18}$$

where $\ _f$ is the total load specific partitioning coeffcent, the lake load is the inputs minus the permanent sinks, the deposition minus sedimentation in the lake:

$$[Hg]_{fish} = \ _f \cdot \frac{A_{lake} + A_{soil}}{A_{lake}} \cdot D - \frac{r_{sed}}{A_{lake}} \tag{19}$$

In the simplest approach, sedimetation will be empirically estimated from lake DOC concentration and retention time. The above equation is rearranged to bring D to the left and set D = Lake Critical Load when the fish content is equal to the limit:

$$Lake\ Critical\ Load = \frac{Limit}{\ _f} \cdot \frac{A_{lake}}{A_{lake} + A_{soil}} - \frac{r_{sed}}{\ _f} \cdot \frac{1}{A_{lake} + A_{soil}} \tag{20}$$

The assumption of direct load partitioning neglects the dilution effects by largely increased amounts of precipitation, and this equation can be expected to perform poorer in high precipitation or arid areas.

The parameterization of these models are still in the development phase, and they await proper evaluation using avalable empirical data. Here the critical load of mercury deposition has the units mg Hg/m^2 yr when the limit is set in mg Hg/kg fish for one-year pike. Required inputs are lake pH, lake area, catchment area and a critical limit. At present, bedrock sources have been ignored, as well as the effect of temperature. The limit currently used for one year pike is 0.5 mg Hg/kg fish. So far, partitioning functions have only been experimentally determined for pike. All non-adronomous fish which grow to old age and which serve as human food should have partitioning functions determined. k_{fish}=0.1 if the limit is in mg Hg per kg fish wet weight.

The advantage of the consept is that it requires very little input data. If we look at equation 17, the only input data reqired is the critical limit, the partition coefficient for the indicator and the lake to catchment area ratio. This arises from the fact that we have no permanent sinks in the catchment included, and that all mercury deposited eventually takes part in fish exposure. In the calculation, the long term net sedimentation to the lake bottom is set to zero. The simplified model ignores at presence of different amounts of DOC in the water, but work is under way in Sweden that could lead to an empirical correction equation. The quantitive effect of other lake depths could be affected by the fact that a larger depth at the same deposition, would lead to a larger dilution in the lake, but this has not yet been determined experimentally.

4.2.7 Data requirements

Required minimum data for use is

1. Lake surface area
2. Catchment surface area
3. Target fish species with limit (in manual) and partition coefficient (in manual)

Optional and not strictly necessary are the following data;

1. Lake DOC for estimation of sedimentation and any modification of k_f
2. Biomass density for modification of k_f
3. Lake retention time of sedimentation

4.2.8 Streams and rivers

For a stream we will have the whole load minus any permnent sinks directly dissolved in the flow at steady state:

$$[Hg]_{tot} = k_f \cdot \frac{D \cdot A_{tot}}{Q} \tag{21}$$

For larger slowly flowing rivers, we need to add sedimentation;

$$[Hg]_{tot} = k_f \cdot \frac{D \cdot A_{tot} - r_{sed}}{Q} \tag{22}$$

We assume partition with the total concentration, convert Q to R, insert partition and the equation we easily rearrange to:

$$Stream\ Critical\ Load = (\frac{Limit}{k_f}) \cdot R \tag{23}$$

and if we adapt it for large, slowly flowing rivers:

$$River\ Critical\ Load = (\frac{Limit}{k_f}) \cdot R - \frac{r_{sed}}{A_{tot}} \tag{24}$$

For a stream, approach 2 does not really make sense, no dilution effects are accounted for, which does not appear as a reasonable assumption.

4.2.9 Data requirements

Required minimum data for use is

1. Specific runoff for catchment
2. Target fish species with limit (in manual) and partition coefficient (in manual)

Optional are, or for special adaptions to large, slow rivers:

1. Catchment surface area for sedimentation scaling
2. Sedimentation rate (slow rivers only)
3. Stream DOC for estimation of sedimentation and any modification of k_f
4. Biomass density for modification of k_f
5. River velocity for modification of sedimentation

4.3 A very, very simple model

A very simple model may be proposed based on a study of dynamic model runs. Tentatively, we could propose:

$$[Hg]_{fish} = a + b \cdot D_{Hg} \tag{25}$$

where a=0.2 and b=0.025 for 1 kg size pike, if mercury content in fish mg/kg and deposition (D_{Hg}) is g/km^2. The physical significance of a is that it indicates the background mercury content in the fish. This we can estimate from semi-independent sources. b is the propotionality of fish content to deposition increase. This we can rearrange to the empirical equation for the critical load:

$$CL = \frac{Limit - a}{b} \tag{26}$$

where $Limit$ is the limit for fish meat content as defined in Tab. 3.2 and a and b are the species specific parameters given above. Important assumption here was that the water concentration was at steady state with the deposition at the time our dataset was measured. This is not certain, and this could cause the value of b to be undersestimated. One further development that could possibly be parameterized on Swedish data would be to include a scaling factor based on lake DOC:

$$[Hg]_{fish} = a + b \cdot D_{Hg} \cdot f(DOC) \tag{27}$$

The effect of f(DOC) would be to increase the fish content above a certain reference DOC level and decrease it below that level. One possible suggestion would be to write:

$$f(DOC) = (\frac{[DOC]_{lake}}{[DOC]_{ref}})^k \tag{28}$$

where the exponent k would be calibrated against data. The value would be in the range of n=0.4-0.6.

Fish	a	b
Pike	0.2	0.025
Eel	0.2	0.025
Baltic cod	0.08	0.009
Herring	0.05	0.006
Salmon	0.01	0.0014

Table 6: *Preliminary parameters a and b of the empirical model, when fish limit is expressed as mg Hg/kg fish and CL is expressed as g Hg/km^2.*

6. ABSTRACTS OF SHORT PRESENTATIONS

6.1 APPLICABILITY OF TRANSFER FUNCTIONS IN HUMUS TO DETERMINE TOXICITY OF HEAVY METALS.

Staffan Åkerblom

Introduction

In heavy metal toxicity studies the question of the biologically relevant fraction is a major issue. The free uncomplexed metal fraction is considered to be most bioavailable. By the use of multiple regression methods the derivation of transfer functions can be used to calculate speciation of heavy metals with easily derived soil data. Calculated metal fractions can in this way be used in toxicity studies of mor layers in field sites.

A dataset based on 8 bulk samples was used to derive transfer functions valid for mor layer.
Proposed transfer functions in UN-ECE/LRTAP are derived from datasets based on soils of minerogenic origin and to some extent organic soils from peats in UK (Groenenberg *et al.* 2002). However, these soils differ in their characteristics from forest mor layers which are high in organic matter and low in pH.

This study has used a lysimetric technique on bulk samples of raw humus to extract pore water. Chemical data from this extraction has been used to derive transfer function connecting the dissolved fraction of Pb and Cu in mor layers with total amount of Pb and Cu, pH and organic matter. These transfer functions has been used in effect studies evaluating the effect of heavy metal load on microbial activity. Proposed transfer functions in the background document has also been used to determine a reactive content and dissolved total metal concentrations.

Material and methods

Humus samples were collected in the vicinity of a major motor highway 15 km north of Stockholm. Sampling area were dominated by Scots pine and Norway spruce on top of a well developed podsol. Contents of Pb and Cu were elevated in this area. A total of 36 humus samples from the top organic mor layer were taken for respiration measurements. Beside the respiration samples a total of 8 larger bulk samples with more humus (app. 1 kg) were also taken.

Humus was taken to laboratory and were sieved (4 mm) and measured for pH (aq.) and organic matter (LOI 550°C). The humus samples were wetted to 100 % WHC and kept for 12 days (20°C, 100 % air humidity) prior to respiration measurement. Respiration was measured as CO_2-evolution captured in NaOH during 24 h in a closed vessel. Respiration was expressed as CO_2-evolution per hour and gram of dry material. After respiration measurement the samples were dried and measured for total content of Pb, Cd, and Cu (7 M HNO_3, AAS).

Bulk samples were treated in exactly the same way as respiration samples, except that respiration was not measured. Soil pore water was extracted using lysimeter and the water extract was measured for total content of Pb and Cu (ICP-MS).

Results from bulk sample analysis were used in multiple linear regression to derive transfer function connecting Pb and Cu-concentration in pore water and total heavy metal content, pH in soil extracts and organic matter.

Linear regression with metal concentration as independant variable was used for determination of the effect of heavy metal load on soil biological activity, expressed as microbial respiration.

Results and discussion

Regression coefficients from multiple regression analysis for Pb and Cu in bulksamples gave the following transfer functions:

$[diss_{Pb}] = 0,541*\ln(total_{Pb})-0,009*(\%OM)-2,170$ $r^2=0,890/**$

$[diss_{Cu}]=0,615*\ln(total_{Cu})-0,159*pH-0,015*(\%OM)-0,193$ $r^2=0,935/**$

Soil pH did not make any improvement in the multiple regression analysis for Pb and was therefore excluded in the derived transfer function valid for Pb. This indicate a more strong relation between organic matter and fractionation of Pb. Speciation of Cu has also been shown to be regulated by organic matter, but not to the same degree as Pb (Sauvé *et al.* 1998).

Results from regression analysis between microbial activity and heavy metal content showed negative correlation with both Pb and Cu indicating toxic effect of Pb and to some extent Cu.
Correlation between microbial activity and heavy metal load was strengthened when soluble fractions calculated from transfer functions were used (table 1).

Table 1.Negative correlations between respiration rates and fractions of Pb and Cu in forest soils. n=36.
Results: for Pb stepwise stronger correlation; for Cu weak, but stepwise stronger correlation
[a]=not significant

Heavy metal / Metal fraction	Pb		Cu	
	r^2	p	r^2	p
Total amount of heavy metal	**0.182**	*	**0.007**	**ns**[a]
Calculated soluble fraction of heavy metal	**0.289**	**	**0.075**	**ns**[a]

By using the proposed transfer function presented in the background document on transfer functions a reactive pool and dissolved total metal concentration of Pb and Cd was calculated for the respiration samples. Correlation between microbial activity and the different Pb and Cd-fractions was strengthened when using reactive and dissolved total metal concentration (table 2).

The results indicate that a soluble fraction is more biological relevant in toxicity studies. It has been denoted that an amount of heavy metal that can react chemically with an extractant is not necessarily the biologically most toxic fraction (De Vries *et al.* 2002). It has been shown here that a reactive fraction both can be described as a chemically reactive fraction, but also as a biological relevant fraction. The calculated soluble fraction (comparable with reactive pool of heavy metal in the proposed transfer functions) for Pb and Cu from the derived transfer function is considered to be a complexed fraction of heavy metal. It is therefore reasonable to think that an even stronger correlation is possible if an uncomplexed fraction (derived from i e WHAM (Tipping 1994)) is used. Therefore it is necessary that forest soils need better evaluation in order to receive transfer functions valid for humus layers.

Table 2.Negative correlations between respiration rates and fractions of Pb and Cd in forest soils calculated from proposed transfer functions.
Results: for Pb stepwise stronger correlation for reactive pool and no improvement with dissolved total Pb-concentration; for Cd stepwise stronger correlation significant for dissolved total Cd-concentration.
[a] *=not significant*

Heavy metal metal fraction	Pb		Cd	
	r^2	p	R^2	p
Total amount of heavy metal	**0.182**	*	**0.102**	**ns**[a]
Calculated reactive pool of heavy metal	**0.18**	**	**0.101**	**ns**[a]
Dissolved total metal concentration of heavy metal	**0.286**	**	**0.146**	*

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6.2 ARE HUMUS LAYERS DIFFERENT? EFFECT LEVELS FOR Pb AND Hg

L. Bringmark[1]

Introduction

There is a long tradition in the Nordic countries to study heavy metal effects in mor layers, i. e. the organic layers on top of podsolic forest soils. This layer, that covers the floor of the vast boreal forest in northern Europe, Asia and America, effectively retains heavy metals deposited from above. The uniformity of the material and locally high metal levels made it of scientific interest to use mor layers for toxicity studies. A large number of investigations around metal industries took place in the seventies and eighties in Sweden and Finland. Basic knowledge on metal behaviour and biological effects was gained in this period. Effect levels in organic layers as well as in other soil strata published until the end of the eighties were summarised by Baath (1989)

Now the focus has shifted to long-range pollution, which means pollution at lower levels but affecting much larger areas than those involved in the earlier research. Pb and Hg are major components of the long-range pollution, which have especially strong bonds to the organic material. They accumulate in the mor layers to a high degree. Although contents remain relatively low at the regional scale compared to local pollution there is still reason to look for adverse effects on soil biota.

In the search for biological indications at low metal levels we focussed on younger material of the upper parts of mor layers. Microorganisms that colonise fresh plant litter could be more sensitive to pollutants than slower organisms associated with old organic material. Higher bioavailability of metals also enhances effects in fresh material. On the other hand, metals tend to accumulate to higher concentrations in old material, as can be seen from the reference samples of different layers in Table 1. In order to test the idea of higher sensitivity in young material, different horizons of a mor layer from a South Swedish site were compared.

Method

In a long-term experiment samples of litter layer, Fm-layer and Hf-layer (uppermost, middle and lowermost part of the mor layer, FAO notation) from a Southern Swedish forest site were exposed to Pb and Hg, added at the start. Dose levels were kept low to be similar to regional pollution (Table 1). Effects observed in the experiment were due to additional loads above the historical pollution already present in the samples. Respiration was monitored for 15 months including two short resting periods with samples frozen. The long measurement period was necessary for negative effects to fully develop at the low dose levels, while effects observed in the early part of the experiment were both positive and negative. The precise addition of metal at low levels is difficult and for Hg there might be evaporative loss, but as a check contents of Pb and Hg were measured in samples of each treatment.

A similar experiment was made with material from the Fm-layer at a North Swedish site. Lower effect levels were expected at this site due to lower original metal contents.

Results and discussion

Southern Sweden is subject to a rather high regional pollution load, resulting in the Pb and Hg concentrations measured in the reference samples (Table 1). Significant effects were observed at doubling of the Pb concentration in the Fm-layer, although effects were small (Table 1). To produce significant Hg-effects a higher dose was required expressed as multiples of the background level. These results were obtained with a traditional method. Nevertheless, observed effect levels were lower than most cases for organic soils reported in literature. The choice of an upper horizon within the mor layer and the long observation period were prerequisites for obtaining effects at low metal levels.

The Hf-layer, having higher mean age, showed weaker effects as expected. However, weak effects were also observed in the litter layer, which contradicted the hypothesis of higher sensitivity in young material. An explanation could be the structural integrity of the litter allowing organisms to

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spatially avoid added metal in the early phase of decomposition. This is relevant to field situations as deposited metals are attached to leaf surfaces.

A calculation of $EC_{5\%}$, i.e. the effect concentration producing 5% reduction of carbon loss over the whole experiment period, resulted in 145 µg/g for Pb in the Fm-layer and 1.7 µg/g for Hg. These values are about 2,5 and 7 times the metal levels of the field situation found for reference samples in Table 1. Experiments on a Northern Swedish Fm-layer resulted in $EC_{5\%}$ values at 50 µg/g for Pb and 0.9 µg/g for Hg. Original field contents in the Fm-layer of this experiment were 21 µg/g for Pb and 0.23 µg/g for Hg.

Table 1. Effects of added Pb and Hg on carbon loss during 450 days, expressed in relation to carbon loss in untreated control (%). Hg and Pb contents include initial amounts. Values significantly different from control indicated with * (p<0.05, Dunnet's test).

Hg-treatment	Hg (µg/g)	Carbon loss (% of control)	Pb-treatment	Pb (µg/g)	Carbon loss (% of control)
1.1 Litter layer:					
None	0.18	100 %	none	21	100 %
Hg1	0.63	98 %	Pb1	64	97 % *
Hg2	1.6	100 %	Pb2	225	95 % *
1.2 Fermenton (Fm layer):					
none	0.26	100 %	none	57	100 %
Hg1	0.50	98 %	Pb1	120	96 % *
Hg2	2.0	95 % *	Pb2	360	90 % *
Humifon (Hf layer):					
none	0.41	100 %	none	145	100 %
Hg1	0.55	98 %	Pb1	205	98 %
Hg2	1.9	100 %	Pb2	465	97 % *

Conclusions

The results show that in mor layers, the age of the organic material is highly relevant for the biological response to metal additions. Effect levels were different for different soil horizons. In general terms it can be concluded that the age and the quality of the organic material are important factors determining the biological response.

If effect levels are shown to be different in different organic materials, it follows that separate critical limits have to be worked out for some soils. The critical limit for the reactive fraction of Pb is now set at 30 µg/g in the background papers of this workshop. This value is very low when applied to organic soils, simply because differences in bulk density makes values incomparable between organic and mineral soils. Recalculation of metal contents per unit organic material does not solve the problem. The value on the critical limit will then be raised 40-fold or more, i. e. much higher than effect levels actually observed in mor layers. This is an argument for developing separate critical limits for forest humus layers. That will mean that we make full use of the knowledge existing on effects in these soils, at least for Pb and Cd. But information on Hg effects will be scarce. A compilation of data on biological effects of Pb, Hg and Cd in organic soils is planned.

Reference

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6.3 THE INFLUENCE OF SOIL PROPERTIES ON DISTRIBUTION AND LEACHING OF AIRBORNE HEAVY METALS IN HIGH MOUNTAINS

J.Čurlík[1]

The accumulation of heavy metals in Slovakian forest soils due to long term atmospheric transport is a large scale environmental problem. From systematic geochemical mapping of soils (Čurlík and Šefčík, 1999) is evident that present day content of some heavy metals (Pb, Cd, Hg, As, Zn, Cu) has been slowly build up especially in high mountainous part of Western Carpathians. High mountains play a filtering role (sink) for heavy metals. The behaviour of heavy metals, their leaching and mobility is dependent on soil properties (pH, humus and carbonates content) and forms of heavy metals occurrence (input sources).

For this study vertical distribution trends and leaching of heavy metals in six soil profiles of mountainous soils was chosen in order to portray the mobility trends of heavy metals which, as is believed have mostly airborne origin. The main soil characteristics are presented in Tab.1

Tab. 1. Soil characteristics of six forest (high mountainous) soils from Slovakia

TAP-1- KMd-Spodo- dystric- Cambisol1915m, gneises and migmatites, TAP-2- KMv-Calcic Cambisol, 1725 m, weathered dolomites, TAP-3-RNk-Ranker, Prašiva, 1735 m weathered granodiorites, TAP-4-RAm– Ortic Rendzina,1380 m limestones, TAP-5- PZo-Histo-humic Podzol, Martinské hole, 1470m, granitic rocks, TAP-6- PZm-Podzol,Babia hora, 1685m, flysh sandstones

Number vzorky	Depth (cm)	Soil unit	Soil pH	Fe ox (%)	Al ox (%)	As tot.	As DTPA	Cd tot.	Cd DTPA	Cu tot.	Cu DTPA	Hg tot.	Hg DTPA	Pb tot.	Pb DTPA	Zn tot.	Zn DTPA
TAP-1	5--10	KMd	3,81	0,24	0,27	7	< 0.1	< 0.3	< 0.3	9	< 1	0,05	< 0.001	58	< 1	37	1
	15--20		4,35	0,43	0,29	2	< 0.1	< 0.3	< 0.3	18	6	0,02	< 0.001	29	< 1	45	2
	35--40		4,73	0,53	0,44	5	< 0.1	< 0.3	< 0.3	9	5	0,02	< 0.001	27	2	53	3
	50--55		4,91	0,38	0,48	4	< 0.1	< 0.3	< 0.3	10	5	0,02	< 0.001	25	2	55	2
TAP-2	5--15	KMv	4,83	1,07	0,71	25	< 0.1	0,5	< 0.3	28	1	0,09	< 0.001	67	1	149	2
	20--30		5,21	1,11	0,87	24	< 0.1	0,3	< 0.3	35	2	0,11	< 0.001	51	2	139	2
	60--70		7,30	0,34	0,37	12	< 0.1	0,3	< 0.3	27	9	0,07	< 0.001	22	2	69	4
TAP-3	10--20	RNk	4,45	0,88	0,50	17	< 0.1	< 0.3	< 0.3	15	< 1	0,07	< 0.001	85	< 1	49	< 1
	30--40		4,23	0,90	0,58	7	< 0.1	< 0.3	< 0.3	18	3	0,04	< 0.001	40	< 1	64	3
TAP-4	5--10	RAm	6,84	0,39	0,52	31	< 0.1	2,3	1,3	24	4	0,16	< 0.001	89	16	136	20
	25--30		7,21	0,21	0,33	20	< 0.1	1,5	1,0	30	9	0,10	< 0.001	42	8	78	10
	50--70		8,09	0,08	0,10	9	< 0.1	0,4	< 0.3	15	8	0,05	< 0.001	7	2	29	5
TAP-5	5--10	PZo	3,00	0,22	0,32	25	< 0.1	1,7	< 0.3	20	< 1	0,36	< 0.001	245	< 1	50	2
	15--20		4,70	0,09	0,43	6	< 0.1	0,3	< 0.3	18	5	0,04	< 0.001	47	2	29	4
	30-40		4,73	0,69	0,79	3	< 0.1	0,3	< 0.3	24	3	0,05	< 0.001	24	< 1	71	2
TAP-6	4--8	PZm	3,30	0,15	0,15	6	< 0.1	0,3	< 0.3	24	< 1	0,22	< 0.001	163	5	53	2
	10--20		4,40	0,04	0,13	2	< 0.1	< 0.3	< 0.3	8	4	0,03	< 0.001	27	16	18	4
	20-25		3,74	0,41	0,38	7	< 0.1	0,3	< 0.3	27	6	0,04	< 0,001	28	< 1	37	4
	30--40		4,55	0,88	0,71	6	< 0.1	0,3	< 0.3	21	1	0,05	< 0.001	19	< 1	61	1

The soils under study were analysed for total and extractable heavy metals content, pH oxalate Fe and Al. Vertical trends of airborne heavy metals distribution (Cd, Pb, Hg, Cu,Zn and As) was

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demonstrating during the presentation. Beside the total content extractable forms of heavy metals (0,05M DTPA) were analysed. From obtained results following conclusions can be drawn:

The role of atmospheric (transboundary ?) input of heavy metals to the soils in highlands part of Western Carpathians (Slovakia) is very significant. High mountains play a barrier (sink) for heavy metals transport.

The potential of soil for heavy metals to accumulate is mostly depending on soil properties. In general topsoils accumulate Pb, Hg and Cd depending on organic matter content (moor) and pH (carbonate status). Pb and Hg are relatively not affected by acidification but Cd is leached from acid (podzolic) soils.

The organic topsoil is the most significant sink for Pb, Hg, and As, but due to organic complexation some metals are mobilized and likely to precipitate in B horizon or completely leached away.

The relation between soil pH and total content of Cd and Zn is close but potential shift to extractable fraction of Cd, Pb and Zn is higher in neutral soils (Ortic Rendzina, Calcic Cambisols). The content of mobile (mobilizable) forms of Cd, Pb, Zn and Cu (in 0,05M DTPA) is higher in neutral soils. This is probably due to deliberation of carbonate bind heavy metals fraction . The rate of both soil acidification and metal leaching depends greatly upon soil and vegetation type.

Literature

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6.4 CRITICAL LOADS, EXCEEDANCE, TEMPORAL TRENDS AND CRITICAL TIMES OF HEAVY METALS IN SOILS OF THE CZECH REPUBLIC

Pačes T.,[1] Sáňka M.,[2] Kadlubiec R. 2) Zapletal M. 2), Chroust, P. 2)

Critical characteristics of Cd, Cu, Pb and Zn in soils of the Czech Republic are calculated in a grid 1x1 km. The method of calculation is described in Paces et. al, 2002, Collection and evaluation of input data is described in a report by Zapletal et al. (2002). We present as an example the maps of lead.

Map 1 illustrates the present concentration of Pb in forest and agricultural soils in extracts by aqua regia. Most of the forest soils contain more lead than it is their critical limit given by the Czech state norms (60 mg/kg). Agricultural soils are mostly below the limit.

Map 2 presents the critical load calculated from the mass balance of lead. The fluxes due to mechanical weathering and erosion are not considered. The critical load is in the range of –10 to more than +10 g/ha/yr. The negative load indicates that it is necessary to remove lead from the Czech soils especially in the eastern part of the country in order to lower the concentration to the critical level.

Map 3 shows that the present atmospheric and agricultural input exceeds the critical load of Pb on the whole territory of the country.

The maps 4 and 5 are more important for decision makers that the critical load maps, because they illustrate the present trends and the critical times when critical levels will be reached.

Map 4 characterises the combination of the pollution status of the soils and future trends if the present inbuts do not change.

Four major groups are defined based on the present concentrations in soils, c0, critical concentration, ccritical, and the trend defined by the difference between the present inputs and outputs, d;

d = F_{atm}+F_{agr}+F_{wea}-F_{up}-F_{run} (F_{atm} – flux due to atmospheric deposition,

F_{agr} – flux due to agricultural inputs,

F_{wea}– flux due to chemical weathering,

F_{up}– uptake by plants and

F_{run} – runoff by water

(1) Light green; c0 < ccritical and d < 0: the critical time is negative and therefore it is not significant ; no environmental problem is expected.

(2) Dark green; c0 < ccritical and d > 0: the critical time shows how long it will take to reach the critical concentration if the present inputs continue; if the steady state concentration will remain under the critical limit, the critical time will not be defined.; environmental problem is ether not expected or it is expected that the critical limit will be reached After certain critical time.

(3) Light brown; c0 > ccritical and d > 0: this is the worst case when the present concentration is high and will still increase in future. The value of the critical time is negative. The time is not significant because the concentration will be always above the critical limit.

(4) dark brown; c0 > ccritical and d < 0: the present concentration is above the critical limit. It will, however, decrease in future even if the present inputs prevail. The critical time is positive and it indicates when the concentration of the metal in soil will reach its critical level; if the critical time is not defined, it means that the steady state concentration in future will remain above the critical limit.

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Map 5 illustrates the critical times. Negative critical times are irrelevant because they indicate when the soil concentration was at the critical level in the past. Presently, the concentration is above the critical level and will still increase. The positive critical times are relevant because they indicate either how fast the presently low concentration of lead will increase to the critical level or how fast the presently high concentrations will decrease to the critical level.

Conclusion

The maps of temporal trends of heavy metals in soils and the maps of critical times indicate more realistically the areas where the pollution of soils with respect to heavy metals deserves our environmental attention and restoration.

Literature

Paces T., Corcimaru S., Emmanuel S., Erel Y., Novak M., Plyusnin A., Vernon A. and Wickham S. (2002) Critical Loads of Hazardous Trace Elements in Soil - Water System. Journal of Field Science No. 1, vol. 1, 15-22, Tokyo University of Agriculture and Technology, Fuchu, Japan, ISSN 1347-3948.

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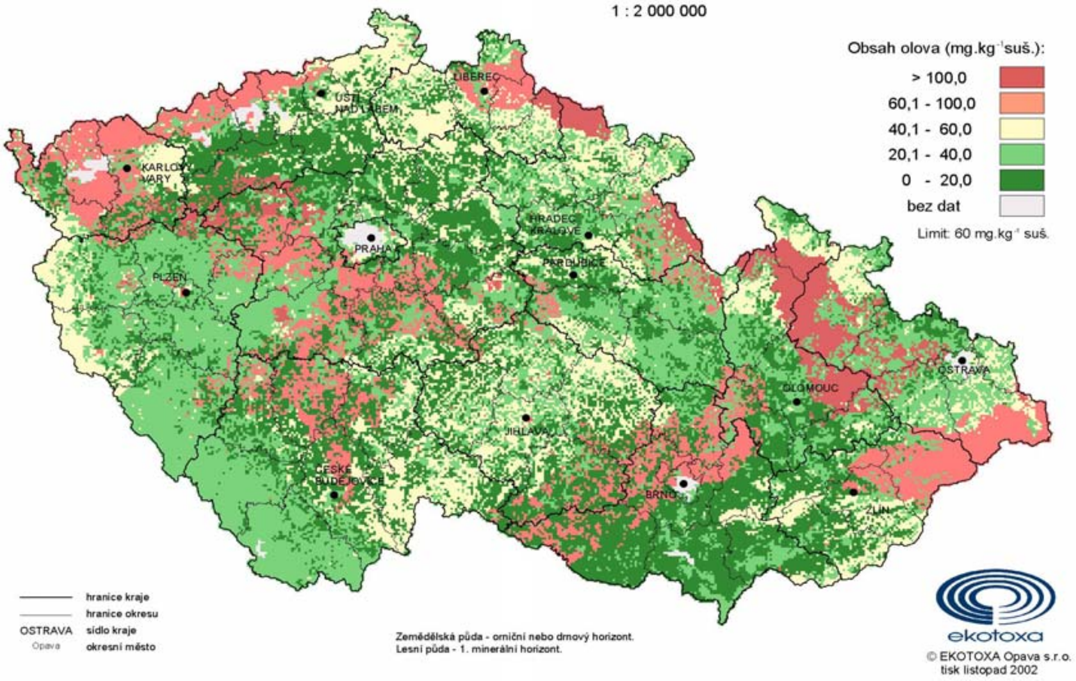
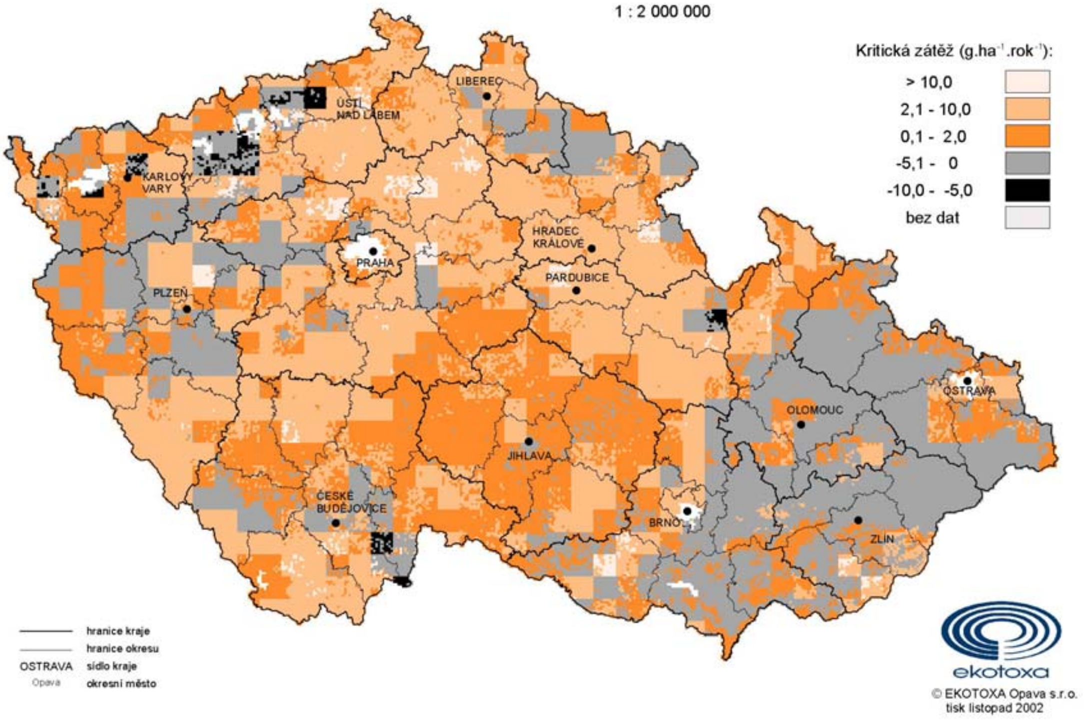
Fugures:

Map 1. Pb content in soil (AR extraction)
Map 2. Pb – critical loads – balance model for the period 1995-2000
Map 3. Pb – exceedance – balance model for the period 1995-2000
Map 4. Pb – variants for calculation the critical times – balance model for the period 1995-2000
Map 5. Pb – time to reach the critical concentration in soil – balance model for the period 1995-2000

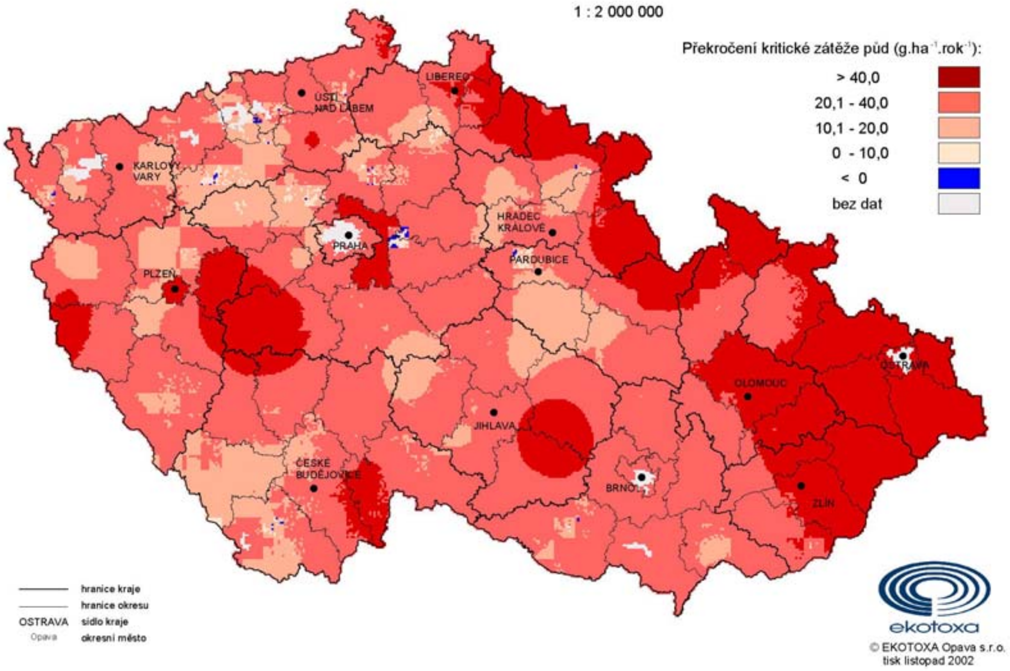
Map 1. Pb content in soil (AR extraction)



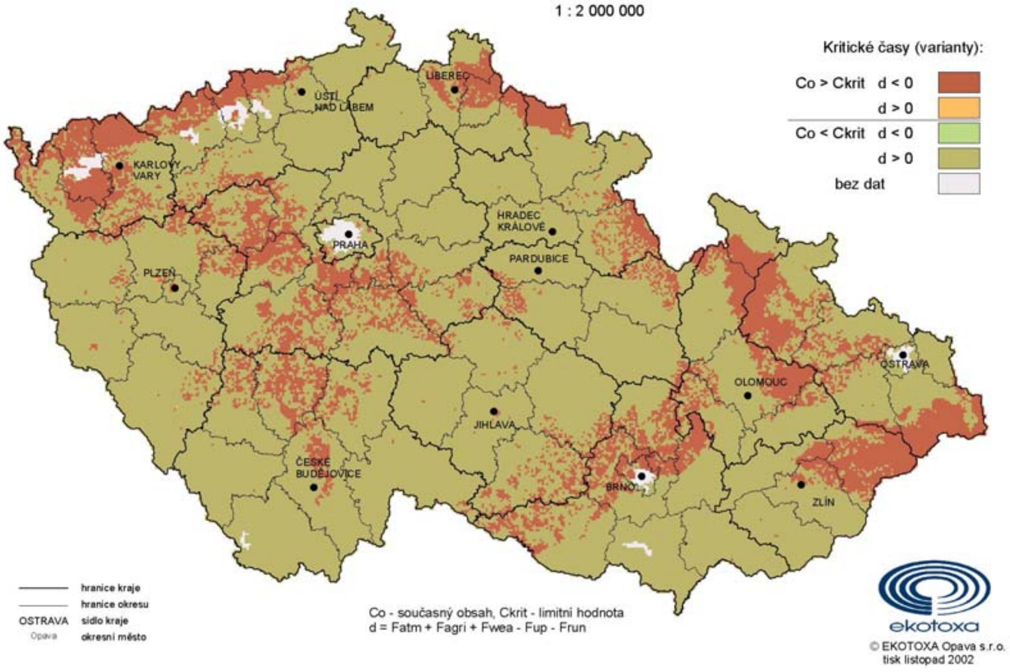
Map 2. Pb – critical loads – balance model for the period 1995-2000



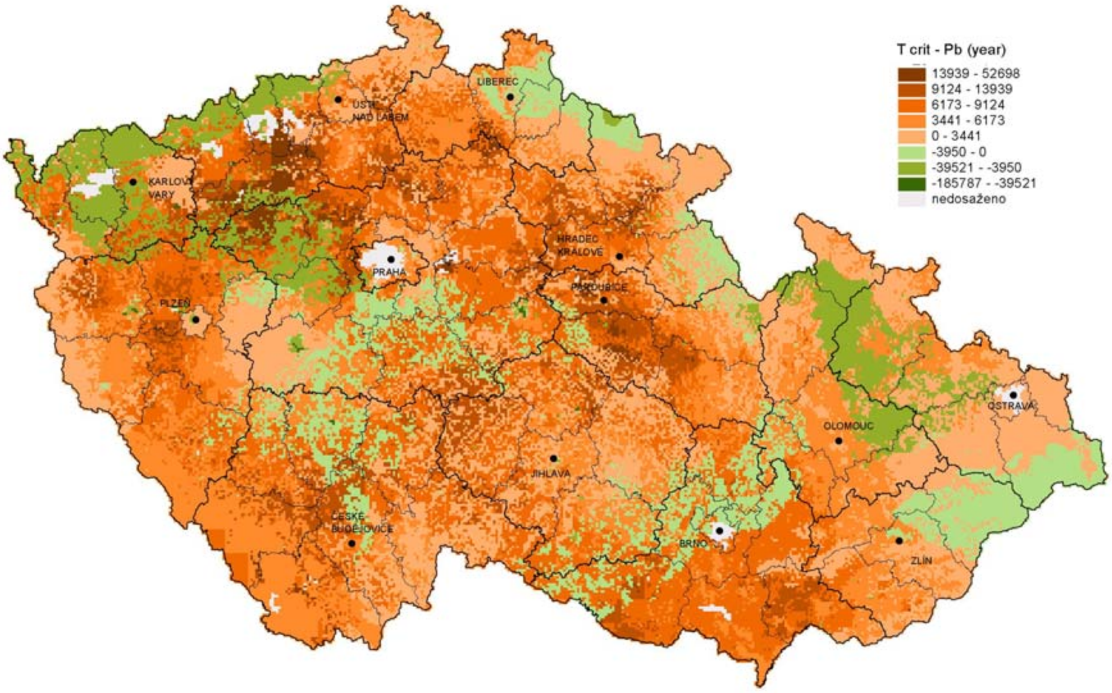
Map 3. Pb – exceedance – balance model for the period 1995-



Map 4. Pb – variants for calculation the critical times – balance model for the period 1995-2000



Map 5. Pb – time to reach the critical concentration in soil – balance model for the period 1995-2000



6.5 NEW FIELD DATA FOR CD AND PB IN CONTAMINATED AND BACKGROUND SOILS: COMPARISON OF EXTRACTION TECHNIQUES AND VALIDATION OF GERMAN TRANSFER FUNCTIONS

Tatiana Pampura[1]

INTAS project N 01- 2213,
NWO project N 047.014.002

Transfer functions link reactive (total) metal content in soil with metal concentration (activity) in soil solution and the main soil characteristics. However there is a number of methods to obtain soil solution and to determine so called reactive and total metal pools in soil. This creates big variability in existing TF. For example Dutch (Römkens et al, 2002) and UK (Tipping et al., 2002) datasets are based on 0.43 HNO3 extractions, whereas German datasets (Pampura et al, 2002, Liebe, 1999, DIN V 19735) are based on weaker 1M NH4NO3 extraction for reactive metals. To approximate soil solution 0.002M CaCl2 extraction, sampling with Rhizon samplers, and soil saturation extracts (BSE) were used in Dutch, UK, and German datasets correspondingly.

In this paper different methods for both soil solution and reactive metal extraction are compared, as well as metal partitioning expressed in different terms. Agreement between different TF derived for German soils (Schuetze, Throl, 2000, Pampura et al., 2002) and the new field data for contaminated and background Russian Podzols (Kola Peninsula) is also presented. Partitioning of Cd and Pb in Podzols (O and B horizons) along pollution gradient created by Monchegorsk Cu - Ni smelter, Kola Peninsula, Russia was investigated. Although the main polluting metals in this area are Cu and Ni, contamination of soil with Cd and Pb also takes place.

Solid phase of soil. "Reactive" metals (Q) were extracted with 0.43M HNO_3 and 1M NH_4NO_3(DIN 19730), "pseudo total pool" was extracted with aqua regia (AR). Soil solution was approximated by 0,002 M $CaCl_2$ extraction ($CaCl_2$) (soil:solution ratio was 1:2 for B horizon and 1:4 for O horizon), and soil saturation extracts (BSE, 100% WHC). Comparison of different extraction methods is presented at Fig. 1. Results demonstrated that for both Cd and Pb NH_4NO_3 extraction is much weaker then HNO_3 extraction. For Pb the difference is much more pronounced than for Cd. Probably 1M NH_4NO_3 extracts mainly exchangeable weakly bound cations, whereas nitric acid destroys also strong complexes with OM and is able to release metals occluded in Fe-(hydr)oxides. Table 1 demonstrates the range of reactive metal fraction with respect to "pseudo total" along pollution gradient. Fraction of "reactive pool" significantly decreased with increasing depth and decreasing level of contamination, fraction of NH_4NO_3 –extractable metal seems more sensitive to contamination in comparison with that of HNO_3. For O horizon metal content in HNO_3 –extractable form is very close to "pseudo total" one, especially in contaminated soils.

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Table 1. Portion of HNO_3 and NH_4NO_3 extractable pool with respect to AR in highly contaminated (7 km from smelter) and background (100-200 km) soils.

Metal	Horizon	HNO_3/ AR (%)	NH_4NO_3/AR(%)
Pb	O	86-(56)	17-(0.4)
	B	39-(20)	0.5-(0.1)
Cd	O	104-(74)	82-(28)
	B	27-(2)	8-(1.7)
Cu	O	89-(29)	16-(0.9)
	B	64-(6)	2-(0.20)

figures for background soil are shown in brackets.

Fig.1 Relation between HNO3, NH4NO3, and Aqua Regia extractable pools of Pb and Cd.

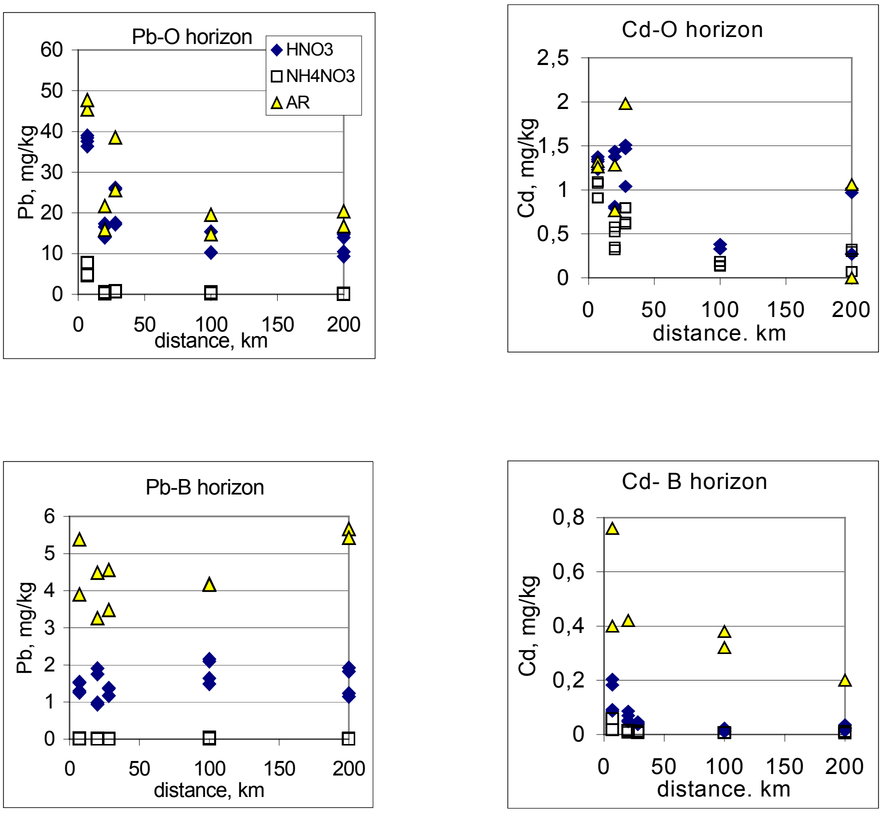


Fig.2. Comparison of concentration of Cd, Pb, DOC , and pH in soil solution approximated with BSE and $CaCl_2$ extraction.

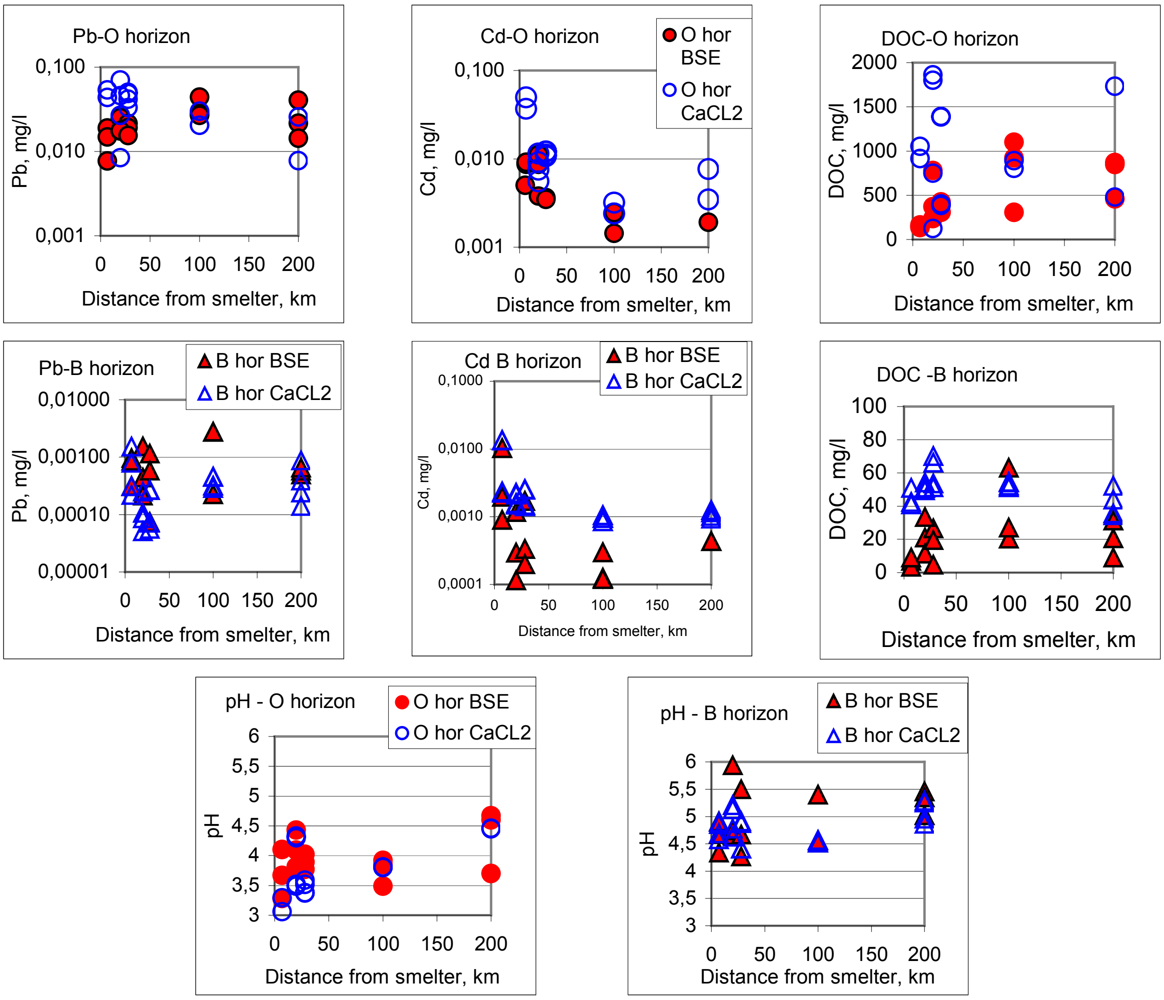
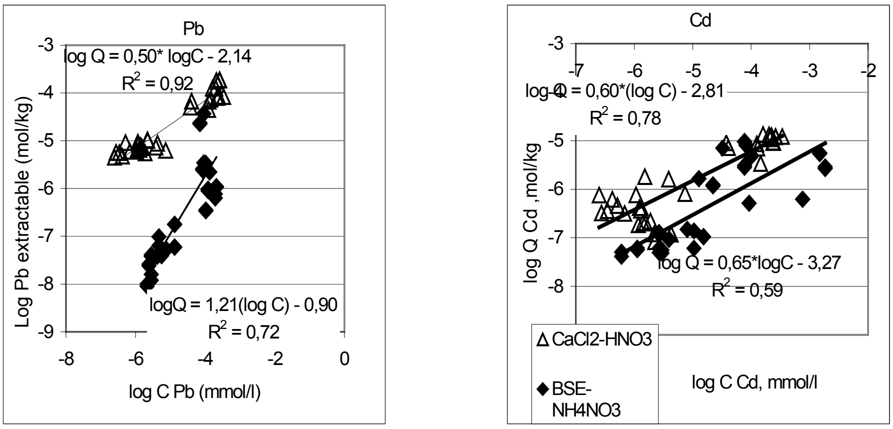


Fig. 3. Comparison of Cd and Pb field partitioning data (KOLA) obtained with different methods

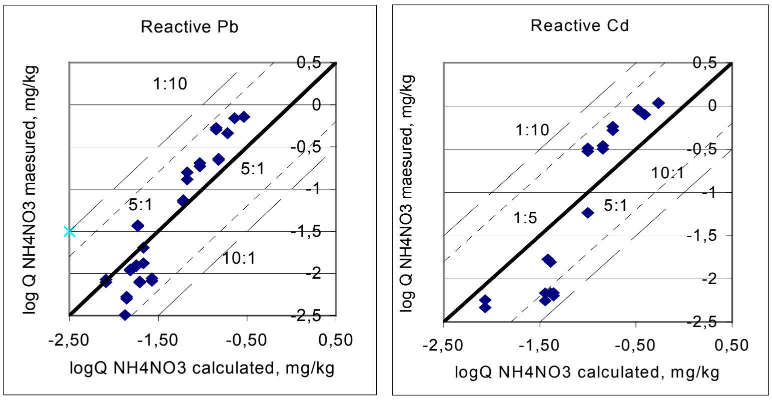


Soil Solution. Difference in Cd, Pb, DOC concentrations and pH of soil solutions approximated with BSE and $CaCl_2$ extractions is presented at Fig. 2. For organic horizon (O) soil solution approximated with $CaCl_2$ had lower pH and higher values of DOC in contaminated soils, which resulted in higher Pb and Cd concentrations. For B horizon values of pH and Pb concentrations were similar for both methods, whereas DOC and Cd concentrations were higher in the case of $CaCl_2$ extraction.

Partitioning. Difference in methods used for reactive metal and soil solution extraction resulted in difference in HM partitioning expressed in different terms (1M NH_4NO_3 – BSE or 0.43M HNO_3-0.002M $CaCl_2$). The difference was much higher in the case of Pb (Fig. 3). The results illustrate that terms “reactive metal” and “soil solution”, as well as TF describing HM partitioning are operationally defined and have to be applied with care.

Transfer functions validation. Applicability of TF linking reactive Q (NH_4NO_3) and pseudo total metals AR (fig. 4) as well as TF linking reactive pool (NH_4NO_3) and concentration in BSE (Fig.5) was studied by comparison of Kola field data with values calculated with different TF derived for German soils. Lines designated as 1:10, 1:5 correspond to the ratio 1:10, 1:5 between observed and calculated values of metal concentrations in soil solution or in soil. Most of measured concentrations had deviation less then one order of magnitude form values calculated with TF, however for BSE trends within different horizons could be different form those predicted with TF (Fig. 5, 6). Concentration of Pb in BSE in O horizon was nearly constant for different levels of contamination perhaps because of strong buffering effect of soil organic layer.

Fig. 4. Agreement between Kola field data (reactive metal in soil, 1M NH4NO3) and TF linking reactive pool (1M NH4NO3) and AR extractable pool (Prinz and Bachmann, 1999 in: Schuetze, Throl, 2000). Most data fall into the interval between 1:5 and 5:1 lines.



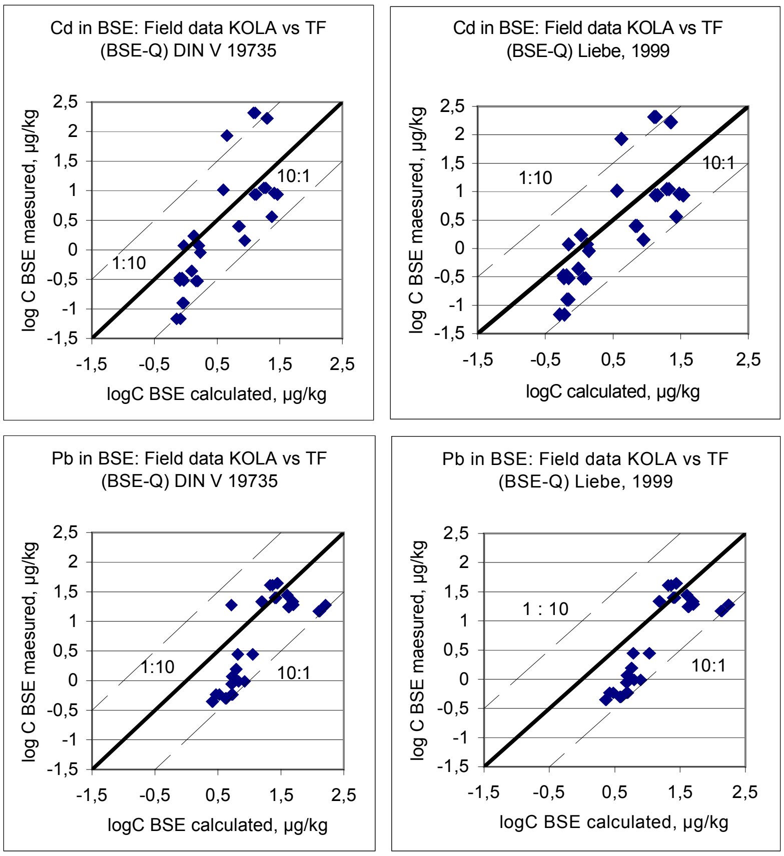


Fig. 5. Agreement between Kola field data (metal concentration in BSE) and German TF (Schuetze, Throl, 2000). Most data fall into the interval between 1:10 and 10:1 lines.

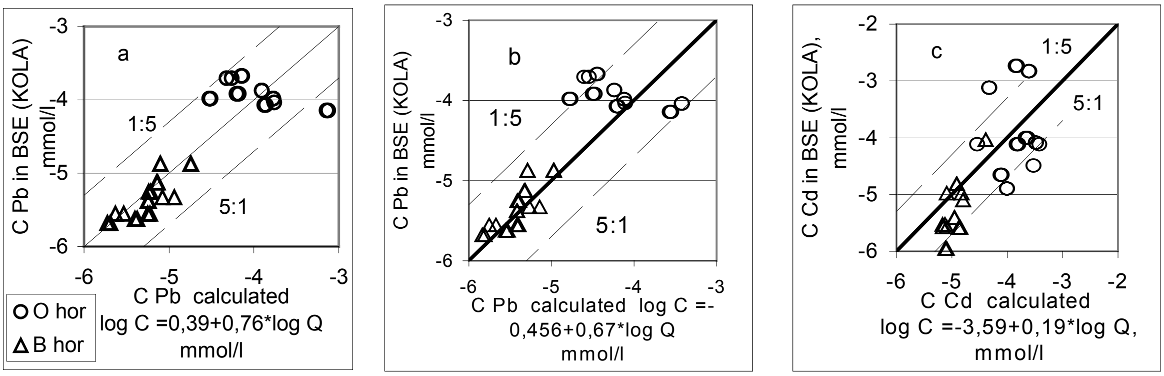


Fig. 6. Agreement between Kola field data (metal concentration in BSE) and German TF (Pampura et al., 2002) Most data fall into the interval between 1:5 and 5:1 lines.
a. TF for Pb based on adsorption-desorption isotherms, b. TF for Pb based on field partitioning data, c. TF for Cd based on field partitioning data.

Acknowledgements. We are grateful to Dr M. Rutgers (RIVM, the Netherlands) for the help in experimental work organization, and to Dr. G. Koptsic, Dr. S. Koptsic (MSU, Russia), Prof. N. Lukina and Prof. V. Nikonov (INEP KSC RAS, Russia) for the help in soil sampling.

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6.6 TRANSFER FUNCTIONS FOR Pb AND Cd: NEW GERMAN DATASET

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This paper presents a set of transfer functions linking Cd and Pb reactive content in soil and concentration (activity) in soil solution (and vice versa) with the main soil characteristics. These transfer functions (TF) are based on field data and laboratory adsorption-desorption study of German soils (Pampura et al, 2002).

Eleven soil samples were collected from 4 sampling sites in Germany (Hessen). The set of samples provides very big variability in soil characteristics responsible for metal binding and retention by soil: SOM (1,61 – 76,6%), pH (3,6-7,8), Clay (0 – 12,4%), CEC effct. (16,4-110,4 mmol/100g), CEC potent. (23,2-317,6 mmol/100g), WHC (24,95 – 172,7 g moisture/100g air dry soil).

Four types of TF (Q_{soil} - $C_{solution}$, $C_{solution}$ - Q_{soil} , Q_{soil} - $a_{solution}$, $a_{solution}$ - Q_{soil}) were derived using procedure of multiple linear regressions. The results are presented in Tables 1-8. Above each table the general equation for regressions is written. Each table contains the values of the equation coefficients corresponding to independent variables (*a, b, c , d , e, n*), equation constant log*K*, coefficient of determination *R2* , and the value of the standard error *se(Y)* for the Y (dependent variable). The different rows of table correspond to the different sets of independent variables included in the equation.

N – the number of data sets

Q_{soil} – reactive metal (NH_4NO_3 1M extraction, DIN 19730), mol/kg

$C_{solution}$ – metal concentration in soil saturation extract (BSE) (100% WHC), mmol/l

$a_{solution}$ – metal activity in soil saturation extract (BSE) (100% WHC), mmol/l

[SOM] – soil organic matter content, %

[Clay] – clay content, %

pH – pH of soil solution observed in the experiment

[DOC] – dissolved organic matter content in soil solution, mol/l

[CEC] – effective cation exchange capacity of soil, mmol/100 g soil

The DOC content in mg/l was recalculated in the concentration of organic acids in mol/l using equation

[DOC, mol/l] = (DOC, mg/l) · f,

where the value of f was set at 5,5 $\mu mol_c.mg^{-1}$ C in accordance with Bril (1995).

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a. Transfer functions: Pb, laboratory adsosrption-desorption isotherms (incubation, low water content)

Log[Q_{soil}] = log$K^{Q\text{-}C}$ + a·log[SOM] + b·pH + c·log[DOC] + d log[CEC] + n·log[$C_{solution}$], N = 36 (3 soils * 6 concentrations* duplicated) [1]

Table 1. Pb: values for coefficients (equation [1])

log$K^{C\text{-}Q}$	*a*	*b*	*c*	*d*	*n*	R^2	*se(Y)*
	SOM	*pH*	*DOC*	*CEC*	$C_{solution}$		
-1.14	-	-	-	-	1.16	0.89	0.30
20.09	-6.18	-2.80	-	-	0.82	0.94	0.27
11.26	-4.67	-2.55	-1.53	-	0.72	0.94	0.27
16.31	/-1.04/	/-0.05/	3.34	-3.34	0.78	0.98	0.15

Log[Q_{soil}] = log$K^{Q\text{-}a}$ + a·log[SOM] + b·pH + c·log[DOC]+ d log[CEC] + n·log[$a_{solution}$], N = 36 [2]

Table 2. Pb: values for coefficients (equation [2])

log$K^{C\text{-}Q}$	*a*	*b*	*c*	*d*	*n*	R^2	*se(Y)*
	SOM	*pH*	*DOC*	*CEC*	$a_{solution}$		
-3.33	-	-	-	-	0.40	0.77	0.50
35.6	-11.1	-4.44	-	-	0.63	0.89	0.35
9.80	-6.08	-3.36	-3.72	-	0.43	0.91	0.33
26.45	-2.79	/-0.04/	4.53	-4.83	0.68	0.98	0.15

Log[$C_{solution}$] = log$K^{C\text{-}Q}$ + a^*·log[SOM] + b^*·pH + c^*·log[DOC]+ d^* log[CEC] + n·log[Q_{soil}], N = 36 [3]

Table 3. Pb: values for coefficients (equation [3])

log$K^{C\text{-}Q}$	*a**	*b**	*c**	*d**	*n*	R^2	*se(Y)*
	SOM	*pH*	*DOC*	*CEC*	Q_{soil}		
0.39	-	-	-	-	0.76	0.89	0.28
-11.55	/3.51/	/1.55/	-	-	0.88	0.90	0.28
-22.57	5.09	/1.63/	/-2.30/	-	0.74	0.91	0.27
-22.99	1.63	/-0.14/	-5.06	3.56	1.03	0.96	0.18

Log[$a_{solution}$] = log$K^{a\text{-}Q}$ + a^*·log[SOM] + b^*·pH + c^*·log[DOC]+ d^* log[CEC] + n·log[Q_{soil}], N = 36 [4]

Table 4. Pb: values for coefficients (equation [4])

Log$K^{a\text{-}Q}$	*a**	*b**	*c**	*d**	*n*	R^2	*se(Y)*
	SOM	*pH*	*DOC*	*CEC*	Q_{soil}		
4.93	-	-	-	-	1.95	0.77	1.10
-28.20	8.87	2.92	-	-	0.85	0.97	0.42
-40.6	10.6	3.01	/-2.59/	-	0.69	0.97	0.41
-41.32	4.44	-0.16	-7.52	6.38	1.22	0.99	0.20

/…/ - insignificant for P=0.95

b. Transfer functions: Pb and Cd, field partitioning data.

$\text{Log}[Q_{soil}] = \log K^{Q\text{-}C} + a\cdot\log[\text{SOM}] + b\cdot\log[\text{clay}] + c\cdot\text{pH} + d\cdot\log[\text{DOC}] + e\,\log[\text{CEC}] + n\cdot\log[C_{solution}]$, N = 33 (11 soils * triplicated) [5]

Table 5. Pb, Cd: values for coefficients (equation [5])

	$\log K^{Q\text{-}C}$	*a*	*b*	*c*	*d*	*e*	*n*	R^2	*se(Y)*
Metal		*SOM*	*Clay*	*pH*	*DOC*	*CEC*	$C_{solution}$		
Pb	-0.42	-	-	-	-	-	1.23	0.83	0.48
Pb	-0.53	-0.37	-	-0.55	-	-	0.48	0.92	0.34
Pb	-4.13	-0.35	-	/-0.26/	-2.00	-	1.41	0.95	0.27
Cd	-2.4	-	-	-	-	-	0.88	0.17	0.66
Cd	-8.61	0.44	/-0.05/	-0.44	-	-	-0.72	0.95	0.18
Cd	-11.83	0.40	-0.21	-0.51	-0.99	-	-0.83	0.97	0.13
Cd	-11.64	0.25	-0.18	-0.54	-0.92	0.34	-0.78	0.98	0.12

$\text{Log}[Q_{soil}] = \log K^{Q\text{-}a} + a\cdot\log[\text{SOM}] + b\cdot\text{pH} + c\cdot\log[\text{DOC}] + d\,\log[\text{CEC}_{effect}] + n\cdot\log[a_{solution}]$,
Pb: N = 33 (11 soils * triplicated)
Cd: N=29 (9 soil *triplicated + 1 soil*duplicated) [6]

Table 6. Pb, Cd: values for coefficients (equation [6])

	$\log K^{Q\text{-}a}$	*a*	*b*	*c*	*d*	*n*	R^2	*se(Y)*
Metal		*SOM*	*pH*	*DOC*	*CEC*	$a_{solution}$		
Pb	-2.40	-	-	-	-	0.48	0.76	0.57
Pb	-3.03	0.32	-1.26	-	-	-0.46	0.93	0.32
Pb	-2.86	0.33	-1.27	/0.07/	-	-0.47	0.93	0.33
Cd	-3.81	-	-	-	-	0.51	0.26	0.65
Cd	-6.47	0.41	-0.45	-	-	-0.26	0.92	0.23
Cd	-9.4	0.60	-0.52	-0.78	-	-0.37	0.93	0.21
Cd	-11.04	0.25	-0.64	-0.95	0.97	-0.46	0.98	0.12

$\text{Log}[C_{solution}] = \log K^{C\text{-}Q} + a^{*}\cdot\log[\text{SOM}] + b^{*}\cdot\log[\text{clay}] + c^{*}\cdot\text{pH} + d^{*}\cdot\log[\text{DOC}] + e^{*}\log(\text{CEC}) + n\cdot\log[Q_{soil}]$,
Pb: N=33, Cd: N=32, [7]

Table 7. Pb, Cd: values for coefficients (equation [7])

	$\log K^{C\text{-}Q}$	*a**	*b**	*c**	*d**	*e**	*n*	R^2	*se(Y)*
Metal		***SOM***	*Clay*	*pH*	*DOC*	*CEC*	Q_{soil}		
Pb	-0.46						0.67	0.86	
Pb	-2.19	0.42	-	-0.30	-	-	0.19	0.94	0.21
Pb	1.56	0.21	-	-0.15	1.20	-	0.29	0.98	0.13
Cd	-3.59	-	-	-	-	-	0.19	0.17	0.30
Cd	-8.36	0.46	/0.05/	-0.38	-	-	-0.72	0.75	0.18
Cd	-11.82	0.42	-0.15	-0.49	-0.99	-	-0.86	0.86	0.13
Cd	-12.34	0.34	-0.15	-0.54	-0.99	/0.23/	-0.92	0.87	0.13

/…/ - insignificant for P=0.95

$\mathrm{Log}[a_{solution}] = \log K^{a-Q} + a^{*}\cdot\log[\mathrm{SOM}] + b^{*}\cdot\mathrm{pH} + c^{*}\cdot\log[\mathrm{DOC}] + d^{*}\log[\mathrm{CEC}] + n\cdot\log[Q_{soil}]$
Pb: N = 33 (11 soils * triplicated)
Cd: N=29 (9 soil *triplicate + 1 soil*duplicated) [8]

Table 8. Pb, Cd: values for coefficients (equation [8])

	LogK^{a-Q}	*a**	*b**	*c*	*d**	*n*	R^2	*se(Y)*
Metal		*SOM*	*pH*	*DOC*	*CEC*	Q_{soil}		
Pb	2.19	-	-	-	-	1.57	0.76	1.02
Pb	-3.55	1.03	-1.40	-	-	-0.43	0.98	0.31
Pb	-0.14	0.85	-1.25	1.09	-	-0.33	0.98	0.28
Cd	-2.13	-	-	-	-	0.52	0.26	0.65
Cd	-10.31	/0.54/	-0.74	-	-	-1.14	0.64	0.48
Cd	-14.27	/0.002/	-1.08	-	1.73	-1.61	0.75	0.40
Cd	-16.82	1.03	-0.83	-2.01	-	-1.18	0.79	0.37
Cd	-20.97	0.49	-1.18	-2.04	1.77	-1.67	0.92	0.24

/…/ - insignificant for P=0.95

Review of TF presented in this paper shows that the high values of coefficient of determination *R2* were obtained in most cases. Taking into account such soil properties as pH , soil organic matter, clay and CEC improved the accuracy of models. It is especially important in the case of Cd where no dependence between reactive pool and concentration in soil solution was found without considering at least SOM, and pH. Introducing DOC in the equations in most cases did not improve the results very much. Taking into consideration difficulty in getting of data on DOC content in soil solution, this variable may be ignored in most cases. Anyway we present here the transfer function for DOC based on field data with pH and SOM as explained variables which can be used for DOC concentration calculations if there is no information on DOC available.
$\log[\mathrm{DOC}] = -2{,}98+0.19\cdot\log[\mathrm{SOM}] - 0.063\cdot\mathrm{pH}$ $R^2 = 0.61$, se(Y)= 0.15, N=33 [9]

Substitution of activity instead of concentration did not affect much the quality of regressions. We have to stress that in this study only calculated activities were used (EPIDIM, Groenedijk, 1995) and validation of speciation model is needed by comparison of measurements and calculated values.

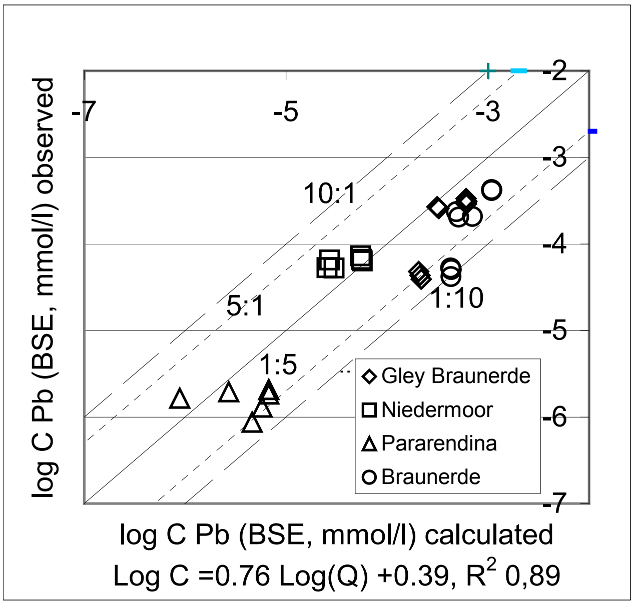

Fig.1. Agreement between Pb concentrations observed in the field soil saturation extracts and calculated with transfer functions based on the laboratory adsorption- desorption isotherms.

Applicability of TF for lead (based on laboratory adsorption-desorption isotherms) were studied by comparison of Pb concentrations in soil solution calculated with TF and those measured in the soil saturation extracts for 11 soil samples. The results for the simplest case of TF (table 3, row 1) are presented on Fig. 1. Even in this case in general values predicted with the regression were in a good agreement with field data. Lines designated as 1:10, 1:5 correspond to the ratio 1:10, 1:5 between observed and calculated lead concentrations in soil solution. The most of data fall into the interval between 1:5 and 5:1 lines.

This investigation was carried out in the frame of Project: UBA - FKZ 201 63 and supported by DAAD fellowship.

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6.7 BIOAVAILABILITY OF HEAVY METALS IN SOIL: THE QUEST FOR A LAB TO FIELD TRANSLATOR FOR RISK ASSESSMENT PURPOSES, THE ZINC BLM AS THE ULTIMATE CHALLENGE

Willie Peijnenburg[1], Rob Baerselman[1], Arthur de Groot[1], Martina Vijver[2]

Introduction

The purpose of ecotoxicological risk assessment is to distinguish between substrates that will or will not produce effects on exposed organisms. Total concentrations are commonly used in environmental risk assessment. Most soil dwelling organisms, however, do not respond to total metal concentrations. Hence, soil quality criteria that are based on total concentrations are unlikely to be predictive of adverse biological effects. It is the variation in critical soil properties that results in a substantially different availability for uptake of compounds by organisms in different soils or sediments. This variation should be taken into account in generic and site-specific risk assessment, to improve the accuracy in predicting (no) effects. Although bioavailability of heavy metals is an important and frequently mentioned issue, the scientific basis for its adequate use in the assessment of ecological risks at contaminated field sites is weak. Important is that bioavailability should be handled as a dynamic process. The dynamic approach of 'bioavailability' should comprise at least three distinct phases: a physico-chemically driven desorption process, a physiologically driven uptake process requiring identification of specific biotic species as endpoint, and toxicodynamic transport processes within the organisms leading to interactions at specific receptor sites (Figure 1). It eventually is the concentration at the receptor that counts in many organisms, as this is directly related with organ-effect levels. Environmental conditions (especially pH) play a crucial role in this whole context since they determine the steady state status, in dependence of the physico-chemical sorption mechanisms and the biologically driven uptake and depuration mechanisms. The environmental conditions, moreover, play a role in the survival and well being of soil organisms. Operationalisation of the three principal processes involved in the concept of bioavailability provides the ultimate tool for extrapolating results of laboratory testing towards field conditions, thus allowing for risk assessment to be based upon truly occurring adverse ecological effects in the field.

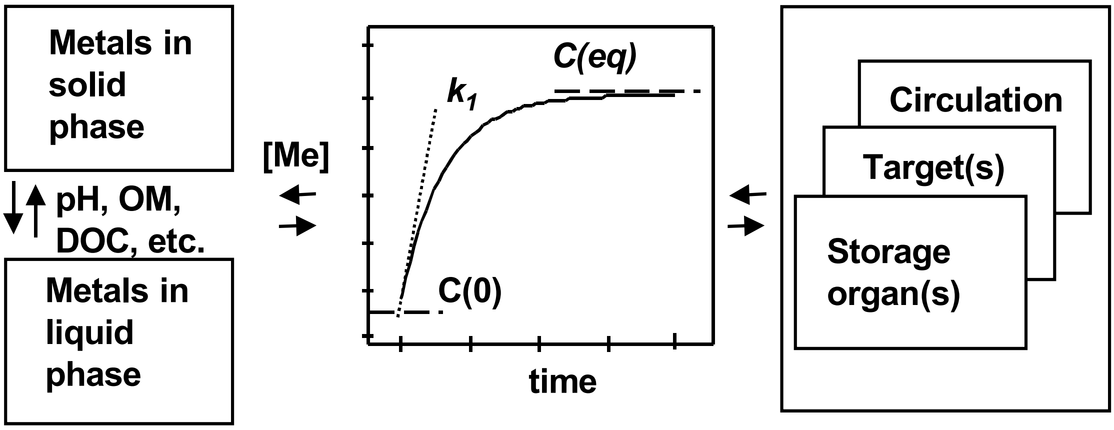

Figure 1. The principal processes involved in the concept of bioavailability. Environmental availability is envisaged as partitioning of heavy metals between the soil solid phase and the pore water (left). The actual uptake (demand of organism) can be defined as bioavailability and is depicted by means of accumulation characteristics (uptake rate constant, k_1, and the equilibrium concentration, C(eq) (middle)). Toxicological bioavailability is shown on the right on the basis of internal recirculation and storage processes of the metals assimilated, resulting in transport to the target sites of toxicity.

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Operationalisation: Zinc as an example
Environmental availability of zinc was studied by sampling 49 Dutch soils, spanning a wide range of soil properties and zinc levels. Apart from the most relevant soil and pore water properties known to affect metal partitioning, zinc levels in both the solid phase and the pore water were measured and partition coefficients (K_p) were calculated. Subsequently, measured K_p-values for each soil were regressed against a range of soil and pore water properties. It was found that pH is the most important soil property and due to competition there is a negative correlation between K_p and pH. Apart from studying zinc partitioning in field soils, we also investigated zinc partitioning in field soils spiked with zinc salts (acetate and chloride, thereby generating a pH-difference due to the counter-ion, and hence a difference in zinc concentrations in the pore water at similar total zinc loadings). In this case, Freundlich isotherms could be well fit through the data and again it was shown that competition with H^+ (and to a lesser extent with Cd^{2+} and Ca^{2+}) dominates the sorption isotherm.

Environmental bioavailability was investigated on the basis of uptake and elimination kinetics for a series of organisms. A key role is played by the mode of uptake of the metal by the different organisms. A clear distinction became visible between organisms exposed via the pore water (dermal uptake) and organisms for which uptake can be best described on the basis of total zinc concentrations in the solid phase (e.g. earthworms versus beetle larvae). Additional studies in which soils were spiked with zinc salts confirmed that especially for earthworms and plants uptake via the pore water is the most important uptake route. Comparable to zinc partitioning it was found that competition with pH, Ca and Mg determines the steady state concentration.

Similar to current developments in the field of aquatic toxicology, we found that competition at the cell membrane determines toxicity and a Biotic Ligand Model (BLM) could be developed for the earthworm *Aporrectodea caliginosa* on the basis of newly generated soil toxicity data. The basis for the BLM is the expression of toxicity in terms of zinc concentrations in the pore water phase as a function of pH. This is graphically illustrated in Figure 2. Toxicity tests with copper in an inert sand matrix (quartz sand, thus excluding uptake from the solid phase) and in water confirm these findings and allow for the development of a quantitative BLM. The concentrations of the most important cations competing for the active sites at the membrane of the worms were systematically varied in these tests. Finally, organism related detoxification mechanisms were studied by assessing metal fractionation in the earthworm. It was found that zinc is evenly distributed among the various operationally defined metal fractions, but nevertheless possibilities for deriving a modified Critical Body Burden model for assessing the effects of zinc were clarified.

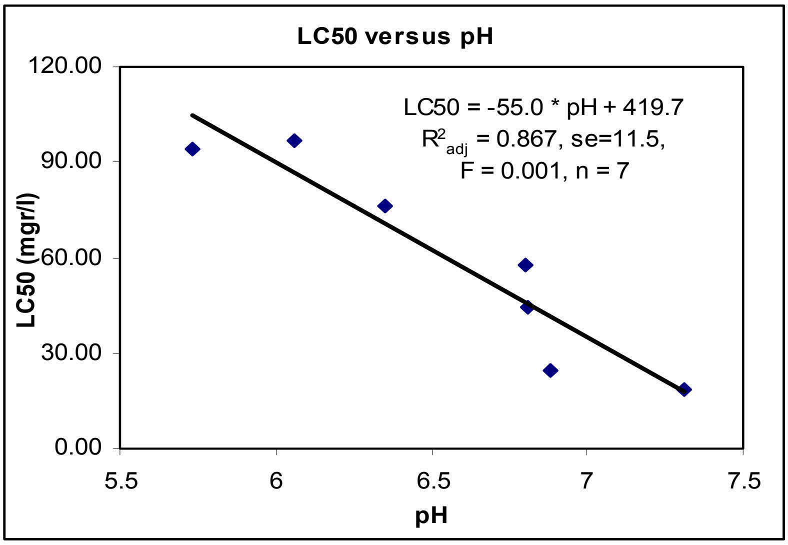

Figure 2. Zinc toxicity (expressed as the total zinc concentration in pore water) for the earthworm *Aporrectodea caliginosa* as a function of pore water pH.

In summary, operationalisation of the bioavailability concept stresses the importance of acquiring detailed knowledge on each of the sub-processes identified. Competitions with cations present in the system and physiological driven detoxification mechanisms in combination with differences between the dominant modes of uptake determine the toxicodynamics of the metals present. Combined insight in all these steps allows adequate assessment of future risk levels explicitly taking bioavailability into account.

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7. ABSTRACTS OF POSTERS

7.1 FURTHER DEVELOPMENT OF AN EFFECTS-BASED APPROACH FOR DETERMINING METAL CRITICAL LOADS IN THE UK.

M.Ashmore, J. Fawehinmi, J.Hall, A.Lawlor, L.Shotbolt, E.Tipping

1. Introduction

Previous research carried out in the UK on critical loads for metals has highlighted:

- the importance of using effects-based critical load determination and therefore the need for better determination of critical limits;
- the importance of incorporating metal dynamics (i.e. transport of metals through soils and into the aquatic system) into the determination of critical loads, particularly in the context of significant historical deposition and large metal pools in many upland UK soils, and;
- the need to extend critical load calculations from the uplands to other acid-sensitive areas of the UK

2. Objectives

The major objectives of current research are:

- To establish critical threshold concentrations of bio-available metals below which there will be no significant effects on a range of taxonomic groups in soils and freshwaters (key findings are presented on the poster by S. Lofts *et al.* "ϕ : a toxicity parameter independent of chemical composition")
- To develop dynamic models to assess the long-term effects of changing patterns of atmospheric deposition on metal concentrations in soils and freshwaters (section 3)
- To develop improved methods for determining and mapping bio-available concentrations (section 4)
- To develop models and mapping procedures for determining and applying critical limits and critical loads of metals in soils and freshwaters in the UK. (section 5).

3. Dynamic modelling

Changes in metal storage within a catchment take place over timescales of decades to centuries and present day metal pools can only be explained through consideration of historical metal deposition, acidification status and other soil and water property changes.

CHUM (Chemistry of Uplands Model) is being used to predict current soil, water and sediment pools through the mathematical description of heavy metal accumulation and transport within soils, transfer to surface waters and accumulation within lake sediments.

The model is being refined and applied to five catchments: Castle How Beck, Cumbria; Cote Gill, Yorkshire Dales; Old Lodge, Sussex; Etherow, South Pennines and Lochnagar, Highlands. The collection of bulk deposition and streamwater chemical data to input into the model is in progress. Soil sampling and characterisation has enabled soil metal pools to be calculated (table 1).

Catchment	Ni	Cu	Zn	Cd	Pb
Castle How Beck	0.2	0.8	1.7	0.03	16.5
Cote Gill	2.9	3.0	47.9	3.40	35.0
Old Lodge	0.3	0.8	4.2	0.05	6.5
Etherow	1.3	4.9	59.6	0.30	862.0

Table 1: Soil metal pools in g m^{-2}

Very high Pb and Zn concentrations in the Etherow and Cote Gill catchment reflect historical contamination, which must, therefore, be input to the model. Reconstruction of deposition histories through the analysis of herbarium moss samples is in progress to improve estimates of historical metal inputs.

Preliminary attempts to predict current soil and water pools show promise, observed and simulated values are in reasonable agreement (table 2).

	Current lake concentrations (nM)		Catchment soil pools (mmol m^{-2})	
	Observed	Simulated	Observed	Simulated
Ni	5.0	17.0	-	4.0
Cu	15.0	7.0	8.0	12.0
Zn	40.0	120.0	95.0	26.0
Cd	-	1.0	0.6	0.2
Pb	3.0	3.0	26.0	20.0

Table 2. Observed and simulated metal concentrations at Lochnagar.

Furthermore, in the Loch Nagar catchment, the lake sediment Cu record shows increased accumulation following a similar trend to the observed data (although somewhat greater in magnitude) (fig. 1). Other metals are under investigation.

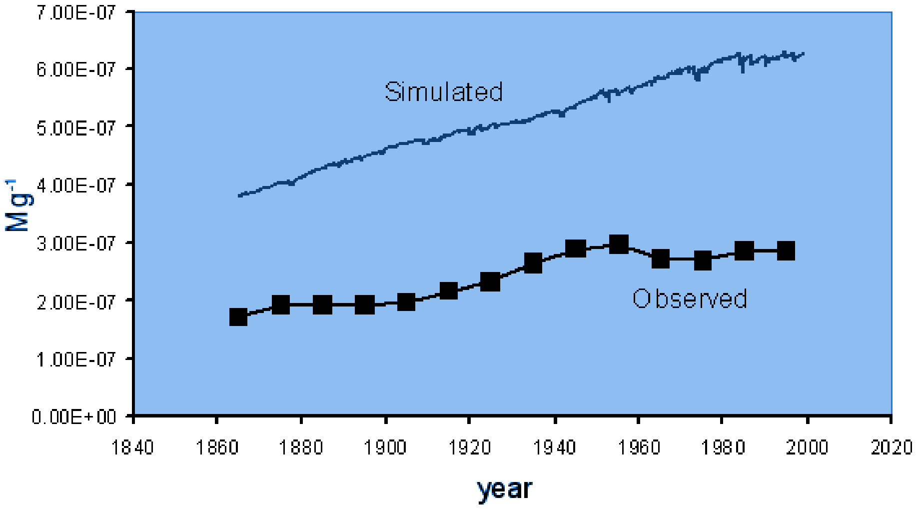


Figure 1. Simulated and observed concentrations of Cu in ^{210}Pb *dated Lochnagar sediments.*

The model can now be run with future deposition scenarios and will improve critical load methodologies by allowing the impact of future changes in metal deposition on soil and water metal pools to be assessed.

4. Modelling bio-available metal concentrations

National soils data for England, Wales, Scotland and Northern Ireland have, under a previous research contract (EPG 1/3/144), been imported into a Geographical Information System (GIS) and linked to produce UK maps and databases of soil types, characteristics and chemistry, and heavy metal concentrations. Bio-available metal concentrations (more specifically soil solution and free-ion concentration) were modelled from soil metal, pH and organic matter content using transfer functions. These transfer functions were developed empirically through extensive field sampling and analysis of soils together with the application of the WHAM chemical speciation model. However, previous research concentrated on upland grassland soils and this needs to be extended to other acid-sensitive soils across the UK.

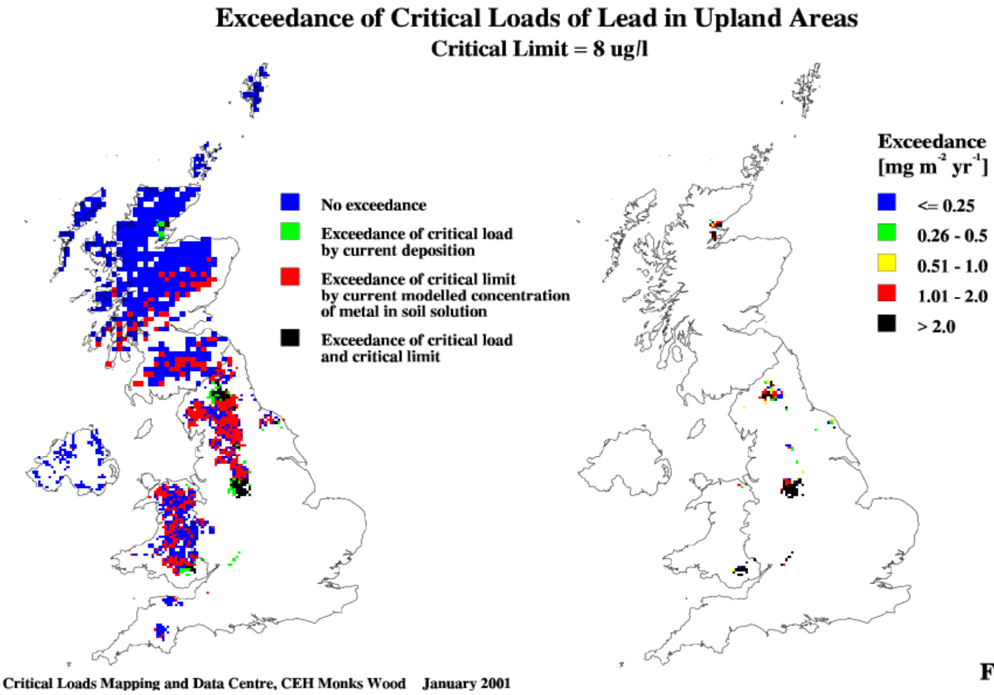
Five new land cover classes potentially sensitive to metal deposition have been selected: upland coniferous forest, lowland coniferous forest, deciduous forest, acid grassland and heathland. Ten sampling locations from each land class have been selected to include a wide geographical spread, a range of deposition loads and inclusion of sites currently monitored for critical loads or environmental change research.

The transfer functions developed under the previous research contract will be tested on this new data set to establish whether a single transfer function can be used across the UK or whether the data must be split according to land class and new regression equations determined. This data can then be used to extend GIS models of critical loads across the UK

5. Mapping critical limits and loads in the UK

Applying the transfer functions derived from field sampling during the previous research phase, critical soil metal concentrations corresponding to a critical soil solution limit of 8 μg Pb l^{-1} have been mapped for upland soils in the UK. The left-hand map in Figure 2 shows significant areas where present soil metal concentrations were found to exceed this value.
Areas where current deposition exceeded critical loads (calculated as precipitation concentrations that would not lead to increased soil metal concentration, i.e. steady state model) were also plotted (right-hand map of Figure 3). Only limited areas of the country show an exceedance based on current deposition. In contrast, most of upland England & Wales, and a significant part of Scotland, show exceedance of the critical limit. This demonstrates both the importance of historical metal inputs to UK soils and deficiencies in the steady state approach to critical load determination in such areas.

Improved and extended mapping of critical metal limits and loads is a key objective of the new project. Furthermore, estimation of the timescales of response to changes in heavy metal deposition based on the dynamic modelling work will also be extended and improved. A simpler model suitable for incorporation in the GIS will be developed based on the more extensive catchment dynamic modelling in progress



Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.9.4

Figure 2 Exceedance of critical limits and loads of lead in the UK uplands.

6. Conclusions

This project is addressing a clear need to extend critical loads calculations to forested areas and lowland areas sensitive to acidification in the UK. It will also improve the basis of critical loads calculations through identification of suitable effects-based critical limits (see accompanying poster), modelling bio-available metal concentrations in soils across the UK, and dynamic modelling. This will enable detailed mapping of critical loads and timescales of response to changes in heavy metal deposition.

Acknowledgements: This work is funded by the Department for the Environment, Food and Rural Affairs (DEFRA) under grant EPG 1/3/18

7.2 HEAVY METALS CRITICAL LOADS FOR ITALIAN SOILS

De Marco A.[1], Daffinà R.[1], Bonanni P.[2] and Silli V.[2]

The deposition of heavy metals (in particular of lead and cadmium) on terrestrial ecosystem is strictly related to impacts to soil organisms and to bioaccumulation in the soil organic layer. Trace metals such as Cd, Cu, Ni, Pb, and Zn are often adsorbed or occluded by carbonates, organic matter and primary or secondary minerals. Determination of total dissolved trace metals may provide useful information on metal bioavailability and toxicity for organisms.

The main input of trace elements to soils are: atmospheric depositions, fertilizers such as phosphates or pesticides. Minor sources of contamination are sewage sludge, municipal solid wastes, and industrial wastes, but they can be also important because their regional or local impact. Because the big importance of depositions, one approach to successful international negotiations on the reduction of atmospheric deposition of pollutants is to determine the maximum atmospheric load that causes no or tolerable damage in the plant ecosystems; this is the concept of *critical load*.

In this work we carried out studies to calculate the critical loads of lead and cadmium for Italian soils, using both the steady state model and the semi-dynamic model described in the "*Manual for calculating critical loads of heavy metals for terrestrial ecosystem, guidelines for critical limits calculation methods and input data*" (SC Report 166, 19998, de Vries and Bakker). All values for the two different applications are calculated separately for each ecosystems (arable lands, coniferous, broad filled and grassland). The results obtained with *stand still model* showed that for the cadmium, the differences in critical loads between maximum and minimum values are about 160 g/ha in three ecosystems (grassland, coniferous, broad filled), whereas in arable lands it is possible observe a grid reaching 253 g/ha.

The fact that grassland is the more sensitive ecosystem is relevant, with lower values respect to the other three ecosystems. The 25% of grids has a critical load lower than 1.4 g/ha, whereas 50% of grids don't exceed 4.3 g/ha. For coniferous, instead, 25% of grids has a critical load lower than 3 g/ha. These considerations are confirmed also for lead with the application of the stand still model. If we carefully observe the results obtained with the semi-dynamic model we can see a net increase of critical load from the value of 9 g/ha for cadmium in coniferous, to 2400 g/ha. These results mean that applying the semi-dynamic model is possible to obtain a very dramatic increase in critical loads, that is reflected in a less sensitivity (about 200 times for lead and 30 times for cadmium) of ecosystems.

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7.3 CRITICAL LIMITS FOR HEAVY METALS IN HUMAN BODY: THE PERSPECTIVE OF APPLICATION IN THE CRITICAL LOADS METHODOLOGY

Evstafyeva H. , Pavlenko V., Evstafyeva I., Slusarenko A., Demchenko V., Krilov D., Glivenko A.

Introduction

Human health is the main indicator to estimate of an acceptable ecological risk therefore inclusion of critical limits related to human health in critical load methodology should be done. For it ADIs, limits for drinking water and food quality criteria are recommended.

It was agreed that a complete model on human exposure pathway is not needed in the critical load methodology and it is enough to use of food quality criteria to convert those limits to soil critical limits. But in this case we are taking account only one way of human exposure and are not considering directly air pollution.

From our point of view the critical limits for human body are more acceptable, because it reflex total metal intake from different connected environmental resources. In this case more important how much of heavy metals there are in biosubstrates of human body (blood, hair, urine) and what kind effect on human body is occurring. Such critical limits remain undefined definitively because the new physiological data appear, but some biomarkers of toxicity effect on the central nervous, cardiovascular and immune systems are recommended by WHO [14].

Methods

The mercury, cadmium, arsenic and lead exposure biomarkers for 60 children (investigation of the central nervous and cardio-vascular systems, age 15 years, boys) and 85 children (investigation of the immune system, age 3-14 years, 46 boys, 39 girls) in town Simferopol (Ukraine) included the metal concentration in hair. A 2-cm proximal hair segment was analyzed by nuclear-absorption spectrophotometers (Hg) and Roentgen-fluorescent analysis (Cd, Pb, Cu, Zn) in the laboratory at Institute of Occupational medicine (Kiev)

Examination of central nervous system contained recording 30 indices of electroencephalograms (EEG) and evoked potentials (EP). Psychological tests included Isenk's questionnaire (children's version) for evaluation teenager's temperament; Schulte's tables for definition peculiarities of attention and working capacity; descriptive method «Building, tree, man» applied for studying personality traits. State of cardiovascular system was assessed by means of computer rheography at physiological rest state and after physical exercises on a veloergometer. The methods has been described in detail before [8,17]. To evaluate the immune state the standard methods were applied: absolute leukocyte number, G, A, M, E immunoglobulins, circulating immune complexes (CIC).

Dependence of these functional parameters on a metal concentration was defined by non-parametrical correlation analysis after Spearman.

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Results

Results of heavy metal content determination in the hair are shown in table 1. Its indicate that averages of all metals were within acceptable limits [22], but many children had the exceedances of the cadmium and lead and deficit of zinc and copper; copper deficit had total character.

Table 1. Metal content in hair of examined teenagers

	Concentration in the hair (mkg/g)			
Element	**Min**	**Max**	**Mid**	**Norm**
Hg	0,06	0,3	0,134	0-2
Pb	1,3	**7,4**	3,9	0-5
As	0,21	2,42	1,4	0-2,5
Cd	0,79	**4,75**	2,61	0-2,7
Zn	**85,4**	133,1	117,6	115-250
Cu	**5,93**	12,47	**8,45**	9-40

Physiological significance of the metals was assumed from a number and hard of correlation coefficients that are shown in the table 2. These data allows conclude that the metals under study have significantly different importance and certain physiological specification.
First of all, extremely wide scope of mercury physiological effect should be considered taking into account that its content did not only exceed the norm, but was approaching to its lowest level. A significant number of functional indices for all examined systems revealed highly significant correlation to the mercury content in hair. In other words, even insignificant increasing of its content within norm limits causes change of wide scope of psychophysiological parameters as well as of cardiovascular and immune systems. At the same time lead affected on several EEG characteristics (gamma-rhythm) and EP (featuring cognitive brain activity), immune indices and stayed indifferent for psychological traits and cardiovascular system.

Neuropsychological tests, evoked potentials and EEG-parameters, immune parameters are good biomarkers of neurotoxicity and immunotoxicity effects [1,2,14,16]. A discussion of revealed connections between physiological parameters and metal contents is not a subject of this article but ones conform to current knowledge, the human and experimental studies about more high doses of heavy metals [3-7,9-13,15,17,19,20,22,23].

Table 2. Results of the correlation analyses of the chemical element content and functional parameters

Parameters	Hg	Pb	Cd	As	Cu	Zn
BRAIN ELECTROPHYSIOLOGICAL PARAMETERS						
α-rhythm on the left (the eyes are closed)	---				-	
α-rhythm on the right (the eyes are closed)	----					
α-rhythm on the left (the eyes are open)	----				--	
α-rhythm on the right (the eyes are open)	----				--	
β-rhythm on the left (the eyes are closed)						-
β-rhythm on the left (the eyes are open)						--
β-rhythm on the right (the eyes are closed)	-					-
β-rhythm on the right (the eyes are open)	-					-
θ-rhythm on the left (the eyes are closed)	--					
θ-rhythm on the right (the eyes are closed)	---				--	---
θ-rhythm on the left (the eyes are open)	----				--	
θ-rhythm on the right (the eyes are open)	----				-	
γ-rhythm on the right (the eyes are closed)		++	+			
γ-rhythm on the right (the eyes are open)		++	+			
γ-rhythm on the left (the eyes are open)		++				
δ-rhythm on the left (the eyes are closed)	--		--		-	--
δ-rhythm on the right (the eyes are closed)	---				--	
δ-rhythm on the left (the eyes are open)	----					-
δ-rhythm on the right (the eyes are open)	----					
Latency P2 (on the right)		++++	+			
Latency P2 (on the left)		+				
Latency P300 (on the left)	+++	+				
Latency P300 (on the right)	+++					
NP on the right	-					
Latency N1 on the left	+++					
Latency N1 on the right	+					
CNV on the left		++				
Reaction time	+++					
PSYCHOLOGICAL PARAMETERS						
Unprotected				---		
Feeling of inferiority	--					
Mental stability	--					
Later work effectivity	+					
Neurotism	+					
Extravertion				-		
Frustration				+++		
Hostility	++		+			

CARDIO-VASCULAR PARAMETERS						
MV2-1 (minute volume amplitude after physical exercises)	++					
MV (minute volume)	+++					
CI2-1(cardio index amplitude after physical exercises)	+++					
CI (cardio index)	++					
WH (work hart)	+					
TPR2-1 (total peripheral resistance amplitude after physical exercises)	---					
TPR2-1/TPR	----					
TPR2 (total peripheral resistant after physical exercises)						++++
MAP2 (middle arterial pressure after physical exercises)						+++
MAP2-1/MAP						+++
HR (hart rate)	+		++			
HR2-1 (hart rate amplitude after physical exercises)	++		++++			
HR2-1/HR	++		++			
CC (cardio cycle)	-		++			
CC2-1 (cardio cycle amplitude after physical exercises)			++			
CC2-1/CC	-		++			
IMMUNOLOGICAL PARAMETERS						
Segmented neutrophils	+					
Strait neutrophils			+			
Monocytes	-				++	
Lymphocytes	-					
T- lymphocytes					+	
T-helpers		+				
B-lymphocytes	---					
0-lymphocytes					----	
Ig G					++	

The note: "+" or "-" means presence of positive or negative correlation at levels of probability: "+" ("-") - 92-94 %, "++" ("--") -95-97 %; "+++" ("---") - 98-99 %; "++++" ("----") - 99-99,9 %.

Conclusion

Central nervous system has higher sensitivity to heavy metals content within norm limits or a little more than the cardiovascular and immune systems of children. Mercury has the most influence to all investigated systems. The results show also that certain heavy metals effect to definite physiological parameters. Absence or insignificant association between some metals and physiological parameters confirms that the adopted critical concentrations at present time are acceptable but in some cases probably should be reconsider of critical limits, in particular taking in account the regional specific (morbidity rate, presence other pollutants etc.). We consider the critical concentrations (critical limits) for heavy metals in human body as the most acceptable criteria to convert those to soil critical limits, as it allows estimate influence to human body by most direct way.

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7.4 HEAVY METALS IN SOME FRENCH FOREST SOILS: DISTRIBUTION, ORIGIN AND CONTROLLING FACTORS

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Journal de Physique IV special issue : XIIth International Conference on Heavy Metals in the Environment (Grenoble, France, May 2003) proceeding (in press).

Abstract. The lowest heavy metal contents are observed in acid soils while the highest contents are in the mollic andosol and in the calcaric cambisol. Cr and Ni concentrations increase with depth in all soils, except the podzol. Co, Cu, Zn behaviour depends on the soil. Cu and Zn decreases with depth in some acid soils. Pb and Cd accumulate in all surface horizons. In the dystric planosol and stagnic luvisol, heavy metals accumulate in deep soil horizons (important clay content). The abundance order of heavy metal contents in soil profiles is: Cr>Zn>Pb>Ni>Cu>Co>>Cd. Almost all heavy metals are mainly correlated to soil pH, iron and aluminum oxides (mainly Cu and Zn), but also to clay content, organic matter and CEC depending on the metal. Ni and Cr are the only heavy metals related to CEC. Pb is related to clay content in acid soils. The highest Pb content concerns a soil located in the N-NE part of France. Pb presents a significant enrichment in surface horizons from various soils in this area which receives significant acid atmospheric pollution. Lead isotopes corroborate the anthropogenic inputs and particularly the influence of leaded gasoline compared to industrial emissions or airborne particles.

1. Introduction

The impact of heavy metal pollution on ecosystems due to anthopogenic activities like smelting or mining have been frequently investigated because of significant local environmental problems [1]. The long range transport of atmospheric heavy metals can lead to pollutant deposition even in pristine areas [2]. However, according to the European Environmental Agency [3], the large-scale impact of heavy metals in forest ecosystems is not clear. Some authors [4] draw attention over the lack of data on the distribution of heavy metals in non heavily polluted areas. It is essential to know the natural contents of heavy metals in soil (pedogeochemical background) before trying to detect the pollution intensity in forest soils and to compare the results with any norm or regulation [5]. The upper horizons of forest soils often show an accumulation of heavy metals as a result of the air-filtering effect of the vegetation, this enrichment in surface could be taken as an indicator of the degree of atmospheric deposition [6]. The total amount of heavy metals do not always prove anthropogenic pollution since high heavy metal accumulations might also result from natural processses. However Sr and Pb isotopes have been demonstrated to be powerful tools to determine the respective contribution of lithogenic and anthropogenic sources in soils [7, 8].

In France, there are by now very few studies dealing with heavy metal behaviour in pristine forest sites, only affected by atmospheric deposition. The objective of this paper is (i) to determine the range, the behaviour and the distribution of heavy metal concentration in the main forest soils, (ii) to assess the main physical and chemical controlling factors of their distribution according to the different soil types, (iii) and finally, to evaluate the anthropogenic *versus* lithogenic contribution in some of the selected soils.

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2. Materials and Methods

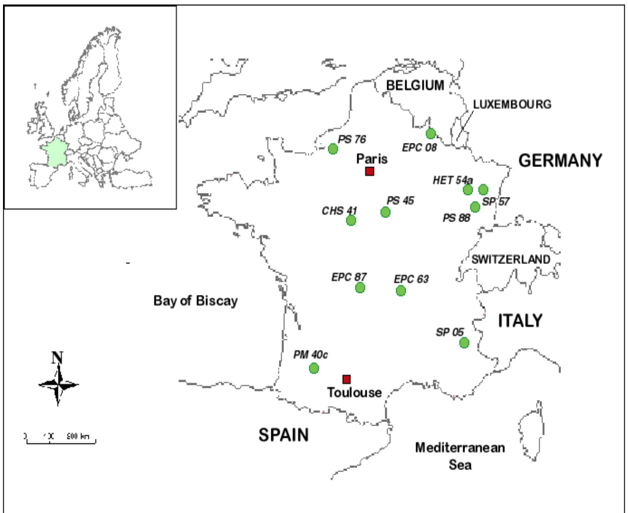


Figure 1. Location of the eleven selected sites

The soil samples concern eleven selected forested sites in France from the French RENECOFOR network (National Network for the long term Monitoring of Forest Ecosystem), managed by the ONF (National Forest Board), reflecting various chemical and physical soil characteristics, as well as different types of atmospheric inputs (fig. 1). One is ferric podzol (PM 40c), five acid soils (cambisols and podzols: EPC 08, EPC 87, PS 76, PS 88, SP 57), two leached soils (luvisol and planosol: CHS 41, HET 54a), one mollic andosol (EPC 63), one dystric planosol (PS 45) and one calcaric cambisol (SP 05). Most of the French forest soil types are represented, however acid soils are dominant because the RENECOFOR network aims to survey the forests mainly located in sensitive areas to acid atmospheric inputs [9].

The major elements were mesured by ICP-AES after complete dissolution by alcaline fusion, the trace elements by ICP-MS (Perkin-Elmer ELAN 6000), after complete dissolution of soil samples by acid digestion on hot plates at atmospheric pressure with a mixture of $HF/HNO_3/HClO_4/H_2O_2$. The isotope ratios were measured by ICP-MS [10]. For calibration and mass fractionation, corrections were based on repeated measurements of Pb standard NIST-SRM 981. The precision of isotopic ratio was 0.3%.

The metal enrichment factor (EF) was calculated using Sc as a stable conservative lithogenic reference element [11].

3. Results

3.1 Heavy metal content and distribution in soil profiles

The abundance order of heavy metal contents in soil samples is: Cr>Zn>Pb>Ni>Cu>Co>>Cd. For almost all the sites, the heavy metal content is lower than the standard values proposed for non-polluted soils and for European norms [12, 13], except Pb (EPC 08), Cr (EPC 08, SP 05) and Ni (SP 05). It is also important to notice that some concentrations are close to (like Cr) or even higher (like Ni, Pb) than the AFNOR critical values for sludge spreading [14]. Acid sandy soils (PM 40c, SP 57 and PS 88) present the lowest heavy metal content. The calcaric cambisol (SP 05) is the most enriched for all heavy metals, except Cd. The behaviour of heavy metal with depth varies according to the element and to the soil type. Cr, Co, Ni, contents increase with depth in all soils except in PM 40c. Cu content increases with depth in EPC 08, EPC 87, PS 45, SP 05 and HET 54a. Cr, Ni and Cu, and Zn slightly accumulates in the Eh-horizon from podzol PM 40c. Zn and Cd content decreases or it remains rather stable within the profile. Zn increases for SP 05, HET 54a, PS 45 CHS 41, and Cd only in CHS 41. Pb content decreases generally with depth, except for PS 45, CHS 41, HET 54a and PM 40c. Like Zn, Cr and Ni, Pb is enriched in the deep layers of PS 45, CHS 41.

3.2 Relationships between trace elements, major elements and the pedological parameters

The content of heavy metals (Cr, Ni, Co, Cu, Zn) is strongly related to the total Al and Fe content ($0.47 \le r^2 \le 0.77$, n= 34), except Cd and Pb. The relationship is particularly significant for Zn and Cu, which indicates the strong affinity between the oxides and these two elements. The relationship between heavy metals and pH_{H2O} is more significant for Ni ($r^2= 0.75$, n=34 $p<0.0001$), Co ($r^2= 0.66$, n=34, $p<0.0001$) and Zn ($r^2= 0.43$, n=34, $p<0.0001$).

The multiparameter linear relationships which were found to be the most significant, between heavy metals and the pedological parameters are presented in table 1. The concentrations of heavy metals, considering all type of soils, are mainly related to Fe and Al oxides, soil pH and frequently to clay content, organic matter, and CEC.

Nevertheless, discrepancies can be observed according to the heavy metals. The relationships are less significant if each parameter is considered separately.

Table 1. Most significant multi-parameter relationships for heavy metals in soil samples

n = 34 , p < 0.0001		r^2
Cr	2.292(Clay) + 0.089(pH $_{H2O}$) + 16.328(Fe%) + 0.809(Al%) – 66.867	0.6969
Co	3.110(CEC) - 0.181(Fe%) + 1.569(Al%) + 0.180(pH $_{H2O}$) - 12.659	0.8682
Ni	0.217(pH $_{H2O}$) + 0.029(Al%) + 0.296(O.M) + 19.204(Clay) - 83.652	0.8409
Cu	0.031(CEC) + 0.578(pH $_{H2O}$)+ 1.227(Fe%) + 3.603(Al%) + 0.105(OM) - 17.130	0.7374
Zn	0.169(pH $_{H2O}$) + 3.684(Fe%) + 1.438(Al%) + 21.302(OM) - 93.253	0.8667
Cd	0.001(pH $_{H2O}$) + 0.060(Al tamm) + 0.008(Fe tamm) + 0.009(OM)+ 0.081	0.8594
Pb	0.415(pH $_{H2O}$) + 0.152(Fe%) + 2.124(Al %) - 3.298(OM) - 6.366(Clay) + 29.685	0.5201

3.3 Enrichment factor for heavy metals and Pb isotopes

With reference to the earth crust Pb content, almost all the soil samples are Pb enriched, except CHS 41 and SP 05 (fig. 2). The most enriched samples concern the surface horizons from the soils located in the north-eastern part of France (EPC 08, HET 54a, PS 88, SP 57). Despite their low Pb content, the soils PM 40c, PS 76, CHS 41 and SP 57 present a rather significant Pb enrichment. Pb isotopes have been analyzed to check if the Pb enrichment has to be related to anthropogenic deposition. Fig. 3 presents the relationship between ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb. The surface horizon of the cambic podzol (EPC 08) has the lowest isotopic value and the highest Pb content. The influence of leaded gasoline seems to be a more important contributor to anthropogenic lead in soils than industrial emissions or airborne particles [15]. The anthropogenic contribution for the Ardennes soil (EPC 08) from top to depth is 83 %, 30% and 11%, whereas it is 68% for the surface horizon of the Alpes soil (SP 05). These data for surface horizons are in agreement with those referenced to earth crust lithogenic data (fig. 2).

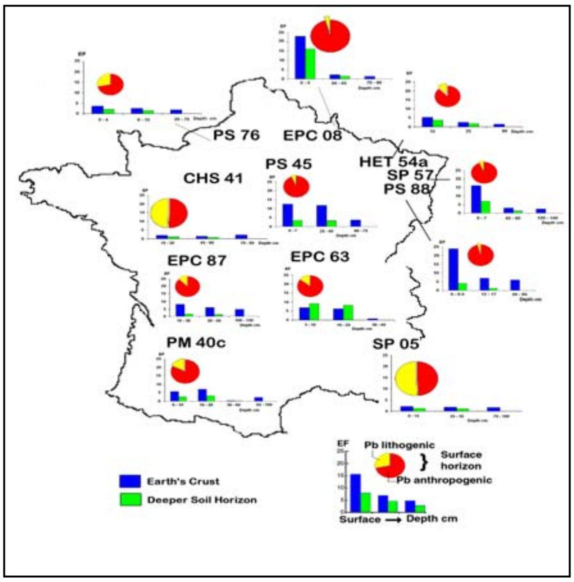
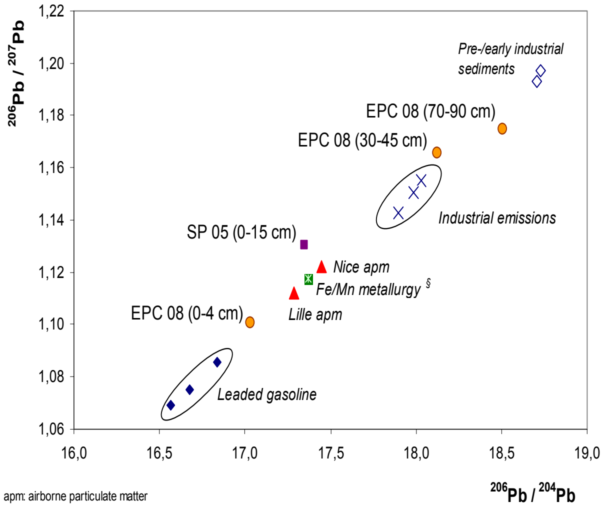


Figure 2. Pb enrichment (EF) in the different soil samples and Pb anthropogenic proportion in surface horizons



apm: airborne particulate matter
Industrial emissions: urban incinerator (Sète, France)
Ref: Monna *et al*., 1997 et Véron *et al*., 1999 §

Figure 3. Pb isotopic composition diagram (^{206}Pb/^{207}Pb vs. ^{206}Pb/^{204}Pb) for EPC 08 profile and SP 05 surface horizon

4. *Discussion and conclusion*

Generally the selected forest soils present low heavy metals content, within the range of concentration for non polluted soils and for the main world soil type [12]. For some soil samples even if they are located faraway from pollution sources, the level of concentration for some heavy metals is is higher than standard values [13, 14]. Soil pH_{H2O} is the parameter which influences mostly heavy metals adsorption, retention and movement in soil samples, showing high significant correlation in single and multiple regression analysis as already shown by Kotaś [16]. In these French forest soils, there is no clear relationship between the level of heavy metal contamination and soil samples properties. A similar pattern has been found by Chlopecka *et al.* [17] for polluted soils in Poland. The relationships between the different parameters and heavy metals in these forest soil samples are complexe and can not be related to only one parameter; nevertheless, pH, iron and aluminium oxides, and clay content play an important role in heavy metals retention and migration. Empirical models allow to identify more clearly the parameters which are the most linked to each heavy metal in the selected forest soils.

One corroborates the metal-trapping character of andosol soil and calcaric soil, the weak heavy metal retention in acid soils, the leaching and trapping character in leached clayed soils, and the migration of heavy metals in the podzol. This study highlights that atmospheric pollution inputs have impacted the soils even in forest areas. Soil surface accumulates heavy metals (Pb particularly) in areas where acid pollutant inputs are significant but also in supposed pristine areas.

Acknowledgements

The authors thanks J. Balouka, R. Rouault and J. Samuel (CGS Strasbourg); S. Aries, R. Freydier, M. Valladon and S. Köhler (LMTG Toulouse) ; the ONF staff (Fontainebleau), G. Landmann “Département de Santé des Forêts (Ministère de l’Agriculture et de la Pêche)”. This work benefits from the CEE-DG VI support (project n° 98.60.FR.006.0) and L. Hernández benefits from a SFERE-CONACYT (Ministère des Affaires Etrangères France-Mexican government) grant.

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7.5 CRITICAL LOADS FOR LEAD IN FRANCE : FIRST RESULTS ON FOREST SOILS

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Journal de Physique IV special issue : XIIth International Conference on Heavy Metals in the Environment (Grenoble, France, May 2003) proceeding (in press).

ABSTRACT

Within the framework of the United Nation Convention on Long Range Transboundary Air Pollution, France is part of the Working Group on Effects which aims at evaluating the impact of atmospheric deposition on ecosystems by calculating critical loads. The “critical loads” are “the highest deposition of compounds that will not cause chemical changes in soil leading to long-term harmful effects on ecosystem structure and function” (Nilsson et al., 1986). A guidance manual for calculation of critical loads for heavy metals (lead and cadmium) has been proposed by the Coordination Center for Effects (executive body of the WGE). French National Focal Center (CNRS and ADEME) aims in this study at evaluating the accuracy of the european methodology for calculation of critical loads for french forest soils. It appears that critical load approach is adapted for France but need to be calibrated at least for calculation of weathering fluxes and determination of critical limits. Stand-still on the contrary is not adequate because of inherent contradictions in the method and too much uncertainties in the transfer functions.

1. Introduction

The United Nation Convention on Long-range Transboundary Air Pollution (UNECE-CLRTAP) has been ratified in 1979 by 34 governments and the European Community to deal with problems of air pollution and to set up an institutional framework, bringing together research and policy.

For this purpose, 3 working groups gathering research centers from involved countries have been created since the signature of the convention :

- the Working Group on Effect which aims at evaluating the sensibility of ecosystems to atmospheric deposition;
- the EMEP steering body which attempts to model the atmospheric transports of air pollutants;
- the Working Group on Strategies and Review which aims at considering different scenarios of pollutant emission and evaluates their financial and ecological impact.

The Working Group on Effects has developed a methodology based on a threshold, determined for a particular receptor, that atmospheric deposition should not trespass : the critical load. The definition of critical load is “the highest deposition of compounds that will not cause chemical changes in soil leading to long-term harmful effects on ecosystem structure and function” [5].

Critical loads of acidity and nitrogen have already been calculated by the european countries and submited to the WGE. Following the same approach, critical loads of lead and cadmium are now being determined by the countries involved in the project.

In this study, we attempt to evaluate the different approaches to determine critical loads of lead for french forest soils. We will focus first on the determination of dissolved lead in soil solution using transfer functions and second on the determination of weathering rates.

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2. Methodology and data sources

2.1 Simple steady-state mass balance

The different approaches for calculation of critical loads for lead (CL_{Pb}) are derived from a simple steady-state mass balance model applied on the topsoil, which is considered as the humus layer for forest soils. The inputs are : weathering (Pb_{we}) and atmospheric deposition. The outputs are : biomass uptakes (Pb_{upt}) and leaching (Pb_{le}). Critical load (CL_{Pb}) is thus calculated as follows [4]:

$$CL_{Pb} = Pb_{le} + Pb_{upt} - Pb_{we} \tag{1}$$

Although other inputs and outputs of lead actually occur in the upper soil horizon, like biomass return, surface runoff, bypass flow and foliar uptake, their determination are difficult due to the lack of data. Hence, they will be neglected in the mass balance.

2.2 Determination of mass balance parameters

The lead weathering rate (Pb_{we}) in the mineral topsoil is derived from the base cation weathering release (BC_{we}), and the ratio between lead (X_Pb) and base cation (X_Bc) contents in the parent material. F_{rt} is a factor that scales down the weathering rate from 1m to the considered depth [4] :

$$Pb_{we} = 5 \cdot 10^{4} \times F_{rt} \times BC_{we} \times \left(\frac{X\_Pb}{X\_bc} \right) \tag{2}$$

Base cation weathering rate has been determined using the PROFILE model [10] on representative french soil samples [6]. The content of lead and base cations in the parent material have been measured [3] on selected french soil samples or taken from the RIVM[2] guidance [4].

The biomass uptake of lead (Pb_{upt}) is derived from the average annual biomass growth (Y) and from the lead content in biomass (X_{hpp}) with an uptake factor (F_{ru}) scaled down to the considered

$$Pb_{upt} = F_{ru} \times Y \times X_{hpp} \tag{3}$$

depth.

Y is determined using the IFN (National Forestry Inventory) data for french forest area and corresponding wood productivity. The average lead content in biomass is from Hettelingh et al. [4].

The leaching of lead from topsoil is calculated using runoff data and dissolved lead concentration in soil solution [6,8].

2.3 Effect-based critical loads and stand-still loads

“Effect-based critical loads” and “stand-still loads” are 2 different approaches for calculation of a treshold for atmospheric deposition, both based on the same steady-state mass balance (eq.1).

2.3.1 Effect-based critical loads

In the “effect-based” principle, the steady state mass balance is used with a critical lead concentration above which the chosen receptor will be damaged. Different approaches for the determination of a receptor and its critical limit for lead are currently discussed in the Working Group on Effects. However, in order to test the effect-based approach, a preliminary critical limit for microbiota has been settled to 8 $mg.m^{-3}$ of dissolved [Pb] in soil solution.

2.3.2 Stand-still loads

In the “stand-still” principle, the steady state mass balance is used with the current lead concentration in topsoils. It allows an atmospheric deposition that just maintains the heavy metal concentration at its present level. Because of the lack of measured total [Pb], we chose

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[2] RIVM : National Institute of Public Health and the Environment (Netherlands)

to apply this approach only on 7 soil samples [7] where total lead concentration is known [3]. To calculate the actual leaching of lead from the topsoil, a dissolved [Pb] in soil solution must be determined from the total [Pb] in soil. For that purpose, a sequence of 3 transfer functions [4] is used (eq. 4, 5, 6, 7).

Transfer function to derive "so-called" lead (Aqua Regia) from total lead[3] [4]

$$\log10(Pb_{so-called}) = a0 + a1 \times \log10(Pb_{total}) \tag{4}$$

Coefficients values : a0=-0,54;a1=1,31 for sandy soils (depend on parent material)

Transfer function to derive reactive lead from "so-called" lead [4]

$$\log10(Pb_{reactive}) = b0 + b1 \times \log10(Pb_{so-called}) + b2 \times \log10(\%MO) + b3 \times \log10(\%clay) \tag{5}$$

Coefficients values : b0=0,063;b1=1,042 ;b2=0,024 ;b3=-0,122

Transfer function to derive dissolved lead from reactive lead [4] (Freundlich coefficient)

$$\log10(Kf) = c0 + c1 \times \log10(\%OM) + c2 \times \log10(\%clay) + c3 \times pH \tag{6}$$

$$Pb_{soilsolution} = \left(\frac{Pb_{reactive}}{Kf}\right)^{1/n} \tag{7}$$

Coefficients values :c0=-3,06;c1=0,85;c2=0,02 ;c3=0,26 ; n=0,67

3. Results and discussion

Preliminary values for critical loads were determined for french forest ecosystems. Effect-based critical loads values range between 4,9 g.ha^{-1}.an^{-1} and 133 g.ha^{-1}.an^{-1}. Stand-still loads values range between 19 g.ha^{-1}.an^{-1} and more than 150 g.ha^{-1}.an^{-1}. For one particular soil, not included in the range, stand-still load is very high (450 g.ha^{-1}.an^{-1}) because of a high lead concentration in the upper horizon (134 mg.kg^{-1}).

In tab.1, we present critical load and stand-still load calculations on 3 french forest sites [7].

Effect-based critical loads are mainly controlled by leaching. The soils where runoff is high (EPC 63) can tolerate a higher atmospheric deposition. This imply important leaching in some coarse soils and damage on draining surface water. For both effect-based and stand-still loads, weathering rates seem neglectables in comparison with leaching and biomass uptakes.

Stand-still approach allows important atmospheric inputs where Pb concentrations are high (EPC 63). This means that stand-still cannot be applied where present concentrations are higher than critical limits.

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[3] *Coefficient values [a0, a1, b0, b1, b2, b3, c0, c1, c2 and c3] are taken from RIVM guidance [4].*

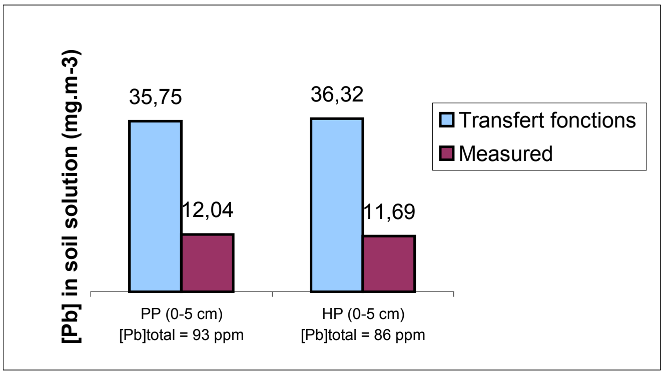
Table 1. Results for the calculation of critical loads and stand-still loads for 3 french forest sites

Site [7]	**PM 40**	**EPC 63**	**SP 57**
Region of France	Landes	Massif Central	Vosges
Parent material	Sand	Basalt	Sandstone
Soil type [1]	Ferric podzol	Mollic Andosol	Dystric cambisol
Pb biomass uptake (g.ha^{-1}.an^{-1})	18,8	16,8	17,2
Pb weathering (g.ha^{-1}.an^{-1})	0,024	0,20	0,032
Net runoff (m.an^{-1})	0,4	0,6	0,4
Critical limit of dissolved lead (mg.m^{-3})[4]	8	8	8
Critical Pb leaching (g.ha^{-1}.an^{-1})	**32**	**48**	**32**
Effect-based critical load (g.ha^{-1}.an^{-1})	50,77	64,6	49,16
Current total lead in topsoil (mg.kg^{-1}) [3]	**3,4**	**51,8**	**26,3**
"So-called" lead (mg.kg^{-1})	1,4	50,8	20,9
Reactive lead (mg.kg^{-1})	0,9	30,7	13,6
Dissolved lead (mg.m^{-3})	0,06	6,07	3,35
Current Pb leaching (g.ha^{-1}.an^{-1})	0,24	36,5	13,4
Stand-still load (g.ha^{-1}.an^{-1})	19	53,1	30,56

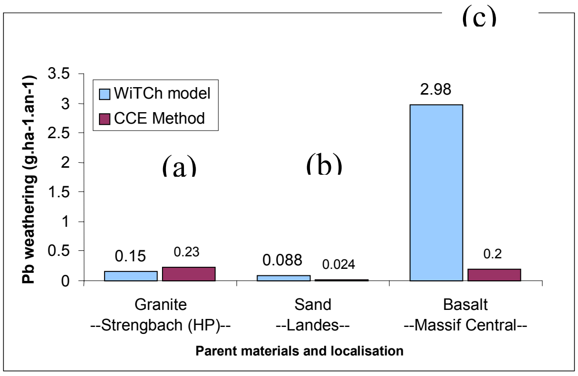
3.1 Discussion on transfer functions

Transfer functions are used in the stand-still approach to derive [Pb] in soil solution from total [Pb] in soil. We compared transfer function results to measured dissolved [Pb] in two granitic sites (PP and HP) in the Strengbach catchment (Vosges, France) where total [Pb] is also known. Soil solutions were collected using zero-tension lysimeter plates. Dissolved lead was measured with ICP-MS on dissolved phase [2].

Transfer functions applied on two granitic soils overestimate the dissolved [Pb] in soil solution (fig. 1). Stand-still load is thus overestimated. Transfer functions must thus be calibrated for french soils.



and calculated [Pb] in soil solution



and CCE recommandations for lead weathering

3.2 Discussion on weathering fluxes

Two different approaches for the determination of lead weathering rate were compared. The first approach refers to equation (2). The second one uses the WiTCh model [9]. WiTCh is a dynamic model of weathering which determines weathering rates using kinetic mineral dissolution. Three soils from very different lithology were chosen to compare the two approaches : a granitic site in the Vosges (HP), a sandy site in the Landes (PM 40) and a basaltic site in the Massif Central (EPC 63) (fig. 2).

The weathering rates determined according to equation (2,a ; 2,b) seems in agreement with the WiTCh model outputs. Exception occurs when the chemical rock composition is different from the proposed standard bedrock composition (equ. 2,c).

Our goal in this study was to evaluate the accuracy of the european methodology for calculation of critical loads for the french forest soils. It appears that critical load approach is adapted for french soils but need to be calibrated at least for calculation of weathering fluxes and determination of critical limits. On the contrary, Stand-still is not adequate se because of inherent contradictions in the method and too much uncertainties in the transfer functions.

Acknowledgments

We want to thank the ADEME for supporting our works.

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7.6 SORPTION AND DESORPTION OF Cd AND Pb IN MEDITERRANEAN ACID SOILS

Rábago Juan-Aracil, I.[1], Moreno García, A.M.,[22] González Parra, J.[2]

Introduction

Previous work was carried out to determine critical load calculation for Cd and Pb on a regional basis (Rábago *et al.*, 2000) and applying the models suggested within the LRTAP Convention (de Vries *et al.*, 1998). The study area was in the west of the region of Madrid (Central Spain) and the corresponding data was gathered and processed separately from different sources (maps, literature or estimated) to transform them to an available format for the calculations. The highest critical loads were obtained for acid soils in areas with high precipitation, whereas lowest for clay soils in less acid conditions and low precipitation. Further work on the application of the methods for modelling critical loads of heavy metals in Spain was suggested, this included determining experimental values for the partition coefficients in Mediterranean conditions.

The work described in this paper is part of a wider project on the study of the behaviour of Cd and Pb in Mediterranean ecosystems and the application of methods to model critical loads for heavy metals in Spain. This paper presents the preliminary results of the study of both soil characteristics and behaviour of Cd and Pb in Mediterranean ecosystems. Soil sampling was done in evergreen forests dominated by *Quercus ilex* subsp. *rotundifolia* Lam.. This type of holm oak is typical of Mediterranean ecosystems, because it can withstand wide temperature range and rainfall variations and diverse types of substrate. In many of the sampling areas, the forest was partially cut, leading to an extensive semi-natural sylvopastoral woodland, called dehesa, formed by isolated trees surrounded by grassland (Joffre *et al.*, 1999 and Ferreras *et al.*1987).

The main soil parameters of these soils were analysed in order to relate them with the sorption-desorption processes. For this purpose, Pb and Cd were added to the soil samples and then extracted to study the relevant processes. Moreover, total metal content in these non-polluted soils and in parent material were analysed in order to establish relationships between both contents and in order to estimate the background level and the reference values of these elements.

Materials and methods

A study area in the central Spain with acid parent material was selected. Soil samples were collected in non-polluted forested (natural and semi-natural) ecosystems below *Quercus ilex* subsp. *rotundifolia* Lam.. In each soil profile two samples according to the upper and lower horizons were taken. The depth for the upper horizon is 0-5/10 cm, and the depth for the lower horizons ranged is 5/10-20 cm. All the samples were air dried, crushed and sieved (<2mm).

Sample analysis for soil characterization were done according to standard methods (ISRIC, 1993): pH in H_2O and KCl (1:2,5); the organic carbon by oxidation with potassium dicromate; the total N by digestion with sulphuric acid and determination by N/C microanalyser; the particle size distribution determined by the standard pipette method (Sand: 2-0.02 mm; silt: 0.02-0.002; clay<0.002) the cation exchange capacity (CEC) by percolation with 1N ammonium acetate pH 7; Ca^{2+} and Mg^{2+} measured by Atomic Absorption (AA); Na^+ and K^+ measured with flame photometry; and clay type analysed by X-ray diffraction. Total metal content was determined after the soil digestions with an acid mixture of $HF/HClO_4/HNO_3$ (5:1:1). Metal concentration in the filtrates, was determined by AA.

Sorption experiments were carried out adding 500 mg L^{-1} and 100 mg L^{-1} of Pb, and 100 mg L^{-1} and 20 mg L^{-1} of Cd separately (1:10 soil/ solution) to 20 samples in batch experiments (Amacher *et al.*, 1986). Suspensions were shaken for 2 h and continued in contact (soil/solution) for 22 h more. After the equilibration period (24 h) the samples were centrifugated and filtered. Desorption

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experiments were carried out adding (three times) 1N ammonium acetate as extracting agent to the contaminated soil samples. Metal concentrations in the filtrates were determined by AA.

In this paper, the sorbed metal was calculated as the total amount of the metal added (in solution) to the soil samples minus the metal in the filtrates after the contamination. The amount of the metal retained was calculated as the difference between the amount of the sorbed metal and the amount of metal in the filtrates extracted with ammonium acetate.

Results

The soils had a slightly acid state and the pH was higher in upper than in lower horizons (Table 1). The samples ranged from sandy loam to loamy sand texture and clay fraction was higher in the upper horizons. The clay fractions had a similar mineralogical composition in all the samples. Within the sheet silicates, the mica-illite, chlorite-vermiculite and kaolinite were the most abundant. Within the framework silicates, the quartz and feldspars were the most frequent minerals.

Table 1: Statistical values of soil characteristics

	Upper Layer					Lower Layer				
	N	Min.	Max.	Mean	S.D.	N	Min.	Max.	Mean	S.D.
pH (H_2O)	10	5.5	7.1	6.1	0.5	10	4.9	6.9	5.8	0.7
pH (KCl)	10	4.4	6.7	5.4	0.6	10	4.0	6.3	4.8	0.7
Organic matter (%)	10	3.2	27.8	11.4	9.4	10	1.2	8.8	3.0	2.2
N (%)	10	0.1	1.2	0.5	0.4	10	0.0	0.4	0.1	0.1
C/N	10	7.8	19.2	13.1	3.0	10	8.7	18.1	13.4	3.5
CEC (cmol$_+$kg^{-1})	10	6.6	77.7	21.9	23.9	10	3.2	10.9	6.1	2.4
Na^+ (cmol$_+$kg^{-1})	10	0.2	0.6	0.3	0.1	10	0.2	1.8	0.4	0.5
K^+ (cmol$_+$kg^{-1})	10	0.5	3.4	1.3	0.9	10	0.3	1.2	0.6	0.3
Mg^{2+} (cmol$_+$kg^{-1})	10	0.4	4.1	1.8	1.3	10	0.2	1.9	1.1	0.5
Ca^{2+} (cmol$_+$kg^{-1})	10	3.9	71.4	28.2	23.6	10	1.4	18.0	9.4	5.4
Σ cations	10	5.1	77.8	31.6	25.6	10	2.1	21.2	11.4	6.2
Sand (%)	6	70.9	90.3	81.8	6.5	8	77.7	92.6	83.8	4.6
Silt (%)	6	3.5	15.1	9.6	4.0	8	3.3	12.0	7.8	3.0
Clay (%)	6	6.1	14.0	8.6	2.9	7	4.2	10.3	7.1	2.1

The organic matter content varied between samples with a range of 3.2-27.8 for upper layers and a range of 1.2-8.8 for the lower layers. The different amount of organic matter of the soils in their upper layer was because of the land characteristics. The differences in the organic matter content in the lower layers were related with the horizons type (AB horizon or Bw horizon). The nitrogen percentage was higher in the upper layers than in the lower, and the C/N ratio gave values between 10 and 14 which indicate an organic matter of a mull-moder type.

The content of Pb in these soils was considered as the background level for this trace element. From this value, the reference value or level A was estimated as the background level plus two times the standard deviation (IHOBE, 1994). The reference value was an indicator of the quality level for the metal and represents the quantity of the element that could be in the soil without generating any loss of the soils multifunctions (Vegter, 1995). According to this, the background level gave a mean value of 60 mg kg^{-1} and the reference level a value of 83 mg kg^{-1}. These values were similar to the ones obtained in other soils located near this study area (Perez *et al.*, 2000 and IGME, 2002).

The total content of Pb in the parent material has also been determined. The mean value was 26.9 mg kg^{-1} (Max: 45.4 mg kg^{-1}, Min: 14.5 mg kg^{-1}) and the relation between the background level and the Pb content in the parent material gave an edaphic accumulation index of 2.2.

Sorption/Desorption

For an added concentration of 500 mg L^{-1} of Pb, the percentage for the sorption was close to 96% in the upper horizons and 78% in the lower horizons. When Pb was added in lower concentration (100 mg L^{-1}) the sorption percentage increased both for the upper and the lower horizons (mean values of 99% and 98% respectively). In both cases of contamination, desorption was higher in lower horizons where the organic matter content was less than in upper layers.

The retention percentage of Pb was higher in the case of 100 mg L^{-1} contamination (77.45% in the upper and 54.53 % in the lower horizons of the profiles) than in the case of 500 mg L^{-1} contamination (53% in the upper and 22 % in the lower horizons of the profiles). In both cases, the retention was greater in the upper horizons due to a greater organic matter content.

The correlation between Pb retention and organic matter in upper layers, for both added concentrations, was significant and positive ($p<0.001$ for Pb100 and Pb 500). This is due to the formation of complexes between organic components and the heavy metal. In lower layers, there was a significant and positive correlation between retention of Pb and silt fraction content, because this metal could form inner sphere complexes with some minerals of this fraction. Exchangeable cations, for both added Pb concentrations, had also a significant and positive correlation with the Pb retained in the upper horizons ($p<0.001$ for Pb100 and Pb 500).

For an added concentration of 20 mg L^{-1} of Cd, the percentage of the sorption was above 96% in the upper horizons and above 85% in the lower horizons. With the same level of contamination the mean percentage of the desorption was 66 % and 83 % for the upper layers and lower layers respectively.

There was a positive and significant correlation between the organic matter and retention for both layers ($p<0.001$). The upper layers had a positive and significant correlation with the cation content.

For an added concentration of 100 mg L^{-1} of Cd, the percentage of the sorption had a mean value of 94% in the upper horizons and 82% in the lower horizons. With this level of contamination the percentage of the desorption was 70% for the upper layers and 83% for the lower ones.

As in the case of 20 mg L^{-1} of contamination, there was a positive and significant correlation between the organic matter and retention for both horizons. The upper layers had a positive and significant correlation with the cation content ($p<0.001$).

Conclusions

The sorption percentage of Pb and Cd, for the added concentrations, was higher in the upper horizons than in the lower horizons. Nevertheless, desorption was higher in the lower than in the upper horizons. The retention percentage of Pb was greater in the case of 100 mg L^{-1} contamination than with the 500 mg L^{-1} contamination.

The organic matter and the exchangeable cations were the principal factors that contributed to the Pb retention in the upper horizons. This metal could be in exchangeable sites and forming complexes with organic matter. In the lower horizons the mineral fraction was the parameter that controlled the Pb retention in these soils.

The retention percentage of Cd was slightly higher in the case of 20 mg L^{-1} contamination than with the 100 mg L^{-1} contamination.

The organic matter and the exchangeable cations were the main factors that contributed to the Cd retention in the upper layer. Nevertheless, the organic matter in the lower horizons also contributed to the Cd retention.

According to the critical load methodology, the sandy texture and the slightly acid state of these soils would give a high value of critical load due to the low capacity to retain these metals. But the organic matter content modifies this result giving a low value of critical load because of the organic matter capacity to retain these pollutants. Nevertheless the management of these semi-natural ecosystems, the dehesas, could lead to a decrease in the organic matter content and therefore, the critical load results would be modified from low to high values.

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7.7 GERMAN EXPERIENCES WITH PROPOSED CRITICAL LIMITS FOR LEAD AND CADMIUM AND THEIR APPLICATION IN FIRST CRITICAL LOADS CALCULATIONS

Gudrun Schütze[1]

Introduction

The German National Focal Centre (NFC) provided its respond to the call for data (Coordination Centre for Effects – CCE, December 2001) on critical loads for cadmium (Cd) and lead (Pb) with 1,222,695 records (Cd) and 1,216,015 records (Pb). Agricultural used land was addressed as well as extensively used semi-natural ecosystems and forests. The calculation of critical loads for Cd and Pb was performed according to the „Guidance“ (De Vries et al. 2001) with some slight deviations. More details are described in Hettelingh et al. (2002). Depending on the type of land use different soil depth have been regarded: arable land 30 cm, grassland 20 cm, forests 10 cm. Because for all processes, considered in the main equation of the critical loads calculation (1) the share of this relevant soil layer was included by a factor (f_{ru} or $f_{we} \leq 1$), the metal fluxes are among others influenced by the land use type.

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

where:

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

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

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

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

In many areas the influence of leaching dominates in the calculation of the critical loads for Cd and Pb. Therefore in this poster the main emphasis is laid on the results of use of critical limits and transfer functions in the calculation of a term for critical or present leaching, respectively.

Plant uptake of Cd and Pb

The net uptake of heavy metals into the harvested parts of the plants has been calculated according to equation (2) of the guidance (De Vries et al. 2001) using German input data. The factor f_{ru}, which is used to describe the share of the relevant soil layer in the net uptake, was derived in a more detailed way than proposed in (De Vries et al. 2001).

Table 1: Statistical parameters describing the distribution of values for net uptake of Cd and Pb in individual ecosystem types of Germany, P = percentile [g ha^{-1} a^{-1}]

Land use	**Cadmium**			**Lead**		
type	**P 10**	**P 50**	**P 90**	**P 10**	**P 50**	**P 90**
arable land	0,39	0,57	0,87	3,0	5,8	9,8
grassland (intensive use)	0,19	0,46	0,96	3,2	7,6	15,9
grassland (dry, ext. use)	0,16	0,27	0,55	2,8	4,6	9,1
grassland (wet, ext. use)	0,22	0,31	0,34	3,7	5,1	5,6
heathland	0,12	0,14	0,30	2,0	2,4	5,0
mesotrophic fens	0,23	0,31	0,36	3,9	5,1	6,0
coniferous forest	0,19	0,28	0,50	3,2	4,8	8,5
deciduous forest	0,06	0,10	0,27	1,8	2,8	7,6
mixed forest	0,14	0,22	0,49	2,6	4,5	9,3

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Table 1 shows 10-, 50-, 90-percentiles of ecosystem type dependent Cd or Pb net uptake. The difference between the ecosystems is not very large. For both metals the highest median values (P 50) were found on agricultural intensively used arable land and grassland, while heathland and deciduous forests showed the lowest values. The categories grassland wet, grassland dry, heathland and mesotrophic fens belong to the natural non forested ecosystem types which are assumed to be used only extensively.

Weathering rates using the method of Vrubel and Paces (1996)

The method of calculation is described in the De Vries et al. (2001), equation (3). Because the relevant soil layer has to be considered, the weathering rates are depending not only on soil properties and chemical composition of parent material, but also on land use. In table 1 typical values for weathering rates are assembled. The ranges of weathering rates were wider for Pb than for Cd due to also wider ranges of Pb contents in parent materials.

Table 2: Weathering rates (or ranges) representing the majority of grids of the related important ecosystem types.[g ha-1 a-1]

Land use type	**Weathering rates**	
	Cd	**Pb**
Arable land:	0,02	5 – 6
Grassland, intensively used:	0,01	2 – 4
Deciduous forest:	0.01	0,5 – 2
Coniferous forest:	0.02	0,5 – 1

Critical and present leaching

The critical and present leaching of lead and cadmium has been calculated according to equation (4) and the transfer functions of the guidance (De Vries et al. 2001). Three different concentrations [mg m^{-3}] in the leaching water were introduced into this equation:

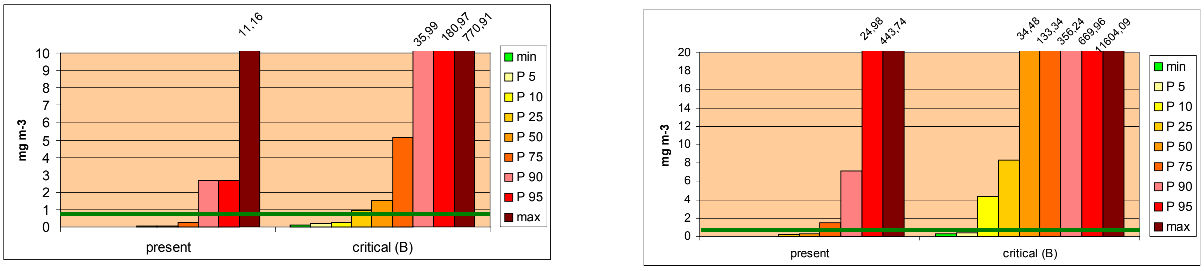
- [M]ss(crit)_a: related to effects on microbiota and plants
- [M]ss(crit)_b: derived by transfer calculations from a critical limit for "reactive" contents of heavy metals in the soil, which are related to effects on soil invertebrates
- [M]ss(pres): derived by transfer calculations from the present content of heavy metals in the soil

Figures 1 a - d present an overview on results of the calculations of critical and present concentrations of Pb and Cd using transfer functions. Only two types of ecosystems are addressed, which however differ clearly in soil properties, relevant in the transfer functions. For both metals [M]ss(crit)_b was in most cases higher than [M]ss(crit)_a. As expected the calculated concentrations in soil solution were higher for (poor and acidic) forest soils than for arable land. The calculated concentrations (present, background) of Cd and Pb in poor and acidic soils are much higher as found in field investigations (e. g. results from measurements of concentration in leaching water at level II forest stands, Nagel et al. 2000). When using the transfer functions, especially for these soils, the possible annual leaching rates of the metals might be overestimated and the critical loads become too high for these sensitive soils.

These results show that

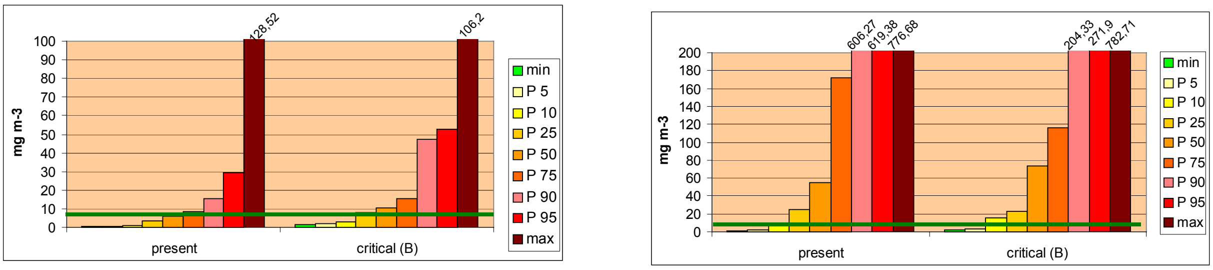
there is some disharmony between the two types of critical limits,

there might be high uncertainties in the transfer functions, especially for soils with low binding capacity.



a) Cd, arable land

b) Cd, coniferous forests



c) Pb, arable land

d) Pb, coniferous forests

Figure 1 a-d: Distribution of calculated present and critical concentration of cadmium and lead in soil solution for two types of ecosystems.
The critical concentration (B) is related to effects on soil invertebrates. The constant bold line indicates the critical limit [M]ss(crit)_a (0,8 mg Cd mg m^{-3}, or 8 mg Pb m^{-3}, respectively) which is related to effects on plants and micro-organisms. P = percentiles

Critical and present Pb and Cd content "reactive" (M_{re})

First approximations for units of the General Soil Map of Germany showed that the critical limit Pb ($Pb_{re(crit)}$= 30 mg kg^{-1}) is often exceeded by 50-percentile background values (Table 2), but there is almost no exceedance of the critical limit of Cd ($Cd_{re(crit)}$= 0,9 mg kg^{-1}).

Table 2: Present contents of lead in selected German soils (50 Percentiles of background values (transformed into contents "reactive", which refers to an extraction with 0.43 M HNO_3)

Present "reactive" content of Pb [mg kg^{-1}]	**Numbers of units of the General Soil Map of Germany**	**General description of the soils**
< 30	1, 4, 10, 12, 18, 19, 21, 22, 24 - 46, 48, 50, 58, 66	Sandy and loamy soils from dunes, fluviatile and glaciale sediments, boulder clay and loess
30 - 50	17, 49, 51, 61 , 62, 64, 68, 69	Stagnic and spodic cambisols from sandstones and conglomerates, clay-and siltstones, rendzic leptosols over lime- and marlstone, alpine soils
> 50	47, 53 - 57, 59, 60, 63, 65, 67	Loamy, sandy and loess soils from basalt, tuffs, igneous and metamorphic rocks, sandstone, quarcite, greywacke, phyllite, claystone, ferrosols

Critical loads and stand-still loads

Critical loads, based on a critical limit “reactive” (CL (b)) as well as stand still loads (SSL) for Pb vary in wider ranges than critical loads based on a constant critical limit for the soil solution (CL (a)), see table 3. An important reason is the use of transfer functions which lead to wide spread values of the concentration in soil solution used in the calculation of the leaching flux. Critical limits “reactive” are seldom exceeded by present contents of Cd, but frequently by present contents of Pb. This is one reason for partly higher values (90-, 95-percentiles) of SSL (Pb) than critical loads (Pb).

	cadmium			**lead**		
Perzentile	**P 10**	**P 50**	**P 90**	**P 10**	**P 50**	**P 90**
CL (a)	2,45	4,49	6	23,68	34,42	62
CL (b)	2,23	17,57	505	17,2	41,69	435
SSL	0,46	0,96	13	7,92	25,91	705

Conclusions and further work

- To protect the whole ecosystem and, in future, human health, we have to use the minimum of all critical limits in the critical load calculation.
- When applying concentrations is soil solution derived from “reactive” by use of transfer functions in the critical load model, soils with high binding capacity for metals become most sensitive, which is not in line with the probability of effects.
- In Germany the critical limit “reactive” of lead is often exceeded, but not for cadmium. We can assume that for many of the soil units of concern pedo-geological sources are mainly responsible for the higher background values. A clear distinction between anthropogenic and non-anthropogenic sources is currently not possible.
- Future work will include updating and complementation of databases for input parameters, consideration of critical limits for human health, testing the models for mercury and searching for methods to quantify current non-atmospheric metal loads.

A research project dealing with determination of background concentrations of soil solutions is in progress on behalf of the Federal Environmental Agency of Germany. Results will be very helpful for the validation of transfer functions. They will become available in 2003. Also research on ecosystem specific sensitivity of biocenoses will continue.

Literature

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7.8 Φ : A TOXICITY PARAMETER INDEPENDENT OF CHEMICAL COMPOSITION

D. Spurgeon[1], St. Lofts[2]

Previous works to derive critical limit concentrations of cadmium, copper, lead and zinc for soils and freshwaters have focused on total metal concentrations. Recently this has become less favoured because of the influence of factors such as pH and soil organic content on the toxicity of these metals. Of soluble fractions, use of the concentration of total dissolved metal for limit calculation may not be most suitable because the presence of dissolved ligands can modify the toxicity of metal present in solution. Further free metal ion is thought to be main uptake form for many organisms. Calculation of the critical limit expressed as the concentration of free metal ion, thus, has the potential to removes the effects of complexation of solution metal (especially by dissolved organic matter). In our work we have investigated the use of free metal ion for the derivation of critical limits for metals. Initial calculation of toxicity expressed as toxic free ion concentration in three data sets (copper toxicity to alfalfa; cadmium toxicity to *Folsomia candida*, and copper toxicity for *Daphnia magna*) revealed significant negative relationships between log free metal ion concentration and pH (as log H^+]. For the study with *Daphnia magna* inclusion of the concentration of further protective ions (log[Na^+], log[Mg^{2+}], log[Ca^{2+}]) as well as log[H^+] improve the prediction of toxic effects. To account for these protective effects, we have adopted a regression based approach, rather than the pseudo-mechanistic biotic ligand model. Based on this finding, we have derived a statistical method to derive expressions for $HC_{5,\ free}$ (the concentration of free metal ion protecting 95% of organisms/microbial effects) as a function of (soil) solution pH and competing cations. On the basis of these regression equations we calculate a partameter (ϕ) as a composition-independent toxic endpoint. When tested for a further set of toxicity data using freshwaters and soils of diverse chemistry, the regression approach produced predictions of toxicity in line with expectations.

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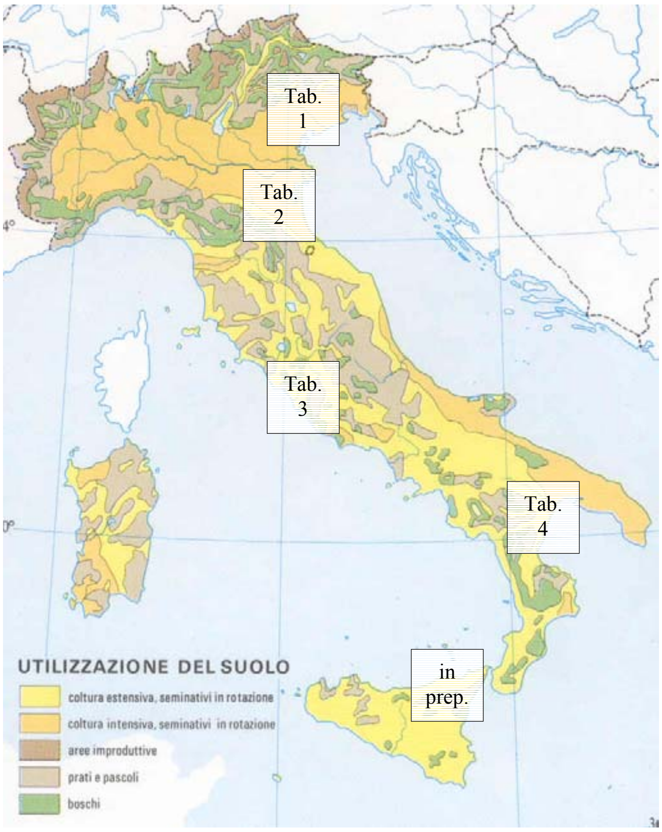
7.9 ANALYTICAL DATA SURVEY CARRYIED OUT BY ENEA MONITORING PROJECTS IN DIFFERENT ITALIAN AREAS

Zappa G. , Portaro N., Troisi L., Barlattani M., Fiocchi G.N., Letardi A., Triolo L.

In the frame of several projects of the last ten years about monitoring the effects of different pollutants in italian district, data on some heavy metals in different soils and crops were collected and analyzed by ENEA facilities. We summarized here some of that data. The analytical procedures were always the same. All soil and crop samples (which are representative of a sampling plan) were dried before analysis. Soil and crop samples dissolution was carried out by Milestone MLS-1200 Mega microwave, high pressure digestion system. Pd and Cd were determined by Electrothermal Atomizer Atomic Absorption Spectrometry (ET-AAS). Certified Reference Materials have been employed to get traceability and comparability of measures in chemical analisys.



Tab.1: Pb in soils of three Friulian areas

	Osoppo	Cividale	S.Giorgio
Pb(ppm)	3*101	6*101	4*101

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[1] ENEA , C. R. Casaccia, U.T.S. BIOTEC SIC, Via Anguillarese 301, I-00100 Roma, Italy

Tab.2: Pb (ppm) in soil and leaf of two sites in Romagna region (standard errors in brackets)

	site A	**site B**
apricot leaf soil	1 (1) $1.2*10^2$ ($0.5*10^2$)	5 (1) $9*10^1$ ($1*10^1$)
peach leaf soil	2 (1) $7*10^1$ ($1*10^1$)	4 (1) $5*10^1$ ($1*10^1$)
vine leaf soil	1 (1) $7*10^1$ ($1*10^1$)	6 (1) $1.2*10^2$ ($0.5*10^2$)
atmosferic deposition (wet+dry) (µg ml-1)	< 0.5	1.1 (0.3)

Tab.3: Pb and Cd (ppm) in grass, root, soil and certified reference materials (CRM) of a Latium area

	Pb	**Cd**
oat	1.3	0.08
oat roots	12	0.25
soil	38	<0.3
wheat	0.5	0.09
wheat roots	12	0.16
soil	71	0.34
grass	1.3	0.02
soil	40	<0.03
CRM V-10	1.2 (0.8 - 1.9)	0.04 (0.02 - 0.05)
CRM 1572	11 (13.3 ± 2.4)	0.03 (0.03 ± 0.01)
CRM Soil-7	70 (55 - 71)	2.5 (1.1 - 2.7)

Tab.4: Pb and Cd (ppm) in crops of a Lucanian area

crop	**sample reference**	**Pb**	**Cd**
strawberry	CAS 101 TLD	<0.3	<0.02
strawberry	CAS 102 TLD	<0.3	<0.02
melon	CAS 201 TLD	<0.3	<0.02
melon	CAS 202 TLD	<0.3	<0.02
apricot	CAS 301 TLD	<0.3	0.08
apricot	CAS 302 TLD	<0.3	0.09
orange	CAS 401 TLD	<0.3	<0.02
orange	CAS 402 TLD	<0.3	<0.02
clementine	CAS 501 TLD	<0.3	<0.02
clementine	CAS 502 TLD	<0.3	<0.02
olive	CAS 601 TLD	0.4	<0.02
lettuce cv. Maral	N44	1.4	0.15
lettuce cv. Erica	N48	3.0	0.28
lettuce cv. Parris	N52	0.9	0.13
lettuce cv. Terra	N53	2.3	0.22
lettuce cv. Conero	N57	<0.3	0.03

7.10 DETERMINATION OF PB AND CD IN SOILS AND VEGETABLES: REFERENCE MATERIALS AVAILABILITY AND EVALUATION OF UNCERTAINTY OF RESULTS

Zappa G.[1], Gatti R., Carconi P., Letardi A., Triolo L.

Certified Reference Materials (CRM) are essential tools to get traceability and comparability of measures in chemical analisys. Since the difficulty to realize and use, in chemistry, representative standards of the base unit (mol) of the amount of substance, the only possibility to obtain comparable measures is to use CRM that is materials sufficiently homogeneous and stable, one or more of whose property values (i.e. content of one or more chemical species) are known, with an assigned uncertainty. RM allow to compare measures made in different places, times, laboratories, and methods.

Routine use of appropriate RM allow systematic analytical offsets to be recognized and related to know procedures or sample matrices. Availability of RM may actually encouurage development and adaptation of new analytical methods as it will allow accurate and consistent comparisons.

To evaluate the uncertainty of measurement it is necessary to identify, quantify and combining uncertainty components of all measurement steps.

Typical sources of uncertainty in chemical analysis are for example: sampling; reagent purity and assumed stoiochemitry; measurement conditions; matrix interferences; measurement standard; calibration certificates; blank correction; random effects. To identify the uncertainty sources it can be helpful to use cause and effect diagrams that permit to list them showing how they relate to each other. Once identified, the uncertainty sources can be quantified by means estimation of individual or group of components and converted into standard uncertainty and combined.

The expression for uncertainty in the measurement of Pb and Cd in solid matrices (as soils, sediments and vegetables) is the following:

$$[u(C_s)/C_s]^2 = [u(A_s)/A_s]^2 + [u(A_g)/A_g]^2 + [u(V)/V]^2 + [u(C_g)/C_g]^2 + [u(m)/m]^2$$

Where:
A_s is the Absorbance mean value of the test sample solution
A_g is the Absorbance mean value of the calibration reference solution
C_s is the unknown concentration in the sample
C_g is the concentration of the calibration reference solution
V is the volume of the test sample solution
m is the mass of the test sample

Moreover it is necessary to consider the contribute of quality control to overall uncertainty.

Reference materials are employed to verify the absence of matrix interferences or other sistematic errors. The uncertainty of the certified reference material employed and the random errors of the measurements are to be considered too.

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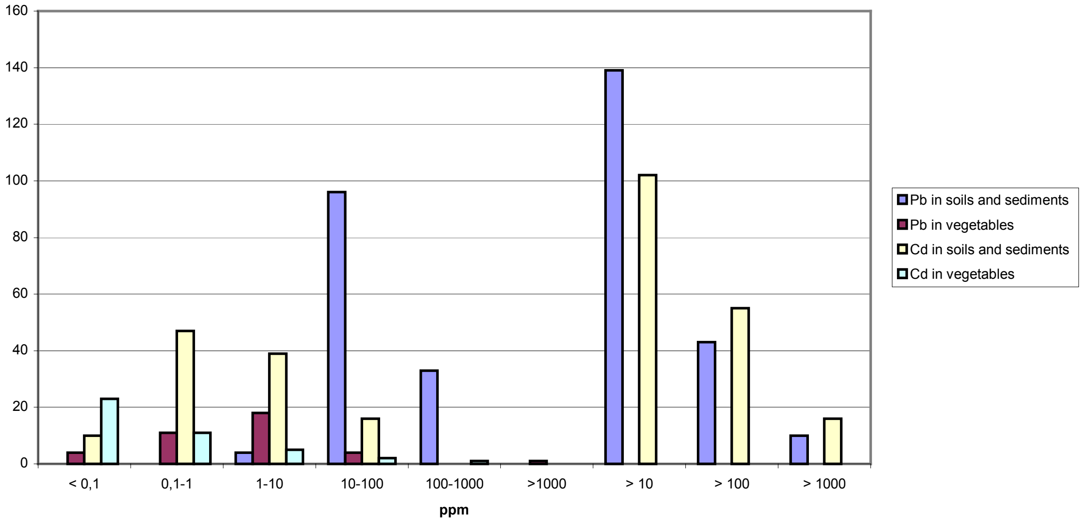
[1] ENEA , C. R. Casaccia, U.T.S. BIOTEC SIC, Via Anguillarese 301, I-00100 Roma, Italy

Availability of CRM for Pb and Cd analysis in soils and vegetables



ENEA facilities for RM setup and for organization and management of laboratory networks

GRINDING IN MICROMILL

PUR chamber (max volume 5,1 l)

47 Kg Zirconia cylinders (1,2x1,2dia cm)

HOMOGENEIZATION in
PP 80 l ROTATING DRUM
96 h (under N_2)

VACUUM EVAPORATOR

V = 100 l
Tmax = 40° C
P= 100mbar

VACUUM FREEZE DRYER

T_{min} = - 40° C
T_{max} = 30°C o 40°C
P_{min} 30 mtorr

ENEA laboratories can produce reference materials of soils, sediments, and lyophilized vegetables in sets of 100 – 1000 units to be employed in laboratory intercomparisons.

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