Arbejdsrapport fra DMU nr. 96

Critical Loads for Lead, Cadmium and Mercury in Denmark

A First Attempt for Soils Based on Preliminary Guidelines

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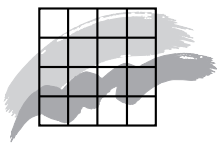

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Contents

Abstract

Critical loads for lead, cadmium and mercury in Denmark have been calculated for soils in accordance with the preliminary guidelines in de Vries and Bakker (1996): Manual for calculating critical loads of heavy metals for soils and surface waters, DLO Winand Staring Centre, Wageningen (The Netherlands). The calculations have been made for arable soils and for forests. For both agricultural crops and forest trees, the removal of heavy metals by harvest has been calculated as the product of the mean concentration in harvested material and the yield. Leaching has been calculated on basis of sorption properties. The calculated values for cadmium and lead are well in agreement with earlier published ranges of critical loads for heavy metals, (e.g. Van den Hout, 1994). There are, however, large uncertainties in the calculation, especially concerning the derivation of critical limits, the estimation of the removal of heavy metals by vegetation uptake, leaching, and for Hg also volatilisation. The available data for mercury has not been considered sufficient to justify a publication of the results. More information is needed on the risk of biomagnification in terrestrial ecosystems and on the amount of volatilisation of mercury from soils.

Summary

In the last decay several calculations of critical loads for acidity and eutrofication have been publicised (e.g. Posch *et al*. 1997), including Danish studies (e.g. Bak 1996). Critical load maps have been used as a basis for the negotiations on air pollution abatement in UN-ECE, latest the 2. Sulphur protocol and the coming protocol on NO_x and other pollutants. Although examples have been presented on calculated critical loads for other air pollutants as heavy metals and persistent organic pollutants (POP's), the quality of these calculations has not as yet allowed critical loads for these substances to be used as a basis for protocol negotiations. It is, however, recommended that coming amendments on the protocols on heavy metals and POP's should be effect based either by the use of critical loads or a more simple risk assessment scheme. It is therefore an obligation for countries which have adopted the heavy metal and POP protocols to support research in effect based control of these pollutants.

As a consequence, a first attempt has been made to calculate critical loads of the heavy metals lead, cadmium and mercury in Denmark. The calculations have been based on a draft manual on mapping, which has been approved by the UN-ECE Task Force on Mapping (de Vries & Bakker 1996). It has further been decided to apply national Danish ecotoxicological soil quality criteria as critical limits in the calculations (Table 2.1) (Scott-Fordsmand & Bruus Pedersen 1995).

Preliminary critical loads for lead and cadmium have been calculated for different types of agricultural farms (farms with pigs, cattle, cattle and pigs, and farms with primarily plant production, Table 3.1) and for different types of forests (spruce, pine, beech, and oak forest, Table 3.2). While the preliminary calculations for lead and cadmium, taking the inherent uncertainties into account, seems to give reasonable results, the quality of the calculations for mercury has not allowed a presentation of the calculated numbers. There are two main problems in the calculation of critical loads for mercury. One is the available critical limits, which only takes direct effects in the soil into account and neglects the possibility of accumulation in the food chain. The other main problem is the quantification of mercury evaporation from the soil. Both problems are essential and may have a large influence on the calculated critical loads. The problems are paralleled for a range of POP's, e.g. PCB. It has therefore been recommended from the latest UN-ECE workshop on heavy metals and POP's, which was held in Bad Harzburg, Germany, the 3.-7. November, 1997, not to base future amendments on the heavy metals and POP protocols for mercury and POP's on critical loads. Instead it is recommended to use risk assessment for selected target groups, e.g. human inhabitants in the arctic, icebears, waterfowls, etc.

The calculated critical loads for lead and cadmium are in agreement with earlier publicised critical load values (van den Hout 1994). As can be seen from Figure 3.1a and 3.2a, the values of the calculated critical loads are highest in Western Denmark. The soils in this part of the country is in general more sandy than the soils in Eastern Jutland, and on the Islands. The Danish production of cattle is concentrated on these areas with poorer, sandy soils, and the higher critical loads are primarily caused by the agricultural practise on farms with cattle. These farms have a higher percentage of area used for grass and green fodder compared to farms with pigs or farms primarily with plant production, and hence also a larger removal of heavy metals by the harvested crop because of the higher production on these areas (Figure 5.5) . In addition, less heavy metals are leached from sandy soils compared to clayey soils (Figure 5.6). The result is a general tendency to higher critical loads on sandy soils. This is problematic from a ecotoxicological point of view, because the biological availability and hence also the toxicity of heavy metals in general is higher in sandy than in clayey soils. In addition, the protection of groundwater is less on these soils. It will therefore be necessary to improve the methodology, especially the applied soil quality criteria, to take these factors into account. The present methodology is probably better suited to predict the risk of accumulation of heavy metals in the soils than to predict environmental effects.

Dansk sammendrag

Grænseoverskridende luftforurening

Der har gennem de sidste mange år været publiceret en række bereg-ninger af tålegrænser for forsurende og eutrofierende stoffer på europæisk niveau (f.eks. Posch *et al.* 1997), herunder danske studier (f.eks. Bak 1996). Disse beregninger har bl.a. været en del af grundlaget i forhandlingerne til FN's svovl- og NO_x-protokoller. Tålegrænseberegninger for andre luftforurenende stoffer som f.eks. tungmetaller og persistente organiske stoffer (POPs) har dog hidtil ikke været udført i sådanne detaljer, at de har været anvendelige i de igangværende UN-ECE forhandlinger om emissionskontrol af disse stoffer. Protokoludkastene anbefaler dog, at fremtidige tilføjelser bør være effektbaserede, f.eks. ved brug af tålegrænser eller simpel risikovurdering. De involverede lande forpligtiger sig derfor til at støtte forskningen inden for effektbaserede områder af tungmetalkontrollen.

Resultater

Derfor er det i dette projekt forsøgt at beregne foreløbige danske tålegrænser for tre tungmetaller: bly, cadmium og kviksølv. Beregningerne bygger på en foreløbig manual for kortlægningen godkendt af UN-ECE's Task Force on mapping (de Vries & Bakker 1996). I dette projekt er det valgt at anvende de danske økotoksikologiske jordkvalitetskriterier (Scott-Fordsmand & Bruus Pedersen 1995) som grænseværdier ("critical limits") for beregningerne af tålegrænser (Tabel 2.1).

Foreløbige tålegrænser for bly og cadmium er opgjort for forskellige typer af landbrugsbedrifter (bedrifter med svin, -kvæg, -kvæg og svin og -planteproduktion, Tabel 3.1) samt for forskellige skovtyper (gran-, fyr-, bøg og egeskov, Tabel 3.2). Mens de foreløbige beregninger for bly og cadmium, trods stor usikkerhed, forekommer rimeligt troværdige, er det vurderet, at usikkerhederne i tålegrænseberegninger for kviksølv i øjeblikket er for store til at retfærdiggøre en præsentation af de foreløbige tal. De væsentligste problemer forbundet med beregningerne af tålegrænser for kviksølv er dels usikkerheden på grænseværdien, der udelukkende tager hensyn til direkte effekter i jordmiljøet og ikke tager hensyn til risikoen for opkoncentrering af kviksølv gennem fødekæden, dels manglende viden om omfanget af kviksølvfordampning fra danske jorder. Begge dele er væsentlige i udregningerne af tålegrænser og kan forskyde resultatet betydeligt. De samme betragtninger gør sig gældende for en række persistente organiske forbindelser (POP'er), f.eks. PCB. Derfor anbefalede den seneste internationale workshop på området (CEC workshop i Bad Harzburg, Tyskland d. 3.-7. november 1997) for POP'er og kviksølvs vedkommende ikke at bygge fremtidige tilføjelser til UN-ECE protokollerne på princippet om tålegrænser, men i stedet benytte en almindelig risikovurdering for udvalgte målgrupper, f.eks. mennesker, isbjørne, vandfugle og andre top-prædatorer.

De beregnede værdier for bly og cadmium er i overensstemmelse med tidligere beregnede tålegrænser (van den Hout 1994). Som det ses på Figur 3.1a og 3.2a er tålegrænserne for begge tungmetaller størst i det vestlige Danmark. Dette skyldes, at dette område, som det også kan ses af Figur 3.3, generelt består af mere sandede jorder end i Østjylland og på Øerne. Da det økonomisk er mindre rentabelt at dyrke afgrøder på

sandede jorder, dækker græs for kvægproduktion en stor andel af landbrugsarealerne i disse områder. Den høstede biomasse på græsarealer er større end for andre afgrøder (Figur 5.5.), hvorfor der alt andet lige vil blive fjernet større mængder tungmetaller. Dette sammen med en generel mindre nedsivning af tungmetaller fra lerjorder (Figur 5.6) gør, at tålegrænsen generelt er højest i områder domineret af sandjorder. Med de anvendte jordkvalitetskriterier kan de beregnede tålegrænser primært bruges til at vurdere risikoen for, at tungmetaller akkumuleres i jorden. Der er ikke taget hensyn til, at biotilgængeligheden og risikoen for nedsivning varierer med jordtypen. Det er dermed problematisk at anvende de beregnede tålegrænser til vurdering af risikoen for miljøeffekter eller for belastning af grundvandet. Dette vil kræve en videreudvikling af de anvendte jordkvalitetskriterier.

1 Introduction

Historical background of the UN-ECE Convention for Long-Range Transboundary Air Pollution

UN-ECE CLRTAP

The history of the UN-ECE convention on Long-Range Transboundary Air Pollution (UN-ECE LRTAP Convention) can be traced back to the 1960's when scientists demonstrated interrelationship between sulphur emission in central Europe and acidification in Scandinavian lakes. Work in the UN-ECE resulted in the signature of the LRTAP Convention by 24 countries in 1979. Later additionally 14 countries have ratified. This was the first international legally binding instrument to deal with problems of air pollution on a broad regional basis. So far protocols for air pollution abatement has included two protocols on the abatement of sulphur emissions, a protocol concerning the control of nitrogen oxide emissions and a protocol concerning control of emission of Volatile Organic Compounds (VOC). Latest work has been done within the Working Group on Strategies under the LRTAP Convention to prepare protocols for emission reduction of heavy metals and persistent organic pollutants (POPs), respectively. The protocols were signed at the meeting of the Executive Body in Århus, 1998

The work activities of the convention is co-ordinated by the Executive Body (EB), which have established a number of intergovernmental bodies open for all parties of the convention, including the Working Group on Effects. Under the Working Group on Effects, several Task Forces of governmental experts have been established, including the Task Force on Mapping and the Co-ordination Centre for Effects (CEC), from which most of the work on critical loads has been initiated.

The critical load concept

A critical load is an ecosystem dependant deposition threshold below which adverse environmental effects is not expected to occur. In the past years many studies have been carried out to assess critical loads of acidifying and eutrophying compounds for forest soils and surface waters on an European scale (e.g. Posch et al. 1997). These calculations have for example been part of the basis for the negotiations of the second sulphur protocol. However, critical load calculations for other air pollutants, such as heavy metals and POPs, have not been available in such details, that they were useful for the negotiations of the first UN-ECE LRTAP protocols on these substances. The drafted protocols are therefore mainly based on emission reductions based on the precautionary principle and best available abatement techniques (BAT). The current draft of both protocols do, however, state that future amendment to the protocol could be based on effect based approaches if sufficiently developed. Such effect based approaches may include critical load calculations.

Decisions made by the Executive Body of the LRTAP convention initiated a Working Group on Effects decision to assess environmental effects of heavy metals and POPs and to develop, if possible, critical loads for these substances. A first attempt to establish direct relationships between atmospheric deposition and environmental effects of heavy metals and persistent organic pollutants on an European scale was the ESQUAD

project : The impact of atmospheric deposition of non-acidifying pollutants on the quality of European forest soils and the North Sea (van den Hout 1994). In that project critical loads of the heavy metals cadmium, copper and lead and the persistent organic pollutants lindane and benzo(a)pyrene, were calculated and compared with present atmospheric deposition. From this and other studies it was concluded that it seems possible to establish relationships between atmospheric deposition and exceedance of evironmental quality criteria and that critical loads can be calculated from these relationships. The methods used in the ESQUAD project has later been refined and presented for heavy metals and POPs, respectively, in the reports by de Vries and Bakker (1996) and Bakker & de Vries (1996). The manual by de Vries and Bakker (1996) have been used as background material for the critical load calculations of cadmium, lead and mercury presented in this report. There is currently not initiated any work for calculating critical loads of POPs in Denmark.

Bad Harzburg Workshop 1997

In order to enable application of the critical load concept in the abatement of heavy metals and persistent organic pollutants, international consensus must be reached on the critical load calculations and on the environmental quality criteria which serve as the basis for these calculations. Therefore, on initiative by The Netherlands and Germany, an international workshop was held within the framework of the LRTAP convention under the Working Group on Effects in Bad Harzburg, Germany, 3-7 November 1997. The overall conclusions of this workshop were that a second stage of Protocols should incorporate effect based approaches, but that the critical load approach could not be recommended for POPs at the moment and that the critical load calculations for mercury is less reliable than for other heavy metals, as a proper methodology for deposition/reemission rates needed to be further developed. Conclusions, issues of discussions and identified knowledge gaps from this workshop have been used as background for a discussion of the limitations and necessary improvements of the methods used in this project.

2 Calculation methods

The methods and the assumptions for calculating critical limits and critical loads are presented in the following paragraphs. It is important to stress that the used ecotoxicological soil quality criteria are not developed with the purpose of critical load calculations and that the calculation methods used for critical loads are based on recommendations in a preliminary guideline document prepared by TNO and DLO Winand Staring Centre, The Netherlands. In November 1997, TNO and the UBA Germany hosted an international workshop on critical limit/load calculations in Bad Harzburg, Germany. Conclusions, discussions and identified knowledge gaps from this workshop have been used as background for a discussion of the limitations and necessary improvements of the methods used in this project.

2.1 **Methods for deriving critical limits**

The first step in critical load calculations for soils is to select or derive quality objectives (critical limits) for the selected receptor, e.g. soil ecosystems. For the calculations presented in this report, the Danish ecotoxicological soil quality criteria for cadmium, lead and mercury are selected (Scott-Fordsmand & Bruus Pedersen 1995).

Table 2.1. Soil quality objectives in Denmark and The Netherlands.

Country	Quality objective	Cadmium mg kg^{-1}	Lead mg kg^{-1}	Mercury mg kg^{-1}
Denmark	Ecotoxicological[1]	0.3	50	0.1
Denmark	Human toxicology[2]	0.5	40	-
Denmark	Sludge regulation[3]	0.5	40	
The Netherlands	Maximum Permissible Concentration[4]	0.0035-0.27	22	0.0033-1.0
The Netherlands	Maximum Permissible Addition[5]	0.76	55	1.9 (0.37 methyl-Hg)
The Netherlands	Target value[6]	0.8	85	0.3
The Netherlands	Intervention value[7]	12	530	10

1) Objective to protect the most sensitive species in vulnerable ecosystems. Derived on basis of extrapolation of toxicity data and information about background concentrations.
2) Objective to protect the most sensitive humans, i.e. normally children, from effects caused by direct soil ingestion or consumption of vegetables grown in the soil.
3) Objective to insure that heavy metals do not accumulate in soil; harm crops or are taken up in food crops in amounts exceeding the recommendation for health protection.
4) The concentration in a standard soil above which risk of adverse effects is considered unacceptable. The value is expressed for a standard soil and change according to soil properties. Extrapolated on the basis of ecotoxicity data. The variation in the MPC is due to the use of different methods, e.g. direct effects or secondary poisoning. New MPC values have recently been calculated on the basic of the added risk approach, i.e. MPC = B.C. + MPA, where B.C equals the background level (i.e. Target value, note 6) and MPA the maximum permissible addition (note 5). See Crommentuijn *et al.* (1997) for a review of Dutch soil quality objectives.
5) The maximum addition in a standard soil above which risk of adverse effects is considered unacceptable. The value is expressed for a standard soil and change according to soil properties. Extrapolated on the basis of ecotoxicity data.
6) The long term quality objective of Dutch soil protection, based on background concentrations in relatively unpolluted areas in the Netherlands. The value is expressed for a standard soil and change according to soil properties.
7) A trigger value leading to remediation, actions to prevent dispersion, or land-use changes.

As these criteria have been developed with the objective to protect soil ecosystems, i.e. microorganisms (soil functioning), plants and soil invertebrates, from adverse effects, the critical loads presented here can only directly be related to soil ecosystems. No consideration of possible effects in connective water systems such as fresh water, marine ecosystems or groundwater as a result of leaching or runoff has been taken into account in the derivation of the ecotoxicological criteria. Furthermore, the critical limits used do not take into account the possible effects of secondary poisoning of top-predators in the terrestrial ecosystems as a result of biomagnification. Neither do they directly aim at protecting humans from heavy metal exposure through soil ingestion or uptake via crops. However, when comparing the ecotoxicological quality criteria for the three heavy metals in question with other Danish and International soil quality objectives (Table 2.1) they seem sufficient low to cover other aspects than structure and functioning of soil ecosystems.

2.1.1 **Approaches for deriving critical limits**

In principle the calculation of critical limits for water and soil ecosystems is based on similar approaches, but with different limitations and uncertainties, with more toxicity data and less parameters controlling toxicity in the aquatic systems. Different approaches for deriving quality objectives exist in different countries, but basically they can be derived by two different methodologies:

Extrapolation methods

1. Applying a safety factor on reviewed toxicity data from laboratory experiments. Minor variation exist in the data requirement between different environmental risk assessment strategies (EU, CSTE[1], USEPA[2] etc.). However, in general an application of a safety factor of 1000 on the lowest acute LC_{50}[3] values or a factor of 100 to the lowest chronic NOEC[4] values is recommended if few data are available. If a sufficient and representative dataset on chronic effects is available, a rather rare situation in terrestrial risk assessment, a safety factor of 10 or 1 (in cases where long term field tests exist), may be applied to the lowest NOEC value.

2. Using a distribution based statistical extrapolation of laboratory toxicity data to derive a PNEC[5]. Several versions of this method exist (Aldenberg & Slob, 1993, Wagner & Løkke, 1991) mainly differing in their assumption of toxicity data being log-logistic or log-normal distributed. The methods are based on statistical analysis of laboratory test data which takes into account the difference in sensitivity of the test species. Based on a probability distribution curve a protection level of e.g. 95% or 50% can be estimated. If the input data to the model have been NOEC values, the estimated PNEC will then in principle protect 95% of the species with a confidence of a chosen value, e.g. 95%. The methods assume that the collection of test spe-

[1] Comité Scientifique consultatif pour l'examen de la Toxicité et de l'Écotoxicité des substances chimiques, Commission Europenne.
[2] United States Environmental Protection Agency
[3] Concentration causing 50% lethality
[4] No Observable Effect Concentration = highest concentration having no observed effect in a an experimental set-up.
[5] Predicted No Effect Concentration

cies represent a random sample of species in the ecosystem in question.

The Danish ecotoxicological soil quality criteria (and the Dutch Target value as well) has not been derived by either of the two mentioned methods as it turns out that both approaches lead to predicted no effect concentrations considerable below the background level of the heavy metals in question. Therefore, the Danish criteria used have been set on the basis of expert judgement of the lowest observed effect concentrations found in the literature, considering available knowledge about bioavailability and background concentrations.

2.1.2 **Uncertainties in critical limit calculations**

Several unsolved problems in the derivation of soil quality objectives (SQO) do exist for the present methods. Most of these are related to the problems in extrapolation from controlled laboratory experiments to field situations. These may include the following aspects:

* *Bioavailability*. The bioavailability of chemicals may be very different from acute laboratory test to field situation, were ageing may reduce the bioavailability. Using one generic guideline value as in Denmark does not take into account the difference in bioavailability and hence toxicity in for example different soil types. Spatial variability in bioavailability is a commonly observed phenomenon, which may be traced back to the existence of different classes of binding sites controlling sorpton/desorption processes in the soil, being a highly heterogeneous medium. Ecotoxicological risk assessment for soils, including the Danish soil quality criteria, is presently based on total concentrations. However, soil organisms or plants do not assimilate metals from the bulk concentrations in the soil. Although species like some earthworms do ingest large quantities of soil material, the most relevant exposure route for most soil living organisms will be through pore water. The application of a generic critical soil concentration imply that the critical load increases with decreasing adsorption as more heavy metal is leached out of the soil leading to lower accumulation rates. This is not coherent with the basic knowledge of ecotoxicity of heavy metals in soil, where highest toxicity in general is observed in acidic sandy soils.

* *Biomagnification*. The Danish ecological risk assessment procedure for the soil compartment does not take into account the potential for biomagnification in terrestrial food chains, e.g. to birds and mammals. However, algorithms and models to include secondary poisoning or biomagnification in the environmental risk assessment of terrestrial food chains have been developed, e.g. in the Netherlands. So far all studies indicate that biomagnification is of less concern in terrestrial food-webs compared to aquatic food-webs, and that for most substances the existing soil quality objectives is sufficient to protect e.g. mammals and birds from secondary poisoning.

* *Mixtures*. The presence of more than one pollutant is the common situation at most contaminated sites. However, standardised ecotoxicity tests are often conducted on single chemicals. The toxic response to a mixture of chemicals may be antagonistic, synergistic or additive,

depending on the concentration and mode of action of the different chemicals.

* *Chronic exposure, adaptation and ecological recovery*. Ecotoxicological tests normally focus on acute short term effects. However, exposure may be of low but chronic character. Several examples of heavy metal adaptation in microorganisms, plants or soil living animals have been observed. These aspects make an extrapolation from short term to long term exposure very complicated.

* *Multiple stress, e.g. combinations of abiotic and chemical stress.* Laboratory experiments are often derived under standardised conditions, to guarantee optimal survival, growth and reproduction of the test animals. In nature, however, organisms may be confronted with large fluctuation in their environment. Large variations in temperature, humidity, food supply or predation may exist throughout the year. A combination of climatic and chemical stress may have influence of the toxicity of a chemical, especially in regions with extreme conditions like in the arctic region, where many compound subjected to long-range transport tend to accumulate, due to the predominant wind directions in the world and decreased degradation and volatilisation in cold climates.

Referring to the bullets above, to increase the reliability critical limits used for critical load purposes should at least

* include aspects of bioavailability, e.g. critical limits for soil solutions
* include potential risk for food chain effects

Standard Soil

One approach to deal with this problem is to relate the critical limit to parameters controlling heavy metal concentrations in the soil solution, e.g. pH, soil texture, cation exchange capacity (CEC), organic matter content (OM) etc. In the Netherlands, both the maximum permissible concentration (MPC) and the target values (TV) are regulated according to the organic matter and clay content of the soil. The standard values are expressed for a standard soil (OECD soil[6]) with a organic matter content of 10 % and a clay content of 20%, i.e.

$$MPC / MPC_{st} = TV / TV_{st} = (a + b \cdot Clay + c \cdot OM) / (a + b \cdot 25 + c \cdot 10)$$

where the metal dependent constants a, b and c are derived specifically from natural geochemical background concentrations in the Netherlands. MPC_{st} and TV_{st} denotes the maximum permissible concentration and the target value derived using standard soil. On the basis of information about the heavy metal concentrations in Danish soils (e.g. Jensen *et al.* 1996, Larsen *et al.* 1996) it should be possible to use a similar approach for the Danish soil quality criteria.

[6] A standard soil composed of 10% sphagnum peat, 20% kaolin clay, 70% quartz sand and some $CaCO_3$ to adjust the pH to ca. 6.0

Soil Solution

An alternative approach would be to use critical limits for soil solution, i.e. pore water concentrations, as the basis of critical load calculations. Critical dissolved metal concentrations may be derived from already available ecotoxicity data and partitioning coefficients. These partitioning coefficients should be expressed as a multivariate function of the most important soil characteristics, e.g. texture and pH, and can be calculated on the basis of experimental measurements of the ratio of heavy metal concentrations in the solid and pore water phase of a (large) number of different soil types.

Secondary poisoning

In the Netherlands a general algorithm to include risk assessment of secondary poisoning in the derivation of critical limits has been developed (Romijn *et al.* 1994). The procedure compares mean concentration factors (BCFs) for the heavy metal in prey (earthworms) with critical food concentrations of the predator (birds or mammals). Romijn *et al.* (1994) concluded that the calculation of critical soil concentrations for secondary poisoning in the terrestrial food chains was only valid in defined situations. By comparing the calculated maximum permissible concentrations (MPC) for secondary poisoning, i.e. top predators, with MPC for direct poisoning, i.e. soil living organisms, they found that secondary poisoning could be a critical pathway for cadmium and methyl mercury. This has been confirmed by others, e.g. Noppert *et al.* (1993). Spurgeon & Hopkin (1996) have later questioned the usefulness of the procedure proposed by Romijn *et al.* as they found that critical limits for secondary poisoning of Cd, Cu, Pb and Zn were exceeded in almost all investigated UK soils, including uncontaminated agricultural soils. Differences in uptake and elimination kinetics to heavy metals are commonly observed in terrestrial organisms. As a consequence, Spurgeon & Hopkin suggests to use critical organ/tissue concentrations instead of toxicity data based on dietary exposure (concentration in food or water) to assess the risk of secondary poisoning, referring to work by e.g. Ma (1987) and Shore & Douben (1994) where links between metal concentration in target organs of predators, levels of heavy metals in earthworms, and soil pH were established.

No matter which method is used, it will at least for cadmium, lead, mercury, and many persistent organic pollutants be important to include possible effects caused by secondary poisoning in the derivation of critical limits used for estimating critical loads.

2.2 **Methods of critical load calculations**

After selecting a critical limit, the critical load for the three selected metals is calculated on the basis of steady state mass balance equations, which describe the major input-output fluxes of heavy metals in the soil. A number of assumptions has to be made to justify the calculation methods. First of all it is assumed that the system is in a steady state, i.e. that the concentrations do not change in time. Furthermore, is it presumed that the soil is homogeneously mixed and the partitioning of heavy metals between the different phases of the soil is in equilibrium. Finally the mass balance equation presented below is based on an assumption that the heavy metals only consists of their divalent

cations. This assumption seriously limits the application of the model to calculate critical loads for mercury, as Hg may exist as mercurous mercury (Hg^{2+}), elemental mercury (Hg^{0}) and organic mercury, e.g. methyl mercury.

In the preliminary guideline for calculating critical loads for heavy metals (de Vries & Bakker 1996) a simplified steady state mass balance for a specific metal (M) is written as:

Agricultural soils : $M_{tl} = M_{sr} + M_{bp} + M_{ru} - M_{we} + M_{le}$

Forest soils: $M_{tl} = M_{td} = - M_{lf} + M_{fu} + M_{sr} + M_{bp} + M_{ru} - M_{we} + M_{le}$

where

M_{tl} = the total load of the heavy metal M (deposition + other loads, e.g. sludge and fertiliser)
M_{td} = the total atmospheric deposition of heavy metal M
M_{sr} = the flux of M by surface runoff
M_{bp} = the flux of M by bypass flow
M_{ru} = the flux of M by root uptake
M_{we} = the flux of M by weathering
M_{le} = the flux of M by leaching
M_{lf} = the flux of M by litterfall
M_{fu} = the flux of M by foliar uptake

Little information about surface runoff and bypass flow is available for Danish arable soils. However, the removal of heavy metals by these sources is considered less important, and the contribution of these processes to the total output of heavy metals from soils have been neglected in the preliminary calculations, leading to more simplified equations. Volatilisation is generally considered an important flow for mercury. It has, however, not been possible to acquire reliable information on the re-emission and species composition of mercury in Danish soils. As a consequence, it has been considered too unreliable to calculate critical loads for mercury.

Figure 2.1 illustrates the various fluxes, and a complete list of symbols is given in Appendix 1.

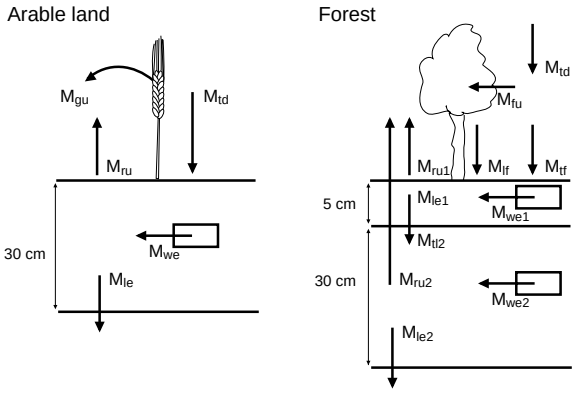


Fig. 2.1 The various fluxes of the heavy metal M in arable land and a forest soil divided in two layers (Topsoil = 1, Mineral layer = 2). For an explanation of symbols and notation please consult the text and appendix 1.

Agricultural soils:
The critical load can be derived as (neglecting surface runoff and bypass flow):

Critical load

$$M_{tl(crit)} = M_{ru} - M_{we} + M_{le(crit)}$$

$$M_{ru} = F_{gr} \cdot [M]_{veg}$$

$$M_{le(crit)} = F_{le} \cdot [M]_{s(crit)}/K_d$$

where

F_{gr} = the annual crop yield
$[M]_{veg}$ = the concentration of metal M in the crop
F_{le} = the yearly water flux from the bottom of the rooting zone
$[M]_{s(crit)}$ = the critical concentration of M in the soil
K_d = the partition coefficient of M between soil and soil solution

$$\log(K_d) = b0 + b1 \cdot pH + b2 \cdot \log(OM\ \%) + b3 \cdot \log(clay\ \%)$$
(de Vries & Bakker 1996, equation 136)

Forest soil:
For forest soils, critical loads can be calculated both for the topsoil (humus layer) and the subsoil (mineral layer).

Topsoil

When neglecting surface runoff and bypass flow, the critical load of the heavy metal M in the top soil (subscript 1) can be described as:

Critical load

$$M_{tl1(crit)} = M_{td} = M_{ru1} + M_{le1(crit)} + M_{fu} - M_{lf}$$

$$M_{ru1} = f_{ru1}(M_{gu} - M_{fu} + M_{lf})$$

$$M_{gu} = F_{gr} \cdot [M]_{veg}$$

$$M_{lf} = F_{lf} \cdot [M]_{lf}$$

$$M_{fu} = f_{fu} \cdot M_{td}$$

$$M_{le1(crit)} = F_{le1} \cdot [M]_{s(crit)}/K_{d1}$$

where

M_{lf} = the flux of M by litterfall
M_{gu} = the flux of M by growth uptake
F_{gr} = average yearly removal by harvest
$[M]_{veg}$ = concentration of M in the parts of the trees which are removed by harvest
$[M]_{lf}$ = concentration of M in litter
M_{fu} = the flux of M by foliar uptake (canopy exchange)
f_{fu} = the fraction of the total deposition of M taken up by foliage

Subsoil

The critical load of the heavy metal M in the subsoil (subscript 2) can be written as:

Critical load

$$M_{tl2(crit)} = M_{le1(crit)} = M_{ru2} - M_{we2} + M_{le2(crit)}$$

where

$$M_{ru2} = f_{ru2}(M_{gu} - M_{fu} + M_{lf})$$

$$M_{le2(crit)} = F_{le2} \cdot [M]_{s(crit)} / K_{d2}$$

Since deposition can only take place in the top soil, the calculated value for $M_{tl2(crit)}$ is assigned to $M_{le1(crit)}$, whereafter $M_{tl1(crit)}$ is recalculated from the equations for the top soil. Whichever value is lowest, this or the critical load calculated for the top soil alone, is used as the critical load for the whole system.

2.2.1 **Input data in the critical load calculations**

Data used in the above equations is presented in Table 2.2-2.9 and is taken from the technical manual (de Vries & Bakker, 1996) or from literature (e.g. McLaughlin, 1996, Coughtrey, 1983, Adriano, 1986).

Table 2.2. Concentrations (mg kg^{-1}) of heavy metals in vegetation

$[M]_{veg}$ ($mg \cdot kg^{-1}$)	cereals	root crops	grass	forest
Pb	0.03	0.04	2.0	3.0
Cd	0.05	0.04	0.10	0.3

Table 2.3. Weathering of heavy metals in different soil types

M_{we} ($mg \cdot m^{-2} \cdot yr^{-1}$)	poor sand	rich sand	loam	heavy clay
Pb	0.17	0.25	0.93	3.1
Cd	0.0003	0.0005	0.0046	0.016

Table 2.4. The fraction of foliar uptake of heavy metals

f_{fu} (-)	deciduous	coniferous
Pb	0.47	0.36
Cd	0.55	0.35

Table 2.5. Concentration of heavy metals in returning litter

$[M]_{lf}$ ($mg \cdot kg^{-1}$)	deciduous	coniferous
Pb	15	15
Cd	0.3	0.3

Table 2.6. Fraction of heavy metals taken up by roots of vegetation

f_{ru} (%)	crops	deciduous	coniferous
5 cm organic	-	20	30
30 cm mineral	100	50	50

Partitioning coefficient

The partitioning coefficient of lead (K_d) between the soil solution and the total soil content is calculated according to the simplified version of equation 136 in the technical manual by de Vries and Bakker (1996) (i.e. neglecting the oxalate extractable Fe content), whereas the partitioning coefficient of cadmium has been calculated according to Danish information in Kjeldsen & Christensen (1996),

$$\log(K_d) = b0 + b1 \cdot pH + b2 \cdot \log(OM\%) + b3 \cdot \log(clay\%)$$

where the constants b_0, b_1, b_2 and b_3 can be found in Table 2.7. The K_d value for Cd in the technical manual is in fair agreement with values calculated for Cd on Danish data. It has not been possible to estimate K_d for Pb or Hg from Danish data.

Table 2.7. Values for coefficients b_0, b_1, b_2 and b_3 used in the simplified relationship between the partition coefficient of Cd and Pb and soil properties from Kjeldsen & Christensen (1996) and de Vries & Bakker (1996), respectively

	b_0	b_1	b_2	b_3
Cd	-3,93	0,48	0,71	-
Pb	-0.95	0.35	-	-

Critical limits

In the critical load calculations Danish soil quality criteria based on ecotoxicological effects in soil have been used as critical limit value (see 2.1 for details). The values used are 0.3 mg kg^{-1} for Cd, 50 mg kg^{-1} for Pb, and 0.1 mg kg^{-1} for Hg.

Aggregation

The critical load calculations have been made on a 1x1 km grid to which all basic data have been aggregated. The calculation has been made for each vegetation type present in the individual grid squares. For arable soils the calculations have been made for the ploughing layer, i.e. the upper 30 cm of the soil. For forests the soil has been divided in a 5 cm organic horizon (topsoil) and a 30 cm layer of the mineral soil (subsoil).

The information sources for the basic input data are presented below.

Soil types:

A basic soil texture map has been applied (Figure 2.2). The soil is divided into 11 classes with different texture and one class for humus soils. The content of clay and organic matter in the soil have been estimated from class definitions and statistics based on a Danish soil library with samples from 1000 soil horizons. pH for the arable land has been estimated on a county level based on information from the agricultural advisory service. For forest, steady state pH values have been taken from the critical load database.

Forest production (M_{gu}):

A national forest map with information on tree species, stand age, and forest production is available. The basic data are from 1986, but some updates have been made on the basis of more recent information. Calculations are made for spruce, pine, beech, and oak.

Table 2.8 Area covered by different forest classes, estimated average production yield and heavy metal removal

	Spruce	Pine	Beech	Oak
Land cover (km^2)	1,884	445	758	92
Production yield (m^3 ha yr^{-1})	12	3	10	6
Average density (kg m^{-3})	460	510	700	700
Production yield (kg m^{-2} yr^{-1})	0.55	0.15	0.70	0.42
Removal of Cd (mg Cd m^{-2} yr^{-1})	0.17	0.05	0.21	0.13
Removal of Pb (mg Pb m^{-2} yr^{-1})	1.65	0.45	2.10	1.26

Agricultural yields (F_{gr}):

The arable land has been divided into areas in rotation and areas with permanent grass. For the areas in rotation, an average distribution of crops have been made for four farm types: farms with pigs, farms with cattle, farms with cattle and pigs, and farms with only plant production. Three categories of crops have been used: cereals, root crops, and grass and green fodder. The distribution of farm types and average yields for each category of crops have been calculated as the county mean from 1985 to 1995. For each grid the distribution of farm types and crops have been estimated from the county mean. Figure 2.3 illustrates a map of total agricultural yield and Table 2.9 contain information used for calculating the removal of heavy metals from different land use classes.

Table 2.9 Area covered by different crops, estimated average production yield and heavy metal removal

	Cereals	Root crops	Grass
Land cover (km^2)	15,319	1,997	5,995
Production yield (kg m^{-2} yr^{-1})	0.78	5.21	3.36
Removal of Cd (mg Cd m^{-2} yr^{-1})	0.039	0.21	0.34
Removal of Pb (mg Pb m^{-2} yr^{-1})	0.023	0.21	6.72

Hydrologi:

A map of mean precipitation for the period 1960-1990 based on values from the Danish net of meteorological stations has been used. Leaching has been calculated from measurements of discharge from 94 streams.

Mean values for the 9 first order coastal areas for the period 1971-1995 has been used. Potential evapotranspiration (E_p) has been calculated at a 40x40 km grid for the period 1971-1995 (Mikkelsen and Olesen, 1991). A map of leaching has been constructed by estimating the vertical water flow (leaching) as the net precipitation subtracted by 0.9 times E_p, and scaling the estimates to equal the measured values in the 9 first order coastal areas. Figure 2.4 illustrates the calculated leaching (F_{le}).

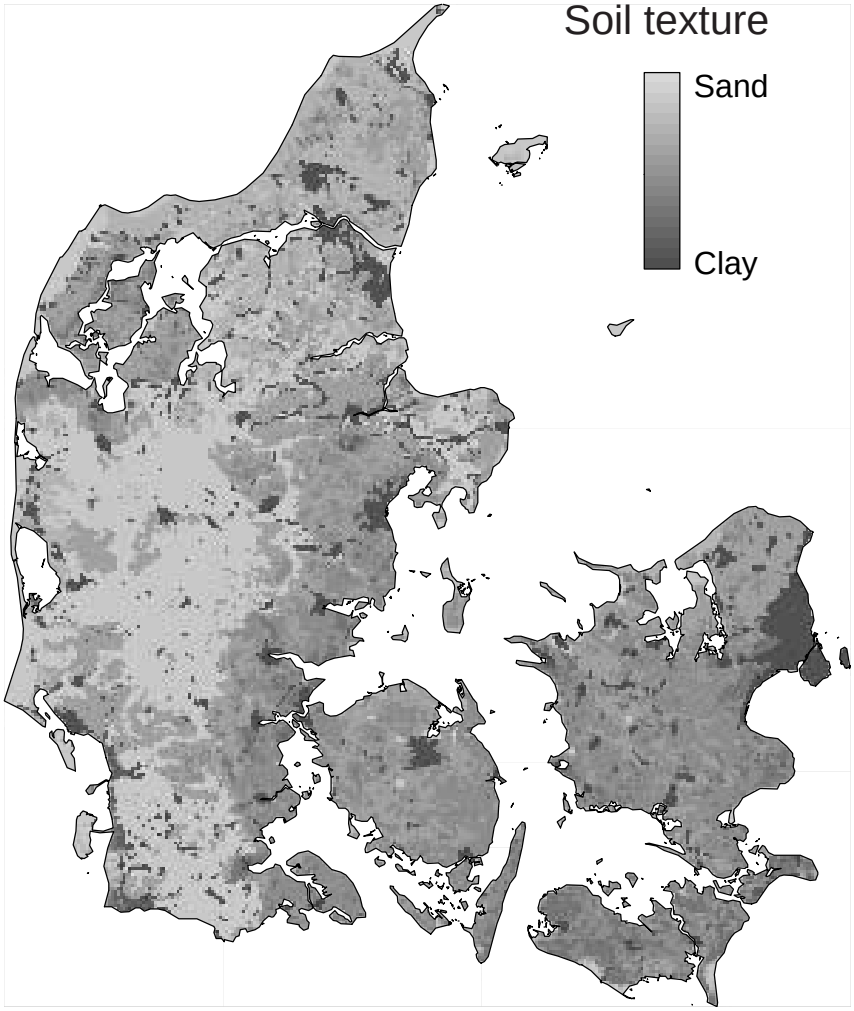


Figure 2.2. Map of soil texture. The map illustrates texture on a linear scale in surface area from sand to loam. Other soil types, cities and other land uses are shown in dark grey.

Figure 2.3. Average agricultural yields. For the calculations, average yields for four different farm types have been applied: farms with pigs, cattle, cattle and pigs, and farms solely with plant production.

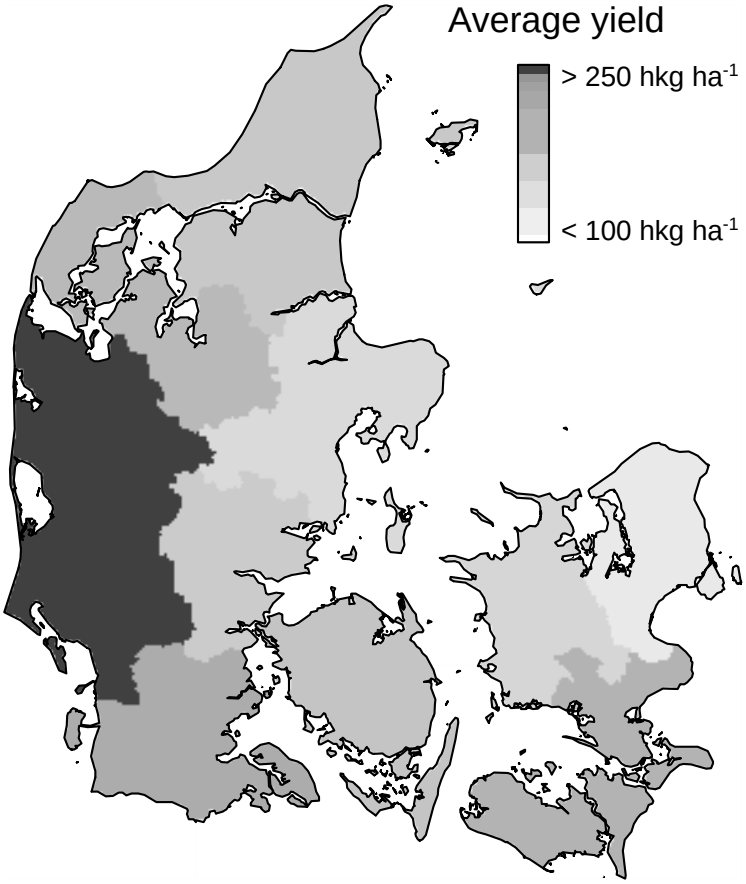
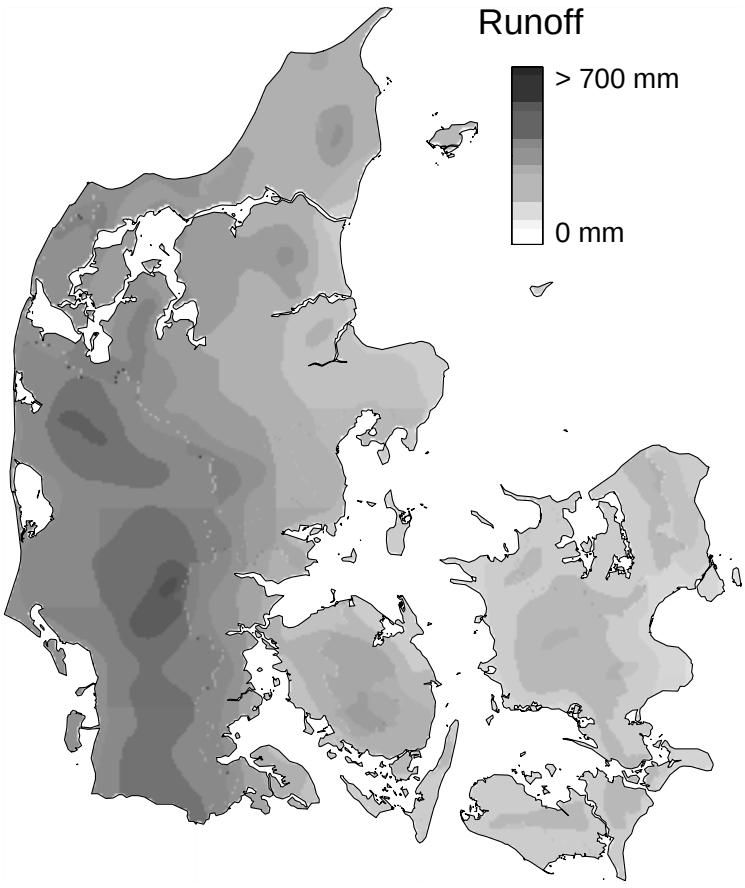


Figure 2.4 Calculated water flux from the bottom of the rooting zone. The flux has been calculated as the actual evapotranspiration subtracted from precipitation.



3 Critical load calculations of cadmium, lead and mercury in Denmark

Critical load for Cd and Pb

The median, 5 -, and 95 percentiles of the calculated critical loads for cadmium and lead are presented in Tables 2.1 and 2.2 and depicted in Figures 2.1 and 2.2. The maps of the 5 percentile critical load values are illustrated on a 20 x 20 km grid-net. For forest soils, this first attempt to calculate critical loads is only valid for the mineral layer. It has been chosen to assume a steady state for the organic layer independently of the deposition level, because no national survey on the heavy metal content of the organic horizon is available, and since the ecotoxicological soil quality criteria in general only consider exposure from mineral soils and not highly organic material as e.g. the upper layer in forest soils.

The maps show the highest critical loads for both heavy metals in the western part of the country (i.e. Western Jutland). This is partly due to a higher leaching rate in the sandy soils dominating in this area of Denmark (Figure 2.4), but also due to a generally higher average agricultural yield (Figure 2.3).

The agricultural structure in Denmark reflects the fact, that production of crops like wheat, rye and other grains is economically most feasible in the clayey and organic soils of Zealand, Funen and East Jutland, while farms with cattle and pigs have been concentrated in Jutland. Especially farms with dairy cows have larger areas with permanent grass cover. As a consequence, the largest areas with permanent grass, and with grass and green fodder in rotation have been placed in the part of the country, where sandy soils are predominating (Figure 2.2). The turnover of biomass and the removal rates of heavy metals is higher from fields with grass, green fodder, or root crops than from cereal fields.Thus, higher removal of heavy metals from the vegetation and hence a higher critical loads are found for grass and green fodder fields.

Critical load for Hg

An attempt has been made to collect relevant data for a critical load calculation for mercury. Reliable information on the species composition of mercury within the soil, i.e. organic mercury, Hg^{+2} or Hg^{0}, and on deposition and re-emission rates of mercury from the soil is, however, generally lacking. Furthermore, as organic mercury may biomagnify in food chains, the most sensitive receptors may not be soil ecosystems but rather top predators, including humans, which are not covered properly by the current critical load approach using soil related quality objectives. As a consequence of the very large uncertainties and the lack of data for even quantifying the overall uncertainty, it has been decided not to present a critical load calculation for mercury at this stage. When more information about the processes is available, critical load calculations for mercury can be made.

Figure 3.1. Calculated critical loads of Pb for Danish forests and arable soils. The map shows 5 percentile values aggregated on a 20 x 20 km grid.

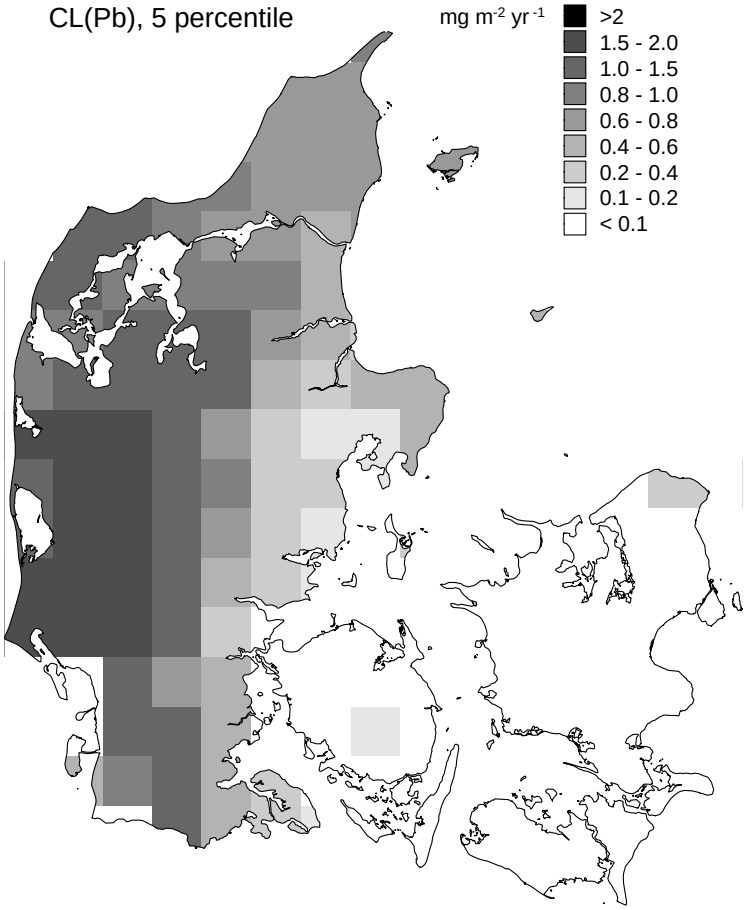


Figure 3.2. Calculated critical loads of Cd for Danish forests and arable soils. The map shows 5 percentile values aggregated on a 20 x 20 km grid

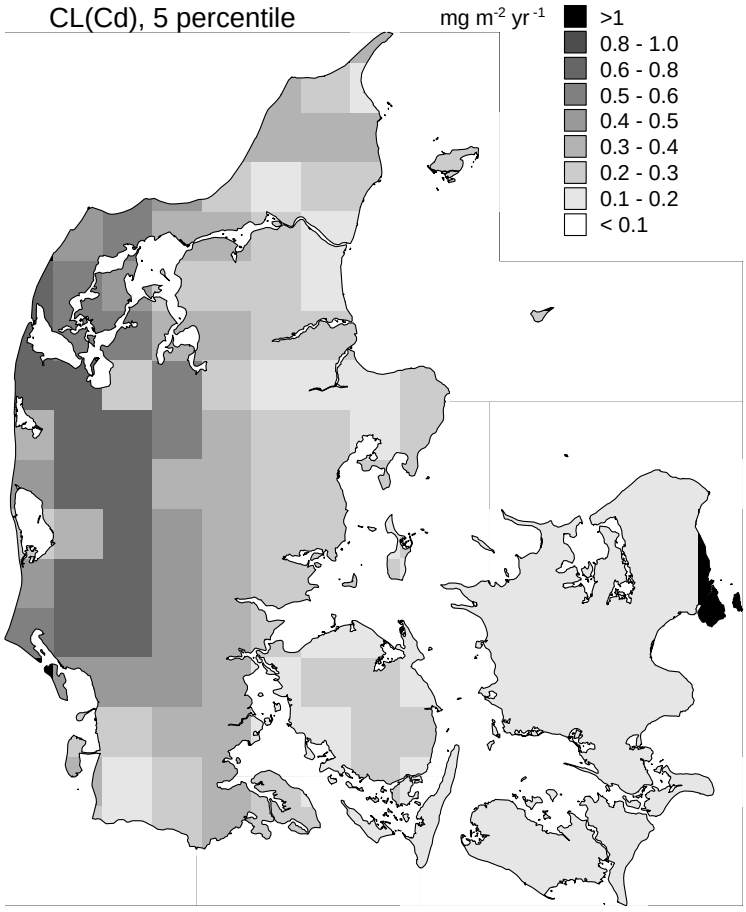


Table 3.1. Critical loads (median, 5 and 95 percentile) for cadmium and lead, differentiated according to farm types.

CL (mg m^{-2} yr^{-1})		farm type			
	percentile	pigs	cattle and pigs	cattle	plant
Lead	5	-0.18[a]	0.12	0.40	-0.13[a]
	50	**0.78**	**1.72**	**2.10**	**1.05**
	95	1.75	2.94	3.48	2.26
Cadmium	5	0.15	0.18	0.20	0.16
	50	**0.34**	**0.43**	**0.47**	**0.37**
	95	0.75	0.87	0.92	0.79

[a] negative values due to high natural contents and/or model artefacts.

Table 3.2. Critical loads (median, 5 and 95 percentile) for cadmium and lead, differentiated according to type of forest

CL (mg m^{-2} yr^{-1})		tree species			
	percentile	spruce	pine	beech	oak
Lead	5	14.9	13.4	13.6	12.4
	50	**19.2**	**18.4**	**15.2**	**14.1**
	95	23.1	21.6	17.8	17.2
Cadmium	5	4.51	4.47	2.17	2.07
	50	**7.95**	**8.71**	**3.24**	**3.05**
	95	11.1	11.0	5.13	5.14

For comparison, soil concentrations of cadmium and lead in Danish soils are presented in Table 3.3. The content of lead and cadmium in the top 30 cm of the soils are given in Table 3.4 assuming an average soil density of 1500 kg m^{-2}.

Table 3.3. Concentration of cadmium and lead (mg kg^{-1}) in Danish soils. The concentration is given as 5, 50 and 95 percentile for the total number of soils and according to soil type. Number of soils is 393. Data from Jensen et al. *(1996) and Larsen* et al. *(1996)*

mg kg^{-1}		5 Percentile	Median	95 Percentile
Cadmium	all soils	0.04	0.16	0.45
	sand	0.03	0.13	0.26
	clay	0.10	0.22	0.61
Lead	all soils	4.5	11.3	19.2
	sand	4.2	10.5	17.7
	clay	5.0	12.1	21.3

Table 3.4. Content of cadmium and lead in the top 30 cm of Danish soils assuming an average soil density of 1500 kg m^{-2}.

g m^{-2}		5 Percentile	Median	95 Percentile
Cadmium	all soils	0.018	0.072	0.20
	sand	0.014	0.059	0.12
	clay	0.045	0.099	0.27
Lead	all soils	2.0	5.1	8.6
	sand	1.9	4.7	8.0
	clay	2.3	5.4	9.6

4 Discussion and conclusions

The calculated critical loads for Cd, Pb and Hg cover large uncertainties both in the calculation method and in the available input data. The largest uncertainty is connected to the export of heavy metals from the soil by leaching, evaporation or uptake of heavy metals in agricultural crops, and to the calculation of critical limits. The uncertainties in calculating critical loads for mercury were considered too large to justify publication of the results (se below for discussion).

General uncertainties

Although the content of heavy metals in agricultural products used for food consumption has been a matter of concern in many countries and hence have been surveyed, the range in the reported values is generally very large. Most surveys have, furthermore, focused on the concentrations of heavy metals in processed food products, making an extrapolation back to concentrations in the removed crops difficult.

Weathering rates seem to be of less importance, since the total influence on the calculated mass balances is low. Sverdrup (1995) has, however, in some soils suggested higher weathering rates for Cd than the values applied in this report. The development of a model for the calculation of soil specific heavy metal weathering would be beneficial for a refinement of the critical load calculations.

The calculated K_d value for cadmium, using Danish data, are in fair agreement with values derived by using the equation given in the draft mapping manual. It has not been possible to estimate K_d for Pb or Hg from Danish data. Pb and Hg take part in several different reactions in the soil, e.g. do Pb participate with especially PO_4,which makes the determination of K_d difficult.

Uncertainties for Hg

A special problem is the volatilisation of Hg, which may have a substantial influence on the mass balance for Hg. Data to calculate partition coefficients for mercury and to reveal relationships between the partition coefficient and soil properties are needed on a national basis. An attempt to calculate a partition coefficient for mercury was based on balance calculations for Swedish IM sites. The calculation based on the available values are, however, extremely uncertain. Volatilisation of mercury from soils with natural concentrations of mercury has not been quantified in details yet. The volatilisation is dependent on temperature, biological processes and on soil characteristics such as texture, pH and organic matter content. In the early 80's the average mercury evaporation from 42 Danish agricultural soils was estimated to approximately 80 µg m^{-2} yr^{-1} adding up to a total of approximately 2.700 kg yr^{-1} from Danish soils outside urban areas, which at that time accounted for approximately 40 % of the total national emission of Hg (Miljøstyrelssen 1987). Compared to the estimated size of other export routes of mercury from the soil at that time (leaching, 10 µg m^{-2} yr^{-1}, and removal of crops, 25 µg m^{-2} yr^{-1}) volatilisation of mercury was a major sources of removal. The volatilisation at that time even exceeded the estimated atmospheric deposition rate of 65 µg m^{-2} yr^{-1}, making soils not only a sink for mercury deposition, but also a significant source of emission. The Danish figures are in agree-

ment with other international studies on mercury emission from soil. Schroeder *et al.* (1989) observed a median emission of mercury from five Swedish and Canadian soils of approximately 10 µg m^{-2} yr^{-1}. Lindenberg *et al.* (1993) found higher emission rates above mercury contaminated forest soils in the US, reaching a level of 750 µg m^{-2} yr^{-1}. Lindenberg *et al.* (1993) also reviewed the emission rate from a number of other studies and reported emission rates in the range of 7-5,700 µg m^{-2} yr^{-1}.

The data presented above is the only data available for emissions of Hg from Danish soils. Since then (1980), emissions of mercury from incinerators, industrial processes, fuel combustion etc. have declined significantly due to replacement of mercury in many products and improved emission control. When excluding soil emissions, the overall emission to air has declined from approximately 4300 kg yr^{-1} in 1980 to 2000 kg yr^{-1} in 1993 concurrently with a general decline in the net consumption of mercury in the Danish society from approximately 20 to 10 tons pr. year (Miljøstyrelsen 1987, 1996). Soil may therefore, in the same manner as for example PCBs (Jones *et al.* 1995), serve as a notable source of mercury emission. A new and comprehensive survey of e.g. the volatilisation rate of mercury under different soil- and climatic conditions is needed before a reliable calculation of critical loads for this metal can be presented.

Another important aspect of uncertainties connected to critical load calculations is the number of problems associated to the derivation and selection of critical limits for relevant target receptors. This was also a key issue of discussion in the latest international workshop on critical loads held in Bad Harzburg, Germany, 3rd to 7th November, 1997.

Many problems associated with the use of critical loads were identified at this workshop, the most important ones being

* to choose the most sensitive receptor and establish a credible source-receptor linkage. As many of these substances are subjected to biomagnification, the most vulnerable receptor is likely to be at the top of the food chains, making an extrapolation from critical levels in the target receptor back to source, e.g. soil concentrations, difficult and uncertain. Predators from the terrestrial environment may take up contaminants from many compartments and sources. For example humans take up mercury from both crops, milk, beef, fish products and breast milk in the case of lactating children. In such cases a dynamic multi-media approach is necessary to calculate reliable critical loads. Presently the methods are by far sophisticated enough to deal with these problems and do perhaps reflect the fact that the critical load concept was developed to solve problems with acidifying compounds, which generally did not result in adverse effects far away from the first receptor, e.g. soils or fresh water ecosystems. As a result of this, it was concluded that a general risk assessment procedure concerning specific target groups, e.g. humans and top predators in the arctic region, was to be recommended as the best and most appropriate effect based approach for mercury and persistent organic pollutants which are subjected for long range transport.

* especially for ionic compounds, such as the prevailing heavy metal species, derivation of critical limits reflecting bioavailability is necessary. Applying a generic limit as for example by using the Danish soil quality criteria, imply that the critical load will increase with a decrease in adsorption constant of the soil, because an increasing heavy metal amount will leach out of the soil. This may be reasonable if the key issue is to prevent accumulation of heavy metals in the soils (Vissenberg & van Grinsven 1995). The present approach is, however, problematic if the aim is to predict environmental effects. Numerous investigations have shown significantly higher toxicity of heavy metals in e.g. sandy soils with low K_d value compared to clay or humic soils (e.g. Peijnenburg *et al.* 1997). In addition, a separate calculation has to be performed to evaluate threats to groundwater.

Conclusions

It can be concluded that for cadmium and lead the data presented in this report represent an acceptable first attempt to calculate critical loads for Danish soils. For mercury more data on re-emission and biomagnification is needed before a first attempt on critical load calculations can be made without too large uncertainties.

Critical limits for other heavy metals

On the basis of the experiences achieved in this study, and on the recommendation from the Bad Harzburg Workshop, the existing preliminary calculation methods is considered sufficient developed to calculate critical loads for a number of other heavy metals. These should involve heavy metals proposed for subsequent addition to a future second stage Protocol for emission abatement of heavy metals under the LRTAP convention, and include for example nickel, copper, zinc and the metalloid arsenic.

5 References

Adriano, D.C. (1986): Trace Elements in the Terrestrial Environment. Springer-Verlag, New York.

Aldenberg, T., Slob, W. 1993. Confidence limits for hazardous concentrations based on logistically distributed NOEC data. Ecotoxicology and Environmental Safety vol. 25, 48-63.

Bakker, D.J., de Vries, W. (1996): Manual for calculating critical loads of persistent organic pollutants for soils and surface waters. TNO-MEP Report no R96/509, The Netherlands.

Coughtrey, P.J., Jackson, D. & Thorne, M. (1983): Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems. A.A. Balkema, Rotterdam.

Crommentuijn, T., Polder, M.D., van de Plassche, E.J. (1997) Maximum permissible concentrations and neglible concentrations for metals, taking background concentration into account. RIVM Report no. 601501001. The Netherlands.

de Vries, W. & Bakker, D.J. (1996): Manual for calculating critical loads of heavy metals for soils and surface waters. Report 114, DLO Winand Staring Centre, the Netherlands.

Jensen, J., Bak, J., Larsen, M. (1996): Tungmetaller i danske jorder. *Heavy metals in Danish soils (In Danish with English Summary)*. TEMA-rapport no 4/96 fra Danmarks Miljøundersøgelser. Miljø- og Energiministeriet.

Johansson, K., Aastrup, M., Andersson, A., Bringmark, L. & Iverfeldt, Å. (1991): Mercury in Swedish forest soils and waters - assessment of critical load. Water, Air, and Soil Pollution 56: 267-281.

Jones, K.C., Johnston, A.E., McGrathg, S.P. (1995). The importance of long- and short-term air-soil exchanges of organic contaminants. International Journal of Environmental Analytic Chemistry 59, 167-178.

Kjeldsen, P., Christensen, T.H. (1996). Kemiske stoffers opførsel i jord og grundvand. Bind 1. Projekt om jord og grundvand fra Miljøstyrelsen. Nr. 20.

Larsen, M.M., Bak, J. & Scott-Fordsmand, J. (1996): Monitering af tungmetaller i danske dyrknings- og naturjorder. DMU, faglig rapport nr. 157.

Lindberg, S.E., Kim, K.-H., Meyers, T.P. & Owens, J.G. (1995): Micrometeorological gradient approach for quantifying air/surface ex-

change of mercury vapor: tests over contaminated soils. Environmental Science and Technology 29 (1): 126-135.

Lindberg, S.E., Kim, K., Meyers, T.P., Owens, J.G. (1993). Micrometeorological gradient approach for quantifying air/surface exchange of mercury vapor: Tests over contaminated soils. Environmental Science and Technology 29: 126-135.

Ma, W.C. (1987). Heavy metal accumualtion in the mole, *Talpa europea* and earthworms as an indicator of metal availability in terrestrial environments. Bulletin f Environmetnal Contamination and Toxicology 39: 933-938.

McLaughlin, M.J., Tiller, K.G., Naidu, R. & Stevens, D.P. (1996): Review: the behaviour and environmental impact of contaminants in fertilizers. Aust. J. Soil Res. 34: 1-54.

Mikkelsen, H.E. & Olesen, J.E. (1991): Sammenligning af metoder til bestemmelse af potentiel vandfordampning. Tidsskrift for Planteavls specialserie, Statens Planteavlsforsøg, Beretning nr. S2157.

Miljøstyrelsen (1987): Kviksølvredegørelse. Redegørelse fra Miljøstyrelsen nr. 5, 1987. Miljø- og Energiministeriet.

Miljøstyrelsen (1996). Massestrømsanalyse for kviksølv. Miljøprojekt nr. 344. Miljø- og Energiministeriet.

Noppert, F., Dogger, J.W., Balk, F., Smits, A.J.M. (1993). Secondary poisoning in a terrestrial food chain: a probabilistic approach. IN: Integrated soil and sediment Research: A basis for propper protection. Eds: Eijsacker, H.J.P., Hamers, T. 303-307.Kluwer Academic Publishers, The Netherlands.

Posch, M., Hettelingh, J.P., de Smet, P.A.M., Downing, R.J. 1997 Calculation and mapping of critical thresholds in Europe. Status Report 1997. Coordination Center for Effects. RIVM Report no. 259101007. The Netherlands
Rühling, Å. *et al.* (1992): Atmospheric heavy metal deposition in Nothern Europe. NORD 12.

Romijn,C.A.F.M., Luttik,R., Canton,J.H. (1994).Presentation of a general algorithm to include effect assesment on secondary poisoning in the derivation of environmental quality criteria. Ecotoxicology and Environmental Safety vol. 24, 107-127.

Schroeder, W.H., Munthe, J. & Lindqvist, O. (1989): Cycling of mercury between water, air, and soil compartments of the environment. Water, Air and Soil Polution 48: 337-347.

Scott-Fordsmand, J.J., Bruus Pedersen, M. (1995): Soil quality criteria for selected inorganic compounds. Working report from Miljøstyrelsen (*EPA)*, no. 48, 1995. Miljø- og Energiministeriet.

Shore, R.F., Douben, P.E.T. (1994). The ecotoxicological significance of cadmium intake and residues in terrestrial small mammals. Ecotoxicology and Environmental Safety 29, 101-112.

Siegel, S.M., Okasako, J., Kaalakea, P. & Siegel, B.Z. (1980): Release of volatile mercury from soils and non-vascular plants. Organic Geochemistry 2: 139-140.

Skovregistreringen (1986). Landbrugsministeriets Arealdatakontor.

Spurgeon, D.J., Hopkin, S.P. (1996).
Risk assessment of the threat of secondary poisoning by metals to predators of earthworms in the vicinity of a primary smelting works. The Science of the Total Environment vol. 187, 167-183.

Sverdrup, H. (1995): Critical loads of cadmium for soils. Note for the 1995 CCE workshop.

van den Hout, K.D. (ed.) (1994): The impact of Atmospheric Deposition on Non-Acidifying Pollutants on the Quality of European Forest Soils and the North sea. RIVM report nr. 722401003, RIVM, the Netherlands.

Vissenberg, H.A., van Grinsberg, J.J.M. (1995): A simple calculation method for the estimation of accumulation and maximum permissible loads of heavy metals and organic compounds in soil (SOACAS). RIVM report no. 715501106 (in Dutch).

Wagner C, Løkke H. (1991). Estimation of ecotoxicological protection levels from NOEC toxicity data. Water Research vol. 25, 1237-1242.

Appendix

Symbol	ECE[7]	Explanation	Unit
$\mathbf{f_{ru}}$	$\mathbf{f_{ru}}$	Root uptake fraction	fraction
$\mathbf{f_{fu}}$	$\mathbf{frM_{fu}}$	Foliar uptake fraction of heavy metal M	fraction
$\mathbf{K_d}$	$\mathbf{K_{p,tot}}$	Partition coefficient between the total content of heavy metal M in the soil and the total concentration in the soil solution	$m^3 \cdot kg^{-1}$
$\mathbf{M_{bp}}$	$\mathbf{M_{bp}}$	Flux of heavy metal M by bypass flow	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{le}}$	$\mathbf{M_{le}}$	Flux of heavy metal M by leaching	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{lf}}$	$\mathbf{M_{lf}}$	Flux of heavy metal M by litterfall	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{fu}}$	$\mathbf{M_{fu}}$	Flux of heavy metal M by foliar uptake	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{gu}}$	$\mathbf{M_{gu}}$	Flux of heavy metal M by growth uptake	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{ru}}$	$\mathbf{M_{ru}}$	Flux of heavy metal M by root uptake	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{sr}}$	$\mathbf{M_{sr}}$	Flux of heavy metal M by surface runoff	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{td}}$	$\mathbf{M_{td}}$	Total deposition of heavy metal M	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{tl}}$	$\mathbf{M_{tl}}$	Total load of heavy metal M	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{M_{we}}$	$\mathbf{M_{we}}$	Flux of heavy metal M by weathering	$mg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{[M]_{lt}}$	$\mathbf{ctM_{lt}}$	Content of heavy metal M in returning litter	$mg \cdot kg^{-1}$
$\mathbf{[M]_{s}}$	$\mathbf{ctM_{s}}$	Total content of heavy metal M in the soil	$mg \cdot kg^{-1}$
$\mathbf{[M]_{veg}}$	$\mathbf{ctM_{veg}}$	Content of heavy metal M in ther harvested part of the vegetation	$mg \cdot kg^{-1}$
$\mathbf{F_{gr}}$	$\mathbf{F_{gr}}$	Growth flux or annual average yield	$kg \cdot m^{-2} \cdot yr^{-1}$
$\mathbf{F_{le}}$	$\mathbf{F_{le}}$	Water flux leaching from the soil	$m \cdot yr^{-1}$
$\mathbf{F_{lf}}$	$\mathbf{F_{lf}}$	Litter fall flux	$kg\ m^{-2} \cdot yr^{-1}$

[7] Notation used in de Vries & Bakker (1996)

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