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Critical loads and excess loads of cadmium, copper and lead for European forest soils

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ABSTRACT

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Recently, concern has arisen about the impact of the dispersion of heavy metals in Europe. Therefore, a study (ESQUAD) was initiated to assess critical loads and steady-state concentrations of cadmium, copper and lead for European forest soils. The calculation methods used strongly resemble those used to compute critical loads for acidifying compounds. Results show that the computed critical loads and associated excess loads for forest soils strongly depend on the threshold values chosen and on the soil phase (adsorbed/dissolved) considered. Further research is needed to improve input data and the modelling of heavy metal adsorption.

Keywords: heavy metal, soil chemistry, soil contamination

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Preface

In 1993 the Dutch Ministry of Housing, Spatial Planning and the Environment commissioned five Dutch research institutes to investigate the effects of non-acidifying substances on forest soils in Europe and the North Sea. A project (Esquad) was carried out in which a first systematic assessment of critical loads, excess loads and steady-state concentrations of three heavy metals and two persistent organic pollutants was made. The results of this study have been reported in the main report of the Esquad project (Van den Hout, 1994).

The emphasis in the main report was put on the results of the study; the methods used in the various computations were only briefly described.

Therefore, it was decided to write a series of background documents in which both the methods and data used in the various parts of the Esquad study (e.g. emission estimates, deposition modelling) and the results are extensively described.

This report serves as one of the two background documents to Chapter 5 in the main report, Forest Soils. In this report an overview is given of the models and the data used to compute critical loads and steady-state concentrations of heavy metals for European forest soils and of the result obtained. Information about the assessments for persistent organic pollutants can be found in Bakker et al., (1994).

Summary

To assess the effects of cadmium, copper and lead on European forest soils, critical loads, excess loads and steady-state concentrations in the soil solution were computed. To calculate a critical load, a threshold heavy metal concentration for either the adsorbed or solute phase is needed. Because internationally accepted standards for maximum allowable heavy metal concentrations in the soil are not available, three different sets with threshold values were used to show the effects of different thresholds on the results. The methods and data used were essentially the same as those used to compute critical loads for sulphur and nitrogen (De Vries et al., 1993). Simple steady-state models were used based on the mass balance principle. However, because heavy metal adsorption in the soil had to be modelled, a geochemical model was used to compute the heavy metal activity in the soil solution.

Regional data on climate, forests and soils were derived from existing data bases (De Vries et al., 1993). Some literature research was carried out to estimate the uptake and the filtering of heavy metals by forests.

Because no readily available data were available that describe heavy metal adsorption in European forest soils, an extensive literature study was carried out to derive (pedo)transfer functions between soil characteristics such as organic matter content and pH and adsorption parameters of heavy metals on soil materials. For cadmium a set of data was available from carefully performed experiments comprising various soil types. Therefore the transfer function that describes cadmium adsorption is considered to be satisfactory. The adsorption function for copper is considered somewhat less reliable, the adsorption model for lead is a first approximation because the model is based on a very limited data set.

The calculations show a strong effect of the threshold value on the results. When the most stringent threshold values are used, critical loads for the organic layer in forests are exceeded almost everywhere in Europe. When the least stringent threshold values are used, the area where deposition exceeds critical loads decreases by a factor eight or more. Furthermore differences exist between critical loads based on thresholds for the soil solution and critical loads based on thresholds for the adsorbed phase because these threshold values were derived independently.

A comparison of the computed steady-state heavy metal contents with measured contents in various European countries showed that the model gives reasonable results, especially for the organic layer. For calcareous soils, the model underestimates heavy metal concentrations.

To improve the critical load and steady-state assessments, more information is needed on the adsorption of copper and lead. Furthermore, adsorption at low pH levels and the role of aluminium and organic anions in the adsorption process should be investigated further.

Because the threshold value has such a profound influence on the results, it is important to improve and harmonize the various experiments to arrive at an internationally accepted set of (ranges of) threshold values.

1 Introduction

In the past years, many studies have been carried out to assess critical loads of acidifying substances for forest soils and surface waters on a European scale e.g. Hettelingh et al., (1991), Downing et al., (1993), De Vries et al., (1993). Impacts of other air pollutants, however, are largely unknown. Recently, concern on the dispersion of non-acidifying substances has arisen and several bodies have been established to address this subject.

To make a first systematic assessments of critical loads for three heavy metals and two persistent organic pollutants, a project was carried out by five research institutes in the Netherlands. This project, ESQUAD (European Soil and sea Quality due to Atmospheric Deposition of selected substances), was commissioned by the Dutch Ministry of Housing, Spatial Planning and the Environment. In this project, critical loads of cadmium, copper, lead, lindane and benzo(a)pyrene were calculated for European forest soils and compared with the calculated, present atmospheric deposition. Furthermore, steady-state concentrations of these substances in forest soils and the North Sea were calculated for both the adsorbed and solution phase and compared with various threshold concentrations. Computations for forest soils were carried out with essentially the same methods and data bases used for the assessment of critical loads for sulphur and nitrogen (De Vries et al., 1993). The objectives of the ESQUAD project were to make a first systematic assessment of critical loads and exceedances of threshold values for pollutants for forest soils and the North Sea, to indicate gaps in knowledge and data and to suggest possibilities for improvement. The results from this study are described by Van den Hout, (1994). This report is one of the background documents written within the framework of ESQUAD. It contains a detailed description of the methods and data used to compute critical loads, excess loads and steady-state concentrations of cadmium, copper and lead in European forest soils and a discussion of the results obtained.

The impact of atmospheric deposition on soil quality can be described in two ways:

1. the difference between present deposition levels and critical loads. A critical load is defined as a deposition level that will not lead to exceedance of threshold values for the quality of the soil or the soil solution
2. quality levels for soil or soil solution that will arise if present deposition levels are allowed to continue (steady-state levels).

In both approaches, the state of the environment can be illustrated with maps. In the first approach, maps can be used to show the relationship between present and critical loads, or areas where critical loads are exceeded. In the second approach, maps show steady-state quality levels at present inputs.

In the first ('critical load') approach, a single threshold value is needed to map a critical atmospheric deposition level. The second ('steady-state') approach, by mapping the environmental impact of present deposition levels on soil or soil solution

quality, allows comparison with various threshold values. Both approaches have their advantages and therefore have been used in this study. The study was confined to forest soils because atmospheric deposition is the main, if not the only, source of heavy metal contamination for these soils.

Critical loads are strongly dependent on the threshold value used, but no internationally accepted standards are yet available. In this reconnaissance study we have used values from three sources:

1. Maximum Permissible Concentrations (MPC) derived from laboratory experiments with soil organisms and plants;
2. Target Values set by the Dutch environment ministry (DTV);
3. critical concentrations in the humus layer (mor horizon) of Swedish forest soils (SMV).

More information on threshold values is given in Chapter 5. For an extensive discussion on threshold values, the reader is referred to Van den Hout, (1994).

Threshold values for the concentration of pollutants depend on the composition of the soil layer being considered. Because both the clay and organic matter contents of the organic layer are often very different from the underlying mineral soil, separate critical loads were calculated for an organic and a mineral layer.

In Chapter 2 the steady-state model to compute critical loads and steady-state concentrations of heavy metals in forest soils is described. Chapter 3 gives a brief overview of the distribution of forest and soil types over Europe and of the data that were used. Chapter 4 contains an overview of the adsorption of heavy metals on soil materials and describes the results of a literature review that was carried out to estimate the adsorption constants. The threshold values for heavy metals in the soil that were used are presented in Chapter 5. In Chapter 6 the modelling results are presented. In Chapter 7 the results are discussed. In Chapter 8 conclusions are drawn and some recommendations for future research are given.

2 The model

2.1 Introduction

As noted before, the impact of atmospheric heavy metal pollution on forest ecosystems was assessed in two ways: by calculating excess loads (present minus critical loads) and by calculating the steady-state heavy metal concentrations in the soil.

To compute a critical load, a threshold value for the metal concentration in either the adsorbed or dissolved phase is used. If a threshold value for the adsorbed phase is used, the associated concentration in the soil solution has to be calculated first using a chemical equilibrium model that computes the partitioning of the metal over the solute and solid phase using a (Freundlich) adsorption function. In this study the geochemical model EPIDIM (Groenendijk, 1994) was used. Such a chemical equilibrium model requires the concentrations of the major cations and anions, together with the concentration of dissolved organic carbon (DOC) and all formation constants of the complexes in the soil solution. Concentrations of the inorganic ions were calculated using mass balance equations (cf Section 2.4.1). DOC was estimated from an empirical relationship between DOC and soil organic matter content (cf Section 2.4.2). From the threshold heavy metal concentrations in the soil solution, the critical load was calculated with mass balance equations. The mass balance equations are discussed in Section 2.2. The Equation to compute a critical load is given in Section 2.6.

Heavy metal concentrations in the soil in steady-state with present deposition levels, were also calculated with mass balance equations. Since metal adsorption is related to the activity of the free metal ions, the speciation of the metals was calculated with the same chemical equilibrium model as mentioned above. Concentrations of the inorganic ions and DOC, needed to calculate metal complexation, were calculated as described above. From the total concentrations of the heavy metals and the concentrations of the inorganic ions and DOC, activities of heavy metals in the soil solution and adsorbed amounts in equilibrium with the soil solution were calculated using a Freundlich adsorption function (cf Section 2.5).

2.2 Mass balance equation for heavy metals

The mass balance of a certain heavy metal X in a forest soil layer (in mol_c ha⁻¹ a⁻¹) equals:

$$X_{td} + X_{ci} + X_{mi} = X_{sr} + X_{bp} + X_{tu} + X_{pr} + X_{le} + \Delta X_{ac} + \Delta X_{ss} \quad (1)$$

where *td* stands for total deposition, *ci* for canopy interaction, *mi* for mineralization, *sr* for surface runoff *bp* for bypass flow (in cracks etc.), *tu* for total uptake by the

trees, pr for net metal precipitation (metal precipitation minus metal dissolution), le for leaching and where ΔX_{ac} and ΔX_{ss} stand for the change in the amount on the adsorption complex and in the soil solution, respectively. Canopy interactions refer to the occurrence of either foliar uptake (X_{ci} is negative) or foliar exudation (X_{ci} is positive). Literature data suggest that foliar uptake is the dominant process for Pb and Cu whereas Cd seems to be relatively inert (Bergkvist et al., 1989). However, in heavily polluted areas, foliar exudation occurs for all three metals (Godt, 1986). Total uptake is equal to maintenance uptake, to resupply the amounts released by litterfall and canopy interactions, plus growth uptake, due to forest growth.

In a steady-state situation ΔX_{ac} and ΔX_{ss} are zero. Furthermore, a steady-state element cycle implies that mineralization equals litterfall and maintenance uptake equals the release by litterfall and canopy interactions. This means that total uptake minus mineralization and canopy interactions equals growth uptake, i.e.:

$$X_{gu} = X_{tu} - X_{ci} - X_{mi} \quad (2)$$

where gu stands for growth uptake.

Combination of Equations (1) and (2) gives:

$$X_{td} = X_{sr} + X_{bp} + X_{gu} + X_{pr} + X_{le} \quad (3)$$

The concentration of heavy metals in forest soils is such that metal precipitation was considered negligible, i.e. $X_{pr} = 0$. Furthermore, bypass flow and surface runoff were not taken into account. Firstly because it was assumed that the presence of a litter layer with a high water adsorbing capacity will prevent substantial bypass flow and surface runoff. A second reason why these two processes were not included is the lack of reliable data describing these processes as a function of the available soil and terrain data.

Equation (3) thus simplifies to:

$$X_{td} = X_{gu} + X_{le} \quad (4)$$

2.3 Interaction fluxes

The interaction fluxes included in Equation (4) are growth uptake and leaching. Growth uptake was assumed to be proportional to the products of water uptake (transpiration rate) and soil solution concentration according to (Boesten and Leistra, 1983):

$$X_{gu} = fX_{up} \cdot E_t \cdot [X]_{tot} \quad (5)$$

where fX_{up} is a preference factor for uptake of heavy metal X (-), E_t is the transpiration rate ($m^3 ha^{-1} a^{-1}$) and $[X]_{tot}$ is the total concentration (free plus complexed) of heavy metal X ($mol.m^{-3}$). In the literature, fX_{up} is sometimes referred to as the transpiration stream concentration factor (Boesten and Leistra, 1983). Values of fX_{up} above one indicate preferential uptake, whereas the opposite is true for values less than one. The latter is the case for the heavy metals considered.

Leaching was described as the product of waterflux and soil solution concentration according to:

$$X_{le} = (P - E_i - E_t - E_v) \cdot [X]_{tot} \quad (6)$$

where P stands for precipitation, E_i for interception evaporation and E_v for the soil evaporation (all in $m^3 ha^{-1} a^{-1}$).

2.4 Steady-state concentrations

2.4.1 Inorganic ions

The concentrations of the inorganic ions i.e. Cl , SO_4 , NO_3 , Ca , Mg , K , Na and NH_4 were calculated with a modified version of the steady-state model START (De Vries, 1991). The leading equation in the modified START model is the charge balance equation:

$$[H] + [Al] + [Ca] + [Mg] + [K] + [Na] + [NH_4] = [NO_3] + [SO_4] + [Cl] + [HCO_3] + [CO_3] \quad (7)$$

where $[]$ denotes the concentration in $mol_c m^{-3}$.

Because SO_4 and Cl were assumed to behave as tracers, the concentration was calculated as:

$$[X] = X_{td} / FW \quad (8)$$

where FW is the water flux ($m^3 ha^{-1} a^{-1}$) which equals (cf Equation (8)):

$$FW = P - E_i - E_t - E_v \quad (9)$$

For X is Ca , Mg , K and Na , the concentration was calculated as:

$$[X] = (X_{td} + X_{we} - X_{gu}) / FW \quad (10)$$

where the subscript we stands for weathering.

The concentrations of NH_4 and NO_3 were also calculated as functions of the total deposition, including the effects of nitrification, denitrification and growth uptake (De Vries, 1991).

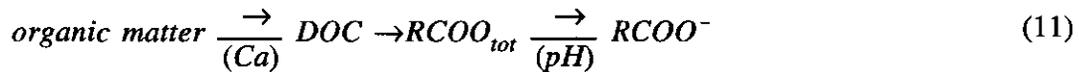
The deposition fluxes of SO_2 , NO_x and NH_4 were computed with the aid of the emission deposition matrices of the RAINS model for acidification (Alcamo et al., 1990) using estimated 1990 emissions. The deposition of the base cations and chloride were estimated by spatial interpolation of the deposition of these ions measured in 1988 at about 60 meteorological stations in Europe (Pedersen et al., 1990).

From the charge balance Equation (7), and the concentrations of Cl , SO_4 , NO_3 , Ca , Mg , K , Na and NH_4 calculated with Equations (8) and (10), the sum concentration of $H + Al - HCO_3 - CO_3$ was calculated. Assuming that Al is in equilibrium with an Al-hydroxide and the amount of inorganic carbon in the soil solution is in equilibrium with gaseous CO_2 , concentrations of Al and inorganic carbon can be expressed in the concentration of H^+ and a combined charge balance for these ions can be used (cf. Section 2.5).

2.4.2 Dissolved organic carbon

To compute heavy metal adsorption in soils, the heavy metal activity in the soil solution must be computed as accurate as possible. Because especially copper and lead form strong complexes with organic anions, the modelling of the dissociation of dissolved organic matter has been included in the chemical equilibrium model.

The following mechanism has been assumed for the relationship between organic matter and organic anion concentration:



where $RCOO_{tot}$ denotes organic acids and $RCOO^-$ denotes organic anions.

To estimate the concentration of dissolved organic carbon (DOC), a regression analysis was carried out using the soil chemical data from the upper mineral layer of about 150 Dutch forest stands (De Vries and Leeters, 1994) and about 50 dune soils with:

- pH (H_2O) values between 3.6 and 7.8
- Organic matter contents between 0.2 and 10%
- DOC concentrations between 3 and 500 $mg.l^{-1}$

This analysis of the relationship between DOC and soil parameters such as the organic matter content and the concentrations of the major cations in the soil solution showed that the DOC concentration in forest soils can be approximated by:

$$\log (DOC) = 1.629 + 0.38 \cdot \log (OM) \quad (12)$$

Where:

OM is the organic matter content of the soil (%)

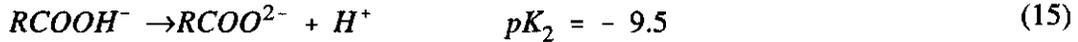
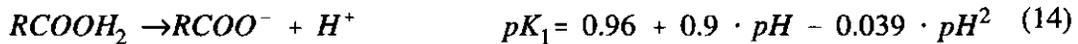
It should be stressed here that this Equation is a very crude approximation of the dissolved organic carbon concentration because the percentage variance accounted for was only about 40%. When this relationship is used for the organic layer with 60% organic matter, the computed *DOC* concentration is about 200 mg.l⁻¹. This value is higher than the measured values by Van Breemen et al., (1988) who found *DOC* concentrations up to 140 mg.l⁻¹.

The relation between dissolved organic carbon and the concentration of organic acids (in μmol_c.l⁻¹) was described by:

$$RCOO_{tot} = m \cdot DOC \quad (13)$$

The value of *m* was set at 5.5 μmol_c.mg⁻¹ C in accordance with Henriksen and Seip, (1980) and Bril, (1994).

The dissociation of the organic acids was described as the dissociation of a dibasic acid according to:



The dissociation constants *PK*₁ and *PK*₂ were derived from Oliver, (1983), and Bril, (1994) respectively (see also Chapter 4).

2.5 Ion speciation and adsorption

The ion speciation in the soil solution was calculated with the chemical equilibrium program EPIDIM (Groenendijk, 1994). In EPIDIM the chemistry of the soil solution is defined by a set of chemical components (such as *H*⁺ and *SO*₄²⁻) and a set of ion species (such as *CaSO*₄ and *HCO*₃⁻) with their associated specific formation constants. The formation of a certain species out of the components can be written as:

with:

*a*_{*i,j*} = stoichiometric coefficient of component *A*_{*i*} in the formation of species *B*_{*j*}
N = number of components

If a species contains a component *A*_{*p*}, the associated stoichiometric coefficient is greater or equal to one; if the species does not contain the component *A*_{*p*}, the stoichiometric coefficient equals zero.

The set of components has to be chosen such that:

- all species can be build from this set
- no component can be build from a combination of other components.

Annex I gives the Table of species used for this application. In this Table the stoichiometric coefficients $a_{i,j}$ are given with i = column number (components) and j = row number (species), the last column contains the formation constants K_j^0 . All stoichiometric coefficients that are equal to zero are left blank in this Table.

The concentration of each species can be expressed in the concentrations of the components according to:

$$[B_j] = K_j \prod_{i=1}^n [A_i]^{a_{ij}} \quad (17)$$

where:

- $[B_j]$ = concentration of species j
- $[A_i]$ = concentration of component i
- K_j = formation constant of species j

For each component the total concentration is:

$$[A_k]^T = \sum_{j=1}^m a_{kj} \cdot K_j \prod_{i=1}^n [A_i]^{a_{ij}} \quad (18)$$

where:

- $[A_k]^T$ = the total concentration of component k
- m = number of species

If the total concentrations are known, we have a set of N Equations (as Equation 17) with N unknowns, the component concentrations. This set of Equations is solved numerically with a Newton Raphson iteration scheme.

To correct for non ideal behaviour of the ions, the formation constants K_j used are conditional constants, corrected for the ionic strength in the soil solution. These modified constants are calculated from the thermodynamic formation constants of the species and activity coefficients of the species and components.

$$K_j = K_j^0 \frac{\left(\prod_{i=1}^n \gamma_i^{a_{ij}} \right)}{\gamma_j} \quad (19)$$

where:

- γ_i = activity coefficient of component i
- γ_j = activity coefficient of species j

K_j = corrected formation constant
 K_j^o = uncorrected formation constant

Activity coefficients are calculated with the Davies equation (Stumm and Morgan, 1981):

$$\log \gamma_i = -0.5 z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 I \right) \quad (20)$$

with:

I = ionic strength
 z_i = valence of ion i

The ionic strength is calculated according to:

$$I = \frac{1}{2} \sum_{j=1}^m z_j^2 [B_j] \quad (21)$$

From the mass balance equations the total concentrations of Cl , SO_4 , NO_3 , Ca , Mg , K , Na and NH_4 are known. For the metal M^{2+} either the total concentration (in solution) or the total amount in the soil is known. DOC concentration is calculated from the regression equation. These ions are all chosen as part of the set of components. From charge balance we also have the sum concentration of $H + Al - HCO_3 - CO_3$. For these ions a combined mass balance is used in EPIDIM. Assuming equilibrium with an Al-hydroxide the concentration of uncomplexed Al can be expressed in the H concentration:

$$[Al^{3+}] = KAl_{ox} \cdot [H^+]^3 \quad (22)$$

With:

KAl_{ox} = solubility product of Al-hydroxide

The solubility of other Al-species such as hydrolysed Al species can be expressed in a similar way. The concentration of inorganic carbon can also be expressed in the H concentration assuming equilibrium with gaseous CO_2 with a fixed partial pressure:

$$[CO_3^{2-}] = K \cdot pCO_2 \cdot [H^+]^{-2} = K_{CO_2} \cdot [H^+]^{-2} \quad (23)$$

$$[HCO_3^-] = K \cdot [H^+] [CO_3^{2-}] = K_{HCO_3} \cdot [H^+]^{-1} \quad (24)$$

Heavy metal adsorption was modelled with the Freundlich equation (cf Chapter 4).

$$Q_M = K_f \cdot (M^{2+})^n \quad (25)$$

where:

$$\begin{aligned} Q_m &= \text{adsorbed metal concentration (mol.kg}^{-1}\text{)} \\ K_f &= \text{Freundlich constant} \\ n &= \text{Freundlich exponent} \\ (M^{2+}) &= \text{heavy metal activity (mol.m}^{-3}\text{)} \end{aligned}$$

The influence of the calcium activity, described in Chapter 4, was included in the adsorption constant K_f . In EPIDIM, adsorbed M^{2+} is treated as a species. However the Freundlich equation differs from Equation (17). The Freundlich exponent n is not equal to the stoichiometric coefficient in the sorption reaction. In order to have a proper mass balance the Freundlich constant K is divided by n . To obtain the adsorbed metal concentration, the adsorbed species concentration calculated by EPIDIM has to be multiplied with n . The Freundlich constant K depends on soil characteristics such as organic matter and clay content and on the pH and Ca activity of the soil solution (cf Chapter 5). The latter two are not known a priori so their estimated values are improved each iteration step. Therefore the model EPIDIM was adapted to update K within each iteration step.

2.6 Critical loads and steady-state concentrations

Combining Equations (4), (5) and (6) yields the Equation to compute a critical load for a heavy metal:

$$CL(X) = fX_{up} \cdot E_t + (P - E_i - E_t) \cdot [X]_{crit} \quad (26)$$

where X_{crit} is the threshold concentration of the heavy metal in the soil solution. This value can be derived from a threshold concentration for the adsorbed phase using the Freundlich Equation (25). For critical loads based on threshold values in the solution phase the values for soil water from Table 9 can be used directly.

The steady-state concentrations in the solution phase at present deposition were computed with the geochemical model EPIDIM. The steady-state adsorbed concentration was computed from the steady-state activity in the soil solution using Equation (25).

3 Input data

In this Chapter an overview will be presented of the input data that were used in the application of the steady-state model described in Chapter 2. Attention will be paid to the distribution of soils and forests over Europe and to data on climate, soil characteristics, heavy metal uptake by forests and atmospheric deposition of heavy metals.

3.1 Distribution of forests and soils

Critical loads and steady-state concentrations of heavy metals were mapped for a grid system of 0.5° latitude * 1.0° longitude. The size of a cell in this grid varies in the east-west direction from 120 km in southern Europe to 60 km in northern Scandinavia, whereas the size in the south-north direction is fixed to 56 km.

Computation were carried out for all combinations of forest and soil within each grid. Two forest types were distinguished, conifers and deciduous forest. Only the percentage of the two forest types per grid cell was known, not their exact location within the grid cell. Soil types were distinguished on the basis of the FAO-Unesco Soil Map of the World on a scale of 1 : 5 000 000 (FAO, 1992). An overview of the different soil types used, is provided in Annex 3.

The FAO-Unesco Soil Map of the World consists of so called mapping units. Each mapping unit consists of one dominant soil unit, some associated soil units and inclusions. Associated soils occupy at least 20% of the mapping unit whereas inclusion occupy less than 20% of the mapping unit. Only very occasionally a mapping unit consists of one soil unit. The texture and slope of the dominant soil of each mapping unit are known. For associated soils and inclusions, texture and slope were assigned using the tables given by FAO. These tables list the prevailing texture and slope class for each soil unit.

The texture of the top soil has been classified into 3 different texture classes:

- 1 course : clay content less than 18%
- 2 medium : clay content between 18 and 35%
- 3 fine : clay content between 35%.

Often, compound texture classes occur within a soil unit comprising two or three of these texture classes.

The slope dominating the terrain where the soil unit is situated, is divided into 3 slope classes:

- a : flat or almost flat, slope less than 8%
- b : undulating, slope between 8 and 30%
- c : steep, slope more than 30%.

Similar to texture, compound slope classes occur comprising two or three of these slope classes.

An overlay procedure with the GIS ArcInfo was applied to obtain the distribution of soils in each grid cell. Taking the dominant soils, associated soils and inclusions into consideration, the number of soils per grid varied between 1 and 25. The mean number of soils per grid cell was 8.37 which is considerably higher than the 2.2 soils per grid which was computed when only the dominant soils were taken into account (De Vries et al., 1993).

The percentage of conifers and deciduous forest in each grid cell was estimated from aeronautic maps (De Vries et al., 1993). Because only the percentage of both forest types was known for each grid but not the exact location, an assignment procedure was applied that allocate forests to soils. It has been assumed that forests are not evenly distributed over all soil types but are mainly located on poor soils and on soils with steep slopes.

Table 1 shows the percentages of forest for each of the European countries.

Table 1 Coverage of coniferous and deciduous forests in the various European countries as a percentage of the land area

| Country | Coniferous forests | Deciduous forests | All forests |
|---------------------|--------------------|-------------------|-------------|
| Albania | 6.2 | 29.4 | 35.6 |
| Austria | 31.2 | 7.0 | 38.2 |
| Belgium | 7.3 | 7.2 | 14.5 |
| Bulgaria | 13.1 | 17.3 | 30.4 |
| Czechoslovakia | 18.9 | 10.9 | 29.8 |
| Denmark | 1.6 | 0.5 | 2.1 |
| Finland | 57.6 | 6.3 | 63.9 |
| France | 12.8 | 6.0 | 18.8 |
| Germany | 17.6 | 7.1 | 24.7 |
| Greece | 10.0 | 5.4 | 15.4 |
| Hungary | 1.5 | 8.3 | 9.8 |
| Ireland | 0.8 | 0.0 | 0.8 |
| Italy | 2.8 | 10.1 | 12.9 |
| Luxembourg | 16.6 | 18.1 | 34.7 |
| Netherlands | 4.0 | 1.8 | 5.8 |
| Norway | 23.2 | 7.6 | 30.8 |
| Poland | 16.7 | 4.4 | 21.1 |
| Portugal | 26.0 | 1.9 | 27.9 |
| Rumania | 6.3 | 14.0 | 20.3 |
| Spain | 16.6 | 11.5 | 28.1 |
| Sweden | 53.8 | 9.0 | 62.7 |
| Switzerland | 20.9 | 7.8 | 28.7 |
| UK | 2.3 | 1.0 | 3.3 |
| USSR (former) | 15.4 | 12.6 | 28.0 |
| Yugoslavia (former) | 4.3 | 31.3 | 35.6 |
| Europe | 18.1 | 10.4 | 28.5 |

The percentage of forest in Europe varies from less than 1% in Ireland to more than 60% in Sweden and Finland. The total area in Europe covered by forests is about 28.5%.

An overview of the results of the procedure that allocates forests to soils is provided in the first column of Table 2. In this Table the percentage of the most important forest soils (soils covered by forest) is listed. In the second column of this Table, the percentages of forest soils are given for the case that forests are not allocated to poor soils and soils with steep slopes but are evenly distributed over all soil types in a grid. With an even distribution, more forest are allocated to the somewhat richer soils such as Podzoluvisols and Luvisols and less forest is allocated to the coarse textured Podzols.

Table 2 Dominant forest soils in Europe as percentages of the total forested areas

| Soil code | Soil Type | Area (%) | |
|-----------|----------------------|---------------------|-------------------|
| | | uneven distribution | even distribution |
| U | Ranker | 0.6 | 1.4 |
| Pl | Leptic Podzol | 0.9 | 0.8 |
| Bh | Humic Cambisol | 0.9 | 0.5 |
| Bk | Calcic Cambisol | 1.2 | 1.2 |
| Ph | Humic Podzol | 1.3 | 0.9 |
| E | Rendzina | 1.3 | 1.8 |
| Lc | Calcic Luvisol | 1.4 | 1.6 |
| Lo | Orthic Luvisol | 1.8 | 2.4 |
| Dd | Dystric Podzoluvisol | 2.2 | 2.5 |
| Pg | Gleyic Podzol | 2.5 | 1.5 |
| I | Lithosol | 2.7 | 2.9 |
| Lg | Gleyic Luvisol | 3.3 | 2.7 |
| Be | Eutric Cambisol | 4.7 | 3.7 |
| Od | Dystric Histosol | 7.1 | 9.4 |
| Bd | Dystric Cambisol | 8.8 | 7.7 |
| De | Eutric Podzoluvisol | 22.7 | 26.1 |
| Po | Orthic Podzol | 31.0 | 24.1 |

3.2 Precipitation and evapotranspiration

To compute the concentration and leaching of compounds in the soil, the (annual) water fluxes through the soil must be known. These water fluxes were derived from meteorological data available for the 1.0° longitude x 0.5° latitude grid. A precipitation data set is described by Leemans and Cramer, (1990), who interpolated selected records of average monthly precipitation from 1678 European meteorological stations for the period 1930-1960 for the 1.0° longitude x 0.5° latitude grid. Details of the interpolation procedure are given in Leemans and Cramer, (1990). Interception of rainwater by the forest canopy was calculated as a function of forest type (tree species) and precipitation amount as described by De Vries et al., (1993).

The sum of soil evaporation and transpiration was calculated by subtracting the canopy interception from the total evapotranspiration, obtained from an IIASA database according to a procedure described by De Vries et al., (1993). No quantitative information was available on the ratio between transpiration and soil evaporation.

Because soil evaporation is normally small compared to transpiration on an annual basis, the sum of evaporation and transpiration (instead of transpiration only) was used to compute the uptake of heavy metals. Based on data on the root distribution over the organic layer and the upper part of the mineral horizon in forest soils (De Vries et al., 1990), it was assumed that 25% of the total water loss from the forest soil by evaporation and transpiration is extracted from the organic layer and 20% from the upper 10 cm of the mineral soil.

3.3 Soil properties

As mentioned before, the texture class and slope class are known for all dominant soils and can be assigned for all associated soils on the FAO soil map. Organic matter content was obtained from selected soil profiles described in FAO, (1981), CEC, (1985) and Gardiner, (1987). Cation exchange capacity, also used in the functions to compute the adsorption constants for heavy metals, was calculated from clay content and organic matter content as described in Breeuwsma et al., (1986).

The nitrification fraction was based on data on nitrification rates in forest soils given by Tietema and Verstraten, (1991). The cumulative nitrification fraction was set to 0.5 for organic layers and 0.8 for mineral layers in acid sandy soils. The nitrification in the mineral layer of calcareous and clay soils was assumed to be complete, so a nitrification fraction of 1.0 was used (Kros et al., 1995).

Denitrification fractions were derived as a function of soil type as described by De Vries et al., (1993). Because these fraction were originally derived for the entire root zone (approx. 50 cm), they were multiplied by 0.5 for the organic layer and by 0.8 for the mineral layer as was done with the nitrification fractions.

3.4 Heavy metal uptake

Because preference factors for uptake for the heavy metals considered were hardly available, they were derived indirectly from data on heavy metal deposition and uptake from several sites in Europe.

Growth uptake can be calculated according to Equations (4), (5) and (6):

$$X_{gu} = \frac{fX_{up} \cdot E_t \cdot X_{td}}{(fX_{up} - 1) \cdot E_t + (P - E_t)} \quad (27)$$

Rearranging Equation (27) yields:

$$fX_{up} = \left(\frac{P - E_i - E_t}{E_t} \right) \cdot \left(\frac{X_{gu}}{X_{td} - X_{gu}} \right) \quad (28)$$

An overview of preference factors thus calculated for Pb, Cd and Cu is given in Table 3. Data on total deposition, growth uptake and throughfall were derived from a literature review on heavy metal fluxes in forest by Bergkvist et al., (1989). Except for two sites in Sweden (Varsjo and Gårdsjon) all data on uptake and total deposition refer to sites located in Germany (mainly the Solling area). Transpiration data were only available for a limited number of sites in the Solling area, indicating an average transpiration rate of 300 mm yr⁻¹. This is a value generally encountered in Central and Northern Europe (Roberts, 1983).

High preference factors (> 1) indicate preferential uptake whereas low preference factors indicate that the tree has no affinity for the element. Preference factors appear to be lowest for Pb with a relative small variance, whereas the opposite is true for Cu. The remarkably high variance in the uptake values for Cu, which is sometimes even higher than the total deposition, can be explained by the fact that Cu is a (minor) nutrient, in contrast to Pb and Cd. Cu deficiency is a well known problem in Dutch forests. This also puts major constraints on the concept of critical loads for copper.

Table 3 Total deposition, growth uptake and preference factors for the uptake of Pb, Cd and Cu in forests in Germany and Sweden

| Tree Species | Site | Through-fall (mm a ⁻¹) | Deposition (g.ha ⁻¹ .a ⁻¹) | | | Uptake (g.ha ⁻¹ .a ⁻¹) | | | Preference factor (-) | | |
|--------------|------------|------------------------------------|---|-----|-----|---|-----|-----|-----------------------|------|------|
| | | | Pb | Cd | Cu | Pb | Cd | Cu | Pb | Cd | Cu |
| Spruce | Solling | 770 | 797 | 44 | 977 | 76 | 3.2 | 300 | 0.17 | 0.12 | 0.69 |
| Spruce | Solling | 742 | 733 | 20 | 659 | 76 | 3.2 | 300 | 0.17 | 0.28 | 1.23 |
| Spruce | Solling | 815 | 408 | 6.0 | 47 | 46 | 2.8 | 7 | 0.22 | 1.5 | 0.30 |
| Spruce | Westerberg | 800 | 341 | 6.0 | 54 | 11 | 0.8 | 4 | 0.06 | 0.26 | 0.14 |
| Spruce | Wingst | 810 | 329 | 5.3 | 66 | 6 | 0.8 | 3 | 0.03 | 0.30 | 0.08 |
| Spruce | Spanbeck | 600 | 199 | 4.2 | 39 | 17 | 3.5 | 64 | 0.09 | 5.0 | * |
| Pine | Heide | 750 | 183 | 4.7 | 39 | 2 | 1.0 | 23 | 0.02 | 0.41 | 2.2 |
| Spruce | Varsjo | 428 | 100 | 2.5 | 10 | 34 | 1.5 | 13 | 0.22 | 0.64 | * |
| Pine | Gårdsjon | 530 | 77 | 3.2 | 9 | 34 | 1.5 | 13 | 0.61 | 0.68 | * |
| Beech | Solling | 771 | 475 | 36 | 697 | 39 | 1.4 | 310 | 0.14 | 0.06 | 1.3 |
| Beech | Solling | 744 | 437 | 16 | 470 | 49 | 1.4 | 310 | 0.19 | 0.14 | 2.9 |
| Beech | Solling | 658 | 335 | 5.0 | 85 | 40 | 0.8 | 24 | 0.16 | 0.23 | 0.47 |
| Oak | Heide | 750 | 199 | 3.1 | 82 | 13 | 1.7 | 17 | 0.11 | 1.8 | 0.39 |
| Beech | Harste | 419 | 161 | 3.0 | 48 | 8 | 1.1 | 30 | 0.02 | 0.23 | 0.66 |

* A value could not be calculated since uptake was higher than the deposition

The variation in preference factors for uptake for the various heavy metals is illustrated in Table 4, using the data given in Table 3.

The median values in Table 4 were used to compute the heavy metal uptake for coniferous and deciduous forests.

Table 4 Minimum, median and maximum preference factors for the uptake of Pb, Cd and Cu in coniferous and deciduous forests

| Forest type | Pb | | | Cd | | | Cu | | |
|-------------|------|------|------|------|------|-----|------|------|-----|
| | min | med | max | min | med | max | min | med | max |
| Coniferous | 0.02 | 0.17 | 0.61 | 0.12 | 0.41 | 5.0 | 0.08 | 0.50 | * |
| Deciduous | 0.02 | 0.14 | 0.19 | 0.06 | 0.23 | 1.8 | 0.39 | 0.66 | 2.9 |
| All | 0.02 | 0.15 | 0.61 | 0.06 | 0.29 | 5.0 | 0.08 | 0.66 | * |

* A value could not be calculated since uptake was higher than the deposition

3.5 Atmospheric deposition and filter factors

The atmospheric deposition of cadmium, copper and lead was computed at RIVM with the transport and deposition model TREND (Van Jaarsveld, 1994). Computations were based on emission estimates for 1990 by TNO (Berdowski and Veldt, 1994).

High cadmium and copper deposition is found in Belgium, the Netherlands, the Ruhr area, southern Poland, Czech Republic and northern Italy. Highest deposition of lead is found in the vicinity of large urban area (e.g. London district, Moscow region, Ruhr area) because gasoline combustion is the dominant source of lead emissions.

Because of their high surface roughness, forests act as a filter for various particles transported in the air. Therefore, rates of deposition of both acidifying compounds and heavy metals on forests can be substantially higher than the deposition on open land. 'Filter factors' were used to account for this effect of forests on the dry deposition of heavy metals. To obtain the deposition on a forest, the average deposition on a grid was multiplied by the filter factor. Filter factors for cadmium, lead and copper were computed from the difference in heavy metal content in the humus layer between sites with coniferous forest and non-forested sites at 7 locations in the Netherlands (Table 5; Winand Staring Centre, unpublished data).

Table 5 Contents of Cd, Cu, and Pb in the humus layer of conifers forests (CF) and non-forested (NF) land at five locations in the Netherlands in 1984

| Location | Contents (mg.kg ⁻¹) | | | | | | Ratio conifers/non-forested | | |
|-----------|---------------------------------|------|----|----|-----|----|-----------------------------|-----|-----|
| | Cd | | Cu | | Pb | | Cd | Cu | Pb |
| | CF | NF | CF | NF | CF | NF | | | |
| De Zilk | 0.70 | 0.47 | 30 | 14 | 145 | 81 | 1.5 | 2.1 | 1.8 |
| Ugchelen | 2.12 | 0.63 | 24 | 10 | 183 | 88 | 3.4 | 2.4 | 2.1 |
| Bathmen | 1.31 | 0.60 | 25 | 8 | 160 | 47 | 2.2 | 3.1 | 3.4 |
| Kootwijk | 1.44 | 0.46 | 32 | 11 | 182 | 83 | 3.1 | 2.9 | 2.2 |
| Doorwerth | 0.96 | 0.23 | 23 | 10 | 139 | 78 | 4.2 | 2.3 | 1.8 |
| Average | | | | | | | 2.9 | 2.6 | 2.3 |

For the three heavy metals considered in this study, the content in the organic top layer at the forested sites was about 2.5 times higher than that at the non-forested sites. Assuming that this difference is due entirely to the difference in deposition, the filter factor then becomes 2.5. This value agrees well with the filter factor of 2.1

for base cations estimated for coniferous forest by Ivens et al., (1989) on the basis of a literature survey of 47 sites in Europe.

As no measurements were available for the comparison of heavy metal contents in organic layers in deciduous forest with non-forested sites, the heavy metals/deciduous forest filter factor was set equal to the base cation filter factor for deciduous forests found by Ivens et al., (1989). This filter factor was estimated as 1.6.

4 Transfer functions between adsorption constants and soil characteristics

A large number of (sorption) experiments with heavy metals (Cu, Pb, Cd) and soils have been performed, and reported in literature. From these experiments a large number of models for the sorption onto soils and/or soil materials have been derived. However, most models do not include the major variables of the soil (pore water and solids), which together determine the sorption behaviour of the metals. Furthermore, most models published are only valid for, or calibrated against data of one or very few soils, thus making a broad applicability questionable.

The aim of this work is to integrate the existing data and knowledge about the sorption process in such a way, that relations are derived which fulfil the following three requirements:

1. The relations are based on a deterministic model of the sorption process.
2. The relations can be calibrated against existing measurements.
3. The relations can be used to estimate the heavy metal sorption behaviour of any soil, with specified error of estimate, when the macro-chemical characteristics of the soil are known (% clay, % organic carbon, cation exchange capacity, pH and pCa) and without the need for specific measurements or extra determinations of soil parameters.

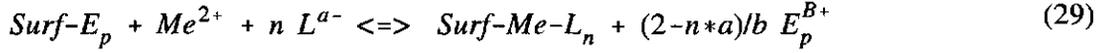
The relations derived in this study can only be applied to oxic conditions. In reduced conditions (sulphate reducing and/or methanogene), sorption relations for the heavy metals studied cannot be applied since the solubility of most of these metals is then regulated by precipitation of sulphide minerals.

4.1 Description of heavy metal adsorption

The sorption model developed is an equilibrium model. This means that the laws of thermodynamic equilibria can be applied. This choice is made for convenience. Furthermore, some kinetic studies show that the rate of adsorption of the metals onto soil materials is fast, with first-order half-times shorter than 10 minutes (e.g. Soldatini et al., 1976).

Secondly the sorption model has to obey the law of electroneutrality: When a metal ion is sorbed from the water phase, either the same amount of negative charge has to be adsorbed also (equivalent to precipitation), or the same amount of positive charge has to be expelled from the adsorption phase (equivalent to cation exchange). The real sorption relation will probably be somewhere in between these extremes. The second requirement for the sorption model is essential, since otherwise charged phases can occur. Since phases can be separated by physical means (e.g. centrifugation and/or filtration), charged water and charged solids can be produced. This is not in accordance with reality.

The equilibrium reaction equation for metal Me with charge $2+$ will be:



where

E_p = any (combination of) cation(s) exchanged with average charge $b+$

L = co-adsorbing ligand with charge $a-$

n = stoichiometric constant of ligand L in the adsorption reaction

Assuming that the stoichiometry of the sorption reaction is constant, we can define $(2-n*a)/b = z$, and applying the law of mass action to this Equation gives relation (30):

$$K_{eq} = (E_p)^z * \{Surf-Me-L_n\} / [(Me) * (L)^n * \{Surf-E_p\}] \quad (30)$$

where $()$ indicate molefractions in the water phase, and $\{\}$ indicate molefractions in the sorption phase. This relation will hold as long as each binding site has the same Gibbs Free Energy (GFE) of binding and the behaviour of the species in this system is thermodynamically ideal. When the surface sites are heterogeneous, as is commonly true for soils, the GFE will change with the amount Me adsorbed. We can correct for this deviation from ideality by introducing an activity correction for the sorbed species. Combining this with the Debye-Hückel theory for the activity correction of dissolved species, we get relation (31):

$$K_{eq} = aE_p^z * \{Surf-Me-L_n\} / [aMe * aL^n * F_{SEp} * \{Surf-E_p\}] \quad (31)$$

where aX denotes the activity in the water phase of X , and F_{SX} is the activity coefficient for the sorbed phase X .

When it is assumed that the activity correction for the sorbed species can be approximated with a power function of the molefraction of the adsorbed species (Langmuir, 1981), which describes the decrease of the GFE of binding of a metal when the amount of metal sorbed is increasing, then the Equation becomes:

$$K_{eq} = aE_p^z * \{Surf-Me-L_n\}^{(1+\alpha)} / [aMe * aL^n * \{Surf-E_p\}^{(1+\beta)}] \quad (32)$$

where

$F_{SMe} = \{Surf-Me-L_n\}^\alpha$, $\alpha \geq 0$ ($\alpha = 0$ means a homogeneous surface)

$F_{SEp} = \{Surf-E_p\}^\beta$

The power α is a measure of the width of the distribution of GFE of binding (large α means a broad distribution, small α a narrow distribution of sorption energies).

Considering the fact that the metal is a micro-chemical, and a change of the amount of metal sorbed will not influence the value of the molefraction of sorbed E_p , the value of $\{Surf-E_p\}^{(1+\beta)}$ can be set to unity.

Linearizing this Equation by taking the logarithm of both sides, and rearranging both sides gives the following relation:

$$\log(\{Surf-Me-L_n\}) = (1+\alpha)^{-1} * [\log(K_{eq}) + \log(aMe) + n * \log(aL) - z * \log(aE_p)] \quad (33)$$

We can change from molefraction to amount sorbed by introducing the total number of sites, N_s (moles/kg soil). When we define

$$\{Surf-Me-L_n\} = M_{me} / N_s \quad (34)$$

and define $(1+\alpha)^{-1} = f$,
then the Equation can be written as:

$$\log(M_{Me}) = \log(N_s) + f * [\log(K_{eq})] + n * \log(aL) - z * \log(aE_p) + f * \log(aMe) \quad (35)$$

This relation is a Freundlich equation, with Freundlich exponent f , dependent on the activity of the metal in solution, and with the Freundlich constant which is the combination of all other terms in this Equation:

$$\log(M_{Me}) = \log(K_F) + f * \log(aMe) \quad (36)$$

The assumptions underlying this model are:

- 1) constant stoichiometry of the sorption reaction,
- 2) the introduction of the power function to describe the surface heterogeneity,
- 3) neglecting the effect of adsorption of Me on the molefraction of the sorbed macroelements.

We can conclude at this point that from thermodynamic equilibrium, combined with the principle of electroneutrality, and the power function, we expect the sorption of the metal onto soils to follow Freundlich type of behaviour, where the Freundlich exponent is a measure of the heterogeneity of the available sites, and the Freundlich constant a function of the Freundlich exponent f and the average binding strength, the co-adsorbing anions, the competing cations and the number of sites available. It further shows that all relations in this system have to be taken as log-log rather than linear.

4.2 Problems with the interpretation of published soil adsorption data

Many metals form extremely strong complexes with dissolved organic carbon (DOC), especially with humic and fulvic compounds (e.g. Mantoura et al. (1978), Stevenson (1976)). Of the metals studied here, especially Cu and Pb form strong complexes with DOC. This fact has often been neglected, or underestimated in adsorption studies published in literature.

Qualitatively, the problem is as follows:

(Ad)sorption studies for metals are performed by shaking soil samples with a solution containing the metal. After some time (usually > 24 h), the solution phase is separated from the solids (centrifugation and/or filtration), and the total dissolved metal concentration is measured (mostly using a carbon rod furnace AAS). The amount sorbed is determined by calculation of the difference between the amount of metal added, and the amount of metal measured in the solution phase. The next step is to construct some kind of isotherm (e.g. linear, Langmuir, Freundlich), connecting the sorbed amounts with the measured dissolved amounts.

The problem is 3-fold:

- 1) many times, the amount of metal already sorbed in the soil itself is not taken into account. This is mostly the lesser of the three errors, since most experiments use concentrations which are much higher than this amount. However, especially at low metal concentrations the contribution from the native metal cannot be disregarded.
- 2) The adsorption of metal changes the pH of the solution (the adsorption releases H^+ from the surface). This in effect leads to a reduced adsorption strength (the adsorption is pH dependent). Therefore, when working with increasing amounts of metal, the sorption curve tends to bend, inherently producing a quasi-Freundlich. This effect can be countered by either adjusting the pH during the sorption experiment, or by recording the pH of the final sorption solution.
- 3) By mixing of soil and some solution, a certain amount of DOC (humic and fulvic compounds) will dissolve from the soil. This DOC will form complexes with the metal. Therefore, the activity of the metal in the solution phase is not equivalent to the dissolved concentration. Worse, the relative amount complexed decreases with higher metal concentration (since the number of sites on the DOC is limited).

An example of errors (1 and 3) acting together to produce results which are difficult to interpret, is given by the adsorption studies for copper of Jarvis (1981) who postulates for each soil investigated two Freundlich curves. The 'high affinity' curve of Jarvis is an artefact of DOC complexation and native metal. The 'real' sorption curve of the soil is more or less represented by his 'low affinity' curves. Other examples of adsorption data which are difficult to interpret are Abd-Elfattah and Wada (1981), Kurdi and Doner (1982), Hassett (1974) and Harter (1979, 1983).

The complexation with DOC is pH dependent. The adsorption to the soil solids is also pH-dependent. It is however not necessarily so that both pH-dependencies are the same. This may introduce a pH dependency in the relation between the activity of the metal and the measured concentration. Therefore, the pH dependency of metal sorption cannot be evaluated without knowledge of the (pH dependency of the) organic complexation, unless it is reasonably safe to assume a negligible contribution of the organic complexes. The amount of DOC released from the solids during the sorption experiment is a function of a) soil properties, b) soil:solution ratio, c) calcium concentration in solution, and d) sodium and potassium concentration. Generally, the amount of DOC increases with an increase of the soil:solution ratio, with an increase of the sodium and potassium concentration, and with a decrease of the calcium concentration in solution (Bril, 1993, *in prep.*).

It is therefore often impossible to assess the activity of the metal, when it is not measured explicitly in the solution. For copper this measurement can be performed with an Ion Selective Electrode (ISE), provided the reference solutions are carefully chosen. A good method is described by Sanders and Bloomfield (1980) and Sanders (1982).

From the above, it can be concluded that principally, the only literature data that can be used for sorption model construction are those article(s) which include the measured activity of the metal, or where it can be reasoned that complexation plays only a minor role in the sorption liquids. For cadmium the last argument often holds, since cadmium forms much weaker complexes with DOC than copper or lead.

4.3 Application of the model to copper sorption

4.3.1 Data sets used to fit the model

An article which provides sorption curves as function of ISE copper activity measurements is by Sanders (1982). Cavallaro & McBride (1977) use ISE measurements too. However, their data are produced in a less accessible way, and thus not easily available (pH is not controlled, it is measured. The data for pH measurements are supplied in a graph which does not allow for more accurate determination than approx. 0.2 pH units. Cu activity has to be measured from the same graph, with the same uncertainty. It then has to be assumed, that an increase in activity corresponds with an increase in concentration, to link the data points to the points in another graph which give the relation between total dissolved and sorbed copper).

Lexmond (1980) uses a resin-method to determine the copper activity. Although possibly less reliable than carefully performed ISE measurements (since more assumptions have to be made, and more steps have to be performed before getting results), these measurements seem to give a good impression of the relation between copper sorption and copper activity.

Other literature data which satisfy the requirements for copper have not been found. However, some 'classical' sorption data can be used. The useability of the classical data depends on the estimated extend of organic complexation. The smaller this is, the better useable the data.

Adsorption data become less reliable (because organic complexation plays a larger role) with higher soil:solution ratios, with lower Ca concentrations, with higher sodium and potassium concentration, and with higher pH. Therefore adsorption experiments with a very small soil: solution ratio, at high calcium concentrations, at relatively low pH and with not to low metal (Cu and Pb) concentrations (higher than the 0-50 ppb level) will be generally useable, since the complexation is then relatively unimportant compared to the total dissolved metal. An article which fulfils these conditions for copper is the article of McLaren and Crawford (1973b). They

use a soil: solution ratio of 1:200, a 'background electrolyte' of 0.05 M CaCl₂, and a pH of 5.5. Furthermore, their experimental concentration range of copper is from 0.1 to 10 mg Cu/L. The combination of these factors effectively suppress the DOC concentration (estimated DOC < 1 mg C/L), and therefore the data can be used to construct the model.

The work of Sanders (1982) is extremely important: It allows for the estimation of pH influences, and Ca competition effects on sorption of copper. It shows clearly that when using the dissolved concentration instead of the activity, one reaches completely different sorption equations, with different slopes.

The sorption of copper is described as a function of the solute activity of copper, not the solute concentration. The relation between the solute activity of copper and the solute concentration of copper has to be assessed with another model. Since the activity of copper in solution is strongly related to complexation, especially with DOC, it has to be kept in mind that use of the model presented here without a decent DOC and complexation model, does not give any relevant results with respect to total dissolved copper concentrations in soil solutions.

4.3.2 Model application

The sorption model presented here is based on combining the results of Sanders (1982) with the results of McLaren and Crawford (1973a,b) as shown in table 6.

Applying Equation (35) to the adsorption data provided by Sanders (1982) gives the following relation (medium = .01 M CaCl₂):

$$\log M_{cu} = (-5.32 \pm 0.044) + (0.70 \pm 0.015) * pH + (0.55 \pm 0.01) * \log a_{Cu} \quad (37)$$

$$R^2 = .99, N = 28$$

pH = pH of adsorbing solution

The fit of this model to the sorption data is given in Figure 1. Any conclusion with respect to other dependencies of $\log K_F$ on soil parameters cannot be determined from these data, since the soils used by Sanders have essentially the same values for key soil parameters (% organic carbon (%OC), % clay minerals (%Cy) and cation exchange capacity (CEC, eq/kg)).

The dependence of the copper sorption on calcium ion activity can be assessed from the measurements presented in Figure 2 (data of Sanders, 1982). The Figure shows the measured activity of copper in water and 10⁻² M CaCl₂ incubates of the same soils as used for the sorption isotherms of Figure 1.

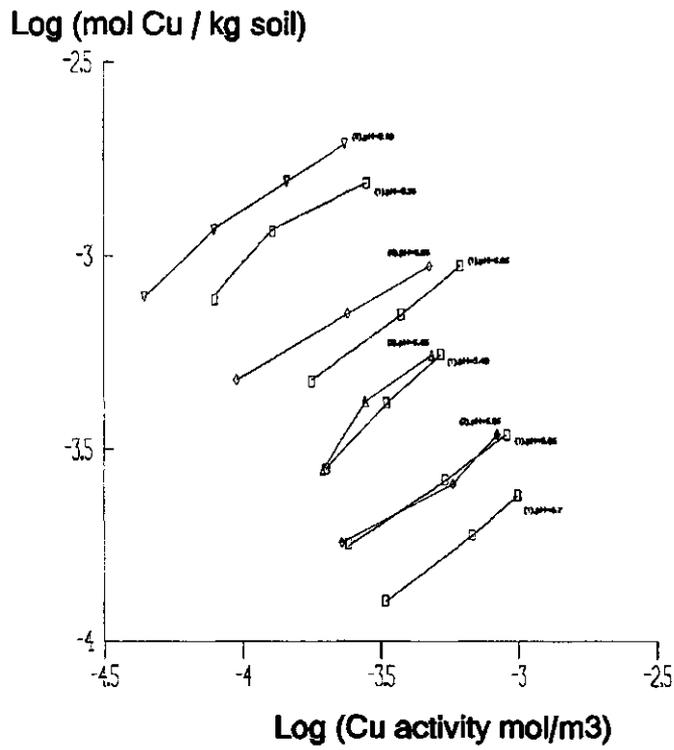


Fig. 1 Sorption data measured by Sanders (1982)

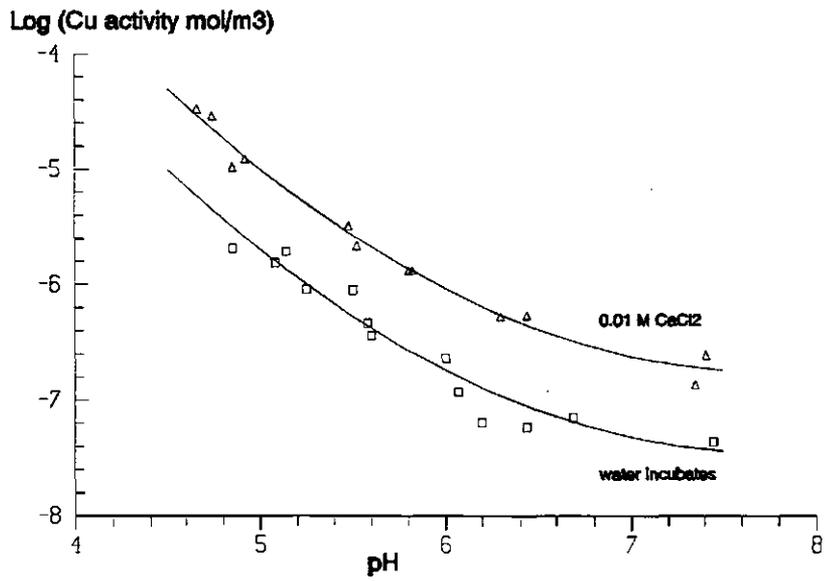


Fig. 2 Measured soil incubation data by Sanders (1982)

Table 6 Soil data used to construct copper sorption model

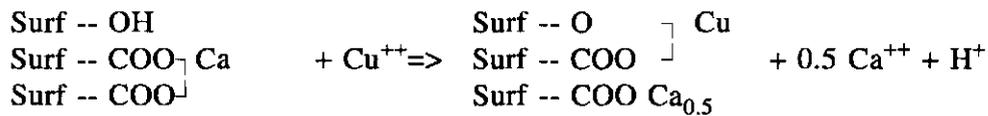
| Soil # | pH-CaCl2 .05 M | %OC eq/kg | %Clay (%Fe) | CEC (%Mn) L/kg | Fe-ox L/mgCu | Mn-ox mgCu/kg | K-lin 'meas' | K-Lang model | Qmax | log(Kf) | log(Kf) |
|--------|-------------------|--------------|----------------|-------------------|-----------------|------------------|-----------------|-----------------|------|---------|---------|
| 1 | 5.0 | 1.9 | 15.2 | .0828 | 1.4 | .026 | 614.8 | 1.06 | 580 | -1.062 | -.917 |
| 2 | 6.1 | 9.1 | 60.2 | .1380 | 2.7 | .057 | 1041.0 | .30 | 3470 | -.589 | -.572 |
| 3 | 4.9 | 0.4 | 37.5 | .1187 | 2.2 | .043 | 326.4 | .96 | 340 | -1.317 | -1.20 |
| 4 | 3.2 | 2.0 | 9.7 | .0413 | 1.9 | .019 | 596.4 | .71 | 840 | -.986 | -1.04 |
| 5 | 5.8 | 2.8 | 9.8 | .1146 | 0.2 | .006 | 1390.0 | 1.39 | 1000 | -.767 | -.738 |
| 6 | 5.9 | 7.2 | 14.4 | .2117 | 0.9 | .006 | 2396.1 | 1.47 | 1630 | -.540 | -.433 |
| 7 | 6.4 | 2.4 | 28.0 | .1402 | 13.5 | .101 | 1037.5 | .83 | 1250 | -.782 | -.788 |
| 9 | 5.9 | 9.1 | 6.7 | .2803 | 0.4 | .005 | 4747.8 | 1.93 | 2460 | -.299 | -.275 |
| 10 | 5.1 | 7.2 | 3.8 | .2391 | 0.2 | .003 | 3894.0 | 1.65 | 2360 | -.353 | -.323 |
| 11 | 6.2 | 1.4 | 6.4 | .0791 | 1.0 | .006 | 583.0 | .53 | 1100 | -.957 | -.935 |
| 12 | 6.0 | 1.9 | 5.6 | .0913 | 0.2 | .003 | 864.0 | .64 | 1350 | -.824 | -.833 |
| 13 | 5.4 | 6.2 | 15.6 | .5134 | 1.5 | .018 | 7109.4 | 1.23 | 5780 | -.030 | .023 |
| 14 | 7.1 | 1.1 | 5.4 | .1288 | 0.7 | .007 | 1233.0 | .90 | 1370 | -.734 | -.862 |
| 15 | 5.9 | 2.2 | 7.2 | .0976 | 0.3 | .004 | 891.0 | .55 | 1620 | -.779 | -.804 |
| 16 | 6.4 | 7.5 | 7.3 | .2331 | 0.3 | .004 | 3783.5 | 1.61 | 2350 | -.360 | -.361 |
| 17 | 7.0 | 3.9 | 20.5 | .2192 | 2.1 | .046 | 2763.3 | 1.51 | 1830 | -.483 | -.570 |
| 18 | 5.3 | 2.9 | 23.5 | .1376 | 2.1 | .047 | 1122.4 | .46 | 2440 | -.645 | -.744 |
| 19 | 5.7 | 5.6 | 19.1 | .2249 | 1.7 | .107 | 2604.0 | 1.20 | 2170 | -.464 | -.487 |
| 20 | 5.4 | 6.6 | 27.1 | .2003 | 3.4 | .159 | 2400.0 | .80 | 3000 | -.415 | -.502 |
| 21 | 6.4 | 3.6 | 27.4 | .1918 | 3.1 | .158 | 1586.0 | .65 | 2440 | -.560 | -.634 |
| 22 | 6.8 | 3.4 | 50.5 | .3339 | 2.1 | .075 | 2058.0 | 1.05 | 1960 | -.544 | -.557 |
| 23 | 6.8 | 2.2 | 12.5 | .1288 | 1.2 | .03 | 788.8 | .58 | 1360 | -.841 | -.775 |
| 24 | 5.6 | 7.6 | 45.8 | .3559 | 2.0 | .032 | 3432.2 | 1.31 | 2620 | -.364 | -.375 |

The calcium activity in 10^{-2} M CaCl_2 solution is estimated at $10^{-2.35}$ M/L (including organic complexation of calcium). The activity of calcium in the water extracts is estimated to be $10^{-3.8}$ M/L. The activity of copper is 0.73 ($\log(\text{mol/m}^3)$) higher in the high calcium solution than in the low calcium solution, irrespective of pH. Since both are in equilibrium with the same solid phase concentration, the effect must totally be contributed to the effect of calcium on the sorption process. If it is assumed that the activity of calcium appears in the Equation as a constant multiplied with the logarithm of the calcium activity, this determines the constant at -0.277.

This number is very close to -0.275. If the number is -0.275, than the Equation (8) can be rewritten as:

$$\log M_{Cu} = \log K_F + (0.70 \pm 0.015) * pH + (0.55 \pm 0.01) * \log (a_{Cu}/a_{Ca}^{0.5}) \quad (38)$$

From a thermodynamic viewpoint the last term in Equation (38) is very interesting: It suggests that with every copper atom adsorbed, there is a release of 0.5 calcium atoms. At the same time the pH term suggests that there is an extra release of 1.27 H^+ atoms. This favours the mechanism of sorption:



The coefficient of H^+ following from this relation would be 1.0, which is less than found. However, the calcium dependency is exactly explained.

Lexmond (1980) finds a slope between pCu (the negative logarithm of the copper activity) and the pH of exactly 1.0 (four copper levels give slopes of resp. 1.07, 0.97, 1.02 and 0.99). Since we feel that ISE measurements need less assumptions, and are therefore more reliable than the resin-method used by Lexmond, these measurements are only referred to as an indication of the validity of the presented model, and not to estimate the pH dependency of the adsorption.

The Freundlich exponent 0.55 is a measure for the decrease in surface binding strength with increased surface coverage with copper. The mechanism also explains why the slope is decreasing for pH values above 7. At such high pH values, the surface OH groups start deprotonizing, thus reducing the amount of protons displaced by the copper ions. The role of aluminum ions at extremely low pH values ($\text{pH} < 4.5$) can be expected to be the same as the role of the calcium ions above pH values of 4.5. There is however no literature on the subject of sorption of copper ions at such low pH values, thus it is impossible to verify the behaviour of copper at these low pH values.

The value of $\log K_F$ in Equation (7) can be assessed from the sorption data of McLaren and Crawford (1973a,b). Table 6 shows the data provided by McLaren and Crawford (1973a,b). For 23 soils from the United Kingdom, with very different characteristics, adsorption curves were constructed for $\text{pH}=5.5$ and $5 \cdot 10^{-2}$ M CaCl_2

electrolyte solution. The data were presented as Langmuir curves. From the Langmuir curves, by assuming the slope of 0.55 with the activity of copper, applying the Langmuir parameters to the concentration range used by McLaren and Crawford in their experiments, and using an ionic strength correction factor of 0.3 for the activity of the Cu^{++} ion, values of $\log K_F$ were calculated. A regressing of $\log K_F$ on soil properties shows a strong relationship between the %OC, CEC and %Cy and $\log K_F$ according to Equation (39):

$$\begin{aligned} \log K_F = & -0.31 \pm 0.075 \\ & + (0.462 \pm 0.060) * \log (\%OC) \\ & + (0.524 \pm 0.097) * \log (CEC, eq/kg \text{ soil}) \\ & - (0.142 \pm 0.050) * \log (\%CY) \end{aligned} \quad (39)$$

$$R^2 = 0.94, N = 23$$

The individual terms in this model can be qualitatively explained: The constant gives the affinity of copper to adsorb. All other terms influence the strength of adsorption because together they define a measure of the number of sites available for copper to adsorb. Equation (39) states that the total number of sites available to copper can be expressed by the %OC and CEC. The clay fraction contributes to the CEC, but the average binding strength to the clay sites is less than the binding strength to the other sites. Therefore the model diminishes the contribution of the clay sites to the CEC (the negative coefficient for %Cy in Equation (39) acts as a weighting factor for the clay sites of the CEC).

The fit of this model is shown in Figure 3. The fit can be improved slightly further by including manganese ($R^2 = 0.95$), which however only changes the coefficient for %Cy (becomes more negative) and the constant, but does not change significantly

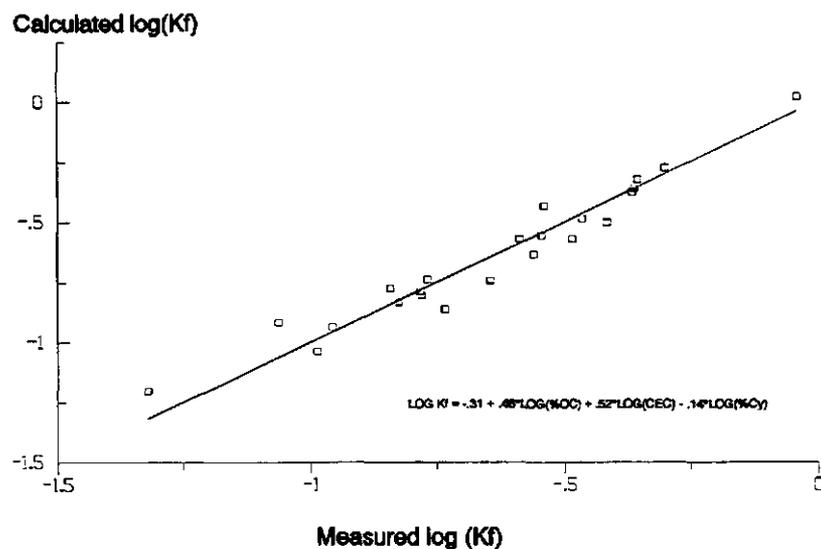


Fig. 3 Fit of copper sorption model

the contribution of %OC and CEC. We feel Equation (39) satisfactory explains the variation in the data of McLaren and Crawford, and it is not necessary to include the manganese content (possibly with the exception of soils very rich in manganese).

Combining Equation (39) with Equation (38) and substituting the appropriate values of pH and calcium activity (the concentration of 0.05 mol CaCl₂/L gives an activity of calcium of 0.015 mol/L = 15 mol/m³) we get the final copper sorption model:

$$\begin{aligned} \log M_{Cu} = & -3.85 \pm 0.08 \\ & + (0.70 \pm 0.02) * pH \\ & + (0.46 \pm 0.06) * \log (\%OC) \\ & + (0.52 \pm 0.10) * \log (CEC, eq/kg soil) \\ & - (0.14 \pm 0.05) * \log (\%C_Y) \\ & + (0.55 \pm 0.01) * \log (a_{Cu}/a_{Ca}^{0.5}) \end{aligned} \quad (40)$$

where

$$\begin{aligned} M_{Cu} &= \text{mol Cu/kg solids} \\ a_{Cu} &= \text{mol Cu/m}^3 \\ a_{Ca} &= \text{mol Ca/m}^3 \end{aligned}$$

Looking back at Equation (36), the final relation for K_F becomes:

$$K_F = 10^{-3.85} * 10^{0.7 * pH} * \%OC^{0.46} * CEC^{0.52} * \%C_Y^{-0.14} \quad (41)$$

The final Freundlich model for the sorption of copper in soils becomes:

$$M_{Cu} = K_F * (a_{Cu}/a_{Ca}^{0.5})^{0.55} \quad (42)$$

It has to be stressed again that this Equation can only be used together with a model which relates the activity of copper to the total dissolved concentration in the soil solution. The activity of copper in normal soil solutions is two to three orders of magnitude lower than the total concentration (Sanders (1982), Hodgson et al., (1966)).

4.4 Application of the model to cadmium sorption

The data to fit the model (Eq. (35), (36)) were taken from Chardon (1984) and Christensen (1989). Data were available for a total number of 14 soils (12 Chardon, 2 Christensen). Some important characteristics of these soils are given in Table 7.

As Chardon and Christensen both showed, H⁺ and calcium are the main competitors for cadmium for sorption sites at the studied pH range (4 < pH < 8). So E_p of Equation (35) is replaced with the activity of H⁺ and Ca²⁺.

$$\log(K_F) = C1 + C2 * \log(\text{soilproperties}) + C3 * pH + C4 * \log(aCa) \quad (43)$$

Table 7 Soil data used to construct cadmium sorption model

| Soil | %Clay | %OC | CEC eq/kg | pH | K_F | f | $\log(K_F)$ | $\log(K_F)$ n=0.82 | $\log(K_F)$ model |
|-------------------------|-------|------|--------------|------|-------|-------|-------------|-----------------------|----------------------|
| sand 1 | 5.2 | 0.9 | 0.060 | 4.01 | 0.019 | 0.818 | -1.717 | -1.719 | -1.619 |
| sand 2 | 2.1 | 0.8 | 0.060 | 4.92 | 0.112 | 0.743 | -0.951 | -1.013 | -1.069 |
| sand 3 | 4.9 | 0.9 | 0.068 | 5.19 | 0.204 | 0.778 | -0.690 | -0.724 | -0.968 |
| sand 4 | 3.6 | 4.0 | 0.160 | 4.92 | 0.284 | 0.827 | -0.546 | -0.540 | -0.699 |
| loess 1 | 5.8 | 1.6 | 0.092 | 4.00 | 0.015 | 0.817 | -1.818 | -1.821 | -1.449 |
| loess 2 | 5.4 | 2.1 | 0.103 | 6.85 | 1.136 | 0.810 | 0.055 | 0.047 | 0.032 |
| peaty clay | 21.2 | 14.3 | 0.560 | 4.00 | 0.232 | 0.901 | -0.634 | -0.569 | -0.800 |
| peat | 0.8 | 40.5 | 1.340 | 4.32 | 0.831 | 0.914 | -0.081 | -0.006 | 0.080 |
| clay 1 | 11.5 | 1.1 | 0.126 | 7.93 | 4.258 | 0.745 | 0.629 | 0.569 | 0.581 |
| clay 2 | 17.9 | 1.7 | 0.164 | 7.73 | 3.618 | 0.817 | 0.558 | 0.556 | 0.549 |
| clay 3 | 40.8 | 1.6 | 0.348 | 5.64 | 0.419 | 0.896 | -0.378 | -0.317 | -0.255 |
| clay 4 | 14.0 | 4.9 | 0.342 | 7.63 | 4.265 | 0.939 | 0.630 | 0.725 | 0.844 |
| sandy loam ^o | 18.0 | 0.3 | 0.176 | 6.00 | 0.447 | 0.836 | -0.350 | -0.337 | -0.286 |
| loamy sand ^o | 6.2 | 0.4 | 0.075 | 6.00 | 0.337 | 0.828 | -0.472 | -0.466 | -0.545 |

From independent measurements of Chardon (1984) the coefficient C4 can be estimated to be -0.41. The value of f found for the different soils varies between 0.75 and 0.9 with an average of 0.83 (± 0.06). This is very close to 0.82, which in turn is exactly -2 times the coefficient for $\log(aCa)$. This makes it very tempting to use instead of the activity of cadmium the ratio $aCd/aCa^{0.5}$ in Equation (36). This means that the mechanism for cadmium sorption equals the mechanism found for copper (c.f. 4.2). Fitting the Ca-adjusted Equation (36) to the adsorption measurements, and using a Freundlich exponent of 0.82, the values found for $\log(K_F)$ are given in Table 7. Fitting these $\log(K_F)$ values to the soil properties and experimental pH values gives the relation:

$$\begin{aligned} \log(K_F) = & -3.15 \pm 0.19 \\ & + (1.00 \pm 0.14) * \log(CEC) \\ & + (0.50 \pm 0.04) * pH \\ & - (0.24 \pm 0.13) * \log(\%Cy) \end{aligned} \quad (44)$$

$$R^2 = 0.96, N=14$$

and

$$M_{cd} = K_F * (aCd/aCa^{0.5})^{0.82} \quad (45)$$

where

M_{Cd} = mol Cd/kg soil

CEC = cation exchange capacity of the soil (Bascomb) in eq/kg

pH = pH of the equilibrium solution

%Cy = percentage < 2 μ m

ac = activity of cadmium in solution, expressed in mol Cd/m³

aba = activity of calcium in solution, expressed in mol Ca/m³

The fit of the model for $\log(K_F)$ is given in Figure 4. Comparing Equation (44) and (45) with Equation (35) and assuming that the CEC term describes the $\log(N_s)$ term of Equation (35) shows that

$$\log(K_{eq}) = -3.84 - 0.29 * \log(\%Cy) - n * \log(aL) \quad (46)$$

If the coefficient of the pH is interpreted as a stoichiometric constant, the value of n is 0.39 ($= 1 - 0.5/0.82$). No further conclusions about the effects of counter-ions can be given, and the term is considered to be constant in the final model.

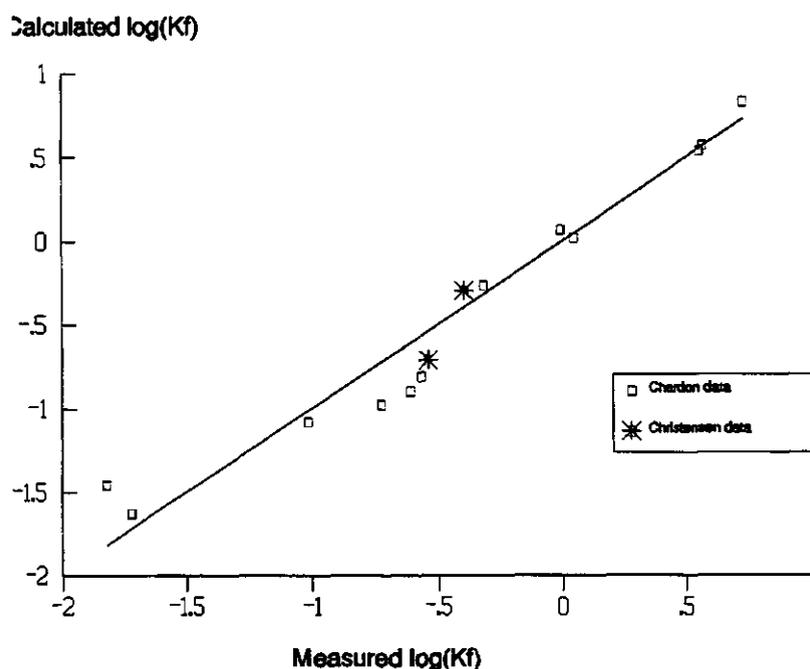


Fig. 4 Fit of cadmium sorption model

The term which describes the effect of the clay fraction can qualitatively be explained: When the contribution of the clay fraction to the total number of sorption sites (CEC) increases, the average binding strength decreases (Equation 46). This means that on average, organic matter is a better cadmium sorbent than clays (c.f. copper sorption, 4.3). It does not, however, exclude the contribution of the clay fraction to the sorption process, as is done by de Haan et al. (1987). This contribution is included in the CEC term.

4.5 Application of the model to lead sorption

Data, necessary to generate a sorption model of lead for soils are scarce in literature. A substantial amount of work has been done to study the sorption of lead onto individual compounds of soils (e.g. Bittel and Miller, 1974, Stevenson, 1976, Brown,

1979). How to use these data for real soil systems is not obvious. Measurements on whole-soils are scarce. Furthermore, a lot of the data which are presented in the literature for whole soils, cannot be used since the most essential parameters influencing the sorption of lead are not taken into consideration, or neglected. Examples are the studies on lead sorption by Hassett (1974) and Harter (1983). Both studies do not control 'background' electrolyte (especially not the calcium activity). Also, pH is measured independent from the sorption experiments (Harter gives pH values measured in a 1:1 soil:water suspension, Hassett does not specify by which method the pH is measured). From the concentrations of lead used in their sorption experiments, it is clear that the pH will strongly be influenced by the sorption process itself. (Hassett used unbuffered adsorption solutions containing 125 to 500 mg Pb/L, Harter up to 150 mg/L). For low concentrations (less than 100 µg/L) organic complexation cannot be ruled out, since the soil:solution ratios are 1:50 resp. 1:100, which allows for 1-5 mg C/L of dissolved organic carbon (higher for higher amount of solids). However, the measurements are all at such high concentrations of Pb that this error can be neglected.

One other source which has been found in literature is Riffaldi et al. (1976), and the companion paper of Soldatini et al. (1976). These papers give sorption measurements for 12 Tuscany soils. 10 of these soils are calcareous, 2 are non-calcareous. The background electrolyte used is 0.05 M CaCl₂ (with Riffaldi et al., 1976). The pH of the sorption experiments is not controlled. However, since they work with a high concentration of CaCl₂, and relatively much less Pb, and most of the soils are well buffered because of the presence of calciumcarbonate, this is less of a problem for the calcareous soils than with the measurements of Harter or Hassett. The pH given in the articles is not specified (probably pH .05 M CaCl₂ or pH water). Since the pH is not controlled during the sorption experiments, substantial changes in pH can be expected for the non-calcareous soils. Therefore, these two soils are not used in the evaluation of model constants. Assuming the pH for all sorption experiments performed with the calcareous soils to be 8.0, the re-fitted sorption data can be regressed against soil parameters (%OC, %Cy, CEC).

Re-fitting is necessary since the published sorption curves are Langmuir isotherms. Based on the behaviour of Pb towards humic acid (Stevenson, 1976), the model which has been derived for the behaviour of copper in soils is taken as the framework in which the Pb behaviour is fitted. Therefore, the Langmuir curves given by Soldatini et al. have been recalculated to fit to a Freundlich exponent of 0.55. Fitting the values of log K_F to the provided soil parameters, and assuming the relation found for copper with respect to Freundlich exponent to hold, we find:

$$\log K_F = (1.5556 \pm 0.150) + 0.624 * \log (CEC) + 0.462 * \log (\%OC) \quad (47)$$

$$R^2 = 0.78, N = 10$$

The fit of this model is shown in Figure 5.

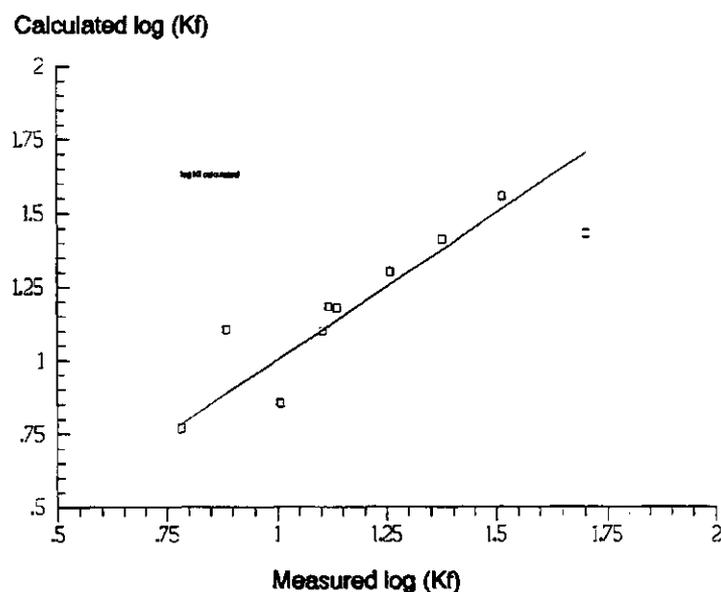


Fig. 5 Fit of lead sorption model

This relation has to be made pH-dependent. Assuming a pH coefficient of 0.6 based on the assumption that the pH coefficient of Pb sorption will be somewhere in between the coefficient of copper (0.7) and cadmium (0.5), and taking into account the estimated pH of the experiments of 8.0, and correcting for the calcium activity, the final sorption Equation for lead becomes:

$$\log M_{pb} = -3.567 \pm 0.25 + 0.6 * pH + 0.624 * \log(CEC) + 0.462 * \log(\%OC) + 0.55 * \log(a_{pb}/a_{Ca}^{0.5}) \quad (48)$$

- M_{pb} = mol Pb/kg soil
- a_{pb} = activity of dissolved Pb, mol Pb/m³
- a_{Ca} = activity of dissolved Ca, mol Ca/m³
- CEC = eq / kg soil
- pH = pH of soil solution

The error in the constant of Equation (48) is estimated from the regression error of Equation (47), combined with a standard error for the estimation of the pH of the sorption experiment of 1/3 pH unit.

It has to be stressed that this model is based on many assumptions (Freundlich exponent, pH, pH coefficient, Ca dependency), and therefore not very reliable. It is however the best possible model we can derive from the available literature data.

4.6 Model calculations for a sandy loam soil

To show the model performance, calculations are performed for an 'example' soil. The soil chosen is a sandy loam. Characteristics are: CEC = .15 eq/kg, %OC = 2.5, %Cy = 10. Furthermore, we have to specify some solution parameters: Total dissolved calcium = .5 mol/m³ (20 mg/L), DOC = 50 g C/m³, dissolved C-inorganic = 1 mol/m³. Next, we need a speciation model for the soil solution, since the sorption model will only provide activities of the dissolved metals.

Table 8 Association constants of complexes used to calculate dissolved metal

| Reaction | | | | log K _{ass} | Reference | |
|------------------|---|-------------------------------|----|------------------------------------|-----------|----------------|
| Ca ⁺⁺ | + | HCO ₃ ⁻ | => | CaHCO ₃ ⁺ | 1.1 | Sposito, 1980 |
| Ca ⁺⁺ | + | CO ₃ ²⁻ | => | CaCO ₃ ⁰ | 3.2 | Sposito, 1980 |
| Ca ⁺⁺ | + | HHUM ⁻ | => | CaHHUM | 2.2 | Mantoura, 1978 |
| Ca ⁺⁺ | + | HUM ²⁻ | => | CaHUM | 4.6 | Mantoura, 1978 |
| Cd ⁺⁺ | + | HCO ₃ ⁻ | => | CdHCO ₃ ⁺ | 2.1 | Ball, 1980 |
| Cd ⁺⁺ | + | CO ₃ ²⁻ | => | CdCO ₃ ⁰ | 5.4 | Ball, 1980 |
| Cd ⁺⁺ | + | HHUM ⁻ | => | CdHHUM | 2.7 | Mantoura, 1978 |
| Cd ⁺⁺ | + | HUM ²⁻ | => | CdHUM | 6.1 | Mantoura, 1978 |
| Cu ⁺⁺ | + | HCO ₃ ⁻ | => | CuHCO ₃ ⁺ | 2.7 | Ball, 1980 |
| Cu ⁺⁺ | + | CO ₃ ²⁻ | => | CuCO ₃ ⁰ | 6.73 | Ball, 1980 |
| Cu ⁺⁺ | + | HHUM ⁻ | => | CuHHUM | 3.9 | Mantoura, 1978 |
| Cu ⁺⁺ | + | HUM ²⁻ | => | CuHUM | 10.0 | Mantoura, 1978 |
| Pb ⁺⁺ | + | HCO ₃ ⁻ | => | PbHCO ₃ ⁺ | 2.9 | Ball, 1980 |
| Pb ⁺⁺ | + | CO ₃ ²⁻ | => | PbCO ₃ ⁰ | 7.0 | Sposito, 1980 |
| Pb ⁺⁺ | + | HHUM ⁻ | => | PbHHUM | 3.7 | Estimated* |
| Pb ⁺⁺ | + | HUM ²⁻ | => | PbHUM | 9.7 | Estimated* |
| H ⁺ | + | CO ₃ ²⁻ | => | HCO ₃ ⁻ | 10.33 | Ball, 1980 |
| H ⁺ | + | HCO ₃ ⁻ | => | CO ₂ + H ₂ O | 6.35 | Ball, 1980 |
| H ⁺ | + | HUM ²⁻ | => | HHUM ⁻ | 9.5 | Bril, 1993 |
| H ⁺ | + | HHUM ⁻ | => | H ₂ HUM | 4.3 | Bril, 1993 |

* = Estimated from Stevenson (1976) after comparison with Mantoura (1978).

We define the molar weight of DOC to be 200 g C/mol humic substance (HUM), and the humic substance is a dibasic acid, H₂HUM, with pKz1 = 4.3 and pKz2 = 9.5. The first constant can be seen as the dissociation of carboxylic groups, whereas the second constant determines the dissociation of phenolic groups. This model is a crude, but reasonable approximation of the titration behaviour of dissolved humic acids, as will be shown in Bril (1994). It enables the calculation of humics as though it is a simple (inorganic) acid. Furthermore, complexation constants have to be defined for the heavy metals and calcium. Table 8 lists all association constants used for the different complexes. Other complexes than inorganic C and humic complexes are not calculated.

Using the constants of Table 8 and the sorption models presented in this study, we can predict the dissolved metal concentrations when the total amount of metal in the sorption phase is known. Please note that although the association constants in Annex I (species table used in EPIDIM) were derived from those in Table 8, they cannot be directly compared to the constants in Table 8 because EPIDIM uses association constants for species, not for components.

Figure 6 gives the calculated dissolved concentration of metal (in ppb = mg/m³) for the 'example soil', for 1 mg Cd/kg ($8.9 \cdot 10^{-6}$ mol Cd/kg), 15 mg Cu/kg ($2.36 \cdot 10^{-4}$ mol Cu/kg) and 15 mg Pb/kg ($7.24 \cdot 10^{-5}$ mol Pb/kg), for pH values of 3 to 9. Figure 7 shows the percentage complexed metal ion in the soil solution as calculated with the speciation model as a function of pH. The model results show that (cf Table 9):

- 1) the dissolved concentration of cadmium is much stronger pH dependent than the dissolved concentration of copper or lead.
- 2) From pH=4.5 upward, both copper and lead are almost completely complexed by humic acids in the soil solution, e.g. at pH=6, only 0.2% of dissolved copper is not complexed. For cadmium, complexation only becomes important at pH values above 7.

Table 9 Effect of changing individual variables

| Variable changed | Effect on dissolved metal |
|-----------------------|---------------------------|
| 2 * Cu-solid | 3.52 * Cu-dissolved |
| 2 * %Cy (Cu) | 0.91 * Cu-dissolved |
| 2 * %OC (Cu) | 0.35 * Cu-dissolved |
| 2 * Ca dissolved (Cu) | see Figure 8 |
| 2 * DOC (Cu) | see Figure 9 |
| 2 * Cd-solid | 2.33 * Cd-dissolved |
| 2 * %Cy (Cd) | 0.86 * Cd-dissolved |
| 2 * %OC (Cd) | 0.54 * Cd-dissolved |
| 2 * Ca dissolved (Cd) | see Figure 8 |
| 2 * DOC (Cd) | see Figure 9 |
| 2 * Pb-solid | 3.52 * Pb-dissolved |
| 2 * %Cy (Pb) | 0.72 * Pb-dissolved |
| 2 * %OC (Pb) | 0.31 * Pb-dissolved |
| 2 * Ca dissolved (Pb) | see Figure 8 |
| 2 * DOC (Pb) | see Figure 9 |

The sensitivity of the model for its individual variables is given in Table 9. It is assumed here, that $CEC (eq/kg) = 0.04 * \%OC + 0.005 * \%Cy$

As Figure 8 shows, the effect of changing the dissolved calcium concentration is not constant for all pH values. This is because calcium not only competes with the metal ions for sorption sites, but also for complexation sites at the DOC. The effect of changing DOC is not constant with pH as well, as Figure 9 shows, since the speciation of DOC, and the complexation of metals is pH-dependent.

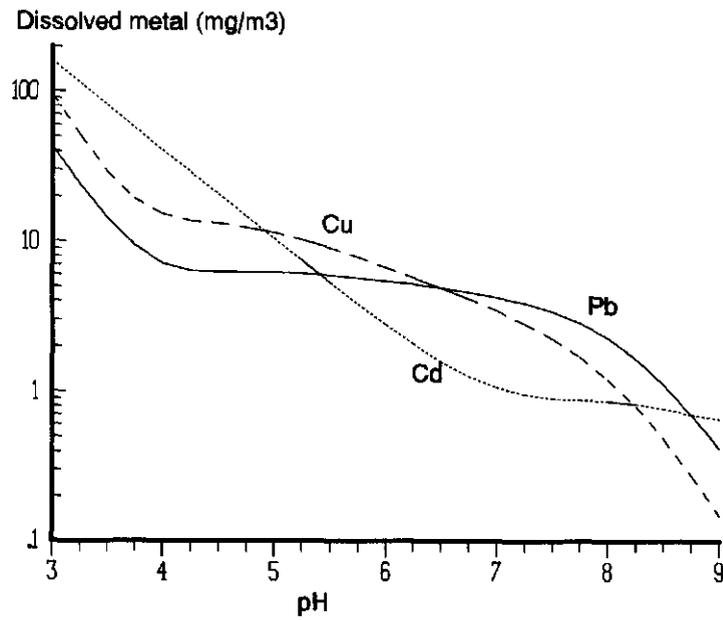


Fig. 6 Calculated dissolved metal concentration for the 'example soil'

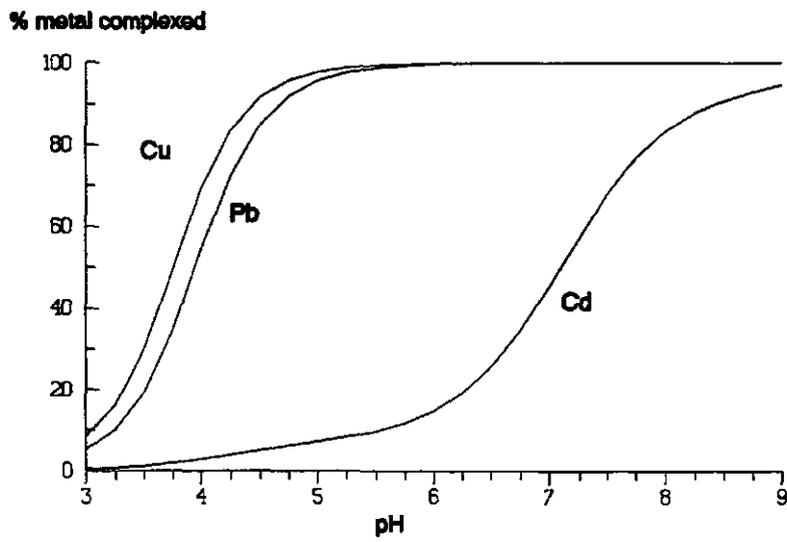


Fig. 7 Percentage of metal complexed in soil solution as function of pH

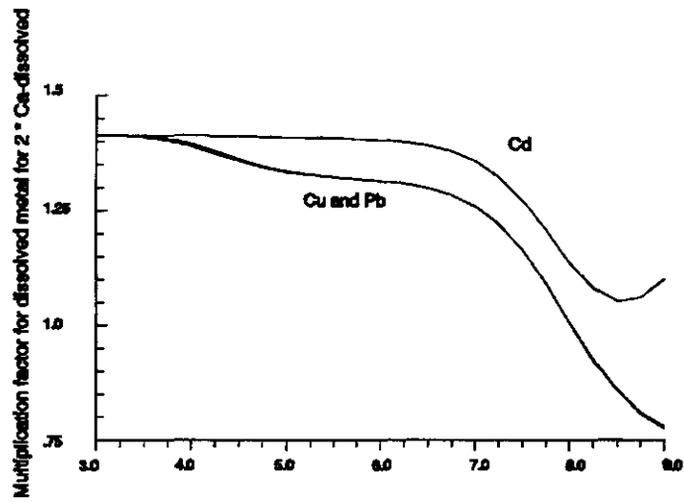


Fig. 8 Effect of calcium on calculated dissolved metal concentration

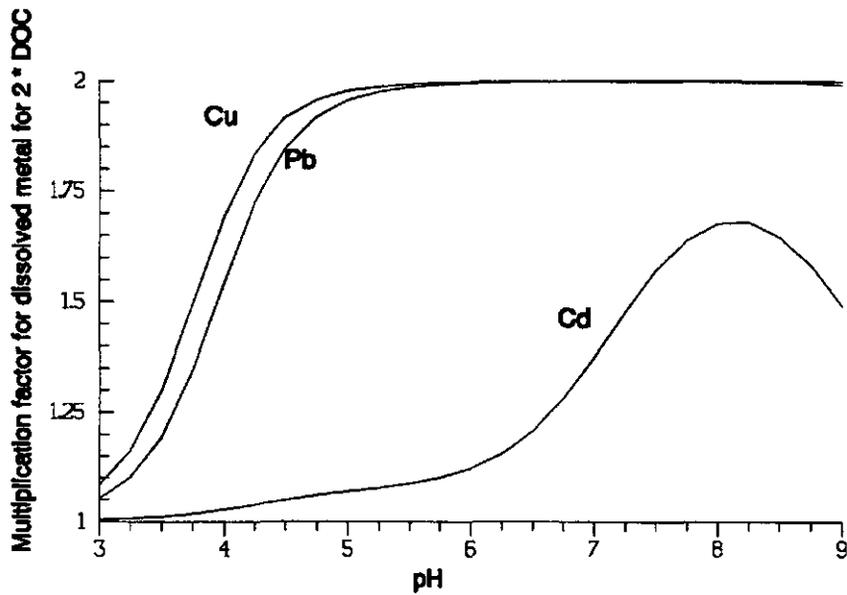


Fig. 9 Effect of DOC on calculated dissolved metal concentration

4.7 Discussion

In this study, a model for the sorption of the heavy metals copper, cadmium and lead onto soils is presented. The model is based on general thermodynamic principles, and fitted to literature data of soil sorption.

The quality of the model derived is $Cd > Cu \gg Pb$.

The model for cadmium is, although only based on 14 soils, considered to be good since the sorption studies were carefully performed, and all major variables influencing the sorption were taken into account.

The copper model is somewhat less reliable, since the data used to fit the model were derived from two different studies, which both focus on a different angle of the sorption process. It is therefore not completely sure, that the combination of these data produces realistic results. Also the pH coefficient of the model is somewhat questionable (comparing results of Lexmond (1980) with Sanders (1982)).

The model for lead is considered to be only a first approximation of reality. Good data to fit the general model Equation (35) were simply not available.

5 Threshold values

In this Chapter a brief overview is given of the threshold values used to compute critical loads. More details on threshold values can be found in Van den Hout, (1994).

The threshold values refer to either the adsorbed phase (adsorbed) or the solution phase (dissolved). An overview of the values used in this study is provided in Table 10. The values for the soil solution phase are based on data for surface water (for MPC) or groundwater (for DTV).

Table 10 Threshold values for soil and soil solution used in this study

| Soil (solution) | Cadmium | Copper | Lead |
|---|---------|--------|------|
| <i>maximum permissible concentration (MPC)</i> | | | |
| Soil dissolved ($\mu\text{g.l}^{-1}$) ¹⁾ | 0.20 | 4.5 | 5.3 |
| Soil adsorbed (mg.kg^{-1}) | 0.26 | 6.0 | 29 |
| <i>Dutch target values (DTV)</i> | | | |
| Soil dissolved ($\mu\text{g.l}^{-1}$) ²⁾ | 0.4 | 15 | 15 |
| Soil adsorbed (mg.kg^{-1}) | 0.8 | 36 | 85 |
| <i>Swedish mor values (SMV)</i> | | | |
| Soil adsorbed (mg.kg^{-1}) | 10 | 50 | 200 |

¹⁾ values for surface water

²⁾ values for groundwater

The MPC values are based on 'no effect concentrations' derived from toxicity measurements with soil and water organisms under laboratory conditions (Van der Meent et al., 1990). Confidence limits for the 'no-effect concentration' were calculated using the method of Aldenberg and Slob, (1991). In experiments with soil organisms, no-effect concentrations and MPC values were corrected for the effects of the soil composition (in particular clay and organic matter content) using the conversion factors used for the Dutch target values (cf Annex IV). The MPC values for soil and soil solution are based on toxicity for soil and freshwater organisms respectively. Because the threshold values for the adsorbed and dissolved phase were derived from experiments with different organisms, the critical load can depend on the soil phase being considered.

The Dutch target values for heavy metals have been derived from background levels in soil and groundwater in relatively uncontaminated areas.

The Swedish mor values are based on a literature review by Tyler, (1992). The values were derived from toxic effects on biological processes and soil organisms in 'mor' horizons, the organic layer of forest soils. The lowest no-effect concentration from these data was used without any statistical treatment.

Adverse effects on vegetation and soil organisms are expected to occur mainly in layers with a high density of fine roots and a high level of microbial activity, ie. the

organic layer on top of the mineral soil and the upper 10 cm of the mineral soil. The latter boundary, which is somewhat arbitrary, was based on a literature review including root distributions in forest soils (De Vries et al., 1990) and on a study of the contribution of different soil layers to nitrogen transformation processes, which gives an indication of microbial activity (Tietema and Verstraten, 1991).

In this study, calculations were performed for the adsorbed and dissolved phase of the organic and mineral layer. Although effects on soil organisms can be more directly related to the soil solution concentration than to the adsorbed concentration, the results for the adsorbed phase in the organic layer are considered to be very relevant. Firstly, the organic layer is most susceptible for pollution and has the highest root and microbial activity. Secondly, threshold values for the adsorbed phase have a direct link with the effects on the ecosystem because they are based on effects on soil organisms. This is not the case for threshold values for the solution phase that were used in this study, because these values are based on effects on surface water organisms (MPC) or background values (DTV). The threshold values for the solution phase were used to provide some information on the long term effects of the atmospheric deposition on groundwater and surface water by leaching from the soil. However, it should be noted that these effects are really long term effects compared to effects in the top soil.

6 Results

The entities used to characterize the impact of atmospheric deposition on soils in maps or tables are summarized in Table 11. The maps show the 5-percentile critical load, i.e. in 95% of the forested area in each grid the critical load is higher than the value on the map and in 5% of the forested area the critical load is lower than the value on the map. A deposition flux equal to the critical load will therefore result in an excess load in 5% of the forested area in each grid: therefore a 5-percentile critical load can be seen as protecting 95% of the forested area in each grid. For this reason, the 95-percentile was used for the mapping of quality levels. This means that the quality levels mapped are exceeded in only 5% of the forested area of each grid.

To restrict the number of figures, maps are only presented for the MPC values (Table 11). Data on Dutch target values and Swedish mor values will be shown in tables. In these tables the range in values is illustrated by the 5, 50 and 95-percentiles.

Table 11 Entities used to characterize the impact of atmospheric deposition on soils

| Entity | Unit | percentile used on maps (%) |
|---|--|-----------------------------|
| <i>Critical loads</i> | | |
| 1. soil | $\text{g}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ | 5 ¹⁾ |
| 2. soil solution | | |
| <i>Relative area exceeding critical loads</i> | % of forested area | |
| 3. soil | | |
| 4. soil solution | | |
| <i>Excess loads</i> | | |
| 5. soil | $\text{g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ | 50 |
| <i>Quality levels at steady-state</i> | | 95 |
| 6. soil | $\text{mg}\cdot\text{kg}^{-1}$ | |
| 7. soil solution | $\mu\text{g}\cdot\text{l}^{-1}$ | |

¹⁾ Corresponds to the use of a 5 percentile critical load as used in soil acidification studies (Hettelingh et al., (1991), Downing et al., (1993)).

6.1 Critical loads based on threshold values for adsorbed concentrations

The calculated 5, 50 and 95 - percentiles of critical loads for heavy metals for the organic layer and mineral topsoil based on adsorbed concentrations are listed in Table 12.

Reference to the Swedish mor values (SMV) is made for the organic layer only because these threshold values are only valid for the organic top layers.

Table 12 The 5, 50, and 95 - percentiles of critical loads for cadmium, copper and lead based on soil quality standards ($\text{g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$)

| | Layer | Cd | | | Cu | | | Pb | | |
|-----|---------------|------|-----|------|------|-----|------|------|------|------|
| | | 5% | 50% | 95% | 5% | 50% | 95% | 5% | 50% | 95% |
| MPC | Organic layer | 0.07 | 0.3 | 2.7 | 0.07 | 0.2 | 1.3 | 0.7 | 2.2 | 8.6 |
| | Mineral layer | 0.3 | 2.0 | 23.6 | 0.3 | 6.4 | 58.4 | 1.0 | 63.5 | 435 |
| DTV | Organic layer | 0.3 | 1.1 | 10.4 | 1.8 | 4.9 | 34.8 | 5.2 | 15.3 | 60.5 |
| | Mineral layer | 1.0 | 8.0 | 89.9 | 6.8 | 166 | 1460 | 7.3 | 447 | 3014 |
| SMV | Organic layer | 1.0 | 4.1 | 38.3 | 1.5 | 4.1 | 29.3 | 16.4 | 47.9 | 189 |

The geographical patterns of the 5-percentile critical loads based on the MPC adsorbed concentrations are shown on maps 1 to 6. The geographical pattern of critical loads is independent of the threshold value and heavy metal chosen; only the magnitude of the critical load differs for the various threshold values and heavy metals. Because one single value was used for the preference factor for uptake for each heavy metal, this factor does not influence the regional pattern of critical loads. The geographical pattern of critical loads can therefore be discussed in general terms that are valid for any combination of metal and threshold value.

In Section 2.2 it was stated that the critical load of a heavy metal is determined on the one hand by precipitation and evapotranspiration and on the other hand by the threshold concentration. Because the threshold metal concentration in the soil solution was calculated from the threshold adsorbed concentration, it is determined by the adsorption characteristics of the soil.

The regional pattern of critical loads is also influenced by the precipitation surplus (precipitation minus evapotranspiration). In high rainfall areas, such as western Norway, Scotland and the Alpine region, critical loads are higher than in dry areas such as central Spain.

6.1.1 Organic layer

For organic layers, a single value for the organic carbon content was used throughout Europe. The cation exchange capacity of this organic layer was linearly related to the organic carbon content and it was assumed that the contribution of clay particles to the CEC in the organic layer can be neglected. Therefore, the difference in the adsorption characteristics of the organic layer are only related to the pH and calcium activity of the soil solution. High pH values lead to strong metal adsorption and thus to low dissolved metal concentrations at a given adsorbed concentration which cause critical loads to be low. High calcium activities give rise to higher dissolved metal concentrations at a given adsorbed concentration which, in turn, lead to higher critical loads.

In our model, the only source of calcium for the organic layer is the atmospheric input. Calcium deposition was estimated by interpolating the 1988 calcium deposition measured at about 60 meteorological stations in Europe (Pedersen et al., 1990). Highest calculated calcium depositions are found in Italy, Greece and the western part of former Yugoslavia. Low deposition of calcium is found in northern Scandinavia. Relatively high calcium deposition can also be found in parts of the atlantic coastal zone: Ireland, western France and northern Spain.

Highest critical loads for organic layers are found in low pH areas, such as southern Poland, the Czech Republic, and Eastern Germany, in areas with high rates of calcium deposition, such as the former Yugoslavia and Italy, and in areas with high precipitation surpluses, such as western Norway, Scotland, the Alps and northwestern Spain. The lowest critical loads are associated with areas of low acid input and thus higher pH values, such as Greece, areas with very low rates of calcium deposition, such as northern Scandinavia, and areas with low precipitation surpluses, such as central and southern Spain.

6.1.2 Mineral layer

The parameters that determine the adsorption of heavy metals are all dependent on soil type. Therefore soil type has a much stronger influence on the heavy metal critical load for mineral layers than for organic layers. The geographical pattern of critical loads for mineral layers is therefore much more fragmented than for organic layers. Highest critical loads are again found in high rainfall areas (western Norway, Scotland and the Alpine regions) and in areas with high acid inputs (Central Europe, UK, Netherlands, Belgium) whereas lowest critical loads are found in areas with clayey soils and in areas with organically rich soils that strongly adsorb heavy metals, such as the peat soils of northern Finland.

6.2 Critical loads based on threshold values for the soil solution quality

The geographical pattern of critical loads which are based on threshold soil solution concentrations (and do not therefore depend on soil parameters) is determined solely by the water fluxes in the soil layers (see also Section 6.3.1). The geographical patterns of these critical loads are therefore identical for all three metals. Because the difference between the critical loads of organic layers and mineral layers is due only to small differences in uptake and leaching between these layers, critical loads and thus excess loads are about equal for the organic layer and the mineral layer.

Table 13 The 5, 50 and 95 - percentiles of critical loads for cadmium, copper and lead based on quality standard for the soil solution ($g \cdot ha^{-1} \cdot a^{-1}$)

| Layer | Cd | | | Cu | | | Pb | | | |
|-------|---------------|-----|-----|-----|------|------|-------|------|------|------|
| | 5% | 50% | 95% | 5% | 50% | 95% | 5% | 50% | 95% | |
| MPC | Organic layer | 0.5 | 0.7 | 1.5 | 12.8 | 19.7 | 39.9 | 10.1 | 15.5 | 32.4 |
| | Mineral layer | 0.4 | 0.6 | 1.5 | 10.9 | 17.9 | 41.5 | 7.3 | 12.4 | 31.4 |
| DTV | Organic layer | 0.9 | 1.4 | 2.9 | 36.2 | 55.8 | 112.3 | 3.6 | 51.1 | 108 |
| | Mineral layer | 0.8 | 1.2 | 2.9 | 30.9 | 50.7 | 117 | 24.3 | 41.3 | 105 |

Table 13 lists critical loads calculated on the basis of threshold concentrations in the soil solution. Differences in the critical loads between the three metals are caused by differences in threshold concentrations (cf Chapter 5) and differences in the preference factor for uptake (cf Syearection 3.4).

Highest critical loads are found in high precipitation areas such as western Norway, Scotland, the Alpine region, the northwestern part of the Iberian peninsula and the western part of former Yugoslavia. Lowest critical loads are found in relatively dry areas such as central Spain and parts of eastern Europe.

6.3 Areas with excess loads related to critical loads based on threshold values for the adsorbed concentration

Excess loads were calculated by subtracting the critical heavy metal loads from the present loads computed by the TREND model. Because critical loads for heavy metals are highly sensitive to the reference values chosen, excess loads also depend heavily on this reference value. Excess loads are therefore discussed in relation to the reference value that the associated critical load is based on. An overview of the areas where critical loads are exceeded, is provided in Table 14, an overview of the magnitude of the excess loads, is provided in Table 15. Negative values indicate that the present load is lower than the critical load.

Table 14 The forested area where critical loads of cadmium, copper and lead based on adsorbed concentrations are exceeded (%)

| Layer | Cd | | | Cu | | | Pb | | |
|---------|-----|------|-----|-----|-----|------|------|------|-----|
| | MPC | DTV | SMV | MPC | DTV | SMV | MPC | DTV | SMV |
| Organic | 32 | 12.9 | 1.4 | 98 | 8.8 | 11.5 | 99.6 | 48.8 | 12 |
| Mineral | 7.0 | 0.3 | - | 14 | 0.1 | - | 17.4 | 3.5 | - |

Table 15 The 5, 50 and 95 - percentiles of excess loads for cadmium, copper and lead based on quality standard for the adsorbed phase ($\text{g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$)

| Layer | | Cd | | | Cu | | | Pb | | |
|-------|---------------|------|-------|------|-------|------|------|-------|------|------|
| | | 5% | 50% | 95% | 5% | 50% | 95% | 5% | 50% | 95% |
| MPC | Organic | -1.3 | -0.08 | 1.0 | 0.12 | 1.3 | 9.3 | 1.5 | 16 | 92 |
| | Mineral | -22 | -1.8 | 0.17 | -54 | -4.1 | 0.9 | -380 | -28 | 15 |
| DTV | Organic layer | -9.1 | -0.9 | 0.53 | -27 | -3.3 | 0.95 | -11.3 | -0.2 | 64. |
| | Mineral layer | -88 | -7.8 | -0.9 | -1000 | -163 | -6.0 | -2950 | -400 | -0.9 |
| SMV | Organic layer | -37 | -3.8 | -0.5 | -22 | -2.5 | 1.6 | -125 | -25 | 19 |

6.3.1 Organic layer

The excess loads for organic layers are presented in maps 7 to 9.

Highest excess loads of cadmium for organic layers of MPC based critical loads occur in areas with high cadmium deposition such as southern and central UK, Netherlands, Belgium, France and western Germany, where the present deposition exceeds the critical load by more than $1 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$. Lower excess loads, usually less than $0.5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ are found in some parts of Scandinavia and Russia. Furthermore, excess deposition occurs in areas with relatively high pH values where critical loads are very low and moderate cadmium deposition is computed: Spain Italy and the Balkans. In these areas the present load exceeds the critical load by $0.5\text{-}1.0 \text{ g}\cdot\text{ha}^{-1}$.

Dutch target value based critical loads for organic layers are exceeded only in parts of Italy, Greece and the former Yugoslavia, where critical loads are very low and moderate cadmium deposition is computed. Critical loads for organic layers based on SMV are only exceeded very locally in northwestern France and small areas in the Balkan region.

The MPC based critical loads of copper for organic layers are so low that they are exceeded throughout Europe. Highest excess loads are found in western and central Europe where the present deposition exceeds the critical load by at least $5\text{-}10 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$. In Scandinavia and southern Europe, excess loads are mostly between 1.0 and $2.5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$.

Critical loads based on DTV are much higher than those based on MPC (cf Table 15). Therefore, excess loads for organic layers are restricted to areas with very high copper deposition such as the Benelux, northern France and the Ruhr area, and to areas in southern Europe and the Balkans with very low critical loads.

For copper, the SMV based critical loads are similar to the critical loads based on DTV. The areas where SMV critical loads are exceeded are therefore almost identical to the areas where DTV based critical loads are exceeded.

For organic layers, excesses of lead over MPC based critical loads occur in almost all forests in Europe. This shows that the threshold concentration of adsorbed lead used to compute critical loads is extremely low, taking into account the strong adsorption of lead in the soil. Highest excess loads are found in densely populated areas where the present deposition exceeds the critical load by more than $100 \text{ g} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$.

Critical loads for organic layers based on DTV are exceeded in all forests in southern, western, central and eastern Europe. Only in central and northern Scandinavia, and on the highly acidified soils of central Europe, are critical loads for lead not exceeded.

The critical load for lead for organic layers based on the SMV is substantially higher than the critical loads for lead based on MPC and DTV (cf Table 13). This is also clearly expressed in the pattern of excess loads. Excesses of lead over SMV based critical loads mainly occur in areas with high or very high lead deposition such as parts of the UK and Ireland, the Netherlands, Belgium, northern France, and western Germany. Critical loads are also exceeded in large parts of Spain, and locally in Italy, Greece and eastern Europe, all areas with moderate lead deposition.

6.3.2 Mineral layer

In the mineral layer, excesses of cadmium over MPC based critical loads are found in areas with very high cadmium deposition such as the Ruhr area and northern Belgium. Excess depositions have also been computed for areas with very low critical loads such as northern France, and parts of Greece and Bulgaria. These areas are dominated by clayey soils that strongly adsorb heavy metals. Critical loads for the mineral layer based on DTV are exceeded only in northwestern France.

Critical loads of copper for the mineral soil, based on MPC, are very low and therefore exceeded throughout Europe except for the western part of Norway and northern Russia. Critical loads based on DTV values are only exceeded in areas both with soils that strongly adsorb copper and a high rate of deposition of copper.

Excesses of lead over MPC based critical loads for mineral layers occurs across 17% of the forested area of Europe. Excess loads occur in northwestern Europe and Spain and in large parts of Sweden and Finland. Critical loads based on DTV are exceeded in areas with clayey soils that strongly adsorb lead. These soils are found typically in northwestern France. Again, excess loads are found in northern Europe, but only in a small percentage of the forests.

Despite the high rate of deposition of heavy metals in central Europe, exceedance is relatively low. This is due to the fact that the soils in this part of Europe are strongly acidified. This might suggest that heavy metals are not a problem in acid soils. However, it should be noted that soils that are less vulnerable to metal accumulation are, at the same time, prone to metal leaching.

6.4 Areas with excess loads related to critical loads based on threshold values for the soil solution

Because the sets of reference values of threshold concentrations in the soil solution used to determine critical loads vary so little from European region to region, excess loads related to these critical loads are strongly determined by present rates of heavy metal deposition.

An overview of the percentages of forest where present loads exceed critical loads is given in Table 16.

Table 16 The forested area (%) where critical loads based on quality standards for the soil solution are exceeded (%)

| Layer | Cd | | | Cu | | | Pb | | |
|---------|------|------|-----|-----|-----|-----|------|-----|-----|
| | MPC | DTV | SMV | MPC | DTV | SMV | MPC | DTV | SMV |
| Organic | 22.4 | 8.9 | - | 1.0 | 0.0 | - | 52.3 | 19 | - |
| Mineral | 27.8 | 12.2 | - | 1.6 | 0.1 | - | 59 | 29 | - |

For cadmium, the area where MPC related critical loads are exceeded, corresponds roughly to the area where presents loads, including the effect of forest filtering, are higher than $1 \text{ g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$. The area where DTV related critical loads are exceeded is smaller and corresponds to the area with cadmium depositions of about $2 \text{ g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$.

Critical loads for copper based on MPC in the soil solution are rarely exceeded in Europe. The present rate of deposition of copper exceeds the critical load only in small areas of Germany, central Poland and the Czech Republic, where loads are over $20 \text{ g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$. Critical loads based on DTV for copper are exceeded in only two grid cells: one in Poland and one in Russia.

The area where the present load of lead exceeds the critical load based on the threshold concentration from MPC, roughly corresponds to the area with present lead deposition over $20 \text{ g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$. DTV related excess loads are found in regions with present loads over $50 \text{ g}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$.

6.5 Steady-state levels in soil and soil solution

Maps 10 to 15 show the 95-percentiles of adsorbed concentrations of heavy metals in organic layers and mineral layers under steady-state conditions at present rates of deposition. An overview of threshold values for both adsorbed and dissolved concentrations is provided in Chapter 6. The legend of the maps is chosen in such a way that each class-limit represents each of the threshold values from MPC, DTV and SMV for a 'standard' soil.

6.5.1 Organic layer

The 95-percentile of adsorbed cadmium concentrations in organic layers varies between less than 0.26 mg.kg^{-1} in areas with no excess loads (based on MPC) to about $2\text{-}5 \text{ mg.kg}^{-1}$ in some areas in Greece and the former Yugoslavia. In most of the area with excess loads, the adsorbed cadmium concentration varies between $0.3\text{-}2 \text{ g.kg}^{-1}$.

The steady-state adsorbed concentration of copper in the organic layer varies between about 20 mg.kg^{-1} in relatively unpolluted areas such as Scandinavia to more than 50 mg.kg^{-1} in areas with high copper deposition and low critical loads such as the Ruhr, northern France, central Spain and Greece.

The adsorbed lead concentration in the organic layer varies between about 60 mg.kg^{-1} in Finland, Norway and most of Sweden to more than 150 mg.kg^{-1} in areas with high lead deposition such as the eastern part of the UK, the Netherlands, Belgium, western Germany, the Madrid area, and the Paris and the Moscow regions.

6.5.2 Mineral layer, adsorbed concentration

The adsorbed cadmium concentration in the mineral soil is below 0.26 mg.kg^{-1} in most forest soils in Europe. Higher adsorbed concentrations, ranging between 0.5 and 10 mg.kg^{-1} are found in areas with low critical loads and intermediate cadmium deposition such as northwestern France, small parts of Spain, Greece and Rumania.

Adsorbed copper concentrations in the mineral soil vary between less than 1 mg.kg^{-1} in strongly acidified sandy soils, such as those found in Poland, to about 200 mg.kg^{-1} in soils that strongly adsorb copper.

The adsorbed concentration of lead in the mineral soil is high in highly polluted areas, but also in other areas with low critical loads of lead, such as southern Sweden.

6.5.3 Mineral layer, soil solution concentration

The steady-state concentration of cadmium in the soil solution exceeds the threshold concentration of $0.2 \mu\text{g.l}^{-1}$ over large areas of Europe. In areas with high cadmium deposition, calculated concentrations in the soil solution are about 2 to $3 \mu\text{g.l}^{-1}$.

The copper concentration in the soil solution is high in areas with a high copper deposition, such as central and southern Poland, eastern Germany, the Czech Republic and the Ruhr area. In these areas, the copper concentration exceeds the threshold value of $4.5 \mu\text{g.l}^{-1}$.

The steady-state lead concentration in the soil solution exceeds the critical limit of $5 \mu\text{g.l}^{-1}$ in most of Europe. Only in Scandinavia are lead concentrations somewhat

lower. The highest lead concentrations in the soil solution, over $100 \mu\text{g.l}^{-1}$, can be found in the vicinity of large urban areas: the area around Paris, western Germany, and the densely populated parts of Hungary and Russia.

7 Discussion

7.1 Comparison with measurements

To evaluate the results of modelled critical loads and steady-state concentrations for heavy metals, the computed steady-state adsorbed metal concentrations in the soil were compared with present heavy metal contents in five European countries.

Although a comparison of computed steady-state adsorbed concentrations with present heavy metal contents will show whether calculated adsorbed concentrations are realistic, it should be noted that there are a number of reasons why steady-state adsorbed concentrations and present concentrations can be different. Firstly, the present situation might not be a steady-state situation. This probably is the case for most mineral soil layers where the total adsorbed amount (in $\text{kg}\cdot\text{ha}^{-1}$) can be large, so that a long period of metal deposition is required to attain steady-state conditions.

A crude approximation of the time needed to reach steady-state was made by dividing the adsorbed heavy metal concentration at steady-state by the atmospheric heavy metal deposition, minus the heavy metal uptake. This showed that, for organic layers, the time to steady-state for copper and lead varies between less than 100 years for areas with medium or high metal deposition to more than 500 years in areas with very low metal deposition or very high steady-state adsorbed metal concentrations. For mineral horizons, the time needed to attain a steady-state is higher. For most of Europe, the time to attain a steady-state for copper varies between 100-400 years. For lead, at least 200-800 years are needed before a steady-state is attained. Much less time is required for the cadmium content to attain a steady-state (usually less than 25 years for organic layers and less than 100 years for mineral horizons). However, because the effect of cadmium leaching has not been taken into account, the computed time to attain steady-state is an underestimate.

The second reason why steady-state adsorbed concentrations can differ from measured concentrations is the pH of the soil solution. Steady-state adsorbed concentrations were calculated using a steady-state pH in the soil solution assuming constant deposition of acidifying compounds at the 1990 level. This steady-state pH is lower than the actual pH because buffering processes in soils result in a relatively slow pH decrease with time, even at high acid inputs.

Thirdly, the present adsorbed concentration is not necessarily determined by atmospheric inputs alone. In the mineral soil natural background levels exist for heavy metals, originating for example from the weathering of parent material. In soils that contain copper holding minerals, the contribution of this native copper to the total copper content might be substantial. Because copper is taken up by the forest as a minor nutrient, copper cycling by litterfall and mineralisation will also contribute to the copper concentrations in the organic layer and upper mineral layer.

Finally, steady-state adsorbed amounts are strongly related to the computed heavy metal deposition. Present adsorbed amounts, however, are also influenced by historical depositions that can be different from the present situation.

An overview of present and the calculated steady-state contents of cadmium, copper and lead is given in Table 17. For organic layers, the agreement between measured contents and steady-state adsorbed concentrations is good. For mineral layers, the steady-state adsorbed concentrations are lower than measured contents, especially in calcareous soils.

This can be (partly) caused by the natural background concentration of heavy metals in the mineral soil that has not been included in the model.

Table 17 Present and calculated steady-state cadmium, copper and lead contents

| Region | Source ¹⁾ | Metal content (mg.kg ⁻¹) | | | |
|---------------------|----------------------|--------------------------------------|-------------------|--------------|----------|
| | | Organic layer | | Mineral soil | |
| | | Calculated | Measured | Calculated | Measured |
| CADMIUM | | | | | |
| Austria | | | | | |
| - non calcareous | 1 | 0.2-1.0 | 0.1-1.5 | 0.0-0.2 | 0.07-0.4 |
| - calcareous | 1 | - | 0.5-2.8 | 0.1-0.2 | 0.3-3.6 |
| Nordrhein Westfalen | 2 | 1.0-2.0 | 0.2-2.0 | 0.1-0.2 | 0.1-1.7 |
| Netherlands | 3 | 0.2-2.0 | 0.3-2.0 | - | - |
| Sweden | 4 | 0-0.5 | 0.5-0.8 | - | - |
| Southern Finland | 5 | 0-0.5 | 0.5 ²⁾ | - | - |
| COPPER | | | | | |
| Austria | | | | | |
| - non calcareous | 1 | 15-30 | 10-22 | 0-5 | 5-35 |
| - calcareous | 1 | - | 10-23 | 0-5 | 10-30 |
| Nordrhein Westfalen | 2 | 40-70 | 10-110 | 5-15 | 3-26 |
| Netherlands | 3 | 40-50 | 6-45 | - | - |
| Sweden | 4 | 10-20 | 5-7.5 | - | - |
| Southern Finland | 5 | 10-20 | 7.2 | - | - |
| LEAD | | | | | |
| Austria | | | | | |
| - non calcareous | 1 | 60-140 | 40-120 | 20-40 | 20-80 |
| - calcareous | 1 | - | 40-170 | 0-20 | 40-170 |
| Nordrhein Westfalen | 2 | 175-250 | 70-500 | 30-80 | 80-200 |
| Netherlands | 3 | 150-250 | 30-280 | - | - |
| Sweden | 4 | 40-90 | 30-60 | - | - |
| Southern Finland | 5 | 40-70 | 40 | - | - |

- 1) Sources 1. Mutch, (1992)
 2. Neite et al., (1991)
 3. De Vries et al., (1992)
 4. Johansson, (1993)
 5. Tamminen and Starr, (1990)

- 2) Median value of all measurements

7.2 Uncertainties

Apart from the sensitivity analysis performed for the adsorption model as described in Chapter 4, a simple sensitivity analysis was carried out on the steady-state model by looking at the effect of a change of 50% of one of the input parameters on the median adsorbed heavy metal concentration for the whole of Europe. Results are given in Table 18.

Table 18 Results of the simple sensitivity analysis for cadmium, copper and lead: effects on the adsorbed concentration in the mineral layer (mg.Kg⁻¹)

| | Cd | Cu | Pb |
|------------------------------|-------|-------|-------|
| Standard run 0.028 | 2.08 | 12.98 | |
| Clay content * 0.5 | 0.025 | 2.02 | 11.03 |
| Clay content * 1.5 | 0.032 | 2.19 | 14.83 |
| Organic carbon content * 0.5 | 0.021 | 1.47 | 8.89 |
| Organic carbon content * 1.5 | 0.034 | 2.63 | 16.75 |
| Precipitation surplus * 0.5 | 0.031 | 2.25 | 14.93 |
| Precipitation surplus * 1.5 | 0.025 | 1.96 | 11.88 |
| MFR scenario | 0.079 | 2.27 | 11.12 |

Table 18 shows that a variation of 50% in clay content, organic matter content, precipitation and resulted in a 10% to 30% change in the median adsorbed heavy metal contents in the mineral layer. If a deposition scenario for acidifying compounds is chosen that aims at a very strong reduction of SO₂ and NO_x by the year 2000 (Maximum Feasible Reductions, MFR), the steady-state soil pH becomes substantially higher than when using the emissions from 1990. Consequently, the median adsorbed cadmium concentrations in the mineral soil layer in Europe increase by a factor 2.9. The effect for copper and lead is much smaller than for cadmium because the activity of these metals strongly decreases with increasing pH, because of complexation with organic anions. This complexation (partly) compensates the stronger adsorption at higher pH values.

7.3 Threshold values

The threshold values used in this study differ widely in their methods of derivation and depend also on the soil phase (adsorbed or dissolved). For each soil phase, threshold values for heavy metals increase from MPC < DTV < SMV. It should be noted that for heavy metals DTV values cannot be compared directly with the ecotoxicologically derived MPC and SMV values, because DTV values are based on background values from relatively unpolluted areas and do not include effects on the ecosystem.

In principle, threshold values should be independent of the soil phase if the ecotoxicological values are based on the same effects and organisms in both phases, and if background data for adsorbed and dissolved phases come from the same soil. In other words, the partitioning of the pollutants over the dissolved and adsorbed phases should be taken into account fully when threshold values are derived. Separate values for adsorbed phase and soil solution are not necessary and even unwanted; they can be derived using the relations between adsorbed and dissolved concentration presented in this study. For soils, this is not yet the case. Critical loads for the different soil phases differ, both for MPC and DTV values because threshold values for soil and soil water, including groundwater, have a different origin.

Moreover, there is also a difference in time scale between the effects on ecosystems in the topsoil and the effects on groundwater in the subsoil. There is often a very

large adsorption capacity for metals between the upper mineral layer and the groundwater level, especially in areas where the groundwater level is low. This will prevent the leaching of heavy metals to the groundwater for a very long time. Leaching to groundwater can, however, occur in soils with shallow groundwater levels and through bypass flow in cracking soils. Furthermore it should be noted that the mixing time in groundwater is very considerable.

MPC for cadmium and copper in groundwater used in this study are more not only more strict than background values in groundwater in the Netherlands (DTV), but also below the WHO guidelines for Cd ($3\mu\text{g.l}^{-1}$) and Cu ($2000\mu\text{g.l}^{-1}$) in drinking water. For Pb, MPC is lower than the WHO guideline for Pb ($10\mu\text{g.l}^{-1}$) whereas DTV is somewhat higher. MPC values therefore sufficiently protect groundwater quality. The same holds for DTV values for Cd and Cu.

In conclusion, MPC values for the adsorbed phase are considered to be the most relevant because:

- In contrast to groundwater standards they are relevant for short term effects.
- MPC values are related to effects on ecosystems.
- The data for the adsorbed concentration have been obtained using soil organisms. MPC values for the soil solution are based on experiments with fresh water organisms that do not occur in soils.

8 Conclusions

The results of this study are highly sensitive to the threshold value. When the most stringent, ecotoxicologically-based MPC values are used, present loads of copper and lead exceed critical loads for organic layers of forest soils throughout Europe. For cadmium, critical loads are exceeded mainly in areas with soils that adsorb heavy metals strongly and in areas with low precipitation surpluses. The area where critical loads are exceeded decreases by a factor 8 or more when the less stringent SMV threshold values are used.

The soil phase (adsorbed or dissolved) affects the threshold values. This is caused by the use of independent toxicity data for the adsorbed and the dissolved metal concentrations. In reality, threshold values for these phases are interdependent and should be derived from the same data set. For heavy metals, the MPC values for the soils solution were derived from toxicity data for surface water organisms. These data are therefore considered to be less useful than the data for the adsorbed phase that were obtained from toxicity data for soils organisms.

Some of the threshold values used for copper lead to very low critical loads. Copper, however, is a minor nutrient for forests. A deposition at the level of such a low critical load leads to very low copper contents in the soil which can be below the copper content required for optimal forest growth. Critical loads for minor nutrients such as copper should therefore be interpreted and used with great care.

Measured contents of heavy metals in the organic layer of European forest soils compare reasonably well with calculated steady-state concentrations. For mineral layers, the steady-state adsorbed concentration is lower than the measured content. The geographical pattern of adsorbed concentrations is predicted rather well; the difference between measured and simulated contents is fairly constant throughout the various regions.

9 Recommendations

Results obtained in this study should be considered as a first approximation. The parameters used in the model to describe the adsorption of heavy metals are based on a very limited number of adsorption experiments that do not cover the full range of soil parameters encountered in the European application of the model. For a more accurate assessment, adsorption data in low pH ranges are essential, and information is needed on the role of aluminium in the adsorption process. Furthermore, simplifications have been made in the modelling of organic anions in the soils due to the limited amount of available data. Because the speciation of copper and lead with organic anions can strongly influence the adsorption of the metals, this subject should be studied further. Furthermore, the effect of forest filtering on the deposition of heavy metals was included in our model on the basis of very few measurements of metal concentrations in forested and non-forested sites. Further research is needed to obtain an accurate assessment of filter factors.

The critical load concept is only valid when a steady-state situation is assumed. For heavy metals, however, it may take hundreds of years before this situation is reached. Therefore, the time taken to reach metal concentrations that exceed threshold values might be more relevant than the ratio between present and critical loads. Further research, using simple dynamic models to evaluate the effects of emission abatement scenarios for both heavy metals and acidifying compounds, is required to enable a quantitative assessment of the time scales on which threshold values for heavy metals in soils would be exceeded.

The threshold values available differ widely in the method of derivation and in magnitude. In principle, ecotoxicologically-based values are to be preferred to background values from relatively unpolluted areas. However, the methods need to be improved to allow these threshold values to be applied in environmental policy. Both the collection and interpretation of toxicity data as well as the extrapolation to field conditions and ecosystems should be improved. Separate values for the adsorbed phase and the soil solution are not necessary. They can be derived from toxicity experiments with soils and soil organisms using the relation between adsorbed and dissolved metal concentrations described in this study.

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Annex I Species table used in EPIDIM

| Components ¹⁾ | | | | | | | |
|-----------------------------------|----------------|------------------|------------------|-------------------------------|------------------|-----------------|-----------------------------------|
| species ²⁾ | H ⁺ | Ca ²⁺ | Mg ²⁺ | SO ₄ ²⁻ | HFA ⁻ | M ²⁺ | logK _j ^{0 3)} |
| OH ⁻ | -1 | | | | | | -14.00 |
| CaHCO ₃ ⁺ | -1 | 1 | | | | | -8.41 |
| CaCO ₃ | -2 | 1 | | | | | -16.69 |
| CaSO ₄ | | 1 | | 1 | | | 2.31 |
| CaHFA ⁺ | | 1 | | | 1 | | 2.20 |
| CaFa | -1 | 1 | | | 1 | | -4.90 |
| MgHCO ₃ ⁺ | -1 | | 1 | | | | -8.44 |
| MgCO ₃ | -2 | | 1 | | | | -16.61 |
| MgSO ₄ | | | 1 | 1 | | | 2.31 |
| Al ³⁺ | 3 | | | | | | 7.00 ⁴⁾ |
| AlOH ²⁺ | 2 | | | | | | 2.01 |
| Al(OH) ₂ ⁺ | 1 | | | | | | -3.10 |
| Al(OH) ₄ ⁻ | -1 | | | | | | -15.70 |
| AlSO ₄ ⁺ | 3 | | | 1 | | | 10.02 |
| Al(SO ₄) ⁻ | 3 | | | 2 | | | 11.92 |
| HCO ₃ ⁻ | -1 | | | | | | -9.51 ⁵⁾ |
| CO ₃ ²⁻ | -2 | | | | | | -19.84 ⁵⁾ |
| H ₂ FA ⁶⁾ | 1 | | | | 1 | | 4.30 |
| FA ²⁻ | -1 | | | | 1 | | -9.50 |
| MHCO ₃ ⁺ | -1 | | | | | 1 | K ₂₅ ^{0 7)} |
| MCO ₃ | -2 | | | | 1 | | K ₂₆ ^{0 7)} |
| MOH ⁺ | -1 | | | | | 1 | K ₂₇ ^{0 7)} |
| MHFA ⁺ | | | | | 1 | 1 | K ₂₈ ^{0 7)} |
| MFA | -1 | | | | 1 | 1 | K ₂₉ ^{0 7)} |
| M _{ads} | | | | | | n ⁸⁾ | logK _F ⁹⁾ |

- 1) The components Na⁺, K⁺, Cl⁻, NH₄⁺ and NO₃⁻ are not in this table because no complexes of these ions were taken into account.
- 2) Species which consist of only one component (e.g. H⁺) are not in this table, their formation constants are equal to 1.
- 3) Values of K⁰ for inorganic species were derived from the WATEQX database (Ball et al., 1980), values for complexes with FA were derived from the values given in table 8 Chapter 4).
- 4) Derived with the assumption that Al³⁺ is in equilibrium with an Al-hydroxide according to the reaction Al(OH)₃ + 3H⁺ = Al³⁺ + 3H₂O
- 5) Derived from equilibrium with gaseous CO₂
- 6) Organic acids are modeled as a diprotic acid schematically represented by H₂FA (see Ch. 5)
- 7) See annex II for formation constants for each of the metals
- 8) Freundlich exponent (see Ch. 5)
- 9) Freundlich constant calculated in EPIDIM (see Ch. 5)

Annex II Formation constants heavy metal complexes

| | Cd ²⁺ | Cu ²⁺ | Pb ²⁺ |
|------------|------------------|------------------|------------------|
| K_{25}^0 | -7.71 | -6.81 | -6.61 |
| K_{26}^0 | -15.44 | -13.11 | -12.84 |
| K_{27}^0 | 2.46 | | |
| K_{28}^0 | 2.7 | 3.9 | 3.8 |
| K_{29}^0 | -3.2 | 0.5 | 0.4 |

Annex III FAO soil types

| | | | | | |
|----|-----------------------|----|--------------------|----|-------------------|
| A | ACRISOLS | I | LITHOSOLS | R | REGOSOLS |
| Ao | Orthic acrisols | | | Re | Eutric regosols |
| Af | Ferric acrisols J | | FLUVISOLS | Rc | Calcaric regosols |
| Ah | Humic acrisols | Je | Eutric fluvisols | Rd | Dystric regosols |
| | | Jc | Calcaric fluvisols | Rx | Gelic Regosols |
| B | CAMBISOLS Jd | | Dystric fluvisols | | |
| Be | Eutric cambisols | Jt | Thionic fluvisols | S | SOLONETZ |
| Bd | Dystric cambisols | | | So | Orthic solonetz |
| Bh | Humic cambisols | K | KASTANOZEMS | Sm | Mollic solonetz |
| Bg | Gleyic cambisols | Kh | Haplic kastanozems | Sg | Gleyic solonetz |
| Bk | Calcic cambisols | Kk | Calcic kastanozems | | |
| Bc | Chromic cambisols | Kl | Luvic kastanozems | T | ANDOSOLS |
| Bv | Vertic cambisols | | | To | Orthic andosols |
| | | L | LUVISOLS | Tm | Mollic andosols |
| C | CHERNOZEMS | Lo | Orthic luvisols | Th | Humic andosols |
| Cg | Glossic chernozems | Lc | Chromic luvisols | Tv | Vitric andosols |
| Ch | Haplic chernozems | Lk | Calcic luvisols | | |
| Ck | Calcic chernozems | Lv | Vertic luvisols | U | RANKERS |
| Cl | Luvic chernozems | Lf | Ferric luvisols | | |
| | | La | Albic luvisols | V | VERTISOLS |
| D | PODZOLUVISOLS | Lg | Gleyic luvisols | Vp | Pellic vertisols |
| De | Eutric podzoluvisols | | | Vc | Chromic vertisols |
| Dd | Dystric podzoluvisols | M | GREYZEMS | | |
| Dg | Gleyic podzoluvisols | Mo | Orthic greyzems | W | PLANOSOLS |
| | | | | We | Eutric planosols |
| E | RENDZINAS O | | HISTOSOLS | Wd | Dystric planosols |
| | | Oe | Eutric histosols | | |
| G | GLEYSOLS Od | | Dystric histosols | X | XEROSOLS |
| Ge | Eutric gleysols | Ox | Gelic histosols | Xh | Haplic xerosols |
| Gc | Calcaric gleysols | | | Xk | Calcic xerosols |
| Gd | Dystric gleysols | P | PODZOLS | Xy | Gypsic xerosols |
| Gm | Mollic gleysols | Po | Orthic podzols | Xl | Luvic xerosols |
| Gh | Humic gleysols | Pl | Leptic podzols | | |
| Gx | Gelic gleysols Ph | | Humic podzols | Y | YERMOSOLS |
| | | Pp | Placic podzols | Yk | Calcic yermosols |
| H | PHAEZEMS | Pg | Gleyic podzols | | |
| Hh | Haplic phaeozems | | | Z | SOLONCHAKS |
| Hc | Calcaric phaeozems | Q | ARENOSOLS | Zo | Orthic solonchaks |
| Hl | Luvic phaeozems | Qc | Cambic arenosols | Zm | Mollic solonchaks |
| Hg | Gleyic phaeozems | Ql | Luvic arenosols | Zg | Gleyic solonchaks |

Annex IV Relation between DTV and soil composition

A. The relation between the Dutch Target Values (DTV) for cadmium, copper and lead and the clay and organic matter content is given in the following table:

| Heavy Metal | DTV | DTV standard soil (mg.kg ⁻¹)(mg.kg ⁻¹) |
|-------------|-----------------------|---|
| Cadmium | $0.4+0.007*(Cl+3*OM)$ | 0.8 |
| Copper | $15+0.6*(Cl+OM)$ | 36 |
| Lead | $50+Cl+OM$ | 85 |

where:

Cl is the clay content (% on weight basis)

OM is the organic matter content (% on weight basis)

A standard soil is defined as a soil with 25% clay and 10% organic matter.

For soils with very low (<2%) or very high (>30%) organic matter content, the organic matter content to compute the DTV value is set to 2% and 30% respectively.

For the organic layer of forest soils, OM was set to 30% and Cl to 0%.

B. MPC values for Cadmium, copper and lead were computed in dependence of clay and organic matter content according to (following (Schobben et al., 1989)):

$$MPC_{(Cl,OM)} = MPC_{(standard\ soil)} * DTV_{(Cl, OM)} / DTV_{(standard\ soil)}$$

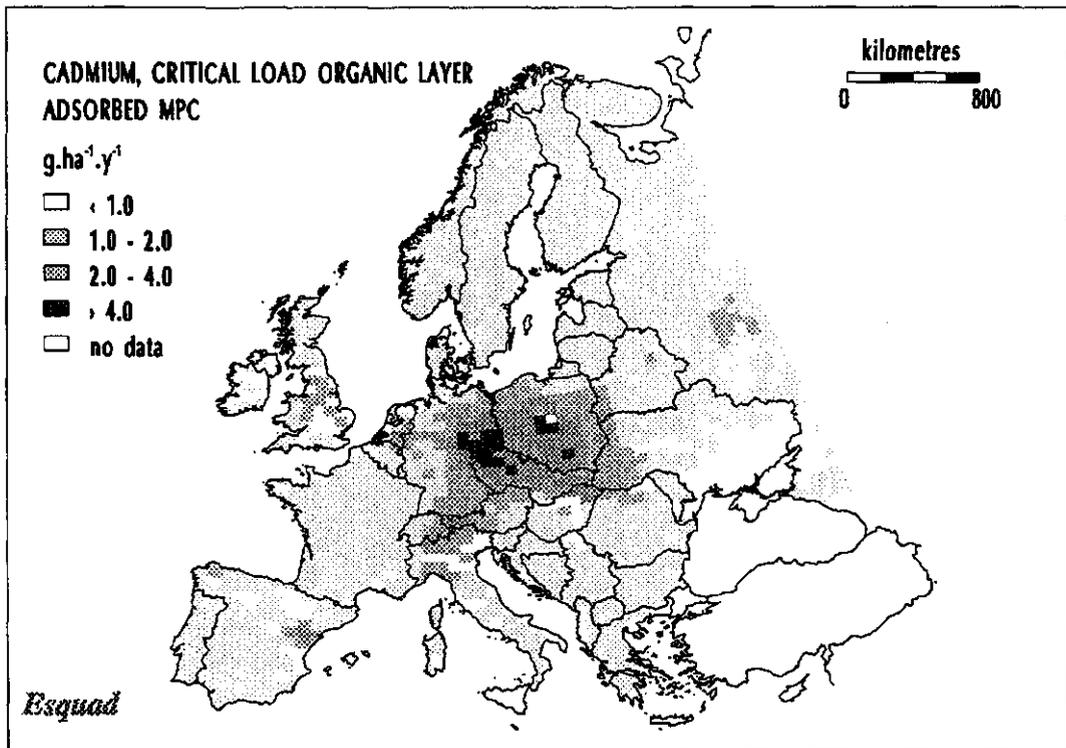
where:

$MPC_{(Cl,OM)}$ = MPC value for a soil with a certain organic matter and clay content

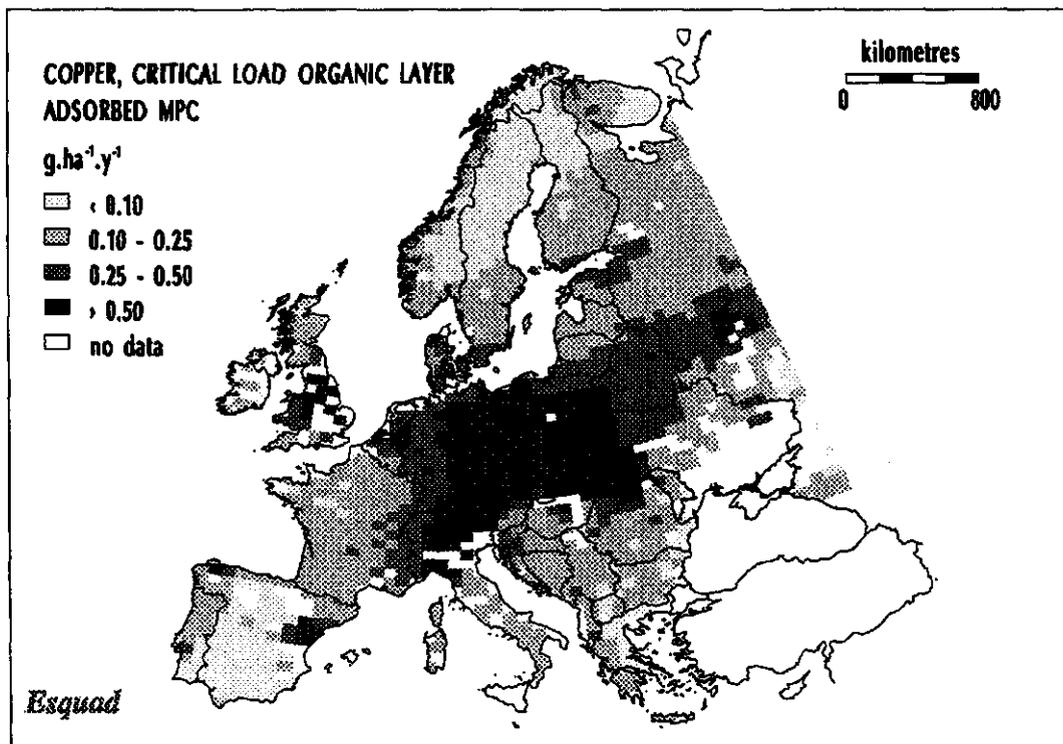
$MPC_{(standard\ soil)}$ = MPC value for a standard soil

$DTV_{(Cl,OM)}$ = DTV value for a soil with a certain organic matter and clay content

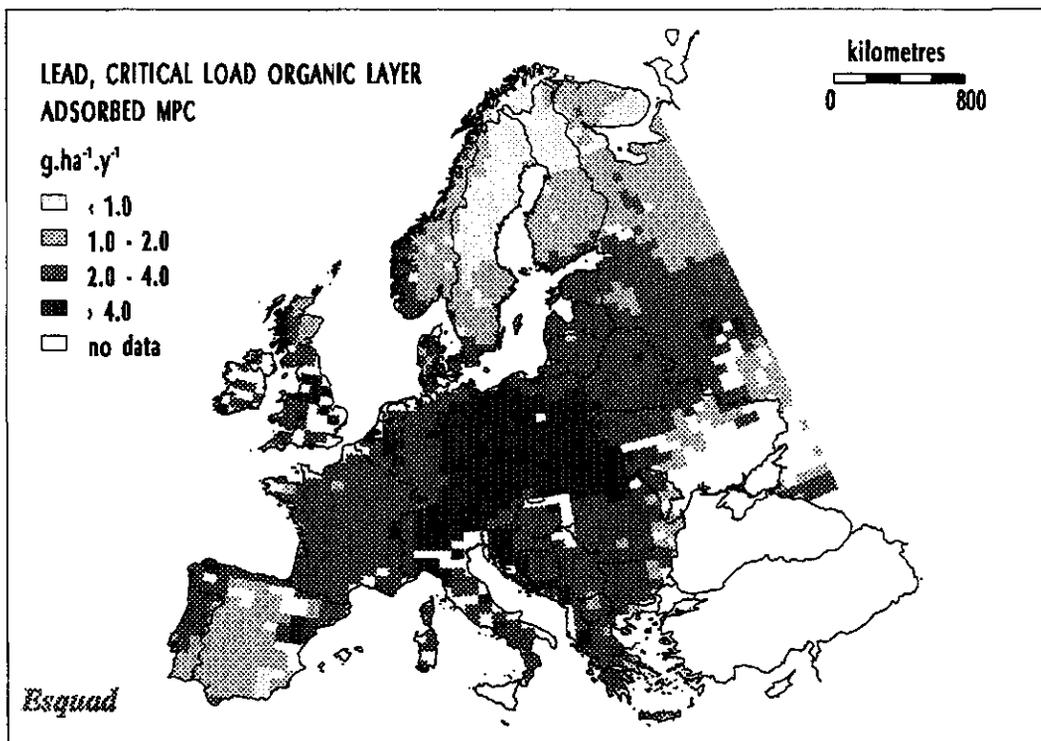
$DTV_{(standard\ soil)}$ = DTV value for a standard soil



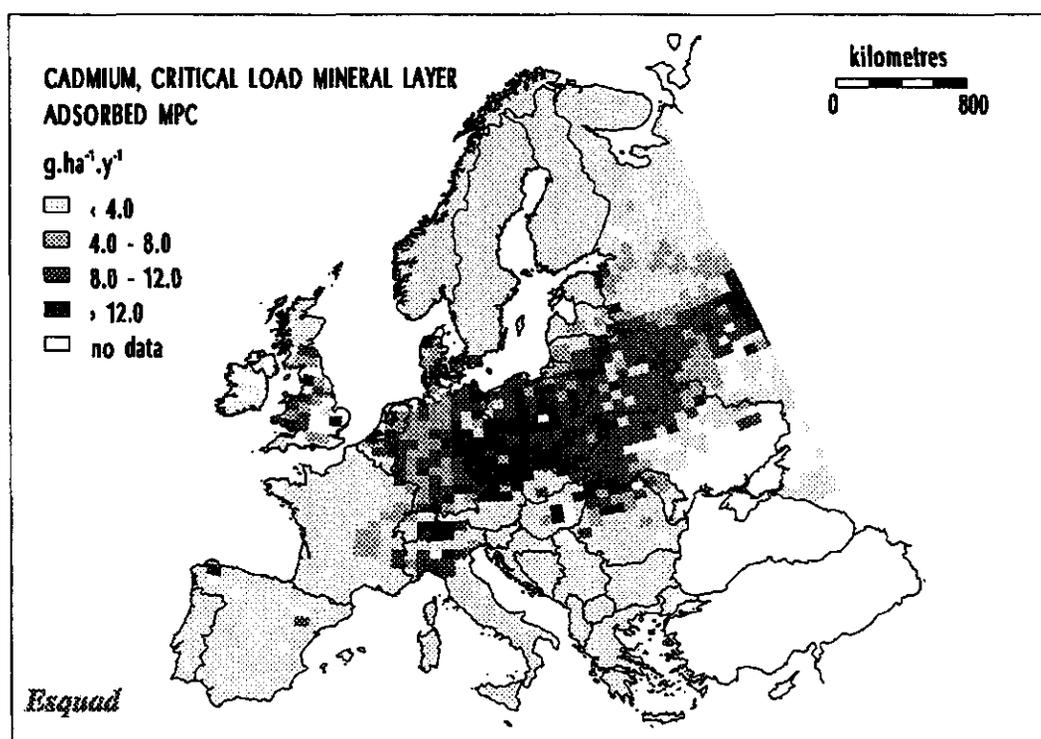
Map 1 Cadmium, critical load organic layer based on adsorbed MPC



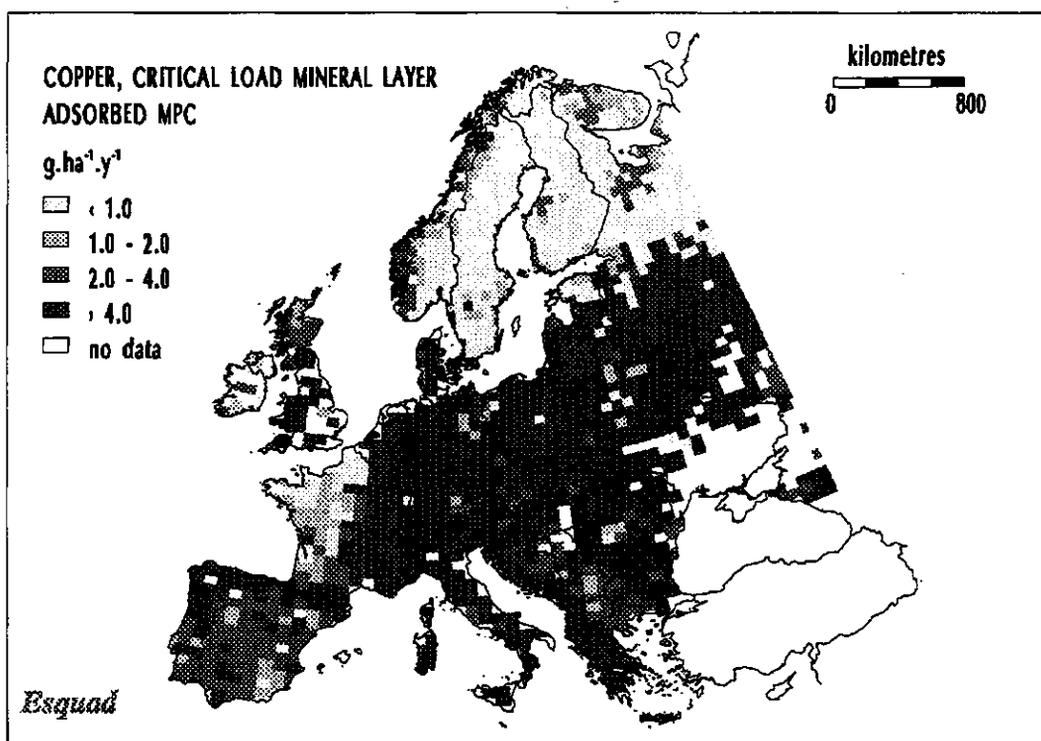
Map 2 Copper, critical load organic layer based on adsorbed MPC



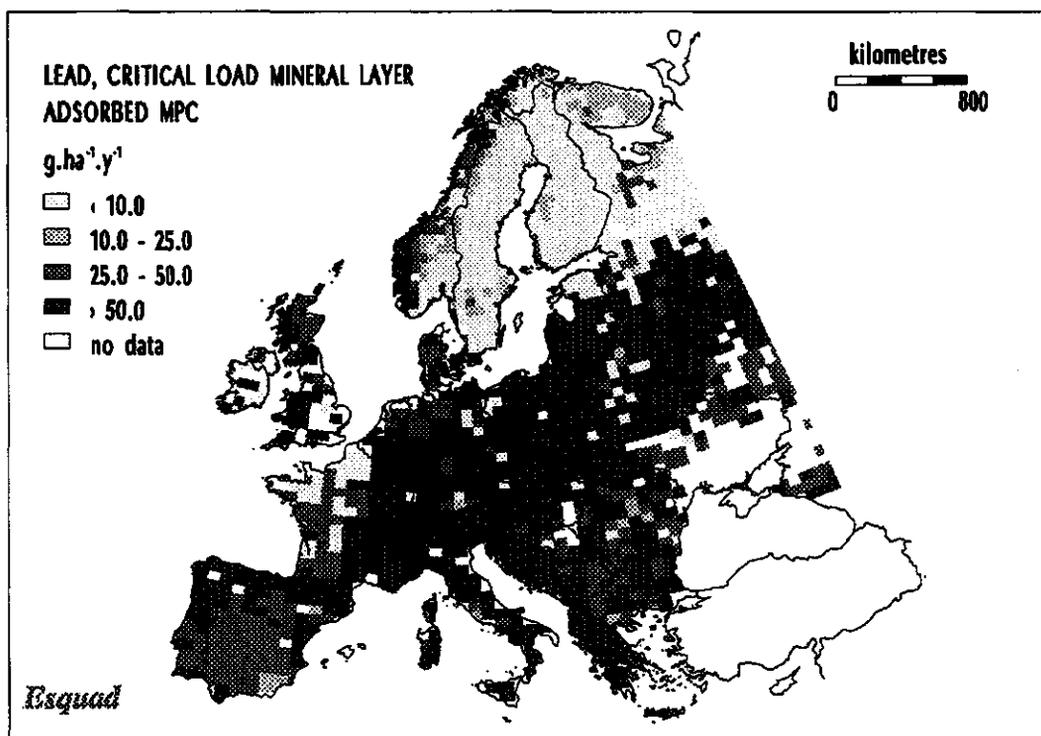
Map 3 Lead, critical load organic layer based on adsorbed MPC



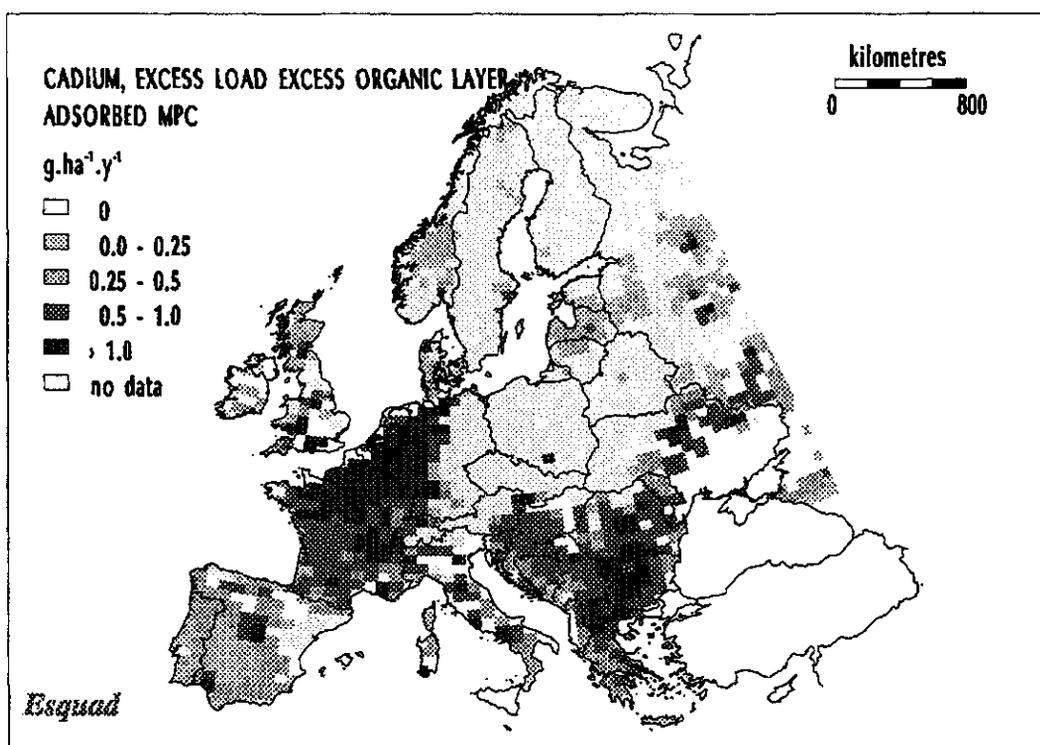
Map 4 Cadmium, critical load mineral layer based on adsorbed MPC



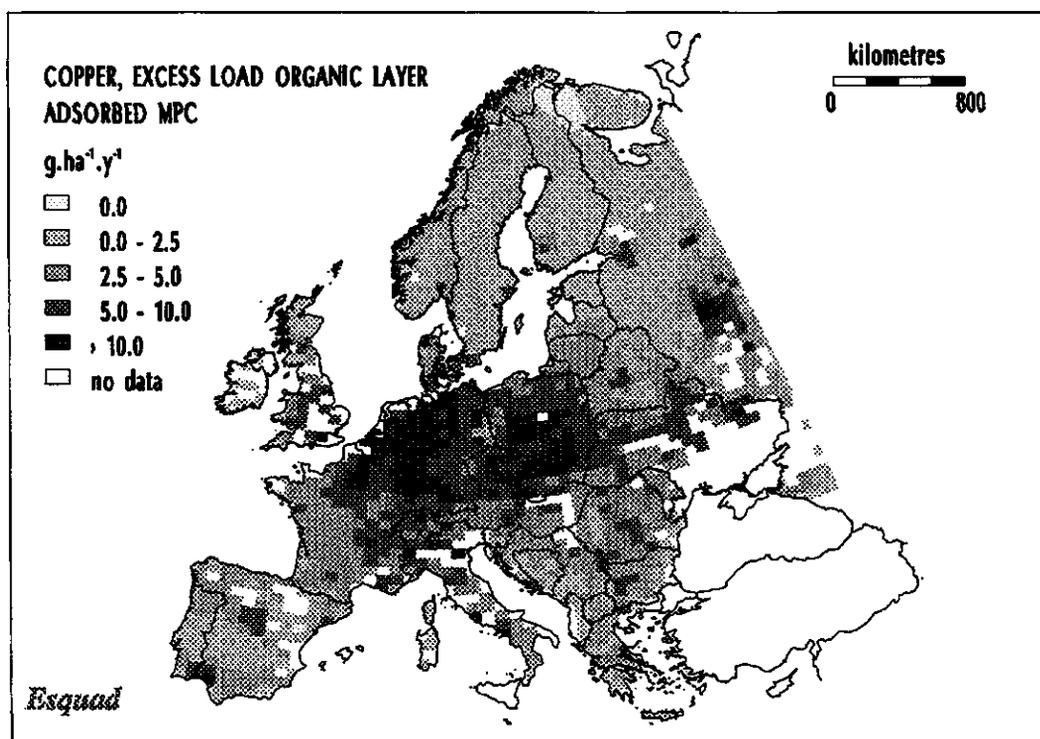
Map 5 Copper, critical load mineral layer based on adsorbed MPC



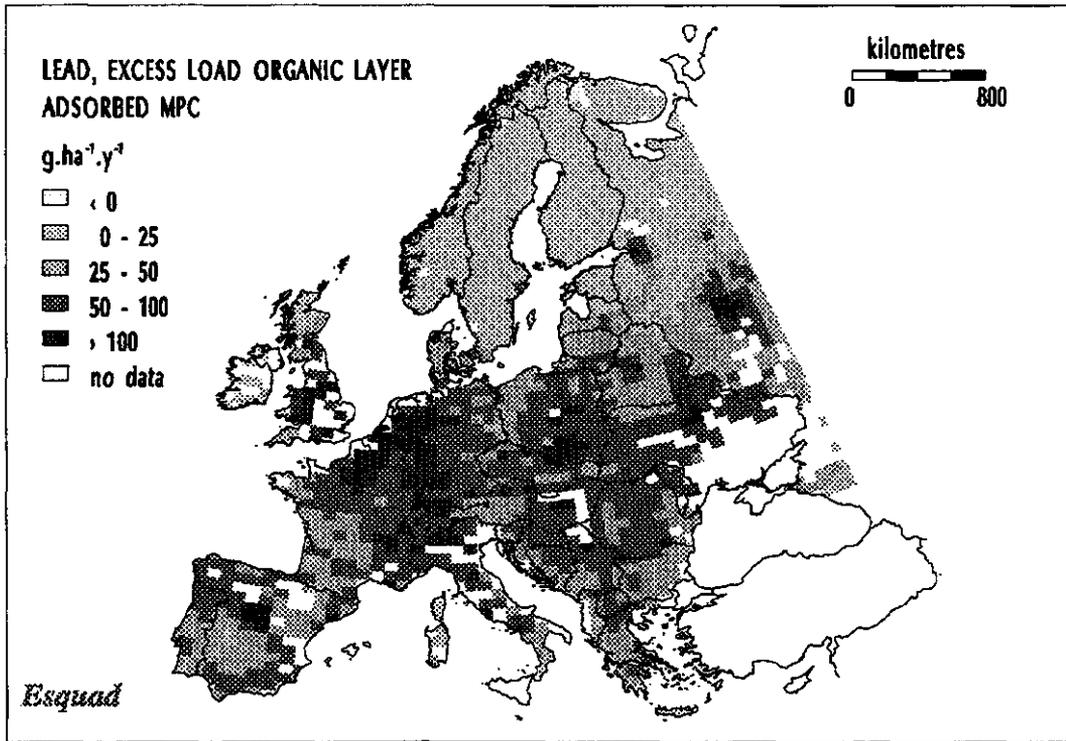
Map 6 Lead, critical load mineral layer based on adsorbed MPC



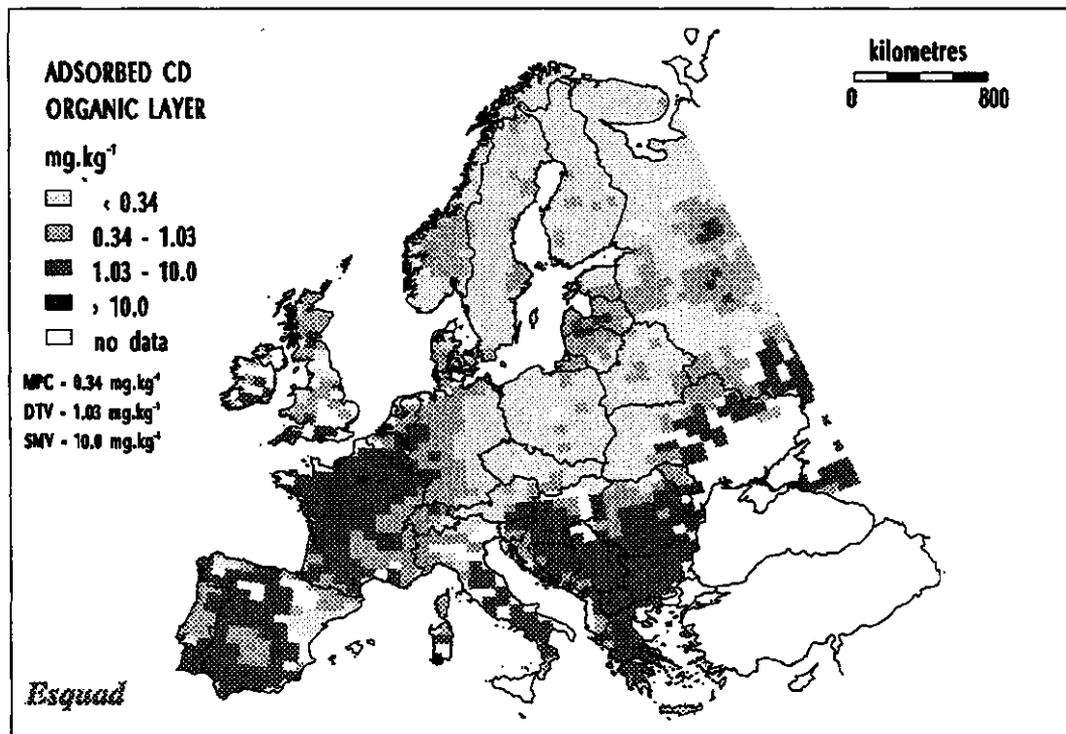
Map 7 Cadmium, excess load organic layer based on adsorbed MPC



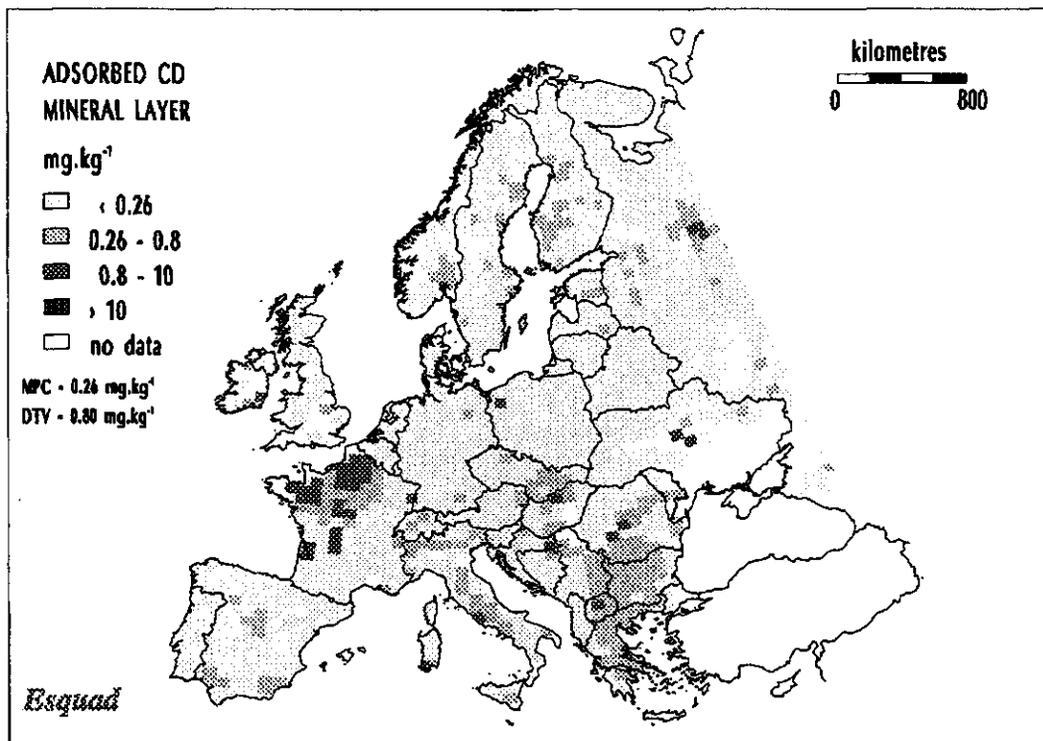
Map 8 Copper, excess load organic layer based on adsorbed MPC



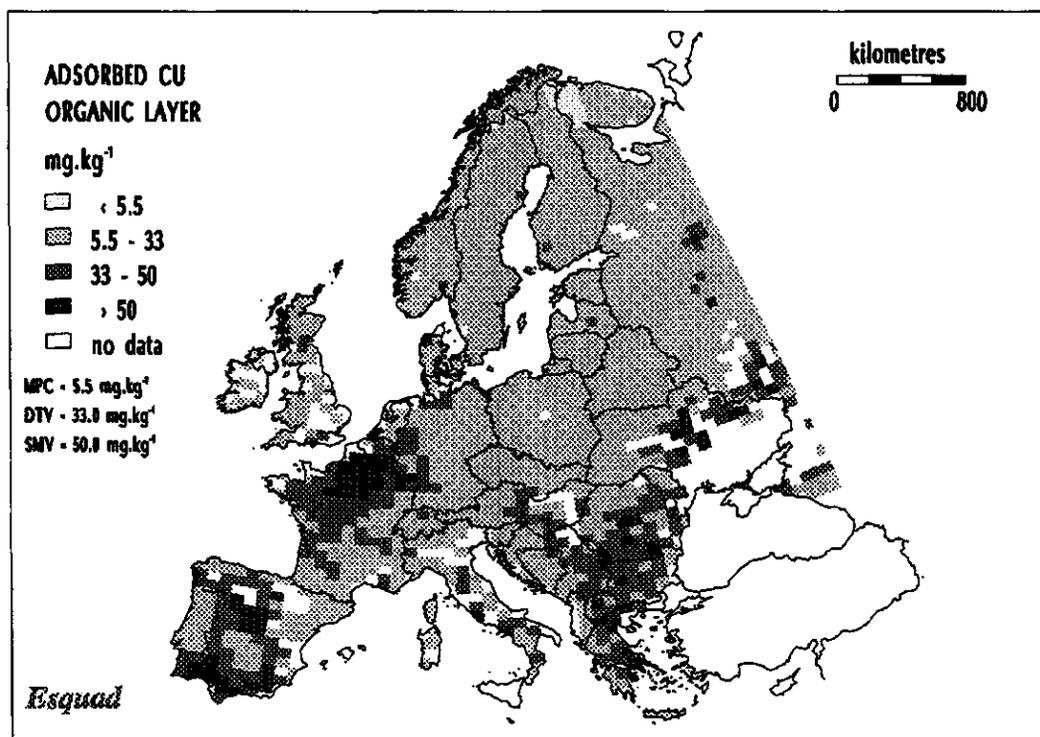
Map 9 Lead, excess load organic layer based on adsorbed MPC



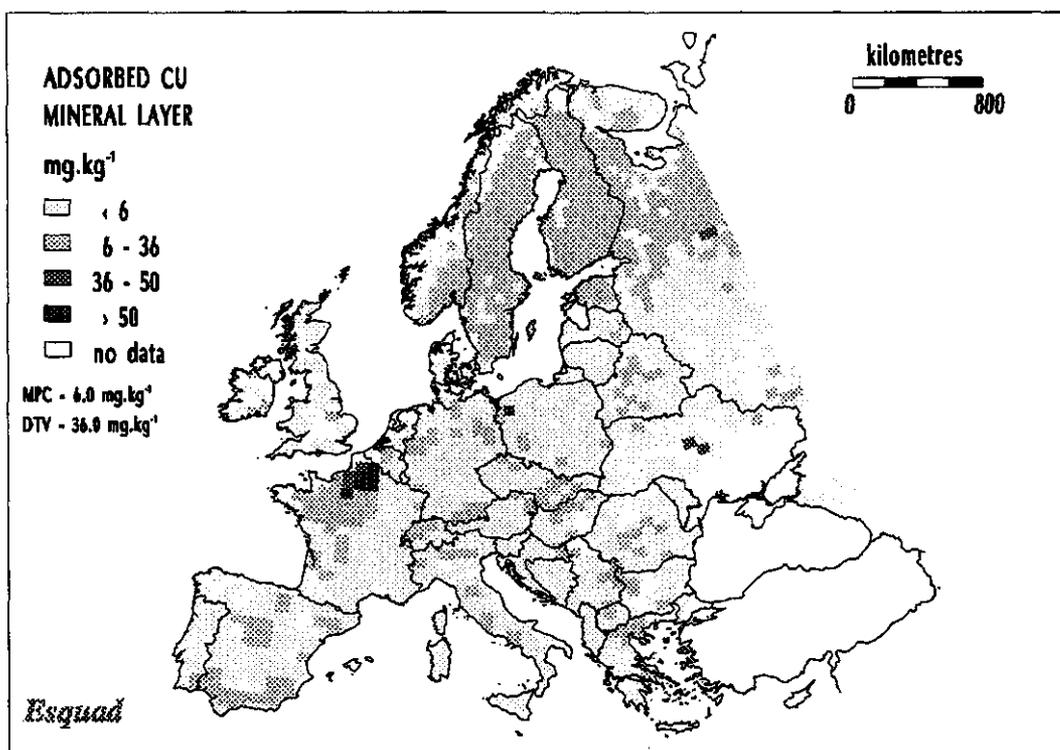
Map 10 Adsorbed cadmium organic layer



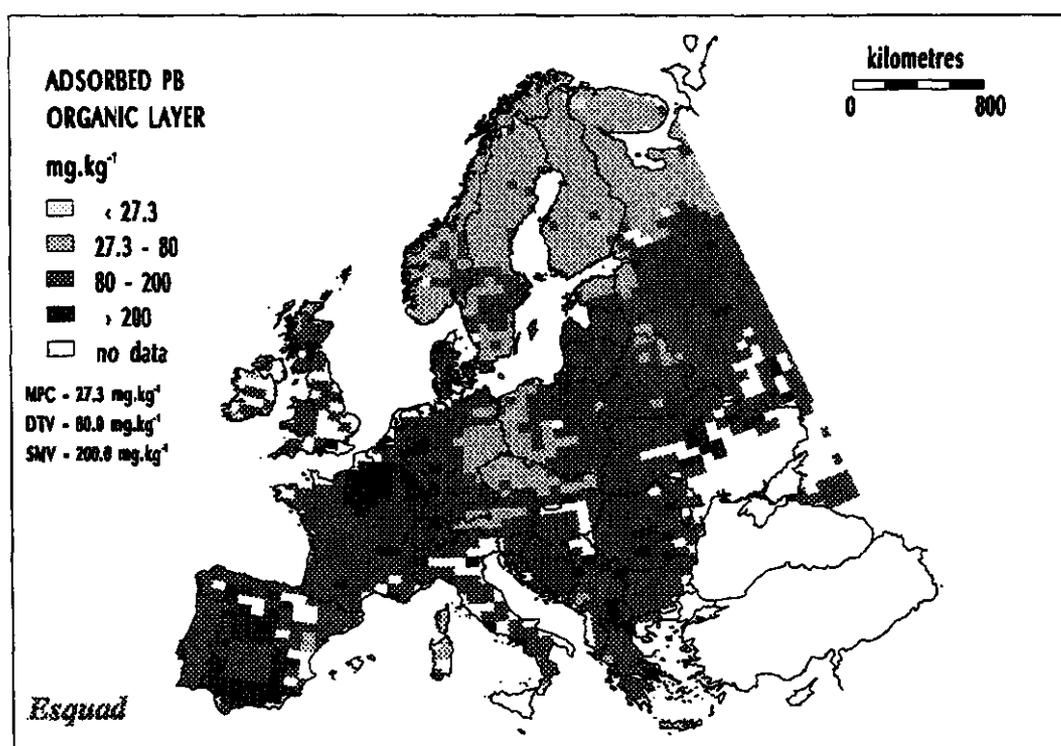
Map 11 Adsorbed cadmium mineral layer



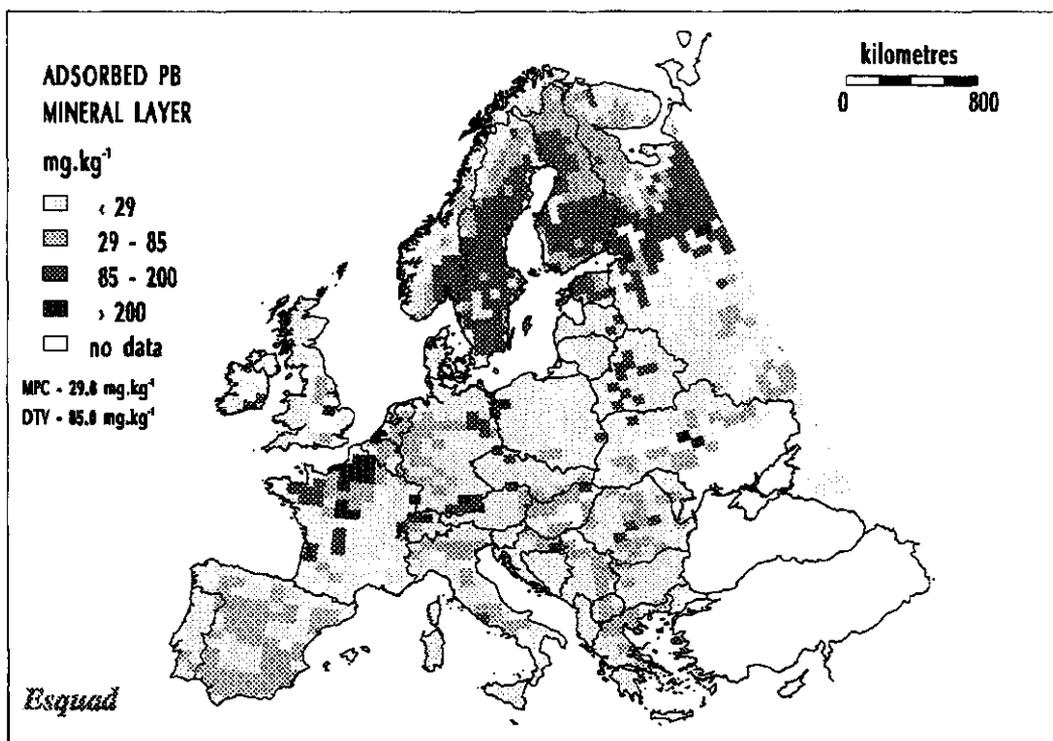
Map 12 Adsorbed copper organic layer



Map 13 Adsorbed copper mineral layer



Map 14 Adsorbed lead organic layer



Map 15 Adsorbed lead mineral layer