Evaluation of models for metal partitioning and speciation in soils and their use in risk assessment

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Evaluation of models for metal partitioning and speciation in soils and their use in risk assessment

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Metals and metalloids are natural constituents of the environment of which many are essential for living organisms. However above certain levels metals may become toxic. Although the largest pool of metals in soils is in the solid phase, uptake by living organisms and migration to soil- and surface water is mainly through the water phase of the soil. Solid solution partitioning of metals is therefore a key process with respect to bio-availability and migration of metals in soils. Both the magnitude of solid/solution partitioning and bio-availability are controlled by the different chemical forms (i.e. speciation) in which metals occur.

In this thesis models were developed and evaluated which describe metal partitioning and speciation in soils. Such models can be distinguished in (i) empirical regression based “partition-relations” which relate the partitioning of metals between the solid phase and soil solution to soil properties like pH and soil organic matter content and (ii) process based “multisurface models”, which describe the various processes and interactions between the soil solution and reactive surfaces by combining separate models for ion-binding to the distinguished reactive surfaces.

Both partition-relations and multisurface models were developed and evaluated on their performance for a large set of elements: including As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V and Zn. Partition relations to predict either the free metal ion concentration (Cd, Cu, Ni, Pb, and Zn) and partition relations for total concentrations (all elements) were shown to be applicable to predict metal concentrations for independent soils outside the data set from which they were derived but within the environmental conditions thereof. The multisurface model is shown to be applicable for a much wider range of conditions and to be a more mechanistically robust model to describe the partitioning of oxy-anions.

Because of the important role of organic matter in the partitioning and speciation of metals in soils, the uncertainties in predicted metal binding to dissolved organic matter (DOM) and speciation by the process based NICA-Donnan model was evaluated. Both composition and binding properties of DOM showed substantial variability. Predicted speciation of metals with a high affinity for organic matter are largely due to the variation in binding constants (the affinity) whereas for metals with a lower affinity, the concentration humic substances and site density (the capacity) are most important.

The use of partition models is successfully demonstrated in two risk assessment studies. The first describes methods to assess: (i) critical (atmospheric) loads of metals to soils i.e. maximum loads without harmful effects, (ii) stand still loads and (iii) target loads which account for a certain time to reach the critical limit. The second example concerns the evaluation of measures to reduce metal inputs by agriculture on metal accumulation in soil and runoff to surface waters in the Netherlands. Scenario analysis on a regional scale show that substantial reductions of Cu and Zn inputs are needed to achieve stand still in their runoff to surface waters. Model evaluation points at an important contribution of partition and/or speciation models to the uncertainty of the model predictions in both examples. To predict metal runoff to surface waters the performance of partition relations at very low organic matter contents, which prevail in deeper soil layers important for runoff, needs to be considered.

Based on the findings of this thesis, it is concluded that empirical partition relations and process based multisurface models can both be used to describe metal partitioning in soils. Because of their simplicity partition-relations are particularly useful in large scale applications and applications to be used by non expert users. Multisurface models are very useful to develop our scientific understanding of trace element partitioning in the complex soil-water system and have the advantage of being applicable to wider ranges of soil properties and environmental conditions.

Key words: trace metals, speciation, solid solution partitioning, risk assessment, reactive transport

Voorwoord

Mijn wens om een proefschrift te gaan schrijven was er al geruime tijd. Jaren geleden heb ik er met Wim de Vries al eens over gesproken en een opzet gemaakt van de verschillende hoofdstukken die er in zouden kunnen komen. Verschillende redenen hebben mij er lange tijd vanaf gehouden om het echt te gaan schrijven. De belangrijkste reden om er dan nu zo'n twee en een half jaar geleden toch aan te beginnen was de wens voor een nieuwe stimulans in mijn werk. De vraag was zoek ik die ergens anders of binnen mijn huidige baan bij Alterra. De extra reistijd die een eventuele andere baan me zou kosten komt al gauw in de buurt van een werkdag per week. Die tijd kun je natuurlijk veel leuker en nuttiger besteden.

En leuk is het geweest om aan dit proefschrift te werken. Gelukkig is mijn werk interessant genoeg zodat ik een aantal artikelen kon schrijven op basis van resultaten uit projecten van de afgelopen jaren. Ik wil daarom Gerwin Koopmans, Luc Bonten, Paul Römkens, René Rietra en Wim de Vries uit ons team hartelijk bedanken voor de goede samenwerking in deze projecten. Job Spijker, Anja Verschoor (RIVM), Joris Dijkstra en Rob Comans (ECN) bedankt voor de goede en prettige samenwerking binnen het UMG project waarin het werk en het schrijven van het artikel over de evaluatie van partitierelaties en multisurface modellen uitgevoerd kon worden. Ik vond het interessant om me eens extra te verdiepen in de type chemische modellen waar we gebruik van maken. Dat heeft geresulteerd in een artikel over de onzekerheid in voorspellingen van het NICA-Donnan model waarvoor ik de werkzaamheden voor het grootste deel buiten werktijd uitgevoerd heb.

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CHAPTER 1

INTRODUCTION AND OUTLINE OF THE THESIS

1 Background

1.1 Metals in soils: functions, toxicity and sources

Metals, and metalloids (further collectively referred to as metals) are naturally occurring constituents in the environment. Several metals are essential for living organisms because of their role in various physiological and biochemical processes whereas some do not have a (known) essential role. Essential elements are usual beneficial up to an optimum level or range. Below this level the metal can be regarded as deficient whereas above this level the metal may become less beneficial and even toxic with increasing levels of availability. Table 1 gives an overview of the most important metals which play a role in biological and physiological processes and which therefore are of importance in risk and deficiency studies. A low availability of essential elements may lead to deficiency problems related to human health. For example, deficiency levels of Se in human nutrition occur in regions with low Se concentrations in soils, such as certain parts of China (*1*), and sub-optimal levels for growth of plants in view of Zn deficiencies occur especially in sensitive crops like rice and maize (*2*). In contrast negative effects are observed for bird-life in regions with high soil Se concentrations, like the San Joaquin valley in California, where it leaches from soils due to irrigation and subsequently accumulates in surface water (*3*). Non-essential elements on the other hand in general may have a level below which they have no effect, above this level toxic effects exert.

Natural concentrations of metals in soils vary on a large scale between geographic or pedogenic regions with parent material and climate as most important factors (*4*). Due to human activities like building, industry, transport and intensive agriculture, metals are emitted to the environment (*5*) leading to elevated concentrations of metals in air, water and soil. Besides highly contaminated soils from (abandoned) industrial, commercial and mining locations, so called brown fields or hot spots, larger areas may be affected at a lower contamination level by diffuse pollution. Well known examples are soils affected by atmospheric deposition of metals from various emission sources. In the Kempen area (Netherlands and Belgium) soils are contaminated with Cd and Zn due to the past emissions of Zn smelters in that area (*6*). Large areas of the Kola peninsula (Russia) are contaminated with Cu, Ni and As due to the emissions from Cu and Ni smelters (*7*). Nearly everywhere in densely populated areas, elevated levels of Pb in soils are found due to the past use of this element in automotive fuels (*8*). In areas with intensive animal husbandry, Cu and Zn in animal feed and feed additives enters the soil by the application of manure leading to elevated levels of these elements in soils (*9*). An important present day source of metals is through the dump and recycling of electronic equipment so called “e-waste” (*10*). Emission of “new” metals or metals in new forms are to be expected from the use of new technologies for example through the use of rare earth metals in high tech products (catalysts, electronic equipment and equipment for solar energy) and metals in produced nano-particles (*11, 12*). Besides anthropogenic sources of metals also natural sources of metals may pose a risk to human health and the environment. These risks are however, mostly initiated through human induced processes. The large scale introduction of tube wells to provide "safe" drinking water to the people in Bangladesh has led to immense health problems due to the high concentrations of As in the pumped groundwater which is due to the natural levels of this element in the soils of Bangladesh (*13*).

TABLE 1 Essentiality and toxicity of metals and metalloids included in this thesis and important anthropogenic sources[a]

Element	important anthropogenic sources	essentiality	eco-toxicity	phyto-toxicity	mamellian toxicity	Chapter
As Arsenic	poultry manure, wood preservative copper smelters	(+)[b]	MH	MH[c]	H	4
Ba Barium	spark plugs, pigments, condensators	-	L	L	H	4
Cd Cadmium	fertilizers, atmospheric deposition, batteries	-	MH	H	H	2,3,4,5,6,7
Co Cobalt	alloys, batteries, pigments	mammals	MH	M	M	4
Cr Chromium	wood preservatives, chrome plating, leather tanning	(+)	MH	H Cr(VI) M Cr(III)	H	4
Cu Copper	organic manure, hoof disinfectants	all organisms	MH	M	M	2,3,4,5,6,7
Mo Molybdenium	fertilizers, fossil fuels	ao	M	M	M	4
Ni Nickel	stainless steel, batteries, plating	(+)	MH	M	M	2,4
Pb Lead	atmospheric deposition, additive in fossil fuels	-	M	H	H	2,3,4,5,6
Sb Antimony	atmospheric deposition, fossil fuels	-	M	H	H	4
Se Selenium	copper refining, production sulfuric acid	mammals, plants	MH	H	H	4
V Vanadium	fertilizers	(+)	H	H	H	4
Zn Zinc	corrosion of metal objects, fertilizers	all organisms	LM	LM	LM	2,3,4,6,7

[a] Information in the table is mainly based on (*4, 14*)
[b](+)=possibly essential, - no known essentiality
[c] L=low, M=medium, H=high

1.2 Pathways of metals in the environment

To evaluate the risks of metal contamination in soils it is necessary to identify the receptors of concern and the pathways of the metal from soil to the receptor. Figure 1 gives an overview of the most important receptors (ovals) and the most relevant pathways. Important pathways for humans and mammals are the intake of metals via food crops, drinking water and in special cases uptake via direct ingestion of soil as with children (*15*) and grazing animals (*16*). Uptake by soil organisms occurs via ingestion of soil and intake of soil water of which the latter is likely the most important route, even for those organisms which ingest substantial amounts of soil, such as earthworms (*17*). Soil water, central in Figure 1, plays a key role in the uptake routes of metals towards biota. Furthermore in most areas the largest amounts of precipitation (rain, snow) feed freshwater reservoirs after contact with soil through surface and subsurface runoff and via leaching trough deeper soil layers and groundwater. The soil thus plays an important role in the quality of water resources. Runoff from soils for example is estimated to contribute between 20% and 50% to the total metal load of surface waters in the Netherlands (*18*). Although the largest pool of metals is in the soil solid phase, metals in the solution phase pose the largest risks. Therefore the transfer of metals from the solid phase to the solution phase as driven by solid solution partitioning is a process of key importance in risk assessment of soil pollution.

1.3 Chemical and biological availability of metals

The bioavailable fraction is the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by (micro)organisms from either the direct surrounding of the organism or by ingestion of food (*20*). The bioavailability of a certain element is dependent on the form in which it is present. Different species containing the same element may have a completely different bioavailability for the same organism (*21*). According to Peijnenburg et al. (*20*) bioavailability can be considered as a three-step approach in which the chemical availability of a metal causes exposure, resulting in actual uptake of metals (so-called bioaccumulation) and subsequently effects due to metals hitting a biological target (so-called toxicological bioavailability). This thesis is limited to the first step i.e. the chemical availability. Uptake of metals from soils by plants and soil organisms is mainly through the solution phase of the soil. The metal concentration in soil solution is therefore the major aspect in the chemical availability of metals in soils

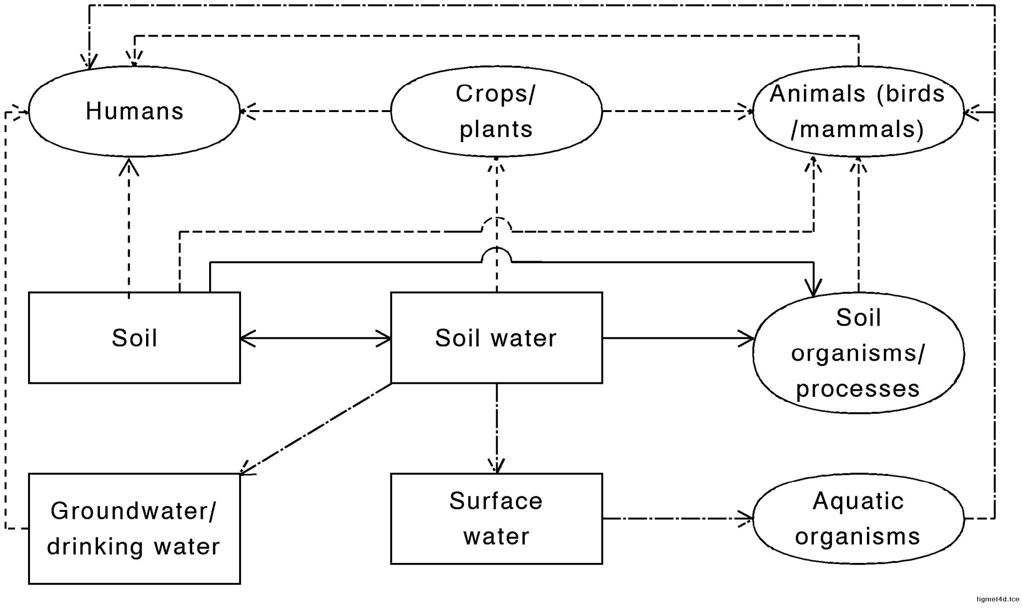

FIGURE 1 Overview of the fluxes and impact pathways of metals from the soil to other compartments in terrestrial and aquatic ecosystems. Boxes are key "pools" and ovals are key "receptors" (19).

The concentration in solution is strongly dependent on the metal concentration in soil and the interaction between the soil solid phase and the solution phase through several chemical processes (Figure 2). Not all metal is available for exchange with the soil solution at time scales relevant for bioavailability. Part of the metals that is occluded in mineral particles (oxides, clay) and organic matter may become only available through very slow processes like weathering. This part is referred to as the inert fraction. The other part, i.e. the reactive fraction is the metal that is available for exchange with the soil solution.

Bioavailability is species (organism) dependent and metal dependent and as such there is no single fraction in soil that dictates the accumulation and effects of metals in organisms (*20*). However, it has been generally accepted that metal bioavailability and toxicity are to a large extent controlled by the free metal ion (FMI) activity in soil solution (*17, 21-25*). Based on these assumptions mechanistically underpinned models like the free ion activity model (FIAM) and the biotic ligand model (BLM) (*24*) were developed. Both models are based on the interaction of the FMI in solution with the organism. According to the concept of the BLM, metal accumulation and or toxic effects are related to the concentration of metal bound to a biotic ligand for which ions compete. The model is therefore capable to account for competition effects of other cations (e.g. H^+ and Ca^{2+}). With the binding of metals the biotic ligand competes with organic and inorganic ligands in solution (like Cl^- and dissolved organic matter) and therefore the BLM needs to include chemical speciation and ion binding models such as NICA-Donnan and WHAM (see next section).

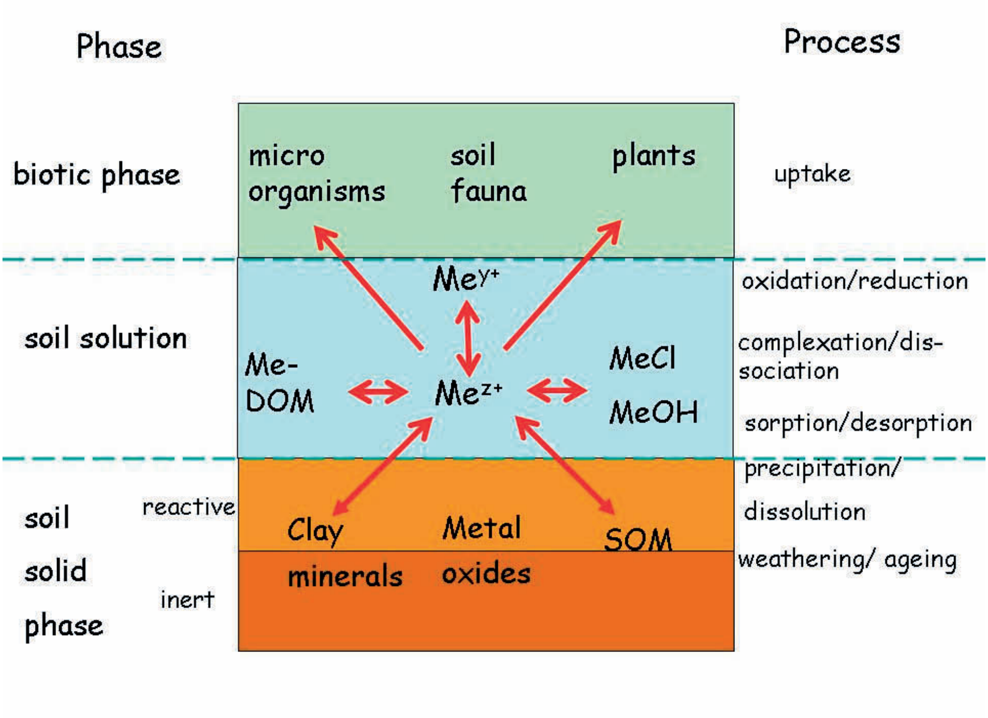

FIGURE 2[1] Schematic representation of the concept of chemical and biological availability of trace metals in soil systems. Me^{z+} symbolizes the free metal ion in solution, the transition of Me^{z+} into Me^{y+} represents a change in redox status of an element (e.g the oxidation of Cr(III) into Cr(VI), MeCl symbolizes inorganic metal complexes, DOM is dissolved organic matter, SOM is organic matter in the solid phase, Me-DOM represents metals bound to dissolved organic matter.

Several analytical methods have been developed to determine the free metal ion concentration or activity in solution, such as ion selective electrodes and several potentiometric and voltametric methods. Disadvantages of these techniques are amongst others single species detection, high detection limits and possible equilibrium shift. To be able to measure multiple elements together methods like Diffusion Gradients in Thin films (DGT) (*26*) and the Donnan Membrane Technique DMT (*27*) were developed. Whereas DGT measurements may also include labile complexes of metals, DMT measures only the free metal ion concentration in solution. Sigg et al. (*28*) give a comparison of analytical techniques for dynamic trace metal speciation in natural waters. It can be concluded that none of these methods are yet available to measure

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[1] Modified figure of E.J.M. Temminghoff used in lectures on soil contamination

metal speciation on a routine basis. The use of thermodynamical equilibrium models for trace metal speciation is therefore an attractive alternative or supplementary method.

1.4 Risk assessment

In risk assessment one can distinguish between risks of actual contamination and precautionary risk assessment, i.e. the assessment of future risks. To evaluate the risks of present pollution it is common to compare present concentrations with critical concentrations at which adverse effects are to be expected. Metal partitioning and speciation play a role in the evaluation of the (bio)-availability of the pollutant (19, 29) and the possible risk of leaching and subsurface runoff towards ground- and surface waters (18). When assessing future risks, metal inputs to soils (e.g. from atmospheric deposition, the application of fertilizer and manure and the leaching of metals from building materials) are to be included, to assess the resulting change in concentration which may exceed critical limits after some time. Methods to asses future risks include the use of dynamic models to predict leaching of metals from soils to ground waters and runoff to surface waters. A recent example is the use of a reactive transport model to set the regulation for the maximum allowed emissions of metals and other elements from building materials in the Netherlands (30). Also steady state models are used to asses future risks. An example is the critical load approach, which is used to asses the risks of atmospheric deposition (31). A critical load is defined as "the highest total input rate of a potential pollutant below which significant harmful effects on defined receptors will not occur in a long-term perspective (at steady state), according to current knowledge"(32). According to its definition, a critical metal load equals the load resulting at steady state in a concentration in a compartment (e.g. soil solid phase, soil solution, groundwater, plant, sediment, fish etc). that equals the critical limit (33). Within the approach of the UN-ECE ICP Modelling and Mapping (32) the critical limit for a soil is a critical free metal ion (FMI) concentration which depends on the pH of the soil to account for bio-availability (22, 34). In order to calculate a critical metal load corresponding with this critical FMI concentration, a speciation model is needed to calculate the total solution concentration depending on solution properties (DOC, pH etc.) as illustrated in Figure 3.

Because of the time it takes to reach steady state concentrations, which is in the order of several hundred years, the use of dynamic model approaches should be considered (35-37). Within the critical load concept, dynamics can be included by defining a target load. This target load is the load which results in the concentration in a compartment that equals the critical limit (in this case the critical FMI concentration in soil solution) within a certain time frame. Figure 3 illustrates the way to calculate such a target load. A critical concentration in the soil solid phase is calculated from the critical FMI in solution using a model to calculate solid solution partitioning. The target load is then calculated from the difference between the present concentration in the solid phase and this critical concentration in the solid phase.

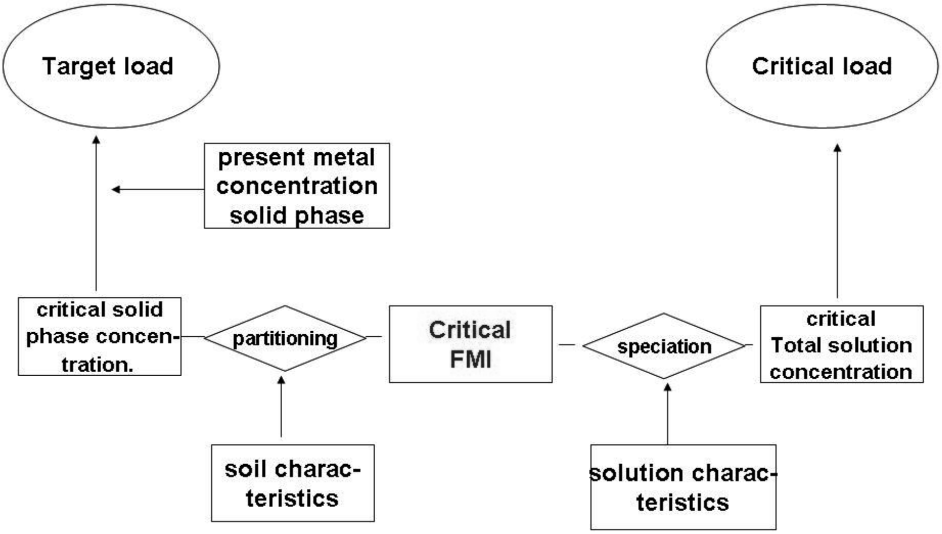

FIGURE 3 Schematic representation of the calculation of a critical load or target load from a critical free metal ion concentration in soil solution.

2 Modeling trace metal partitioning and speciation in soils

In this thesis we develop and evaluate models to describe metal partitioning and speciation in soils with special emphasis on their use in risk assessment studies. Two distinct approaches to model metal partitioning and speciation in soil are used at present:

1. Empirical models: these models relate soil solution concentrations to total or reactive metal concentrations either by using a constant distribution coefficient (K_d) (*38*) or by directly relating solution concentrations to metal contents in soils and soil properties like pH and SOM (*39*) or by relating sorption constants to soil properties (*40-42*). Model coefficients for such relations are derived using (multiple) linear regression analysis.
2. Process based multisurface models: these models describe the separate processes and interactions between the soil solution and reactive surfaces by combining separate models developed for the distinguished reactive surfaces (*43-46*). Because interactions between reactive soil constituents are largely unknown they are usually neglected and additivity of parallel operating processes is assumed.

Empirical K_d models and regression models, frequently termed "partition relations" or "transferfunctions" are widely used to predict metal transport in soils. Strengths of these models are their easiness of use and the numerous studies that are available for these models together with model parameters for various metals (*39-41, 47-50*). Because of there simplicity and their low demand for model input they are used in several regional modeling studies (*18, 51-54*) and Decision Support Systems or web applications to be used by a broad public (*55*). A weak point of these models is their conditional character. Empirical partition relations are conditional resulting from:

1. the parameters incorporated in the model e.g. from a constant distribution constant (K_d) which is only applicable to the soil for which it was derived to regression models, including either only few parameters like pH (*56*), pH and SOM (*39, 50*) or many parameters such as pH, SOM, clay and hydrous Al and Fe oxides (*41*);
2. the types of soils included in the derivation set, ranging from a specific group of soils e.g. only organic rich (SOM>10%) upland soils in the UK (*50*) to a data set including a large variety of soil types (*41, 48*);
3. the simplifications of the model, lumping several processes in one parameter. For example, the pH dependence of binding to organic matter and oxides, hydrolysis reactions and the concentration of important competing cations like Al, Fe and Ca are described by one coefficient for pH;
4. the optimization method used to derive the model, which influences the resulting relation (*48*)
5. the variety in experimental conditions in the derivation data set (e.g extraction of metal and the way the solution is obtained).

Therefore it should be tested under which conditions the derived partition relations are applicable.

Process based multisurface models, also denoted as "assemblage models", were developed in the past decade (*43-45, 57*) but are used sparsely up till present, which might be due to their apparent complexity and greater input data demand. Furthermore, the much longer run time on computers, due to the iterative solution method needed for these models, makes them less attractive to use in regional model studies. The strength of these models is their sound scientific basis for the description of the chemical processes which determine metal partitioning and speciation in soils. These models are therefore in principle suitable to take account of competing effects between different elements and variation in the environmental conditions. These models are however parameterized for isolated "model" soil constituents. Interactions between the different constituents which are neglected in this approach may however also affect metal partitioning and speciation (*58*). To feed the models with the required input parameters, a translation has to be made from (routinely) measured but operationally defined soil characteristics, such as soil organic matter content and oxalate extractable iron, to the concentrations of individually reactive surfaces of well defined model constituents like humic- and fulvic acid and hydrous ferric oxide (HFO). Furthermore natural variation in physical and chemical properties of the reactive soil constituents leads to a certain, but not yet quantified, uncertainty of model predictions. The section below summarizes the state of the art with respect to process based modeling as a background to the research questions posed in section 1.3.

2.1 Sorption of metals to soil constituents

Sorption is a general term for the accumulation of a substance at the interface of two phases i.e. in case of metal sorption in soils the solid solution interface. In soils a mixture of elements is sorbed to a mixture of soil constituents. Even in case of sorption to isolated soil constituents it is often hard to distinguish between phenomena like adsorption, (chemisorption and electrostatic sorption), surface precipitation and the formation of solid solutions due to the often gradual transition between the processes (*59*). For a long time general adsorption models like the Langmuir and the Freundlich van Bemmelen equation were used to describe metal binding to soil constituents (*59*). In the past decades several process oriented models were developed to describe sorption of metals to single metal binding constituents in soil. Below the most important reactive soil constituents with respect to binding of metals are discussed together with the models used to describe metal binding to them.

Organic matter is present in both the solid phase of the soil (soil organic matter or SOM) and in the solution phase (dissolved organic matter or DOM). Organic matter is a mixture of several organic compounds i.e. high molecular weight organic substances, termed humic substances, and low molecular weight organic molecules (organic acids, carbohydrates, lipids, amino acids *etcetera*) (*60*) of which the humic substances (HS) are assumed to be the most relevant fraction for metal binding. HS are high molecular weight substances with a variety metal binding groups. HS can be divided in humic acid (HA) and fulvic acid (FA). The most advanced models to describe ion binding to HS are the NICA-Donnan model (*61*) and WHAM Model VI (*62*) These models include specific binding of cations taking into account the heterogenic character of HS. Non specific electrostatic binding is accounted for by a Donnan model. The models are parameterized for binding of large number of metal ions to FA and HA based on measurements for isolated systems (*62, 63*). Besides HS also low molecular weight organic acids can play a role in metal binding in soil solution (*64*). In the acid to neutral pH range, organic matter is generally the most important binding constituent for metal cations.

Oxides, hydroxides and oxy-hydroxides of Fe, Al and Mn, further referred to as oxides, have the capacity to specifically bind both metal cations and anions. For anions these oxide minerals are generally the most important binding phase in soils. The surface charge of the oxide surfaces depends on pH. Especially the less crystalline oxides have a large capacity to bind metals because of their structural disorder and larger surface area. The Generalized Two Layer Model (GTLM) of Dzombak and Morel (*65*) is a surface complexation model which was developed to describe cation and anion binding to hydrous oxides. The model includes proton exchange, cation and anion binding via ligand exchange at surface hydroxyl sites and surface precipitation at the oxide surface, taking into account electrostatic interactions and ion binding in a diffuse double-layer. It was parameterized for ion binding to hydrous ferric oxide (HFO) for various metal cations (Ag, Ba, Ca, Cd, Co, Cr(III), Cu, Hg, Ni, Pb, Sr and Zn) and anions (As, Cr(VI), Se, V) and the macro-anions PO_4 and SO_4 and for the divalent metal cations to hydrous manganese oxide (HMO) (*66*). The charge distribution model CD-MUSIC (*67*) was developed to describe ion binding to oxides mechanistically, based on the coordination and structure of adsorbed ions as derived from spectroscopic data. The model was parameterized for the binding of Cd, Co, Cu, Ni, Pb and Zn to goethite and HFO (*68*) and for several oxy-anions like As (*69*), Se and S (*70*) on goethite. However an extended and consistent parameter set is still lacking. The present parameterization of the model seems to underestimate Cu and Pb binding in the low, but for natural systems highly relevant, concentration range because the parameterization was derived from spectroscopic data at relatively high metal levels (*68*). At present a complete dataset for metal binding to Al oxides is lacking and was therefore either omitted (*71*) or modeled similar to sorption to HFO (*44*).

Clay and layer silicates have a permanent negative charge through which metal cations can be bound electrostatically. The electrostatic binding of metals is generally modeled with a simple Donnan model (*44, 45, 57*)

2.2 Inorganic complexation and mineral equilibria

In addition to complexation with organic ligands, which is generally most important for cationic metal speciation, ion pair formation with inorganic ligands like Cl^- and HCO_3^- and hydrolysis reactions play a role in metal speciation Together with precipitation/ dissolution, which may especially be important at high concentration levels, these reactions can be modeled with the law of mass action using thermodynamic equilibrium models. The models used in this thesis, i.e. WHAM (*62*) and ORCHESTRA (*72*), both facilitate the computation of these reactions and include extended thermodynamic databases.

2.3 Oxidation/reduction.

Oxidation reduction reactions may have a large influence on the availability and mobility of metals such as Se and Cr. Se(IV) as selenite or Cr(III) as the Cr^{3+}-ion are strongly retained in soils whereas Se(VI) as selenate and Cr(VI) as chromate are highly mobile and therefore prone to uptake by plants and leaching to ground- and surface waters. In strongly reduced soils metals may be very immobile due to the formation of insoluble metal sulfides like ZnS. Redox reactions are relatively slow processes and in order to describe these processes accurately kinetics should be included. In this thesis we however limit ourselves to the redox state in (moderately) oxidized soils by fixing the sum of pe and pH at a value of 15 based on measurements in wet aerobic soils (*14*). An overview of biogeochemical redox processes and their impact on contaminant dynamics is given in a recent review by Borch et al. (*73*). The BIOCHEM-ORCHESTRA model (*74*) includes empirical relations to calculate the redox potential depending on the water level in the soil and couples the calculated redox dependent speciation in soil and solution to metal uptake by plants and invertebrates.

3 Research aims and outline of the thesis

The objectives of this study are to evaluate the performance, strengths and weaknesses of both mechanistic process based models and empirical regression models. The main question is under which conditions these two concepts are applicable to predict metal partitioning and speciation in soils. What is their accuracy and how do these methods compare to each other? The limitations of empirical models due to their conditional character has already been mentioned. However, assumptions also need to be made when applying process based multisurface models to real soil systems assumptions, specifically with respect to the composition of reactive soil constituents. For example, amounts of reactive Fe and Al oxides in soil are derived from Al and Fe extractions with several extractants (*44, 71*). Measures of the organic matter content like loss on ignition (LOI) or organic carbon have to be translated to the reactive model constituents HA and FA which are used in the model. For both approaches a choice has to be made on the method which is used to quantify the reactive metal concentration in soil e.g. extraction with 0.43 M HNO_3 (*44, 50*), extraction with EDTA (*75*) or by isotopic dilution (*76*).

In this thesis the assumptions to be made will be addressed together with their consequences for the results. Important questions to be addressed are:

1. What are the implications of the mathematical form of empirical partition relations with respect to their possible application and the accuracy of their predictions
2. How general is the applicability of empirical partition relations? What is the ability of these models to predict metal partitioning for soils outside the domain of soil properties for which the model parameters were derived.

3. What is the accuracy of predicted metal partitioning in soils using process based multisurface models when using generic model parameters?
4. How does the predictive power of both type of models compare to each other? Are partition relations capable to predict metal partitioning under changing environmental conditions and what is the additional value of process based models?
5. What is the effect of natural variability in chemical properties of reactive soil constituents and uncertainty in the quantification of model inputs on the uncertainty in predicted metal binding and speciation when using process based models?
6. What are the consequences of the previous knowledge questions concerning the modeling of metal speciation for (regional) risk assessment modeling?

The first part of the thesis (Chapter 2-5) focuses on the modeling of trace element speciation and partitioning in soils. Models are derived (empirical models) or assembled and parameterized (process based models) and subsequently evaluated for their applicability to predict metal partitioning and speciation in soils taking account the choices to be made amongst model input and uncertainties of the model and model input. The second part (Chapter 6-7) deals with the application of both types of models in risk assessment. Both examples deal with future risks of pollution due to present emissions. The first of which is focused on the use of steady state models in risk assessment whereas the second is an example of the use of a dynamic model.

Chapter 2 focuses on the derivation and testing of empirical solid solution partition relations. Transfer functions in terms of metal partitioning between the free metal ion in solution and the reactive metal concentration in the soil solid phase were derived for Cd, Cu, Ni, Pb and Zn. The derivation was based on measured and modeled (using WHAM Model VI) free metal ion activities in soil solution extracts of a large number of soil solution samples, the reactive metal concentration in the soil, the pH in the solution extract and the soil organic matter content. The transferfunctions thus derived were tested on a large set of independent published and unpublished data.

Chapter 3 evaluates the applicability of an assemblage model to predict metal concentrations in soil solution from measured metal concentrations in the solid phase and contents of reactive soil constituents and pH. The model combines sorption models for reactive soil constituents, i.e. soil- and dissolved organic matter (NICA-Donnan), hydrous ferric and aluminum oxides (GTLM-model of Dzombak and Morel) and clay (Donnan model) and a model for inorganic speciation in soil solution, including precipitation/ dissolution reactions. The applicability is evaluated by comparing measurements and model predictions of solution concentrations of Cd, Cu, Pb and Zn for a large number of soil samples with a large variety in soil properties and metal concentrations. Special emphasis is given to determine the sensitivity of the model to inputs in reactive fractions of organic matter and the influence of the macro chemical composition of the soil solution on predicted solution concentrations of trace metals.

In **Chapter 4** a comparison is made between process based and empirically derived solid solution partitioning models. The models are compared with respect to their ability to predict metal partitioning of As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Ni, Pb, Sb, Se and V in independent samples of soil solution extracts and in batch experiments in which the pH was varied between pH 3-8, i.e. the normal pH range encountered in soils.

Chapter 5 evaluates the uncertainty in the prediction of Cd, Cu and Pb speciation in the soil solution with respect to binding of these metals to dissolved organic matter using the NICA-Donnan model. Uncertainties are due to natural variability of binding properties (capacity and affinity) of humic substances (HS) with respect to trace metal binding. Furthermore the usually unknown concentrations of HS in dissolved organic matter (DOM) are another source for uncertainties in predictions. Model predictions are compared with measured speciation in solutions in which also the concentrations FA and HA were determined

In **Chapter 6** approaches are evaluated to calculate critical loads and target loads for forest soils using partition relations derived in Chapter 2. In order to set target levels for metal inputs at which critical limits are reached within a certain time frame, a simple dynamic model is applied to predict the change in the metal concentration in the soil solid phase. Within the calculation of critical loads and target loads, WHAM Model VI is used to calculate the total solution concentration corresponding with the critical free metal ion concentration in soil solution. To calculate target loads partition relations were used additionally to calculate the reactive soil metal concentration in equilibrium with the critical free metal ion concentration. This approach is evaluated by comparing measured and predicted total solution concentrations, calculated by the model from measured free metal ion activities.

Chapter 7 deals with the risks of future Cd, Cu and Zn inputs, in response to various manure management policies, on long term accumulation and leaching of cadmium, copper and zinc in Dutch agricultural soils. Solid solution speciation in deeper soil layers is one of the key processes in the prediction of metal runoff to surface waters. Therefore we evaluated the predictions of dissolved Cd, Cu and Zn concentrations in some representative soil profiles and in ground water.

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CHAPTER 2

Transfer functions for solid-solution partitioning of cadmium, copper, nickel, lead and zinc in soils: derivation of relationships for free metal ion activities and validation with independent data

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Summary

Models to predict the solid-solution partitioning of trace metals are important tools in risk assessment, providing information on the biological availability of metals and their leaching. Empirically based models, or transfer functions, published to date differ with respect to the mathematical model used, the optimization method, the methods used to determine metal concentrations in the solid and solution phases and the soil properties accounted for. Here we review these methodological aspects before deriving our own transfer functions that relate free metal ion activities to reactive metal concentrations in the solid phase. One single function was able to predict free metal ion activities estimated by a variety of soil solution extraction methods. Evaluation of the mathematical formulation showed that transfer functions derived to optimize the Freundlich adsorption constant (K_f), in contrast to functions derived to optimize either the solid or solution concentration, were most suitable for predicting concentrations in solution from solid phase concentrations and *vice versa*. The model was shown to be generally applicable on the basis of a large number of independent data, for which predicted free metal activities were within one order of magnitude of the observations. The model only over-estimated free metal ion activities at alkaline pH (> 7). The use of the reactive metal concentration measured by 0.43 M HNO_3 rather than the total metal concentration resulted in a close correlation with measured data, particularly for nickel and zinc.

1 Introduction

Solid-solution partitioning and solution speciation of metals are key factors influencing the accumulation, mobility (retention and transport) and bio-availability of metals in soils. Recent model concepts for metal toxicity in soils such as the terrestrial Biotic Ligand Model (*1*) assume that free metal ions are the key determinant in metal toxicity on the basis of evidence that toxic effects of trace metals on soil fauna and flora are more directly related to free-metal ion concentrations than to the whole soil metal pool (*2-4*).

At present two major types of models are used to predict the dissolved total or free-metal ion (FMI) activity: mechanistic models and empirically-derived transferfunctions relating FMI activity to soil metal contents and properties (*3, 5-8*). Compared with mechanistic models transfer functions require fewer input data and since no iterations are needed, they use far less computing time. They are, therefore, particularly suitable in large-scale applications (*9-12*) and/or when limited data are available. Transfer functions were used because of limited data by Lofts *et al*. (*13*) and De Vries *et al*. (*14*) to derive FMI-based critical limits from published toxicity experiments. These studies modeled the FMI activities from added total metal concentrations, soil organic matter (SOM) content and pH.

The most recent examples of mechanistic models to predict metal partitioning in soils are multi-surface models that combine separate adsorption models for different reactive soil phases (clay, organic matter, (hydr)oxides) (*15-18*). Although such mechanistic models are very promising, the use of empirical models can be favored in certain studies by the computational advantages, limited data availability and, in some cases, by a lack of process understanding.

Most of the publications on transfer functions are limited to specific metals for example Cu (*4*) and Cd (*19*), and/or soil properties for example organic soils (*20*). Experimental and methodological approaches in these studies differ widely in terms of:

1. extraction of soil solution. Methods include dilute salt extractions (*3, 6, 7*) and *in situ* solution sampling (rhizon samplers used by *20*);
2. extraction of metals in the solid phase with methods ranging from pseudo-total concentration determination using *Aqua Regia* (*4*) or nitric acid digestion (*6, 7, 21*) to reactive concentration determination using 0.43 M HNO_3 (*20*);
3. the use of sorption (e.g. *22*) versus desorption data (*6, 7, 20, 21*);
4. the soil and soil solution properties accounted for, which range from pH only (*8*) to a combination of pH, SOM, clay, (hydr)oxides and dissolved organic carbon (DOC) (*23*);
5. the explained variable of the model which varies from solution concentration (*3, 6, 7*) or solid phase concentration (*22*) to sorption constants such as K_d (*20*) and K_f (*24*) and
6. transfer functions for total solution concentrations (e.g. *23*) compared with FMI activities in solution (*3, 6, 7*).

The above methodological and conceptual differences restrict the general applicability of empirical transfer functions. While the derivation of case-specific partitioning equations, as is the case at present, is possible, uncertainty about their wider applicability limits their potential for use in the assessment of soil metal contamination. There would be clear advantages in developing a single, generic, transfer function for each metal which would cover a large range of soils and experimental conditions. The aim of this paper is, therefore, to develop and test such transfer functions for solid-solution partitioning. We first provide an over-view of the various different approaches used in published studies to derive transfer functions including the different mathematical formulations, extraction protocols and explanatory variables. Following this, three published datasets encompassing a range of soil types and metal extraction protocols are used to derive single transfer functions for Cd, Cu, nickel (Ni), lead (Pb) and Zn (zinc). Three different regression equations are used to derive transfer functions. The ability of these equations to predict solid and solution phase metals are tested against several independent datasets.

2 Review of relevant methodology

2.1 Mathematical formulation and optimization techniques

Several different forms of empirical models for metal partitioning are described in the literature as the basis of transfer functions. The most basic model describes metal partitioning with a constant distribution coefficient according to:

$K_d = Q/C$, (1)

where K_d = distribution constant (liters kg^{-1}), Q = metal concentration in the solid phase (mol kg^{-1}) and C = metal concentration in the solution phase (mol $liter^{-1}$). The K_d values can vary over several orders of magnitude for a given metal as a function of soil properties (*25*). Therefore several authors have related K_d to soil and soil solution properties (X_i) according to:

$$\log K_d = \alpha_0 + \sum \alpha_i \log(\mathrm{X}_i) \qquad (2)$$

Because pH is already log-transformed its value is used as such in Equation 2 and the following equations. Soil properties included range from pH and SOM (*5*), to a combination of clay content, cation exchange capacity, organic carbon content, dithionite-extractable iron (Fe) and aluminum (Al), and oxalate-extractable manganese (Mn) contents (*23, 26*).

Transfer functions can also account for non-linear sorption, by using extended Freundlich-type equations. The basis for these equations is the Freundlich-van Bemmelen equation (*27*):

$Q = K_f . C^n$, (3)

where the exponent *n* describes the variation in bonding strength with metal loading. As with the linear relations, Freundlich equations can be determined as a function of specific soil properties such as pH (*19*), pH and SOM (*3, 6-8*), or a larger set of soil properties such as pH, SOM, clay content, Fe and Al oxide contents and DOC (Elzinga *et al*., 1999; Römkens *et al*., 2004). Various optimization techniques are used to obtain the coefficients for the explanatory variables. The most common approach is to optimize either the concentration in solution (referred to as *C-Q* relation, Equation 4) or the concentration in the solid phase (*Q-C* relation, Equation 5) while using the concentration in the other phase and soil properties as explanatory variables:

$$\log C = \alpha_0 + \alpha_1 \log(Q) + \sum \alpha_i \log(\mathrm{X}_i) \qquad (4)$$

$$\log Q = \beta_0 + \beta_1 \log(C) + \sum \beta_i \log(\mathrm{X}_i) \qquad (5)$$

Although equations (4) and (5) are mathematically equivalent, least squares optimization does not give the same results in each case, because regression coefficients for a *C*-*Q* type relation minimize errors in *C*, whereas the coefficients in a *Q*-*C* relation minimize the error in the estimate of *Q*. Often it is not explicitly reported which variable (*C* or *Q*) was used for optimization, which results in errors when using a *Q*-*C* relation to calculate solution concentrations from *Q* or *vice versa*. Examples of *Q*-*C* relations are the transfer functions used by Elzinga *et al.* (*22*) for Cd, Zn and Cu. Tye *et al*. (*28*) have derived *C*-*Q* relations for FMI activities of Cd and Zn, Sauvé *et al*. (*6-8*) have derived *C*-*Q* relations for both total dissolved metal and FMI activities of Cu, Pb and Cd

An alternative to the optimization of solid or solution concentrations is the optimization of the Freundlich constants K_f and *n*:

$$\log K_f = \gamma_0 + \sum \gamma_i \log(\mathrm{X}_i) = \log Q - n \log C \qquad (6)$$

Whereas *C*-*Q* and *Q*-*C* and K_d relations can be derived by simple linear regression of the log transformed values, K_f relations also require the power term *n* to be optimized. So far K_f relations have only been derived by Römkens *et al*. (*29*) and Tye *et al*. (*24*). Römkens *et al*. (*29*) optimized *n* and simultaneously regressed K_f against soil properties while minimizing the error in K_f whereas Tye *et al.* (*24*) minimized the error in *C*. Sometimes it has been suggested that K_f optimized relations have been derived, when actually *C*-*Q* or *Q*-*C* relations were fitted (e.g. Elzinga *et al*. (*22*)). A novel approach is to derive the coefficients by means of Total Least Squares regression (TLS). Whereas in ordinary regression techniques the independent variable is assumed to be error-free, the TLS technique takes observational errors in both dependent and independent variables into account (*30*). In the present study we derive transfer functions using *C*-*Q*, K_f and TLS relations and compare the resulting functions.

2.2 Choice of experimental conditions and extractions

Several studies have shown hysteresis between sorption and desorption isotherms for metals e.g. Zn (*31*) and Cu (*32*) Hysteresis in batch studies may result from kinetic retention behavior (*33*) and/or irreversible sorption. Several studies show an increase in the magnitude of sorption/desorption hysteresis with longer sorption periods, also referred to as ageing (*34*). Because the transfer functions to be derived are primarily aimed at the prediction of solution concentrations from solid phase concentrations, we have decided to use only data from unspiked soils.

Various analytical procedures are used for the extraction of metals from soils. These include pseudo-total extractions (*Aqua Regia*, nitric acid digestion), as well as many single extraction methods to extract ‘available’ metals in soils. Only some of the metal in the solid phase is available for interaction with the soil solution at short time scales through fast processes such as sorption/desorption and (surface) precipitation reactions. This we tentatively refer to as the reactive fraction. The other ‘inert’ component is not readily available because it is occluded in the matrix of soil constituents such as (hydr)oxides, clay minerals and SOM either because of its geogenic origin or through processes such as ageing. The inert metals are assumed to be released from the soil matrix only by very slow processes such as weathering. For transfer functions we are interested in the (pseudo) equilibrium between the solid and solution phases which is established within short times of days at the longest. Therefore, only the reactive metal pool is considered here. The use of isotopically exchangeable metals as a measure of chemically reactive metals (*33, 35*) is probably the most suitable technique to determine the reactive pool. However, at present it is not widely available for routine analysis and not available for all metals because of the lack of a suitable isotope (*36*). Single extractions with EDTA or dilute acid extractions (0.43 M HNO_3) are likely to provide the most easily used measures of reactive metal concentrations. Extraction with 0.43 M HNO_3 has been used by several authors (*16, 37, 38*). Good agreement between EDTA and 0.43 mol l^{-1} HNO3 extracted metal has been shown by Tipping *et al*. (*20*) for organic soils (>10% SOM), and by Groenenberg *et al*. (*39*) and De Vries *et al*. (*40*) for a large range of forest and agricultural soils. With the 0.43 M HNO_3-extracted metal as input, Dijkstra *et al*. (*17*) obtained good geochemical modeling predictions of soil solution concentrations (for Cd, Cu, Pb, Zn and Ni) from batch experiments ranging in pH from 2–12 using their multisurface model. In our study we therefore use the results of 0.43 M HNO_3 extractions to quantify the reactive metal concentration in soils.

A range of methods is also used for estimating the dissolved metal concentrations in the soil solution. Concentrations of DOC and metals may vary significantly amongst the different methods used (*41*). In this study we make use of data for i) soil solutions obtained by dilute salt extracts with electrolyte concentrations in the range from 0.002 to 0.01 M, which is realistic for field conditions between field capacity and wilting point (*42*) and ii) solutions obtained from soils at field capacity by centrifuging or sampling with Rhizons (small-scale tension lysimeters).

2.3 Choice of explanatory variables

Experimental sorption and desorption studies have revealed the importance of soil properties such as pH, SOM, clay, DOC, Fe/Al (hydr)oxides and ionic strength for the retention of metals in soils (*32, 43*). For metals such as Cd and Zn, pH appears to be the most important explanatory variable (e.g. *8, 26, 44, 45*). Organic matter appears to be the most dominant metal-sorbing constituent in soils for Cd (*5, 46*) and Cu (*38*). Recently the dominant role of organic matter in the binding of copper was confirmed by Strawn and Baker (*47*) using X-ray absorption near-edge and extended X-ray absorption fine-structure spectroscopy studies. The results of mechanistic multisurface models (*15-18*) also show that organic matter is the most important metal sorbent in soils. Furthermore, ionic strength has shown to influence metal partitioning (e.g. *48, 49*) because of competition with cations and complexation with anions (for example Cl^-) and effects on DOM concentration (*50*).

The aim of our present study was to derive transfer functions that can be applied easily in large-scale studies. The choice of explanatory variables was therefore restricted to those that are most important and easily accessible from soil maps and soil-monitoring studies. Hence we selected pH and SOM content as the prime variables. However, we also evaluated the effect on the model performance of adding the additional variables of clay and Al and Fe-(hydr)oxide contents.

3 Materials and methods used for the derivation of transfer functions

3.1 Soils and sampling

Three published soil datasets were used to derive new transfer functions, here named NL1, NL2 and UK. NL1 is a dataset for soils from the Netherlands described in detail in De Groot *et al*. (*51*) and Römkens *et al.* (*29*). Briefly, it contains 49 topsoil samples (0 – 20 cm) of various soil types and degrees of metal contamination, from clean soils to heavily contaminated soils. NL2 (*29*) contains 69 soil samples from all diagnostic horizons down to 120 cm (between two and six horizons depending on soil type) from soil profiles at 11 locations in the Netherlands. Metal concentrations range from background levels to moderately increased levels from diffuse sources. Both datasets include sandy soils, clay soils, peat soils and a loess soil. The UK dataset (*20*) contains samples of surface soils (0 – 5 cm) collected from upland moorland sites in the UK with large organic matter contents (>10%). Soil properties and metal concentrations of the three data sets are summarized in Table 1.

TABLE 1 Range of solid phase characteristics for the three sets of soil samples used to derive the transfer functions (total metal concentrations extracted with *aqua regia*)

Dataset		OM	clay	Fe-ox	Al-ox	pH	Cd	Cu	Ni	Pb	Zn
		(%)		(mmol kg^{-1})					(mg kg^{-1})		
NL1 (n=49)	minimum	2.0	0.8	6.6	6.6	3.7	0.03	0.6	0.5	5.0	5.9
	median	4.9	4.5	44	24	5.6	0.48	16.7	12.7	38.0	110
	maximum	13.3	27.0	155	58	7.3	21.2	326	64.5	1473	7563
NL2 (n=69)	minimum	0.5	1.0	11.4	1.3	4.1	0.01	0.1	0.4	1.0	2.8
	median	2.9	7.0	39	38	5.0	0.37	10.9	13.7	22.0	46
	maximum	36	42	117	160	6.6	10.9	129	51.7	1663	3770
UK (n=98)	minimum	9.0		-	-	3.3	0.1	1.7		10.9	1.9
	median	40.1		-	-	4.4	0.5	7.7		85.3	20.6
	maximum	97.8		-	-	8.3	44.9	144.0		9660	2460

3.2 Soil solution extraction and chemical analyses

For datasets NL1 and UK, soil solution was extracted from field-moist soils. Soil solution from NL1 was obtained from 2 kg of soil which was moistened with a 2 mM $Ca(NO_3)_2$ solution up to a pF-value of 2. The moistened samples were stored for three weeks at 5° C (*52*). Thereafter, pore-water was obtained by centrifugation at 7500 rpm (6000 g) at 5° C. After centrifugation, the pore-water was filtered through a 0.45 µm membrane filter and the pH measured. The pore-water was divided between two polyethylene bottles, one used for determination of anions and DOC and the other was acidified with concentrated nitric acid to pH 2 for metal analysis. For the UK samples, blocks of field moist soils were brought to field capacity by adding high purity water and stored at 4° C to equilibrate for a week. Thereafter they were left for two days at room temperature after which the pore water was extracted over night with diagonally inserted rhizon samplers. Dried soil samples from both Dutch sets (NL1 and NL2) were equilibrated with solutions of 0.002 and 0.01 M $CaCl_2$ or 0.002 M $Ca(NO_3)_2$. The extraction conditions are summarized in Table 2. In addition to their natural pH, samples from set NL2 were also extracted at two amended pH levels, approximately 0.5 to 1 and 1.5 to 2 pH units more acidic than the initial soil pH, by adding nitric acid at the same ionic strength as the background electrolyte in the soil-solution mixture. The soil-solution ratio was kept constant by reducing the volume of salt solution by the equivalent amount of acid added. The samples were shaken continuously in an end-over-end shaker to ensure complete contact between soil and solution (approximately 30 rpm) for 48 hours. Thereafter, the solutions were allowed to settle in the centrifuge tubes and after one hour, the pH was measured in the tube directly before filtration. The supernatant-soil mixture was centrifuged at 3000 rpm followed by filtration through a 0.45 µm filter using syringes and screw filters. The extracts were stored at 4° C until further analysis.

TABLE 2 Summary of weak salt extractions used in the datasets to assess soil solution concentrations

Extraction solution	Soil : solution ratio	Dataset	Number of extractions	Analysis of metals	Analysis of anions
0.002 M $CaCl_2$	1:2	NL1	49	ICP-AES	FIA
0.01 M $CaCl_2$	1:4	NL1, NL2	118	ICP-MS	-
0.002 M $Ca(NO_3)_2$	1:2	NL1, NL2	187	ICP-AES	-
0.002 M $Ca(NO_3)_2$ + nitric acid	1:2	NL2	276 (two pH values)	ICP-AES	-
0.002 M $Ca(NO_3)_2$	1:2 DMT	NL1	23	ICP-MS	-

Table 3 summarizes the analytical methods used for the analyses of the soils, soil solutions and salt extracts. Samples from NL1 were also used by Weng *et al*. (*53*) to determine the FMI activities in a 0.002 M $CaCl_2$ solution percolating through a column using the Donnan Membrane Technique (DMT) (Temminghoff *et al*., 2000). From the NL2 set, three soil profiles, a sandy, peat and clay soil) were selected in which measurements were made of fulvic (FA), humic (HA) and hydrophilic acids in a 0.002 M $CaCl_2$ extract (1:2 soil to solution ratio) for all the horizons using a batch procedure developed by van Zomeren & Comans (*54*).

TABLE 3 Data sets for deriving transfer functions: summary of methods for extracting and characterizing the soil solid phase and for analysing the soil solution

Soil solid phase	UK	NL1	NL2
soil organic matter	LOI	LOI	LOI
total metal	nitric acid and perchloric acid digestion	aqua regia,	aqua regia,
reactive metal	0.43 M HNO_3 (1 g: 10 ml); 0.1 M Na_2EDTA (1 g: 10 ml)	0.43 M HNO_3 0.05 M Na_2EDTA	0.43 M HNO_3 0.05 M Na_2EDTA
clay content	-	sedimentation (pipette method)	sedimentation (pipette method)
Fe and Al oxides	-	oxalate extraction	oxalate extraction
Soil solution			
pH	combination glass-calomel electrode	combination glass-calomel electrode	combination glass-calomel electrode
DOC	Dohrmann DC-190 TOC analyser	Dohrmann DC-190 TOC analyser	Shimadzu TOC analyser
trace metals and major cations[a]	filtered (0.2 um) and acidified: ICP-MS	filtered (0.45 um) and acidified: Cd, Ni, Pb GF-AAS; Cu, Zn Flame-AAS; Major cations ICP-AES	filtered (0.45 um) and acidified: ICP-AES/ ICP-MS (including P and S)
anions	-	Cl, NO_3, SO_4: IC PO_4: FIA	-

[a] Al, Fe, Ca, Mg, K, Na

3.3 Speciation modeling

Speciation modeling was used to estimate FMI activity for both the derivation of the transfer functions and testing against independent samples, for those datasets where only total dissolved concentrations were measured. We calculated chemical speciation using the WHAM/Model VI which is parameterized for fulvic and humic acids from an extensive set of experimental data (*55*). For Al and Fe(III) we used the revised parameter values from Tipping *et al*. (*56*). Measured pH and concentrations of the trace metals (Cd, Cu, Ni, Zn and Pb) and major cations (calcium, magnesium, sodium, potassium, Al and Fe) in solution were used as inputs to the model. Using the average FA and HA fractions of DOM measured in 0.002 M $CaCl_2$ extracts from three soil profiles of NL1, we modeled dissolved organic matter (DOM) as 40% FA and 10% HA. DOM was calculated from DOC by assuming it to be 50% C by weight. Concentrations of NO_3^- and Cl^- were made equal to the concentration of the background electrolyte or calculated from the anion deficit. Concentrations of PO_4^{3-} and SO_4^{2-} were set equal to total P and S as measured with ICP-AES. Major cations (especially Al and Fe) can compete significantly with trace metals for binding with humic substances (*56*):

therefore the measured Al and Fe concentrations were used for samples which were under-saturated with respect to $Al(OH)_3$ ($pK_{so,25}$=8.5) and $Fe(OH)_3$ ($pK_{so,25}$=2.5), otherwise FMI activities corresponding to the assumed maximum solubility were used for speciation calculations.

3.4 Derivation of transfer functions

We used multiple linear regression analysis to derive the regression coefficients for the *C-Q* relations (Equation 4) as is done in most other studies. New approaches were used to derive K_f-relations (Equation 6) either by optimization with TLS or by the simultaneous optimization of K_f and the Freundlich exponent *n*. The latter was done by an iterative procedure in which K_f was regressed against soil properties while optimizing n with the Solver routine in Microsoft Excel to maximize the variance explained (R^2).

3.5 Validation of transfer functions on independent data

To test the validity and applicability of the derived transfer functions, the models were applied to published and as-yet unpublished independent solid-solution partitioning data, summarized in Table 4. In common with the derivation of the transfer functions, only data from desorption studies were used. For all metals, measured free ion activities were available, although methods of detection varied among metals. Methods to determine FMI activities included DMT (DMT, *57*), ion selective electrodes (ISE, *4*) and differential pulse anodic stripping voltammetry (DPASV, *6*). Different methods to obtain the soil solution were also used among the studies (see Table 4). If available, the reactive metal concentration was used in the calculation but datasets with only measurements of the total metal concentration (measured with strong acid extractions) were also used. Although relationships between reactive and total metal concentrations have been derived (*40*), we decided to use the original data without correction because firstly those relationships were derived from data from clean and diffusely-polluted soils only and secondly, relationships were not available for all the different extracts used in the partitioning studies.

To quantify the fit of the transfer functions to independent data we used statistical measures. The mean error (ME) indicates whether on average the model gives an under-prediction (negative value) or over-prediction (positive value). The mean absolute error (MAE) and the root mean square error (RMSE) give the average deviation of the model results, the latter giving a greater weight to data points with a large deviation.

TABLE 4 Overview of data used for validation of transferfunctions and numbers of samples within the data sets (n)

metal(s)	Solid phase extraction	Solution phase extraction	FMI activity determination	n	Description	Reference
Cd, Cu, Ni, Pb, Zn	0.43 M HNO_3	centrifugation	WHAM	20	two profiles forest soils	Goody *et al.* (*37*)
Cu	*Aqua Regia*	rhizon samplers	Cu-ISE	22	Cu contaminated soils: UK, Chile and China	Vulkan *et al.* (*4*)
Cd, Cu, Pb and Zn	*Aqua Regia*	centrifugation rewetted soils	DMT	27	agricultural soils Australia and contaminated soils Australia and US	Nolan *et al.* (*58*)
Cd	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	61	contaminated agricultural and urban soils: US and Canada	Sauvé *et al.* (*8*)
Pb	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	84	contaminated agricultural and urban soils: US and Canada	Sauvé *et al.* (*6*)
Zn	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	66	contaminated soils: North America and Europe	Stephan *et al.* (*59*)
Cu	HNO_3 digestion	0.01 M $CaCl_2$ extract	Cu-ISE	68	contaminated soils: US, Canada and Denmark	Sauvé *et al.* (*7*)
Cd, Cu, Ni, Pb, Zn	2 M HNO_3	percolation 0.002 M $Ca(NO3)_2$	SC-DMT	26	sandy, agricultural soil: Netherlands	Weng *et al.* (*53*)
Cu		0.002, 0.01 and 0.05 M $Ca(NO_3)_2$ extractions at three amended pH values	Cu-ISE	126	agricultural soils at different pH values by addition of HNO_3: Hungary	Murányi *et al.* (*60*)
Cd, Cu, Ni, Pb	0.43 M HNO_3	percolation 0.002 M $Ca(NO3)_2$	DMT (Cu-ISE)	19	contaminated forest soils (smelter) including organic horizon: Russia	Pampura *et al.* (*61, 62*)
Cd, Pb	0.43 M HNO_3	water extract/ lysimeter	WHAM	33	forest soils: Germany/ contaminated forest soils: Russia	Pampura *et al. (61)*
Cd, Cu, Pb, Zn	0.43 M HNO_3	percolation 0.002 M $Ca(NO3)_2$	DMT	27	contaminated soil (smelter): France	Cancès *et al.* (16)

continued on next page

TABLE 4 Overview of data used for validation of transferfunctions and numbers of samples within the data sets (n)

metal(s)	Solid phase extraction	Solution phase extraction	FMI activity determination	n	Description	Reference
Cd, Pb, Zn	0.43 M HNO_3	0.002, 0.01 and 0.05 M $Ca(NO_3)_2$ extractions at 3 amended pH levels	WHAM	126	agricultural soils, different pH levels by addition of HNO_3: Hungary	Murányi *et al.* (*60*)
Cd, Cu, Ni, Pb, Zn	0.05 M EDTA	Rhizon samplers	WHAM	56	soils from different land uses: UK	Shotbolt and Ashmore (*63*)
Cd, Cu, Pb, Zn	0.02 M EDTA/ NH_4Ac	water extracts (1:10)	WHAM	225	forest soils: Switzerland	Luster, unpublished data
Cd, Cu, Ni, Zn	0.43 M HNO_3	0.002 M $CaCl_2$ extract (1:10)	DMT	6	contaminated soils: Netherlands, Denmark and China	Koopmans *et al. (64)*
Cd, Cu, Ni, Pb, Zn	0.43 M HNO_3	0.002 M $CaCl_2$ extract (1:10)	DMT	4	contaminated soils	Chapter 5 (*65*)

4 Results and discussion

4.1 Speciation calculations

The transfer functions derived below were based on FMI activities calculated with WHAM/ Model VI from datasets NL1, NL2 and UK. Calculated FMI activities ranged from approximately 2 to 80% of total dissolved concentrations for Cd, Ni and Zn, from as little as 0.00003% to 80% for Cu and from 0.001% to 80% for Pb. Metal binding to DOC was crucial for solution speciation whereas binding to inorganic anions proved to be unimportant except for Cd and Pb in 0.01 M $CaCl_2$ solutions. Speciation calculations for the 0.01 M $CaCl_2$ extractions show strong complexation of Cd with Cl, with chloride complexes contributing 40 – 49% to the total concentration. Complexation of Pb with Cl varied strongly from 0.2 to 26%, (average 12.6%) of the total dissolved Pb concentration depending on pH, with almost no chloride complexation at alkaline pH because of strong complexation with humic substances. For the other elements, chloride complexes contributed only approximately 2.5% (with little variation) to the total solution concentration.

4.2 Validation of calculated free metal activities (FMI)

Because the derivation of transfer functions relies heavily on the speciation model used, we also tested the goodness of fit of WHAM/Model VI for datasets with FMI activities measured with the DMT (57) and with sufficient data to perform the speciation calculations. We used data from Weng et al. (53) for 32 of the 49 samples of dataset NL1, Pampura et al. (61, 62) including O and B horizons of forest soils, Koopmans et al. (64) and Chapter 5. FMI activities were calculated as described above. Figure 1 gives a comparison between FMI activities calculated with WHAM and the measured FMI activities. Table 5 gives an overview of the performance measures for the different metals. Note that the measurements refer to log activities. On average, WHAM gave a reasonably good prediction of the FMI activity with a MAE from 0.2 to approximately 0.6 on a logarithmic scale. The largest deviations were found for Cu and Pb, which have the greatest affinity for binding to DOM. However, the DMT measurement is not itself error free. Comparison between DMT measured and calculated FMI activities in the well-defined systems of Cd with Cl and Cu with EDTA showed differences ranging from negligible values up to 0.3 on a log scale (57). Because the ME was close to zero, there was no bias in the FMI activity predictions for Cd, Pb and Zn, whereas WHAM over-estimated FMI activities for Cu and Ni (0.14 – 0.23 on a logarithmic scale). Errors in the predictions with WHAM will have contributed to error in the derived transfer functions. Because of the small or negligible bias, the error will only have contributed to the unexplained variance of the derived transfer functions.

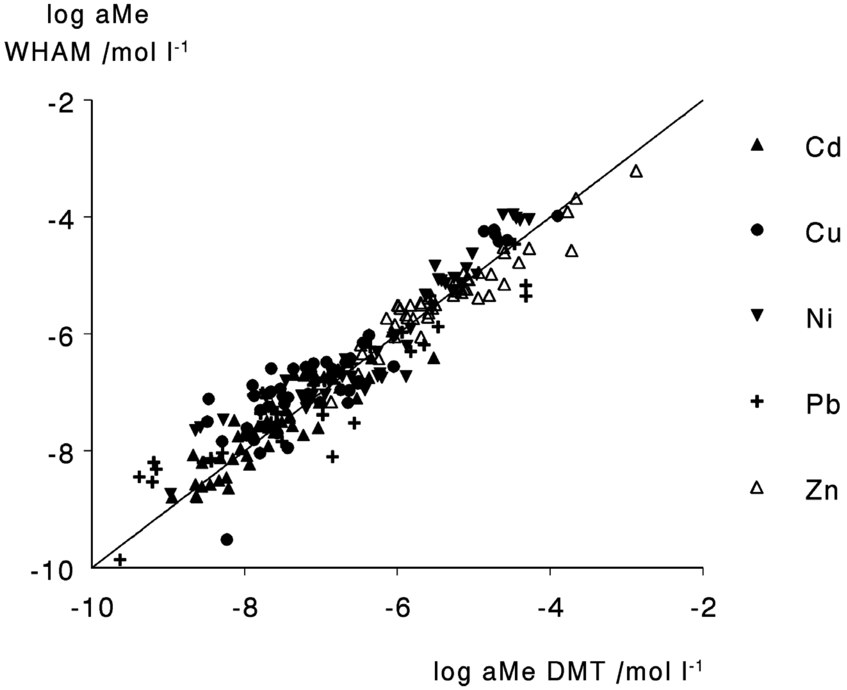

FIGURE 1 FMI activities calculated with WHAM/Model VI compared with DMT measurements

TABLE 5 Summary of parameters for the performance of WHAM speciation calculations, as compared to DMT measurements (49 samples)

	Ni	Cu	Zn	Cd	Pb
RMSE	0.40	0.54	0.27	0.32	0.72
MAE	0.29	0.45	0.21	0.25	0.56
ME	0.14	0.23	-0.02	0.02	0.08

4.3 Transfer functions

Transfer functions for the combined data sets NL1, NL2 and UK were derived with different regression models using measured (if available) or modeled FMI activities, pH in the soil solution, reactive metal contents (extracted with 0.43 M HNO_3), and organic matter content. Optimized regression coefficients are summarized in Tables 6, 7 and 8 for the C-Q relationships (Equation 4), K_f-relationships (Equation 6) and TLS relationships, respectively. Coefficients for TLS relations are presented, such that these can be used in Equation 6 (K_f relation). In general the regression results indicate that the limited number of properties included (organic matter and pH) were able to explain a considerable part of the variation in the FMI activities. The variance explained (R^2) was always 80% or greater higher, except for Ni for which the fit of the C-Q relation was relatively poor with R^2 = 68%. This difference might be because of the relatively small range in Ni concentrations in the data used to derive the transfer functions

TABLE 6 Regression coefficients, variance accounted for, standard error of the regression and mean absolute errors for the prediction of C for the C-Q relations (Equation 4)

	α_0	α_1 Q	α_2 (SOM)	α_3 (pH)	R^2	se_y	MAE C
Cd	1.34	1.1	-1.0	-0.49	0.78	0.44	0.32
Cu	0.48	0.81	-0.89	-1.00	0.83	0.65	0.47
Ni	-0.98	0.74	-0.51	-0.42	0.68	0.33	0.25
Pb	2.24	0.81	-1.07	-1.21	0.87	0.78	0.58
Zn	0.81	0.99	-0.75	-0.50	0.80	0.46	0.34

TABLE 7 Regression coefficients, Freundlich coefficients, variance accounted for, standard error of the regression and mean absolute errors for the prediction of *C* for the K_f relations (Equation 6)

	γ_0	γ_1 (SOM)	γ_2 (pH)	n	R^2	se_y	MAE C
Cd	-2.04	0.84	0.41	0.78	0.82	0.36	0.34
Cu	-2.26	0.90	0.89	0.85	0.87	0.58	0.51
Ni	-1.81	0.82	0.43	0.81	0.86	0.33	0.32
Pb	-3.06	1.17	1.21	1.0	0.88	0.78	0.60
Zn	-1.44	0.72	0.46	0.86	0.81	0.41	0.35

TABLE 8 Regression coefficients and mean absolute errors for the prediction of *C* for the Total Least Square optimization reported according to Equation 6

	γ_0	γ_1 (SOM)	γ_2 (pH)	n	MAE C
Cd	-2.71	0.91	0.41	0.70	0.38
Cu	-3.37	0.87	0.64	0.57	0.61
Ni	-1.76	0.91	0.45	0.84	0.30
Pb	-3.46	1.35	0.96	0.84	0.70
Zn	-1.67	0.84	0.46	0.84	0.39

In Figure 2, FMI activities predicted with the K_f-based transfer function are compared with measured activities and FMI activities calculated from total solution concentrations. Broken lines indicate a one-order of magnitude deviation. The relationship gave good fits over large ranges of FMI activities, from four orders of magnitude for Cd to nine orders of magnitude for Cu and Pb, i.e. the metals with the strongest affinity to DOM. Logarithmic mean absolute errors were less than 0.6 for the K_f relations which is good, especially when the simplicity of the model, which does not account for electrostatic effects and competition of other cations such as Ca, Al and Fe, is considered. To some extent this is accounted for by correlation of these effects with pH which is included in the equations. However, the review of published data by Tipping (66) showed that although Al activity strongly follows pH, there is considerable scatter, and the same effect will probably apply to Ca and Fe. This will produce differences between soils and will show itself in the transfer functions as scatter. Large deviations (>>1 order of magnitude) for Cd and Pb occurred mainly in soils with small (<2%) SOM contents when other metal-binding soil constituents become more important. Figure 2 shows that the K_f relations were able to predict FMI activities for the different methods of solution extraction with rhizons and centrifugation, and with dilute salt solutions (0.002 M $Ca(NO_3)_2$ and 0.01 M $CaCl_2$). Differences resulting from different concentrations of complexing anions (Cl^-) and organic ligands (DOC), which vary substantially between the different extraction methods because of drying (67) and the use of different soil solution ratios (41), were largely accounted for by using FMI activities instead of total solution concentrations. DMT-measured data, however, seemed to be under-estimated by the transfer functions for Cd and Cu.

4.4 Comparison of mathematical models

We evaluated the three mathematical models (C-Q, K_f and TLS) by comparing their ability to fit i) the measured solution activities using solid phase concentrations as input, and ii) solid phase concentrations using solution activities as input. Table 9 gives the RMSE of the predicted versus measured solution activities (C) and solid phase concentrations (Q) for the different transfer functions. Mean errors were close to zero for all mathematical models. The C-Q and K_f relations produced similar fits for the solution activities with a slightly better fit for the C-Q relations. C-Q and K_f produced better predictions than the TLS-relations, especially for Cu and Pb for which the TLS relation produced large deviations of predicted solution activities. On the other hand, solid phase concentrations were best predicted by TLS relationships, followed by those for K_f. C-Q relationships had large errors in predicted solid phase concentrations, again with the largest deviations for Cu and Pb. This is illustrated in Figure 3 with the fit for Q using the C-Q relation (A) and the K_f relation (B) of copper. Although using TLS, neither C or Q were optimized, results showed a bias for the optimization of solid phase concentrations. We think that this can be explained by the strong correlation between solid phase concentrations and the organic matter content. By optimizing K_f this correlation is successfully suppressed. K_f relations provided the best fits when both solution activities and solid phase concentrations were considered, and are therefore particularly suitable for predictive calculations, for example in the dynamic modeling of soils subjected to varying inputs of metals, and for the calculation of metal leaching from soils.

TABLE 9 Root Mean Squared Errors (RMSE) for the prediction of *C* and *Q* for the different optimizations

	K_f		*C-Q*		TLS	
	C	*Q*	*C*	*Q*	*C*	*Q*
Cd	0.46	0.36	0.44	0.40	0.50	0.35
Cu	0.63	0.59	0.61	0.80	0.79	0.46
Ni	0.41	0.33	0.33	0.44	0.40	0.34
Pb	0.75	0.75	0.74	0.91	0.87	0.73
Zn	0.48	0.41	0.46	0.46	0.52	0.43

4.5 Evaluation of addition of other explanatory variables

To improve the fit of the regression equations, additional explanatory variables could be used. The best candidates are the concentrations of other metal-binding soil constituents such as clay minerals and Al and Fe (hydr)oxides. We evaluated the improvement of the fit by adding the clay content and oxalate-extractable Al and Fe to the variables for the NL1 and NL2 sets which include these data. The effect of the inclusion of these additional variables was minimal with an increase of 1 – 3% of the explained variance and a decrease in the standard error of the prediction (se_y) of 0.02 – 0.05 units. These results confirm the dominant effect of pH and SOM on the partitioning of metals. However, it cannot be concluded that the contribution of sorption on other constituents than SOM was negligible. Strong correlations between SOM and clay content or oxalate-extractable Al and Fe might mask their contribution. Nonetheless, the importance of SOM as the most important sorbent for data sets NL1 and NL2 has been confirmed by Bonten et al. (15) (Chapter 3) by calculations with their mechanistic multisurface model.

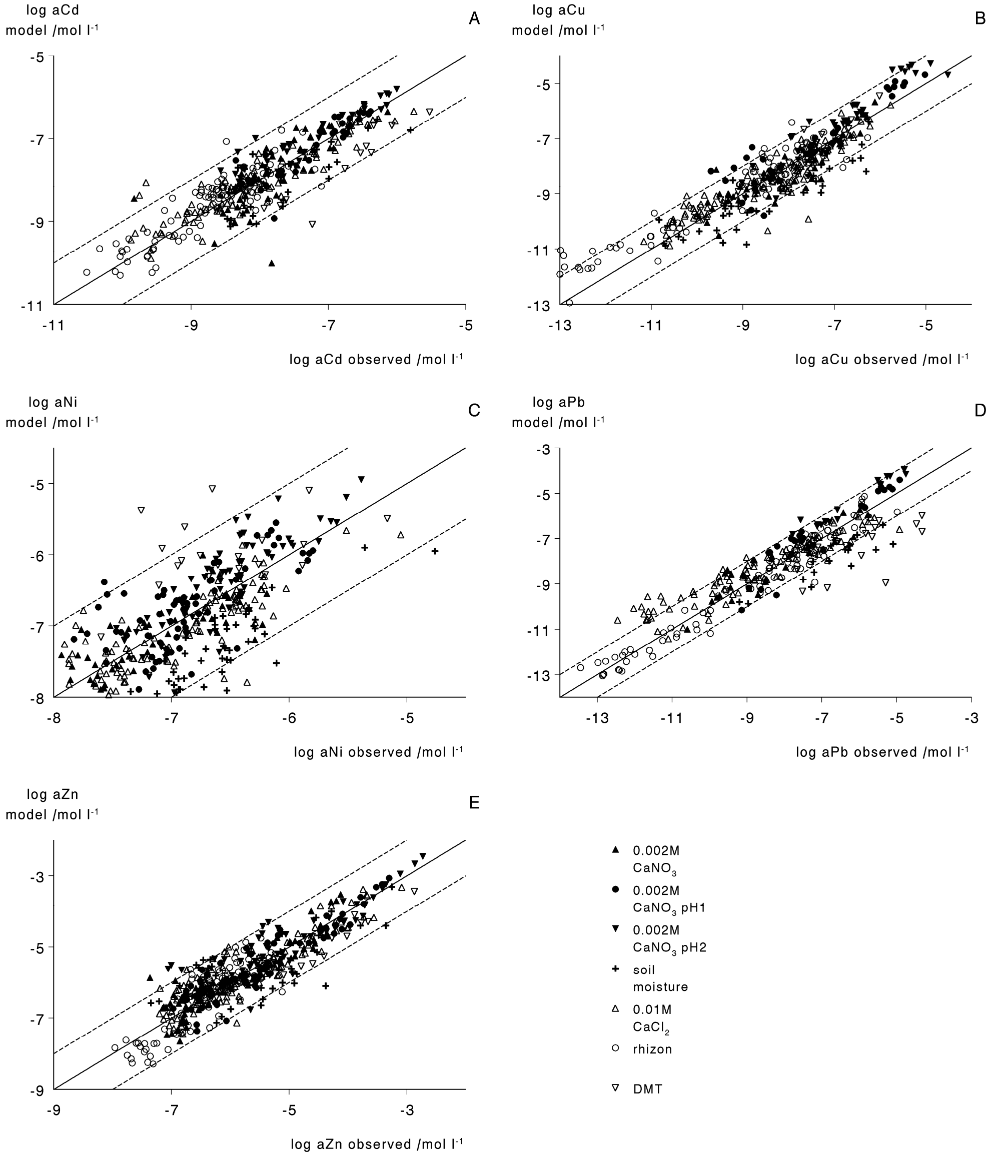

FIGURE 2 FMI activities predicted with K_f transferfunctions compared with FMI activities calculated with WHAM or measured with DMT for Cd (A), Cu (B), Ni (C), Pb (D) and Zn (E) . The solid line indicates a 1:1 fit; dotted lines give 1 order of magnitude deviation

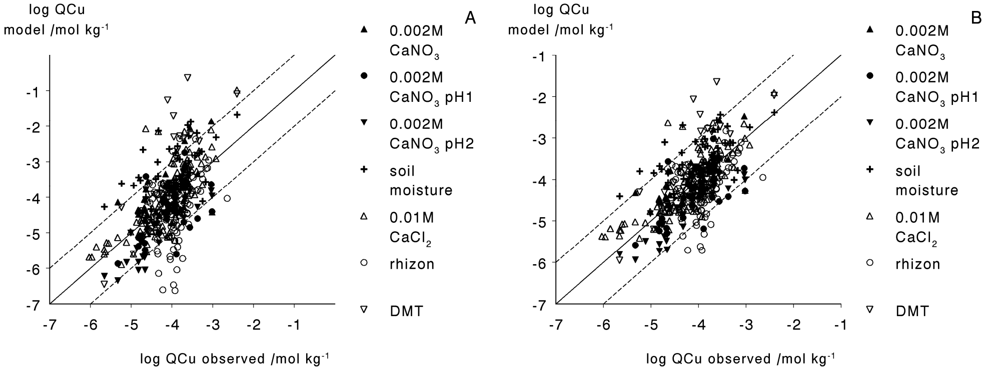

FIGURE 3 Solid phase concentrations predicted with the *C-Q* (A) and the K_f relation (B). The solid line indicates a 1:1 fit; dotted lines give 1 order of magnitude deviation.

4.6 pH dependence of metal binding

As a result of analyzing only desorption data for unspiked soils, only a single observation of solid phase concentration per sample was available. For most soil samples, desorption data were only available at the native pH of the soil solution. Therefore, the pH coefficient and the Freundlich exponent were optimized by comparing different samples with different metal concentrations and different pH, rather than by optimizing the change in solid solution partitioning for a single soil over ranges of pH and metal loadings, as can be obtained from sorption experiments. This means that the pH coefficient in the transfer functions did not necessarily reflect the change in partitioning for a particular soil with changing pH. We evaluated the pH dependence of metal binding per soil sample by using dataset NL2 for which we had desorption data for each sample at three pH values; one data point at the native pH of the solution and two data points for samples acidified with HNO_3 to between 0.5 – 1 and 1.5 – 2 pH units more acidic than the native pH. We calculated the pH dependence as the ratio of the change in log FMI with the change in pH. This ratio equaled the negative value of the ratio of the pH coefficient in the K_f relation (γ_2) and the Freundlich exponent (n):

$$\frac{\Delta \log_{10} a_{Me}}{\Delta pH} = -\frac{\gamma_2}{n} \qquad (7)$$

According to van Riemsdijk et al. (68), the left hand side of Equation 7 equals the proton/metal exchange ratio in a binary system, which changes with pH and metal loading. The calculated pH dependence (data not shown) varied considerably among the different samples. These results showed that the pH coefficient of the K_f relation reflects an average pH response rather than the particular response of a specific sample at a certain pH. pH-dependent leaching/desorption data such as those of Dijkstra et al. (17), obtained over a wider range of pH values, can give more information on the pH response for individual soils.

4.7 Validation of transfer functions on independent data.

To test the validity of the derived transfer functions, we compared predictions of dissolved FMI activities with observations for a large set of independent samples. The observations were based on WHAM calculations, using measured total dissolved metal concentrations, and measurements of FMI activities. The comparison is summarized with statistical measures in Table 10. Figure 4 compares predictions with independent measurements. In general, the transfer functions were able to predict FMI activities for all metals within one order of magnitude (MAE ≤1), which is comparable to the precision of mechanistic models when used with their default parameters. Errors in predicted FMI activities using the transfer functions for the complete set of independent data used here (RMSE ranging from 0.7– 1.2) appear to be larger than those calculated with a multi-surface model (69) for a small data set with just one type of soil (RMSE ranging from 0.3 – 0.9). Errors in predictions with WHAM/Model VI for the whole UK dataset (20) were within one order of magnitude, comparable to the errors of the transfer functions. Mean errors show that the transfer functions over-estimated FMI activities for most metals of the independent data. This is partly explained by the fact that the independent data were generated using stronger metal extractants than the 0.43 M HNO_3 which was used to obtain the data from which the transfer functions were derived.

TABLE 10 Summary of parameters for the performance of K_f transfer functions and the number of data points (n) used in the evaluation

metal	Fit of transfer function based on measured free ion activities				Fit of transfer function based on modelled free ion activities			
	MAE	RMSE	ME	n	MAE	RMSE	ME	n
Cd	0.85	1.1	0.61	156	0.54	0.75	0.0	219
Cu	0.68	0.85	0.30	298	0.82	1.05	0.48	260
Ni	0.99	1.0	0.94	51	0.50	0.71	0.30	76
Pb	0.87	1.1	-0.68	151	0.61	0.98	-0.01	366
Zn	1.0	1.2	0.94	153	0.57	0.72	0.50	278

Comparison of predicted Cd free ion activities with WHAM-calculated (Figure 4A) and measured free ion activities (Figure 4B) shows that the transfer function was able to predict Cd for most soils within one order of magnitude. Larger deviations were observed for soils with pH >7. These observations include soils with $CaCO_3$ from the unpublished results of J. Luster and soils with pH >7 in the data set of Sauvé et al. (8). The over-estimation of Cd^{2+} activities in the data from Sauvé may result in part from the nitric acid digestion method that they used to measure metal contents in the solid phase, which extracts more Cd than 0.43 M HNO_3.

Predicted copper free ion activities compared very well with the independent data, both for the WHAM-predicted (Figure 4C) and measured free metal activities (Figure 4D). Apparently there was no great effect on the quality of the prediction resulting from the different methods applied, i.e. copper ion selective electrodes (4, 7, 60) and DMT (53, 61, 62). Some points (9 out of 302 of measured Cu FMI activity) showed a larger deviation (>>1). These are almost exclusively free Cu^{2+} activities measured with DMT by Nolan et al. (58) at pH 6 and greater. According to Nolan et al. (58), predictions with WHAM for alkaline soil solutions (7.5<pH<8.5) were 1 – 4 orders smaller than was measured with DMT. This mismatch between model calculations and measurements contradicts the good agreement found by Vulkan et al. (4) between WHAM and ion selective electrodes for alkaline solutions. At alkaline pH the Cu concentration in the acceptor solution used in the DMT, which is open to the air, may be much larger than the concentration of the free Cu^{2+} ion alone, because of complexation with HCO_3. We have estimated from speciation calculations, assuming a pCO_2 in equilibrium with the air, that Cu concentrations in the acceptor may be more than three orders of magnitude greater than the FMI concentration depending on pH. Therefore, we conclude that the mismatch between DMT measurements and WHAM reported by Nolan results from problems with the interpretation of the measurements rather than to an over-estimation of Cu complexation by WHAM.

Mean average errors for Ni indicate that there was approximately half an order of magnitude deviation between the transfer function predictions and the WHAM-predicted activities (Figure 4E) and one order of magnitude between transfer function predictions and measured FMI activities (Figure 4 F). For the measured data this is mainly the result of the large over-prediction of the data from Weng et al. (69), who used a stronger 2 M HNO_3 extraction. Differences between extractions were particularly large for Ni: we found for dataset NL1 and NL2 that 0.43 M HNO_3 extracted only 20% of the amount extracted by Aqua Regia.

Free ion activities of Pb calculated with the transfer function were within one order of magnitude for almost all data (Figures 4G and 4H). Comparison with both calculated and measured Pb activities showed good agreement for soils with pH <7. Within the set of calculated activities, larger deviations than 1.0 were found for some points from the dataset of J. Luster (Figure 4G) for which the transfer function over-estimated the FMI activity. These points are exclusively from samples with pH pH >7 and containing carbonate. For most soils containing solid calcium carbonate, solution concentrations were below the detection limit of the ICP-MS (< 0.04 ug $liter^{-1}$). For all cases with measurable solution concentrations, deviations were larger than 1.5 log units. In the set of measured FMI activities, however, the transfer function gives a smaller estimate than measured for samples with alkaline pH (see Figure 4g) which were mainly in the data from Sauvé et al. (6). According to Ge et al. (70), who have modeled the solution speciation of the data from Sauvé et al. (6) and calculated smaller FMI activities with WinHumic V than were measured with, this discrepancy may result from to overestimation of free metals by differential pulse anodic stripping voltammetry at alkaline pH.

Comparison of predicted Zn FMI activities with WHAM-calculated free ion data (Figure 4I) from soil solution measurements show good agreement, except for data in the lower range, which are mostly samples with pH > 7, for which the transfer functions over-estimates FMI activities. The transfer function predicts greater FMI activities than those measured for the data sets with strong extractants to determine soil metal contents for example Stephan et al. (59) who used a nitric acid digestion, Weng et al. (69) who used 2 M HNO3 and Nolan et al. (58) who used Aqua Regia (Figure 4J). The over-estimation by the transfer functions was greater for uncontaminated soils, where a larger part of the total metal is not reactive, than for contaminated soils. For the data sets in which 0.43 M HNO3 was used we did not observe this over-prediction of FMI activities.

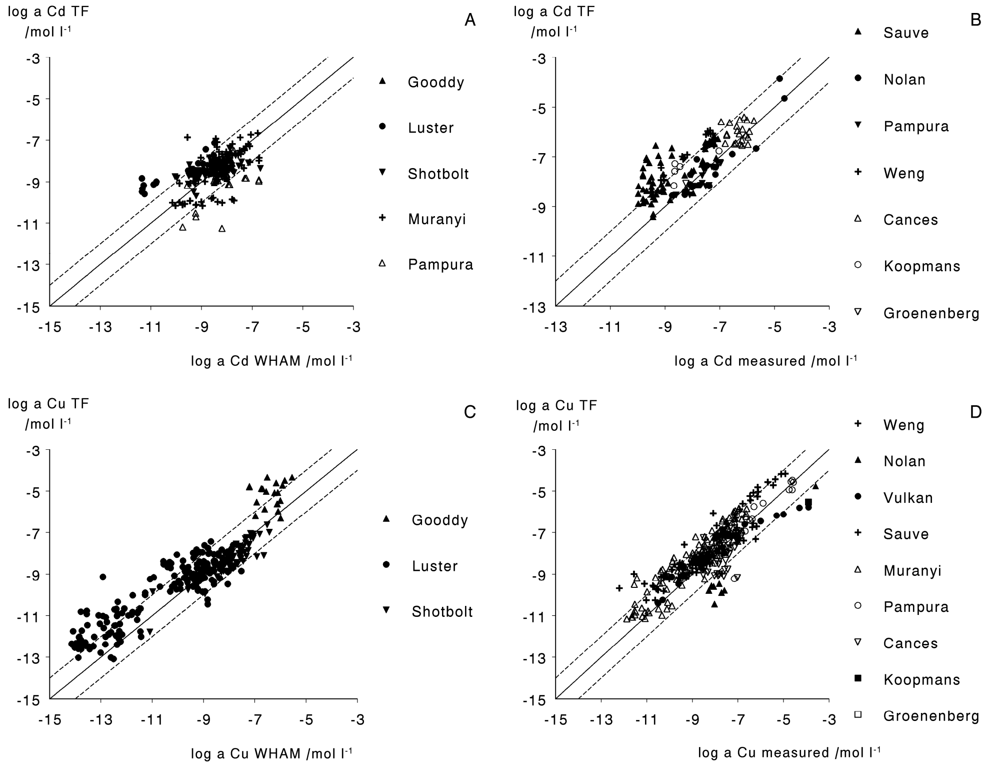

FIGURE 4 FMI activities predicted with the K_f transferfunctions compared with WHAM predictions (left) or measurements (right) for Cd (A,B), Cu (C,D)

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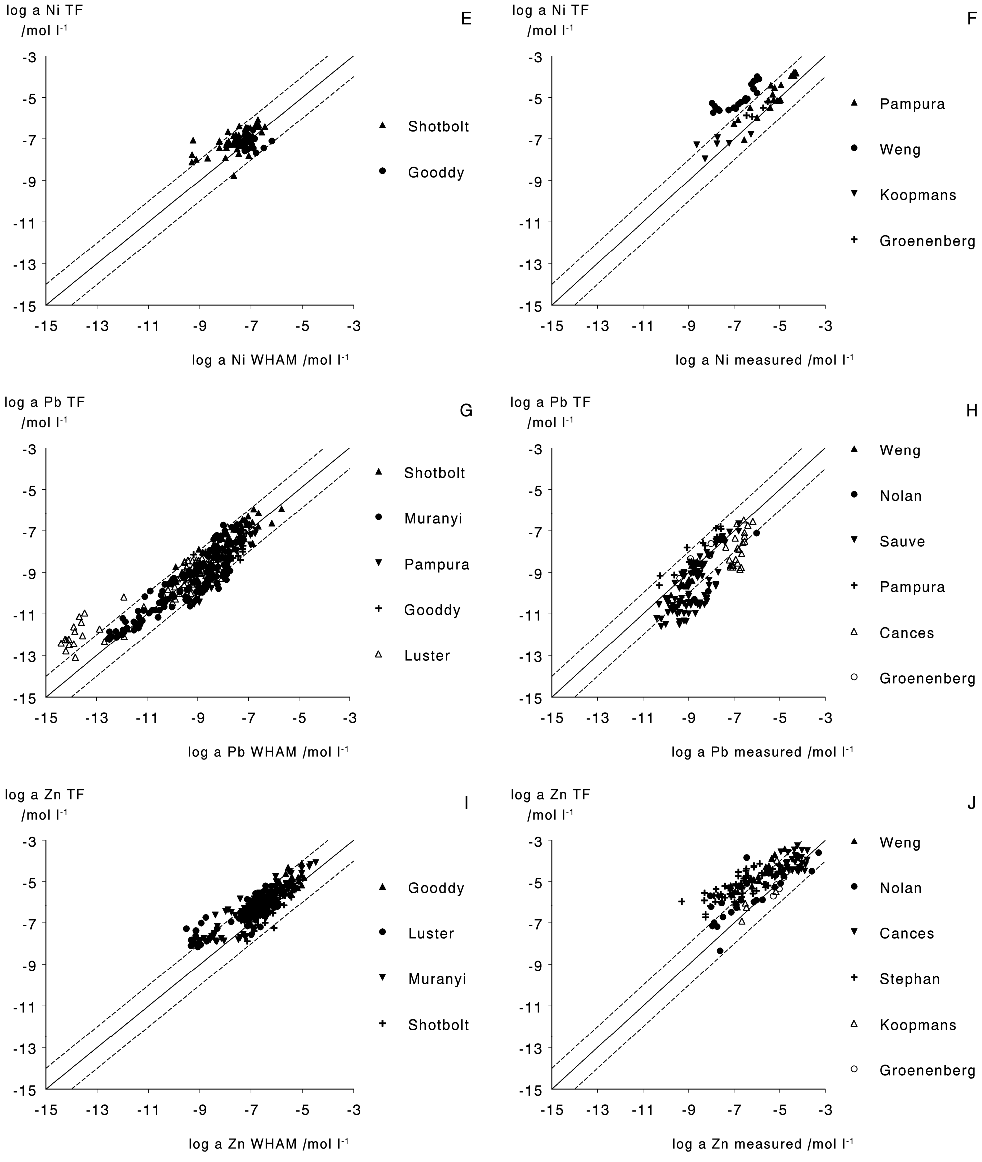

FIGURE 4 (continued) FMI activities predicted with the K_f transferfunctions compared with WHAM predictions (left) or measurements (right) for Ni (E, F), Pb (G,H) and Zn (I,J)

5 Conclusions

Free metal ion activities were predicted well by a single transfer function for a variety of soil solution extracts including solutions obtained by centrifugation of field-moist soils, *in situ* pore-water samples from rhizon samplers, and dilute salt extracts of dried soils. Differences in metal concentrations due to different concentrations of complexing anions (Cl^-) and organic ligands (DOC) were largely accounted for by using FMI activities instead of total solution concentrations

FMI activities for Cd, Cu, Pb, Ni and Zn can be predicted within one order of magnitude from the 0.43 M HNO_3 extractable metal concentration using transfer functions which use only pH and SOM as explanatory variables. This confirms the dominant role of SOM and pH in the partitioning of metals in soils; additional soil properties such as Al and Fe oxide contents only marginally improved model performance.

Of the mathematical formulations tested, K_f relations provided the best fits when predictions of both solution and solid phase concentrations were considered. K_f functions are particularly suitable for predictive calculations, for example in the dynamic modeling of soils subjected to varying inputs of metals and for the calculation of metal leaching from soils.

The pH coefficient in the transfer function represents an average pH response for all soils rather than the pH dependence of metal binding for individual soils. Adsorption at pH>7 tends to be over-estimated by the transfer functions.

The transfer functions derived in this study also are applicable to soils other than those for which they were derived. Comparison of predicted FMI activities with independent data shows, on average, some over-estimation which is partly because of the use of stronger extractants in the independent data than the 0.43 M HNO_3 extraction used for the derivation of the transfer function. This was particularly the case for Ni and Zn.

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CHAPTER 3

Use of speciation and complexation models to estimate heavy metal solubility in soils

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Abstract

The development of speciation and surface complexation models to calculate partitioning of metals between the soil solid phase and soil solution has made a large progress. We evaluated the use and practical applicability of an assemblage of complexation models to predict heavy metal sorption. We used 353 samples which cover a wide range of soil properties and metal concentrations. For sorption of cations to solid and dissolved organic matter the NICA-Donnan model was used, to clay minerals a non-specific Donnan type exchange model, and to metal(hydr)oxides a two-site DDL model. Calculated solution concentrations agree well with measured concentrations, except for Pb where calculations overestimate concentrations by one order of magnitude on average. Some highly Zn contaminated samples show relatively large deviations between measured and calculated concentrations. This is most likely caused by Zn containing minerals which are included in the total amount of reactive metals in the soil as determined by acid extraction. Hence, such models can be used for practical applications if one is aware of the possible complications. When the "total reactive metal concentration" includes a substantial amount of precipitated metals, which may occur for heavily contaminated soils, the model tends to overestimate concentrations in solution.

1 Introduction

Heavy metals in soil systems can be a threat to groundwater and surface water systems, food crops and ecosystem health. To assess these risks or define measures to prevent or diminish risks, computer models that describe metal partitioning between soil solid phase and soil solution are often used. In general, partitioning and speciation of heavy metals in soil systems depend both on the properties of the heavy metal and on the composition of the solid phase and the soil solution. To predict metal partitioning and speciation, various kinds of models have been used, ranging from simple empirical relations between soil and solution composition and heavy metal concentrations (*1-3*), to advanced process based models using a detailed description of soil surface complexation and solution chemistry (*4-8*).

Because of their simplicity empirical relations are often used in practical applications like soil remediation, risk assessment and mass transport calculations (*1, 9-11*). Yet, these models provide little or no understanding of the processes determining heavy metal behavior in soils. Also, use of these models is restricted to the range of data they have been derived from, unless it has been proven that they are applicable outside this range, as extrapolation outside this range is often not reliable.

A different approach is the use of mechanistic based speciation modeling including advanced surface complexation models for ion adsorption to soil particles. During the last decade there has been a large progress in the development of these kinds of models. Especially the description of metal ion sorption to solid and dissolved organic matter has been improved considerably with models like NICA-Donnan (*12*) and Model V and VI (*13*). This is of great importance because solid and dissolved organic matter determine metal behavior in many soil and water systems. The development of these organic matter models promoted the development of mechanistic models describing heavy metal speciation in soil. Of further importance is that sets of generic model parameters have been derived which enable the use of these models for a wide range of different soils (*14*). So called assemblage or multi-surface models have been proposed which are comprised of several advanced models for calculating ion sorption to different soil surfaces including solid and dissolved organic matter. Lofts and Tipping (*4*) described metal sorption to two suspended particulate matter samples with their SCAMP model, an assemblage model comprising ion adsorption to solid and dissolved organic matter, clay minerals and metal hydroxides. Weng et al. (*7*) and Dijkstra et al. (*8*) calculated the speciation of several heavy metals in sandy soils with an assemblage model, comprising ion adsorption to solid and dissolved organic matter, amorphous and crystalline iron hydroxides and clay. Cancès et al. (*6*) used an assemblage model to calculate free metal ion concentrations and the distribution of sorbed metal ions among the different surfaces for one clayey soil sample; the calculated distributions could be confirmed by EXAFS measurements. A similar approach was used by Schröder et al. (*15*) for heavy metal distribution in flood plain sediments.

So far the assemblage models have only been tested for a relative small number of datasets with few samples and/or little variation in soil or sediment properties. Now, in this paper we evaluated the use of such models to predict solid solution partitioning of metal ions using generic model parameters by applying an assemblage model for a wide range of both soil properties and metal concentrations. Compared to the often used empirical models, these assemblage models generally require several parameters that are not available from standard soil investigation studies, especially concentrations of macro ions and dissolved organic matter in the soil solution. Therefore we also looked at consequences for model predictions due to uncertainty in these concentrations and whether it is possible to use estimated values for these.

2 Materials and Methods

2.1 Soil datasets

In this study, four soil datasets were used. The first and second dataset consist of 46 and 69 soil samples, respectively, taken from all over the Netherlands. Samples are from non-polluted rural areas as well as from polluted areas like near zinc smelters and the flood plains of the river Rhine and Maas. Both datasets were previously used to determine empirical relations between metal partitioning and soil properties (Chapter 2), (*16*). The first dataset contains only topsoil samples, whereas the second dataset also contains samples from greater depths, till 120 cm below soil surface level. Solid organic matter (loss on ignition), iron and aluminum oxides (oxalate extraction) and clay contents in these soils have been determined and the analytical methods are described in Römkens et al. (*16*). Solid phase 'reactive' metal concentrations were determined using a 0.43 M HNO_3 extraction (liquid:solid=10:1). This is a weaker extraction than the Aqua Regia extraction which is generally applied to determine total metal concentrations. We used this weaker extraction because we expected that, using this extraction, mainly reactive metals which are readily available for exchange with the soil solution are extracted and to a much lesser extent metals incorporated in mineral lattices which are not directly available for dissolution. Metal concentrations in solution were determined using a 0.01 M $CaCl_2$ extraction in both a 4:1 and a 10:1 liquid to solid ratio. Dissolved organic matter (TOC-analyzer) and concentrations of heavy metals and macro elements (Na, Ca, SO_4, PO_4) in these extractions were measured (ICP-MS) (*16*).

The third dataset consists of 32 sandy soil samples from several depths between 0 and 100 cm below the surface level from an experimental field near Wageningen, the Netherlands. In 1982 copper sulfate was added to part of the field leading to very high Cu concentrations in some samples. This dataset has previously been used for calculation of heavy metal speciation with an assemblage model (*7*). Total metal concentrations using a 2M HNO_3 extraction (liquid:solid=10:1), concentrations of metals, Ca, SO_4 and PO_4 in 0.002M $Ca(NO_3)_2$ solution (liquid:solid=2:1) were measured. Additional soil properties as solid and dissolved organic matter content, clay content, crystalline and amorphous iron oxides content were also determined. Analysis methods of the soil samples are described in Weng et al. (*7*).

The last dataset consists of 206 samples collected from 40 different forest sites in Switzerland with a large variety in soil properties. This dataset contains both topsoil and subsoil samples. For this dataset reactive metal concentrations in the solid phase were derived by extraction with 0.02 M EDTA buffered at pH 4.65 with a 0.5 M NH_4Ac/HAc solution. Concentrations in solution of both heavy metals and macro ions (ICP-MS for cations, ion chromatography for anions) were determined after an extraction with double-deionized water (liquid:solid = 10:1). Further, solid organic matter (loss on ignition), dissolved organic matter (TOC-analyzer), aluminum and iron (hydr)oxide contents (oxalate extraction) and clay contents were measured.

The reactive metal concentration is estimated with different methods for the datasets. A 0.43 M HNO_3 extraction for datasets 1 and 2, a 2 M HNO_3 extraction for dataset 3 and EDTA extraction for dataset 4. Because of these different methods, results for the different datasets might not be comparable. Now, for dataset 2 we also performed a 2 M HNO_3 extraction and an EDTA extraction. Extraction efficiencies for all methods appeared to vary little. Efficiencies for all metals were on average 60% higher for the 2 M HNO_3 extraction compared to the 0.43 M HNO_3 extraction and on average 10% lower for the EDTA extraction. For individual samples efficiencies were at most 100% higher or 50% lower, respectively. Data from the 2 MHNO_3 and EDTA extractions of dataset 2 were not further used in the model calculations.

2.2 Model description

Metal partitioning between solid and solution phase was modeled using a multi-surface assemblage model. This assemblage model incorporated metal ion sorption to three reactive surfaces: organic matter, clay minerals and metal (hydr)oxides. Within the model we assume simple additivity, which means that ion sorption to various surfaces is calculated separately and is summed to calculate total sorption. Interactions between various surfaces and their effects on metal ion adsorption are then neglected. For the solution phase, inorganic complexation reactions for components in solution according to the MINTEQA2 database (*17*) and sorption to dissolved organic matter (DOM) were incorporated. The sorption calculations accounted for competition between all components in solution (macro ions, Fe, Al, and heavy metals) for binding to solid organic matter (SOM), DOM, clay and metal (hydr)oxides. As input for the model we used the reactive metal concentrations estimated with HNO_3 (dataset 1, 2 and 3) or EDTA (dataset 4) extractions, solid organic matter and clay contents, Fe and Al contents measured with oxalate extraction, dissolved organic carbon concentrations and concentrations of macro elements in solution. The chloride or nitrate concentrations as set in the extraction solutions were used for datasets 1, 2 and 3. For dataset 4, measured Cl concentrations were used.

Sorption to solid and dissolved organic matter

Metal sorption to both SOM and DOM is described by the NICA-Donnan model (*12*). Here specific binding is described using two types of binding sites each having a continuous distribution of binding strengths. Electrostatic effects are accounted for using a Donnan approach, where the Donnan volume depends on the ionic strength of the solution. Parameters were used from the datasets for generic purified humic acid (HA) and fulvic acid (FA) as derived by Milne et al. (*14*). Previous studies used various assumptions to apply the NICA-Donnan model to real soil systems concerning the site density and composition of SOM and DOM. As a starting point, we followed the approach used by Weng et al. (*7*) where SOM was assumed to consist of HA with a site density of 31% relative to generic HA. DOM was assumed to consist of 30 % FA, 30% HA and 40% non-reactive material. SOM and DOM were assumed to contain 50% organic C. These reactivities for SOM and DOM have proven so far to provide good modeling results. Cancès et al. (*6*) and Dijkstra et al. (*8*) used higher reactivities for both SOM and DOM, but obtained good results as well. Further, we tried to optimize SOM site density and DOM composition to improve our modeling results.

Sorption to clay.

Metal sorption to clay was calculated using a non-specific cation exchange model. Accumulation of metal ions depends only on their charges and their concentration in the bulk solution and is described by a Donnan model. Specific sorption of cations, most likely because of binding to clay edges, and selectivity in cation exchange was neglected, which is reasonable because sorption to clay is expected to play small role for most samples. A site density of 0.25 moles per kg was used, which is the average site density of illites, the most dominant clay type in the Netherlands. The Donnan volume of illites was estimated as 1.0 L kg^{-1} based on the interlattice distance and surface area of illites (*18*). Although illite might not be the most important clay type for the samples from Switzerland (dataset 4), we used the same parameters values for sorption to clay for this dataset, because specific information on clay type is not available.

Sorption to metal (hydr)oxides

Iron and aluminum (hydr)oxides were considered the reactive metal (hydr)oxide surfaces. Complexation was modeled using the two site diffusive double layer model for HFO from Dzombak and Morel (*19*). Sorption to aluminum (hydr)oxide was treated similar as sorption to iron (hydr)oxide. Total surface areas were calculated based on total oxalate extractable amounts of Fe and Al, which in the model were allowed to precipitate as amorphous ferric hydroxide (log K = 3.16) and gibbsite (log K = 8.77) respectively. The specific surface area of iron and aluminum (hydr)oxides is assumed as 53.5·103 m^2/mole Fe or Al, which is equivalent to the value of 600 m^2/g for HFO given by Dzombak and Morel. We neglected the more crystalline iron oxides like goethite, because total surface areas of crystalline iron (hydr)oxides are in most Dutch soils much smaller than amorphous surfaces. Sorption to other surfaces like manganese oxides or silicon oxides was not included as well, because in most soils iron and aluminum (hydr)oxides are the two most abundant oxide surfaces. Also, only for a small number of the samples data on the amount of crystalline iron (hydr)oxides and manganese and silicon oxides are available.

Modeling environment

Calculations for the model were performed using the model framework ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport) (*20*). The object-oriented structure of this framework facilitated the implementation of advanced models in aquatic and soil chemistry, like NICA-Donnan.

3 Results and discussion

3.1 Analytical results

Table 1 shows median values and 10 and 90 percentile values for the soil solid phase composition for all four datasets. Samples for datasets 1 and 2 have a wide variety in soil properties. Samples range from poor sandy soils to peat soils or heavy clay soils. Because these datasets contain samples from contaminated sites, maximum heavy metal concentrations are often higher than in samples from the other two datasets. The range in soil properties of dataset 3 is small, because the samples were taken from a single field. All samples are sandy soils with a maximum clay content of 4.9% and maximum SOM content of 4.2%. The high Cu concentrations in some samples are caused by an earlier addition of copper sulfate to part of the field. Also, dataset 4 shows a large spread in soil properties but heavy metal concentrations are low; in many samples concentrations were below the detection limit. Different from other datasets, this dataset also contains samples with very high pH values; the highest value being 9.0.

TABLE 1 Solid phase characteristics for used sets of soil samples

dataset		OM	clay	Fe-ox	Al-ox)	DOC	pH	Cd	Cu	Pb	Zn
			%	mmol.kg^{-1}		mgC.L^{-1}		mg.kg^{-1}			
1 (n=46)	10-percentile	2.0	0.8	6.6	6.6	7.7	3.7	0.19	1.2	10.4	3.2
	median	4.9	4.5	44	24	17	5.6	0.82	9.6	35	47
	90-percentile	13.3	27.0	155	58	43	7.3	4.2	32	219	638
2 (n=69)	10-percentile	0.5	1.0	11.4	1.3	5.1	4.1	0.04	0.46	0.9	1.5
	median	2.9	7.0	39	38	15	5.0	0.31	4.4	12.9	14.6
	90-percentile	36	42	117	160	152	6.6	1.6	17.5	73	115
3 (n=32)	10-percentile	0.4	2.5	3	7	8	3.9	0.008	0.6	1.2	0.9
	median	1.1	3.3	11	16	15	5.5	0.07	6.9	2.5	3.3
	90-percentile	4.1	4.8	38	34	26	5.9	0.25	106.7	24.1	10.2
4 (n=206)	10-percentile	0.2	5.0	12	21	4.3	4.3	< d.l.	< d.l.	< d.l.	< d.l.
	median	2.7	17.1	41	60	25	5.2	< d.l.	0.77	3.3	0.85
	90-percentile	19.7	41.0	111	255	137	8.2	0.61	3.0	18.1	10.4

< d.l. = below detection limit

3.2 Comparison between Calculated and Measured Concentrations.

The calculated concentrations of Cd, Cu, Pb and Zn in the soil solution are compared with the measured concentrations in Figures 1a to 1d. The dotted line is the 1:1 line. As a measure for absolute error between calculated and measured values, root-mean-squared-errors (RMSE) were calculated. We also calculated mean-errors (ME) to tell whether the model on average overestimates (ME > 0) or underestimates (ME < 0) the measurements. Values for RMSE and ME for each metal are shown in Table 2.

TABLE 2 Root mean squared error (RMSE) and mean error (ME) of calculated metal concentration in solution (logarithm)

	Cd	Cu	Pb	Zn
RMSE	0.57	0.34	1.31	0.44
ME	0.41	-0.02	1.19	0.19

Zinc. Calculated Zn concentrations deviate for most data points no more than 0.5 log unit (RMSE = 0.44, ME = 0.19). On average, concentrations are slightly overestimated. Only for a small number of samples of dataset 1 the assemblage model overestimates measured concentrations by more than one log unit. All of these samples have relatively high Zn concentrations, neutral or near neutral pH and were taken from contaminated floodplains or areas close to zinc smelters or zinc processing industries. In this case, the “total reactive metal concentration” in soil estimated by acid or EDTA extracted metals may also include Zn dissolved from Zn containing precipitates in addition to Zn adsorbed to reactive surfaces. However, using Zn activities estimated from Zn in soil solution and solubility of Zn minerals from literature, in these samples Zn activities are too low for formation of precipitates, like Zn (hydr)oxides, phosphates or carbonates. Meima and Comans (*21*) showed that including surface precipitation reactions improved the prediction of Zn sorption at neutral pH values. However, in our calculation the inclusion of surface precipitation using parameters from Dzombak & Morel (*19*) did not have a large effect on the calculated zinc concentrations, although the calculated surface coverages of Fe and Al hydroxides by Zn were very high (10-35% of total surface sites). Some authors (*22, 23*) have suggested the relative ease of formation of Zn-Al layered double hydroxides or Zn containing phyllosilicates in soils at near neutral pH. Thermodynamic data for these compounds are scarce. Nevertheless, formation of layered double hydroxides of Zn was predicted for these samples when using recently presented log K values by Allada et al.(*24*). However the model now underestimated concentrations for the specific samples by approximately one log unit. EXAFS measurements of highly zinc contaminated soils showed surface precipitation of Zn as well as the formation of Zn containing layered double hydroxides and phyllosilicates (*25*).

Copper. Cu concentrations are predicted well by the model (RMSE = 0.34, ME = -0.02). In the low concentration range some deviations are found, which might be caused by analytical errors, because measured concentrations are close to detection limits.

Cadmium. Cd concentrations are on average overestimated by the assemblage model; RMSE is 0.57 log unit, ME is 0.41 log unit. This suggests that binding constants for Cd are a little too low. This can also be due to the fact that interactions between SOM and minerals are at present neglected. Such interactions can lead to more Cd adsorbed than the linear additivity model predicts (*26*).

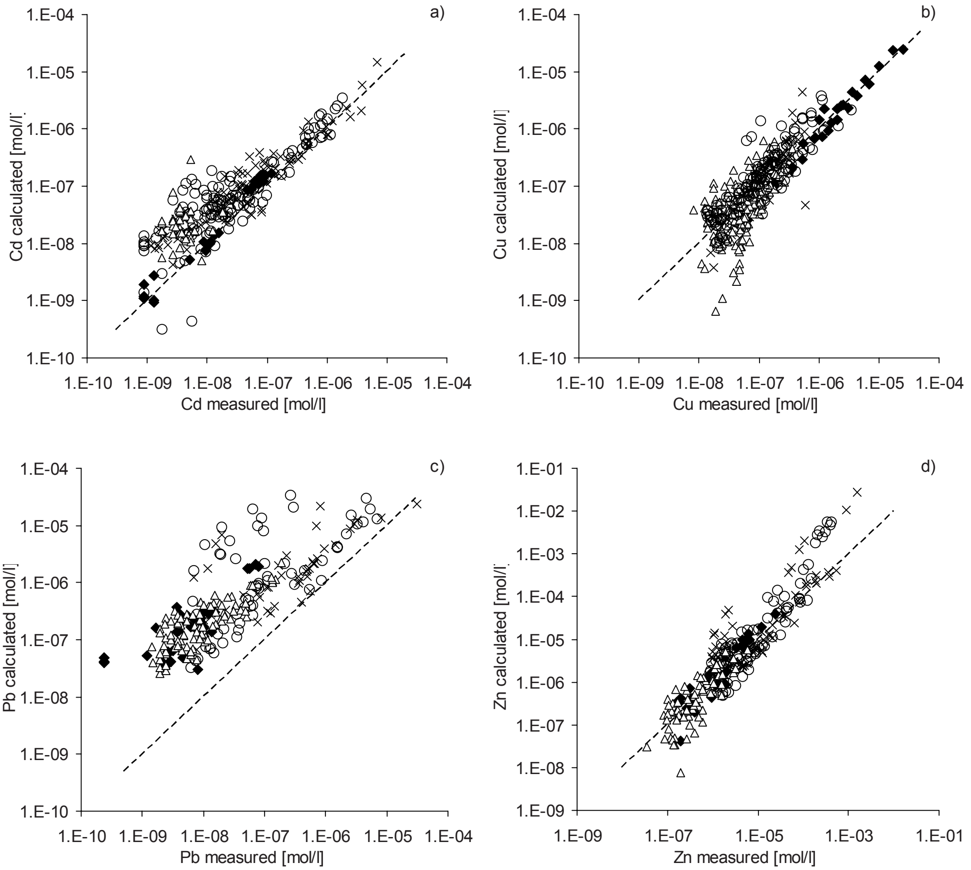

FIGURE 1 Metal concentrations in soil solution calculated with the speciation model vs measured concentrations. Cadmium (a), copper (b), lead (c), and zinc (d). Samples are from four datasets: ×=dataset 1, ○=dataset 2, ◆=dataset 3 and △=dataset 4. Dotted line is 1:1-line.

Lead. The model overestimates Pb concentrations (RMSE = 1.31, ME = 1.19). This corresponds with other studies which also show an overestimation of Pb concentrations (*7, 15, 21*). Weng et al. (*7*) assumed in their paper that concentrations were overestimated because extraction with 2 M HNO_3 might lead to an overestimation of the reactive amount of Pb. However, also for samples from the other three datasets, which were determined using the weaker 0.43 M HNO_3 extraction (dataset 1 and 2) or 0.02 M EDTA extraction (dataset 4), calculated concentrations are too high. The use of higher log K values for Pb sorption at HFO, as suggested by Dijkstra et al. (*8*) and (*27*), did not increase Pb sorption enough to fit the data (data not shown). Additional calculations showed that formation of Pb precipitates, of which Pb phosphates are the most likely, was predicted for a few samples of dataset 1 only. This means that either the sorption parameters for Pb are not correct, to organic matter or to aluminum hydroxide, which is treated similarly as iron hydroxide, or that important sorption processes are not incorporated in this model. A possible candidate is complexation by manganese oxides, which is not included in these model calculations, because data for sorption to manganese oxides are rare and generic parameter values for sorption to manganese oxides are consequently not available[2]. Yet, several authors have found that Pb is strongly complexed by manganese oxides (*4, 6, 28, 29*). A different explanation is suggested by Schröder et al. (*15*) who used the formation of a ternary lead-phosphate species on goethite to improve estimates of Pb sorption. Another possible explanation for the failure of the model for Pb can be caused by the influence of SOM on Pb adsorption to oxides. Similar to what has been suggested for Cd, adsorption of SOM to oxide minerals can lead to synergistic effects on Pb adsorption to oxides surfaces.

3.3 Metal speciation in soil solution and contribution of individual surfaces to metal sorption.

The contribution of the different sorption surfaces to the sorption of heavy metals calculated using the assemblage model is shown in Figure 2. This figure shows that for most samples and all metals sorption predominantly takes place at the SOM surface in the considered range of soil properties e.g. SOM and pH. This sorption is mainly specific binding to reactive groups of SOM. Electrostatic binding in the Donnan phase of SOM contributes little to total sorption. For Pb and to a lesser extent for Zn, sorption to iron and aluminum (hydr)oxides plays an important role in total sorption. Sorption to clay makes up a significant contribution to total sorption only in case of Cd and Zn for a few samples which have high clay contents compared to SOM and metal (hydr)oxides contents. Others (*4, 6, 30*) also found that SOM was the most important sorption surface. Further, Weng et al. (*30*) found that sorption to iron (hydr)oxides is an important process for Pb. Lofts and Tipping (*4*) and Cancès et al. (*6*) included in their

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[2] After publication we found the following published model parameters available : Tonkin, J.W.; Balistrieri, L.S.; Murray, J.W., Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Appl. Geochem.* **2004**, *19*, 29-53.

calculations sorption to manganese oxides and found that this was especially important for Pb.

The calculated speciation in the soil solution for the various metals is given in Figure 2. This figure shows that Zn occurs mainly as free ions in the soil solution, while Cu is almost completely complexed by DOM. Cd and Pb show intermediate behavior depending on conditions in the soil solution. Cd is also present as inorganic complexes, mainly $CdCl^+$ and $CdCl_2$.

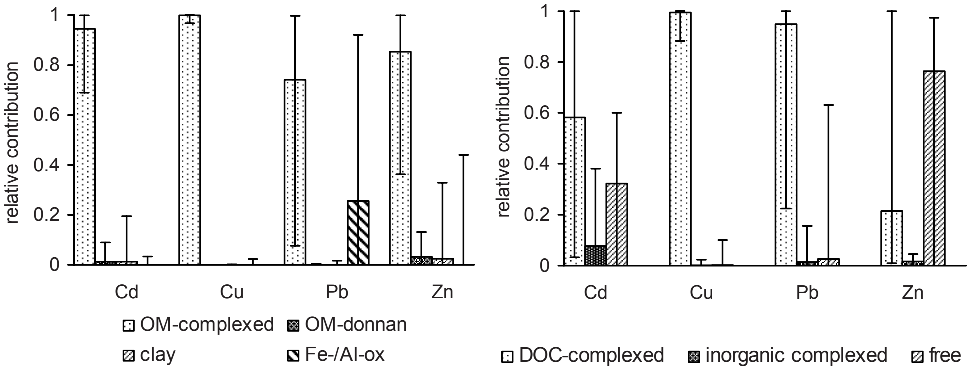

FIGURE 2 Calculated contribution of soil sorption surfaces to heavy metal sorption (left) and calculated heavy metal speciation in soil solution (right); error bars indicate 10 and 90 percentile values.

3.4 Optimization of SOM and DOM reactivities.

The values for the site density of SOM and the FA and HA contents of DOM were quite arbitrarily taken from Weng et al. (*7*). Hence we also tried to optimize these values to improve our modeling results. It can however be expected that SOM site densities and DOM composition will be different for different soil samples. For example, Tipping et al. (*3*) showed that the reactive fraction of SOM is smaller in soils with high organic matter than in soils with low organic matter. Consequently, optimization will provide only optimal average values for the presented datasets. During optimization, it proved impossible to simultaneously optimize results for copper and lead. The optimal values for copper and zinc did not improve modeling results very much compared to the results using the initial chosen reactivities. However, optimizing lead concentrations would require much higher site densities for SOM and much lower HA contents of DOM. Cu concentrations, and also Cd and Zn, were then highly underestimated.

TABLE 3 Optimal values for site density of SOM and DOM composition for Cd, Cu, Pb and Zn and RMSE between calculated and measured concentrations at optimal values

	site density SOM[a] (%)	HA (% of DOM)	FA (% of DOM)	RMSE (log units)
Cd	54	20	24	0.44
Cu	39	50	11	0.33
Pb	90	9	29	0.66
Zn	39	58	24	0.44

[a] relative to site density of generic HA (*14*)

3.5 Applicability of the Model.

On average the model predicts solution concentrations of Cu, Cd and Zn very well for the large soil sets studied that cover a wide range of soil properties and source of pollution. This is promising because the modeling uses generic parameters and average values for reactivities of SOM and DOM. Our approach requires no fitting and therefore it is a pure prediction. The good predictions of total solution concentrations allow the model to be used in calculations in which total concentrations are important, like reactive transport modeling. Additionally and different from empirical regression models, the model also predicts free ion concentrations, which are important for calculating risks for e.g. soil micro-fauna, many aquatic organisms and plant uptake. The distinction between total dissolved and free concentrations is very important, because their dependency on pH can be very much different as is shown in Figure 3. This figure shows that total concentrations of Cu are nearly independent of pH whereas free concentrations of Cu decrease greatly with increasing pH.

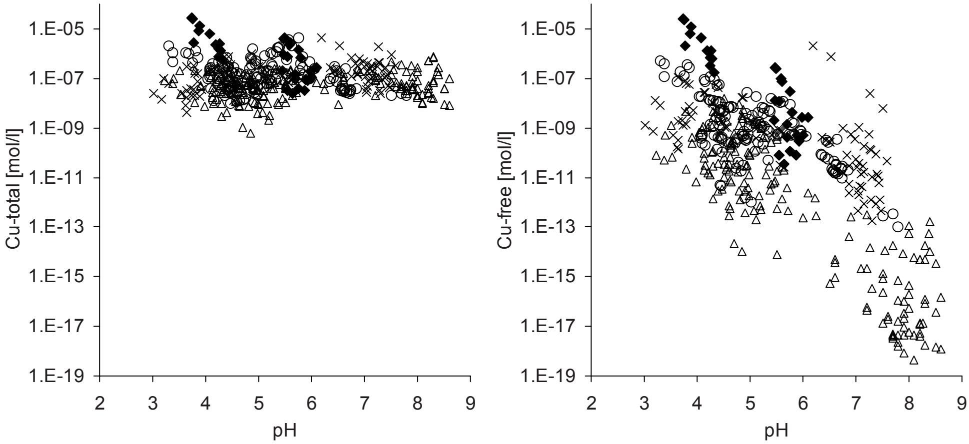

FIGURE 3 Calculated total copper concentrations in soil solution (left) and free copper concentrations (right) as a function of solution pH. Samples are from four datasets: ×=dataset 1, ○=dataset 2, ◆=dataset 3 and △=dataset 4.

In practice the "total reactive metal concentration" is operationally measured with acid or EDTA extractions, which can also dissolve certain amounts of metal containing precipitates present in the soil. When the contribution of these dissolved precipitates to the total reactive concentration is substantial and when the solid phase under concern is not included in the model calculations, the model will overestimate metal concentrations in solution. This is probably the reason of the large deviations between the model predictions and the measurement found in some samples with high heavy metal concentrations, especially Zn. Including the formation of precipitates in the model is in principle possible. But this requires knowledge of the precipitates present and reliable thermodynamic constants, which are not always available. The prerequisite for using process-based modeling is the incorporation of all relevant processes. However for extreme conditions like very high metal concentrations, some processes might become important that are not incorporated in the model, leading to erroneous results. This is especially important for industrial contaminations, which often have extreme conditions, like high heavy metal concentrations, or a very high or very low pH.

The practical applicability of models also depends on the kind and amount of data that are available as input. The input required for the assemblage model is relatively limited and mostly available from standard soil investigation studies, except for concentrations of DOC and of major cations and anions in the soil solution. Effects of uncertainties in DOC concentrations on estimates of metal concentrations are nearly linear for Cu, which is most strongly complexed by DOC, and less than linear for Cd, Pb and Zn. Because estimates of DOC concentrations are probably within a factor 3, its effects on uncertainties in metal concentrations are less than a factor 3, what is relatively small in perspective of the range in metal concentrations[3]**.** Additionally the fraction of humic substances, the predominant metal binding fraction of DOC, may vary significantly (Chapter 5). Together this may lead to substantial uncertainty in predicted metal concentrations, especially for Cu. The effect of major cation and anion concentrations on the calculated concentrations of heavy metals is small and acts primarily through the ionic strength effects on the activity coefficients and on the electrostatic contributions of sorption. This is illustrated in Figure 4 in which we performed calculations for 25 randomly selected samples, where concentrations of major cations and anions were multiplied with 0.25 and 4. Error bars indicate deviations due to the higher and lower ion concentrations. This figure shows that using a 'best guess' for these concentrations instead of measurements still would lead to reasonable estimates of heavy metal concentrations. Calculations for other metals (not shown) gave similar results.

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[3] Additionally the fraction of humic substances, the predominant metal binding fraction of DOC, may vary significantly (Chapter 5). Together with the uncertainty in the DOC concentration this may lead to substantial uncertainty in predicted metal concentrations, especially for Cu.

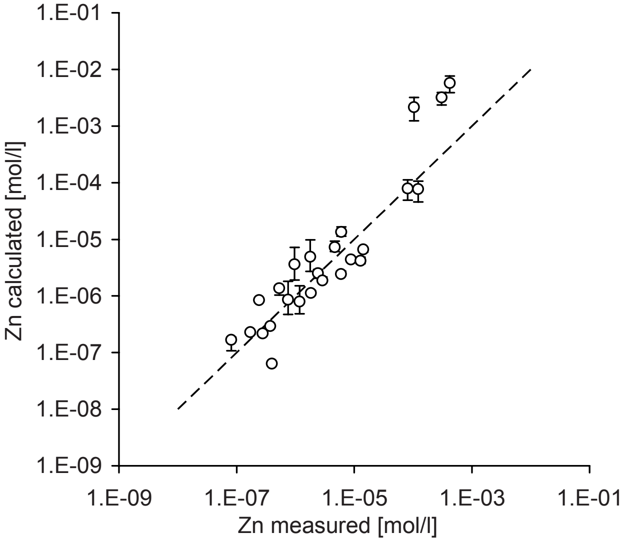

FIGURE 4 Calculated zinc concentrations with a surface complexation and speciation model vs measured concentrations. Error bars indicate calculations with 4 times higher and 4 times lower concentrations of macro elements in solution

Overall it can be concluded that the progress in the development and parameterization of process based models allows reasonable predictions of the solid-solution distribution of most heavy metals without fitting. However the description of all relevant processes is sometimes incomplete, which may lead to predictions of dissolved concentrations that are higher than the reality. The model calculations can be based on data of standard soil analysis, and the uncertainties resulted from best-guess regarding to DOC and major ion concentrations are relatively small[4].

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[4] Uncertainties in predicted concentrations due to uncertainties in the concentration and composition of DOC need further attention.

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CHAPTER 4

Evaluation of the Performance and Limitations of Empirical Partition-Relations and Process Based Multisurface Models to Predict Trace Element Solubility in Soils

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Jan E. Groenenberg, Joris J. Dijkstra, Luc T.C. Bonten, Wim de Vries and Rob N.J. Comans. Evaluation of the Performance and Limitations of Empirical Partition-Relations and Process Based Multisurface Models to Predict Trace Element Solubility in Soils

Abstract

Here we evaluate the performance and limitations of two frequently used model-types for reactive transport and ecotoxicological risks of trace elements in soils: regression based "partition-relations" and thermodynamically based "multisurface models", for a large set of elements. For this purpose new partition-relations were derived for As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V, Zn. Both approaches were evaluated by applying these partition-relations and a multisurface model, including aqueous speciation, mineral equilibria, sorption to organic matter, Fe/Al-(hydr)oxides and clay, on independent datasets for a wide variety of conditions. We conclude that Freundlich-based partition-relations are robust predictors for most divalent cations and can be used for independent soils outside the derivation dataset but within the environmental conditions thereof. The multisurface model is shown to be able to successfully predict solution concentrations over a much wider range of conditions. Predicted trends for oxy-anions agree well for both approaches but with larger (random) deviations than for cations. The multisurface model is shown to be more mechanistically robust for these elements. The results of this study enable a well-informed choice between model types depending on the purpose and conditions of the particular study, and provides suggestions for model improvements

1 Introduction

Solid solution partitioning and solution speciation largely determine the availability of trace elements to biota and their mobility in soils. Models are frequently used tools to evaluate trace metal speciation in soils, for instance in relation with leaching and runoff (1, 2) and bioavailability (3). Two distinct approaches are used to describe solid-solution partitioning in soils: (i) *Empirical "partition-relations"* relate the partitioning of elements to soil properties like pH and SOM. Model coefficients for such relations are generally derived from data of soil and corresponding solution extracts using (multiple) linear regression analysis (4); (ii) *Process based "multisurface models"* describe the various processes and interactions between the soil solution and reactive surfaces by combining separate models for ion-binding to the distinguished reactive surfaces (5). Intrinsic model parameters are derived from laboratory experiments on isolated or synthesized model systems (6, 7). In the development of these two categories of models different choices have been made that determine their performance and the width of their applicability.

Empirical partition-relations: Sorption data of trace elements to individual soils have been fitted successfully using Langmuir or Freundlich type models or a constant distribution coefficient (Kd) for a limited concentration range. Such empirical partition-relations lump sorption mechanisms including chemisorption, electrostatic sorption and surface precipitation to various reactive surfaces including organic matter, clay and metal oxides. Adsorption constants may vary by orders of magnitude among soils and environmental conditions (4). To widen the applicability of partition-relations to various soils and environmental conditions, distribution coefficients (Kd-relation) (4, 8) have been related to soil properties. Also Freundlich type partition-relations have been derived by relating Kf to soil properties (Kf-relation) (9), or by directly relating solution concentrations to solid phase concentrations and soil properties (C-Q relation) (4) or vice versa (Q-C relation) (10). Relations are available both to predict either the total (4, 8) or the free metal ion concentration in solution (9, 11). Methodological aspects are described in two recent publications (9, 12). The empirical approach is popular because of its simplicity, low data demand and short computing time which makes these models easy to use in large scale (regional) applications (1, 13) and broadly accessible web-applications.

Process based multisurface modeling: Multisurface models combine thermodynamic models for inorganic speciation and mineral equilibria with separate models for ion binding to various reactive surfaces, which distinguish between electrostatic binding and specific binding. The intrinsic model parameters of the surface complexation models are usually derived for a large range of element concentrations and conditions (6, 7). Within model applications to natural waters and soils (5, 11, 14-20) a few models are notably frequently used. The NICA-Donnan model (21), WHAM-Model V/VI (22) or related models (23) are most often used to describe ion binding to organic matter. Ion binding to Al/Fe/Mn-(hydr)oxides is frequently modeled using the generalized two layer model (GTLM) (6) developed for cation and anion binding to hydrous ferric oxide (HFO) and/or CD-MUSIC (24) that was developed originally for ion-binding to crystalline ferric oxide. The strength of multisurface models is their chemical-process basis which makes them in principle generally applicable as long as generic intrinsic model constants are used. The availability of extended sets of generic model parameters for the NICA-Donnan model (7) and the GTLM model (6) has strongly facilitated their applicability. To date, multisurface models have been used primarily to aid to the development of our understanding of complex natural systems. However, their generic basis makes them also suitable for generic risk assessments, e.g., as successfully demonstrated for the derivation of limits for contaminant emission from construction materials to protect soil and groundwater (25).

Generic model application and aim of the study: In this study we compare the performance of both types of models independently in view of their application in science, risk assessment and legislation. For these purposes generic models are required. Although fitting of models may give better results for individual cases from which the fitted parameters are derived, it also leads to conditionality. Here we have explicitly selected generic models because we aim for a generic applicability. When applying partition models, attention should be paid to conditionality resulting from: (i) the choice of parameters incorporated in the model, which may vary from one parameter, e.g. pH (4), or few parameters e.g. pH, SOM (4, 9) to multiple parameters

(8, 10); (ii) the soil types included in the derivation set, ranging from a specific group of, e.g. organic, soils (11) to a large variety of soil types (9); (iii) the simplicity of the model which lumps several processes, e.g. by using just one coefficient for the pH dependence of ion-binding to both organic matter and oxides, hydrolysis and the pH-dependent concentration of important competing cations such as Al, Fe and Ca, and (iv) the optimization method of the model, which allows either the prediction of solution concentrations (C-Q), solid phase concentrations (Q-C) or sorption constant (Kd/K_f) (9). Multisurface models are hypothesized to be less conditional and give better predictions. This because of their process based formulation, the use of intrinsic model parameters and their explicit account of competition for surface sites. Some conditionality may, however, arise from the choice of reactive surfaces included and the need to choose the appropriate mineral equilibria that control the element solubility at high concentrations (5).

It is not yet clear to which extent the conditional character of partition- relations limits their use to predict trace element solubility for soils outside the domain of the derivation set and whether such relations can predict changes in solution concentrations with changing environmental conditions (e.g. pH) for individual soils. In the context of their generic application, the aim of this study is to independently evaluate both approaches for a large range of elements, including metal cations and oxy-anions, on their accuracy to predict solution concentrations together with the ranges of conditions for which they can be applied. Past studies were either limited to the evaluation of multisurface models (5, 17, 26, 27) or partition-relations separately. Moreover, past studies only evaluated the performance of partition relations to fit the data from which they were derived. We found only one study, limited to one soil type, in which both approaches were evaluated to predict metal concentrations (Cd, Cu, Pb, Zn) on independent data (28). Here we derived partition-relations for a large number of elements, i.e. As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V, Zn, and tested both partition relations and multisurface models on independent data for a large range of element concentrations, soils and environmental conditions.

2 Materials and methods

Derivation of Partition-relations: We derived Freundlich-type partition-relations, specifically C-Q relations as being the most representative presently used (4, 9, 11, 28, 29) and the best predictor for solution concentrations (4, 9). We used an extended set of parameters (see Equation 1) and a dataset with a large variety in soil types, soil properties, element concentrations and environmental conditions for the derivation of the partition-relations, to minimize the conditionality with respect to points (i, ii) listed in the introduction:

$$\log C = \alpha_0 + \alpha_1 \cdot \log Q + \alpha_2 \cdot \log SOM + \alpha_3 \cdot \log clay + \alpha_4 \cdot \log AlFe_{ox} + \alpha_5 \cdot \log DOC + \alpha_6 \cdot pH \tag{1}$$

With C = element concentration in solution (mol.L-1), Q = (reactive) element concentration, extracted with 0.43 M HNO_3 (mol.kg^{-1}), SOM (%), DOC (mg.L^{-1}), clay (%), and AlFeox the sum of oxalate extractable Al and Fe (mmol.kg^{-1}). The coefficients of Equation 1 were derived by multiple regression (Genstat Release 12.1) using dataset NL (9). This dataset includes reactive element concentrations, soil properties for 118 soils, analyses of various corresponding solution extracts for Cd, Cu, Ni, Pb and Zn. Additionally, for a subset of 70 soils , 0.01 M $CaCl_2$ extracts were analyzed for the other elements (see supporting information)

Multisurface model: The multisurface model setup was adopted from Dijkstra et al. (17). The model includes the NICA-Donnan model (21) for ion binding to SOM and DOM, the generalized two layer model (GTLM) (6) for ion binding to Fe /Al(hydr)oxides and a Donnan model for binding to clay. SOM and DOM were modeled as a generic humic acid (HA). We used generic model parameter for the NICA-Donnan (7) and GTLM (6) models with some parameters for additional elements from Dijkstra et al (17).

Model evaluation: We evaluated model performance on independent data without any parameter fitting prior to their application. Dataset NL that was used to derive the partition relations, was therefore excluded from the evaluation of model performance of the partition relations. We used four datasets, all with "reactive" element concentrations extracted with 0.43 M HNO_3 (9, 11, 17), contents of reactive soil constituents and corresponding solution data. A detailed description is given in the original publications and the supporting information. Subsets were used of datasets NL (9) and PRT (29) using only the filtered 0.01 M CaCl2-extracts of dried soils with data for all elements (see supporting information). Dataset NB contains solution data obtained from field moist samples by centrifugation and extraction with 0.002 M $CaCl_2$. Dataset pH-stat contains solution data obtained from pH-static experiments (pH 2 – 12) previously used to evaluate the multisurface model (17). This dataset was used to explicitly test the models on their ability to predict the pH dependent solubility of individual soil samples.

3 Results and discussion

3.1 Partition-relations.

Together with the study by Rodrigues et al. (29) this is the first study with partition-relations for such a large set of elements. The optimized coefficients for the partition-relations are summarized in Table 1, including the explained variance (R^2) and the Root Mean Square Error (RMSE) of the fit to the solution concentrations The explained variance and RMSE are generally good (R^2> 0.62, RMSE<0.41) except for Cr, Cu, Mo, (low R^2) and Pb (RMSE=0.67) and similar to previous studies for Cd, Cu, Ni, Pb and Zn (4, 10). Coefficients for solid phase concentrations are always positive but are low for Cr, Sb and Se, indicating a small influence of the solid phase concentration on solution concentrations. The sign of the regression coefficients is consistent with their known soil chemistry. For the cationic metals, coefficients for pH are always negative, reflecting an increasing metal binding with pH resulting from a decreasing competition of protons for binding to SOM and Al/Fe-(hydr)oxides. Conversely, pH-coefficients for oxy-anions are always positive, when significant, reflecting a decreasing sorption due to a decrease of positive surface charge of Al/Fe-(hydr)oxides with increasing pH. Coefficients for SOM are always negative for cationic species, consistent with their binding to organic matter. Coefficients for DOC were positive for both cations and oxy-anions. For cationic metals, this relationship is consistent with their binding affinity for DOC, with high coefficients for Cu, Pb and V which have a particularly high affinity to bind to organic matter. A possible explanation for the positive relation between DOC and oxy-anion concentrations is the decrease in oxy-anion binding to Fe-oxide and soil (18, 30) through site-competition and charge neutralization at the oxide surface by organic matter sorption (31). The positive relation with DOC is possibly also due to the very similar behavior of the oxy-anions and DOC in their binding to oxide surfaces. The small values of the regression-coefficients for the reactive solid phase concentrations of Cr, Sb and Se could reflect either depletion of these elements in the solid phase, as a result of the high liquid to solution ratio (LS10), or solubility control by a mineral phase. However, depletion is only likely for Sb of which on average 45% of reactive metal was dissolved, but not for Cr and Se for which dissolution was 10% or less. Further, concentrations of Sb and Se are most likely regulated by sorption reactions (32) and not by mineral equilibria. Only Cr may be controlled by the solubility of Cr containing oxides (32), however the used multisurface model predicted Cr concentrations to be controlled by sorption to organic matter (17). Altogether this means that we have no plausible explanation yet for the very small values of the regression-coefficients for Cr, Sb and Se.

TABLE 1 Coefficients Partition Relations (Equation 1)

	α_0	α_1 **(Q)**	α_2 **(SOM)**	α_3 **(Clay)**	α_4 **(AlFe)**	α_5 **(DOC)**	α_6 **(pH)**	**R^2**	**RMSE**
As	-4.99	0.57	-	-0.19	-0.49	0.88	-	0.73	0.34
Ba	-2.16	0.71	-	-0.30	-	-	-0.15	0.67	0.35
Cd	1.60	1.11	-0.62	-	-0.39	0.29	-0.41	0.82	0.34
Co	1.49	0.93	-0.20	-	-	-	-0.79	0.90	0.25
Cr	-5.69	0.23	-	0.15	-0.21	0.23	-0.17	0.53	0.22
Cu	-3.7	0.62	-0.29	-0.14	-0.63	0.76	-0.013	0.57	0.41
Mo	-12.4	0.07	1.23	-0.77	-	-	0.67	0.58	0.40

Continued on next page

TABLE 1 Coefficients Partition Relations (Equation 1)

	α_0	α_1 **(Q)**	α_2 **(SOM)**	α_3 **(Clay)**	α_4 **(AlFe)**	α_5 **(DOC)**	α_6 **(pH)**	**R^2**	**RMSE**
Ni	-1.95	0.80	-0.77	-0.17	-	0.63	-0.25	0.62	0.40
Pb	-2.08	0.79	-0.40	-	-0.83	0.88	-0.29	0.63	0.67
Sb	-6.43	0.20	-	-	-0.29	0.33	-	0.62	0.18
Se	-8.56	0.11	-	-	-	0.57	0.07	0.69	0.20
V	-2.67	0.98	-	-0.64	-1.06	1.24	-	0.71	0.43
Zn	0.93	0.99	-0.43	-0.22	-0.14	0.12	-0.46	0.83	0.39

3.2 Evaluation partition-relations.

Figure 1 compares model results with measurements for the elements As, Cd, Cr and Cu. It shows predictions of the partition-relations for the pH-stat data and predicted vs. measured concentrations for both the partition-relations and multisurface mode for all data sets. Results for all elements are shown in Figure S-1 and S-2 of the supporting information. Model performance is quantified using the RMSE and the mean error (ME) of the predictions (Table 2). The figures show that the partition-relations predict the concentration level of the metal cations Cd, Co, Cu, Ni, and Zn well in the most relevant pH range 3-8, without any trend in the errors with pH except for Co. This is also reflected by the remarkably well predicted pH dependence for individual soils (Figure S-1 of the supporting information), which allows the use of partition-relations in predictive simulations under changing pH. This was not a priori known, because the pH-coefficient is optimized by comparing different samples at their natural pH, rather than by optimizing the solution concentration for individual soils over a range of pH (9, 11). The performance (RMSE) for these elements on the independent datasets is similar to that for the dataset from which the relations were derived (Table 1). Predictions for the other cations Pb, V (predominantly present as VO^{2+} under acidic conditions according to multisurface model calculations (17)), Ba and Cr have a larger RMSE. The partition-relation fails to predict Ba, likely because of the various mechanisms which control its solubility in the pH rage 3-8 According to the multisurface model calculations solubility is controlled by barite and sorption to clay under acidic conditions and sorption to SOM under neutral and alkaline conditions (17). The partition-model overestimates Pb concentrations in the low concentration range whereas it underestimates concentrations in the higher concentration range. A similar, much more pronounced, effect is observed for Cr. Outside the pH range 3-8 the partition-relations show a clearly lower performance especially in the high pH range. At high pH the partition-relations underestimate solution concentrations which increase due to hydrolysis reactions and stronger binding to DOM. At very low pH the model underestimates concentrations of Cu, Pb and V, i.e. the cations which bind very strongly to SOM. Predicted concentrations of weakly binding cations such as Cd, Co and Zn now sometimes exceed the total amount present because the partition relation does not account for the mass balance. Remarkably, the partition relations adequately predict pH-dependent solubility of Se and As. This is especially clear from the pH-stat data (Figure S-1 of the supporting information). Given that the pH-coefficient was either insignificant or very small, the high value for the DOC coefficient supports our previously stated hypothesis that this performance results from the similar, and therefore strongly correlated, pH dependence of DOC and oxy-anion binding to oxide-surfaces. For Mo and Sb a somewhat different relation was found, including a positive pH-coefficient, however, their concentrations are increasingly underestimated with decreasing pH. Overall, the partition-relations give rather good predictions for most metal cations and As, reasonable predictions for Pb and the oxy-anions Mo, Se and V, whereas predictions for Cr and Sb are poor. Model performance for oxy-anions for the independent data-sets was however systematically lower than for the dataset from which the relations were derived.

TABLE 2 RMSE and ME of the Model Predictions

	Partition relations[1]				**Multisurface model**			
	pH 2-12		pH 3-8		pH 2-12		pH 3-8	
	RMSE	ME	RMSE	ME	RMSE	ME	RMSE	ME
As	0.68	-0.51	0.69	-0.53	1.02	-0.34	0.99	-0.28
Ba	0.74	0.24	0.73	0.49	0.94	0.64	0.94	0.64
Cd	1.01	-0.31	0.37	0.04	0.45	-0.16	0.36	-0.07
Co	1.88	-0.66	0.75	-0.18	0.98	0.66	1.02	0.76
Cr	1.28	-0.79	1.01	-0.53	0.45	0.01	0.41	0.07
Cu	1.61	-0.36	0.35	-0.09	0.32	-0.19	0.30	-0.12
Mo	1.52	0.98	0.60	-0.19	1.13	-0.47	1.33	-0.77
Ni	1.06	-0.48	0.45	-0.31	0.42	-0.06	0.42	0.09
Pb	2.15	-0.53	0.77	0.16	0.98	0.33	1.01	0.74
Sb	0.53	0.18	0.55	0.39	0.82	0.36	0.80	0.31
Se	0.67	-0.40	0.58	-0.29	0.70	-0.05	0.71	0.04
V	1.06	-0.73	1.09	-0.86	0.94	0.0	0.77	0.21
Zn	0.98	-0.44	0.42	-0.15	0.55	-0.02	0.54	0.05

[1] measures for the partition are calculated for the three independent datasets (Portugal, Noorderbos, pH-stat) for the multisurface model also dataset NL was included

3.3 Evaluation multisurface model.

Figure 1 shows compares model predictions for As, Cd, Cr and Cu with measurements for all datasets. Results for the other elements are shown in Figure S-2 of the supporting information. Performances are listed in Table 2. The model predicts concentrations well to very well over the entire pH-range (2-12) for most divalent cations, i.e. Cd, Cu, Ni and Zn. For other cations, results are generally poorer. For Pb, predicted concentrations are generally too high in the pH range 2-5 where the multisurface model predicts Pb to bind predominantly to SOM. Conversely, concentrations are underestimated above pH 6 where Pb is predicted to bind predominantly to Al/Fe-(hydr)oxides. Concentrations of Ba are specifically overpredicted when the solubility is not predicted to be controlled by equilibrium with barite but by sorption to SOM which is thus likely too low. For Co both sorption to SOM (the dominant process at low pH) and sorption to HFO (the dominant process at high pH) are likely underestimated.

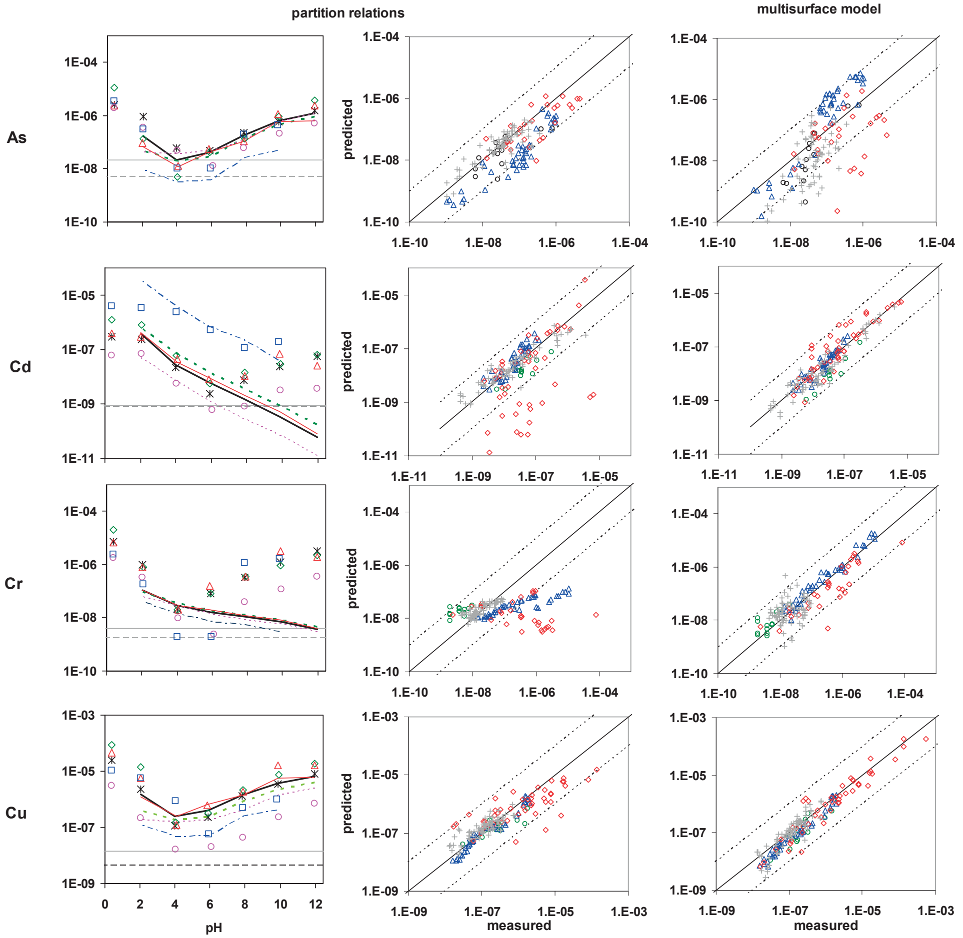

FIGURE 1 Measured concentrations and predictions of the partition relations of the pH-stat data as function of pH (left panels; symbols represent measurements, lines represent model predictions for soils I, II, III, IV and V). Total reactive concentrations, recalculated to mol/L, are shown at pH 0.5 ; Comparison of predictions of the partition-model (middle panels) and multisurface model (right panels) with measurements for datasets pH-stat (red diamonds); NB(blue triangles); PRT(green circles) and NL (grey crosses).

Despite the fact that binding-constants for Cr have been derived from linear free energy relations (LFER) (7) the model gives very good predictions. The model appears to be rather insensitive to the exact value of the binding constants. Varying the binding-constants of Cr to HA in the NICA-Donnan model by a factor 100 around their nominal value leads to a change of only -9% and +2% in solution concentrations. For elements with such high affinity, the model predicts almost complete binding to organic matter and the solution concentration is therefore largely determined by the ratio of DOM and SOM.

Predictions for the oxy-anions As, Mo, Sb and Se reflect the trend of the solubility well but with a relatively large deviation (RMSE 0.7 – 1) compared to the cations. The influence of DOM on oxy-anion binding (18, 30), which is not included in the model, may be a confounding factor. No specific relations were found between the error in the prediction and pH, except for As that is underestimated at high pH. Concentrations for Sb were systematically overestimated.

3.4 Comparison between partition-relations and multisurface modeling and implications for their use in risk assessment

Generally the multisurface approach provides better predictions than partition-relations over the entire pH range from 2-12 for the metal cations. Within the relevant pH range for most soils, i.e. pH 3-8, partition-relations perform equally well for these elements. Partition-relations derived for the pH range 3-8 are less useful under extreme conditions such as at very low pH e.g. after oxidation of sulfidic sediments, and under alkaline conditions e.g. calcareous soils and soils in contact with cementitious construction materials or after cement-stabilization. Partition-relations are, however, shown to be robust predictors for concentrations of most of the evaluated divalent cations (Cd, Co, Cu, Ni, Pb and Zn) for a large variety of soils and conditions, e.g. with liquid to solid ratios varying between 0.2 an 10. The derived coefficients of the relations comply with our mechanistic picture of the controlling processes as described above. Furthermore, partition-relations are able to describe the pH-dependence adequately within pH 3-8. Considering these pH boundaries, this performance legitimates the use of such relations in large scale applications of risk assessment models for these elements.

Predictions for oxy-anions seem to be somewhat less successful both by the partition-relations and the multisurface model, with larger deviations, although the concentration trends are predicted well. Predictions of the partition-relation for these elements are sensitive to the concentration of DOC that is input to the model but which is not necessarily due to a mechanistic interaction. In this respect the multisurface model are mechanistically more robust than the partition-relations for these elements.

Relations of the elements for which the predictions are relatively poor and for which the concentration ranges are relatively small, as for the oxy-anions and Cr, can possibly be improved by extension of the datasets. For the elements which are already predicted well, i.e. the metal cations, no large improvements can be expected, because the dataset used in this study already covers a large range of element concentrations, soil properties and conditions. The simplicity of partition-relations, however, puts limits on the extent of their potential improvement. Extension of the datasets to larger ranges of conditions, e.g. pH, will not necessarily lead to improvement. The dominant solubility controlling mechanisms vary with conditions and it is unlikely that this can be described adequately by a single function. This variation in mechanisms is, however, covered by the multisurface approach in which the various processes are modeled explicitly. The multisurface approach has a greater potential for further improvement. For some elements model parameters can be improved, especially for those elements for which model parameters were derived from relatively few data or using LFER; suggestions are listed in Dijkstra et al. (17). Further improvements can be made by including the interaction of DOM with oxide surfaces and its effect on oxy-anion binding (18, 30). However, for most metal cations that are already predicted well, the extent of further improvements will be limited by a certain uncertainty that will always remain, given the heterogeneous character of natural organic matter (33) and other reactive soil constituents.

The great advantage of multisurface models is their process based character in combination with generic parameters. These features make them very suitable as research tools and applicable beyond the domain of the partition-relations. Examples are the use of multisurface models for very acid and alkaline systems, e.g. acid-mine-drainage (16) and MSWI-bottom ash. (34). However, the various choices made to quantify reactive element concentrations and reactive surfaces lead to a certain conditionality. Reactive element concentrations are quantified by acid extracts ranging from 0.22M HNO_3 (14) to Aqua Regia (26) or synthetic ligands such as EDTA (5). The concentrations of HS are rarely measured, but usually estimated to be a fraction of OM between 50 (19) and 100% (14). Also the Al/Fe/Mn-(hydr)oxide contents are quantified by various extracts, e.g. oxalate (5) or a combination of dithionite and ascorbate(17). Bonten et al. (5) (Chapter 3) have shown that multisurface models may also obtain a conditional character at high element concentrations when appropriate minerals are to be chosen in the absence of independent mineralogical analyses. To consolidate their relatively unconditional character, insight is needed in the effects of the different options to quantify the reactive metal concentration and reactive surfaces like SOM, DOM and Al/Fe-(hydr)oxides. Apart from the aforementioned advantages and constraints, multisurface models can predict the speciation of elements in the solid and the solution phase. Such information is required in (terrestrial) Biotic Ligand Models (3) and in models which account for kinetic binding to a certain constituent, e.g. models for the slow kinetic binding of trace metals by hydrous oxides (35). Another great potential is the use of multisurface models in the dynamic forward prediction of the macro chemistry of natural systems and their subsequent effect on the solubility of trace elements, e.g. in case of acidification (36, 37). In this respect one of the greatest challenges is to adequately predict the concentration of DOM, especially of the most important components therein with respect to ion-binding, which are at present input to the models.

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Supporting Information

Description of the datasets:

Dataset NL (1) consists of two subsets of Dutch soils: NL1 containing 49 topsoil samples and NL2 with 69 soil samples from different horizons of 11 soil profiles, of uncontaminated and contaminated soils. Soil data include 0.43 M HNO3 extractable element concentrations, SOM, oxalate extractable Al and Fe and clay content. Soil solution was obtained by centrifugation from field moist soils of NL1. Dilute salt extracts (0.002/0.01 M $CaCl_2$/$Ca(NO_3)_2$) were obtained from dried soils of both NL1 and NL2. Recently this data set, which originally included Cd, Cu, Ni, Pb and Zn, was extended for 70 of the 118 samples with measurements of As, B, Ba, Be, Co, Cr, Mo, Sb, Se and V in 0.43M HNO_3 and 0.01M $CaCl_2$ extracts with a liquid to solid ratio (LS) of 10 according to Groenenberg et al. (1). Element concentrations in the extracts were measured using HR-ICP-MS (Thermo Element 2). All data from dataset NL were used for the derivation of the partition-relations but only the subset of 70 soils with 0.01 M CaCl2 extracts, including all elements, was used in the validation.

Dataset PRT consists of 0.01 M $CaCl_2$ extracts from 15 samples selected from a large dataset of uncontaminated and contaminated areas in Portugal (2). The original solution data were not used because they were obtained from unfiltered extracts. New 0.01 M $CaCl_2$ extracts (LS 10) were obtained from the selected soils and filtered through a 0.45 µm TOC-free filter prior to analysis of the trace elements (HR-ICP-MS Thermo Element 2) and TOC. Soil data include 0.43 M HNO_3 extractable element concentrations, SOM, DOC, oxalate extractable Al and Fe and clay content. Filtration had a significant effect on the solution concentrations of various metals.

Dataset NB consists of field data from two soil profiles sampled for every 10 cm until a depth of 150 cm. The two profiles were sampled from two research plots at the location Noorderbos, a contaminated former wastewater infiltration field. One of these field plots was artificially acidified by applying elemental sulfur. Field moist samples were centrifuged to obtain soil solution for 10 minutes at 7000 rpm and filtered over 0.45 µm. Field most soils were also extracted with 0.002 M $CaCl_2$ at a liquid to solution ratio of 10 for 1 hour and filtered over 0.45 µm . Measured soil and solution properties include the content of humic substances (HS) of organic matter in soil and soil solution (measured according to van Zomeren et al. (3)), SOM (loss on ignition), DOC, clay content, oxalate extractable Al and Fe and dithionite and ascorbate extractable Fe, element concentrations (trace elements, major cations, S, P) in 0.43 M HNO_3 and in the solution extracts using HR-ICP-MS (Thermo Element 2)

Dataset pH-stat (4) consists of 8 moderately to strongly polluted soils. Data include the content of HS in SOM, 0.43 M HNO_3 extractable metal concentrations, oxalate extractable Al and Fe and dithionite and ascorbate extractable Fe and solution concentrations of elements and DOC in soil solutions from pH-static experiments with pH in the range 2-12. Table S-1 gives an overview of ranges of soil properties and metal concentrations of the datasets used in this study.

With the evaluation of both the partition relations and multisurface model we used "reactive" concentrations of trace metals and oxy-anions as measured with 0.43 M HNO_3. For the partition-relations we used furthermore measured oxalate extractable Al, Fe, clay content, SOM, pH and DOC to predict the solution concentrations with the newly derived partition relation (Equation 1, Table 1). For organic matter in the multisurface model we used measured concentrations of HS (sum of HA and FA) for datasets pH-stat (DOM only) and NB (SOM and DOM). In data sets NL and PRT (SOM and DOM) and pH-stat (DOM), OM was assumed to consist of 50% HS based on the measured fraction of humic substances in previous studies (16, 31). Measured concentrations of major cations and anions were used as input to the model. For datasets NL, NB and PRT we used however fixed ion activities for Al and Fe because measurements were frequently below detection limits. Ion activities at the appropriate pH were calculated from the solubility products of $Al(OH)_3$ (pKso,25=8.5) and $Fe(OH)_3$ (pKso,25=2.5), being representative for soil solutions (32). For dataset NL and PRT, HFO was estimated using oxalate extractable Fe. For datasets NB and pH-stat crystalline Fe-oxides as extracted with dithionite were taken into account and HFO was calculated as the difference between ascorbate and dithionite extractable Fe.

TABLE S-1. Overview of datasets with ranges of soil properties and reactive element concentrations (µmol.kg^{-1})

	Solution extracts			
	NL[1]	PRT	NB	pH-stat
system	dried soils	dried soils	field moist soils	pH-static titration
# samples	118 / 70[2]	15	30	8
# solution extracts	403 / 70	15	42	48
reference	(*1*)	(*2*)		(*4*)
$\mathrm{Al_{ox}}$ (mmol.kg^{-1})	1.3 - 160	8.04 - 240	25.6 – 80.0	2.36-109
$\mathrm{Fe_{ox}}$ (mmol.kg^{-1})	6.6 - 155	11.3 - 159	4.11 – 48.0	5.99-105
SOM (%)	0.5 - 36	2.2 – 10.6	0.1 -11.1	0.33-4.5
lutum (%)	0.8 - 42	3.6 - 33	2-13	<1-9
pH	3.7 – 7.3	4.3 – 7.2	4.0 – 6.1	2-12
DOC (mg.L^{-1})	2.31 - 1325	4.4 – 39.3	0.64 - 175	1.3-1966
As	0.13 - 318	4.10 - 1032	1.74 - 182	3.74 – 42.3
Ba	0.28 - 1915	30.8 - 836	13.9 - 1164	25.2 - 224
Cd	0.18 - 155	0.085 – 6.17	0.18 – 17.9	0.12 – 46.8
Co	0.17 - 114	1.18 - 120	0.34 – 26.3	3.25 – 79.2
Cr	0.38 - 835	3.79 – 96.9	29.0 - 9366	3.64 - 2081
Cu	0.94 - 4413	19.3 - 1727	9.92 – 1039	6.13 - 1198
Mo	0.08 – 0.92	0.11 – 0.41	<dl[4]	0.17 – 3.23
Ni	0.17 - 302	5.53 - 143	8.86 - 1119	7.89 -2932
Pb	0.58 - 7228	14.1 - 456	5.07 - 676	5.72 - 656
Sb	0.0004 – 18.1	0.056 – 3.65	0.47 – 1.37	0.009 – 6.40
Se	0.003 – 5.07	0.15 – 3.86	0.01 – 28.2	0.71 – 3.44
Sn	<dl[4]	0.019 – 0.99	<dl[4]	0.001 – 5.31
V	1.24 - 626	nm[3]	8.45-106	9.26 - 224
Zn	1.89 - 148415	33.7 -1404	22.9 - 4174	24.8 -17002

[1] There are also data based on pore water obtained by centrifugation of field moist soils for a subset of 49 soils in dataset NL and 12 samples in dataset NB; [2] 118 soils Cd, Cu, Ni, Pb and Zn; 70 soils with all elements, [3] nm = not measured [4] <dl = below detection limit

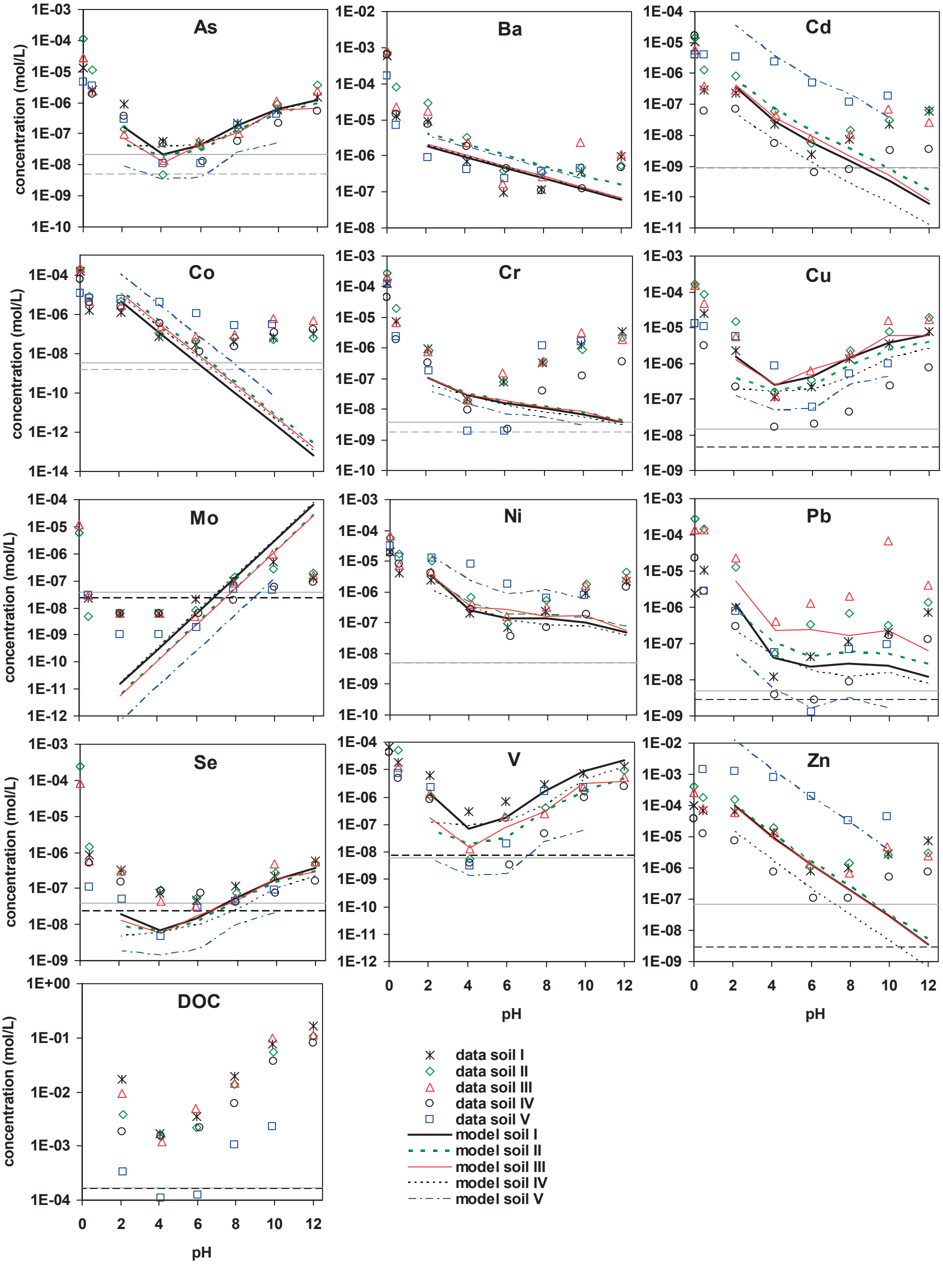

FIGURE S-1. Measured concentrations and model predictions with partition relations as a function of pH and measured concentrations of DOC in the pH-stat experiment for soils I-V (4). The two most left points indicate the amounts extracted with Aqua Regia and 0.43 M HNO3 respectively Horizontal lines indicate the detection limit.

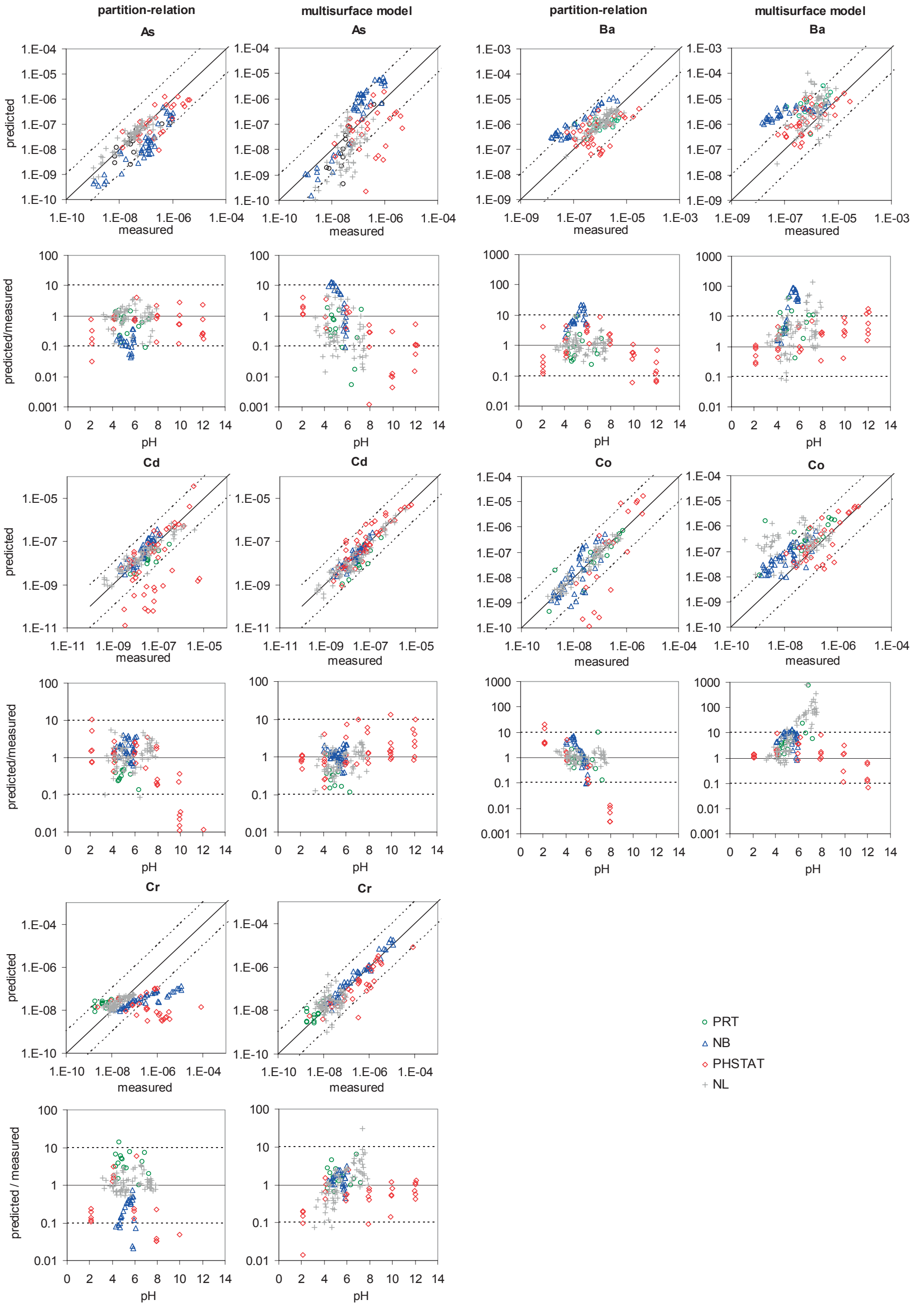

FIGURE S-2. Diagrams showing measured (x-axis) vs. predicted concentrations (y-axis, upper Figures) and predicted/measured concentration ratio as a function of pH (lower Figures) for the partition-relation (left) and multisurface model (right). Solid lines indicate predicted/measured = 1; the dashed lines indicate one order of magnitude over- or underestimation. Data below detection limit have been excluded from the Figures.

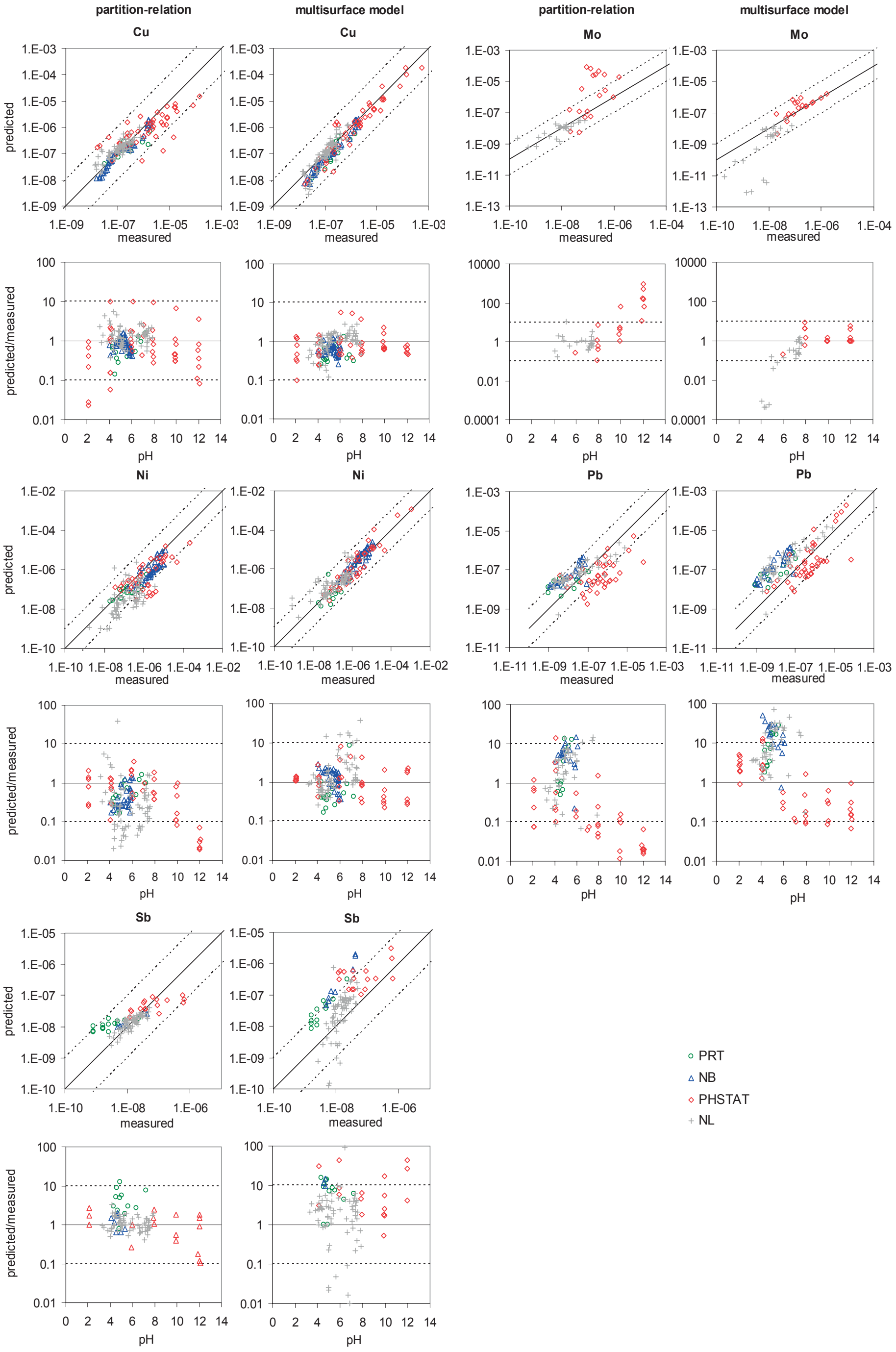

FIGURE S-2 Continued

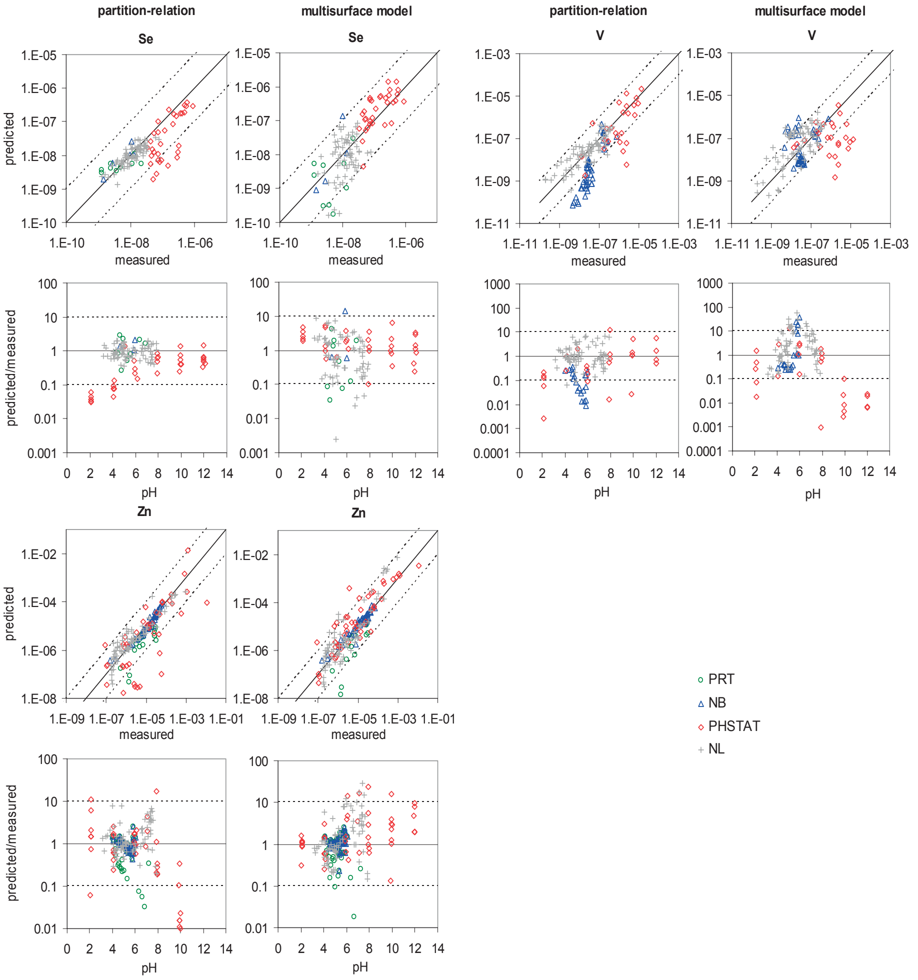

FIGURE S-2 Continued

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CHAPTER 5

Uncertainty Analysis of the Non Ideal Competitive Adsorption-Donnan Model: Effects of Dissolved Organic Matter Variability on Predicted Metal Speciation in Soil Solution

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Abstract

Ion binding models like NICA-Donnan and Model VI successfully describe laboratory data of proton and metal binding to purified humic substances (HS). In this study model performance was tested in more complex natural systems. The speciation predicted with the NICA-Donnan model and the associated uncertainty were compared with independent measurements in soil solution extracts, including the free metal ion activity and fulvic (FA) and humic acid (HA) fractions of dissolved organic matter (DOM). Potentially important sources of uncertainty are the DOM composition and the variation in binding properties of HS. HS fractions of DOM in soil solution extracts varied between 14 and 63% and consisted mainly of FA. Moreover, binding parameters optimized for individual FA samples show substantial variation. Monte Carlo simulations show that uncertainties in predicted metal speciation, for metals with a high affinity for FA (Cu, Pb) are largely due to the natural variation in binding properties (i.e. the *affinity*) of FA. Predictions for metals with a lower affinity (Cd) are more prone to uncertainties in the fraction FA in DOM and the maximum site density (i.e. the *capacity*) of the FA. Based on these findings, suggestions are provided to reduce uncertainties in model predictions.

1 Introduction

Speciation of metals is highly important for their bioavailability and mobility in soils and waters. Chemical speciation models are being used within ecotoxicological effect models such as the Biotic Ligand Model (*1*) and in reactive transport models to calculate metal leaching from soils to ground- and surface waters (*2*). In such models ion-binding to organic matter is a key processes and Model VI (*3*) and the NICA-Donnan model (*4*) are at present the most advanced models for ion-binding to humic substances (HS).

These models have been shown to successfully describe laboratory data of proton and metal binding to HS in binary and ternary systems with either purified humic (HA) or fulvic acid (FA), data which have also been used to derive generic model parameters (*3, 5, 6*). However, when applying these models to natural soil- and surface water, predictions are likely to become more uncertain, because natural systems are more complex: there will be an increasing number of competing cations and a more heterogeneous composition of dissolved organic matter (DOM) being a mixture of FA, HA and other organic substances.

Such uncertainties can be categorized according to their origin: (i) conceptual uncertainty; (ii) uncertainty in model parameters and (iii) uncertainty in input variables. Conceptual uncertainty has e.g. become apparent from differences between predictions of Model VI and NICA Donnan for natural systems (*7, 8*) despite the fact that both models are about equally successful in fitting the common data from which they are parameterized (*9*). A possible important source of parameter uncertainty is the use of generic parameters (*3, 5, 6*) while ignoring the variability in ion binding that may exist for HS of different origin (*5*). Uncertainties in input variables may be due to the incomplete characterization of the solution being modeled. In particular, the characterization of DOM is nearly always missing. Consequently estimates of the percentage of FA and HA in DOM are required, which vary between 40-100% (*7, 8, 10-13*), resulting in an associated uncertainty in model predictions that is not quantified to date. Insight into the uncertainties of model predictions and their causes provides a reference to interpret deviations between models and measurements and may help to find directions for model improvement, including the parameterization and required input.

Our aim in this paper is to: (i) validate NICA-Donnan predictions of metal speciation in soil solutions, taking into account the uncertainties in input variables and model parameters, (ii) quantify the variation in binding properties of HS, (iii) quantify the variation in the composition of DOM, (iv) quantify the uncertainty in model predictions due to the variations in binding properties and DOM composition both separately and together.

To validate the NICA-Donnan model, speciation measurements are presented, obtained with the Donnan Membrane Technique (DMT) (*14*) in solutions extracted from eight soils with a broad range in metal concentrations and soil properties. To be able to distinguish between model parameter uncertainty and uncertainty in input variables we also measured the FA and HA concentrations with the rapid batch technique of van Zomeren and Comans (*15*). The variability of the model parameters for proton and metal binding to FA, which appeared to be the dominant metal binding fraction of DOM in the studied soil extracts, was assessed by optimizing the model parameters for individual samples of FA followed by determination of their variation amongst FA samples. Uncertainties were quantified by Monte Carlo (MC) simulations for each sample. Additionally, we evaluated the dependence of the uncertainty on pH, FA and metal concentrations using model scenarios with a broad range in pH, FA and metal concentrations for systems with a (i) fixed total dissolved metal concentration and (ii) fixed free metal ion (FMI) activity in solution. The first system is representative for cases where FMI activities are to be calculated e.g. to assess metal bio-availability. The second system represents cases where the total concentration in solution is to be calculated from the FMI activity for example in (reactive transport) models assuming equilibrium of the FMI with the solid phase or when calculating critical loads for metals which are related to a critical FMI activity in solution (*16*).

2 Materials and Methods

2.1 Measurement of metal and DOM speciation in soil extracts

Eight soils from contaminated sites were used in this study (Table 1). Samples were oven-dried at 40°C and sieved (<2 mm) before further use. Metal concentrations (Aqua Regia and 0.43 M HNO_3-extractable metal) and soil properties were determined using standard analytical procedures. Soil solution extracts were obtained by extraction of soil with 0.002 M $Ca(NO_3)_2$ and 0.001 M NaN_3 (to inhibit microbial activity) at a 1:10 (w/v) solid to liquid ratio (*17*). FMI activities in the supernatants of the batch extracts were determined with the DMT (*14, 17*). DOM composition in the donor solutions sampled at t = 8 d of the DMT experiment was determined by measurement of the HA, FA and Hydrophilic acid (Hy) concentrations using a rapid batch technique (*15*). For four soil samples concentrations of Low Molecular Weight Organic Acids (LMWOA) (i.e. citric- and oxalalic acid), Cl, NO_3, and ortho-P were measured in the donor solutions, using a Dionex ICS-2500 high performance liquid chromatography system (*18*).

TABLE 1 Soil Properties and Metal Concentrations

	SOM	clay (%)	total soil metal concentration Aqua Regia (μmol.kg^{-1})			0.43 M HNO_3-extractable metal concentration (μmol.kg^{-1})		
			Cd	Cu	Pb	Cd	Cu	Pb
Zlatitza	4.8	13	16.4	22448	687	4.0	14806	653
Wildekamp	3.4	2	1.5	1435	114	0.56	1282	94.9
Hygum	7.1	10	4.6	12142	144	2.9	10344	95.6
Zhejiang	6.9	13	71.2	11627	7042	69.8	13215	8059
Noorderbos 1	12.9	-	15.7	1158	763	12.7	705	517
Noorderbos 1A	12.5	-	7.30	943	637	5.9	625	533
Noorderbos 2	5.2	-	2.4	167	162	3.1	139	144
Noorderbos 2A	5.7	-	0.80	181	195	0.91	105	141

2.2 NICA-Donnan model

The NICA-Donnan model (*4*) is a combination of the Non-Ideal Competitive Adsorption Model (NICA), which describes competitive binding of protons and metal cations to FA and HA taking into account ion specific nonideality, and a Donnan equilibrium model that describes nonspecific electrostatic adsorption. The model accounts for binding site heterogeneity by distinguishing two different groups of binding sites each with their own continuous affinity distribution: type 1 and type 2 binding sites, the first with a relatively low and the second with a relatively high affinity to bind cations. The amount bound Q_i (mol.kg^{-1}) of a component *i* at solution concentration c_i (mol.L^{-1}) is given by:

$$Q_i = \frac{n_{i1}}{n_{H1}} \cdot Q_{\max 1,H} \frac{(\widetilde{K}_{i1} c_i)^{n_{1i}}}{\sum_i (\widetilde{K}_{i1} c_i)^{n_{i1}}} \cdot \frac{\left[\sum_i (\widetilde{K}_{i1} c_i)^{n_{i1}}\right]^{p_1}}{1+\left[\sum_i (\widetilde{K}_{i1} c_i)^{n_{i1}}\right]^{p_1}} +$$

$$\frac{n_{i2}}{n_{H2}} \cdot Q_{\max 2,H} \frac{(\widetilde{K}_{i2} c_i)^{n_{12}}}{\sum_i (\widetilde{K}_{i2} c_i)^{n_{i2}}} \cdot \frac{\left[\sum_i (\widetilde{K}_{i2} c_i)^{n_{12}}\right]^{p_2}}{1+\left[\sum_i (\widetilde{K}_{i2} c_i)^{n_{i2}}\right]^{p_2}} \qquad (1)$$

Four parameters are characteristic for the FA or HA: $Q_{max1,H}$ and $Q_{max2,H}$ give the proton site density for the two considered groups of binding sites; p_1 and p_2 are a measure for the widths of the affinity distributions and describe the intrinsic heterogeneity of the humic material. Four ion specific parameters for each considered component describe the median affinities ($\widetilde{K}_{i1}$, $\widetilde{K}_{i2}$) and nonidealities (n_1 and n_2) of the ion binding to both distributions. The charge of the humic particle is counteracted by the attraction of counter-ions and the exclusion of co-ions within the Donnan volume V_D (L.kg^{-1}), which is calculated according to:

$$\log V_D = b(1 - \log I) - 1 \qquad (2)$$

With b an empirical constant and I the ionic strength (mol.L^{-1}).

2.3 Speciation modeling

Metal speciation in solution was calculated using ORCHESTRA (*19*) including the NICA-Donnan model. For the uncertainty analysis, we used the sampled NICA parameters for H, Cd, Cu and Pb. Generic parameters (*6*) were used for all other elements except for the binding of Fe^{3+} to FA for which we used the parameters from Hiemstra and van Riemsdijk (*20*). Inorganic speciation and binding to LMWOA was calculated on the basis of the MINTEQ database (*21*), the parametric uncertainties of which were not included in this study.

Measured values of either the total concentrations or ion activities of Cd, Cu and Pb were used to calculate the speciation in the soil extracts together with measured pH, concentrations of major cations (Al, Ca, Fe, K, Mg, Mn, Na), additional trace metals (Cr, Ni, Zn) and FA and HA. When available, we used measured concentrations of anions (Cl, NO_3, PO_4) otherwise the NO_3 concentration was set to that of the background electrolyte.

2.4 Uncertainty analysis

Parameter sampling and statistical analysis of the Monte Carlo (MC) simulations were done using the software package UNCSAM (*22*). For each simulation, 1000 random parameter sets were sampled from the derived distributions in NICA parameters and FA fractions using the Latin Hypercube Sampling method assuming a normal distribution. Correlations between parameter values were imposed in the sampling procedure to avoid unrealistic parameter value combinations that might lead to overestimations of uncertainty. From the output of the MC runs, the individual contribution of each parameter to the uncertainty in model outputs was then derived by the linear correlation coefficient (LCC) of the least squares linear regression of model outputs as a function of the varied parameters.

2.5 Modeling scenarios.

The uncertainty in the predicted metal speciation at various levels of pH, concentrations FA, Cd, Cu and Pb was evaluated using MC simulations for model scenarios in the pH range 3-8. Realistic levels (low, medium, high) of total metal concentrations or FMI activities and DOM concentrations were chosen based on measured data of 118 samples with a large range in soil properties and metal concentrations (*23*) (Table S-1, Supporting Information). For Al and Fe we used Al^{3+} and Fe^{3+} activities calculated with solubility products of $Al(OH)_3$ ($pK_{so,25}$=8.5) and $Fe(OH)_3$ ($pK_{so,25}$=2.5) representative for soil solutions (*24*). We evaluated model scenarios to obtain the uncertainty in predicted metal speciation due to: (i) the uncertainty in NICA parameters by MC simulations with sampled NICA parameters for H, Cd, Cu and Pb, (ii) the uncertainty in the fraction FA by MC simulations with sampled fractions of FA and (iii) the combined uncertainty due to uncertainty in NICA binding parameters and FA fractions.

The average fraction FA and its variability has been derived from compiled studies (Table S-2, Supporting Information) in which the FA, HA and Hy fraction were measured in soil extracts with water or 0.002 M $Ca(NO_3)_2$. DOM was modeled comprising 41% FA being equal to the average HS content of these extracts.

2.6 Variability in NICA parameters of fulvic acids

The variation in the maximum proton site densities $Q_{max1,\mathrm{H}}$ and $Q_{max2,\mathrm{H}}$ and variation in $\log \widetilde{K}$ values for proton binding were derived from the individual fits for proton binding to FA (*5*). The variation in binding properties for metals was derived from the binding properties determined for individual FA samples from the data compiled by Milne et al. (*6*), using FIT, a nonlinear least-squares optimization code (*25*). Only for Cd, Cu and Pb were we able to fit the NICA parameters for three or more FA samples. Because it was not always possible to optimize all parameters independently due to the incomplete definition of model parameters using the available data (*6*), we selected the parameters for which the model is most sensitive based on a sensitivity analysis taking into account all parameters, except p_1 and p_2, two parameters that cannot be determined independently from n_1 and n_2 for individual samples of FA. The most sensitive parameters for Cu and Pb are the affinity constants $\widetilde{K}_1$ and $\widetilde{K}_2$ and the distribution coefficients n_1 and n_2, whereas for Cd only $\widetilde{K}_{Cd1}$ and n_1 are sensitive. The Donnan constant *b* was not a sensitive parameter for any of the metals. Based on these results, we have limited the parameters to be optimized to $\widetilde{K}_{i1}$ and $\widetilde{K}_{i2}$ and n_{i1} and n_{i2}. The intrinsic heterogeneity parameters p_1 and p_2 and the constant *b* to calculate the Donnan volume were kept at their generic values (*6*). The available data for Cd and Pb did not allow us to fit all four parameters freely. Therefore, we reduced the number of parameters by fixing the least sensitive parameters to their generic values. For Cd, we fixed the parameters of the type 2 high affinity sites $\widetilde{K}_2$ and n_2 because the model is insensitive to variation in these parameters. For Pb, we fixed the parameters n_1 and n_2 similar to Milne et al. (*6*), who used the *n* values derived for HA. Fixing these parameters for Cu showed a limited decrease (≤20%) in the variation of model output.

Because no data sets were available for FA samples with both proton and metal binding data, we had to use the generic values of $Q_{\mathrm{max1,H}}$ and $Q_{\mathrm{max2,H}}$, $\widetilde{K}_{H1}$ and $\widetilde{K}_{H2}$ when optimizing the NICA parameters for metals. To be able to derive the correlation between the *Q*s and other parameters, we also optimized the parameters with preset values of $Q_{max1,\mathrm{H}}$ and $Q_{max2,\mathrm{H}}$ at their generic values plus or minus their standard deviation (SD).

3 Results and Discussion

3.1 Metal and DOM Speciation in Soil Solution Extracts.

The soil extracts show considerable variation in their measured composition (Table 3). Total metal concentrations ranged from a factor 30 for Cd and Pb to a factor of 1000 for Cu between lowest and highest concentrations. There is also considerable variation in the fraction free metal, which varied between 18-95% of the total concentration for Cd, between 3-87% for Pb and between 0.1-87% for Cu.

DOM mainly consisted of FA (average 38%) and Hy (average 60%), whereas the HA fractions in the extracts were very low (average 2%). This is in agreement with the compilation of DOM fractions in soil extracts (Table S-2, supporting information), in which FA (average 34%) and Hy (average 61%) are the dominant fractions and the fraction HA (average 5%) is low. The fraction Hy contains LMWOA, sugars and amino acids (*26*). Concentrations of citric and acetic acid, two of the prevailing LMWOA in soils (*27*), were negligible (≤0.11% of DOC).

3.2 Variability in NICA Parameters of Fulvic Acids

Variation in NICA parameters for proton and metal binding to be used in the uncertainty analysis were derived from individual fits of the NICA Donnan model to proton binding data (*5*) and the newly derived individual fits for metal binding data for various FA samples from the compilation by Milne et al. (*6*). Parameters derived for each FA sample individually (Table S-4, Supporting Information) describe the data more precisely than the generic parameters according to their lower RMSE (Table 2) compared to those based on generic parameters (*6*). The distributions of the NICA parameters are close to a normal distribution and can, therefore, be described with their mean value and SD. The highest variation was found for the NICA parameters related to the high affinity sites i.e. $Q_{max2,\mathrm{H}}$ for protons, log $\widetilde{K}_2$ for Cu and Pb and n_2 for Cu. The obtained parameter variation appears to be within realistic ranges according to the ratios derived for $n_{\mathrm{Me}}/n_{\mathrm{H}}$, which can be interpreted as the inverse of the stoichiometry of the exchange between the metal cation and proton. The obtained values are almost within the theoretical range between a minimum of 0.5 (maximal 2 protons exchanged) and a maximum of 1 (minimal 1 proton exchanged) for divalent cations (*9*) ($0.6 \leq n_{\mathrm{Cu}1}/n_{\mathrm{H}1} \leq 1.2$; $0.9 \leq n_{\mathrm{Cd}1}/n_{\mathrm{H}1} \leq 1.2$; $0.4 \leq n_{\mathrm{Cu}2}/n_{\mathrm{H}2} \leq 1.1$). Therefore, we have used the obtained ratios as an additional constraint in the sampling of *n*.

Statistical analysis of the optimized parameters shows medium to strong negative correlation between several parameters e.g. between $\widetilde{K}_1$ and $Q_{max2,\mathrm{H}}$ for Cd and Cu. Such correlations can be explained statistically since several parameter value combinations fit the data about equally well. Alternatively, the correlation between $n_{\mathrm{Cu}2}$ and $Q_{max\mathrm{H}2}$ can also be interpreted physically: an increase in the site density of the high affinity sites ($Q_{max\mathrm{H}2}$) increases the probability of multidentate binding, resulting in a decrease of $n_{\mathrm{Cu}2}$ which is related to the inverse of the stoichiometry (*9*). The correlations have been imposed on the sampling of parameters for the uncertainty analysis to avoid overestimating uncertainty.

TABLE 2 Fitted NICA-Donnan Parameters

element	$Q_{max1,H}$ (eq.kg^{-1}) mean SD	$Q_{max2,H}$ (eq.kg^{-1}) mean SD	$\log K_1$ mean SD	$\log K_2$ mean SD	n_1 mean SD	n_2 mean SD	RMSE
H	5.66 1.24	2.37 1.67	2.65 0.432	8.60 0.781	-[a]	-	0.08
Cd	-	-	-1.12 0.638	-	0.689 0.0527	-	0.13
Cu	-	-	-0.139 0.647	8.03 2.41	0.525 0.145	0.597 0.387	0.07
Pb	-	-	-0.308 0.679	6.46 1.27	-	-	0.11

[a] – = parameter was not optimized

3.3 Uncertainty in modeled speciation resulting from variation in NICA parameters

The variation in predicted concentrations of metal bound to FA decreases with increasing pH for each of the three metals (Figure 1). Because of the skewed distribution of model outputs from the Monte Carlo simulations, with median values of FMI activities being closer to the p5 than to the p95, we used the interquantile range (IQR), the difference between the 75 and 25 percentiles of the results, instead of the SD. The simulated variation appears to be within realistic ranges when comparing the average standard deviation ranging from 0.11 to 0.25 (used here only because of its comparability with RMSE) with the RMSE of the generic fits, ranging from 0.16 to 0.28 (*6*). The trend of decreasing uncertainty with increasing pH is consistent with the decreasing deviation between predicted and observed values with increasing pH for acid/base titration data of a solution with Cu and FA (*28*) using generic parameters (*6*). Uncertainty is high when concentrations of metals bound to FA are relatively small, (i) at low pH, (ii) at low concentrations FA (Figure 1) or (iii) when concentrations of metals are high (results not shown), i.e. at high metal to FA ratios.

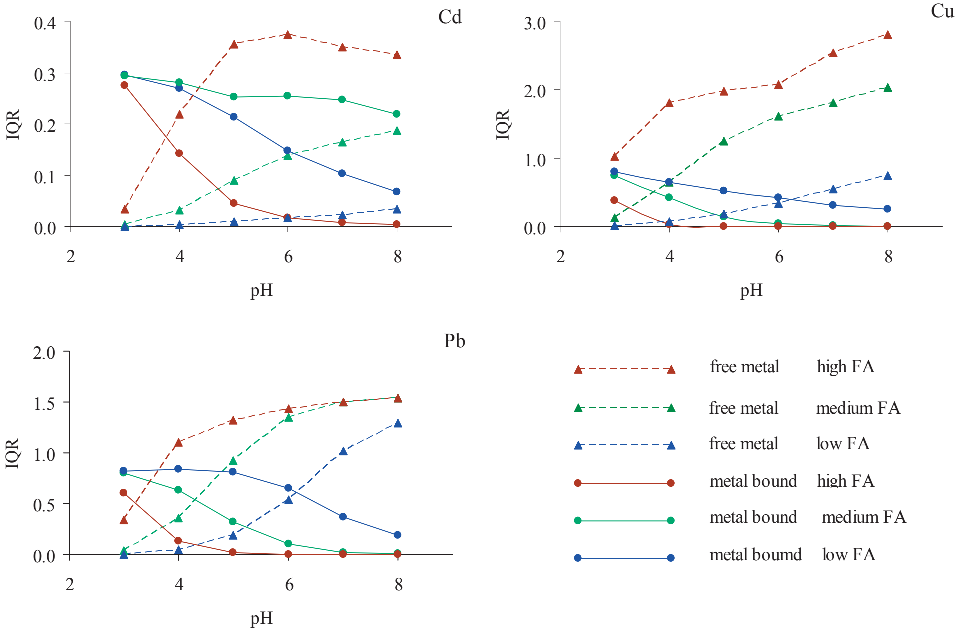

FIGURE 1 Inter quantile ranges (IQR) of the model predictions from the Monte Carlo simulations for log concentrations of metal bound to FA (lines) and the free metal ion (dotted line) as a function of pH for various concentrations of FA (high = 200, medium = 20 and low = 2 mg.L-1) for Cd, Cu and Pb

Variations in the predicted FMI activities are considerably higher than variations in concentrations of metal bound to FA. Opposite to the trend found for metals bound to FA, the uncertainty in FMI activities increases with increasing pH. At high pH, the largest fraction of the metals is bound to FA. Hence a small change in this concentration results in a large change in the FMI concentration to fulfill the mass balance constraint. This observation also explains the increasing uncertainty with increasing concentrations FA or decreasing total metal concentrations.

TABLE 3 Composition of the Solution Extracts

sample	pH	DOC (mg.L^{-1})	%HA	%FA	%Hy	Cd	Cu	Pb
						total metal[a] FMI (log mol.L^{-1})		
Zlatitza	4.67	9.4	1.7	24.4	73.8	-7.05	-4.09	nm[b]
						-7.03	-4.15	
Wildekamp	5.22	15.2	2.0	27.3	70.7	-7.77	-6.10	nm
						-8.51	-7.61	
Hygum	5.86	31.2	1.0	30.7	68.3	-8.40	-5.50	nm
						-8.64	-7.32	
Zhejang	7.23	9.1	3.8	27.7	68.4	-7.21	-5.59	-6.77
						-7.41	-8.74	-8.27
Noorderbos 1	5.23	36.1	0.9	41.8	54.1	-7.45	-6.43	-7.93
						-7.63	-8.05	-8.65
Noorderbos 1z	4.58	22.9	0.5	41.5	54.7	-7.32	-6.63	-7.59
						-7.50	-7.79	-7.74
Noorderbos 3	5.69	32.7	1.2	48.3	45.2	-8.01	-6.97	-8.22
						-8.28	-8.97	-9.11
Noorderbos 3z	4.71	17.5	1.3	35.7	59.2	-7.99	-7.28	-7.75
						-8.15	-8.65	-7.80

[a] total concentrations in bold, *FMI in italics*

[b] nm=not measured

3.4 Uncertainty in modeled speciation resulting from uncertainty in DOM composition

According to the compilation of DOM composition in batch extracts (Table S-2, supporting information), the percentage HS varies between 14 and 63%, with an average value of 39% and a standard deviation of 13%. Fractions of HS thus vary considerably and the fractions of HS obtained from our measurements are significantly lower than those assumed in most other studies, which vary between 40-100% (*7, 8, 10-13*).

Because the HS fraction contains mainly FA (average 90%) we evaluated the variation in HS assuming that it consists totally of FA. Uncertainties due to variation in the fraction of FA show similar trends as those observed for the variation in NICA parameters; increasing uncertainties in predicted FMI activities with increasing pH, and FA and decreasing total metal concentrations. For Cd, the uncertainties due to parameter uncertainty and uncertainty in FA concentrations are about equal in magnitude (Table 4). However, uncertainties in Cu and Pb activities of FMI due to variation in the fraction FA are considerably lower than the uncertainty due to model parameter variability.

Because of the large Hy fraction, we evaluated the possible contribution of LMWOA to the binding of trace metals for LMWOA being 10% of DOC, which must be considered a maximum (*27*). In addition, a scenario was calculated in which the total hydrophilic fraction (50%) was assumed to have binding properties similar to LMWOA. Based on measured concentrations LMWOA in A-horizons of soils (*27*) we considered LMWOA as 70% mono-, 20% di- and 10% tri- carboxylic acids represented by fumaric- oxalic- and citric acid, respectively, the first with a low and the two latter with a relatively high metal binding affinity. Including LMWOA in the speciation calculations for the scenario with medium concentrations of metals and FA lowered the log activity of free Cu^{2+} with 0.2-0.5 (10% LMWOA) or 0.6-1 units (50% LMWOA) below pH 6 (Table S-6, Supporting Information). LMWOA did not affect metal speciation of Cd and Pb and had no effect on Cu above pH 6.

3.5 Combined uncertainty and contributions of the different sources.

The total uncertainty in model output due to the sources of uncertainty investigated in this study, i.e. the uncertainty in NICA parameters and the uncertainty in FA concentrations, is clearly not additive (Table 4). IQRs for the total uncertainty are only slightly higher than those for the source with the highest uncertainty contribution alone. For Cu and Pb, the contribution of parameter uncertainty is most important whereas for Cd, uncertainty in the FA fraction contributes most to uncertainty.

TABLE 4 Maximum values Inter Quantile Range (IQR)[a]

metal	NICA[b]	FA[c]	NICA + FA[d]
Cd	0.19	0.23	0.29
Cu	2.04	0.56	2.06
Pb	1.54	0.33	1.58

[a] at medium levels of metal and FA concentration in the pH range 3-8

[b] scenario varying the NICA parameters

[c] scenario varying the concentration FA in DOM

[d] scenario varying the NICA parameters and concentration FA together

Ranking the parameters according to the absolute value of the linear correlation coefficient (LCC) (Table 5) shows that variation in the NICA parameters ($\log\widetilde{K}$ and *n*) contributes most to the uncertainty of model outputs of Cu and Pb. The parameters with the largest contribution to the uncertainty shift from the parameters related to the type 1 low affinity sites to those related to the type 2 high affinity sites with increasing pH. For Cd, the fraction FA is the most important source of uncertainty, followed by $\log\widetilde{K}_{H1}$ and $\log\widetilde{K}_{Cu1}$ due to competition with H and Cu. Additionally, the maximum proton site density $Q_{max\mathrm{H}1}$ appeared to be important for Cd. It appears that the number of binding sites, which depends on the maximum site density, and the FA fraction are the most important factors for metals that have a relatively low affinity

($\log\widetilde{K}$) for binding to FA, such as Cd, whereas for metals with a high affinity $Q_{max\mathrm{H1}}$ and the fraction FA appear to be of lower importance than $\log\widetilde{K}$ and *n*.

TABLE 5 LCC of the three variables that contribute most to the uncertainty

pH 3			pH 6			pH 8		
Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb
FA*	n_{Cu1}	K_{Pb1}	FA*	n_{Cu1}	K_{Pb2}	FA*	K_{Cu2}	K_{Pb2}
0.62	-0.74	0.75	0.68	-0.37	0.60	0.68	0.26	0.44
K_{H1}	K_{Cu1}	K_{Pb2}	K_{H1}	FA*	K_{Pb1}	K_{Cu1}	FA*	K_{Pb1}
-0.50	0.36	0.73	-0.30	0.34	0.57	-0.23	0.26	0.39
n_{Cd1}	FA	K_{H2}	K_{Cu1}	K_{Cu1}	K_{H2}	$Q_{max,\mathrm{H1}}$	n_{Cu1}	K_{H2}
-0.25	0.32	-0.35	-0.25	0.28	-0.26	0.13	-0.18	-0.15

* FA = the fraction FA in DOM

3.6 Comparison of predicted speciation and associated uncertainty with speciation measurements.

Figure 2 shows the comparison of modeled FMI activities (A) and total concentrations (B), including their uncertainty, with measurements. Modeled FMI activities using the average parameter values derived in this study show comparable agreement with measurements, as reported in other studies (*7, 13, 29-31*), according to their RMSE. Predicted total metal concentrations show a somewhat smaller variation than FMI activities and the distribution is less skewed (Figure 2).

The uncertainty in the predicted FMI activity is highest for Cu and Pb, which bind strongly to FA, and is less pronounced for Cd. Results of the model scenarios (see Figure 1) show considerable uncertainty in predicted FMI activities already at pH values around 4 for Cu and Pb whereas for Cd uncertainty starts to become important at pH 6 and higher. Because most extracted soil solutions have a pH below 6 the uncertainties for Cd are low, consistent with the observed small deviation between model predictions and the measurements. The larger deviations for Cu and Pb are consistent with the larger uncertainties for both metals. Although the differences between the model predictions and measurements for Cu lie within the error bars, the FMI activities tend to be overestimated since all predictions (using either average or generic parameters) are systematically higher than the measurements. FMI activities of Cu in soil solutions tend to be overestimated in other studies as well (*7, 31, 32*). Most likely these systematic differences are due to deviations in log*K* and *n,* the parameters that contribute most to the uncertainty. Meanwhile, predictions for Pb are systematically too low. Other studies however show both underestimation (*7*), overestimation (*32*) or no systematic deviation (*29*) in predicted Pb^{2+}.

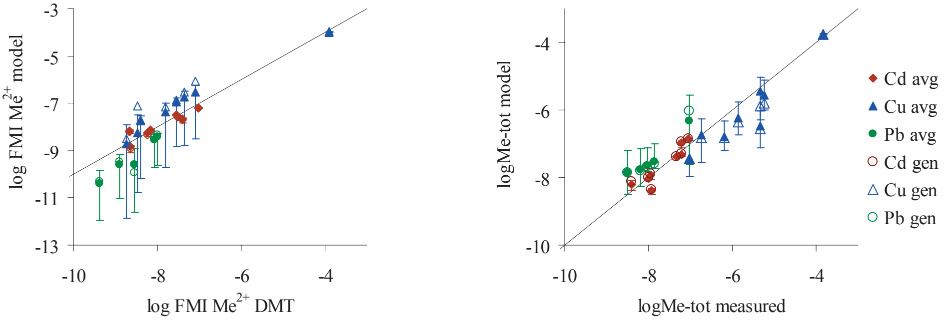

FIGURE 2 Comparison between calculated and measured log free metal ion concentrations (left) and total concentrations (right) for Cd, Cu and Pb. Error bars indicate p5 and p95 of the Monte Carlo simulations, closed symbols represent calculations with average values of the parameters (avg), open symbols represent calculations with the generic parameters of Milne et al. (gen)

The uncertainty in NICA parameters of competing cations may also affect the uncertainty in predicted trace metal speciation. We evaluated this additional uncertainty for the important competitors Al^{3+} and Fe^{3+} (*24*) with MC simulations of the FMI predictions for the soil extracts. The measured dissolved Fe and Al concentrations in these extracts (Table S-3, Supporting Information) enable an explicit analysis of the additional effect of uncertainty in the parameters for Al and Fe binding to FA. Binding parameters were varied according to the SD reported for Fe (*20*), assuming a similar variation for Al, for which no data were available. Differences between the uncertainties (Table S-9, Supporting Information) of the MC calculations with and without variation in the Al and Fe parameters were insignificant, implying that with the present parameter uncertainty for Cd, Cu and Pb, the parameter uncertainty of Al and Fe does not lead to additional uncertainty in the predicted speciation.

3.7 Implications for model use and improvement.

HS fractions extracted from different soils vary between 14% and 63% of total DOM. Considerable variation is shown to exist in NICA-model parameters for various samples of FA. This natural variation in binding properties and DOM composition creates considerable uncertainty in the predictions of metal speciation when using ion binding models like NICA-Donnan. The variability in model parameters is the most important source of the uncertainty in predicted speciation of metals with a relatively high affinity to bind to organic matter (Cu and Pb), whereas the variation in the composition of DOM is most important for metals with a relatively low affinity (Cd). It is, therefore, worthwhile to investigate the extent to which uncertainties can be reduced by restricting the variability of the (dissolved) organic matter composition and model parameters by determining their ranges for certain groups of soils, soil- and surface waters and other materials in which metal binding to HS is important. However, due to the heterogeneous nature of (dissolved) organic matter a certain level of variability is to be accepted. For example the observed fivefold temporal variation in Cu-binding affinity of DOM in leachates from a single soil (*33*). The large uncertainties at low FMI activities (e.g. at high pH and/or low total metal concentration and/or high FA concentration) are unlikely to be substantially improved because these uncertainties are mainly the result of the difference between two relatively large numbers: the total metal concentration and the concentrations of metal bound to FA. However, the practical need for further precision at these very low FMI activities may be questioned.

It is also important to note that the contribution of LMWOA should be considered when modeling Cu speciation in acid soils, while the effect was found to be insignificant for Cd and Pb and higher pH.

When new model parameters are derived, their uncertainty can be reduced when proton and metal binding data are determined for the same HS sample. At present there are almost no samples for which both data are available. Our results show a clear difference (Figure 2) between the predicted speciation using either the average values from this study or the generic values of the NICA parameters as derived by Milne et al. (*6*). Their method employed to derive the generic parameters weighs the data points according to their quality, possibly leading to a strong bias for HS samples with many data points, although the particular HS may show far from average behavior. Because of the existing variability in binding properties, we advocate a method in which the separate HS samples are weighed equally.

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Supporting Information

Soils. Eight soil samples were collected from field-contaminated sites in Bulgaria, the Netherlands, Denmark, and China. The soil from Bulgaria was taken from the topsoil of a yard in Zlatitza. Soils in the area around Zlatitza have elevated Cu levels from pedogenic origin and from atmospheric deposition of metal-bearing dust from a nearby Cu smelter (N.S. Dinev, 2007, personal communication). The first soil from the Netherlands was collected from the Wildekamp experimental site near Wageningen. In 1982, the experimental site was established as a randomized block design of four pH adjustments (nominal pH of 4.0, 4.7, 5.4, and 6.1) and four Cu concentrations (0, 250, 500, and 750 kg $CuSO_4$ ha^{-1}) (*1*). From 1978 onward, the experimental site was used as arable land. We used a soil sample taken in 2005 from the 0-20 cm layer of the treatment with the lowest pH level and the highest Cu application.

The other samples from the Netherlands (Noorderbos) are sandy soils from a location with former wastewater infiltration fields which were used to remove nutrients from wastewater from the city of Tilburg before discharge into surface waters. The soils are contaminated with As, Cd, Cr, Cu, Ni and Zn. Each wastewater infiltration field is about 100 x 100 m with at one end an inlet for wastewater. Each field has a clear concentration gradient of metals and organic matter with the highest concentrations close to the inlet. Some field plots were artificially acidified by adding elemental sulfur. Here we used two samples with high metal and organic matter levels of which one is at its original pH and the other artificially acidified and two soils from the low end of metal and SOM contents again 1 with the original pH and 1 acidified.

The soil from Denmark was taken in 2003 from the plow layer of a site near Hygum. Timber preservation with $CuSO_4$ from 1911 to 1924 caused contamination of the soil with Cu. The site was used as arable land and left fallow after 1993 (*2*). The soil from China was taken from the 0-15 cm layer of a paddy field in Zhejiang province. Due to atmospheric deposition of metal-bearing dust from nearby Cu smelters and application of wastewater irrigation, the soil was contaminated with multiple heavy metals (*3*).

Donnan Membrane Technique. For the Wildekamp, Hygum, and Zhejiang soils, purified humic acid from the Tongbersven forest near Oisterwijk in the Netherlands (*1*) was added to the acceptor solutions at a DOM concentration of 30 mg L^{-1} to accumulate metals in the acceptor solutions to levels above the detection limit of the inductively coupled plasma mass spectrometer (ICP-MS) (*2*) . ORCHESTRA (*3*) including the NICA-Donnan model was used to calculate the free metal activities in the acceptor solutions based on total metal concentrations, the concentration of the added purified humic acid (PHA, samples 1-4, other samples were measured without PHA addition), and pH at t = 8 d. The nitrate concentration was fixed at 4 mM. For H, Ca, Cd, Cu, Ni, and Zn, specific NICA-Donnan parameters of the PHA were taken from Kalis et al. (*2*). For other metals, generic parameters were used (*4*). The free metal activities were corrected for differences in ionic strength between donor and acceptor solutions (*5*) with Na.

TABLE S-1 Metal and Fulvic Acid concentrations used in the scenarios

	high	medium	low
FA (kg.L^{-1})	2.10^{-4}	2.10^{-5}	2.10^{-6}
Cd tot (mol.L^{-1})	1.10^{-6}	3.10^{-8}	1.10^{-9}
Cu tot (mol.L^{-1})	1.10^{-5}	3.10^{-7}	1.10^{-8}
Pb tot (mol.L^{-1})	3.10^{-5}	3.10^{-7}	6.10^{-8}
Cd FMI (mol.L^{-1})	5.10^{-7}	1.10^{-8}	5.10^{-10}
Cu FMI (mol.L^{-1})	1.10^{-6}	1.10^{-8}	1.10^{-11}
Pb FMI (mol.L^{-1})	3.10^{-5}	1.10^{-7}	1.10^{-11}

TABLE S-2 DOM Composition of Soil Solution Extracts

Sample	%HA	%FA	%Hy	%HS
Zlatitza[1]	1.7	24.5	73.8	26.2
Wildekamp[1]	2.0	27.3	70.7	29.3
Hygum[1]	1.0	30.7	68.3	31.7
Zhejang[1]	3.8	27.8	68.4	31.6
Noorderbos1[1]	0.5	45.1	54.4	45.6
Noorderbos1z[1]	1.4	48.7	49.9	50.1
Noorderbos3[1]	0.9	38.3	60.8	39.2
Noorderbos3z[1]	1.1	39.4	59.5	40.5
Sand 0-30[2]	13.7	36.1	50.2	49.8
Sand 30-60[2]	3.0	41.9	55.0	45.0
Sand 60-90[2]	0.0	60.3	39.7	60.3
Sand 90-120[2]	11.6	51.3	37.1	62.9
Clay 0-40[2]	2.0	45.9	52.1	47.9
Clay 40-80[2]	24.2	29.2	46.6	53.4
Clay 80-120[2]	14.2	0.0	85.8	14.2
Peat 0-15[2]	3.2	37.6	59.2	40.8
Peat 10-40[2]	2.8	34.4	62.7	37.3
Ll1986[3]	0.9	17.2	81.9	18.1
Ll2005[3]	0.0	16.0	84.0	16.0
Hl1986[3]	1.5	37.3	61.3	38.7
Hl2005[3]	0.0	39.3	60.7	39.3
minimum	0.0	0.0	37.1	14.2
maximum	24.2	60.3	85.8	62.9
average	4.3	34.7	61.1	38.9
SD	6.3	13.4	13.4	13.4

[1] This Study

[2] Spijker *et al.(6)*

[3] Fest *et al*. (7)

Table S-3 Concentrations of major cations and trace metals in the soil solution extracts (log mol.L^{-1})

sample	Na	Mg	Al	K	Ca	Cr	Mn	Fe	Ni	Zn
Zlatitza	-2.99		-5.06	-4.33	-2.78		-4.27	-6.15	-6.19	-5.10
Wildekamp	-3.00		-5.44		-2.74		-5.09	-5.97	-7.34	-6.34
Hygum	-2.98		-5.38	-3.55	-2.71		-4.71	-6.14	-6.90	-6.15
Zhejang	-2.95		-5.67	-4.02	-2.55		-5.84	-6.46	-7.45	-5.01
Noorder-bos 1	-3.00	-3.88	-4.78	-3.82	-2.76	-5.66	-4.72	-5.47	-5.14	-4.46
Noorder-bos 1z	-3.08	-4.18	-4.84	-3.80	-2.88	-5.69	-5.00	-5.09	-5.41	-4.81
Noorder-bos 3	-2.99	-3.79	-4.96	-3.84	-2.74	-6.01	-5.00	-5.66	-5.87	-5.11
Noorder-bos 3z	-3.04	-4.39	-5.07	-4.30	-2.83	-6.10	-5.45	-5.12	-5.94	-5.42

TABLE S-4 Individually optimized NICA parameters for Cd, Cu and Pb, the R^2 and root mean squared error (RMSE) of the fit and the number of data in each set. (sample codes are those from Milne et al. (*4*)) ; the fit for all samples together and minimum and maximum values for the parameters obtained. Sets printed in Italics did not give a fit or resulted in unrealistic parameter values and were not used. Numbers in bold are generic parameters (*4*)

Cd

Set	**log K_1**	**n_1**	**log K_2**	**n_2**	**R^2**	**RMSE**	**n**
FCd-01	-1.35	0.65	**0.50**	**0.50**	1.00	0.04	223
FCd-02	-0.60	0.73	**0.50**	**0.50**	0.99	0.05	227
FCd-03							96
FCd-04	-1.47	0.67	**0.50**	**0.50**	0.40	0.29	70
FCd-05							10
FCd	-1.06	0.66	**0.50**	**0.50**	0.94	0.16	520
MIN	-1.47	0.65	0.50	0.50			
MAX	-0.60	0.73	0.50	0.50			

continued on next page

Cu

Set	log K_1	n_1	log K_2	n_2	R^2	RMSE	n
FCu-01	0.44	0.79	7.18	0.54	0.98	0.07	237
FCu-02	-0.75	0.50	8.62	0.39	0.95	0.15	23
FCu-03	-0.08	0.40	11.25	0.32	0.98	0.03	69
FCu-04	*-7.18*	*0.09*	*13.35*	*0.37*	*0.99*	*0.06*	*11*
FCu-05	-0.47	0.18	5.92	0.80	0.99	0.03	43
FCu-06	-1.27	0.47	10.91	0.26	1.00	0.01	24
FCu-07	*-27.83*	*0.53*	*13.18*	*0.27*	*0.93*	*0.22*	*15*
FCu-08	-0.31	0.68	5.24	0.86	0.98	0.08	18
FCu-09	*0.04*	*0.41*	*-25.70*	*0.36*	*1.00*	*0.02*	*15*
FCu-10	0.05	0.51	8.27	0.43	1.00	0.06	60
FCu-11	0.57	0.55	7.70	0.44	1.00	0.03	56
FCu	0.23	0.56	8.19	0.36	0.91	0.18	541
MIN	-1.27	0.18	5.24	0.26			
MAX	0.57	0.79	11.25	0.86			

Pb

Set	log K_1	n_1	log K_2	n_2	R^2	RMSE	n
FPb-01	-0.10	**0.60**	6.40	**0.69**	0.95	0.09	60
FPb-02	*-0.48*	***0.60***	*-11.87*	***0.69***	*0.96*	*0.07*	*10*
FPb-03	*-21.89*	***0.60***	*7.60*	***0.69***	*0.95*	*0.08*	*41*
FPb-04	-0.30	**0.60**	7.30	**0.69**	0.96	0.10	66
FPb-05	-1.31	**0.60**	4.09	**0.69**	0.99	0.04	23
FPb-06	0.21	**0.60**	7.01	**0.69**	0.95	0.07	16
FPb-07	-1.03	**0.60**	6.57	**0.69**	0.99	0.07	305
FPb-08	-0.13	**0.60**	6.33	**0.69**	0.94	0.18	58
FPb	-1.11	0.60	6.89	0.69	0.92	0.22	579
MIN	-1.31	0.60	4.09	0.69			
MAX	0.21	0.60	7.30	0.69			

TABLE S-5 Correlations between optimized NICA parameters (medium to strong correlations as used in the sampling of the parameters are printed in bold)

H	Q_{max1H}	Q_{max2H}	$\log_{KH1}$
Q_{max2H}	-0.28		
$\log_{KH1}$	-0.27	-0.17	
$\log_{KH2}$	0.35	0.34	-0.05

Cu	LogK_{Cu1}	Q_{max1H}	n_{Cu1}	LogK_{Cu2}	Q_{max2H}
Q_{max1H}	**-0.56**				
n_{Cu1}	0.28	-0.16			-0.08
LogK_{Cu2}	**-0.40**	0.08	-0.14		-0.11
n_{Cu2}	0.29	-0.07	0.06	**-0.72**	**-0.47**

Cd	LogK_{Cd1}	Q_{max1H}
Q_{max1H}	**-0.78**	
n_{Cd1}	**0.91**	**-0.70**

Pb	$\log_{KPb1}$	$\log_{KPb2}$
LogK_{Pb2}	**0.66**	
Q_{max1H}	-0.35	-0.16
Q_{max2H}	-0.31	**-0.50**

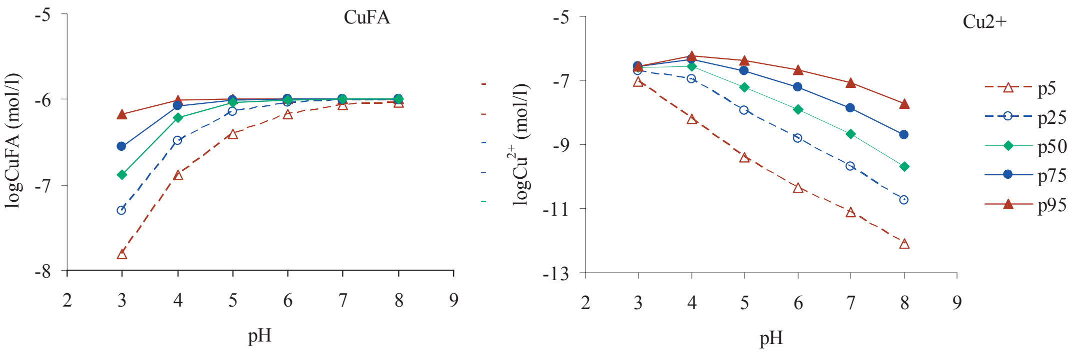

FIGURE S-1 Model outputs of predicted Cu bound to FA (CuFA) and free Cu^{2+}-ion concentrations for the Monte Carlo Simulations for a system with fixed total concentrations of Cu at medium levels of Cu and FA concentration.

Table S-6 Log FMI activity for the scenario calculations with medium levels of FA for various concentrations of Low Molecular Weight Organic Acids[a]

element	pH	0% LMWOA	10% LMWOA	50% LMWOA
Cd	3	-8.27	-8.27	-8.28
	4	-8.29	-8.29	-8.30
	5	-8.38	-8.39	-8.40
	6	-8.52	-8.52	-8.54
	7	-8.67	-8.67	-8.68
	8	-8.82	-8.82	-8.84
Cu	3	-6.31	-6.52	-6.94
	4	-6.58	-7.04	-7.65
	5	-7.20	-7.47	-8.02
	6	-8.10	-8.15	-8.40
	7	-9.26	-9.27	-9.29
	8	-10.63	-10.63	-10.64
Pb	3	-7.26	-7.26	-7.27
	4	-7.37	-7.38	-7.39
	5	-7.78	-7.79	-7.80
	6	-8.79	-8.79	-8.80
	7	-9.88	-9.88	-9.89
	8	-10.92	-10.92	-10.93

[a] LMWOA were modeled as 70% mono-, 20% di- and 10% tri- carboxylic acids represented by fumaric- oxalic- and citric acid, respectively

Table S-7 Root Mean Squared Errors of predicted free metal ion concentrations (logM) in this and other studies

source	Cd	Cu	Pb	model	%FA
this study (average)	0.21	0.47	0.60	NICA	measured
this study (generic)	0.22	0.79	0.65	NICA	measured
Ge *et al.* (*8*)	0.67	-	0.82	NICA	65
Pampura *et al.* (*9, 10*)	0.35	0.39	0.54	Model VI	65
Ponizovsky *et al.*(*11*)	-	0.77	-	Model VI	40 (optimized)
Weng *et al.* (*12*)	0.35	0.28	0.71	NICA	65
Weng *et al.*(*12*)	0.26	0.40	0.38	Model VI	65

TABLE S-8 NICA-Donnan Parameters of Al and Fe and the Standard Deviation used in the Monte Carlo simulations

element	***$logK_1$***	***$logK_2$***	***n_1***	***n2***
	mean	mean	mean	mean
	SD	SD	SD	SD
Fe[a]	2.7	8.3	0.36	0.23
	1.1	3.5	(0.05)[c]	(0.09)[c]
Al[b]	-4.11	12.16	0.42	0.31

[a] parameter values according to Hiemstra and Van Riemsdijk (*13*)

[b] SD for Al were set equal to those for Fe

[c] not used in the MC simulations

Table S-9 Uncertainties in terms of the Inter Quantile Range (IQR) for the Monte Carlo Simulations of the FMI activity Predictions for the Soil Solution Extracts due to variation in NICA parameters of the trace metals (TM) and variation in the NICA parameters of the TM together with those for Al and Fe (TM+Al Fe)

sample	Cd		Cu		Pb	
	TM	TM + Al Fe	TM	TM + Al Fe	TM	TM + AlFe
Zlatitza1	0.0054	0.0054	0.0095	0.0089	-	-
Wildekamp1	0.058	0.059	1.24	1.25	-	-
Hygum1	0.15	0.15	1.29	1.31		
Zhejang1	0.11	0.11	2.24	2.23	1.56	1.56
Noorderbos11	0.042	0.044	1.52	1.52	0.97	0.99
Noorderbos1z1	0.014	0.016	0.99	0.93	0.60	0.57
Noorderbos31	0.086	0.090	2.04	2.04	1.08	1.11
Noorderbos3z1	0.016	0.018	1.18	1.28	0.55	0.53

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CHAPTER 6

Evaluation of approaches to calculate critical metal loads for forest ecosystems

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Abstract

This paper evaluates approaches to calculate acceptable loads for metal deposition to forest ecosystems, distinguishing between critical loads, stand still loads and target loads. We also evaluated the influence of including the biochemical metal cycle on the calculated loads. Differences are illustrated by examples of Cd, Cu, Pb and Zn for a deciduous forest on five major soil types in the Netherlands. Stand still loads are generally lower than critical loads, which in turn are lower than the target loads indicating that present levels are below critical levels. Uncertainties in the calculated critical loads are mainly determined by the uncertainty in the critical limits and the chemical speciation model. Including the metal cycle has a small effect on the calculated critical loads. Results are discussed in view of the applicability of the critical load concept for metals in future protocols on the reduction in metal emissions.

1 Introduction

In Europe, there are large areas of forest soils that have been polluted by various metals through atmospheric deposition (*1*) both from industrial emissions (*2*) and traffic emissions (*3*). In situations of extreme metal pollution, such as occurring in the Kola Peninsula in Russia, various impacts have been observed on forest ecosystems, including a decrease in forest productivity, vitality, biodiversity and stand structure (*4-6*). Elevated concentrations of metals have been found to damage root growth and functions both in pot experiments or hydroponic cultures (e.g. *7*) (*8, 9*)and in the field situation (e.g. *10, 11*), impairing the water relations of affected plants (*11, 12*).

While the above mentioned effects are limited to severe metal pollution, impacts on soil organisms related to anthropogenic enhanced accumulation in the organic layer occur at much lower concentrations of metals (specifically cadmium and lead) in forests (*13-15*). This has lead to the derivation of critical limits for total metal concentrations, either in the humus layer or the mineral soil, based on No Observed Effect Concentrations (NOECs) from laboratory studies with plants and soil organisms, such as soil microbiota and soil invertebrates (e.g. *16*).The risks from metal pollution, however, depends on their availability which in turn is influenced by soil properties such as pH, CEC, clay and organic matter content etc (e.g. *17, 18, 19*). Recently, critical dissolved free metal ion (FMI) concentrations were thus derived in view of ecotoxicological effects on soil organisms and plants, based on NOEC soil data and soil properties (pH, organic matter content), affecting its availability (*20, 21*).

Common practice in risk assessment is to compare present concentrations with critical concentrations at which adverse effects are not to be expected. With this approach it impossible to assess future risks due to metal inputs which may cause accumulation and possibly leads to future exceedance of critical limits. A method to assess future risks is the critical load approach. This approach determines the maximum level of constant atmospheric deposition that causes no or tolerable damage, ("long-term acceptable load" or "critical load"). It has been applied successfully in international negotiations on the reduction of atmospheric emissions of nitrogen and sulfur. Its potential use in international negotiations on the reduction in metal emissions is under debate. According to its definition, a critical load (CL) for metals equals the load resulting at steady state in a concentration in a compartment (soil solid phase, soil solution, groundwater, plant, sediment, fish etc.), that equals the critical limit set for metals, thus preventing 'significant harmful effects on specified sensitive elements of the environment' (*22*).

In defining a CL one aims at long-term sustainability of the ecosystem. In this context, sustainability can be defined as the situation where (i) no further net accumulation of metals occurs (stand still load) or (ii) accumulation of metals is below critical limits in defined ecosystem compartments (e.g. soil solid phase, soil solution; CL). The method to calculate CLs of metals is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a future steady state situation. First approaches were described in a "manual" for calculation of critical loads of metals in terrestrial ecosystems (*23*), including various approaches to calculate critical loads. In 2004, The UNECE ICP Modelling & Mapping published a formal manual (*24*), focusing on Cd, Pb and Hg, with related background report describing the various details (*25*). Because of the time it takes to reach steady state concentrations, the use of dynamic model approaches should be considered (*26*). A particular example of a dynamic model approach is the calculation of a target load, which is defined as the load resulting in a concentration in a compartment that equals the critical limit set for metals within a defined time period

Maps of critical loads for metals have been published for Europe (*27*) and Canada (*28*), using various approaches, but an evaluation of the various concepts in terms of their assumptions and effects has not yet been published. This paper aims at such a review. It summarizes and evaluates possible approaches to calculate acceptable loads for metal deposition to forest ecosystems, distinguishing between critical loads, stand still loads and target loads. These approaches differ with respect to the criterion used on which the maximum load is based in either (i) using present metal concentrations for the soil solid phase (stand still loads) or effect based critical limits (critical loads and target loads) and (ii) with respect to the time scale used, applying a steady-state approach (infinite timescale) for CLs and stand still loads and a finite time scale with a dynamic approach to calculate target loads. We also evaluate the influence of the complexity of the models with respect to inclusion of the plant metal cycle (metals in litterfall and uptake to replenish litterfall) on the calculated loads. Differences are illustrated by calculation examples of Cd, Cu, Pb and Zn for a generic deciduous forest, where the metal load is due to atmospheric deposition only. Results are discussed in view of the applicability of the CL concept for metals in future protocols on the reduction in metal emissions.

2 Calculation methods

2.1 Steady-state model approach to assess stand still loads and critical loads

Stand still loads and CLs are calculated with a mass balance model on the basis of a present or critical metal leaching rate, respectively, which in turn is defined by a present or critical metal concentration in soil solution.

Steady-state mass balance equation

In deriving CLs use was made of a steady-state mass balance model according to:

$$M_{td} = -M_{lf} + M_{fu} + M_{ru} + M_{le} \tag{1}$$

where M_{td} is the total load of metal M by atmospheric deposition and where M_{lf}, M_{fu}, M_{ru} and M_{le} are the fluxes of metal M by litterfall, foliar uptake, root uptake and leaching, respectively (all in $mg.m^{-2}.yr^{-1}$). Apart from the assumption of a steady-state situation, implying that the calculated CL is intended to be valid for an indefinitely long period, various assumptions apply to the model, such as: (i) the soil system is homogeneously mixed which implies that the CL can only be calculated for a distinctive homogeneous layer, (ii) the soil is in an oxidized state and metal partitioning can be described with equilibrium sorption and complexation with DOC, (iii) transport of water and metals only takes places in vertical direction (no seepage flow, surface runoff and bypass flow), (iv) metal weathering and erosion is not considered and (v) the metal deposited is chemically reactive and is 100% available for exchange with the solution phase. The related limitations due to these assumptions are discussed in De Vries et al. (*25*).

Calculation of metal fluxes

The various fluxes included in Eq. (1) are litterfall, foliar uptake, root uptake and leaching. The flux of metals in litterfall is calculated as a function of the total metal deposition according to:

$$M_{lf} = M_{lf}(nd) + frM_{lf} \cdot M_{td} \tag{2}$$

Where $M_{lf}(nd)$ is the flux of metal M in litterfall at negligible deposition ($mg.m^{-2}.yr^{-1}$) and frM_{lf} is the litterfall fraction (-). Foliar uptake of metals is described as a fraction of the total deposition according to:

$$M_{fu} = M_{fu}(nd) + frM_{fu} \cdot M_{td} \tag{3}$$

Where $M_{fu}(nd)$ is the foliar uptake flux of metal M at negligible deposition ($mg.m^{-2}.yr^{-1}$) and frM_{fu} is a foliar uptake fraction (-). Root uptake in the layer for which the CL is calculated is described as a fraction of the maintenance uptake, to resupply the amount released by litter fall minus foliar uptake, and uptake due to net growth according to:

$$M_{ru} = fr_{ru} \cdot (M_{lf} - M_{fu} + M_{gu}) \tag{4}$$

where fr_{ru} is a depth dependent cumulative root uptake fraction in the root zone (-) and M_{lf}-M_{fu} is the flux of metal M needed to maintain a constant metal concentration in the foliage ($mg.m^{-2}.yr^{-1}$). At the bottom of the root zone, fr_{ru} equals 1. Growth uptake is derived by the multiplication of the forest yield and the metal content in stem wood, according to:

$$M_{gu} = Y \cdot ctM_{st} \tag{5}$$

Where Y is yield ($kg.ha^{-1}.yr^{-1}$) and ctM_{st} is the metal content in stem wood ($mg.kg^{-1}$). Leaching is described as the product of water flux and soil solution concentration according to:

$$M_{le} = Q_{le} \cdot [M]_{tot,ss} \tag{6}$$

Where Q_{le} is the water flux leaching from the soil ($m.yr^{-1}$) and $[M]_{tot,ss}$ is the total metal concentration in soil solution ($mg.m^{-3}$). The water flux at steady-state is calculated according to:

$$Q_{le} = (1 - fr_i) \cdot P - E_{se} - fr_{ru} \cdot E_t \tag{7}$$

Where P is precipitation ($m.yr^{-1}$), E_{se} is soil evaporation ($m.yr^{-1}$) and fr_i is interception fraction (-).

Calculation of critical loads

The steady-state dissolved concentration of a certain metal can be calculated by combining the mass balance equation (Eq. 1) with Eq. (2)- Eq. (7) according to:

$$[M]_{tot,ss} = (fr_{re} \cdot M_{td} - M_{re}) / Q_{le} \tag{8}$$

With:

$$fr_{re} = (1 - frM_{fu}) - fr_{ru} \cdot (frM_{lf} - frM_{fu}) + frM_{lf} \tag{9}$$

$$M_{re} = (-1 + fr_{ru}) \cdot M_{lf}(nd) + (1 - fr_{ru}) \cdot M_{fu}(nd) + fr_{ru} \cdot Y \cdot ctM_{st} \tag{10}$$

Where fr_{re} is a deposition dependent removal fraction (-) and M_{re} is a deposition dependent removal flux of metal M ($mg.m^{-2}.yr^{-1}$). For a given critical value of $[M]_{tot,ss}$ i.e. $[M]_{tot,ss}$(crit), a CL (deposition level), M_{td}(crit), can be derived according to (cf. Eq. 8-10):

$$\mathrm{M_{td}(crit) = (M_{re} + Q_{le} \cdot [M]_{tot,ss}(crit)) / fr_{re}} \tag{11}$$

The calculation of CLs with Eq. (11) requires a critical total metal concentration in soil solution $[M]_{tot,ss}$(crit), When neglecting the plant metal cycle, fr_{ru} = 1. Inserting this value in Eq. (8)- Eq. (11) leads to:

$$\mathrm{M_{td}(crit) = Y \cdot ctM_{st} + Q_{le} \cdot [M]_{tot,ss}(crit)} \tag{12}$$

We used both approaches (Eq. 11 and 12) to assess the influence of the metal cycle on the critical metal load.

2.2 Simple dynamic model approach to assess target loads

Mass balance equation

The inclusion of an acceptable net accumulation or reduction of metals during a given time period is an approach, which implies that the steady-state principle is left and Eq. (1) changes into:

$$M_{td} = -M_{lf} + M_{fu} + M_{ru} + M_{le} + \rho_s z_s \frac{d}{dt} ctM_{re} + \theta z_s \frac{d}{dt}[M]_{tot,ss} \tag{13}$$

Where ctM_{re} is the reactive metal concentration in the soil solid phase ($mg.kg^{-1}$), ρ_s is the bulk density of the soil ($kg.m^{-3}$), θ is the water content ($m^3.m^{-3}$) and z_s is the thickness of the soil layer (m). Here we consider only changes in the adsorbed pool of metals.

Calculation of target loads

Using a dynamic model, a target load can be calculated by solving the mass balance equation (Eq. 13). In the case of a linear relation between the metal concentration in the solid phase and the concentration in solution, an analytical solution of the mass balance equation is available and the target load can be calculated according to Eq. 14 (for a derivation see Appendix 1)

$$\mathrm{M_{td}} = \frac{\left[\mathrm{M_{re}} + \frac{\mathrm{Q_{le}}}{1-\mathrm{e}^{-\mathrm{b}\cdot\mathrm{t}}}\left([\mathrm{M}]_{\mathrm{tot,ss}}(\mathrm{crit}) - [\mathrm{M}]_{\mathrm{tot,ss}}(\mathrm{init}) \cdot \mathrm{e}^{-\mathrm{b}\cdot\mathrm{t}}\right)\right]}{\mathrm{fr_{re}}} \tag{14}$$

With $$b = \frac{Q_{le}}{\rho_s z_s k_d + \theta z_s} \qquad (15)$$

Note that, unlike a steady-state approach, a dynamic approach always requires the inclusion of solid-solution partitioning. To be able to solve the equation to calculate the target load, we used a k_d value in the concentration interval between the present concentration and the critical concentration, according to:

$$k_d = \frac{ctM_{re}(crit) - ctM_{re}(present)}{[M]_{tot,ss}(crit) - [M]_{tot,ss}(present)} \qquad (16)$$

This approach can be used irrespective of the models used to calculate metal speciation and partitioning. Here, we calculated ctM_{re}(crit) in equilibrium with the critical FMI in solution and ctM_{re}(init) from the initial total metal concentration using regression relations (see section 2.3).

2.3 Modeling solid solution partitioning and metal speciation in soil solution

Need for modeling interactions between and in soil and soil solution

The need for modeling interactions between soil and soil solution is illustrated in Figure 1, presenting the approaches to calculate stand-still loads, CLs and target loads. A critical metal concentration in soil solution can directly be used to derive a CL. To calculate a stand still load the present (initial) metal concentration in solution needs to be calculated from the present metal concentration in soil. Inversely, critical reactive soil metal concentrations have to be calculated from a critical metal concentration in soil solution, in order to derive a target load (Figure 1).

The interrelationships that are accounted for in the modeling are illustrated in Figure 2. Part of the metals in the solid phase is assumed to be inert with respect to solid solution partitioning, referred as immobile metal, whereas the part of metals in the solid phase which controls soil solution concentrations is referred to as reactive metal. Going from total to reactive soil metal concentrations, an immobile metal correction is needed (see relation 1 in Figure 2). We assume that metal partitioning over the soil solid phase and soil solution can be described with equilibrium partitioning, using a transfer function between free metal ion (FMI) concentration in soil solution and the reactive metal concentration in the solid phase (see relation 2 in Figure 2). To calculate a total concentration in solution from the critical FMI concentration, a speciation model is needed to account for metal speciation in the soil solution (see relation 3 in Figure 2).

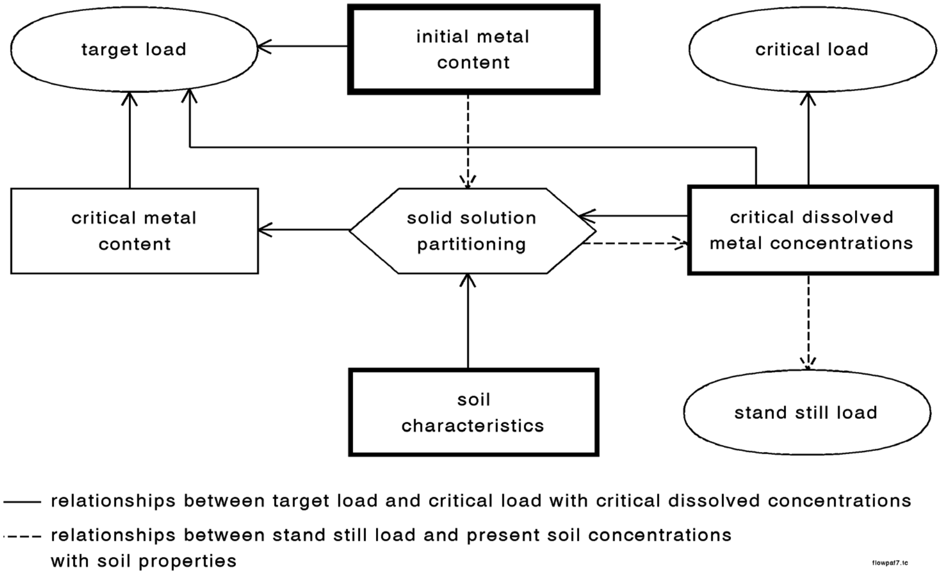

FIGURE 1 Overview of the three different approaches, used in calculating steady-state stand-still loads and critical loads and a target load

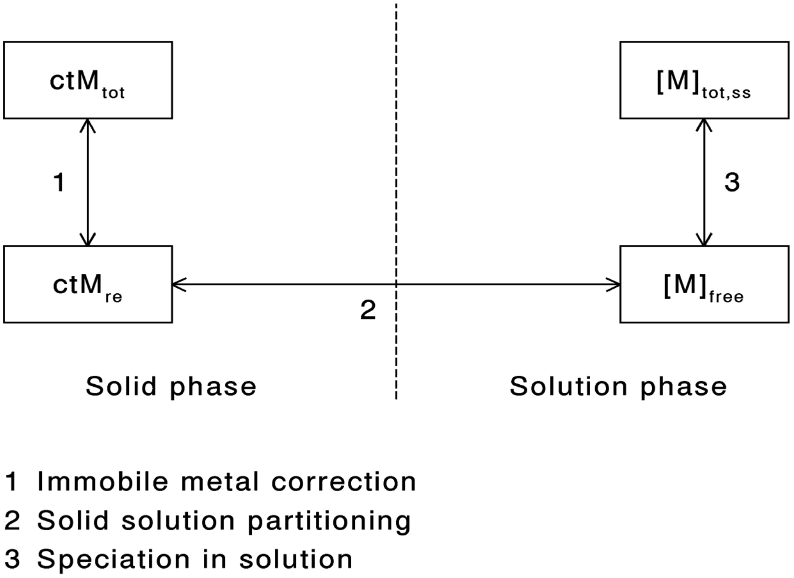

FIGURE 2 Overview of relations between metal concentrations in soil solid phase and soil solution

The assessment of a stand-still load requires application of all relations in figure 2 to come from a present total soil metal concentration to a related present total metal concentration in solution. The same is true for the assessment of a target load. With the calculation of the target load the reactive metal pool changes (increase or decrease) from its initial value to its final (critical) value. The initial reactive metal concentration is calculated from the total reactive metal concentration (relation 1) and the critical reactive metal concentration is calculated from the critical FMI with relation 2. The total solution concentrations in equilibrium are calculated from the FMI concentrations using a chemical speciation model (relation 3). In the case of deriving CLs, the starting point is a critical FMI concentration that needs to be converted to a critical total dissolved metal concentration. The assessment of stand-still loads, CLs and target loads thus always requires modeling of speciation in the soil solution.

Assessment of critical free metal ion concentrations

To assess CLs, there is a need for critical limits for metals in soil solution. Up to now, critical limits are mostly related to total metal concentrations, either in the humus layer or the mineral soil, based on NOEC (No observed effect concentrations) data from laboratory studies with plants and soil organisms (soil microbiota and soil invertebrates) (*16, 29, 30*). The use of a single soil metal concentration as a critical limit for ecotoxicological effects upon soil organisms has been criticized (*31*) since it does not account for observed variations in the toxicity of cationic metals among soils of differing chemistry (e.g. *32*). The hypothesis is that variations in toxicity arise since for many organisms uptake and consequent toxicity of metals occurs via the soil solution (e.g. *33*). Specifically, the free metal ion (FMI) in soil solution is likely the form that is available for interactions with organisms. This is the basis for the free ion activity model (FIAM) (*34*). Because other cations may compete for uptake (*35*); the Biotic Ligand Model (BLM) was developed (*36, 37*). This model is however only parameterized for very few terrestrial organisms (e.g. *38*). To make use of existing toxicity data critical dissolved FMI concentrations in view of ecotoxicological effects on soil organisms and plants were derived, based on NOEC data and soil properties affecting its availability (pH, organic matter concentration), using a procedure described in Lofts et al. (*20*) and De Vries et al. (*21*). The critical FMI concentrations were derived as a function of pH, according to:

$$\log[\mathrm{M}]_{\mathrm{free(crit)}} = \alpha_{\mathrm{crit}} \cdot \mathrm{pH}_{\mathrm{ss}} + \gamma_{\mathrm{crit}} \tag{17}$$

Values used for the empirical coefficients α_{CRIT} and γ_{CRIT} are given in Table 1. These critical dissolved metal concentrations are based on: (i) data sets with both NOEC or EC10 toxicity data for soil from major organisms including information on soil properties affecting bioavailability, (ii) transfer functions, describing the relation between FMI concentration and reactive metal concentration (assumed to equal the added metal concentration in the toxicity test) and (iii) statistical approaches, deriving limit functions using a bootstrapping technique and applying a 95% protection level (HC_5). More information on the approach and the data sets used is given in Lofts et al. (*20*) and De Vries et al. (*21*).

TABLE 1 Values for α_{CRIT} and γ_{CRIT} used to calculate critical limits for FMI concentrations in soil solution

Metal	FMI concentration	
	α_{CRIT}	γ_{CRIT}
Cd	-0.32	-6.34
Cu	-0.91	-3.80
Pb	-1.23	-2.05
Zn	-0.31	-4.63

Metal partitioning in the soil solid phase: derivation of reactive metal concentrations

When assessing stand still loads and target loads, the reactive metal concentration ctM_{re} has been derived from the total metal concentration, ctM_{tot} using a log linear relation accounting for the impact of soil characteristics (clay content and organic matter content) according to (*39*):

$$\log ctM_{re} = \beta_0 + \beta_1 \cdot \log ctM_{tot} + \beta_2 \cdot \log(\%OM) + \beta_3 \cdot \log(\%clay) \qquad (18)$$

The coefficients for mineral soils are based on 630 soil samples in which the reactive metal concentration was derived by extraction with 0.43 $Mol.L^{-1}$ HNO_3 and the (pseudo) total metal concentration by Aqua Regia (Table 2,where ctM_{tot} and ctM_{re} are expressed in $mol.kg^{-1}$). For the organic layer, the reactive metal concentration was assumed to be equal to the total metal concentration. This was based on measurements of Aqua Regia - and EDTA extractable metals in organic layers of 11 forest soils in the Netherlands, showing that the inert fraction of metals in organic layers is negligible (Groenenberg, unpublished data).

TABLE 2 Value for the regression coefficients in the relationship between reactive metal concentration (extracted by 0.43N HNO_3 versus total metal concentration (extracted by aqua regia) and soil properties (39)

Metal	β_0	β_1	β_2	β_3	R^2	se-y_{est}[a]
Cd	0.225	1.075	0.006	-0.020	0.82	0.26
Cu	0.400	1.152	0.023	-0.171	0.93	0.13
Pb	0.063	1.042	0.024	-0.122	0.88	0.17
Zn	0.428	1.235	0.183	-0.298	0.96	0.16

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

Metal partitioning over solid phase and soil solution: relating reactive metal concentration and free metal ion concentration

To calculate the metal partitioning between soil (reactive metal concentration) and soil solution (FMI) we used a Freundlich equation, according to :

$$ctM_{re} = K_f \cdot [M]_{free}^{n} \tag{19}$$

where ctM_{re} is reactive metal concentration in the soil ($mol.kg^{-1}$), $[M]_{free}$ is FMI concentration in the soil solution ($mol.l^{-1}$), K_f, is the Freundlich constant ($mol^{1-n}.kg^{-1}.l^{3n}$) and n is the Freundlich exponent. We used a transfer function, relating the Freundlich adsorption constant to easily available soil properties, because these relations are applicable to a large range of soils, need a limited set of input parameters that are generally available (*19*):

$$\log K_f = \alpha_0 + \alpha_1 \cdot pH + \alpha_2 \cdot \log[OM] \tag{20}$$

where pH is the pH in soil solution and OM is the organic matter content in %. Groenenberg et al. (*19*) derived transfer functions on the basis of two sets of desorption experiments (*39, 40*) including both mineral and organic soils. Free metal ion concentrations were calculated from measured total concentrations using WHAM. The reactive metal concentration was determined with 0.43 $Mol.L^{-1}$ HNO_3. Values used for the various regression coefficients are shown in Table 3.

TABLE 3 Values for the Freundlich exponent (n) and coefficients in the transfer function with the Freundlich adsorption constant K_f (19).

Metal	α_0	α_1	α_2	n	R^2	se-y
Cd	-2.04	0.41	0.84	0.78	0.82	0.36
Cu	-2.26	0.89	0.90	0.85	0.87	0.58
Pb	-3.06	1.21	1.17	1.0	0.88	0.60
Zn	-1.44	0.46	0.72	0.86	0.81	0.35

Metal speciation in soil solution: relating total and free metal ion concentration

To calculate CLs and stand still loads it necessary to calculate the total metal concentration in soil solution, $[M]_{tot,ss}$ in equilibrium with the FMI concentration, $[M]_{free}$.. In our calculations, metal bound to suspended particulate matter is neglected. Total metal concentrations in soil solution are thus determined as the sum of the concentration of (i) the FMI, $[M]_{free}$, (ii) dissolved inorganic complexes, $[M]_{DIC}$, such as MOH^+, $MHCO_3^+$, MCl^+, and (iii) metals bound to dissolved organic matter, $[M]_{DOM}$:

$$[M]_{tot,ss} = [M]_{free} + [M]_{DIC} + [M]_{DOC} \cdot [DOM] \tag{21}$$

where [DOM] is concentration of dissolved organic matter ($kg.m^{-3}$). By assuming geochemical equilibrium, the partitioning and speciation of metals over the various fractions can be calculated. Given the free metal activity ([M]free) the concentrations of the other metal species were estimated with the equilibrium speciation model WHAM6 (*41*). The calculation takes into account the dependence of metal binding to DOM on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe (*42, 43*). A customized program (W6-MTC), based on WHAM 6 was used, for a detailed description of the calculation procedure (see de Vries et al., *25*). Binding of metals to DOM is calculated assuming that 65% of DOM acts as fulvic acid and 35% of DOM is not involved in metal binding. This fraction is based on application of WHAM6 to field and laboratory data for waters and soils involving Al (*42, 44*), Cu (*45-47*), and Cd (*48*). DOM is calculated assuming a carbon content of 50% by taking 2* DOC.

In the calculation we use fixed free cation concentrations of the metals and fixed FMI concentrations for Al^{3+} (estimated with regression functions (*43*) and Fe^{3+} (from a solubility product, *42*) and a fixed total concentration of Na of 0.001 $Mol.L^{-1}$, the pCO_2 is kept constant at 15 times atmospheric pressure. For anions the total initial concentration is set to 0.001 $Mol_c.L^{-1}$ in equal ratios of Cl^- and SO_4^{2-}. The calculation procedure iteratively solves the charge and mass balance in solution. During the iteration procedure the charge balance is adjusted after each calculation step by increasing Ca^{2+} in case of a cation deficit and Cl^- and SO_4^{2-} (in equal ratios) in case of an anion deficit.

3 Input data

In this paper we illustrate the differences in the assessment of CLs, stand still loads and target loads, including and excluding metal cycling, while using generic data for a generic deciduous forest on major soil types in the Netherlands. The reason for using data for deciduous forests is because they grow on all kinds of soil types (sand, clay and peat) and we wanted to illustrate the impact of soil type on CLs, stand still loads and target loads. The data that were used are described below.

Metal and land use related data

Metal and land use related data include all data related to metal cycling in the ecosystem, i.e. litterfall, foliar uptake and growth uptake. Data used in the model calculations are summarized in Table 4. All data have been based on data for total deposition, throughfall, litterfall and growth uptake for four deciduous forests (beech and oak) sites in Germany (*1*). M_{lf}(nd) and M_{lf} were derived from a linear regression between litterfall and total deposition. (R^2_{adj} 0.73-0.96, depending on metal). M_{fu}(nd) and M_{fu} were derived by subtracting throughfall from total deposition and relating the resulting canopy exchange fluxes to the total depositionR^2_{adj} 0.94-0.98) (*23*). It has to be realized, however, that the relationships were derived in a high deposition range.

Relationship may be worse in the lower deposition range, occurring in most parts of Europe, including the Netherlands. Yield data are 0.21, 0.35 and 0.49 kg.m^{-2}.yr^{-1} for Dutch forests based on sand, clay/peat and loamy soils, respectively.

TABLE 4 Metal cycling parameters for deciduous forests used in the model calculations.

Metal	M_{lf}(nd) (mg.m^{-2}.yr^{-1})	frM_{lf} (-)	M_{fu}(nd) (mg.m^{-2}.yr^{-1})	frM_{fu} (-)	ctM_{st} (-)
Cd	0.094	0.05	0.0	0.55	0.3
Cu	3.3	0.07	0.0	0.77	5
Pb	0.0	0.25	0.0	0.47	5
Zn	113	0.08	0.0	0.64	25

Hydrological data

Hydrological data include precipitation, soil evaporation, transpiration and the interception- and root uptake fraction. For precipitation we used a 30-year average value of 780 mm.yr^{-1}. The soil evaporation was set at 55 mm.yr^{-1}, whereas transpiration was set at 325 mm.yr^{-1} for deciduous forests (oak) on sand and loess soils and at 400 mm.yr^{-1} for clay and peat soils, based on model calculations. The interception fraction was set at 0.2 based on Tietema and Verstraten (*49*). For the root uptake fraction a value of 0.3 was used for the organic layer and 0.5 for both the organic layer and mineral layer up to 10 cm depth. More information is given in De Vries et al. (*25*). The water fluxes (Q_{le}) thus derived are given in Table 5.

TABLE 5 Soil properties and soil solution characteristics of the organic layer and the mineral layer(0-10 cm) of the four soils used in the various calculations.

Soil type	Q_{le} (mm.yr^{-1})	$\rho_s.z_s$ (kg.m^{-2})	OM (%)	Clay (%)	pH-H_2O	DOC (mg.l^{-1})
Organic layer[a]	470	6.5	66	-	3.8	90
Sandy soil[b]	405	140	5.4	2.7	3.8	94
Loess soil[c]	370	124	8.7	12	4.3	17
Clay soil[c]	370	143	7.8	25	6.1	58
Peat soil[c]	370	16	92	-	3.7	83

[a] Refers to the organic layer of a sandy soil. Averages are based on data for the organic layer of 150 non-calcareous sandy soils (*60*).

[b] Averages are based on data for the top 0-10 cm of 200 non-calcareous sandy soils (*61*).

[c] Averages are based on data for the top 0-10 cm of 40 peat soils, 30 loess soils and 30 clay soils (*62*).

Soil data, present and background soil metal concentrations

The soil and solution data needed to calculate the critical limit and speciation and solid solution partitioning are summarized in Table 5. The pH values and DOC concentrations are based on measurements in soil solution obtained by centrifugation of field moist soil samples. Present soil metal concentrations, and the calculated present dissolved metal concentrations in equilibrium with the metal concentration, used in the calculation of stand still loads, are given in Table 6. Information on the derivation of the data is given in the Tables. Present reactive metal concentrations, calculated from the total metal concentrations according to equation (18) and reactive critical metal concentrations are presented in Table 7.

TABLE 6 Present metal concentrations in soil and corresponding calculated total metal concentrations in soil solution of the organic layer and the four mineral layers, used to calculate stand still loads

Soil type	Present soil metal concentration (mg.kg^{-1})				Dissolved total metal concentration (mg.m^{-3})			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Organic layer[a]	0.7	20	120	75	1.67	14.2	74.5	485
Sandy soil[b]	0.17	4.1	12	17	0.88	2.14	61.3	65
Loess soil[c]	0.15	16	71	53	0.44	2.64	31.6	205
Clay soil[c]	0.61	26	70	146	3.49	55.0	13.4	325
Peat soil[c]	1.4	17	125	87	3.00	7.53	58.2	463

[a] Averages based on metal concentrations in the organic layer of 150 non-calcareous sandy soils (*60*).

[b] Averages based on metal concentrations in the top 0-10 cm of 200 non-calcareous sandy soils (*61*).

[c] Averages based on metal concentrations in the top 0-10 cm of 40 peat soils, 30 loess soils and 30 clay soils (*62*).

TABLE 7 Present and critical reactive metal concentrations of the organic layer and the four mineral layers, used to calculate target loads

Soil type	Present reactive metal concentration (mg.kg^{-1})				Critical reactive soil metal concentration (mg.kg^{-1})			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Organic layer	0.7	20.0	120	75	1.54	78.4	72	24.7
Sandy soil	0.07	0.96	2.9	12.0	0.19	8.24	3.85	4.07
Loess soil	0.10	4.6	45.8	18.9	0.34	10.3	9.39	7.31
Clay soil	0.41	12.0	41.4	51.1	0.62	4.40	27.5	16.2
Peat soil	1.4	17	125	87	1.95	110	99.3	29.9

4 Examples of critical load calculations

Here we illustrate the impacts of differences in various model approaches by calculation examples for Cd, Cu, Pb and Zn for a deciduous forest on four major soil types, being a non-calcareous sandy soil and a loess-, clay and peat soil, using the generic data described. We calculated CLs, stand still loads and target loads including and excluding the plant metal cycle.

Critical loads, stand still loads and target loads for a non calcareous sandy soil

The results (Table 8) show that for all metals, except for Pb and Zn in the organic layer and Pb in the mineral layer, CLs are higher than stand still loads, independent of the soil layer or inclusion of a plant metal cycle. This means that for those cases present concentrations are lower than critical concentrations, which implies that target loads that are to be reached in the defined time span of 100 years, are higher than critical loads. On average, CLs and stand-still loads are higher for the organic layer than for the mineral topsoil. This is due to both the higher present and critical dissolved metal concentrations and the larger water leaching flux calculated for the organic layer compared to the mineral topsoil. For target loads, however, the difference between organic layer and mineral topsoil is much smaller because the higher capacity of the mineral layer to bind metals reduces the differences.

TABLE 8 Critical loads, stand still loads and target loads for Cd, Cu, Pb and Zn excluding and including the plant metal cycle for a non calcareous sandy soil.

Soil layer	Metal	Critical load (mg.m^{-2}.yr^{-1})		Stand still load (mg.m^{-2}.yr^{-1})		Target load (mg.m^{-2}.yr^{-1})	
		Including	Excluding	Including	Excluding	Including	Excluding
Organic layer	Cd	3.0	2.4	1.1	0.90	3.0	2.4
	Cu	51	35	9.2	8.2	51	35
	Pb	26	24	43	38	26	23
	Zn	89.	72	333	248	89	72
Mineral layer of sandy soil	Cd	1.8	1.5	0.48	0.44	1.8	1.5
	Cu	15	12	0.33	2.0	23	18
	Pb	10	9.6	30	28	5.0	5.0
	Zn	52	47	35	34	52	47

The difference between target loads and critical loads is determined by the difference between the critical and present metal pools, which can be derived from the multiplication of the amount of soil ($\rho_s.z_s$ in kg.m^{-2} presented in Table 5) and the present and critical metal concentrations, presented in Table 6 and 7 respectively. Division of that pool by 100 year (the target period) gives the average yearly change in the reactive metal pool due to sorption or desorption (mg.m^{-2}). This flux is however much larger than the difference between the target load and the critical load, because the change in the metal concentration also causes solution concentration changes. When present metal concentrations are lower than critical concentrations the annual average leaching flux of metals in the 100 year period of the target load approach, is lower than the critical metal leaching. The sum of the average adsorption and average leaching rate determines the difference between target load and critical load. For Cd and Zn, differences between target loads and CLs are very small, whereas the effect is much more pronounced for the stronger bound metals Cu and Pb. Differences are larger for the mineral layer because of the higher capacity of the mineral layer compared to the organic layer (on a volumetric basis) to bind metals.

Including or neglecting the plant metal cycle has a clear effect on the calculated critical- stand still- and target loads (Table 8). However in most cases the differences are small (within 10-30%). The results show that including the plant metal cycle for the investigated soils always resulted in higher critical loads and target loads. The effect can, however, be different depending on the parameters for foliar uptake, growth uptake and litter fall and their contribution relative to the critical leaching flux. Opposite effects are shown in case of the stand still loads for copper in the mineral layer. The change in the value of $M_{re,d}$ compared to the value of $[M]_{tot,ss(crit)}$ which depends on the metal and chosen criterion determines whether the calculated load is higher or lower when the plant metal cycle is included.

The calculated stand still load for Pb in the mineral layer while including the plant metal cycle is negative for loess and clay soils (results not shown). A negative load results from the fact that the critical metal leaching flux at 0.1 m depth is lower than the calculated metal flux induced by litter fall corrected for uptake up to 0.1 m depth. Such inconsistencies may be the result of the use of inadequate empirical relationships for metal fluxes in litter fall and foliar uptake at low deposition levels. Since a negative CL is meaningless in policy making, a further evaluation of the inclusion of the plant metal cycle and the uncertainty it brings with it is necessary.

Impacts of soil type on critical loads, stand still loads and target loads

The influence of soil type on the critical loads, stand still loads and target loads for Cd, Pb, Cu and Zn in the mineral layer is illustrated in Table 9 for calculations without the plant metal cycle. The differences in CLs are the combined result of differences in forest growth (yield) determining metal uptake (beware that metal contents in stem wood are assumed to be equal), differences in water flux (Q_{le}), and differences in critical dissolved metal concentrations which are influenced by pH and DOC concentrations (see Eq. 12). Critical loads for Cd and Zn do not differ too much for the different soils, but for Cu and Pb a larger variation is found. This is due to the fact that the total concentration of these metals (including metal bound to DOC) depends much stronger on pH and DOC concentration than the Cd and Zn concentrations. The highest CLs are calculated for peat soils because of their high DOC concentration.

TABLE 9 Critical loads, stand still loads and target loads for Cd, Cu, Pb and Zn for different soil types, excluding the plant metal cycle

Soil type	Critical load ($mg.m^{-2}.yr^{-1}$)				Stand still load ($mg.m^{-2}.yr^{-1}$)				Target load ($mg.m^{-2}.yr^{-1}$)			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Sandy soil	1.5	12	9.6	47	0.44	2.0	28	34	1.5	18	5.0	47
Loess soil	1.0	5.0	5.0	39	0.32	3.5	15	93	1.1	11	-35	38
Clay soil	2.7	14	5.6	53	1.6	26	7.6	150	2.7	8.2	-13	35
Peat soil	1.9	28	20	62	1.3	4.7	25	191	1.9	34	18	62

The variation in stand still loads is larger. Apart from differences in yield and water flux, these loads are determined by the present soil metal concentrations and the organic matter content, clay content and pH, that determine the relationship with the dissolved metal concentration (see Eq. 19 and Eq. 20). The relative differences between the present soil metal concentrations among soil types are slightly higher than differences in stand still loads (Compare Table 6 and 9), due to the differences in soil properties affecting the related dissolved metal concentrations.

The impact of soil type on the target loads is limited. For Cd the target loads are highest for clay soils whereas the reverse is true for Cu and Zn. For Pb the lowest target loads are negative and were calculated for loess soils. The differences between the critical soil metals concentration among soil types are clearly larger than differences between target loads (Compare Table 6 and 9). It are specifically the differences in critical and present metal pools that determine the differences and in the case of peat soils, the much lower bulk density reduces the effect of a much higher critical metal concentration

5 Discussion

The major issue regarding using critical loads is its reliability and its applicability in policy making in terms of a need for reduction of metal emissionsor not.

5.1 Reliability of critical loads, stand still loads and target loads

Parameters influencing the reliability

The reliability of critical loads, stand still loads and target loads mainly depends on the reliability of the various models and parameters determining these loads, as presented in Table 10 for the distinguished metal loads excluding a metal cycle. An expert judgement indication of the variation coefficient (standard deviation divided by the mean) of the various parameters is also given. All loads are influenced by metal uptake (yield and metal content in stem wood) and the water flux leaving the root zone. In the case of CLs, the uncertainty is further influenced by the critical dissolved metal concentration, for stand still loads this is the present metal concentration in soil and the Freundlich adsorption constant, K_f, while target loads are influenced by all these three parameters. As such it is thus likely that target loads are more uncertain than CLs or stand still loads. The uncertainty in stand still loads is likely to be small if applied for a local situation where present metal concentration and soil properties affecting K_f are known, but on the regional scale it is possibly less reliable than the Cl.

Ashmore et al. (50) concluded from uncertainty analysis that the uncertainty in the terms α_{CRIT} and γ_{CRIT} in the critical limit function dominates the uncertainty in critical loads. As mentioned by these authors, this reflects the limited database available for derivation of the critical limit function. Of the other parameters critical loads were most sensitive to variation in the pH and DOC and to a lesser extent to the water flux. Apart from the uncertainty in parameters influencing the critical FMI concentration in soil solution (α_{CRIT}, γ_{CRIT}, pH), the uncertainty in the critical metal leaching flux is also due to the uncertainty in the chemical speciation model calculating total metal concentrations from free metal concentrations and the pH and concentration DOC which are input in the speciation model. For target loads and stand still loads, the uncertainties in coefficients of the transfer function for solid-solution partitioning and uncertainties in soil properties (pH and soil organic content), determine the uncertainty in the derived K_f. The uncertainty in both critical total metal concentrations and K_f is much larger than for the other parameters (see Table 10 and also Ashmore et al. (50)). Both aspects are discussed in more detail below.

TABLE 10 Parameters determining the uncertainty in critical loads, stand still loads and target loads

Parameters influencing loads	Reliability (vr)	Critical load	Stand still load	Target load
Yield, Y	High (+/- 25%)	x	x	x
Metal content in stems, ctM^{st}	High (+/- 25%)	x	x	x
water flux, Q_{le}	High (+/- 25%)	x	x	x
Critical total metal concentration in soil solution, $[M]_{tot,ss}$ (crit)[1]	Low (+/- 100%)	x		x
Present metal concentration in soil, $ctM_{tot,\ pres}$	High (+/- 25%)		x	x
Freundlich adsorption constant, K_f[2]	Low (+/- 100%)		x	x

[1] T he uncertainty in this value is determined by the uncertainty in α_{CRIT} and γ_{CRIT} in the critical limit function and in the speciation model and pH and DOC determining the relation between the critical free metal ion concentration and total dissolved metal concentration.

[2] The uncertainty in this value is determined by the uncertainty in regression parameters and in organic matter content and pH (Eq. 20). Furthermore, the uncertainty in regression parameters and in clay content in view of the relation between reactive and total metal concentration is relevant (Eq. 19).

Speciation modeling in soil solution

The uncertainty of the calculation of total metal concentrations from free metal concentrations with a chemical speciation model, such as W6-MTC, is due to uncertainties in the model approach, the model inputs (DOC, Al en Fe concentrations in solution) and the parameterization of the model. To get an idea of the adequacy of this approach, we calculated total metal concentrations from FMI activities, similar to the approach in the CL calculations, for datasets in which both total and FMI concentrations in solution were measured (*51-53*). The input data to W6-MTC are the FMI activity, the organic matter content, the pH and DOC. Because DOC is usually not available for CL mapping we also made calculations in which DOC was set to standard values according to the mapping manual (*25*) i.e. 35 $mg.L^{-1}$ for organic horizons of forest soils, 20 $mg.L^{-1}$ for the forest mineral top soil, 15 $mg.L^{-1}$ for grassland soils and 10 $mg.L^{-1}$ for arable soils. Figure 3 shows that the model gives reasonable predictions for the total concentrations in solution, The Mean Absolute Error of the log concentration (MAE see Table 11) varies between 0.11 for Zn and 0.45 for Pb when using the measured DOC concentrations. This means that the concentrations on a linear scale vary with a factor 1.3-2.8. The error is largest for the strong complexing metals Cu and Pb for which calculations are also most sensitive to variation in estimated DOC concentrations (compare DOC measured and DOC default in Table 11). The error in the calculated total concentration is most likely due to natural variation in the affinity of DOC to bind metals. The fact that the critical leaching flux is the largest contribution to the CL (51%-97%, average 85%) in combination with the relative large error in both the critical limit function and the calculation of a critical total concentration from the critical limit implies that the calculation of the critical limit in terms of a total concentration is the most uncertain aspect in the critical load calculation.

TABLE 11 Mean Absolute Errors of dissolved total metal concentrations (mg.m^{-3}) calculated with W6-MTC compared to measured concentrations using measured and default values for DOC

Metal	Mean Absolute Error (log concentration)	
	DOC measured	DOC default
Cd	0.32	0.38
Cu	0.40	0.57
Pb	0.45	0.55
Zn	0.11	0.13

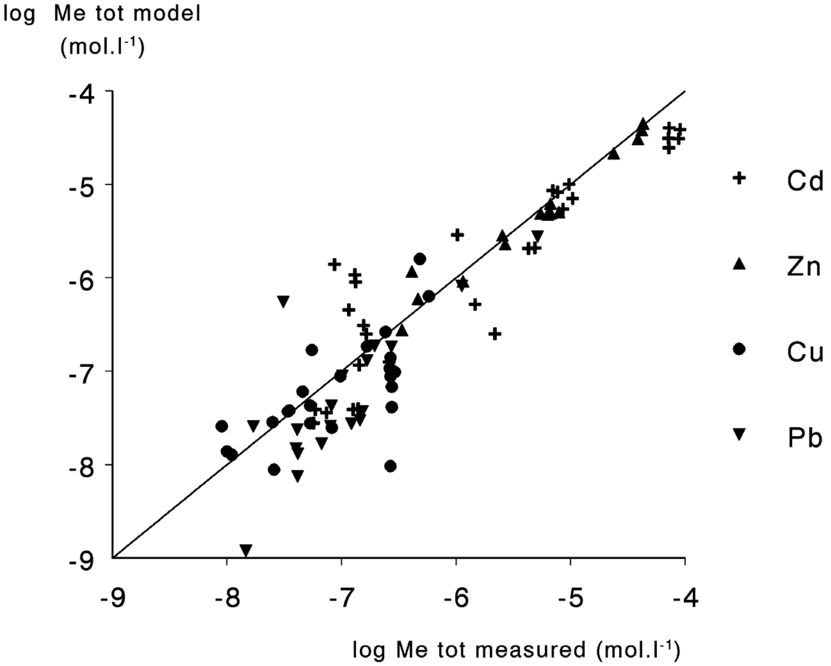

FIGURE 3 Comparison of total solution concentrations calculated from FMI activities using W6-MTC with measured concentrations in soil solution extracts

Partition relationships between soil and soil solution

Unlike CLs, stand still loads and target loads, are strongly influenced by the transfer functions for solid solution partitioning of metals. Earlier sensitivity and uncertainty analysis show that uncertainties in the parameterization of such transfer functions are highly important (*23, 50*). We choose to use partition relations in terms of FMI activities instead of partition relations that relate total metal concentrations in solution to solid phase concentrations because equilibrium is expected between the activity of metals in soil and soil solution and not between total concentrations. Groenenberg et al. (*54*) showed that activity relations had a higher explained variance than total soil solution concentration relations. However in the calculation of a stand still load, the calculation of the total metal concentration in solution with activity relations requires an additional step i.e. the calculation of total concentrations from FMI concentrations with a chemical speciation program (e.g. WHAM). To get an indication of the adequacy of the combined use of all relationships used in modelling metal speciation in and between soil and soil solution (see Figure 2: reactions 1-3), we compared results for calculated total dissolved metal concentrations, based on present total soil metal concentrations, with results of the measured metal concentrations in soil solution obtained in the field situation. We used independent data, i.e. data not used to derive the relationships, from 56 soil samples of 5 land-use types (acid grassland, heathland, upland and lowland coniferous forest and deciduous woodland) collected from 'background' sites in the UK (*50*).

Results (see Table 12) show that the ranges (5-95% percentile) of calculated total metal concentrations correspond well with measured ranges for all Cd and Cu. Median values were however overestimated by a factor 4-5 for Pb and Zn. The MAE of the log concentration is mostly between 0.3 and 0.5 (a factor 2-4 on a linear scale) which is within the error ranges calculated for the transfer function which relates metal activities in solution to the reactive soil metal concentration (*19*). This implies that the extra steps in this calculation do not lead to an increase in the error.

TABLE 12 Calculated and measured dissolved total metal concentrations in the mineral topsoil of 56 soil samples in 5 land-use types in the UK Values are medians with the range between the 5% and 95% percentile between brackets.

Metal	Dissolved total metal concentration (mg.m^{-3})	
	Calculated	Measured
Cd	0.6 (0.1-4.3)	0.6 (0.07-5.7)
Cu	5.5 (0.9-71)	8.2 (2.5-28)
Pb	53.1 (6.7-599)	12.0 (1.2-125)
Zn	216 (33.2-723)	44 (12-195)

In the assessment of a target load, we used a K_d value in the range between the present and critical concentration instead of using a non linear K_f function to allow a direct solution. By use of numerical modeling we evaluated the effect of this linearization of the K_f value and this appeared to be insignificant.

5.2 The applicability of the critical load concept in view of uncertainties in and differences between present and critical metal loads

The present CLRTAP protocol on metal emission abatement under the UN/ECE is based on flat rate reductions using best available abatement techniques, ignoring differences in susceptibility of receptors. The calls that have been made by the Co-ordination Centre for Effects of the UN-ECE ICP Mapping for the calculation of CLs for Cd, Pb and Hg makes the question urgent whether this approach is already suitable for policy application. If the uncertainty is such that results can be completely inside or outside the present range of metal deposition, it is not worthwhile to include the CLs concept in the present protocol. Recently, the CL method excluding metal cycling was applied on a European scale by Slootweg et al. (*27*). In this approach, results of the W6-MTC model were used to convert critical FMI concentrations to critical total dissolved metal concentrations. Comparison of the CLs and the estimated atmospheric loads on terrestrial ecosystems in 2000 showed a high risk for Hg (51% of the area being exceeded), a considerable risk for Pb (29% of the area being exceeded) and no risk for Cd (practically no exceedance).

The above mentioned results are in line with those obtained for Cd and Pb in this study, focusing on the Netherlands. The average range in present loads on forests, as compared to the range in CLs based on the averages for the different soil types in the above given examples, is presented in Table 13. The present loads refer to the year 2000 and are based on model calculations (*55*), while correcting for forest filtering (see *23*). The results show that the present loads in this country lie below the range of the CLs except for Pb. The fact that Cu and Zn, which are both much less toxic than Cd and Pb, do not lead to toxicity problems is to be expected for non-agricultural ecosystems. It might even be so that in forests Cu and Zn deficiency in view of tree growth (not considered in these calculations) might even be more relevant than Cu and Zn toxicity (*56, 57*). However, in heavily manured agricultural systems, such as in the Netherlands, the large input of Cu and Zn by animal manure can cause both Cu and Zn toxicity problems in the long run as predicted in various studies (*58, 59*). A CL approach for terrestrial ecosystems thus seems useful for Cd and Pb, whereas the concept seems also of relevance for Cu and Zn in agricultural systems. By including uncertainty analyses, the possible exceedance of a CL can be evaluated in a probabilistic manner rather than as a deterministic value, which might provide a stronger basis for future policy evaluation, considering the uncertainty in the calculations.

TABLE 13 A comparison of the range in critical loads in the example calculations and in present loads on Dutch forests

Type of load	Load (mg.m^{-2}.yr^{-1})			
	Cd	Cu	Pb	Zn
Present load	0.08-0.42	0.8-4.0	0.2-7.4	5.8-32
Critical load	1.0-2.7	5.0-35	5.3-20	39-62

6 Conclusions

The following conclusions can be drawn regarding the impacts of different approaches on the resulting critical- stand still- and target loads, focusing on the calculation examples for the Netherlands:

In the calculation examples, the stand still loads are generally lower than the CLs, which in turn are lower than the target loads for Cd, Cu, Pb and Zn, independent of the soil layer or use of a plant metal cycle. Considering these examples as representative for the Netherlands, it implies that present soil metal concentrations are generally lower than critical soil metal concentrations.

- Both CLs and stand still loads are higher for the organic layer and for peat soils than for the mineral soil. Both CLs and stand still loads are generally higher for clay soils than for sand and loess soils.
- In general including or neglecting the plant metal cycle leads to small differences in CLs and target loads (within 10-30%). The inclusion of the plant metal cycle may sometimes lead to negative CLs or stand still loads. This makes the method less robust and inclusion of a plant metal cycle in the calculation of the CL is therefore not recommended.
- A comparison of present loads and CLs for forest soils indicates a possible exceedance for Pb but not for Cd, Cu and Zn.
- Uncertainties in critical loads are mainly determined by the critical total dissolved metal concentration. This in turn is influenced by the uncertainty in the critical limit function for free metal ions and the chemical speciation model used to calculate the related total dissolved metal concentration. The uncertainty in target loads is largely influenced by the uncertainty in the transfer function relating metals in the soil to those in soil solution and in soil properties affecting this relation (specifically pH, and soil organic matter content).

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Appendix on Derivation of target load

The mass balance for a homogeneous soil layer is given by (see also Eq.1):

$$M_{td} = -M_{lf} + M_{fu} + M_{ru} + M_{le} + \rho_s z_s \frac{d}{dt} ctM_{re} + \theta z_s \frac{d}{dt}\left[M\right]_{tot,ss} \quad \text{(A1)}$$

By defining:

$$\mathrm{M_{in}} = \mathrm{M_{td}} + \mathrm{M_{lf}} - \mathrm{M_{fu}} \quad \text{(A2)}$$

And inserting root uptake according to Eq. (4) and leaching according to Eq. (6) and assuming a linear solid solution partition relation according to:

$$ctM_{re} = k_d \cdot [M]_{tot,ss} \quad \text{(A3)}$$

and defining:

$$A = \frac{M_{in}}{\rho_s z_s k_d + \theta z_s} \quad \text{(A4)}$$

$$b = \frac{Q_{le}}{\rho_s z_s k_d + \theta z_s} \quad \text{(A5)}$$

equation (A1) can be written as an ordinary differential equation:

$$\frac{d[M]_{tot,ss}}{dt} + b \cdot [M]_{tot,ss} = A \quad \text{(A6)}$$

Solving Eq. A6 and setting the initial concentration $[M]_{tot}$ (t=0) at $[M]_{tot,init}$ gives:

$$[M]_{tot,ss}(t) = \left([M]_{re}(init) - \frac{A}{b} \right) \cdot e^{-bt} + \frac{A}{b} \quad \text{(A7)}$$

Setting the total concentration after the considered time period to $[M]_{tot,crit}$,including A/b as M_{in}/Q_{le} (see Eq. A4 and A5) and rearranging Eq. A7 gives:

$$M_{in} = \frac{Q_{le}}{1 - e^{-b \cdot t}} \left([M]_{tot,ss}(crit) - [M]_{tot,ss}(init) \cdot e^{-b \cdot t} \right) \quad \text{(A8)}$$

Combination with Eq. 11 gives:

$$M_{td}(t\arg et) = \frac{\left[M_{re} + \frac{Q_{le}}{1-e^{-b\cdot t}}\left([M]_{tot,ss}(crit) - [M]_{tot,ss}(init)\cdot e^{-b\cdot t}\right)\right]}{fr_{re}}$$

(A9)

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CHAPTER 7

A regional dynamic modeling approach to calculate Cadmium, Copper and Zinc accumulation in soils and runoff to surface waters

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ABSTRACT

Cadmium, copper and zinc inputs to agricultural land in excess of crop uptake lead to accumulation in soil and runoff to surface waters. We used a regional scale dynamic model to evaluate long-term effects of measures reducing metal inputs by manure and fertilizers on metal concentrations in soils and surface waters in the Netherlands. Present inputs will increase soil concentrations by 23-133% and runoff to surface waters by 25-340% after 100 years. Soil concentrations of Cd, Cu and Zn and concentrations of Cd in runoff will not exceed ecological thresholds. The area where concentrations in runoff exceed surface water criteria, however, increases to 20% for Cu and 54% for Zn. A substantial reduction of Cu and Zn in animal food with a total ban on discharge of Cu containing hoof disinfectants is required to stop soil accumulation and achieve stand-still of metal concentrations in runoff to surface waters.

1 Introduction

Sustainable use of land and water is an important issue within the policy goals of national governments and supra national organizations like the FAO and EU (*1*). Current input levels of Cd, Cu and Zn in manure from animal husbandry pose a threat to such a sustainable use. In the Netherlands approximately 80% of the total Cu and Zn inputs to arable soils is due to animal manure application (*2*). For Cd, P fertilizers are an important source for agricultural land, contributing about 30% to the total input. Several studies have shown that present inputs lead to net positive balances and consequent accumulation of heavy metals in agricultural systems in Europe and North America (*3-6*). Accumulation of metals in the topsoil may lead to increased metal concentrations in food crops (*7*), decrease of ecosystems functions, such as mineralization and nitrification, and a loss of microbial biodiversity (*8*). Aside from the impact on crop quality and soil ecosystems, metal losses towards groundwater and surface waters will increase. Rozemeijer and Broers (*9*) showed that inflow of metals from groundwater contributes substantially to Cu and Zn in surface water leading to exceedances of surface water criteria in a region of the Netherlands with intensive animal husbandry. Present concentrations of Cu and Zn already exceed national ecological threshold levels in surface water throughout the Netherlands (*10*). Metal runoff from agricultural land to surface waters was estimated to contribute between 20% and 40%, depending on the metal, to the total metal load of surface waters in the Netherlands (*11*). On a local scale, in areas without emission from industrial activities or waste water treatment plants, however, the contribution of runoff can even be close to 100%.

Regionally applicable dynamic mass balance models can be a great help to identify problem areas which are at risk considering metal accumulation and runoff and to evaluate measures that reduce metal inputs. Models developed so far are confined mostly to the top layer of the soil (*6, 12-14*) and are therefore unsuitable to assess metal runoff from soils to surface waters. In this study we combined a dynamic mass balance approach, which takes into account both sources and sinks of metals (*12, 13*), with a multilayer transport model which includes both vertical migration of metals to underlying soil layers and lateral transport to surface waters (*11*).

This model was used to evaluate the effects of various scenarios, with measures that reduce metal inputs to Dutch agricultural systems, on soil and water quality for a period of 100 years (2000-2100). We evaluated the effects on metal loads to soils, net soil metal balances, soil metal concentrations and runoff to surface waters. Furthermore, calculated metal concentrations in soil and runoff were compared with critical values for agricultural and ecological functioning to assess the effectiveness of measures to avoid unwanted metal levels in both soil and water. The plausibility of the model was assessed by comparing: (i) the calculated metal inputs with national statistics, (ii) calculated pore water concentrations with measurements and (iii) predicted trends of metal accumulation with measured accumulation rates in field studies.

2 Model approach, input data and scenarios

Figure 1 gives a schematic overview of the model approach which will be described in separate sections below.

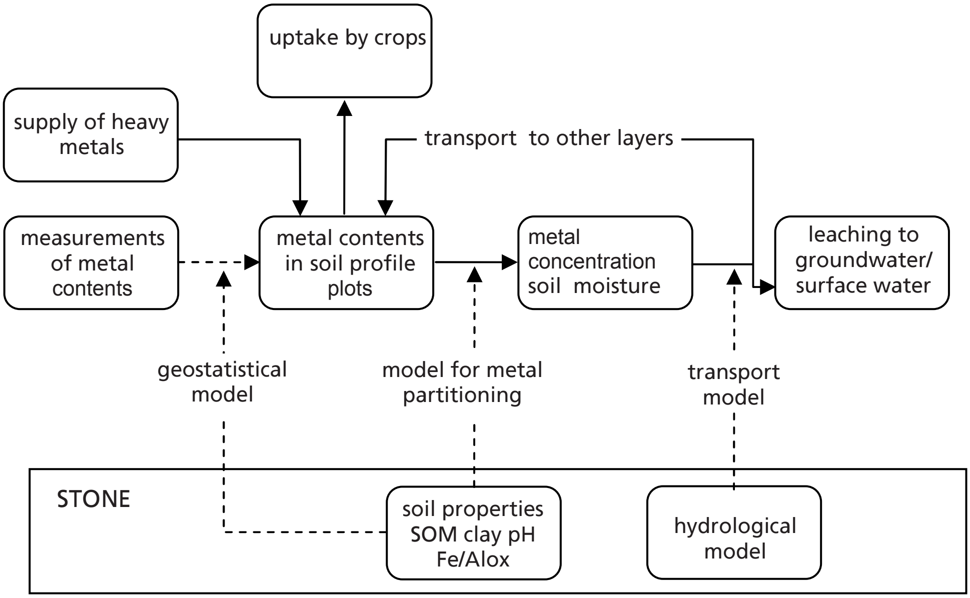

FIGURE 1 Schematic presentation of the model for dynamic calculations of soil metal concentrations and leaching to ground- and surface waters

2.1 Spatial schematization, soil properties and soil metal concentrations

Starting point of the simulations is a spatial schematization, to allow spatially explicit calculations of changes in soil metal concentration and metal runoff fluxes in time. The Netherlands was divided into 6405 unique spatial units to account for regional variations in soil properties, land use, hydrological characteristics, meteorology (*15*) and present soil metal concentrations (*11*). The units vary in size between 1 ha and more than 20000 ha in case of very homogenous areas. Vertically the soil is divided into soil layers until 13 m depth, with varying thickness from 5 cm in the top soil up to a few meters for the deepest soil layers (*15*). Soil properties of the units were based on the Dutch soil information system. For each unit, the soil organic matter (SOM) content, clay content, oxalate extractable Al and Fe content, and pH-KCl were attributed to diagnostic soil horizons to a depth of 13 m below the surface level (*16*).

Initial Cu, Zn and Cd concentrations in the top soil (0-30 cm for arable soils and 0-10 cm for grasslands and natural areas) of each unit were calculated based on the soil organic matter content, clay content and pH, followed by a kriging procedure to adjust the initial estimates using measurements of 4000 data points from a large national database, as described in detail by Bonten et al. (*11*). In contrast to the topsoil, few data were available to describe the vertical metal profile with depth. Here we assumed that the metal levels decrease with soil depth till levels equal to the natural background level. The natural metal background level for each unit was calculated using regression relations that relate the metal concentration to the clay content based on data from 308 subsoil samples with no known pollution history from the Netherlands (*17*)

$$\mathrm{Me}_{\mathrm{soil,bg}} = \alpha_0 + \alpha_1 * \mathrm{clay} \qquad (1)$$

with $\mathrm{Me}_{\mathrm{soil,bg}}$ = total metal background concentration ($\mathrm{mg.kg^{-1}}$) and clay = clay content (%). Values of the coefficients are listed in Table S-1 of the supporting information. The metal profile between the topsoil and the subsoil was derived with a regression function using data from 260 soil profiles, which relates the metal concentration at a certain depth to the metal concentration in the top soil and soil properties (SOM, clay content and pH) for the corresponding depth, according to :

$$\begin{aligned} \log \mathrm{Me(z)}_{\mathrm{soil,tot}} &= \beta_0 + \beta_1 \log(z) + \beta_2 \log Me(z=0)_{soil,tot} + \\ &\beta_3 \log(SOM(z)) + \beta_4 \log(clay(z)) + \beta_5 \cdot pH_{KCl}(z) \end{aligned} \qquad (2)$$

with: $\mathrm{Me(z)}_{\mathrm{soil,tot}}$= total metal concentration in soil ($\mathrm{mg.kg^{-1}}$) at depth z; z = depth (m), SOM = soil organic matter content (%) and $\mathrm{pH_{KCl}}$ = pH-KCl in the soil (-). Together with a minimum value equal to the local background level in case Equation 2 predicts lower levels. Values of the coefficients are listed in Table S-2 of the supporting information.

2.2 Metal inputs

Metal inputs included in the model are atmospheric deposition and application rates of manure, compost and inorganic fertilizers. Atmospheric deposition was based on model predictions for a nationwide 5 x 5 km grid in the year 2000 (*18*).

The production and distribution of animal manure was based on a national geographic database (GIAB) which contains amongst others the locations and type of farms in the Netherlands, numbers and types of animals, farm size, type of crops. The production of animal manure and the corresponding excretion of N, P and metals was calculated on the basis of the numbers of animals for 65 animal categories and the manure production and composition for each distinguished animal category (*19*). The manure distribution was based on the allowed application of N and P per municipality according to the local land use. The application of other organic substances (compost, sewage sludge etc.) was based on national numbers published by the Central Bureau for Statistics (CBS) for 2004 which was divided equally over the entire agricultural area. Metal concentrations in manures and fertilizers considered are listed in Table 1.

TABLE 1 Metal contents in manure (mg metal/kg dry matter) (20) and metal contents in fertilizers (mg metal/ kg P or N) used in the simulations.

manure/fertilizer type	Cd	Cu	Zn
		$mg.kg^{-1}$ dry matter	
cattle manure (slurry)	0.27	182	248
pig manure (slurry)	0.39	444	990
poultry manure	0.22	86	297
		$mg.kg^{-1}$ N or P	
N-fertilizer[1]	0.36	8.4	25
P-fertilizer[2]	105.2	178.4	2242

[1] pers comm. W. De Vries

[2] pers. Comm. EMFA (European Fertilizer Management Association)

2.3 Metal uptake

The net removal of metals by agricultural crops was calculated according to:

$$F_{Me,upt} = Y \cdot \frac{Me_{plant}}{1000} \quad (3)$$

with $F_{Me,upt}$ = net metal removal by harvesting ($g.ha^{-1}.a^{-1}$); Y = the yield (kg dry matter.$ha^{-1}.yr^{-1}$) and Me_{plant} = metal concentration of the crop ($mg.kg^{-1}$ dry matter).

Contens of Cd and Zn in crops were calculated with soil-plant-relations, accounting for the impact of soil properties like pH, SOM and clay, according to (*21*):

$$\log(Me_{plant}) = a_0 + a_1 \cdot \log(SOM) + a_2 \cdot \log(clay) + a_3 \cdot pH_{KCl} + a_4 \cdot \log(Me_{soil,tot}) \tag{4}$$

with Me_{plant} = metal content of harvestable crop parts (mg.kg^{-1} d.m.). Coefficients for the distinguished crops (grass, maize, potatoes, sugar beet, other crops, wheat and other cereals) can be found in Table S-3 of the supporting information. For Cu and for the category other crops, for which no good relations ($R^2 < 0.4$) were available, the median value of measured metal contents was used (see Table S-4 supporting information).

Yields were based on a data compilation of optimal yields of harvestable parts of the distinguished crops for the three main soil types i.e. sand, clay and peat, subdivided over three hydrological classes i.e. dry, moist and wet according to the average highest groundwater table (see Table S-5 supporting information). The calculated metal uptake (mg.kg^{-1}.ha^{-1}.a^{-1}) was subtracted from the total soil metal pool in the root zone (0-10 cm for grasslands, 0-30 cm for maize and arable crops).

2.4 Metal partitioning between the soil solid phase and soil solution

Metal partitioning between the soil and soil solution was modeled using empirical relations which relate metal partitioning to soil properties based on the Freundlich-van Bemmelen equation (*22*):

$$Me_{react} = K_F \cdot [Me]_{ss}^{n} \tag{5}$$

with: Me_{react} = reactive metal concentration in the soil, $[Me]_{ss}$ = total metal concentration in soil solution (mg.L^{-1}); K_F = Freundlich constant (mg^{1-n}.L^{n}.kg^{-1}) and n = Freundlich exponent (-). To account for differences between soils, K_f can be related to soil properties according to (*23, 24*) :

$$\log K_F = \alpha_0 + \sum \alpha_i \log(X_i) \tag{6}$$

where X_i represent soil properties like organic matter, clay and Al/Fe-(hydr)oxide contents. However, this can lead to erroneous estimates of K_F in case of low levels of either SOM, clay or oxides. To overcome this limitation we used a function where the impact of soil properties on metal sorption was calculated in an additive way rather than a multiplicative way:

$$\log K_F = \log(\alpha_1 \cdot SOM + \alpha_2 \cdot clay + \alpha_3 \cdot AlFe_{ox}) + \alpha_4 \cdot pH_{ss} + \alpha_5 \cdot \log(DOC) \qquad (7)$$

with $AlFe_{ox}$ = the sum of the oxalate extractable Al and Fe content of the soil (mmol.kg^{-1}); pH_{ss} = *p*H of the soil solution(-) and *DOC* = dissolved organic carbon concentration (mg C.L^{-1}). Combination of equation 5 and 7 yields:

$$\log Me_{react} - n \cdot \log[Me]_{ss} = \log(\alpha_1 \cdot SOM + \alpha_2 \cdot clay + \alpha_3 \cdot AlFe_{ox}) + \alpha_4 \cdot pH_{ss} + \alpha_5 \cdot \log(DOC) \qquad (8)$$

Coefficients in Equation 8 were derived using solid solution partitioning data from Dutch data sets described in Groenenberg et al. (*24*). Parameters α_1 to α_5 together with the Freundlich coefficient n, (see Table 2) were optimized by minimizing the sum of the squared differences between left and right hand side of Equation 8.

TABLE 2 Coefficients used in the transfer functions for solid solution partitioning of metals (Equation 8)

Metal	b_0 (SOM)^a	b_1 (clay)	b_2 (Ct_{AlFeox})^b	b_3 (pH)	b_4 (DOC)^c	n	R^2	RMSE
Cd	0.0801	0.00314	0.00381	0.235	-0.151	0.445	0.85	0.54
Cu	7.98	0.720	0.325	0.111	-0.389	0.545	0.66	0.60
Zn	0.100	0.0239	0.00540	0.385	-0.163	0.752	0.84	0.43

^{a} soil organic matter content (SOM) and clay content (%)

^{b} oxalate extractable aluminum and iron (mmol.kg^{-1})

^{c} dissolved organic carbon concentration (mg.L^{-1})

In Equations 5 and 8, the reactive rather than the total metal concentration is used. This reactive metal concentration is the total amount of metal that is available for exchange with the soil solution (*24, 25*). Reactive metal concentrations were calculated from total metal concentrations according to (*26*):

$$\log Me_{soil,re} = c_0 + c_1 \cdot \log(SOM) + c_2 \cdot \log(clay) + c_3 \cdot \log Me_{soil,tot} \qquad (9)$$

Coefficients for Equation 9 are listed in Table S-6 of the supporting information. Concentrations of DOC were estimated using a regression equation derived from DOC measurements in pore water extracted using ceramic suction cups, pH and SOM (*17*):

$$\log(DOC) = 2.48 + 0.365 \cdot \log(SOM) - 0.203 \cdot pH_{ss} \qquad R^2=0.82, \qquad (10)$$

The pH of the soil solution, which is required in Equations 8 and 10 to calculate the solution concentrations of metals and DOC, was estimated from the pH-KCl according to (*27*):

$$pH_{solution} = 0.82 \cdot pH_{KCl} + 1.79 \qquad R^2=0.83 \qquad (11)$$

2.5 Metal transport

Metal inputs were distributed homogeneously over the top soil to account for processes such as manure injection, ploughing and bio-turbation, which were shown to result in a homogeneous distribution of contaminants within the top soil (*28*). Metal inputs were added to the geochemical reactive pool of the soil solid phase. Transport of soil water and resulting metal fluxes were calculated for a soil column down to 13 m below the surface level, taking into account lateral transport to surface waters. To enable metal transport calculations, average water fluxes including seepage, lateral drainage, evaporation, and transpiration were calculated using the hydrological model SWAP (*29*) for each of the 6405 plots from the STONE model for the period 1971-2003 (*15*). From these average water fluxes the metal fluxes and the metal concentrations were calculated for each time-step (36 per year), using a semi-analytical solution for the conservation and transport equation (*30*). Each time step after the transport calculations new equilibrium concentrations were calculated using Equation 8. Metal loads discharged to surface waters were calculated by summation of the product of the calculated solution concentration with the lateral drainage flow for each layer. Metal concentrations in run-off were subsequently calculated by dividing metal loads to surface waters by the lateral water flow.

2.6 Critical limits

The predicted concentrations in soil and surface waters were compared with critical concentrations (threshold levels) to protect agricultural functions for soils and ecological functions for soils and surface water. Critical limits to protect agricultural functions (Table 3) were based on the Dutch advisory limits for agricultural soils "LAC-2006" (*21*) which aim to protect (human) food quality, animal health and agricultural production. The methodology to derive these limits is described in de Vries et al. (*31*). Critical soil limits to protect ecological functioning were set to the Predicted No Effect Concentration (PNEC) as developed under the EU risk assessment process (*32*). These standards are based on the 5 percentile of the species sensitivity distribution (HC_5) of No Observed Effect Concentrations (NOEC) from both laboratory and field derived NOEC data. The bio-availability is accounted for by normalization according to the effective cation exchange capacity (eCEC), i.e. the CEC at the actual pH of the soil. Here we calculated PNEC values for each spatial unit from the eCEC as calculated from the pH, soil organic matter content and clay content (*33*) using the PNEC calculator (*32*). PNEC values for representative agricultural sand, peat and clay soils are given in Table 3. For surface waters, maximum tolerable risk (MTR) values (Table 4), based on NOEC data for impacts on aquatic organisms were based on recent European Risk Assessment (EU-RAR) reports for Cd, Cu and Zn by the European Chemicals Bureau (*34*), the European Copper Institute (*35*) and RIVM (*36*) respectively.

TABLE 3 Critical concentrations in soil (mg.kg^{-1}) to protect agricultural functions (LAC-2006) (*21*) and ecological functions (PNEC) (*32*) and estimated background concentrations (using Equation 1) for a generic agricultural sand, clay and peat soil

	Limit	Sand	Peat	Clay
SOM (%)[1]		3	30	3
Clay (%)[1]		3	15	25
pH[1]		5.5	6.0	6.5
metal				
Cd	LAC grass	1	3	2
	LAC maize	1	3	2
	LAC arable crops	1	3	2
	PNEC	1	1	1
	background	0.06	0.1	0.12
Cu	LAC grass[2]	30/50	30/80	30/80
	LAC maize	50	80	80
	LAC arable crops	50	200	160
	PNEC	40	218	103
	background	2.7	6.8	10.2
Zn	LAC grass	150	720	660
	LAC maize	150	720	660
	LAC arable crops	150	350	350
	PNEC	53	148	186
	background	10.3	32.7	51.3

1 These soil properties were used in the calculation of the PNECs, LACs and background concentrations

[2] The first value applies to sheep, the second to other cattle

TABLE 4 Critical limits for surface water

Metal	Critical limit surface water (µg.l^{-1}) EU RAR
Cd	0.19
Cu	7.8
Zn	8.8[1]

[1] The EU-RAR value for Zn is based on a PNEC-added of 7.8 µL^{-1} ((*37*)) and a background correction of 1.0 µgL^{-1}

2.7 Scenario studies

We defined five scenarios for the period 2000-2100 to evaluate emission reduction measurements on their effects on metal concentrations in soils and runoff:

1. Business As Usual (BAU), with continued metal inputs according to the load of the year 2000

2. Manure Legislation (ML), with reduced manure and fertilizer addition based on reductions in maximum N and P addition according to Dutch manure legislation for the year 2015 and the assumption that elemental composition of manure will be constant.
3. Manure legislation in combination with a 50% reduction of animal intake of Cu and Zn (ML+) and a reduction of the Cd content in P fertilizers to 20 mg.kg^{-1} P_2O_5 , being the proposed lower limit by the working group fertilizers (DG Enterprise of the European Commission March 2006). The 50% reduction of Cu and Zn was arbitrarily chosen to evaluate the potential effect of such measures. It is however, not based on data of Cu and Zn requirements for animal health or production. Because more than 90% of metal intake via food is excreted by the animals (*38*), we assumed an equivalent reduction of the metal content in manure.
4. Manure legislation in combination with a reduction of Cu in food additives and a total ban on the current practice of discharging Cu containing hoof disinfectants to manure (ML+-hd). The average reduction of Cu contents in cattle manure was estimated to be 61 mg.kg^{-1}on the basis of a survey among farmers on the use of hoof disinfectants amongst a small group of farmers (*39*). This scenario only affects Cu inputs.

2.8 Model evaluation

Results of model studies as those presented here always include a certain extent of uncertainty. Uncertainty in predictions may be the result of (i) uncertainty due to conceptual model errors and (ii) uncertainty in the input and model parameters.

A potential conceptual error is the assumption that all metal inputs are 100% geochemically reactive and that there is no exchange between the inert and geochemical reactive metal pool. The possible influence of metal immobilization by slow kinetic sorption to Al- and Fe-(hydr)oxides and clays (aging) on predicted runoff to surface waters was evaluated by assuming a re-distribution of total metal over the reactive and inert metal pool at the end of each year. This re-distribution was calculated with the regression relation (Equation 11) which was also used to calculate the initial concentration of reactive metal from the total metal concentration in soil. We used this approach rather than the recently developed aging model of Buekers et al. (*40*) which demands a more mechanistic modeling approach of the soil chemistry.

The impacts of models inputs and model parameters on the plausibility of the model results were assessed by comparing (i) calculated metal inputs with national statistics, (ii) calculated concentrations in pore water in major soil classes with measurements and (iii) metal accumulation with measured accumulation rates in field studies, as summarized below.

Important sources of input uncertainties are the inputs of metals to soil, the spatial variation of metal concentrations and soil properties, uncertainties in metal contents in crops and uncertainties in the solid solution partitioning of metals (*41*). To assess the quality of input data we compared predicted inputs from our study with independent estimates. Such independent data were, however, not available for metal uptake. Metal uptake is in our study based on regression relations or average crop contents derived from measured metal contents in crops and soils in the Netherlands. Although these relations may lead to substantial uncertainty at the plot level due to uncertainties in soil concentrations (*42*), uncertainties are most likely averaged out at the regional level.

Solid solution partitioning of metals was found to be an important source of uncertainty in predicted metal accumulation (*41*) Furthermore the calculated runoff to surface waters depends strongly on the predicted solid solution partitioning. The performance of the partition-model was assessed by comparing predicted solution concentrations with measurements for specific locations. Furthermore we tested the whole chain in our model approach to predict solution concentrations by comparing model predictions with regional groundwater quality data. Solution concentrations were calculated for 5 soil profiles (3 sandy soils, 1 peat soil and 1 clay soil) based on measured: total metal concentrations in soil, organic matter content, clay content, oxalate extractable Al and Fe and the pH and DOC concentration in pore water. Pore water was extracted with suction cups during 1.5 years at 5 depths between 20-150 cm below the soil surface. To calculate solution concentrations we first calculated the reactive soil metal concentration from the total concentration using Equation 9. Thereafter solution concentrations were calculated using the measured pH and DOC for each sampling using Equation 8. Finally we compared the (time) averaged predictions of solution concentrations with averaged measurements.

To compare model predictions with regional groundwater data we calculated metal concentrations in solution of the lowermost soil layer of STONE. Calculations include the prediction of: the vertical distribution of metal concentrations (Equation 2), the reactive metal concentration from the total concentration (Equation 9), the concentration DOC (Equation 10) and finally the prediction of metal partitioning using Equation 8. Predicted concentrations were then clustered and compared with measured concentrations in groundwater in the Netherlands as clustered to 27 hydrological units (*43, 44*). These studies were aimed to give the natural background level of metal groundwater concentrations. All samples with a possible anthropogenic influence were dismissed.

Quantification of the overall model performance requires comparison of model predictions with long term monitoring data. Monitoring data with sufficient information on metal inputs, soil data and time series of metal concentrations in soil, soil water and runoff water for a quantitative model evaluation were however not available. To test the plausibility of our model results we compared calculated soil accumulation with results from long term field studies.

3 Results and discussion

3.1 Scenario analyses

Impact of measures on metal fluxes and changes in soil metal concentrations

Figure 2 shows the contribution of different sources to the total input for each scenario. The items contributing to the metal balance of the top soil (0-10 cm for grass, 0-30 cm for maize and arable land) are summarized in Table 5 for the year 2050, i.e. the mid-term value for the simulation period. Metal pool changes (positive in case of accumulation and negative in case of release) were calculated as the sum of inputs (manure, fertilizer, organic amendments and deposition) minus crop uptake and leaching from the topsoil. Soil pool changes were classified as substantial positive or negative when they were greater than 10% or less than -10% of the total inputs respectively (see Table S-7 of the supporting information). Figure 3 gives a geographical picture of top soil metal concentrations in the year 2000 and the changes thereof for the BAU scenario in the year 2100. Median changes in soil metal concentrations for all scenarios are summarized in Table 6. The metal balances and changes in soil metal concentrations are discussed per element below.

Cadmium. Almost half of Cd in present inputs (BAU) is from P-fertilizers (Figure 2). Other important sources are atmospheric deposition and animal manure. The strongest decrease in cadmium inputs is achieved with the foreseen reduction of manure and fertilizer inputs according to the manure legislation (ML scenario). The additional reduction in Cd inputs by reducing the maximum Cd content in P fertilizers (ML+ scenario) is small (4%). This because present Cd contents in P-fertilizers (23 mg.kg^{-1} P_2O_5) in the Netherlands are already close to the desired level of 20 mg.kg^{-1} . Most of the incoming Cd is either retained in the top soil or taken up by crops. Therefore only a small part (12%) of total Cd inputs leach from the topsoil to deeper soil layers and surface water.

With the BAU scenario, Cd accumulates substantially (balance>+10% of inputs) in 85% of the total area. Cd always accumulates in clay soils, whereas significant parts of peat soils and sandy soils have a negative accumulation (release) for maize and arable crops. The increase in Cd soil concentration is, however, rather small (Figure 3, Table 6). Reduction of manure and fertilizer inputs reduces Cd accumulation substantially. In a relative sense, reductions are largest in sandy soils (Table 5).

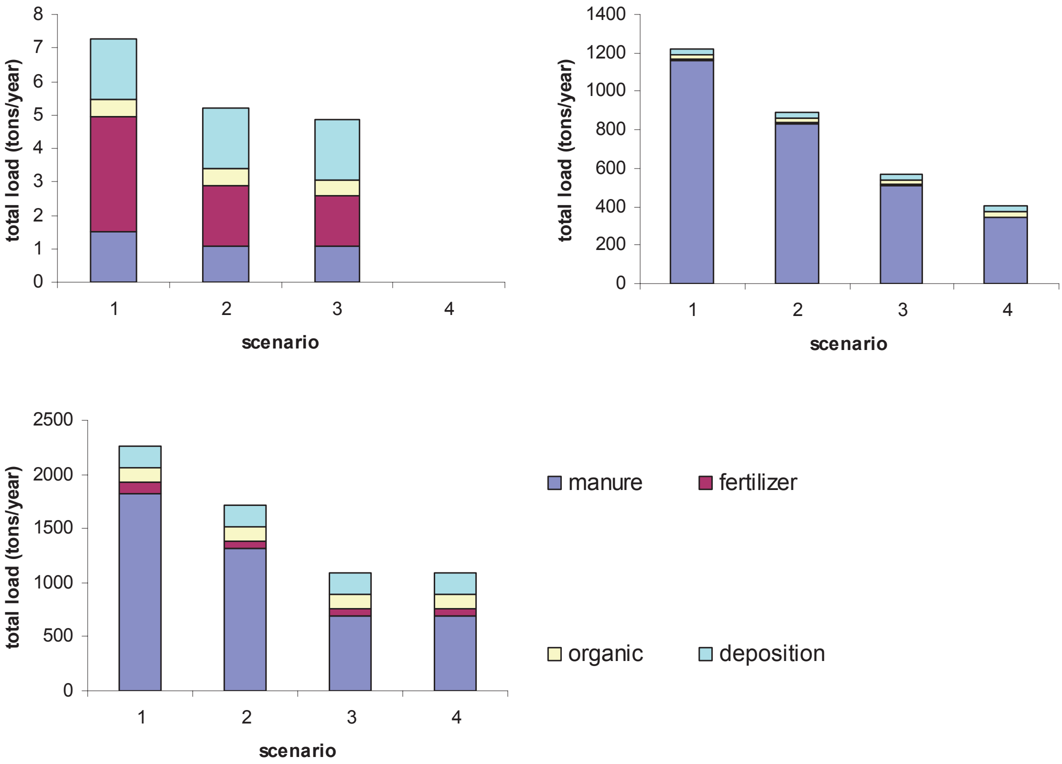

FIGURE 2 Total inputs of Cd, Cu and Zn (tons yr^{-1}) to agricultural land in the Netherlands for different scenarios: 1 BAU; 2 ML; 3 ML+, 4 ML+-hd

TABLE 5 Terms of the metal balance for Cd, Cu and Zn in the top soil for the various scenarios in the year 2050 (g.ha^{-1}.a^{-1})

	BAU					ML			
Cd	dep[1]	man	upt	leach	acc	man[1]	upt	leach	acc
clay	0.6	2.7	0.9	0.2.	2.3	1.6	0.9	0.2	1.2
peat	0.6	2.7	2.1	0.2.	1.0	2.1	2.0	0.2	0.7
sand	0.7	3.0	1.5	1.0	1.1	1.7	1.5	0.8	0.1
Cu									
clay	10.2	499	103	54.8	351	408	103	42.0	273
peat	10.4	558	96.6	82.8	389	421	96.6	62.1	273
sand	10.7	774	115	318	352	493	100	196	207
Zn									
clay	70.8	899	342	114	514	746	338	100	379
peat	71.1	863	449	228	256	669	435	198	107
sand	72.2	1350	655	551	215	873	603	341	1.5

continued on next page

TABLE 5 Terms of the metal balance for Cd, Cu and Zn in the top soil for the various scenarios in the year 2050 ($g.ha^{-1}.a^{-1}$)

	ML+					ML+-hd			
Cd	man[1]	upt	leach	acc	man[1]	upt	leach	acc	acc
clay	1.5	0.9	0.2	1.0	-	-	-	-	1.2
peat	1.9	2.0	0.2	0.3	-	-	-	-	0.7
sand	1.5	1.5	0.8	-0.1	-	-	-	-	0.1
Cu									
clay	256	103	32.2	131	179	103	27.4	59	273
peat	274	96.6	46.3	141	172	96.6	37.2	48	273
sand	302	91.4	135	86.4	214	86.5	110	27.4	207
Zn									
clay	448	333	86.0	100	-	-	-	-	379
peat	395	419	163	-116	-	-	-	-	107
sand	497	564	220	-215	-	-	-	-	1.5

[1] dep = atmospheric deposition; man i= the sum of metal inputs by manure, fertilizer and sludge; upt = plant uptake; leach = leaching from the topsoil; acc = accumulation in the topsoil

TABLE 6 Median changes in soil metal concentrations in the top-soil in the period 2000-2100 for the different scenarios (%)

metal	soil type	BAU	ML	ML+	ML+-hd
Cd	clay	33	21	19	-
	peat	28	18	14	-
	sand	25	8	6	-
	all	27	13	11	-
Cu	clay	95	79	47	30
	peat	154	124	78	45
	sand	155	107	65	45
	all	133	95	56	37
Zn	clay	33	25	10	-
	peat	41	23	0	-
	sand	45	14	-11	-
	all	40	20	-4	-

Copper. Animal manure dominates Cu inputs (Figure 2). Implementation of foreseen manure legislation (ML) reduces Cu input with 28%. The 50% reduction of the Cu content in animal food inputs (ML+) reduces Cu inputs by 56%. With a ban on discharge of Cu in hoof disinfection solutions (ML+-hd), Cu inputs are further reduced to 71%. Most of Cu added to the soil accumulates in the topsoil (Table 5). Predicted soil metal concentrations are highest in the clay and peat soils (Figure 3). The largest increases in Cu concentrations were predicted for peat soils and secondly for the sandy soils located in the southern, central and eastern parts of the Netherlands (Figure 3), which are the areas with intensive animal husbandry. With the BAU scenario Cu accumulates in nearly all plots. Lowering of manure and fertilizer inputs reduces the area with accumulation with only 0.4%. With the maximum reduction scenario (ML+-hd), the area with substantial Cu accumulation decreases significantly but is still rather high (77%) due to low leaching losses.

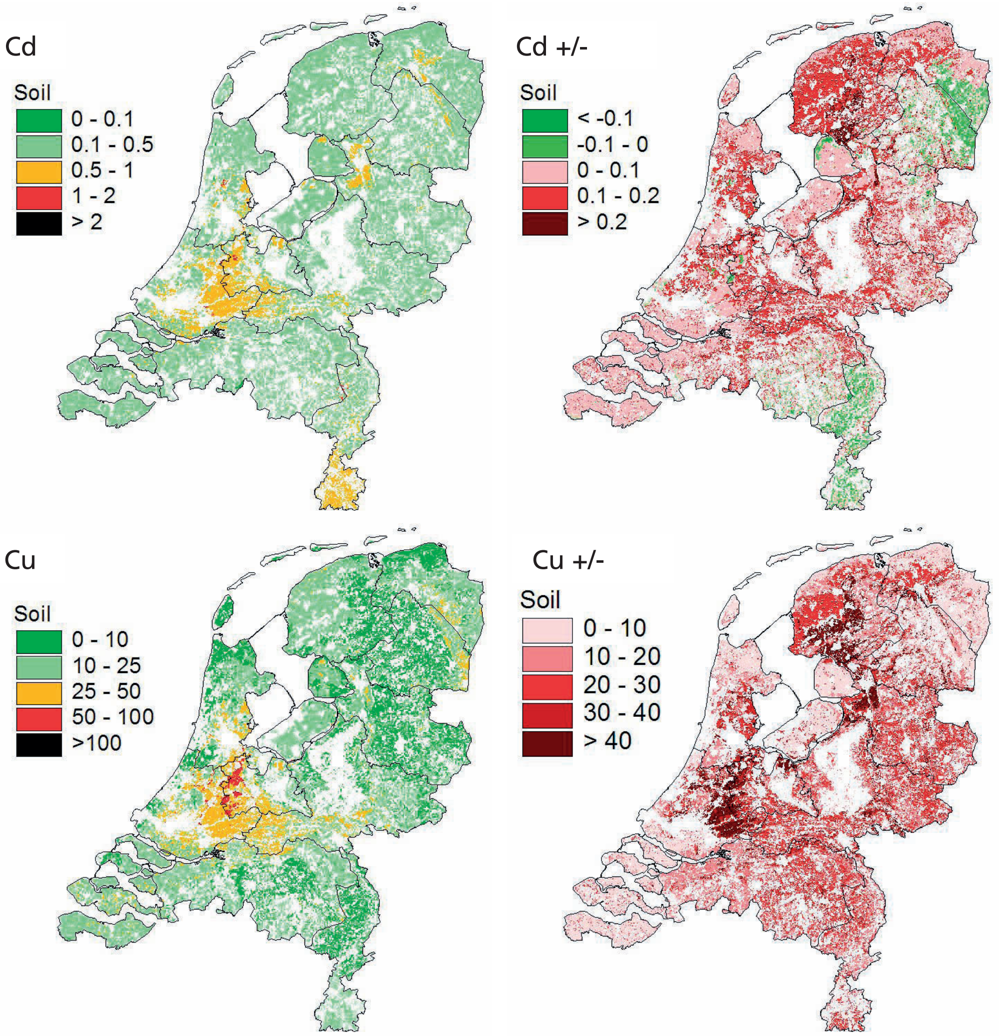

FIGURE 3 Cd, Cu concentrations in soil (mg.kg^{-1}) in 2000 (Left) and changes in soil metal concentration in 2100 (Right) for the Business As Usual scenario

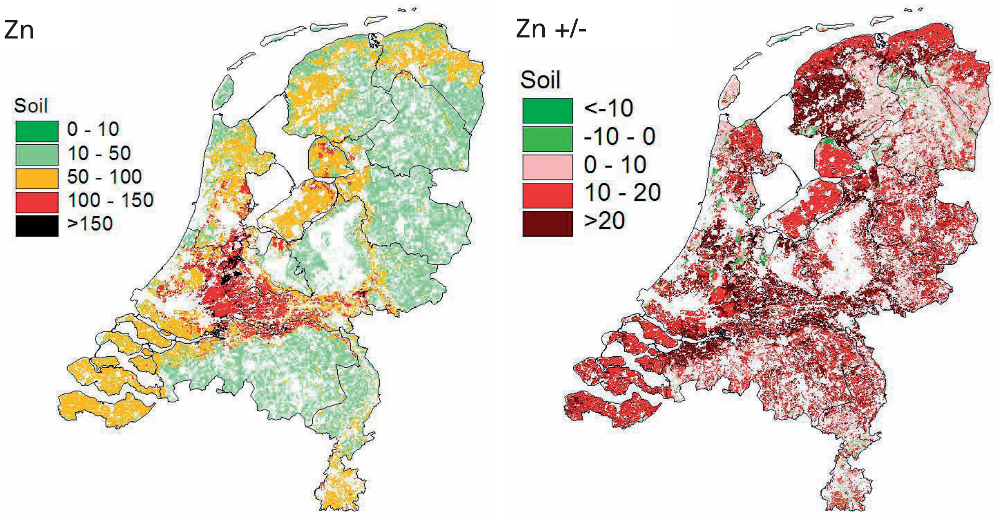

FIGURE 3 Zn concentrations in soil (mg.kg^{-1}) in 2000 (Left) and changes in soil metal concentration in 2100 (Right) for the Business As Usual scenario

Zinc. As with Cu, manure is also the major source of Zn inputs to agricultural land. Reduction of manure gifts (ML scenario) reduces Zn inputs with 28%. An additional reduction of Zn contents in animal food further reduces Zn inputs to soils up to 62%. Zn concentrations are highest in clay and peat soils. The largest increase in metal concentrations was predicted for clay soils due to their low leaching losses. Similarly high increases of soil Cu concentrations were predicted for sandy soils due to the high inputs in the areas with intensive animal husbandry. Uptake of Zn by crops is the most important sink, which amounts 43% of total inputs under the BAU scenario. With lower inputs the relative importance of uptake increases to 83% under the ML+ scenario. The contribution of leaching to the mass balance is rather constant among the scenarios (26-29%). At present inputs, Zn accumulates substantially in 79% of the plots. Manure legislation (ML scenario) leads to a stand still for sandy soils due to relatively high Zn leaching losses which are related to their low pH. Results for scenario ML+ for Zn including 50% reduction in Zn in animal food, show that an on average stand still can be achieved, although balances may vary considerable amongst plots resulting in an area with positive balances of 33% and an area with negative balances of 50%.

Impact of measures in view of critical limits in soil

In the year 2000, soil Cd, Zn and Cu levels were below the ecological critical limit (PNEC). After 100 years with the highest inputs of Cd, Cu and Zn (BAU-scenario), PNEC levels were exceeded only in 0.1% of the total area for Cd (mainly grassland) whereas for Cu and Zn, soil metal concentrations remain well below PNEC levels (Compare Figure 3 with Table 3; Table S-8 of the supporting information).

Metal concentrations in the year 2000 were all below the critical limits for agriculture (LAC-2006). Predicted soil Cu concentrations in the year 2100 exceed this limit in 20%

of the total area but in case of the BAU scenario. This is almost entirely due to exceedances of the rather strict critical limit for grassland soils to protect sheep health (30 mg.kg^{-1}). The second critical limit for grassland that relates to all other grazing animals (80 mg.kg^{-1}) was only exceeded in 1.7 % of the plots. Under the most stringent scenario (ML+-hd) this exceedance is reduced to 12% of the area. Actual levels and predicted future levels of Cd and Zn in the topsoil stay well below critical limits for agriculture.

Impact of measures on metal runoff to surface waters and excess of water quality criteria

The effects of the four scenarios on runoff towards surface waters are shown in Figure 4. Table 7 gives the area where predicted metal concentrations in runoff towards surface waters exceed critical limits for surface water for the various scenarios distinguished per soil type. Present loads of metals (BAU) will result in an increase of total metal runoff from agricultural soils towards surface waters for all metals (Figure 4). In case of Cd the increase in predicted runoff under the BAU scenario is rather small and differences between the scenarios are small.

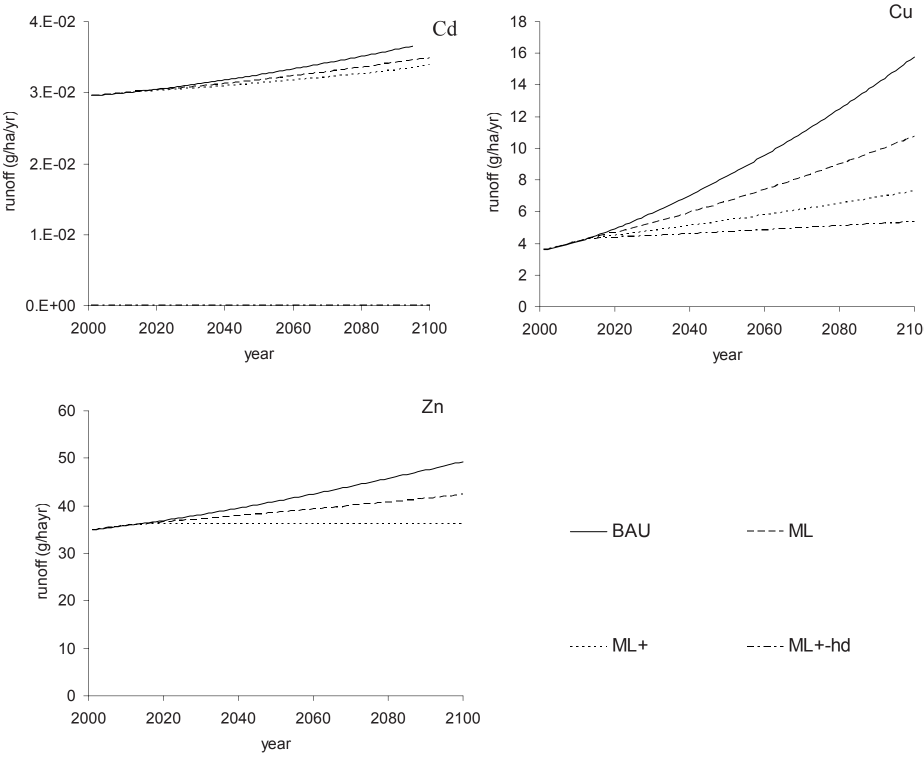

FIGURE 4 Area weighed runoff fluxes of Cd, Cu and Zn from agricultural land to surface waters in the Netherlands for the various scenarios

TABLE 7 Area of land (%) from which metal concentrations in runoff exceed critical limits for surface waters for the year 2000 and in 2100 for the various scenarios

metal	soil type	2000	BAU	ML	ML+	ML+-hd
Cd	clay	1.3	1.3	1.3	1.3	-
	peat	0.2	0.4	0.4	0.4	-
	sand	0.4	0.6	0.4	0.4	-
	all	0.7	0.8	0.8	0.8	-
Cu	clay	0.4	7.3	4.1	1.7	0.9
	peat	9.3	42.6	38.9	31.6	22.8
	sand	0.2	22.3	6.3	2.0	0.9
	all	2.2	20.2	12.3	8.1	5.1
Zn	clay	23.2	27.5	26.1	25.0	-
	peat	67.5	76.8	74.7	71.3	-
	sand	25.3	72.2	60.8	46.9	-
	all	33.3	54.2	49.0	42.8	-

Copper runoff at present loads increases strongly with a factor of three in 100 year which leads to an increase of the area with exceedances of critical limits from 2.2 to 20.2%. With a reduction of manure and fertilizers application (ML scenario) the increase in runoff is 50% lower than under the BAU scenario. With the most stringent scenario (ML+-hd) a nearly stand still in the average metal runoff is achieved. The area with exceedances of critical limits increases 2.2% in the year 2000 to 5.1% in 2100.

For Zn already large areas with exceedances (Table 7) are calculated for the Zn concentration in runoff water in the year 2000, especially for peat soils where the Zn concentration in runoff exceeds critical limits for surface water for 67% of the peat area. With present inputs this area increases to 77%. By decreasing manure application together with a lowering of the amount of Zn in animal feed (ML+), stand still is obtained

3.2 Model evaluation

Effects of redistribution between reactive and inert metal pools

In our study we added metal inputs from atmospheric deposition, manure and fertilizers to the geochemically reactive metal pool. This is in line with the results of Vijver et al. (*45*) who found that anthropogenic enrichments were represented by a cold 2M HNO_3 extraction which they used as a measure for geochemically reactive metal. According to Bonten et al. (*46*), 2M HNO_3 extracts about 60% more than a 0.43 M HNO_3 extraction. Similar to other dynamic modeling studies (*47-49*) we did not include exchange between geochemical reactive and inert metal pools. Monitoring studies of soils applied with manure in which both total and reactive metal pools were monitored show, however, that only part of the accumulated metal is in a geochemically reactive form (*50, 51*) as measured with a Mehlich 3 and 0.01 M EDTA extraction. Apparently, part of the metals in manure added to soils is not in a reactive form and/or part of the reactive metal is immobilized due to slow sorption reactions to oxides and clays. Calculations including redistribution between the reactive and inert metal pool lead to a substantial lower predicted runoff for Cu and Zn under the BAU scenario (Figure 5), whereas the effect for Cd appeared to be relatively small because of the large fraction of reactive Cd.

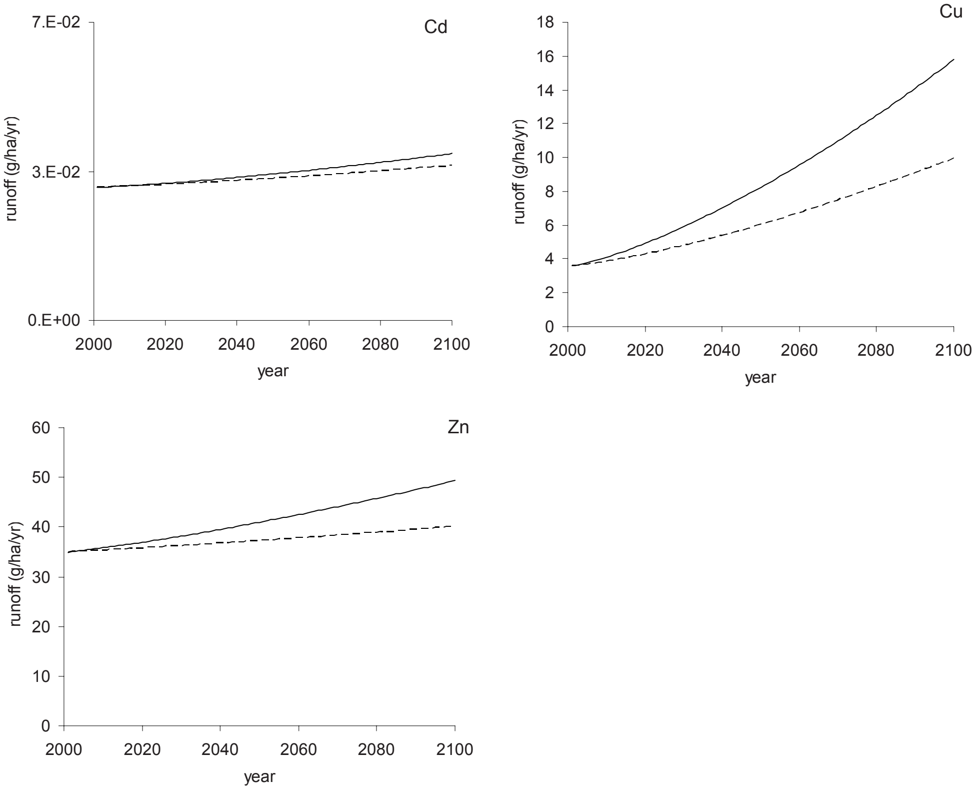

FIGURE 5 Area weighed runoff fluxes of Cd, Cu and Zn from agricultural land to surface waters in the Netherlands for the BAU scenario without aging (solid line) and with aging (broken line)

Metal inputs and uptake

Computed metal inputs were compared with figures of Statistics Netherlands (CBS) which calculates metal inputs from gross national data. The calculated metal inputs for the year 2000 (excluding atmospheric deposition) of 5.5 tons for Cd and 2060 tons for Zn compare well with the CBS data (*2*) of 5 and 2100 tons respectively. The computed input of Cu of 1190 tons substantially exceeds CBS estimates of 760 ton. The CBS estimate is however likely to be an underestimation since their estimated decrease of Cu in manure is based on assumed reductions of Cu contents in animal feed as enforced by EU regulations in the year 2000. This is, however, not in agreement with actual data of Cu in manure in 2008 (*20*), which show no decrease of Cu in manure compared to

1996 (*52*). Possibly the decrease of Cu in animal feed is (partly) compensated for by the use of Cu additions to fodder or drinking water at the farms themselves and the use of Cu and Zn as a substitute for antibiotics. Furthermore the CBS figures do not include Cu in manure originating from hoof disinfectants

Solid solution partitioning

Figure 6A compares model predictions of solution concentrations for the five soil profiles. Model predictions are within one order of magnitude from measurements in case of Cu and Zn. The model however generally underestimated Cd concentrations by one order of magnitude.

The average levels of the groundwater concentrations for the 27 hydrological clusters in the Netherlands (Figure 6B) were predicted within one order of magnitude for all three metals. Note that the uncertainty in predicted solution concentrations includes uncertainties in estimated background soil metal concentrations, soil properties (pH, SOM, clay, and oxalate extractable Al and Fe) used in the regression relation to predict the solid solution partitioning and the uncertainty of the parameters of the used regression relation itself.

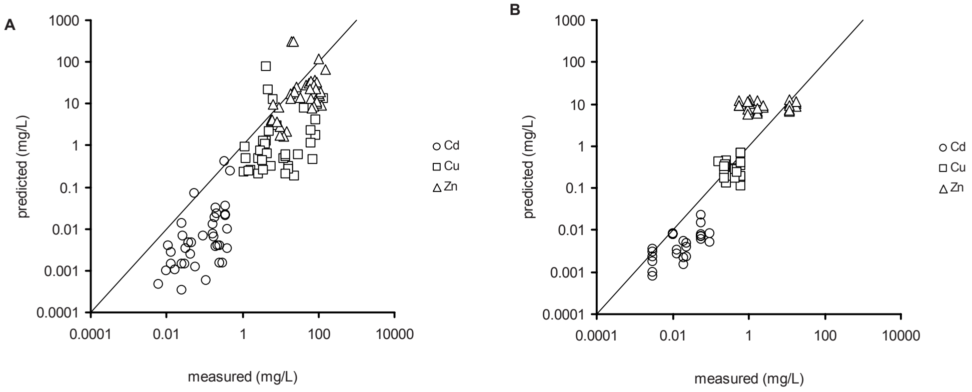

FIGURE 6 Comparison of predicted pore water concentrations with measurements in 5 soil profiles (A), comparison of predicted groundwater concentrations with scaled measurements of hydrological clusters in the Netherlands (B)

Comparison of model results with measured accumulation in field studies

Several field studies show increasing Cu and Zn levels in soils due to application of cattle, swine and poultry manure (*50, 51, 53-56*). Due to the heterogeneity of the composition of the applied manure and receiving soils, soil metal budgets based on changes in metal concentrations from studies of a few years up till 10 years are highly uncertain and therefore fractions of Cu and Zn measured in soil relative to total applied amounts reported or estimated from published data may result in unrealistic fractions exceeding 100% (*51, 53*). Therefore only long-term field studies (> 10 years) were used to evaluate the plausibility of our modeling results

A long term field study in the Czech Republic (*56*) in which the effects of 52 years manure application were analyzed on a permanent arable field (Luvisol) shows a very limited and non significant increase in total Cu and Zn concentrations. Copper inputs of 23 and 104 $g.ha^{-1}a^{-1}$ are, however, much lower than the inputs in our model study. These inputs are within the range of the computed uptake by crops of 68-103 $g.ha^{-1}a^{-1}$ in our study (Table 5). Also Zn inputs of 132 and 778 $g.ha^{-1}a^{-1}$ are similar or somewhat above the calculated uptake of Zn by crops in our study which range from 328-572 $g.ha^{-1}a^{-1}$. Additionally Zn leaching is another important sink. Significant increases are therefore not to be expected and are in line with our results

For a 25 year field study in Canada (*50*), in which cattle manure was applied to arable land (clay loam soil) at zero level and 3 different rates of 526, 1050 and 1580 $g.ha^{-1}a^{-1}$ Cu and 1510, 3010 and 4520 $g.ha^{-1}a^{-1}$ Zn, the changes in the storage of metals in the top 30 cm in soils were estimated from changes in measured soil concentrations and average bulk densities of the soils as reported by (*57*). The two lowest application rates are similar to the range of Cu application rates in our model study. For these application rates about 66% of the applied Cu accumulated in the top soil layer. This is comparable but is in the lower end of the range in predicted accumulation rates of 65- 89% in our modeling study. Their highest application rate exceeds inputs in our study. For this application rate about 50% of the applied manure accumulated in the top soil. The relatively lower accumulation rate at higher inputs is likely due the result of increased leaching losses at higher Cu inputs due to a decrease in the remaining metal binding capacity at higher Cu concentrations which is in line with our model simulations. The accumulated fraction of Zn in the field monitoring study was between 20 and 30% depending on the addition rate. This is within the wide range of predicted accumulation rates between -1 - 76% in our study.

4 Conclusions

Comparison of model results of the regional dynamic model with measurements of metal accumulation of long-term monitoring studies, solid solution partitioning data from field studies and regional monitoring data show that model predictions are within realistic ranges. This gives confidence in the predicted trends of metal accumulation in soil and runoff to surface waters, which makes it possible to identify problem areas and to evaluate the effects of measures on soil and water quality. However, a certain extent of uncertainty in model predictions has been shown to exist due to uncertainties in model inputs and in process modeling. Uncertainties in the geochemically reactive fraction of metals due to slow sorption processes possibly lead to overestimation of runoff to surface waters. Besides, long-term changes which influence metal inputs to soil or change bio-geochemical processes, such as changes in land use and climate (hydrology), will also affect the accumulation and runoff of metals from soils in the coming 100 years.

Model results clearly showed that with present inputs, soil metal concentrations and metal concentrations in runoff will increase continuously. With present inputs the average soil concentration of Cd increased with 23%, Cu with 133% and Zn with 41% in 100 year. Despite the increase, both present (2000) and future (2100) metal concentrations of Cd and Zn were all below agricultural and ecological thresholds. Also Cu will stay below ecological thresholds, but will increase to above agricultural thresholds with respect to grazing sheep for a substantial area (20%).

Present Cd concentrations in runoff hardly exceed critical limits in surface waters (less than 1%) and this is still the case in 2100 using present inputs, since the increase in predicted runoff is small. Present Cu and Zn concentrations in runoff, however, exceed those of critical limits in surface waters and these exceedances will further increase with present loads. The area with concentrations in runoff water which exceeds surface water criteria increases from 2% to 20% for Cu and from 33% to 54% for Zn from 2000 to 2100. Scenario analyses show that substantial reductions, which only can be achieved by a combination of measures, are needed to reverse the trends of increasing metal loads to surface waters.

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Supporting information

TABLE S-1 Coefficients to be used to calculate total background metal concentrations from clay content using Equation 1 (*1*)

Metal	α_0	c_2 (clay)	R^2
Cd	0.0517	0.0029	0.26
Cu	1.71	0.339	0.47
Zn	4.76	1.86	0.76

TABLE S-2 Coefficients to be used to calculate total metal concentrations for the soil profile at different depths using Equation 2 (*2*)

Metal	β_0	β_1 (z)	β_2 ($Me_{soil,tot}(z=0)$)	β_3 (SOM)	β_4(clay)	β_5(pH_{KCl})	R^2
Cd	–0.496	–0.354	0.382	0.174	0.261	0.011	0.44
Cu	0.364	-0.351	0.102	0.372	0.650	0.009	0.64
Zn	0.343	-0.111	0.146	0.320	0.466	0.071	0.69

TABLE S-3a Coefficients to be used in the plant-soil relations (Equation 4) for Cd (*3*)

Crop	a_0	a_1 (SOM)[a]	a_2 (clay)[a]	a_3 (pH)	a_4 ($Ct_{Me,soil}$)[b]	R^2
Grass	1.45	0	0	-0.38	1.22	0.63
Maize	0.9	0	-0.32	-0.21	1.08	0.50
Potatoes	0.97	-0.41	-0.2	-0.21	0.81	0.78
Wheat	0.22	-0.33	-0.04	-0.12	0.62	0.64
Sugar beet	1.33	0	-0.31	-0.21	0.62	0.83
other cereals	0.22	-0.33	-0.04	-0.12	0.62	0.64

TABLE S-3b Coefficients to be used in the plant-soil relations (Equation 4) for Zn (*3*)

Crop	a_0	a_1 (SOM)[a]	a_2 (clay)[a]	a_3 (pH)	a_4 ($Ct_{Me,soil}$)[b]	R^2
Grass	2.19	0	-0.49	-0.15	0.47	0.49
Maize	1.35	-0.14	-0.25	-0.17	0.81	0.68
Potatoes	1.23	-0.07	-0.15	-0.09	0.34	0.36
Wheat	1.32	0	-0.24	-0.06	0.45	0.56
Sugar beet	2.69	-0.71	-0.37	-0.41	1.13	0.67
other cereals	1.32	0	-0.24	-0.06	0.45	0.56

[a] soil organic matter content (SOM) and clay content (%)

[b] metal conten in soil ($mg.kg^{-1}$)

TABLE S-4 Median concentrations of copper in all crops and of cadmium and zinc in other arable crops (mg.kg^{-1}) (*4*)

soil type	Cd	Cu	Zn
sand	0.34	5.9	64
clay	0.11	11.3	83
peat	0.4	8.3	79

TABLE S-5 Optimal yields of harvestable product (tons dry matter.ha^{-1}) as a function of crop type, soil type and hydrology compiled by (*4*)

soil type	hydrological class^{1}	yield (tons dry matter.ha^{-1})						
		grass^{2}	maize	potatoes^{3}	wheat^{3}	sugar beet^{3}	other cereals^{4}	other crops ^{4}
sand	dry	11	13	10	6.4	12.2	5.1	7.5
	moist	11	16	10	6.4	12.2	5.1	7.5
	wet	10	16	10	6.4	12.2	5.1	7.5
clay	dry-moist	11	16	11.5	7.4	13.8	5.5	7.5
	wet	10	13	11.5	7.4	13.8	5.5	7.5
peat	dry-moist	10	11	10	6.4	12.2	5.1	7.5
	wet	9	10	10	6.4	12.2	5.1	7.5

1 according to the average highest groundwater level (HGL): wet (HGL<40 cm), moist (40<HGL<80 cm), dry (HGL>80 cm); ^{2} Aarts et al. (*5*); ^{3} Schröder et al. (*6*); ^{4} CBS-Statline

TABLE S-6 Coefficients to be used to calculate geochemical reactive metal concentrations from total metal concentrations (mg.kg^{-1}) and the soil organic matter and clay content (%) using Equation 9 (*7*)

Metal	c_0	c_1 (SOM)	c_2 (clay)	c_3 ($Ct_{Me,\ soil}$)	R^2
Cd	-0.089	0.022	-0.062	1.075	0.96
Cu	-0.331	0.023	-0.171	1.152	0.93
Zn	-0.703	0.183	-0.298	1.235	0.96

TABLE S-7 Percentages of the area with a substantial positive accumulation (>+10% of inputs), negative accumulation (<-10% of inputs) or equilibrium (-10% < accumulation <+10%)

metal	BAU			ML			ML+			ML+-hd		
	+	-	0	+	-	0	+	-	0	+	-	0
Cd	85	8	7	72	21	7	70	22	8			
Cu	100	0	0	100	0	0	94	0	6	77	7	16
Zn	79	1	20	62	10	28	33	50	17			

TABLE S-8 Median ratio of metal concentration to PNEC for the year 2000 and in 2100 for the various scenarios

metal	soil type	2000	BAU[1]	ML[1]	ML+[1]	ML+hd[1]
Cd	clay	0.29	0.43	0.39		
	peat	0.40	0.50	0.46		
	sand	0.21	0.27	0.23		
	all	0.25	0.35	0.31		
Cu	clay	0.14	0.33	0.31	0.25	0.22
	peat	0.12	0.30	0.27	0.21	0.17
	sand	0.16	0.44	0.36	0.29	0.26
	all	0.14	0.37	0.33	0.26	0.23
Zn	clay	0.25	0.34	0.32	0.28	
	peat	0.18	0.26	0.23	0.18	
	sand	0.21	0.30	0.24	0.18	
	all	0.22	0.31	0.27	0.22	

[1] BAU = business as usual (present loads); ML = reduction in application of manure and fertilizers to meet maximum gifts for N and P according to manure legislation; ML+ = same as previous and an additional reduction in Cu and Zn contents in animal feed; ML$^+$hd = same as previous but with additional measurers to ban Cu in hoof disinfection baths.

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CHAPTER 8

Synthesis and recommendations

1 Major conclusions of the study

In this thesis, the strengths and weaknesses of two different approaches to model metal partitioning and speciation in soils have been evaluated, i.e.: (i) empirical based partition models and (ii) thermodynamical multisurface models. Furthermore, their application has been demonstrated and evaluated in two risk assessment studies. On the basis of the results obtained in the different chapters of this thesis, the research questions as formulated in the introduction (Chapter 1) are addressed in the section below, followed by a future outlook and recommendations for possible improvement of the modeling approaches.

1.1 Implications of the mathematical form of partition relations

When applying partition relations the choice of their mathematical form needs careful consideration. Various studies have derived empirical partition relations based on the Freundlich-van Bemmelen equation and generalized their applicability by the inclusion of relevant soil properties. It was shown in Chapter 2 that such partition models can be distinguished according to their formulation and method of optimization. Freundlich-type models which are derived using multiple linear regression were categorized as C-Q, Q-C and K_f relations. C-Q relations are models in which the concentrations in solution are predicted from metal concentrations in the solid phase and soil and soil solution properties (e.g. organic matter content and pH), whereas in Q-C relations the solid phase concentration is predicted from the solution concentration and soil and solution properties. In K_f relations, the adsorption constant K_f is related to soil and solution properties. When using multiple linear regression, the sum of the squared residuals is thus minimized for C in C-Q relations, for Q in Q-C relations and for K_f in K_f-relations. Partition relations can also be derived by using an alternative statistical technique i.e. total least squares (TLS), as illustrated in Chapter 2. Whereas the independent variable is assumed to be error-free in ordinary regression techniques, the TLS technique takes observational errors in both dependent and independent variables into account. The advantage of TLS and K_f relations is that they can be used to predict both solution concentrations and solid phase concentrations. The performance of the TLS relation to predict solution concentrations of free metal ions (FMI) was shown to be poor and comparable to that of Q-C relations. This is likely to be caused by the strong correlation of solid phase metal concentrations with the content of SOM and pH, i.e. the thus derived relations relate element solid phase contents to soil properties rather than to solid solution partitioning. Despite the fact that C-Q relations are optimized for C, the model performance of the K_f relations to predict FMI solution concentrations was only slightly less than that of the C-Q relations for metal cations. K_f-relations are, therefore, particularly useful in dynamic models, predicting metal leaching from soils subjected to varying inputs of trace elements.

1.2 Applicability of partition-relations

It was shown by evaluation of partition relations on independent data that K_f relations for both FMI activities of Cd, Cu, Ni, Pb and Zn (Chapter 2) and C-Q relations for total concentrations of these elements and As, Ba, Co, Cr, Mo, Sb, Se, V (Chapter 4) can be used for soils outside the data set from which the partition relations are derived. However, their use is limited to the range of environmental conditions, such as pH (Chapter 4) and organic matter content (Chapter 7), for which the relations were derived. Partition relations (C-Q) were remarkably successful to describe the pH dependent solubility for individual soils for the elements As, Ba, Cd, Cu, Ni, Pb, Se, Pb, V and Zn within the pH-range 3-8 (Chapter 4). In contrast with the C-Q relations, it was not possible do derive meaningful K_f relations for Mo, Sb and Se and predictions for As by the K_f-relations were poor (Chapter 4, results not shown). It is not yet clear what the reasons are. However it can be concluded that the partition relations (both C-Q and K_f) are more successful to predict concentrations of metal cations, i.e. ions which bind predominantly to organic matter than Pb and oxy-anions, for which binding to Al/Fe-(hydr)oxides is important. Partition relations for divalent cations are shown to be robust models to predict trace element solubility in soils. This legitimates their use in (regional) risk assessment studies for which computing time is to be considered and in applications (e.g. decision support systems) to be used by non specialists as long as the domain for which they are valid is delimited.

1.3 Evaluation of multi-surface models

Two almost similar multisurface models with separate models for ion speciation in solution, ion binding to organic matter, Al/Fe(hydr)oxides and clay were evaluated on various datasets of solution extracts (Chapter 3 and 4). The two models which were evaluated include the NICA-Donnan model for ion binding to particulate and dissolved organic matter, the Generalized Two Layer Model (GTLM) for binding to AL/Fe-(hydr)oxides and a Donnan model for electrostatic binding to clay. The models differed somewhat with respect to the choices made to quantify reactive surfaces (see Table 1). The models showed to be good predictors of the concentrations of especially Cd, Cu, Zn (Chapter 3 and 4), Ni and Cr (Chapter 4). Root mean square errors (RMSE) for the logarithm of solution concentrations for these elements were close to 0.5 or lower, which means that 95% of the predictions is within one order of magnitude. For As, Ba, Co, Mo, Sb, Se ,V (Chapter 4) and Pb (Chapter 3 and 4) a larger scatter was observed ($0.7 < \text{RMSE} < 1.3$). For most elements there was no systematic over- or under-prediction of solution concentrations except for Pb and Sb concentrations which were generally overpredicted by the model. A further improvement of the binding constants for these elements, which are usually based on less extensive datasets or estimated from linear free energy relationships, will likely improve their predictions. For the oxy-anions, part of the larger scatter is possibly explained by the fact that the (competitive) influence of organic matter adsorption to the oxide surfaces is not included in the models. As observed for the partition relations, multisurface models are most successful to predict the concentrations of metal cations which bind predominantly to organic matter whereas predictions for Pb and oxy-anions, for which binding to Al/Fe-(hydr)oxides is important, are less successful. The applicability of these models in generic risk assessment depends on the required and available input data. Most of these data are available from standard soil investigations except for solute concentrations of DOC and major cations and anions (Chapter 3). It was shown in Chapter 3 that it is possible to reduce the required input of the multisurface model to calculate metal (Cd, Cu, Pb and Zn) solubility by using estimates of the solution concentrations of major cations and anions when such information is missing. This because the model was not very sensitive to such inputs for the evaluated soils. However, this has to be done with caution and not used for more extreme conditions e.g. in case of saline soils. With the use of multisurface models to calculate oxyanion solubility, information on solution or solid phase concentrations of the major anions (SO_4^{2-}, PO_4^{3-}) is however required.

1.4 Comparison between partition-models and multisurface models

It was shown in Chapter 4 that partition relations and multisurface models have a similar performance for divalent cations in the pH range 3-8. Multisurface models, however, give substantially better predictions than partition relations at low and high pH, i.e. outside the range of the datasets from which the partition relations were derived. Because of their fundamental process-oriented basis, it is expected that multisurface models are in general more widely applicable than partition relations, and able to cover a large range of environmental conditions. Examples are: (i) saline soils due to competition with cations and complexation with inorganic ligands, (ii) extremely acidic soils and waters, such as acid sulfate soils and acid mine drainage, (iii) calcareous soils, soils in contact with cementitious materials or cement stabilized waste materials with high pH, (iv) soils with very low concentrations of organic matter such as sandy subsoils or (v) soils with very high concentrations of contaminants when precipitation is likely to occur. Another advantage of multisurface models is the prediction of the speciation of elements in the solid and the solution phase. This makes it possible to combine multisurface models with models which require such information as input. Examples are the implementation of (terrestrial) Biotic Ligand Models for the assessment of metal bio-availability and the combination of multisurface models with kinetic models for example to describe the long term immobilization of trace metals in soils by hydrous oxides and/or clay minerals. Another great potential is the use of multisurface models in the dynamic forward prediction of the macro chemistry of natural systems together with their effect on the solubility of trace elements, e.g. in case of acidification.

1.5 Natural variability of dissolved organic matter and its consequences for model predictions

Because of the important role of organic matter, the effect of natural variability in chemical properties of organic matter and uncertainty in model inputs thereof on the uncertainty in output of the NICA-Donnan model was evaluated. Important sources of uncertainty are the organic matter composition and the variation in binding properties of HS. NICA binding parameters that were optimized for individual FA samples showed substantial variation. Monte Carlo simulations showed that uncertainties in predicted metal speciation, for metals with a high affinity for FA (Cu, Pb) are largely due to the natural variation in binding properties (i.e. the affinity) of FA. Predictions for metals with a lower affinity (Cd) are more prone to uncertainties in the fraction FA in DOM and the maximum site density (i.e. the capacity) of the FA. To reduce parameter uncertainty it is strongly advised to determine proton and metal binding data for the same HS sample (Chapter 5). At present there are almost no samples for which both proton and metal binding data are available. DOM composition can be measured and is facilitated by the rapid batch technique of van Zomeren and Comans (*1*). However, it seems not feasible to determine the composition of organic matter for each sample to be modeled. Therefore, it is worthwhile to investigate the extent to which uncertainties can be reduced by restricting the variability of the organic matter composition and model parameters by determining their ranges for certain groups of soils and surface waters and other (e.g. waste) materials in which metal binding to HS is important.

1.6 Use of partition-relations and multisurface models in risk assessment

To calculate critical loads of metals for soils, WHAM/Model VI was used to calculate the total metal concentration in equilibrium with the critical free metal ion concentration (Chapter 6). It was shown that uncertainties in calculated critical loads result for a large part from uncertainties in the calculation of solution speciation, largely due to the uncertainties in the binding parameters and fractions HS in DOM used in the ion-binding model, in line with results in Chapter 5. Additional uncertainty in geographical applications is due to the uncertainty in DOC concentration of soils. With the calculation of target loads an additional uncertainty arises from the use of partition relations which are needed to calculate the metal concentration in the soil solid phase. To reduce uncertainties in regional assessments of critical loads, it is recommended to get information on the geographic variation in DOC concentrations. It is therefore recommended to include DOC measurements in the standard measurements of geographic (monitoring) systems and to extend present systems with these measurements. When information is available it is worthwhile to test whether it is possible to derive relations which adequately predict DOC concentrations based on data available in geographical information systems.

Empirical partition models were used in a regional-scale model to predict the leaching of Cd, Cu and Zn from soils to surface waters (Chapter 8). The results revealed substantial limitations when applying partition models to subsoils, which are particularly important for the leaching of metals from soils to surface waters. The reason for this is that in deeper soil layers, soil organic matter contents can be very low. The dataset from which partition relations were derived have relatively high contents of soil organic matter (p5 = 3.4%) compared to that of sub-soils which may have median SOM contents up to ten times lower, especially in sandy soils. In the previous sections it was concluded that partition-relations showed particularly good performance for systems in which metal binding to organic matter was the dominant solubility controlling process. In systems with low organic matter contents, binding to oxides becomes more important. However, also due to the mathematical form of the equations it is difficult to describe the various dominant processes depending on conditions adequately. In its present mathematical formulation, the adsorption constant K_f depends in a multiplicative way on the considered metal-binding soil constituents. At low contents of a particular constituent this dependency is likely to lead to an underestimation of metal binding. To overcome this problem, new partition relations were derived which relate K_f in an additive way to the metal-binding soil constituents (SOM, clay and Al/Fe-(hydr)oxides). The newly derived relations need, however, to be tested on subsoil samples to see whether they provide better estimates than the "traditional" K_f relations. Another option would be the use of multisurface models, although computing time for such large regional/national applications is still a major obstacle.

2 Future outlook and recommendations

2.1 Future directions for improvement of empirical models

Most risk assessment studies use partition relations because of their easiness of use, short computing time and assumed lower data demand. Because partition relations need no iterative calculation procedure, the calculation procedure is very robust whereas multisurface models may not find a solution incidentally due to convergence problems. Furthermore partition relations are, due to their simplicity, more transparent to non-expert users. Robustness and transparency are non scientific but practical advantages which are important for example in decision support systems that are to be applied by non expert users. An example of such a DSS is the risk toolbox – an instrument to support site-specific management of soil quality and soil use in the Netherlands (*2*).

Empirical relations are mostly limited to the range in soil properties for which they were derived and are less successful for oxy anions. The domain for which partition relations can be used can in principle be enlarged by using derivation sets with a larger domain. It is worthwhile to test the possibilities thereof, however, it may be limited by differences in the dominant processes between certain ranges of environmental conditions or metal concentrations. Binding of most metal cations is dominated by binding to organic matter in the pH range 3-7 but shifts to binding to Al/Fe-(hydr)oxides at higher pH as predicted by Dijkstra et al. (*3*) with their multisurface model. Similarly, extension to partition data at high metal concentrations may be limited at a certain point at which precipitation, rather than sorption, takes over to be the concentration regulating process (*4*). It is unlikely that the various dominating processes can be described adequately by just a single empirical relation. Moreover, when precipitation is the regulating process, there is no relation between C and Q. For the extension of the application range to very low soil organic matter contents, as can be found in subsoils, a new type of partition relation was proposed (Chapter 7). It should be tested whether this type of relation, in which K_f is a function of the sum of the reactive surfaces, is able to extend the applicability of these relations to soils with a low organic matter content, where binding of metals to Al/Fe-(hydr)oxides is the dominant process rather than binding to organic matter. A limitation that might appear is that the pH-dependent binding to SOM and to Al/Fe-(hydr)oxides is not adequately described by just a single pH coefficient.

The development of partition relations for oxy-anions needs further attention. At present only few studies exist with such relations derived from solution extraction of field soils (e.g. Chapter 4, (*5*)) These relations, however, do not fully comply with the general mechanistic picture of oxy-anion binding to soils. Although these relations include Al and/or Fe (hydr)oxide contents, i.e. the dominant soil constituents to bind oxy-anions, there was usually no clear relation with pH, the potential determining cation, or with P which is known to be an important competitor (*6*). The relations as derived in Chapter 4 were successful to describe the pH dependence of the oxy-anions by the inclusion of DOC as an explaining variable, which showed to have a very similar pH dependence. Because this is not necessarily due to a causal relation, it is advised to derive relations including coefficients for soil properties according to our mechanistic understanding of the oxyanion sorption processes. Possibly, the inclusion of datasets with larger ranges of Al/Fe/Mn-(hydr)oxide contents and environmental conditions will help to derive better relations. Furthermore, the use of the extractant 0.43 M HNO_3, which was used to determine the reactive element contents, needs further evaluation for oxy-anions. Only few studies (Chapter 4) (*3, 5, 7*) have used this extraction, which was developed for metals originally, to quantify the geochemically reactive pool of oxy-anions. The low pH of this acid extraction increases the positive surface charge of the Al/Fe/Mn-(hydr)oxides, thereby increasing oxy-anion binding, whereas protonation of oxy-anions and dissolution of the oxide surface promote oxy-anion solubility. According to the results of Chapter 4 and the study by Dijkstra et al. (*3*) the solubility of most oxyanions, with the exception of Mo, can be predicted well using the amount extracted with 0.43 M HNO_3

To apply partition relations, but this holds for multisurface models equally well, the concentration of DOC is one of the key-input parameters. When applying such models in regional risk assessment models, measured DOC concentrations are not available but have to be estimated. Yet, there are only few conditional relations to predict DOC from soil and soil solution properties (e.g. Chapter 7). It is therefore strongly recommended to make an inventory of DOC concentrations and its composition across soil types, soil horizons, hydrological and climatic conditions. Process oriented research is needed to unravel the most important processes regulating DOC concentrations in soils. Such information should then be used in the design of the inventory and finally in the development of empirical relations and mechanistically based models to predict DOC in soils. It is important to pay attention to the method to sample soil solution from soils. Several studies have shown that the sampling method and sample preparation have a strong influence on the concentration and composition of DOC (*8-11*)

2.2 Future directions for improvement of multisurface models

At present there are relatively few cases of risk assessment modeling in which (multi)surface-complexation models have been used. Examples are the use of WHAM/Model VI in the calculation of maximal permissible loads of Cd and Pb (*12, 13*) and the use of a reactive transport model, including a multisurface model, to set the regulatory emission limits for metals and other elements from construction materials, including soil and sludge, in the Dutch Soil Protection Decree (*14*). The extra data demand for multisurface models compared to partition models is, however, more a perception than a fact. With the use of generic constants, which are provided by various model frameworks such as ECOSAT, ORCHESTRA (*15*), Visual-Minteq and WHAM, not much extra information is required as compared to the use of extended partition relations which include SOM, $AlFe_{ox}$ clay, pH and DOC. When the change in the macro chemistry has to be included, the use of multisurface models may even reduce the amount of input, as shown by various researchers (*16-18*) who used multisurface models to predict changes in the macro chemistry of soils and trace elements under changing atmospheric deposition of NO_x, SO_x and trace elements. The approach avoided the need to determine or calibrate conditional cation exchange constants as is common practice in standard soil acidification models (*19, 20*). Computing time is, however, still an issue which may hinder the use of multisurface models in large scale applications. With the ongoing improvement of computers and the resulting increasing computing speed, this will become of minor importance in the future although I expect that it will be an issue at least for the coming decade. Multisurface models have been developed and evaluated with field and laboratory measurements during the last 15 years. Table 1 gives an overview of such applications. Within the various applications different choices were made with respect to the quantification of the reactive metal concentration in the solid phase (soil or particulate matter in surface waters) the reactive surfaces included, i.e. organic matter, Al/Fe/Mn-(hydr)oxides and clay and their quantification. This variety in used extractions brings along a certain conditionality and uncertainty in the use of multisurface models. Therefore, it is recommended to evaluate the various quantification methods with respect to uncertainty of model outcome and applicability.

Extraction techniques to quantify reactive element concentrations

Most studies with surface complexation models have used geochemically reactive metal concentrations rather than total metal concentrations. Acid extracts have been used frequently to determine the reactive element concentrations, especially HNO_3-extracts of various strength. Furthermore, the synthetic ligand EDTA is used in several applications. Good agreement between EDTA and 0.43 mol l^{-1} HNO_3 extracted metal has been shown by Tipping et al. (*21*) for organic soils (>10% SOM), and by Groenenberg et al. (*22*) and De Vries et al. (*23*) for a large range of forest and agricultural soils. An advantage of the 0.43 M HNO_3 extraction is that it possibly can be used for both cationic and anionic species as was shown in Chapter 4 and by Dijkstra et al. (*3*). However, a more thorough evaluation of this extract is needed and it is therefore strongly recommended to evaluate various extraction techniques with respect to their effect on model predictions, uncertainties and applicability.

Methods to quantify reactive surfaces

Also the quantification of site densities of reactive surfaces of especially oxides and organic matter needs further attention.

Al/Fe/Mn-(hydr)oxides. In most of the applications listed in Table 1, the amount of Al/Fe/Mn-(hydr)oxides is estimated by selective, but operationally defined, extraction of Al, Fe or Mn-(hydr)oxides. The amount of hydroxides can also be calculated by the multisurface model from the total reactive amount of Al, Fe and Mn and the solubility of the assumed oxide phases (*24, 25*). The model then calculates the fractions of the total amount bound to reactive surfaces an the fraction which is precipitated. For surface waters Al/Fe/Mn-(hydr)oxide contents are also determined by the difference of the total amount of Al/Fe/Mn (including particulate matter) minus truly dissolved concentrations of these elements as determined after filtration of the sample. For all these three methods assumptions are then to be made on the mineral form of the oxide and its corresponding specific surface area. According to Hiemstra et al. (*26*) the ion binding behavior (affinity) of the various Al and Fe oxides is rather similar and ion binding can be modeled using a single model oxide when taking into account the different surface areas of the oxides. An alternative, recently developed, approach is to determine the effective reactive surface area using a probe anion (PO_4^{3-}) under well defined conditions (*26*). With this method reactive surface areas were found corresponding with 630±470 m^2/g Fe/Al-oxide for Al and Fe extracted with a dithionite extraction. The reactive surface area of 600 m^2/g HFO as frequently used (*3, 24, 25*) is nearly similar to the average value. However, the variation is not taken into account when using single selective extractions. Part of the variation can be accounted for when using several extractions to distinguish between various mineral forms e.g. to distinguish between amorphous and crystalline oxides taking into account their specific surface area (*3, 25, 27-30*). Further studies are needed to determine the sensitivity of cation and anion sorption to this variation and to study the applicability of the various methods. Selective extraction procedures are attractive because they are not laborious and therefore suitable for routine measurements. To reduce uncertainties within generic model applications for which only standard soil data are available from e.g. geographical information systems it is needed to get information on the variation of reactive surface areas of oxides amongst soils and environmental conditions. When such information is available it is worthwhile to discover whether it is possible to relate this variation to soil properties and environmental conditions which are available from standard soil investigations.

Organic matter. Natural organic matter (particulate and dissolved) is a mixture of organic substances containing high molecular weight or humic substances and low molecular organic molecules (organic acids, carbohydrates, lipids, amino acids *etcetera*) (*31*) of which the humic substances (HS) are assumed to be the most relevant fraction for metal binding. Natural organic matter composition, and therewith its binding properties, varies amongst samples from different locations or even between different sampling times at the same location (*32*). When applying ion binding models for organic matter, the reactive part of organic matter with respect to metal binding is usually assumed to be a fixed percentage varying between 30-100% of total organic matter (*9, 25*) (see also Table 1). The results in Chapter 5 confirm this with the large spread in the composition of DOM with HS ranging from 14-63% of total DOM. The reactive part of organic matter can be estimated as the fraction of HS in organic matter, being the most important fraction with respect to metal binding (*3, 33*), which can be determined by fractionation techniques (*1, 34*). Although the role of the hydrophilic fraction for bulk soil solutions seems limited (*33*), more attention is needed with respect to the quantitative role of this fraction in metal binding. It is important to take into account that various, but operationally defined, fractionation techniques e.g (*1, 34*) yield fractions which will differ in their composition to some extent. To obtain a picture of the variation in the content of HS in field soils (solid and solution phase) it is advised to analyze the HS content for various soils and soil horizons under different environmental conditions i.e. for different soils and different climate and hydrological conditions.

Improvement of model parameters

Another important aspect is the variation in binding properties within humic materials. The uncertainty in binding properties is both due to the variation in the intrinsic binding properties of the humic substances and to the uncertainty in the determination of these binding properties which is usually done by fitting titration data with the model (see Chapter 5). The number of parameters to be optimized in the model fit is, however, generally too large to find an unconditional fit using titration data (*35-38*). Reducing parameter uncertainty can be achieved by parameter constraints (*35, 36, 39*) and by using extra information (*38*). For example van Zomeren et al. (*40*) used a two step procedure after de Wit et al. (*41*) in which they separately optimized the model constants for intrinsic and electrostatic affinities. Similarly Lenoir et al. (*35*) developed a three step procedure, in which they also separate electrostatic and intrinsic affinity, to constrain model fits “to convergence toward chemically and physically realistic values”. Parameter uncertainty with respect to metal binding can be further reduced by using datasets which include both proton and metal titration data for the same sample of humic material (Chapter 5). To reduce the uncertainty for generic applications of the model, the variation in binding parameters amongst different samples of humic materials from different origin should be further quantified and if possible related to soil and/or environmental properties

Improvement of process modeling

A possible improvement with respect to the modeling of oxy-anions is to include organic matter sorption to Al/Fe-(hydr)oxides, which was not taken into account in the studies listed in Table 1. Part of the surface may be occupied by organic matter, which may influence oxyanion sorption by changing the electrostatic potential near the oxide surface and by competition for binding sites (*38*). Sorption of organic matter to oxide surfaces was shown to play a role in the binding of arsenate and phosphate to synthetic oxides (*42, 43*) and arsenate binding to soils (*44*). The modeling of organic matter sorption to oxides is also an important step to be taken in the predictive modeling of DOC concentrations in soils, which will increase the applicability of multisurface models to simulate the effects of changing environmental conditions.

TABLE 1 Overview of applications of process based (multi)surface models to natural soil and water systems

	model(s)	system	elements	metal concentration	reactive organic matter	oxide surface	ref
1	NICA-Donnan	lake water, soil solution extracts	Cd, Cu (FMI in lake water, total concentration in soils)	0.43 M HNO_3 (soils)	optimized to fit the data	-	(*45*)
2	WHAM-SCAMP, constant capacitance, Donnan	batch adsorption suspended articulate matter in river water	Co, Ni, Cu, Zn, Sr, Cd, Cs, Eu, Pb	-	soluble OM 50% FA, 50% HA	oxalate Fe, hydroxylamine Mn Si	(*46*)
3	WHAM-SCAMP	river water	Co, Ni, Cu, Zn, Pb	1% v/v HNO_3 (=0.24 M)	DOM:50% FA, 50% inert; POM 50% FA, 50% HA	non filterable Fe and Mn	(*47*)
4	WHAM/Model V	titrations of soil with acid and base 3≤pH≤6	H, Al	0.1 M $CuCl_2$ (Al)	DOM 100%/FA or adjusted amount inert DOM to fit the data	-	(*48*)
5	NICA-Donnan, GTLM, CD-MUSIC, Donnan	soil column DMT	Cd, Cu, Ni, Pb, Zn (prediction FMI)	2 M HNO_3	SOM as HA with estimated site density from CEC (average 31% of generic HA according to (*49*)	HFO = oxalate Fe – org. bound; goethite = DCB – oxalate Fe	(*30*)
6	NICA-Donnan, GTLM, CD-MUSIC, Donnan	soil column DMT	Cd, Cu, Ni, Pb, Zn total concentrations	2 M HNO_3	SOM as in (5); DOM as 30%FA +30%HA or as 65% FA	HFO = oxalate Fe – org. bound; goethite = DCB – oxalate Fe	(*29*)
7	NICA-Donnan, CD-MUSIC, mineral equilibria (Zn/Al)	soil solution extract	Cd, Cu, Pb, Zn total concentrations and FMI	0.43 M HNO_3	SOM as HA with site density derived from CEC; DOM as 50% FA and 50% HA	HFO: 15% of Fe-tot, HMnO: 50% of Mn-tot	(*50*)
8	WHAM/Model VI	pore water organic rich soils	Cd, Cu, Pb, Zn	0.43 M HNO_3	SOM: HS (84% HA, 16% FA) optimized to fit measured pH; DOM as 65% FA	-	(*21*)
9	NICA-Donnan, GTLM, Donnan, mineral equilibria	batch titrations of soils with acid/base (pH 2-12)	Cd, Cu, Ni, Pb, Zn	0.43 M HNO_3	SOM: as HA from measured HS; DOM as 100% HA	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate	(*25*)

TABLE 1 Overview of applications of process based (multi)surface models to natural soil and water systems

	model(s)	system	elements	metal concentration	reactive organic matter	oxide surface	ref
10	NICA-Donnan, mineral equilibria	soil solution extracts	DOM,Al, Cd	0.1 M HCl (Al); Cd added	SOM: as HA from measured HS; DOM as HA (DOM predicted with model)	HFO = 1.7 * oxalate Fe	(*51*)
11	NICA-Donnan, CD-MUSIC, GTLM	titration soils with acid (pH 3-6)	H, Al, Ca, Mg, Cd, Cu, Ni, Zn	0.43 M HNO_3	SOM as HA with 31% site density of generic HA; DOM as 65% FA	HFO = oxalate Fe; crystalline = DCB – oxalate Fe	(*27*)
12	NICA-Donnan, CD-MUSIC, GTLM	pore waters river floodplain	Cd, Cu, Zn, Pb, As, Fe, Mn	Aqua regia	SOM as 30% HA, DOM as 50% FA	HFO and HMnO calculated from solubility	(*52*)
13	WHAM/ Model VI	titrations soils with acid/base (pH 4-8)	H, Al, Ca, Mg, Cd, Cu, Zn	0.22 M HNO_3	SOM: 50% HA + 50% FA; DOM 65% FA	-	(*53*)
14	NICA-Donnan, GTLM, Donnan	soil solution extracts	Cd, Cu, Pb, Zn	0.43 M HNO_3/ EDTA	SOM as HA with 31% site density of generic HA, DOM as 30% FA+ 30% HA	HFO and HAlO calculated from solubility	(*24*) / Ch. 3
15	NICA-Donnan/ SHM, GTLM, Gaines-Thomas	batch titrations	Cd, Cr Cu, Mn, Pb, Zn	EDTA	DOM as 43.5% FA and 43.5% HA, SOM as HA and FA fitted to measured CEC	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate	(*28*)
16	SHM, DLM	column studies	Cd, Cr, Cu, Hg, Ni, Pb, Zn	sequential extraction including EDTA	SOM different estimates for different soils based on literature; DOM as 87% FA	??	(*54*)
17	NICA-Donnan, GTLM, Donnan, mineral equilibria	batch titrations soils with acid/base (pH 2-12)	Cd, Cu, Ni, Pb, Zn, Sn, Cr, Co, Ba, S, As, Se, Sb, Mo, V	0.43 M HNO_3	SOM: as HA from measured HS; DOM as 50% HA	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate	(*3*)
18	NICA-Donnan/ SHM GTLM *	surface water acid mine drainage impacted stream	Cu, Zn	total acid soluble	DOM as 71% FA	HFO and HMO as difference between total acid-soluble and dissolved Fe and Mn	(*55*)
19	NICA-Donnan,	$CaCl_2$ extracts,	Cd, Cu, Ni, Pb,	0.43 M HNO_3	SOM and DOM from	crystalline Fe =	Ch. 4

TABLE 1 Overview of applications of process based (multi)surface models to natural soil and water systems

model(s)	system	elements	metal concentration	reactive organic matter	oxide surface	ref
GTLM, Donnan, mineral equilibria	centrifuged pore water, pH static titrations	Zn, Cr, Co, Ba, As, Se, Sb, Mo, V		measured HS/ SOM and DOM as 50% HA	ascorbate; HFO = dithionite-asc/ oxalate extractable Fe; HAlO = oxalate extractable Al	

NICA = NICA-Donnan model (*37*) for ion binding to organic matter
WHAM = Windermere Humic Acid Model (*39*) for ion binding to organic matter
SHM = Stockholm Humic Model (*56*) largely similar to WHAM except for electrostatics
GTLM = generalized two layer model for HFO (*57*); *parameterization HMnO according to (*58*)
DLM = Double layer model (roughly similar to GTLM)
CD-MUSIC = charge distribution model for ion binding to oxides (*59*)

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Summary

Background

Metals and metalloids (shortly metals) are naturally occurring constituents in the environment. To certain concentration levels, many metals have an essential role for biota but higher levels may lead to phytotoxicological and ecotoxicological effects. In soils the largest stock of these elements is located in the soil solid phase. However, their most important uptake route is via the soil solution. Also migration of metals from soils to ground- and surface waters takes place via the water phase. Solid solution partitioning of metals is, therefore, a key process with respect to the bio-availability and migration of metals in soils. The magnitude of the solid/liquid partitioning and bioavailability of metals is controlled by the different chemical forms (i.e. the speciation) in which they occur in a particular soil. Models for metal transport and uptake, including toxicological risks or deficiencies should thus include partitioning and speciation. Models for metal partitioning can be distinguished in: (i) empirical regression based "partition-relations", which relate the partitioning of elements to soil properties like pH and soil organic matter content and (ii) process based "multisurface models", which describe the various processes and interactions between the soil solution and reactive surfaces by combining separate models for ion-binding to the distinguished reactive surfaces.

This study focuses on the (further) development and critical evaluation of both model approaches and their use in environmental risk assessment studies. The models are evaluated with regard to their performance to predict metal concentrations in the soil solution. Furthermore, their use is demonstrated and evaluated in two risk assessment studies. The following specific research issues are addressed in this study: (i) the implications of the mathematical form of partition relations with respect to their applicability and accuracy; (ii) the extent to which partition relations and multisurface models can be generally applied to predict metal partitioning in soils, and the associated accuracy and limitations; (iii) the effect of natural variability in the composition and metal binding properties of dissolved organic matter on the uncertainty in predicted metal speciation, and (iv) the consequences of the previous questions for the suitability of the use of partition-relations and multisurface models in generic risk assessment studies.

Empirical partition models

Empirically based models for metal partitioning, frequently denoted as "transfer functions" or "partition-relations", relate the partitioning of elements to soil properties. Model coefficients for such relations are generally derived from data obtained from measurements in both the solid phase and a corresponding (extracted) soil solution, using (multiple) linear regression analysis. Empirical "partition-relations" published to date differ with respect to their mathematical form, the optimization method, the methods used to determine metal concentrations in the solid and solution phases and the soil properties that are accounted for. In Chapter 2, these methodological aspects were reviewed with an emphasis on the optimization method. Solid/liquid partitioning data of trace elements in soils have been fitted by relating either a distribution coefficient (Kd-relation) or a Freundlich type coefficient (Kf-relation) to soil properties, or by directly relating solution concentrations to solid phase concentrations and soil properties (C-Q relation) or vice versa (Q-C relation). Furthermore, new transfer functions have been derived that relate free metal ion (FMI) activities to reactive metal contents in the solid phase using a Kf relation. Although functions optimized with respect to the solution concentration (C-Q relation) give the best prediction for solution concentrations, the performance of K_f-relations was only slightly less while this relation is suitable for predicting both concentrations in solution from solid phase concentrations and vice versa. The K_f-relation has been shown to be generally applicable, on the basis of a large number of independent data, for which predicted free metal activities were within one order of magnitude of the observations. The model only over-estimated free metal ion activities at alkaline pH. The use of the reactive metal content measured by 0.43 M HNO_3 rather than the total metal content resulted in a close correlation with measured data, particularly for nickel and zinc.

Multisurface models

The use and practical applicability of a multisurface model to predict solution concentrations of metals was evaluated in Chapter 3. For this evaluation 353 samples have been used, which cover a wide range of soil properties and metal contents. The NICA-Donnan model was used to describe the sorption of cations to solid and dissolved organic matter, a non-specific Donnan type exchange model for the sorption to clay minerals, and a two-site diffuse double layer model for the sorption to metal(hydr)oxides. Calculated solution concentrations have been found to agree well with measured values, except for Pb where concentrations were on average overestimated by one order of magnitude. Relatively large deviations between measured and calculated concentrations have also been found for some highly Zn contaminated samples. This deviation is most likely caused by the presence of Zn containing minerals, included in the total reactive metal content of the soil as determined by acid extraction, and the solubility of which is not properly reflected in the (sorption-based) multisurface model. The study has shown that multi-surface models can be used for practical applications unless the “total reactive metal content” includes a substantial amount of precipitated metals, which may occur in heavily contaminated soils. In such cases, the model tends to overestimate concentrations in solution.

Comparison between partition relations and multisurface models

In Chapter 4 the performance and limitations of "partition-relations" and a "multisurface model" were evaluated for a large set of elements including As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V and Zn. The multisurface model combines thermodynamic models for aqueous speciation and mineral equilibria, models for sorption to particulate and dissolved organic matter (NICA-Donnan model), adsorption to clays (Donnan model) and sorption to Fe/Al-(hydr)oxides (Generalized Two Layer Model, GTLM). Both approaches were evaluated using independent datasets for a wide variety of conditions. The Freundlich-based partition-relations were shown to be robust predictors for most divalent cations of which the empirical parameters are consistent with our present mechanistic picture. The relations were demonstrated to be applicable for soils outside the data set from which they were derived, but within the environmental conditions thereof. The multisurface model, however, did also enable successful prediction of solution concentrations outside the domain of the partition-relations, e.g. at very low and very high pH. Predicted trends for oxy-anions agree well for both approaches but with a larger deviation compared to the cations. Unlike the partition relations for cations, the relations for oxy-anions do not fully comply with our present mechanistic view of their solid/liquid partitioning processes . The results of Chapter 4 enable users to make a deliberate choice of the model type depending on the specific purpose and conditions of the particular study.

Effects of dissolved organic matter variability on predicted metal speciation in soil solution

The Ion binding model NICA-Donnan successfully describes laboratory data of proton and metal binding to purified humic substances (HS). In Chapter 5 the performance of this model was tested in more complex natural systems. The speciation predicted with the model and the associated uncertainty was compared with independent measurements in soil solution extracts, including the free metal ion activity and fulvic (FA) and humic acid (HA) fractions of dissolved organic matter (DOM). Results showed that the DOM composition and the variation in binding properties of HS are potentially important sources of uncertainty. HS fractions of DOM in soil solution extracts varied between 14 and 63% and consisted mainly of FA. Moreover, binding parameters optimized for individual FA samples have been found to show substantial variation.

Monte Carlo simulations have shown that uncertainties in predicted metal speciation, for metals with a high affinity for FA (Cu, Pb) are largely due to the natural variation in binding properties (i.e. the affinity) of FA. Predictions for metals with a lower affinity (Cd) are more prone to uncertainties in the fraction FA in DOM and the maximum site density (i.e. the capacity) of the FA.

Critical loads and target loads of heavy metals

In Chapter 6 approaches were evaluated to calculate acceptable loads of metal deposition to forest ecosystems, distinguishing between critical loads, stand still loads and target loads. Both empirical partition relations and the speciation model WHAM, including Model VI for ion binding to dissolved organic matter, were used for this purpose. To enable the assessment of critical loads, critical limits are required for metals in soil solution. Until recently, critical limits are mostly related to total metal contents, either in the humus layer or the mineral soil, based on NOEC (No Observed Effect Concentrations) data from laboratory studies with plants and soil organisms (soil microbiota and soil invertebrates). This study used dissolved free metal ion (FMI) concentrations as critical limit, which were pH dependent, to account for the effect of pH on bio-availability. The limit was set such that 95% of the considered soil organisms and plants are protected. Using the critical free metal concentration as a function of pH, the corresponding total critical solution concentration, which is needed to calculate a critical load, was then calculated using a the chemical speciation model WHAM Model VI. Evaluation of WHAM Model VI showed that total solution concentrations were predicted from free metal ion concentrations within one order of magnitude. The corresponding critical metal content in the solid phase, which is needed to calculate stand still- and target loads, was calculated with empirical partition-relations. The approach was illustrated by examples of Cd, Cu, Pb and Zn for a deciduous forest on five major soil types in the Netherlands. Stand still loads are generally lower than critical loads, which in turn are lower than the target loads indicating that present levels are below critical levels. Uncertainties in the calculated critical loads are mainly determined by the uncertainty in the critical limits and the chemical speciation model. Including the plant metal cycle i.e. release of metals by litterfall and metal replenishment by plant uptake had a small effect on the calculated critical loads.

Modeling cadmium, copper and zinc accumulation in soils and runoff to surface waters

Cadmium (Cd), copper (Cu) and zinc (Zn) inputs on agricultural land in excess of crop uptake lead to accumulation in soil and runoff to surface waters. In Chapter 7 a regional scale dynamic model was used to evaluate long-term effects of measures to reduce metal inputs by manure and fertilizers on metal concentrations in soils and surface waters in the Netherlands. The regional model uses empirical relations to calculate metal uptake by plants and empirical partitioning-relations to calculate metal leaching. To overcome problems encountered with the application of partition-relations at very low organic matter contents, a new type of partition relation was introduced in which the binding constant is a function of the sum of reactive soil constituents, DOC and pH. Evaluation of the newly derived partition relations on measured pore water concentrations in five soil profiles showed that predictions were within one order of magnitude. Cadmium concentrations were however underpredicted. Calculated groundwater calculations, including the complete model chain from the spatial schematization of soil metal contents in the Netherlands towards the prediction of solution concentrations in groundwater were within one order of magnitude from average measured concentrations of hydrological units in the Netherlands. Dynamic model results show that present metal inputs will increase soil contents by 23-133% and runoff to surface waters by 25-340% after 100 years. Soil contents of Cd, Cu and Zn and surface water concentrations of Cd will not exceed ecological thresholds. The area where concentrations in runoff exceed surface water criteria, however, increases to 20% for Cu and 54% for Zn. A substantial reduction of Cu and Zn in animal food with a total stop of discharge of Cu containing hoof disinfectants is required to reduce soil accumulation and achieve stand-still of metals in runoff to surface waters.

Synthesis

Based on the total findings of this thesis, it is concluded that both empirical partition relations and process based multisurface models to describe metal partitioning and speciation in soils can fulfill specific functional roles in risk assessment studies. The multisurface approach has specific advantages in the development of our understanding of the processes that regulate trace element partitioning and speciation in the complex soil-water system. Empirical partition relations, particularly those for metal cations, have been shown to be robust predictors for solution concentrations, with comparable performance to multisurface models, within the range of conditions for which they were derived. Given their greater simplicity, these models are particularly useful in regional scale applications and in applications to be used by non-specialist users. Multisurface models have been demonstrated to have the advantage of being more widely applicable among soils and environmental conditions, and to provide additional information with respect to the speciation of elements in the solid- and solution phase. This thesis has identified specific gaps in the parameterization, performance and application domain of the investigated models, which have led to recommendations for further model improvement. The process based multisurface approach is thought to have the largest potential for improvement. Given its identification as a major influential input parameter, both types of models would particularly benefit from greater knowledge of the DOC concentrations and composition across soil types, soil horizons, hydrological and climatic conditions

Samenvatting

Evaluatie van modellen voor partitie en speciatie van metalen in bodems en hun gebruik in risicobeoordeling

Achtergrond

Metalen en metalloïden (hier verder met metalen aangeduid) zijn natuurlijk voorkomende elementen in het milieu. Tot een zeker concentratie niveau zijn vele metalen essentieel voor levende organismen (micro-organismen, planten, dieren), maar hogere niveaus zijn mogelijk giftig en kunnen leiden tot gezondheidsproblemen en ecologische effecten. De grootste voorraad metalen in de bodem bevindt zich in de vaste fase van de bodem (klei, organische stof). De belangrijkste opnameroute van metalen door levende organismen is echter via de waterfase van de bodem. Ook het transport van metalen door de bodem en uitspoeling naar grondwater en oppervlaktewater vindt plaats via de waterfase van de bodem. De verdeling van metalen over de vaste fase en de waterfase (vast/vloeistof partitie) van de bodem is daarom een sleutelproces in de biologische beschikbaarheid en mobiliteit van metalen in de bodem. De vast/vloeistof partitie en biobeschikbaarheid worden bepaald door de verschillende chemische vormen (speciatie) waarin metalen in de bodem(oplossing) voorkomen. Modellen voor het berekenen van transport door de bodem en voor het berekenen van metaalopname door organismen, en de als gevolg daarvan optredende tekorten of vergiftiging, moeten daarom modellen voor het berekenen van partitie en speciatie bevatten. Modellen voor vast/vloeistof partitie kunnen onderscheiden worden in: (i) empirische op regressie gebaseerde “partitie-relaties“, die de partitie relateren aan bodemeigenschappen zoals de zuurgraad (pH) en het organische stof gehalte en (ii) op processen gebaseerde “multi-reactieve-oppervlak-modellen” of “multisurface” modellen, die de verschillende processen en interacties tussen de bodemoplossing en meerdere reactieve oppervlakken (klei, organische stof en ijzer- en aluminium-oxiden) beschrijven door combinatie van verschillende modellen voor ion-binding aan de onderscheidden reactieve oppervlakken.

Dit onderzoek richt zich op de (verdere) ontwikkeling en kritische evaluatie van de beide modeltypen en het gebruik daarvan in milieu risico studies. De beide typen modellen zijn geëvalueerd met betrekking tot hun prestaties van het voorspellen van de metaalconcentraties in de bodemoplossing. Daarnaast is het gebruik van de modellen gedemonstreerd en geëvalueerd in twee risico studies. De volgende specifieke onderzoeksonderwerpen komen aan bod in dit onderzoek: (i) de implicaties van de mathematische vorm van de empirische partitie-relaties met betrekking tot hun toepasbaarheid en accuratesse; (ii) de condities waaronder de beide modeltypen generiek toepasbaar zijn voor het voorspellen van metaalpartitie en de daarbij behorende nauwkeurigheid en beperkingen; (iii) het effect van natuurlijke variabiliteit in de samenstelling en metaalbindende eigenschappen van de in de bodemvloeistof aanwezige opgeloste natuurlijke organische stof op de onzekerheid van de met het model voorspelde speciatie; en (iv) de gevolgen van de hiervoor aan de orde gekomen onderwerpen voor de bruikbaarheid van de beide modeltypen in generieke risico studies.

Empirische partitierelaties

Empirisch gebaseerde modellen voor metaalpartitie, die vaak aangeduid worden met de begrippen "transferfuncties" of "partitie-relaties", relateren de vast/vloeistof partitie van de elementen aan bodemeigenschappen. De modelcoëfficiënten van deze relaties worden in het algemeen afgeleid van data met metingen in zowel de vaste fase als de daarbij behorende (geëxtraheerde) bodemoplossing door gebruik te maken van statistische methoden (multiple lineaire regressie). De tot nu toe gepubliceerde empirische partitie-relaties verschillen onderling met betrekking tot de mathematische vorm, de optimalisatie methode, de methoden die gebruikt zijn om de concentraties metalen in de vaste en vloeistoffase te bepalen en de verschillende bodemeigenschappen die in de relaties meegnomen worden. In Hoofdstuk 2 zijn deze methodische aspecten kritisch besproken en geëvalueerd met een nadruk op de optimalisatie methode, Vast/vloeistof partitie data van bodems zijn in verschillende studies gefit door een constante distributiecoëfficiënt (K_d-relatie met een lineaire relatie tussen de concentratie in de vaste fase en de vloeistoffase), een Freundlich-type relatie (K_f-relatie, niet lineair) of door directe relaties tussen concentraties in oplossing (C) en vaste fase concentraties (Q) en bodemeigenschappen (C-Q-relatie) of vice versa door hete relateren van vaste fase concentraties aan concentraties in oplossing en bodemeigenschappen (Q-C-relatie). Optimalisatie voor verschillende grootheden (K_f, C of Q) leidt tot verschillende waarden van de parameters in de afgeleide vergelijkingen. Er zijn nieuwe partitierelaties afgeleid die vrije metaal concentraties van cadmium (Cd), koper (Cu), nikkel (Ni), lood (Pb) en zink (Zn) relateren aan het reactieve gehalte van metalen in de vaste fase door middel van een K_f-relatie. Alhoewel relaties die geoptimaliseerd zijn met betrekking tot de concentratie in oplossing (C-Q) de beste voorspelling geven van de concentratie in oplossing was de prestatie van de afgeleide K_f-relaties slechts iets minder terwijl deze relatie zowel geschikt is om concentraties in oplossing te voorspellen op basis van concentraties in de vaste fase en vice versa. De goede resultaten van de K_f-relatie in het voorspellen van vrije metaalconcentraties voor een groot aantal onafhankelijke data, waarbij de voorspelde waarde binnen een orde van grootte (factor 10) van de gemeten waarde lag, laten zien dat deze relaties algemeen toepasbaar zijn. De partitierelaties gaven alleen een overschatting te zien van de vrije metaalconcentraties bij hoge pH (pH>7). Het gebruik van de reactieve metaal concentratie gemeten met 0.43 M HNO_3 in plaats van het totaalgehalte metalen leidde tot een goede correlatie met gemeten waarden, in het bijzonder voor nikkel en zink.

Multisurface modellen

Het gebruik en de praktische toepasbaarheid van een multisurface model om de concentraties van metalen in oplossing te voorspellen is geëvalueerd in Hoofdstuk 3. Voor deze evaluatie is gebruik gemaakt van data van 353 monsters die een brede range omvatten van bodemeigenschappen en metaalconcentraties. Het NICA-Donnan model is gebruikt om de sorptie van metalen aan de vaste en opgeloste organische stof te beschrijven, een ion aspecifiek Donnan model is gebruikt voor de binding aan kleimineralen en voor de binding van metalen aan aluminium en ijzer(hydr)oxiden is het oppervlakte complexatie model (GTLM) van Dzombak en Morel gebruikt. De voorspelde concentraties kwamen goed overeen met metingen, behalve voor lood waarvoor de concentraties met een orde van grootte overschat werden. Verder werden relatief hoge afwijkingen gevonden voor een aantal monsters met hoge zink concentraties. Deze afwijking is waarschijnlijk het gevolg van de aanwezigheid van zinkhoudende mineralen, die geëxtraheerd worden met de zure 0.43 M HNO_3 extractie voor de bepaling van het reactieve metaalgehalte maar waarvan de oplosbaarheid niet goed gemodelleerd wordt door het op sorptie gebaseerde multisurface model. Deze studie heeft aangetoond dat multisurface modellen gebruikt kunnen worden voor praktische toepassingen zolang het totale reactieve metaalgehalte geen substantiële hoeveelheid geprecipiteerde metalen bevat, die voorkomen in zwaar verontreinigde bodems. In dergelijke gevallen is de kans groot dat het model de concentraties overschat.

Vergelijking tussen partitierelaties en multisurfacemodellen

In Hoofdstuk 4 zijn de prestaties en beperkingen van partitierelaties en een multisurface model geëvalueerd voor een uitgebreide set elementen: arseen (As), barium (Ba), cadmium (Cd), kobalt (Co), chroom (Cr), koper (Cu), molybdeen (Mo), nikkel (Ni), lood (Pb), antimoon (Sb), seleen (Se), vanadium (V), en zink (Zn). Het multisurface model combineert thermodynamische modellen voor speciatie in oplossing en oplosbaarheid van mineralen met modellen voor sorptie aan vaste en opgeloste organische stof (NICA-Donnan model), sorptie aan kleimineralen (Donnan model) en sorptie aan Fe/Al-(hydr)oxiden (GTLM). Beide model methoden zijn geëvalueerd met onafhankelijke datasets met daarin een brede variatie in omstandigheden (bodemeigenschappen, zuurgraad, metaalconcentratie). De Freundlich-type partitierelaties bleken robuuste voorspellers voor de meeste divalente kationen waarbij de afgeleide empirische coëfficiënten consistent waren met ons mechanistische beeld. De partitierelaties bleken toepasbaar te zijn op bodems die geen deel uitmaakten van de set waarop de partitierelaties afgeleid zijn, mits binnen de omgevingsfactoren (zoals pH) daarvan gebleven werd. Het multisurface model maakte ook succesvolle voorspellingen mogelijk buiten het domein van de partitierelaties zoals bij zeer lage en zeer hoge pH. De voorspelde trends van de concentraties oxy-anionen komen goed overeen bij beide methoden maar wel met een grotere spreiding dan bij de kationen. Anders dan bij de partitierelaties voor kationen komen de relaties voor oxy-anionen niet geheel overeen met ons huidige beeld van hun vast-vloeistof partitieprocessen. De resultaten van Hoofdstuk 4 maken het mogelijk voor de gebruikers van dergelijke modellen een weloverwogen keuze tussen de modeltypen te maken afhankelijk van de specifieke doelstellingen en omstandigheden van de studie.

Effecten van de variabiliteit van opgeloste organische stof op de voorspelde metaalspeciatie in oplossing.

Het NICA-Donnan model voor ion-sorptie aan organische stof is in staat gebleken laboratoriumdata van de binding van protonen en metalen aan gezuiverde humeuze stoffen (HS) goed te beschrijven. In Hoofdstuk 5 zijn de prestaties van dit model in meer complexe natuurlijke systemen getest. De met het model voorspelde speciatie en de daar bijbehorende onzekerheid zijn vergeleken met onafhankelijke metingen in bodemextracten van de vrije metaalconcentratie en de fulvo- (FA) en humus-zuur (HA) fracties (samen HS) van de opgeloste organische stof (DOM). De resultaten lieten zien dat de samenstelling van DOM en de variatie in bindingseigenschappen van HS potentieel belangrijke bronnen zijn van de onzekerheid. HS fracties in DOM van bodemextracten varieerde tussen de 14 en 63% en bestonden voornamelijk uit FA. Daarnaast bleken de bindingsparameters zoals deze waren geoptimaliseerd voor individuele FA monsters een substantiële variatie te vertonen. Monte Carlo simulaties lieten zien dat de onzekerheden in de voorspelde metaalspeciatie voor metalen met een hoge affiniteit voor FA (Cu en Pb) voornamelijk het gevolg zijn van de natuurlijke variatie in bindingseigenschappen (de affiniteit) van FA. Voorspellingen voor metalen met een lagere affiniteit (Cd) zijn met name gevoelig voor de onzekerheid in de fractie FA in DOM en de totale bindingscapaciteit (de capaciteit) van FA.

Kritische belasting en streef-belasting van zware metalen

In Hoofdstuk 6 zijn methodes geëvalueerd voor het berekenen van de acceptabele belasting van bos-ecosystemen met depositie van zware metalen. Hierbij is een onderscheid gemaakt tussen kritische belasting, stand-still belasting (belasting waarbij geen verandering optreed in de concentratie van metalen in de bodem) en streefbelasting. Voor het berekenen hiervan zijn zowel empirische partitierelaties als het speciatie model WHAM, met daarin het procesgebaseerde Model VI voor ion-sorptie aan opgeloste organische stof gebruikt. Het uitgangspunt voor het bepalen van een acceptabele belasting is een kritische metaalconcentratie in de bodemoplossing. Tot op heden werden kritische niveaus echter in het algemeen gerelateerd aan totaalconcentraties in de vaste fase van of de strooisellaag of de minerale grond. Deze kritische concentraties zijn gebaseerd op NOEC (hoogste concentratie waarbij nog geen effect meetbaar is) data uit laboratorium studies met planten en bodemorganismen (micro-organismen en invertebraten). In deze studie is als kritisch niveau gebruik gemaakt van de vrije ion concentratie van metalen in oplossing, in afhankelijkheid van de zuurgraad (pH) om de effecten van de pH op de beschikbaarheid van de metalen te verdisconteren. De kritische niveaus zijn zo gekozen dat 95% van de bodemorganismen en planten beschermd zijn. Om de kritische belasting te berekenen behorend bij een bepaalde kritische vrije metaal concentratie moet eerst de corresponderende totaalconcentratie berekend worden. Hiervoor is gebruik gemaakt van het chemische speciatiemodel WHAM Model VI. Evaluatie van WHAM Model VI liet zien dat uit de vrije metaal concentratie berekende totaalconcentraties binnen één grootteorde correct werden voorspeld. De met de vrije metaal concentratie corresponderende totaalconcentraties in de vaste fase, die nodig zijn voor het berekenen van stand-still en streef belastingen, zijn berekend met empirische partitierelaties. De aanpak is geïllustreerd met voorbeelden van berekeningen voor de metalen Cd, Cu, Pb en Zn voor een loofbos op de vijf belangrijkste bodemtypen in Nederland. Berekende stand-still belastingen waren in het algemeen lager dan kritische belastingen die weer lager waren dan streef belastingen wat aangeeft dat de huidige belastingen beneden de kritische belastingen liggen. Onzekerheden in de berekende kritische belasting zijn met name het gevolg van de onzekerheid in de kritische metaalconcentraties en van het chemische speciatiemodel. Het meenemen van de plant-metaal cyclus, bestaande uit het vrijkomen van metalen door bladval en de aanvulling daarvan door gewasopname, had maar een klein effect op de berekende kritische concentraties.

De modellering van cadmium, koper en zink accumulatie in bodems en uitspoeling naar oppervlaktewater.

Cadmium (Cd), koper (Cu) en zink (Zn) belasting van landbouwgronden groter dan de gewasopname daarvan leidt tot accumulatie in de bodem en uitspoeling naar oppervlaktewater. In Hoofdstuk 7 is gebruik gemaakt van een dynamisch model voor de regionale schaal voor de evaluatie van lange termijn effecten van maatregelen, die de metaalbelasting van landbouwgronden door mest en kunstmest toediening beperken, op de concentraties van metalen in de bodem en uitspoeling naar het oppervlaktewater. In het regionale model worden empirische relaties gebruikt voor het berekenen van de metaalopname door planten en empirische partitierelaties voor de berekening van de metaaluitspoeling. Vanwege problemen bij het gebruik van de eerder ontwikkelde partitierelaties bij zeer lage gehalten organische stof, zijn nieuwe partitierelaties ontwikkeld waarin de bindingsconstante een functie is van de som van de reactieve bodembestanddelen (organische stof, Al/Fe-(hydr)oxiden en klei), DOC en pH. De evaluatie van deze nieuw afgeleide relaties op gemeten bodemvochtconcentraties laat zien dat de voorspelde concentraties binnen een orde van grootte kloppen met gemeten concentraties. De voorspelde concentraties Cd waren echter te laag. Berekende grondwaterconcentraties, berekend op basis van de gehele modelketen uitgaande van de ruimtelijke schematisatie van metaalgehalten in de bodem van Nederland, zijn binnen een grootteorde gelijk aan de gemiddelde gemeten grondwaterconcentraties van hydrologische eenheden in Nederland. Dynamische model voorspellingen laten zien dat de huidige belasting met metalen leidt tot een verhoging van de bodemgehalten (in de bouwvoor) met 23-133% en een verhoging van de uitspoeling met 25-340% in 100 jaar. De bodemgehalten van Cd, Cu en Zn en de concentratie in uitspoeling zullen in die 100 jaar geen ecologische limieten overschrijden. Het oppervlak van bodems waarin de concentratie in uitspoeling de oppervlaktewater criteria overschrijden stijgen tot 20% voor Cu en 54% voor Zn. Om bodemaccumulatie en een toename in uitspoeling te stoppen is een substantiële reductie vereist van Cu en Zn in diervoeders en supplementen en een totale stop van de afvoer van koperbevattende hoefontsmettingsmiddelen

Synthese

Gebaseerd op de bevindingen van deze thesis kan worden geconcludeerd dat zowel empirische partitierelaties als procesgebaseerde multisurface modellen voor de beschrijving van partitie en speciatie in de bodem een specifieke rol kunnen spelen in risicostudies. Multisurface modellen hebben specifieke voordelen in de ontwikkeling van onze kennis van de processen die de partitie en speciatie van sporenelementen bepalen in het complexe bodem-water systeem. Empirische partitierelaties, met name die voor metaal kationen, zijn robuuste voorspellers gebleken van elementconcentraties in oplossing met een vergelijkbare prestatie als die van de mulstisurface modellen, zolang binnen de grenzen gebleven wordt van de omstandigheden waaronder de relaties zijn afgeleid. Vanwege hun sterke vereenvoudiging zijn partitierelaties bij uitstek bruikbaar in toepassingen op regionale schaal en in toepassingen anders dan door experts. De aangetoonde voordelen van multisurface modellen zijn hun bredere toepasbaarheid voor verschillende bodems en omgevingsfactoren. Daarnaast voorzien deze modellen in aanvullende informatie over de speciatie van de elementen in de vaste- en vloeistoffase van de bodem. In dit proefschrift zijn lacunes geïdentificeerd in de parameterisatie, prestatie en toepasbaarheid van de onderzochte modellen. Op basis hiervan zijn aanbevelingen geformuleerd voor modelverbetering. Hierbij wordt de grootste potentie voor verbetering gezien voor multisurface modellen. Op basis van het feit dat DOC een zeer belangrijke input parameter is, zullen beide typen modellen profiteren van een betere kennis betreft de concentratie en samenstelling van DOC voor verschillende bodemtypen, bodemhorizonten, hydrologische en klimatologische condities.

Curriculum Vitae

Jan Engelbert (Bert-Jan) Groenenberg was born in Oppenhuizen (municipality Súdwest Fryslân) on 31 July 1961. He attended the middle school (HAVO) at the "Scholengemeenschap Johannes Calvijn" in Rotterdam. In 1980-1981 he did the propaedeuse at the "Rijks Hogere Landbouwschool" in Groningen. After that year he started his study Environmental Sciences at the "Landbouwhogeschool Wageningen", which he finished in 1988 at "Wageningen Agricultural University" with majors in soil pollution and hygiene, colloid chemistry and a minor in mathematics. After working some months as an assistant at the practical training for physical chemistry he started as a researcher at the Winand Staring Centre, one of the precursors of Alterra, working on the modeling of chemical processes in acid sulfate soils. Thereafter he worked mainly on integrated soil-plant-atmosphere models to study the effects of atmospheric nitrogen and sulfur deposition. The last 10 years he worked mainly on risk assessment and the modeling of trace metal chemistry and transport in soils.

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