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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 contents 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 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.

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 (Thakali *et al*., 2006) 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 (Minnich *et al*., 1987; Sauvé *et al*., 1998a; Vulkan *et al*., 2000).

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 transfer functions which predict total solution concentrations or FMI activity from soil properties (Gerritse & van Driel, 1984; Sauvé *et al*., 1997a,b, 1998a, 2000). Compared with mechanistic models transfer functions require fewer input data and because no iterations are needed, they use far less computing time. They are, therefore, particularly suitable in large-scale applications (De Vries *et al*., 1998; Groenenberg *et al*., 2006; Bonten *et al*., 2008b; De Vries *et al*., 2008) and/or when limited data are available. Transfer functions were used because of limited data by Lofts *et al*. (2004) and

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De Vries *et al.* (2007) to derive FMI-based critical limits from published toxicity experiments. These studies modelled 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) (Weng *et al.*, 2001a; Cances *et al.*, 2003; Dijkstra *et al.*, 2004; Bonten *et al.*, 2008a). Although such mechanistic models are very promising, the use of empirical models can be favoured 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 Boekhold *et al.* (1993) for cadmium (Cd) and Vulkan *et al.* (2000) for copper (Cu), and/or soil properties, for example Tipping *et al.* (2003) for organic soils. Experimental and methodological approaches in these studies differ widely in terms of:

1. extraction of soil solution; methods include dilute salt extractions (Sauvé *et al.*, 1997a,b, 1998a) and *in situ* solution sampling (rhizon samplers used by Tipping *et al.*, 2003);
2. extraction of metals in the solid phase, with methods ranging from pseudo-total content determination using *aqua regia* (Vulkan *et al.*, 2000) or nitric acid digestion (Sauvé *et al.*, 1997a,b, 1998b) to reactive content determination using 0.43 M HNO_3 (Tipping *et al.*, 2003);
3. the use of sorption (e.g. Elzinga *et al.*, 1999) versus desorption data (Sauvé *et al.*, 1997a,b, 1998b; Tipping *et al.*, 2003);
4. the soil and soil solution properties accounted for, which range from pH only (Sauvé *et al.*, 2000) to a combination of pH, SOM, clay, (hydr)oxides and dissolved organic carbon (DOC) (Janssen *et al.*, 1997);
5. the defined variable of the model, which varies from solution concentration (Sauvé *et al.*, 1997a,b, 1998a) or solid phase concentration (Elzinga *et al.*, 1999) to sorption constants such as K_d (Tipping *et al.*, 2003) and K_f (Tye *et al.*, 2004); and
6. transfer functions for total solution concentrations (e.g. Janssen *et al.*, 1997) compared with FMI activities in solution (Sauvé *et al.* 1997a,b, 1998a).

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 overview 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 zinc (Zn). Three different regression equations are used to derive transfer functions. The ability of these equations to predict solid and solution phase metals is tested against several independent datasets.

Review of relevant methodology

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:

$$K_d = \mathrm{Q/C}, \tag{1}$$

where K_d = distribution constant (litre kg^{-1}), Q = metal concentration in the solid phase (mol kg^{-1}) and C = metal concentration in the solution phase (mol litre^{-1}). The K_d values can vary over several orders of magnitude for a given metal as a function of soil properties (Allison & Allison, 2005). Therefore several authors have related K_d to soil and soil solution properties (X_i) according to:

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

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 (Gerritse & van Driel, 1984) to a combination of clay content, cation exchange capacity, organic carbon content, dithionite-extractable iron (Fe) and aluminium (Al), and oxalate-extractable manganese (Mn) contents (Anderson & Christensen, 1988; Janssen *et al.*, 1997).

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 (Sposito, 1989):

$$Q = K_f C^n, \tag{3}$$

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 (Boekhold *et al.*, 1993), pH and SOM (Sauvé *et al.*, 1997a,b, 1998a, 2000), 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.* (1999) for Cd, Zn and Cu. Tye *et al.* (2003) have derived $C-Q$ relations for FMI activities of Cd and Zn; Sauvé *et al.* (1997a,b, 2000) 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 $C-Q$, $Q-C$ 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.* (2004) and Tye *et al.* (2004). Römkens *et al.* (2004) optimized n and simultaneously regressed K_f against soil properties while minimizing the error in K_f whereas Tye *et al.* (2004) 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 (Elzinga *et al.*, 1999). 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 (Van Huffel & Lemmerling, 2002). In the present study we derive transfer functions using $C-Q$, K_f and TLS relations and compare the resulting functions.

Choice of experimental conditions and extractions

Several studies have shown hysteresis between sorption and desorption isotherms for metals (Selim & Amacher, 2001 for Cu; Carrilo Gonzalez *et al.*, 2005 for Zn). Hysteresis in batch studies may result from kinetic retention behaviour (Comans, 1987) 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 (Buekers *et al.*, 2007). 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 (Comans, 1987; Smolders *et al.*, 1999) 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 (Young *et al.*, 2000). 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 (Gooddy *et al.*, 1995; Temminghoff *et al.*, 1997; Cances *et al.*, 2003). Good agreement between metal extractions with EDTA and with 0.43 M HNO_3 has been shown by Tipping *et al.* (2003) for organic soils (>10% SOM), and by Groenenberg *et al.* (2003) and De Vries *et al.* (2005) for a large range of forest and agricultural soils. With the metal extraction with 0.43 M HNO_3 as input, Dijkstra *et al.* (2004) obtained good geochemical modelling predictions of soil solution concentrations (for Cd, Cu, Pb, Zn and Ni) from batch experiments ranging in pH from 2 to 12 using their multisurface model. In our study we therefore use the results of extractions with 0.43 M HNO_3 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 (Fest *et al.*, 2008). 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 (Bolt & Bruggenwert, 1976), and (ii) solutions obtained from soils at field capacity by centrifuging or sampling with Rhizons (small-scale tension lysimeters).

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 (McBride, 1994; Selim & Amacher, 2001). For metals such as Cd and Zn, pH appears to be the most important explanatory variable (e.g. Anderson & Christensen, 1988; Ma & Lindsay, 1993; Salam & Helmke, 1998; Sauvé *et al*., 2000). Organic matter appears to be the most dominant metal-sorbing constituent in soils for Cd (Gerritse & van Driel, 1984; Hooda & Alloway, 1998) and Cu (Temminghoff *et al*., 1997). Recently the dominant role of organic matter in the binding of copper was confirmed by Strawn & Baker (2008) using X-ray absorption near-edge, and extended X-ray absorption fine-structure, spectroscopy studies. The results of mechanistic multisurface models (Weng *et al*., 2001a; Cances *et al*., 2003; Dijkstra *et al*., 2004; Bonten *et al*., 2008a) also show that organic matter is the most important metal sorbent in soils. Furthermore, ionic strength has been shown to influence metal partitioning (e.g. Shuman, 1986; Naidu *et al*., 1994) because of competition with other cations and complexation with anions (for example Cl^-) and effects on DOM concentration (Römkens & Dolfing, 1998).

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.

Materials and methods used for the derivation of transfer functions

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*. (1998) and Römkens *et al*. (2004). 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 (Römkens *et al*., 2004) 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 contents 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 (Tipping *et al*., 2003) 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 contents of the three datasets are summarized in Table 1.

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 3 weeks at 5°C (Houba & Novozamsky, 1998). Thereafter, pore-water was obtained by centrifugation at 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 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 2 days at room temperature, after which the pore-water was extracted overnight 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 0.5–1 and 1.5–2 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

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

Dataset (number)		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

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 м $CaCl_2$	1:2	NL1	49	ICP-AES	FIA
0.01 м $CaCl_2$	1:4	NL1, NL2	118	ICP-MS	–
0.002 м $Ca(NO_3)_2$	1:2	NL1, NL2	187	ICP-AES	–
0.002 м $Ca(NO_3)_2$ + nitric acid	1:2	NL2	276 (two pH values)	ICP-AES	–
0.002 м $Ca(NO_3)_2$	1:2 DMT	NL1	23	ICP-MS	–

Table 3 Datasets 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 (loss on ignition)	LOI	LOI
Total metal	Nitric acid and perchloric acid digestion	*aqua regia*	*aqua regia*
Reactive metal	0.43 м HNO_3 (1 g: 10 ml); 0.1 м Na_2EDTA (1 g: 10 ml)	0.43 м HNO_3, 0.05 м Na_2EDTA	0.43 м HNO_3, 0.05 м 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 µm) and acidified: ICP-MS	Filtered (0.45 µm) and acidified: Cd, Ni, Pb GF-AAS; Cu, Zn Flame-AAS; Major cations ICP-AES	Filtered (0.45 µm) 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.

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 for 48 hours. Thereafter, the solutions were allowed to settle in the centrifuge tubes and after 1 hour, the pH was measured in the tube directly before filtration. The supernatant-soil mixture was centrifuged at 2500 ***g*** 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 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*. (2001b) to determine the FMI activities in a 0.002 м $CaCl_2$ 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 м $CaCl_2$ extract (1:2 soil to solution ratio) for all the horizons using a batch procedure developed by van Zomeren & Comans (2007).

Speciation modelling

Speciation modelling 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 WHAM/Model VI, which is parameterized for fulvic and humic acids from an extensive set of experimental data (Tipping, 2002). For Al and Fe(III) we used the revised parameter values from Tipping *et al*. (2002). 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 м $CaCl_2$ extracts from three soil profiles of NL1, we modelled 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 (Tipping *et al*., 2002): therefore the measured Al and Fe concentrations were used for samples that 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.

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).

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 (Temminghoff *et al*., 2000), ion- selective electrodes (Vulkan *et al*., 2000) and differential pulse anodic stripping voltammetry (Sauvé *et al*., 1997a). Different methods to obtain the soil solution were also used among the studies (see Table 4). If available, the reactive metal content was used in the calculation but datasets with only measurements of the total metal content (measured with strong acid extractions) were also used. Although relationships between reactive and total metal concentrations have been derived (De Vries *et al*., 2005), 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.

Results and discussion

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.

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 DMT (Temminghoff *et al*., 2000) and with sufficient data to perform the speciation calculations. We used data from Weng *et al*. (2001b) for 32 of the 49 samples of dataset NL1, Pampura *et al*. (2006, 2007), including O and B horizons of forest soils, Koopmans *et al*. (2008) and unpublished results of J. E. Groenenberg. 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 an 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 (Temminghoff *et al*., 2000). 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.

Transfer functions

Transfer functions for the combined datasets NL1, NL2 and UK were derived with different regression models using measured (if available) or modelled 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

Table 4 Overview of data used for validation of transfer functions and numbers of samples within the datasets (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	Gooddy *et al*. (1995)
Cu	*aqua regia*	Rhizon samplers	Cu-ISE	22	Cu contaminated soils: UK, Chile and China	Vulkan *et al*. (2000)
Cd, Cu, Pb and Zn	*aqua regia*	Centrifugation rewetted soils	DMT	27	Agricultural soils Australia and contaminated soils Australia and US	Nolan *et al*. (2003)
Cd	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	61	Contaminated agricultural and urban soils: US and Canada	Sauvé *et al*. (2000)
Pb	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	84	Contaminated agricultural and urban soils: US and Canada	Sauvé *et al*. (1997a)
Zn	HNO_3 digestion	0.01 M KNO_3 extract	DPASV	66	Contaminated soils: North America and Europe	Stephan *et al*. (2008)
Cu	HNO_3 digestion	0.01 M $CaCl_2$ extract	Cu-ISE	68	Contaminated soils: US, Canada and Denmark	Sauvé *et al*., (1997b)
Cd, Cu, Ni, Pb, Zn	2 M HNO_3	Percolation 0.002 M $Ca(NO_3)_2$	SC-DMT	26	Sandy, agricultural soil: Netherlands	Weng *et al*. (2001a)
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*. (2003)
Cd, Cu, Ni, Pb	0.43 M HNO_3	Percolation 0.002 M $Ca(NO_3)_2$	DMT (Cu-ISE)	19	Contaminated forest soils (smelter) including organic horizon: Russia	Pampura *et al*. (2006, 2007)
Cd, Pb	0.43 M HNO_3	Water extract/lysimeter	WHAM	33	Forest soils: Germany/contaminated forest soils: Russia	Pampura *et al*. (2007)
Cd, Cu, Pb, Zn	0.43 M HNO_3	Percolation 0.002 M $Ca(NO_3)_2$	DMT	27	Contaminated soil (smelter): France	Cances *et al*. (2003)
Cd, Pb, Zn	0.43 M HNO_3	0.002, 0.01 and 0.05 M $Ca(NO_3)_2$ extractions at three different Ph	WHAM	126	Agricultural soils, different pH levels by addition of HNO_3: Hungary,	Murányi *et al*. (2003)
Cd,Cu, Ni,Pb, Zn	0.05 M EDTA	Rhizon samplers	WHAM	56	Soils from different land uses: UK	Shotbolt & Ashmore (2004)
Cd, Cu, Pb, Zn	0.02 M EDTA/NH_4Ac	Water extracts (1:10)	WHAM	225	Forest soils: Switzerland	J. 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.* (2008)
Cd, Cu, Ni, Pb, Zn	0.43 M HNO_3	0.002 M $CaCl_2$ extract (1:10)	DMT	4	Contaminated soils	J.E. Groenenberg, unpublished data

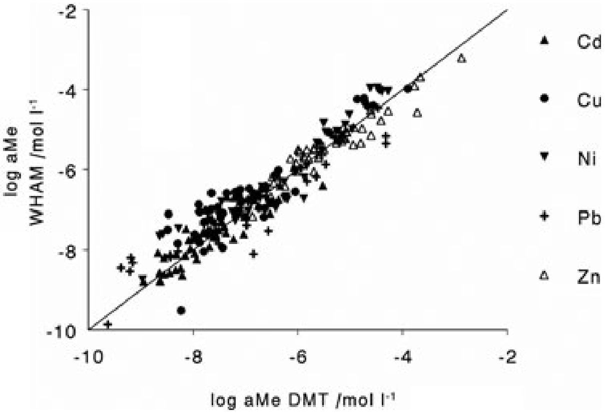

Figure 1 FMI activities calculated with WHAM/Model VI compared with DMT measurements.

Table 5 Summary of parameters for the performance of WHAM speciation calculations, as compared with 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

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

in Tables 6–8 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 larger, 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 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 (2005) 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 ($\gg 1$ 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 (Amery *et al.*, 2007) and the use of different soil solution ratios (Fest *et al.*, 2008), 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.

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

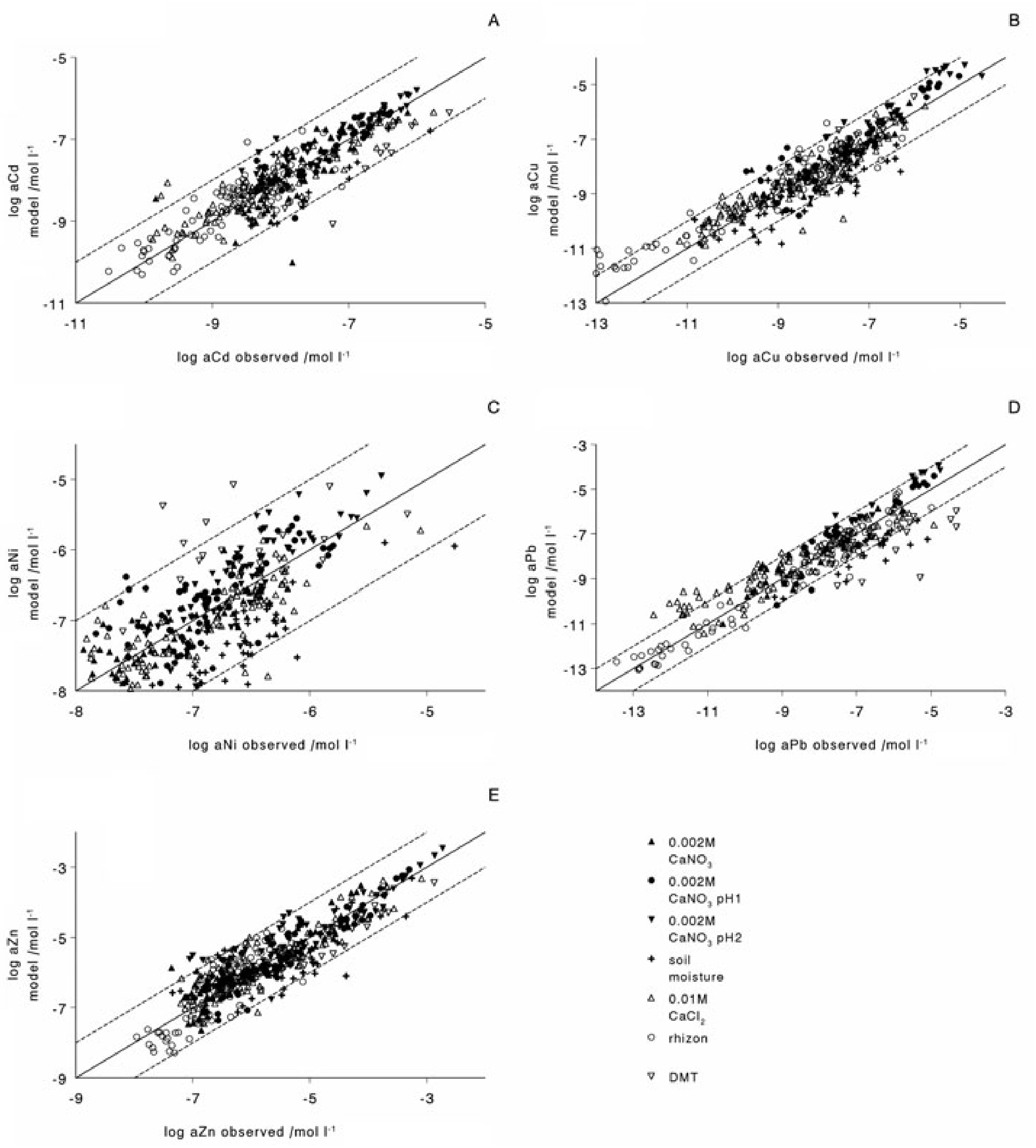

Figure 2 FMI activities predicted with K_f transfer functions compared with FMI activities calculated with WHAM or measured with DMT for Cd (a), Cu (b), Ni (c), Pb (d) and Zn (e) . The solid line indicates a 1:1 fit; dotted lines give one order of magnitude deviation.

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, with neither C nor Q being optimized, results showed a bias for the optimization of solid phase concentrations. We think that this can be explained by

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

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 modelling of soils subjected to varying inputs of metals, and for the calculation of metal leaching from soils.

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 that 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 datasets NL1 and NL2 has been confirmed by Bonten *et al.* (2008a) by calculations with their mechanistic multisurface model.

pH dependence of metal binding

As a result of analysing 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 equalled the negative value of the ratio of the pH coefficient in the K_f relation (γ_2) and the Freundlich exponent (n):

$$\frac{\Delta \log_{10} a_{Me}}{\Delta pH} = -\frac{\gamma_2}{n}. \tag{7}$$

According to van Riemsdijk *et al.* (2006), 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

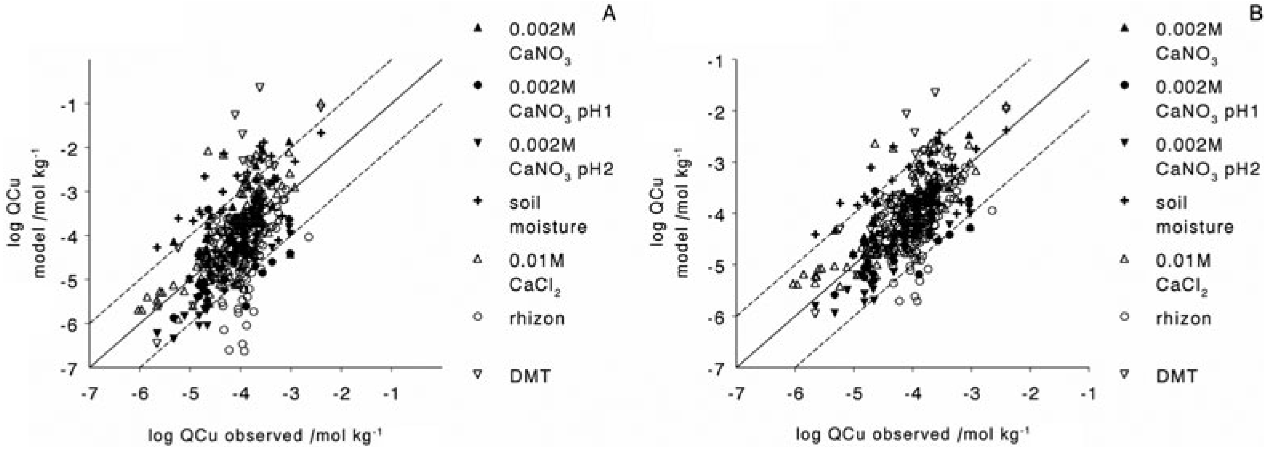

Figure 3 Solid phase concentrations predicted with the C-Q (a) and the K_f relation (b). The solid line indicates a 1:1 fit; dotted lines give one order of magnitude deviation.

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*. (2004), obtained over a wider range of pH values, can give more information on the pH response for individual soils.

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 $\leq$ 1), which is comparable with 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 to 1.2) appear to be larger than those calculated with a multi-surface model (Weng *et al*., 2002a) for a small dataset with just one type of soil (RMSE ranging from 0.3 to 0.9). Errors in predictions with WHAM/Model VI for the whole UK dataset (Tipping *et al*., 2003) were within one order of magnitude, comparable with 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 that was used to obtain the data from which the transfer functions were derived.

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 dataset of Sauvé *et al*. (2000). The over-estimation of Cd^{2+} activities in the data from Sauvé *et al*. 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 (Sauvé *et al*., 1997b; Vulkan *et al*., 2000; Murányi *et al*., 2003) and DMT (Weng *et al*., 2001b; Pampura *et al*., 2006, 2007). Some points (9 out of 302 of measured Cu FMI activity) showed a larger deviation ($\gg 1$). These are almost exclusively free Cu activities measured with DMT by Nolan *et al*. (2003) at pH 6 and greater. According to Nolan *et al*. (2003), predictions with WHAM for alkaline soil solutions ($7.5 < pH < 8.5$) were one to four orders smaller than that measured with DMT. This mismatch between model calculations and measurements contradicts the good agreement found by Vulkan *et al*. (2000) 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 complexing 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 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 4f). For the measured data this is mainly the result of the large over-prediction of the data from Weng *et al*. (2002b), who used a stronger 2 M HNO_3 extraction. Differences between extractions were particularly large for Ni: we found for datasets 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

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

	Fit of transfer function based on measured free ion activities				Fit of transfer function based on modelled free ion activities			
Metal	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

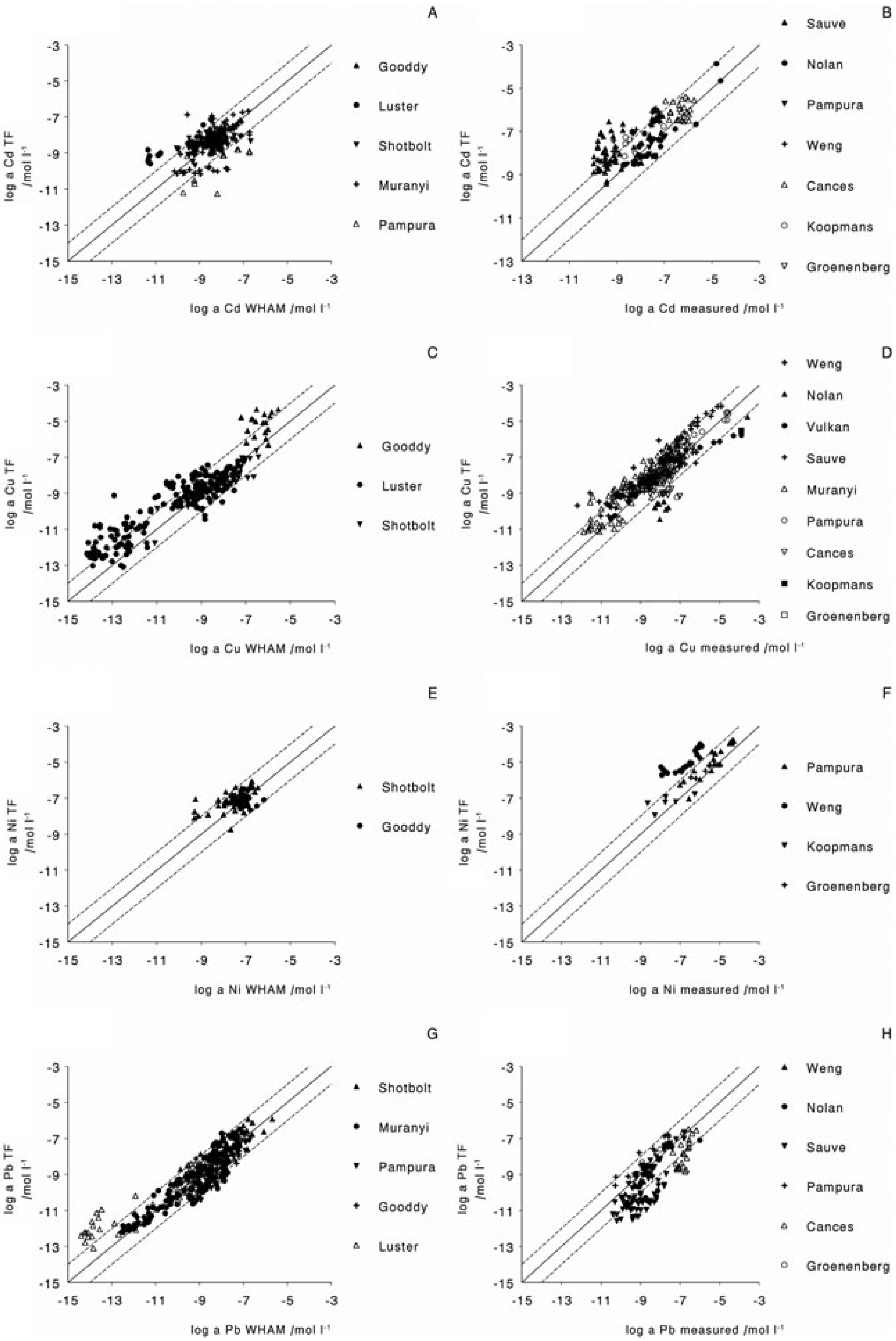

Figure 4 FMI activities predicted with the K_f transfer functions compared with WHAM predictions (left) or measurements (right) for Cd (a,b), Cu (c,d), Ni (e,f), Pb (g,h) and Zn (i,j).

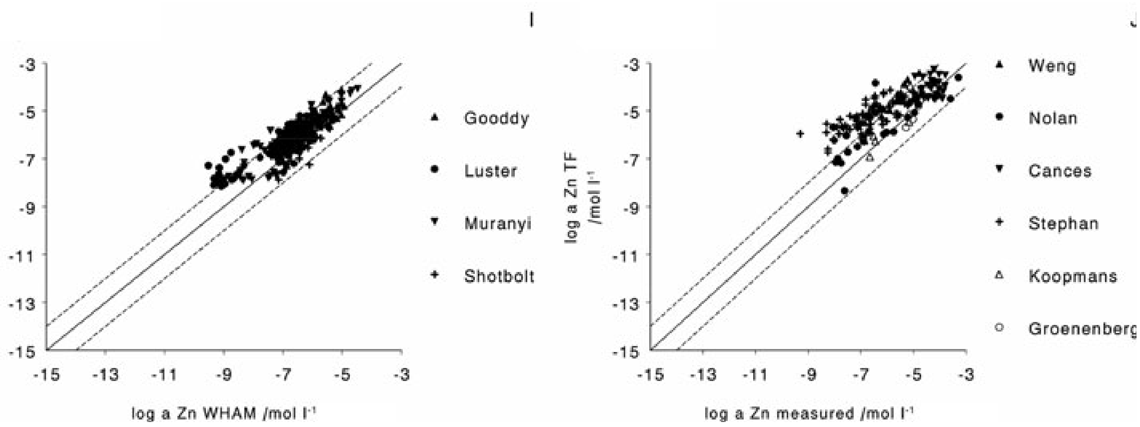

Figure 4 Continued

(Figure 4g,h). 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 > 7 and containing carbonate. For most soils containing solid calcium carbonate, solution concentrations were below the detection limit of the ICP-MS (<0.04 μg litre^{-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.* (1997a). According to Ge *et al.* (2005), who have modelled the solution speciation of the data from Sauvé *et al.* (1997a) and calculated smaller FMI activities with WinHumic V than were measured, this discrepancy may result from an over-estimation 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 shows 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 datasets with strong extractants to determine soil metal contents, for example Stephan *et al.* (2008), who used a nitric acid digestion, Weng *et al.* (2002a), who used 2 M HNO_3, and Nolan *et al.* (2003), 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 datasets in which 0.43 M HNO_3 was used we did not observe this over-prediction of FMI activities.

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 content using transfer functions that 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 modelling 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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