Validation of transfer functions predicting Cd and Pb free metal ion activity in soil solution as a function of soil characteristics and reactive metal content.

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Abstract

According to recent insight, the toxicity of metals in soils is better related to the free metal ion (FMI) activity in the soil solution than to the total metal concentration in soil. However, the determination of FMI activities in soil solution is a difficult and time-consuming task. An alternative is to use empirical equations (so called transfer functions (TFs)) that relate FMI activity in solution to the reactive metal concentration in the solid phase and to soil properties (pH and organic matter content). Here we test the applicability of two sets of TF for Cd and Pb using independent data from a wide range of soil types and regions that are not represented in the datasets used to derive the TFs. From these soils, soil solution was extracted using four different methods. For all these extracts, FMI

activities were calculated from total concentrations in solution using the speciation program WHAM VI. In some of the soils, Cd and Pb FMI activities were also measured using a Donnan membrane technique. Most of these FMI activities deviated from the TF predictions by less than one order of magnitude and were within the 95% confidence interval of the TFs, irrespective of the method used to extract soil solution. Predictability was higher for Pb than for Cd and differed also between the two TF sets.

Keywords: heavy metals, free metal ion, activity, , critical limit, transfer function, soil solution extraction, Donnan membrane technique

1. Introduction

Risks of high industrial inputs of cadmium and lead to terrestrial ecosystems are related to negative impacts on plants and soil organisms and the (bio)accumulation of these metals in the soil organic layer (Bringmark et al., 1998; Palmborg et al., 1998). One approach to successful international negotiations on the reduction of atmospheric deposition of pollutants is to determine the maximum level of constant atmospheric pollution that causes no or tolerable damage ("long-term acceptable load" or "critical load"). Currently, this critical load approach is being used for Cd, Pb and Hg across Europe (ICP Modelling and Mapping, 2004; De Vries et al., 2005).

Crucial for critical load calculations is to define a metal concentration in soil or soil solution below which no long-term damage to the ecosystem occurs. This concentration is called the critical limit (De Vries et al., 2005).

The most significant uptake route of many cationic metals by soil biota is via the soil solution in the dissolved form, and especially as the free metal ion (Allen, 1993; Sauvé et al., 1994; McGrath et al., 1999; Vulkan et al., 2000; 2001; Di Toro et al., 2001). The derivation of critical limits or environmental quality standards based upon the free metal ion in soil solution, where possible, is therefore a desirable goal of metal risk assessment. However most ecotoxicological data at present are based on laboratory experiments where effects are expressed in terms of total added metal (data are summarized in Schütze and Throl, 2000; Lofts et al., 2004). In order to relate the free metal ion activity in soil solution to the metal concentration in soil, linear regressions relations (transfer functions) have been proposed by several authors (e.g. Sauvé et al., 1998b; 2000; Groenenberg et al., 2003; Pampura, 2003a, b; Tipping et al., 2003; ICP Modelling and Mapping, 2004; Römkens et al., 2004). Sauvé et al. (1998a) proposed a methodology for calculating the effects of metals on soil processes, based on the free metal concentration alone as the best predictor of toxicity, while Lofts et al. (2004) proposed the use of a critical free metal ion activity as a function of soil solution pH, in order to consider the competing effect of cations. Both methodologies use existing ecotoxicological data, where endpoints are expressed as a metal concentration added to the soil. In both cases the added metal in the toxicity

studies was considered reactive metal in the solid soil and was related to metal activity in soil solution using transfer functions.

Heavy metal soil solution activity-effect relationships are the basis for critical limit derivation within the critical load approach (ICP Modelling and Mapping, 2004; Lofts et al., 2004; De Vries et al., 2005). Recently, two sets of TFs have been proposed to calculate free metal ion concentrations. The two transfer functions have the same general form but differ with respect to the data they were derived from: TF1 (Groenenberg et al., in prep.) is based on solid solution partitioning data obtained in the United Kingdom and the Netherlands (Tipping et al., 2003; Römkens et al., 2004), TF2 (Lofts et al., 2004) is based on data from Canada, the Netherlands and the United Kingdom (Sauvé et al., 1998b; Sauvé et al., 2000; Weng et al., 2001; 2002; Tipping et al., 2003). All free metal ion activities used to derive TF1 were calculated from the total dissolved metal concentration using a speciation model WHAM/ Model VI (Tipping, 1998). TF2 are based on both calculated and measured metal activities. Both sets contain data from a wide range of soils, necessary for the derivation of robust TFs. However, forest soils are rather underrepresented in both data sets, whereas they are important receptors in Europe. There is thus a need to test the applicability of the TFs to European forest soils in particular. Here we test the validity and applicability of transfer functions on independent data for different types of soil, including many forest soils from Germany and Russia.

2. Materials and methods

2.1. Soil and soil solution sampling and analyses

Soil samples were collected in Germany (Hessen) and Russia (Oka river basin and Kola Peninsula) and analysed during the period 2000-2003. Detailed information about soil type, location, land use, horizon, and sampling depth is presented in Table 8 of the Appendix. Kola Peninsula soils were collected at different distances from the Monchegorsk Cu-Ni smelter along a pollution gradient.

Soil organic matter was determined using standard methods: loss on ignition (LOI) (Kola soils), DIN 38409 H1-3 (German soils), method by Tyurin (Arinushkina, 1973) (Oka river soils).

Reactive metal contents in solid soil were determined using a 0.43 mol.L^{-1} HNO_3 extraction (Houba et al., 1985). Air-dry soil was shaken for 4 hours with 0,43 mol?L^{-1} HNO3 solution with a soil–solution ratio (SSR) 1:10, followed by centrifuging (3000 rpm, 10 min.) and filtering of solution via cellulose nitrate 0.45 mµ membrane filter (Schleicher&Schüll). Extracts were analyzed for Cd, Pb using: ICP-MS for German and Kola soils and GF AAS for Oka river basin soils (for detailed info see Table 1).

Soil solution concentrations were approximated using four different methods:

- *Soil saturation extract (BSE)* (German and Kola soils). Soils (air dry for German soils and at field moisture content in the case of Kola soils) were passed through 3mm sieve, and were equilibrated in plastic containers

with deionised water added to bring soil to a moisture content of 100% of the water holding capacity (WHC). After 48 hours (room temperature) the soils were centrifuged at 3000 rpm during 10 minutes. The obtained solutions were filtered through 0.45µm cellulose nitrate 0.45 µm membrane filter (Schleicher&Schüll). The pH was measured after soil solution separation before and after filtering through a membrane filter.

- *Dilute salt solution extraction ($CaCl_2$)* (Kola and Oka river basin). Air dried soil material and a dilute salt solution (0.002 $mol.L^{-1}$ $CaCl_2$) were put in polypropylene centrifuge tubes and were gently shaken continuously (about 30 rpm) for 48 hours as it is recommended in (Houba et al., 1985). We used a soil : solution ratio (SSR) of 1:2 for mineral horizons and 1:4 for organic horizons. Thereafter the samples were centrifuged at 3000 rpm during 10 minutes and the supernatant was filtered though a cellulose nitrate 0.45 µm membrane filter (Schleicher&Schüll). The pH was measured after centrifuging in the supernatant before and after filtering.
- *Lysimetric waters* (Kola soils). Lysimetric waters were collected with gravitational lysimeters below O_h and B_{hf} horizons of Podzols (unpublished data of N. Lukina (CEPF, Russia). Water samples were collected during the same time period and at the same sampling sites as soil samples used for soil solution extractions.
- *Soil column -Donnan membrane technique (DMT)* (Kola soils). This method allows the simultaneous determination of the free metal ion concentration of several metals in a soil solution (approximated here with

0.002M $Ca(NO_3)_2$) which is equilibrated with the soil by continuous pumping of the solution through a soil column.

After sampling soil samples were transported at field moisture content in a cool box at a temperature about +10°C. In the laboratory samples were passed though 3mm plastic sieve without drying and were kept in the dark at a temperature +4°C during 8-12 months. Moisture content (at 40°C) was determined before the experiments and taken into consideration for soil: solution ratio calculations needed for soil column DMT experiment. More information is given below in the section "Metal activity measurement".

Soil solution pH was measured using a combination pH electrode (semimicro research-grade pH-electrode U-05711-11, Orion). For the BSE and $CaCl_2$ extracts, pH was measured both before and after filtering of the obtained solution extract. No significant differences were found, and here we present data on pH after filtering.

Table 1 gives an overview of the different extraction techniques and chemical analyses used for the different soil data sets.

Table 1

2.2. Determination of free metal ion activities

Metal activity calculation. Free ion activities of Cd and Pb in BSE, $CaCl_2$-extracts and lysimetric waters were calculated from total metal concentrations in solution, concentrations of major cations, anions, DOC, and pH using the speciation model WHAM/Model VI (Tipping, 1998). We assumed that dissolved organic matter

(DOM) can be modelled as 65% active fulvic acid, which is an average value found by optimizing the model for binding of Cu to natural DOM in surface waters (Bryan et al., 2002) and is a reasonable estimate for the binding of several metals including Cd and Pb to DOM in soil solutions (Weng et al., 2002). DOM was calculated by assuming it to comprise 50% C by weight.

Metal activity measurement. For several samples (Podzols, organic and mineral horizons, Kola Peninsula), metal activities were not only calculated, but also measured using the Soil Column -Donnan Membrane Technique (DMT) described in Temminghoff et al. (2000) and Weng et al. (2001; 2002). The method is based on the assumption of (pseudo) equilibrium between a donor and an acceptor solution in a Donnan cell separated by a cation exchange membrane (55165 2U, BDH Laboratory Supplies, UK). The membrane allows fast transport of free cations but hinders the transport of complexed cations and anions. For both the donor and acceptor parts of the cell we used 0.002M $Ca(NO_3)_2$ solutions which were circulated using peristaltic pumps (Desaga and Gilson Minipuls 2 with tygon tubes, 2.06 1.D.) with a speed of 2 ml/min. The donor solution was in contact with the soil and circulated continuously from the bottom to the top through the soil column and the donor part of Donnan exchange cell. The acceptor solution circulated through the acceptor part of the Donnan cell. The experiment was run for 48 hours as recommended by Weng et al. (2001), who showed that in most cases this time was enough to reach equilibrium in the soil system and Donnan cell.

For mineral soils a SSR of 1:2 according to Weng (2001; 2002) was used. For organic horizons we had to increase this ratio to 1:7 because of the extremely high water holding capacity of the organic material. We also modified the column using a piston to prevent organic material from floating at the surface and disturbing the constant circulation of solution though the column. After 48 hours solution samples were collected from both donor and acceptor parts of the cell. The pH was measured in the soil column using a combination pH electrode. Activities of Cd and Pb ($a_{M\ don}$) in donor part (soil column) were calculated from the activity of the metal in the acceptor part ($a_{M\ acc}$) corrected for differences in ionic strength using the ratio of Na activities in donor and acceptor (equation 1, (Temminghoff et al., 2000)). The activities of Cd and Pb in acceptor and activities of Na in donor and acceptor were calculated from all measured total concentrations using WHAM VI.

$$\left[\frac{a_{M_don}}{a_{M_acc}}\right]^{1/2} = \left[\frac{a_{Na_don}}{a_{Na_acc}}\right], \quad (1)$$

where a_M and a_{Na} are respectively the activities of metal (Cd^{2+} or Pb^{2+}) and Na, in the donor (don) or acceptor (acc) solution ($mol.L^{-1}$)

2.3. Transfer functions

The general equation for both sets of transfer functions is:

$$\log (a_{Me}) = a_0 + a_1 \cdot \log(Q_{Me}) + a_2 \cdot \log (\%SOM) + a_3 \cdot pH \quad (2)$$

where:

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

a_{Me} = free metal ion activity ($mol.L^{-1}$)

%SOM = soil organic matter (weight %)

pH = pH of soil solution extract

Both sets of transfer functions give a direct relation between the activity of the free metal ion in soil solution and the metal content, organic matter content in the soil solid phase and pH of the soil solution. The explanatory variables were limited to parameters available in all the data sets.

The following sets of transfer functions were validated:

TF1 (the Netherlands- UK).

These transfer functions were derived by Groenenberg et al. (in prep.) and presented at the Workshop on Critical Loads of Heavy Metals, UNECE Convention on Long-range Transboundary Air Pollution ICP Modelling & Mapping, Potsdam, Germany, 4-5 March 2004. Data for derivation were limited to datasets in which reactive metal was measured with 0.43 $mol.L^{-1}$ HNO_3 to have a consistent dataset. Two large datasets (Tipping et al., 2003; Römkens et al., 2004) were used. The data set from Tipping et al. (2003) consists mainly of samples from the top upland soils (United Kingdom) with high organic matter content. The data set from Römkens et al. (2004) consists of a range of soils from the Netherlands and includes also samples from deeper soil horizons. Free ion activities were calculated using WHAM/Model VI.

TF2 (the Netherlands- UK-Canada) (ICP Modelling and Mapping, 2004; Lofts et al., 2004).

These transfer functions were derived by Lofts et al. (2004) with the aim of covering the ranges of Cd and Pb concentrations found in toxic endpoint data, and to include data as far as possible based on measured free metal ion. Soil metal contents for the different data set used are extracted with different methods. Data are confined to data from top soils. Transfer functions are based on the results of studies carried our in Canada, the Netherlands, and the United Kingdom.

For more information on the datasets see Table 2, for details one is referred to the original publications. The regression coefficients are summarized in Table 3.

Table 2

Table 3

2.4. Data analysis

We quantified the performance of both transfer functions with statistical measures. The Mean Absolute Error (MAE) is the average of the difference between predicted and actual value in all test cases; it is the average prediction error:

$$MAE = \frac{\sum_{i=1}^{n} |p_i - o_i|}{n}, \qquad (2)$$

where p and o are respectively the predicted and actual values of $\log(a_{Me})$.

The coefficient of residual mass (CRM) indicates the tendency of the model to bias in prediction and is calculated as:

$$CRM = \frac{\sum_{i=1}^{n}(p_i - o_i)}{\sum_{i=1}^{n} o_i} \quad (3)$$

A positive CRM indicates positive bias in prediction (tendency to overestimate actual values) and vice versa.

3. Results and discussion

3.1. Reactive metals

Our use of 0.43 mol.l^{-1} HNO_3 extraction as an approximation of reactive metal content in soil was determined in order to maintain measurement consistency, given the fact that this method was used for the most soils in the datasets for TF derivation (100% in the case of TF1 and 45% for Pb and 52 % for Cd in the case of TF 2, Table 2). Extraction with 0.43 mol.L^{-1} HNO_3 to determine the 'reactive' or 'geochemical active' metal in soil was used by several authors (Gooddy et al., 1995; Temminghoff et al., 1997; Cances et al., 2003). Good agreement between EDTA and 0.43 mol.L^{-1} HNO_3 extracted metal was found by Tipping et al. (2003) for organic soils (>10% SOM), by Groenenberg et al. (2003) and De Vries et al. (2005) for a large range of forest and agricultural soils. With the 0.43 mol.L^{-1} HNO_3–extracted metal as input Dijkstra et al. (2004) found good predictions of soil solution concentrations (Cd, Cu, Pb and Zn) from pH batch titrations ranging in pH from 2-12 using their "multisurface" model. However, we would like to note that the use of 0.43 mol.l^{-1} HNO_3 for soils with high pH, and especially

calcareous soils, could result in overestimation of reactive metal content due to dissolution of carbonates. Probably for neutral soils and soils with high pH an alternative would be to use a chelating agent e.g. EDTA, or an isotope exchange method (Degryse et al, 2004, 2006, 2007, Young et al., 2000, Tye et al., 2003).

3.2. Comparison of different soil solution extraction methods

Comparison of "soil solutions" extracted using different methods demonstrates in some cases very big difference in DOC concentration and total metal concentration. This difference can be illustrated using data on Kola Podzols collected along a pollution gradient, where different extraction techniques were applied to the same soil samples (Table 4; Tables 10-11, Appendix).

The methods we used for soil solution extraction differed in terms of extract solution composition, soil:solution ratio (SSR), method used for solid and liquid phases separation (centrifuging and filtering (BSE, $CaCL_2$), or only filtering (DMT, Lysimetric waters)), soil pre-treatment (dry soil or moist).

DOC and pH in different extracts.

Organic horizon. Mean DOC concentrations followed the trend $CaCl_2$ extracts > BSE extracts > DMT extracts> lysimetric. Concentrations of DOC in lysimetric water were lowest of all (on average about ten times lower then in $CaCl_2$ extract). We did not find any significant dependence of DOC concentration on soil sampling site distance from the smelter. The pH in different extracts consistently

decreased in soils in the vicinity of the smelter, but there were no significant differences in pH among different soil extracts, probably due to the pH buffering effect of DOC (Table 4).

Mineral horizon. DOC concentrations in all extracts from the mineral horizons were much lower than those in organic horizon extracts. Mean values followed the trend $CaCl_2$ ~ lysimetric > DMT ~ BSE. In general pH was highest in $CaCl_2$ extracts and lowest in lysimetric waters.

The high DOC concentration in $CaCl_2$ and BSE compared to DMT extracts and especially lysimetric waters is probably due to mobilisation of organic matter from the soil due to centrifuging (Tiensing et al., 2001). The effect appears especially pronounced for horizons with very high organic matter contents. In mineral horizons, BSE extractions and lysimeters resulted in solutions with similar DOC concentrations.

The soil:solution ratio (SSR) can also influence the amount of extracted DOC. For example, You et al. (1999) and Ponizovsky et al. (2006) observed positive correlations between DOC concentration and SSR. In our organic horizons, SSR was 1:7 for DMT (1:7), 1:4 for $CaCl_2$ extractions, and a mean of 1:3.7 for BSE (where soils were saturated to water holding capacity thus giving soil–specific SSRs). For the mineral horizons, the SSR was 1:2 in the DMT experiment and for $CaCl_2$ extraction, and on average 1:1.69 (0.59) for BSE.

Higher concentrations of DOC in $CaCl_2$ extractions compared to BSE could be due to the use of dried soils for $CaCl_2$ extractions, and field-moist soil for BSE

and DMT experiments; soil drying has been shown to increase the mobilisation of soil organic matter on extraction (Kaiser et al., 2001).

Metal concentrations and activities in different extracts.

Difference between extracts in DOC resulted in a big difference in metal concentration. In general metal concentrations in extracts were higher where DOC concentrations were highest. However, this does not necessarily imply a direct cause–effect relationship. The highest Cd and Pb concentrations were found in $CaCl_2$ and BSE extracts, and the lowest in lysimetric waters (O_h horizon) and DMT (Cd - B_{hf} horizon). The variability in metal and DOC concentrations, across different soil solution extracts, was notably greater in the organic horizons than the mineral horizons.

Variability in lead FMI activity in the O horizons was smaller than for total soil solution lead, probably due to the overriding influence of the total soil organic matter content and pH on speciation of this metal in these soils. For Pb in O horizon (and Cu - our unpublished data) we could not find any significant difference in activity between different extracts. This effect was not observed for Cd in the O and B horizons, nor for Pb in the B horizon. This suggests that other soil and solution parameters, such as DOC and the total soil metal, were affecting the FMI activities in these soils. In more details the effect of different techniques used for soil solution extraction will be discussed in our next paper.

3.3. Dataset used for transfer function validation

The complete dataset consists of four groups of data: “German soils”, “Kola soils”, “Kola soils – DMT” and “Oka river basin soils”. A complete description of the datasets is presented in the Appendix, Tables 8 – 12. Table 5 gives a summary of the dataset: ranges of soil solution pH, soil organic matter, reactive metal content, dissolved metal concentrations (before and after exclusion of samples with reactive or dissolved metal content below detection limits). In the case of lead, the following samples were excluded, mostly because of undetectable concentrations of dissolved Pb: all samples of Rigosol-Pararenzina (Germany) with pH (BSE) 7.61-7.76, Podzols (B horizon) from Kola Peninsula ($CaCl_2$ extract, DMT), and Chernozem, Luvisols, and half of Podzoluvisols from Oka river basin with pH higher then 4.6 ($CaCl_2$). This resulted in a decrease of the pH range of the dataset from 2.98–7.75 to 2.98–5.36 (Table 5). In the case of Cd, seven samples were excluded due to undetectable concentrations in the soil solution: Rigosol-Pararenzina (30-60cm) with pH (BSE) 7.71 (Germany), Chernozem with pH 6.47 from Oka river basin, and some mineral horizon samples from the Kola Peninsula (DMT) were excluded due to Cd concentration in acceptor being below detection.

Table 5

3.4. Validation of FMI activities calculated with WHAM VI using the results of DMT experiments.

Metal speciation calculations using WHAM were verified by comparing calculated FMI total activities with ones measured using DMT. Activities of Pb^{2+}

and Cd^{2+} were calculated using data on total dissolved metal concentrations, pH and DOC measured in soil column in the end of DMT experiment.

Table 6

Fig 1

The mean absolute error (MAE) in the calculation of the log FMI for cadmium was 0.37 for Cd and 0.46 for Pb (Table 6). The results indicated a tendency for WHAM to underestimate DMT–measured metal activities in the lower part of the observed range of activities, and to overestimate in the higher part of the observed range (Figure 1).. For the B horizon only a limited number of data points, for Cd only, were available. Predicted activities were consistently higher than observations. However according to the low CRMs calculated for both metals (respectively -0.02 and 0.005) there was on average no significant over- or underestimation in predicted activities compared to measurements with DMT (Table 6).

The deviations between predicted and measured Cd^{2+} and Pb^{2+} activities were as approximately equal to the deviations observed by Weng et al. (2002) in their comparison of model–predicted and DMT–measured FMI activities. This deviation was due both to errors in the model predictions as well as errors in the activity measurements. In another paper (Pampura et al., 2006) we showed mean absolute deviations between Cu^{2+} activities measured with DMT and those calculated with WHAM VI and NICA of 0.3 and 0.4 respectively.. We also demonstrated an MAE of 0.4 between activity values determined using DMT and measured with a Cu-selective electrode.

3.5. Transfer function validation

The applicability of both transfer functions was evaluated using a comparison of TF-predicted and observed free metal ion concentrations (computed from measured total concentrations (WHAM VI) or measured free ion concentrations (DMT)) (Figure 2.). The graphs show both the one order of magnitude interval and the 95% confidence interval of the regression function. The 95% confidence interval is calculated from the standard error of prediction (se(Y)) of each transfer function according to:

$$\text{Conf . Interval} = \text{Y-est.} \pm t_{n-2}\text{se(Y)} , \quad (4)$$

where Y-est is the predicted activity of the transfer function, and t_{n-2} is equal to 1.96 (n>120) for a 95% confidence interval. The width of the band shows how well the TF fits the data it is derived from.

It should be noted that TF2 was partly derived in terms of the free ion concentration $[M^{2+}]$ since some of the data used free ion expressed as a concentration rather than activity, whereas TF1 and our experimental dataset express free metal ion in terms of activity. This disagreement does not significantly influence the results. In soil solution extracts the difference in log(FMI activity) and log(FMI concentration) is expected to be around 0.13

(calculated with the Davies equation, Stumm and Morgan, 1981) with activities lower than concentrations.

Figure 2

Visual evaluation shows considerable scatter for both Cd and Pb. However transfer functions for Pb give better predictions than those for Cd for which the scatter is largest (Figure. 2). This is also reflected by the smaller MAE computed for Pb for both TF1 and TF2 (Table 7).

Table 7

Cd. From the computed CRM it follows that both TF1 and TF2 underestimate the log FMI activity for Cd by on average 7% and 4%, respectively. On the basis of the MAE, TF2 gives better results for Cd than TF1 because the average deviation is smaller for TF2 than for TF1 (Table 7). For TF1 about 23% of the points are outside the one order of magnitude interval and 9% for TF2. To see if there is any systematic deviation we looked for which soils the deviation is larger than the MAE. For both TFs the error is systematically larger for B horizons (Podzols, Brown soils) and it is nearly always smaller for O and A horizons. Errors for B horizons are especially large in case of TF1. If B horizons are left out the both TF's perform about equal. Specifically the agreement is poor for TF1 for all samples of Rigosol-Pararendzina, samples from B horizons of Eutric and Gleyic Cambisols (BSE extraction) and partially samples of Kola Podzol (BSE and $CaCl_2$ extraction). For TF2 predictions are poor for B_v horizons of Eutric Cambisol, Rigosol-Pararendsina (30-60cm) and some BSE extracts of O horizon of Kola Podzols.

Pb. The results for Pb show considerable scatter, however the predicted values are generally within an order of magnitude of observation for both transfer functions, and for both functions nearly all the data are within the 95% confidence intervals. TF1 on average overestimates the Pb FMI activities slightly whereas TF2 tend to underestimate the log FMI. According to the MAE (Table 7), TF2 gives somewhat better predictions than TF1. Again the error in the prediction is in general larger for the B horizons, but far less pronounced than for Cd. TF2 shows a larger than average prediction deviation for peat soils.

Comparison of metal activity prediction with transfer functions and with WHAM VI using the results of DMT measurements.

We tested the performance of TF2 and compared it with the performance of the WHAM VI model to predict FMI activities for those solutions in which the activity was measured using DMT. Table 6 gives the model performance parameters for WHAM VI and TF2.

Table 6

For Cd predictions with TF2 and WHAM VI are about equal with a slightly better prediction with WHAM. For Pb FMI activity prediction is better in the case of WHAM, although even with this model the average deviation on a log scale is 0.46.

Comparison of TF-predicted and observed activities in different types of soil solution extracts.

Figure 3 illustrates the scatter of free metal concentrations resulting from the use of different approaches to approximate soil solution in Podzols of the Kola Peninsula (BSE, $CaCl_2$, lysimetric waters, DMT).

Figure 3

Comparison of TF2–predicted Cd^{2+} and Pb^{2+} activities with observed values in different soil solution extracts (calculated from total dissolved concentrations with WHAM VI in BSE, $CaCl_2$ and lysimetric waters, and measured with DMT) demonstrates that for nearly all samples and for both metals, agreement is within one order of magnitude. This range of variation corresponds quite well to the 95% confidence intervals of TF2. For lead, the prediction for $CaCl_2$ extracts and lysimetric waters was a little better than for soil saturation extracts and DMT measurement. In the case of Cd, a high variability of FMI activities was found in BSE extracts, and predictions were poorer compared to $CaCl_2$, and lysimetric waters. A reasonable agreement between values predicted with TF2 and values measured with DMT was found, however in all cases Pb activities measured with DMT were lower and Cd activities were higher than those predicted with transfer functions. The variation due to different methods of soil solution sampling is within the variation of the transfer functions.

We would draw the following main conclusions from this work:

- Since a significant amount of data was excluded from the Pb dataset because of undetectable dissolved metal concentrations in soil solutions, the validation of the transfer functions for Pb was limited to the acid and slightly acid pH range.

- for Cd predictions are poor for the B horizon especially for TF1. Transfer function predictions for organic and A horizons are reasonably good. Best agreement between predicted values and those observed (either measured or calculated from total concentrations using WHAM VI) was found for TF2;
- for Pb reasonable agreement was found between activity of free metal ion predicted by both TF1 and TF2 and FMI activity measured or calculated from total concentrations in soil solutions;
- prediction with transfer functions is better for Pb than for Cd, and for organic horizon than for mineral one;
- deviations between values of free metal (Cd and Pb) ion activities observed in different soil solution extracts (BSE, $CaCl_2$, Lysimetric waters, DMT) and those ones predicted with TF are within the 95% confidence interval of the transfer functions. Transfer functions can be used equally well for all these extracts;
- comparison of FMI activity measured with DMT with activity predicted using WHAM VI and TF2 demonstrated that for Cd both models (WHAM and TF) were nearly equal. In the case of Pb WHAM-predictions demonstrated better agreement with DMT measurements than TF-predictions.

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Appendix

Table 8. Description of a complete dataset: soil type, location, land use, horizon, sampling depth.

N	Code	Location	Soil Type	Horizon (depth, cm)	Land use	note
1	DC1, DC2	Mörfelden, Germany	Gleyic Cambisol	O_f/O_h	Forest (Beech)	
2	DC4, DC5	Mörfelden, Germany	Gleyic Cambisol	A_{eh}	Forest (Beech)	
3	DC7, DC8	Mörfelden, Germany	Gleyic Cambisol	B_{hv}	Forest (Beech)	
4	DC10, DC11	Mörfelden, Germany	Gleyic Cambisol	B_v	Forest (Beech)	
5	DC13, DC14	Rohwiesen, Gernsheim, Germany	Sapric Histosol	H_n (0-10)	Forest (Poplar and Alder)	Alluvial forest
6	DC16, DC17	Rohwiesen, Gernsheim, Germany	Sapric Histosol	H_n (10-30)	Forest (Poplar and Alder)	Alluvial forest
7	DC19, DC20	Heppenheim, Germany	Rigosol-Pararendzina (Loess)	(0-30)	Vineyard	Hill slope on the border with vineyard
8	DC22, DC23	Heppenheim, Germany	Rigosol-Pararendzina (Loess)	(30 - 60)	Vineyard	Hill slope on the border with vineyard
9	DC25, DC26	Königstein (Taunus), Germany	Eutric Cambisol	O_f/O_h (3-5)	Forest (mixed Beech and Spruce)	
10	DC28, DC29	Königstein (Taunus), Germany	Eutric Cambisol	A_h (0-1/3)	Forest (mixed Beech and Spruce)	
11	DC31 DC32	Königstein (Taunus), Germany	Eutric Cambisol	B_v (3/5 – 30)	Forest (mixed Beech and Spruce)	
12	166, k-7 k-8 k-9	Monchegorsk, Russia	Al-Fe Humus Podzol	O_h	Forest (Spruce)	7 km from Cu-Ni smelter, the border between barren land and sparse forest
13	167, k-13 k-14 k-15	Monchegorsk, Russia	Al-Fe Humus Podzol	B_{hf}	Forest (Spruce)	7 km from Cu-Ni smelter, the border between barren land and sparse forest
14	k-16 k-17	Monchegorsk, Russia	Al-Fe Humus Podzol	O_h	Forest (Spruce)	20 km from Cu-Ni smelter, defoliating forest
15	k-22 k-23	Monchegorsk, Russia	Al-Fe Humus Podzol	B_{hf}	Forest (Spruce)	20 km from Cu-Ni smelter, defoliating forest
16	177, k-25	Monchegorsk, Russia	Al-Fe Humus	O_h	Forest (Spruce)	28 km from Cu-Ni smelter, defoliating

N	Code	Location	Soil Type	Horizon (depth, cm)	Land use	note
	k-26, k-27		Podzol			forest
17	k-31 k-32	Monchegorsk, Russia	Al-Fe Humus Podzol	B_{hf}	Forest (Spruce)	28 km from Cu-Ni smelter, defoliating forest
18	29, 32, 157, 160, k-34, k-36	Monchegorsk, Russia	Al-Fe Humus Podzol	O_h	Forest (Spruce)	100 km from Cu-Ni smelter, undisturbed forest
19	158, 161 k-40, k-41	Monchegorsk Russia	Al-Fe Humus Podzol	B_{hf}	Forest (Spruce)	100 km from Cu-Ni smelter, undisturbed forest
20	140, k-43	Monchegorsk, Russia	Al-Fe Humus Podzol	O_h	Forest (Spruce)	200 km from Cu-Ni smelter, undisturbed forest
21	141, k-49 k-50	Monchegorsk, Russia	Al-Fe Humus Podzol	B_{hf}	Forest (Spruce)	200 km from Cu-Ni smelter, undisturbed forest
22	501	Moscow reg. Serpukhov distr. Gryzlovo, Russia	Luvisol	A1	Forest (mixed, small-broadleaves)	
23	504	Moscow reg. Serpukhov distr. Gryzlovo, Russia	Luvisol	B il-fe	Forest (mixed, small-broadleaves)	
24	506	Kaluga reg. Satino, Russia	Podzoluvisol	A1A2	Forest (mixed, Spruce with Birch)	
25	510	Kaluga reg. Zaseki, Russia	Podzoluvisol	A1	Forest (mixed, coniferous-small-leaves)	
26	511	Kaluga reg. Zaseki, Russia	Podzoluvisol	E	Forest (mixed, coniferous-small-leaves)	
27	512	Kaluga reg. Zaseki, Russia	Podzoluvisol	A1	Forest (mixed, coniferous-small-leaves)	
28	521	Tula region, Russia	Luvic Cherozem	A1	Natural pasture	
29	671	Moscow reg.	Podzoluvisol	A1	Forest	

N	Code	Location	Soil Type	Horizon (depth, cm)	Land use	note
		Prioksko-Terrasnyi biosphere reserve, Russia	il-Fe		(mixed, Spruce with Birch and Pine)	
30	673	Moscow reg. Prioksko-Terrasnyi biosphere reserve, Russia	Podzoluvisol il-Fe	E	Forest (mixed, Spruce with Birch and Pine)	
31	701	Moscow reg. Serpukhov distr., Russia	Luvisol	A1	meadow	
32	703	Moscow reg. Serpukhov distr., Russia	Luvisol	A1A2	meadow	
33	711	Moscow reg., Pushchino IPBPSS, Russia	Luvisol	B il	agricultural	

Table 9. Dataset “German soils”: soil organic matter (DIN 38409 H1-3), soil solution pH (soil saturation extract), dissolved organic carbon (TOC/TN-analyzer, UBA-Langen), reactive metal content (0,43M HNO_3, ICP-MS, WUR), dissolved metal (GF-AAS, UBA-Langen), metal free ion activity (calculated with WHAM)

N	Code	Soil organic matter OM, %	pH	Dissolved organic carbon DOC mgL^{-1}	Reactive Pb Q_{Pb} $mgkg^{-1}$	Dissolved Pb C_{Pb} μgL^{-1} DL: 0.5	Pb free ion activity $-loga_{Pb}$ (M)	Reactive Cd, Q_{Cd} $mgkg^{-1}$	Dissolved Cd C_{Cd} μgL^{-1} DL: 0.2	Cd free ion activity $-loga_{Cd}$ (M)
1	DC1	22.6	3.97	278	49.3	55.6	7.91	0.22	1.3	8.66
2	DC2	22.6	3.82	279	47.7	53.4	7.84	0.20	1.4	8.61
3	DC4	21.6	3.73	228	60.1	64.2	7.41	0.13	1.4	8.32
4	DC5	21.6	3.66	235	57.2	69.3	7.32	0.12	1.7	8.21
5	DC7	12.1	3.85	224	21.1	64.8	7.42	0.02	2.3	8.12
6	DC8	12.1	3.86	223	21.8	62.6	7.46	0.02	2.0	8.18
7	DC10	2.1	4.02	142	7.9	3.6	8.51	0.01	8.1	7.46
8	DC11	2.1	4.05	132	8.1	2.8	8.56	0.01	9.0	7.39
9	DC13	40.3	4.57	165	13.2	15.1	8.27	0.60	3.3	8.03
10	DC14	40.3	4.55	157	13.5	13.2	8.29	0.62	3.0	8.07
11	DC16	40.7	5.34	310	3.5	10.9	9.63	0.39	1.9	8.46
12	DC17	40.7	5.36	301	4.2	11.0	9.65	0.38	1.3	8.63
13	DC25	76.6	3.75	181	52.8	48.7	7.55	0.21	2.2	8.13
14	DC26	76.6	3.89	163	57.8	42.4	7.65	0.23	1.9	8.20
15	DC28	35.4	3.66	209	78.5	85.4	7.17	0.12	1.7	8.17
16	DC29	35.4	3.58	215	88.5	86.9	7.12	0.14	1.4	8.26
17	DC31	9.3	4.11	95.5	21.3	10.5	7.84	0.03	2.7	6.86
18	DC32	9.3	4.04	106	36.1	10.9	7.81	0.04	2.9	6.85
19	DC19	1.6	7.75	76.5	DL	DL	DL	0.01	0.2	9.51
20	DC20	1.6	7.76	90.9	DL	DL	DL	0.01	0.3	9.55
21	DC22	3.2	7.71	52.8	DL	DL	DL	0.01	DL	DL
22	DC23	3.2	7.61	54.8	DL	DL	DL	0.01	2.0	8.46

DL - below the detection limit

Table 10. Dataset "Kola soils", contaminated and background soils collected along pollution gradient of Monchegorsk Cu-Ni smelter: soil organic matter (LOI, MSU), soil solution pH (soil saturation extract, $CaCL_2$ 0.002M extract SSR 1:2 O horizon, 1:4 B horizon, Lysimetric waters), dissolved organic carbon (NPOC, TC-analyzer, RIVM), reactive metal content (0,43M HNO_3, ICP-MS, RIVM), dissolved metal (ICP-MS, RIVM), metal free ion activity (calculated with WHAM VI)

N	Code	Soil organic matter OM* %	pH	Dissolved organic carbon DOC mgL^{-1}	Reactive Pb Q_{Pb} $mgkg^{-1}$ average from two values	Dissolved Pb C_{Pb} μgL^{-1} DL: 0.2	Pb free ion activity -log a_{Pb} (M)	Reactive Cd Q_{Cd} $mgkg^{-1}$ average from two values	Dissolved Cd C_{Cd} μgL^{-1} DL: 0.04	Cd free ion activity -loga_{Cd} (M)
Soil solution is approximated with soil saturation extract										
1	K-7	61.3	3.28	166	38.7	18.9	7.64	1.36	8.7	7.38
2	K-8	61.3	3.67	148	36.9	14.8	7.89	1.28	9.2	7.38
3	K-16	61.6	4.43	782	16.9	25.0	8.86	1.41	8.6	7.99
4	K-17	61.6	3.81	238	14.0	17.5	8.24	0.80	11.1	7.49
5	K-25	61.6	3.77	425	17.3	21.5	8.21	1.04	166.8	6.34
6	K-26	61.6	3.89	311	26.0	19.1	8.38	1.49	3.6	8.07
7	K-34	71.3	3.92	921	15.3	44.0	8.46	0.38	2.5	8.62
8	K-36	71.3	3.49	309	10.2	27.7	7.96	0.33	1.4	8.39
9	K-43	71.1	4.6	847	9.9	21.6	9.00	0.99	207.8	6.58
10	K-44	68.7	4.67	873	14.3	40.7	8.89	0.27	85.1	7.12
11	K-13	7.3	4.34	7.1	1.5	1.0	8.50	0.19	10.3	7.16
12	K-14	7.3	4.68	3.5	1.3	0.9	8.47	0.09	0.9	8.16
13	K-22	8.2	4.66	21.1	1.0	0.4	8.94	0.08	1.2	8.13
14	K-23	8.2	4.75	11.4	1.8	1.6	8.24	0.05	0.30	8.65
15	K-31	8.2	4.27	26.6	1.4	1.2	8.47	0.04	1.7	7.96
16	K-32	8.2	4.67	4.7	1.2	0.6	8.67	0.04	0.33	8.60
17	K-40	2.6	4.56	20.4	1.6	2.8	8.01	0.02	0.30	8.67
18	K-41	2.6	4.52	27.2	2.1	2.8	8.02	0.01	0.13	9.04
19	K-49	3.5	5.02	20.7	1.2	0.5	9.24	0.03	0.44	8.68
Soil solution is approximated with $CaCl_2$ 0.002M, SSR 1:2										
1	k-7-1+2	61.3	3.06	1053	38.7	53.9	7.62	1.36	49.5	6.82
2	k-8-1+2	61.3	3.29	915	37.7	43.6	7.77	1.28	36.9	6.96
3	k-16-1	61.2	4.33	1860	16.5	45.9	8.90	1.44	9.2	8.30
4	k-16-2	61.2	4.30	1802	17.3	70.4	8.50	1.38	11.5	7.99
5	k-17-1	61.6	3.52	749	14.0	26.8	8.14	0.79	7.5	7.71
6	k-17-2	61.6	3.49	125	14.0	8.4	7.95	0.81	5.5	7.52
7	k-25-1	61.6	3.38	1390	17.5	48.6	8.01	1.04	12.1	7.60
8	k-25-2	61.6	3.37	1384	17.2	50.4	7.98	1.04	12.0	7.61
9	k-26-1	61.6	3.52	402	25.9	33.2	7.75	1.51	10.7	7.38
10	k-26-2	61.6	3.59	384	26.2	41.6	7.69	1.47	11.1	7.37
11	k-34-1	71.3	3.80	891	15.3	29.9	8.27	0.38	3.2	8.17
12	k-34-2	71.3	3.81	804	15.3	20.4	8.49	0.38	2.4	8.34
13	k-43-1	71.1	4.45	1734	9.3	25.8	9.03	0.97	7.6	8.16
14	k-43-2	71.1	4.46	481	10.5	7.8	8.95	1.01	3.5	8.02
15	k-13-1	7.3	4.58	42.5	1.5	0.80	8.71	0.18	13.4	7.17

N	Code	Soil organic matter OM* %	pH	Dissolved organic carbon DOC mgL^{-1}	Reactive Pb Q_{Pb} $mgkg^{-1}$ average from two values	Dissolved Pb C_{Pb} μgL^{-1} DL: 0.2	Pb free ion activity -log a_{Pb} (M)	Reactive Cd Q_{Cd} $mgkg^{-1}$ average from two values	Dissolved Cd C_{Cd} μgL^{-1} DL: 0.04	Cd free ion activity -loga_{Cd} (M)
16	k-13-2	7.3	4.69	41.0	1.5	0.31	9.13	0.20	13.6	7.16
17	k-14-1	7.3	4.86	50.9	1.3	0.22	9.71	0.09	2.3	7.98
18	K-14-2	7.3	4.90	51.1	1.3	1.52	8.74	0.09	2.4	7.93
19	k-22-1	8.2	5.13	51.1	1.0	DL	DL	0.07	1.6	8.14
20	k-22-2	8.2	5.21	49.6	0.9	DL	DL	0.09	1.5	8.16
21	k-23-1	8.2	4.78	54.2	1.7	0.25	9.34	0.05	2.1	7.99
22	k-23-2	8.2	4.63	50.8	1.9	DL	DL	0.05	2.3	7.94
23	k-31-1	8.2	4.41	70.2	1.4	0.27	9.15	0.05	2.5	7.90
24	k-31-2	8.2	4.42	66.1	1.4	0.27	9.15	0.04	2.5	7.90
25	k-32-1	8.2	4.91	51.3	1.2	DL	DL	0.04	1.5	8.16
26	k-32-2	8.2	4.88	53.8	1.2	DL	DL	0.04	1.4	8.18
27	k-40-1	2.6	4.57	51.4	1.6	0.29	9.09	0.02	0.86	8.35
28	k-40-2	2.6	4.52	52.4	1.5	0.32	9.04	0.02	1.06	8.26
29	k-41-1	2.6	4.53	54.2	2.2	0.45	8.91	0.01	0.96	8.31
30	k-41-2	2.6	4.56	54.5	2.1	0.46	8.90	0.01	0.97	8.31
31	k-49-1	3.5	5.26	43.9	1.2	DL	DL	0.04	0.94	8.38
32	k-49-2	3.5	5.29	52.3	1.1	0.39	9.50	0.02	1.0	8.36
33	k-50-1	4.7	4.96	34.5	1.9	0.24	9.42	0.02	1.2	8.25
34	k-50-2	4.7	4.87	35.5	1.8	0.88	8.82	0.01	1.3	8.21
Soil solution is approximated with lysimetric waters**										
1	166	61.3	3.54	68.89	37.7	2.06	8.10	1.32	2.5	7.72
2	177	61.6	3.44	79.82	21.2	1.67	8.30	1.24	2.2	7.79
3	29	71.3	3.81	36.97	12.5	4.09	8.12	0.35	0.36	8.66
4	32	71.3	3.89	69.55	12.5	2.2	8.45	0.35	0.44	8.58
5	157	71.3	3.63	50.41	12.5	3.85	8.04	0.35	0.5	8.48
6	160	71.3	3.89	15.26	12.5	2.16	8.33	0.35	0.5	8.47
7	140	71.1	4.54	30.03	11.9	0.58	9.52	0.52	0.1	9.33
8	167	7.3	4.18	6.48	1.4	0.15	9.37	0.13	1.6	7.92
9	158	2.6	4.26	27.11	1.8	0.3	9.00	0.02	0.6	8.38
10	161	2.6	4.05	23.33	1.8	1.22	8.34	0.02	0.5	8.44
11	141	4.0	4.84	7.87	1.5	0.19	10.17	0.02	0.1	9.56

DL - below the detection limit, *- data on OM – reported by G. Koptsik, Moscow State University, ** data on pH, OM, TC, CCd, CPb - reported by N. Lukina, CEPF RAS, Moscow

Table 11. Dataset “Kola soils -DMT”, contaminated and background soils collected along pollution gradient of Monchegorsk Cu-Ni smelter: soil organic matter (LOI, MSU), soil solution pH ($Ca(NO_3)_2$ 0.002M solution in soil column – DMT), dissolved organic carbon (TC- analyzer, NPOC, ALTERRA), reactive metal content (0,43M HNO_3, ICP-MS, WUR), dissolved metal ($Ca(NO_3)_2$ 0.002M solution in soil column – DMT experiment, ICP-MS, WUR), metal free ion activity (measured with DMT).

N	Code	Soil organic matter OM* %	pH in Donor	Dissolved organic carbon DOC mgL^{-1}	Reactive Pb Q_{Pb} $mgkg^{-1}$ average from two values	Dissolved Pb, C_{Pb} μgL^{-1} in Donor DL: 0.2	Pb free ion activity -log a_{Pb} (M)	Reactive Cd Q_{Cd} $mgkg^{-1}$ average from two values	Dissolved Cd, C_{Cd} μgL^{-1} in Donor DL: 0.04	Cd free ion activity -loga_{Cd} (M)
Soil-column – Donnan membrane technique experiment, $Ca(NO_3)_2$ 0.002 M										
1	k-9-a	61.6	3.39	130.4	37.8	31.5	7.77	1.32	30.1	7.23
2	k-9-b	61.6	3.39	138.4	37.8	30.1	7.88	1.32	30.9	7.35
3	k-16	61.6	4.09	279.8	16.9	8.56	9.16	1.41	6.0	7.83
4	K-26	61.6	3.49	308.4	26.0	8.61	8.55	1.49	11.0	7.46
5	k-7-a	61.6	2.98	91.0	38.7	25.3	7.71	1.36	32.9	7.09
6	k-7-b	61.7	3.04	134	38.7	16.6	7.79	1.36	29.8	7.08
7	k-7-c	61.7	3.07	124	38.7	16.9	7.57	1.36	30.1	6.96
8	k-43-a	71.1	4.39	218.0	9.87	4.17	DL	0.99	6.0	8.06
9	k-43-b	71.1	4.41	339.0	9.87	3.11	DL	0.99	11.0	7.69
10	k-43-c	71.1	4.34	209	9.87	3.5	DL	0.99	5.15	7.69
11	k-43-d	71.1	4.34	351	9.87	4.6	DL	0.99	6.20	7.39
12	k-17	61.6	3.45	81.6	14.0	3.03	9.19	0.80	30.1	8.14
13	k-27	61.6	3.53	244.2	21.7	8.30	8.44	1.26	30.9	7.74
14	k-13	7.4	4.67	9.26	1.53	DL	DL	0.19	3.94	DL
15	k-23	8.3	4.64	6.72	1.83	DL	DL	0.05	0.19	DL
16	k-31	8.3	4.22	11.91	1.37	DL	DL	0.04	1.38	DL
17	k-40	2.6	4.48	11.41	1.56	DL	DL	0.02	0.18	DL
18	k-49	3.5	4.89	19.09	1.19	DL	DL	0.03	0.22	DL
19	k-15	7.3	4.13	7.6	1.40	DL	9.63	0.14	9.26	7.64
20	k-22	7.3	4.42	13.6	0.96	DL	DL	0.08	2.90	8.09

DL - below the detection limit,
a, b, c, d -replicates
**- data on OM – reported by G. Koptsik, Moscow State University

Table 12. Dataset “Oka river basin soils”: soil organic matter (by Tuyrin, IBPPSS), soil solution pH ($CaCl_2$ 0.002 M, SSR 1:2), dissolved organic carbon (NPOC, TC- analyzer, ALTERRA), reactive metal content (0,43M HNO_3, GFAAS, TEST, Pushchino), dissolved metal ($CaCl_2$ 0.002 M, SSR 1:2, ICP-MS, WUR), metal free ion activity (calculated with WHAM)

N	Code	Soil organic matter OM %	pH	Dissolved organic carbon DOC mgL^{-1}	Reactive Pb Q_{Pb} $mgkg^{-1}$ average from two values	Dissolved Pb C_{Pb} μgL^{-1} DL: 0.2	Pb free ion activity -log a_{Pb} (M)	Reactive Cd Q_{Cd} $mgkg^{-1}$ average from two values	Dissolved Cd C_{Cd} μgL^{-1} DL: 0.04	Cd free ion activity -loga_{Cd} (M)
1	501-a	4.7	5.81	155	2.06	DL	DL	0.42	0.70	8.67
2	501-b	4.7	5.78	199	2.06	DL	DL	0.42	0.71	8.72
3	504-a	0.6	4.93	9.4	2.12	DL	DL	0.02	0.16	9.05
4	504-b	0.6	4.91	8.5	2.12	DL	DL	0.02	0.16	9.03
5	506-a	0.4	4.70	12.5	1.03	DL	DL	0.22	7.61	7.34
6	510-b	2.9	4.07	117.2	2.81	2.49	-8.44	0.04	2.01	8.00
7	510-b	2.9	4.05	99.8	2.81	2.47	-8.36	0.05	2.04	7.98
8	511-a	0.2	5.60	9.0	0.17	DL	DL	0.01	0.41	8.65
9	512-a	3.4	4.62	166.1	2.39	1.28	-8.83	0.04	1.84	8.05
10	512-b	3.4	4.60	168.1	2.39	0.97	-9.06	0.05	1.85	8.06
11	521-a	4.6	6.47	43.6	1.99	DL	DL	0.08	DL	10.82
12	521-b	4.6	6.47	43.9	1.99	DL	DL	0.09	DL	10.88
13	671-a	1.7	3.36	51.0	1.49	5.25	-7.80	0.02	1.62	8.00
14	671-b	1.7	3.36	58.3	1.49	5.49	-7.79	0.01	1.63	8.00
15	673-a	0.4	4.14	11.8	0.20	0.44	-8.84	0.002	0.30	8.73
16	673-b	0.4	4.15	11.3	0.20	0.45	-8.84	0.002	0.29	8.74
17	701-a	4.1	6.54	11.6	1.17	DL	DL	0.17	0.12	9.31
18	701-b	4.1	6.56	47.2	1.17	DL	DL	0.16	0.13	9.41
19	703-a	1.8	5.75	12.8	0.69	DL	DL	0.11	0.13	9.19
20	703-b	1.8	5.81	11.9	0.69	DL	DL	0.11	0.14	9.18
21	711-a	0.7	5.30	6.0	1.02	DL	DL	0.02	0.08	9.32
22	711-b	0.7	5.35	6.1	1.02	DL	DL	0.03	0.08	9.36

DL - below the detection limit
a, b -replicates

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Figures

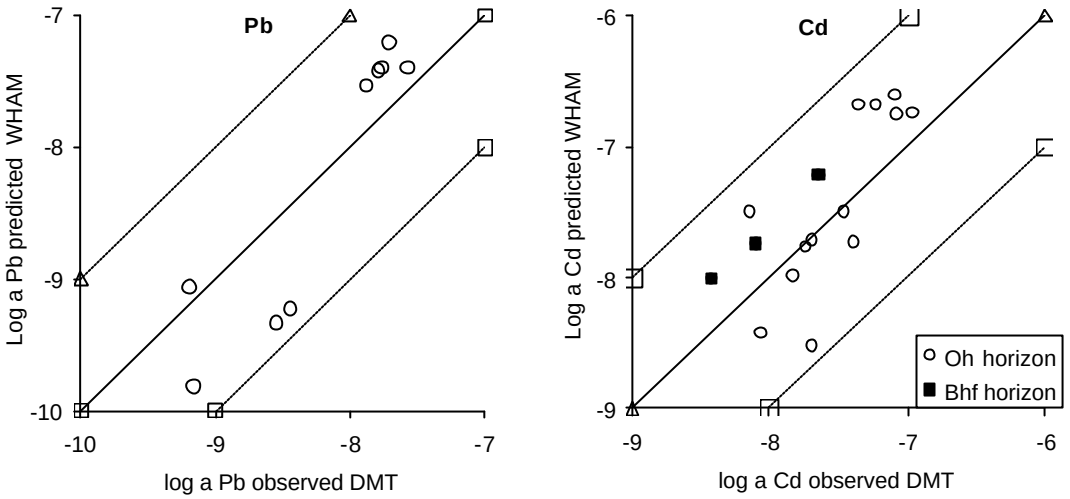

Figure 1

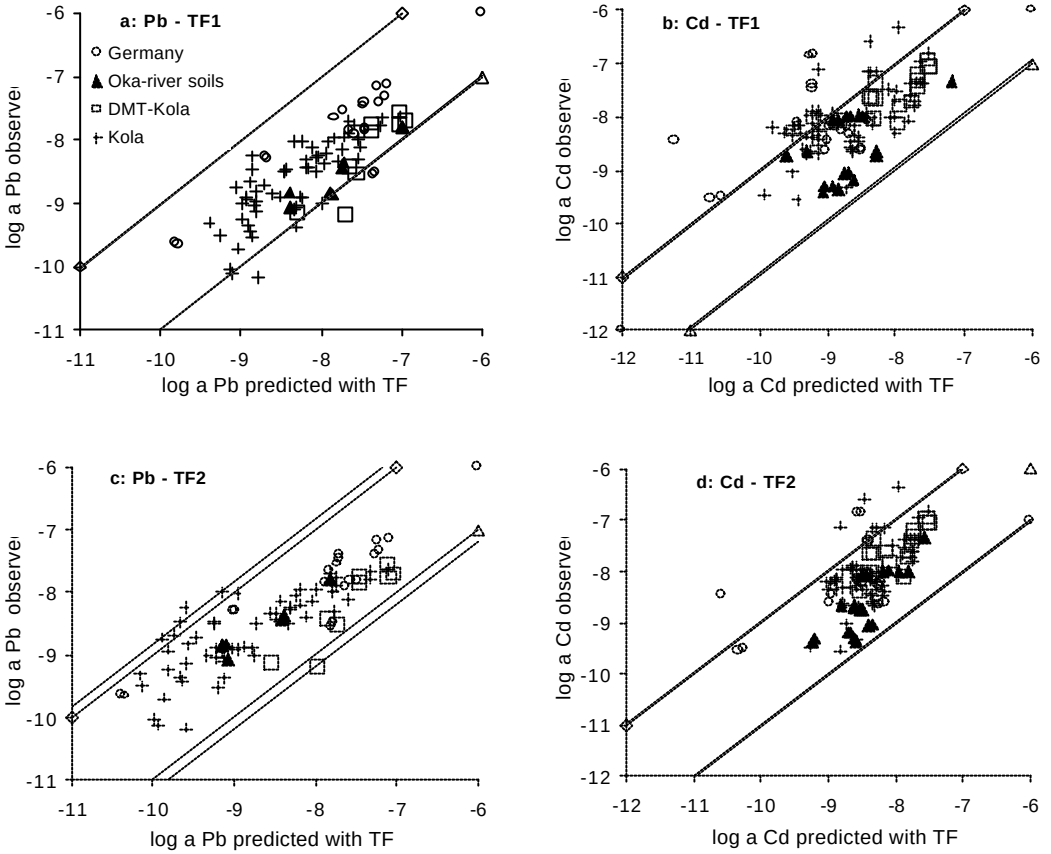

Figure 2

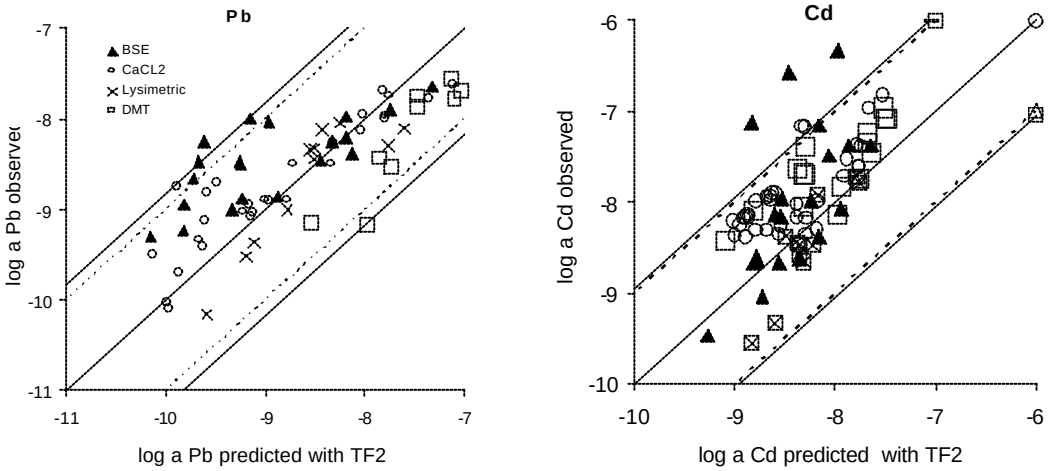

Figure 3

Figure captions

Figure1. DMT-soil column experiment: ?omparison of DMT activity measurements with FMI activities calculated with WHAM. Activities were calculated from total dissolved metal concentrations, pH and DOC measured in soil column solution.

Figure2. Comparison of free ion activities predicted by transfer functions with activities observed in soil solutions (calculated using WHAM VI and measured with DMT). Solid lines indicate 95% confidence intervals of predicted values. Dotted lines indicate ± one order of magnitude

Figure3. Comparison of free ion activities predicted by TF2 with activities observed in different types of soil solution extracts of Podzols from Kola Peninsula, Russia. Dotted lines indicate ± one order of magnitude. Solid lines indicate 95% confidence intervals of predicted values.

Tables

Table 1. Overview of the different extraction techniques and chemical analyses.

dataset	solution extraction	Pb and Cd	Cations, S,P	SO_4,NO_3, Cl	DOC	FMI	Cd, Pb HNO_3
Germany	**BSE**	**GFAAS**[1]	**ICP-OES**[2]	**IC**[3]	**TOC analyzer**[4]	**WHAM**	**ICP-MS**[5]
Oka-river	**$CaCl_2$**	**ICP-MS**[5]	**ICP-AES**[6]	**IC**[7]	**TOC analyzer**[8]	**WHAM**	**GFAAS**[12]
Kola	**BSE**	**ICP-MS**[9]	**ICP-MS**[9]	**IC**[10]	**TOC analyzer**[11]	**WHAM**	**ICP-MS**[9]
Kola	**$CaCl_2$**	**ICP-MS**[9]	**ICP-MS**[9]	**IC**[10]	**TOC analyzer**[11]	**WHAM**	**ICP-MS**[9]
Kola	**Lysimeter**	**GF??S**[14]	**S, P - Calorimetry**[15]	**-**	**Organic C digestion**[16]	**WHAM**	**ICP-MS**[9]
DMT-Kola	**DMT**	**ICP-MS**[5]	**ICP-AES**[6]	**est**[13]	**TOC analyzer**[8]	**DMT**	**ICP-MS**[9]

[1] GFAAS Perkin Elmer 2100 (UBA-Langen); [2] ICP OES Perkin Elmer Optima-3200DV (UBA-Langen); [3] Ion chromatography IC, Dionex DX 100 (UBA, Langen); [4] TOC/TN analyzer, Analyticjena AG multi N/C 3000 (UBA, Langen) as difference between total and inorganic C
[5] ICP-MS, Perkin Elmer, ELAN 6000 (Wageningen University);[6] ICP-AES (ALTERRA, Wageningen)
[7] IC (Alterra, Wageningen);[8] Shimadzu TC-5000 (ALTERRA, Wageningen), NPOC method
[9] ICP-MS, HP 4500plus, Hewlett Packard (RIVM, Bilthoven); [10] IC (RIVM, Bilthoven);[11] Dorhmann DC-190 (RIVM, Bilthoven), NPOC method;[12] GF AAS Spectra AA 250 plus, Varian, ("TEST", Pushchino);[13] Estimated from charge balance; [14] GF? ? S Aanalyst-800, INEP, Apatity, Russia (data of N. Lukina);[15] Calorimetry , INEP, Apatity, Russia (data of N. Lukina); [16] Total carbon determination with organic carbon digestion , INEP, Apatity, Russia (data of N. Lukina)

Table 2. Summary of data sets used for derivation of transfer functions

TF	Dataset used for TF derivation	Soil metal extraction	Method for extracting soil solution	Determination of free ion	Range of soil metal concentration* (mg/kg)	Range SOM (%)	Range pH	nr of data
TF1	Römkens et al. (2004)	0.43M HNO_3	0.002 and 0.01 M $CaCl_2$ SSR 1:2	WHAM	Cd: 0.01- 20.3 Pb: 6.1-1570	0.5-45.7 0.5-74.1	2.5-7.9 2.5-7.9	863 535
TF1 TF2	Tipping et al. (2003)	0.43M HNO_3	Saturated soil extracted with Rhizon samplers	WHAM	Cd:0.12-44.9 Pb: 10.9-9660	9-99	3.3-8.3	98 98
TF2	Weng et al. (2001)	2M HNO_3	0.002M $Ca(NO_3)_2$ soil column - DMT	DMT	Cd: 0.01-0.28 Pb: 0.99-25.76	0.4-4.1	3.8-5.8	25 19
TF2	Weng et al. (2002)	Aqua Regia	0.002M $Ca(NO_3)_2$ soil column - DMT	DMT	0.05-6015 8.8-105	0.3-13.7	3.1-6.1	10 10
TF2	Sauvé et al. (2000)	Conc. HNO_3	0.01M KCl, SSR 1:2	DPASV	Cd: 0.1-38.1	1.6-21.5	3.5-8.5	61
TF2	Sauvé et al. (1998b)	Conc. HNO_3	0.01M KCl, SSR 1:2	DPASV	Pb: 10.1-14861	0.9-21.5	3.5-8.1	84

* The range of metal concentrations is that found using the extraction method given

Table 3. Regression coefficients for transfer functions

	a_0	a_1 (Q_{me})	a_2 (SOM)	a_3 (pH)	R^2	se(y)
TF1						
Cd	**1.73**	**1.28**	**-0.93**	**-0.42**	**0.69**	**0.48**
Pb	**-0.50**	**0.56**	**-0.72**	**-1.02**	**0.91**	**0.50**
TF2						
Cd	**-1.88**	**0.60**	**-0.60**	**-0.53**	**0.62**	**0.53**
Pb	**1.17**	**1.05**	**-0.69**	**-1.02**	**0.85**	**0.60**

se(y) = the standard error of the y-estimate on a logarithmic basis

Table 4. Dissolved organic carbon (DOC) concentration in different soil solution extracts

Extract	**DOC, mg.L^{-1}: average± STD (STD %)**		**SSR**		**Conditions**
	O_h horizon	***B_{hf} Horizon***	**O_h horizon**	***B_{hf} horizon***	
0.002 M $CaCL_2$	**1000±570** ***(56%)***	**51 ± 9** ***(17%)***	**1: 4**	**1 : 2**	**Centrifuging** ***dry soil***
H_2O BSE	**50 0 ± 315** ***(63%)***	**16 ± 9** ***(63%)***	**1: 3.7**	**1 : 0.59**	**Centrifuging** ***wet soil***
Lysimetric waters	**50 ± 24** ***(48%)***	**16 ± 11** ***(63%)***			**Gravitational waters**
0.002M $Ca(N0_3)_2$	**200 ± 95** ***(46%)***	**11 ± 4** ***(63%)***	**1: 7**	**1 : 2**	***DMT-soil column***

Table 5. Summary of data used for transfer function validation

Dataset	n	Range of reactive metal concentration 0.43M HNO_3 $mg \cdot kg^{-1}$	Range of dissolved metal concentration $\mu g \cdot l^{-1}$ (type of soil solution extract)	Range of pH of soil solution extract (type of soil solution extract)	Range of soil organic matter %
Cd					
Complete	125	1.51-0.002	207.8 (BSE)– <0.04 ($CaCl_2$)	2.98 (DMT)- 7.75 (BSE)	76.6-0.2
>detection limit	118	1.51-0.002	207.8 (BSE)– 0.08 ($CaCl_2$)	2.98 (DMT)- 7.75 (BSE)	76.6-0.2
Pb					
Complete	125	88.5- <0.002	86.9 (BSE) - < 0.2 ($CaCl_2$, BSE, DMT)	2.98 (DMT)- 7.75 (BSE)	76.6-0.2
>detection limit	94	88.5- 0.2	86.9 (BSE) - 0.2 (Lys)	2.98 (DMT)- 5.36 (BSE)	76.6-0.4

Table 6. Statistical measures to quantify the performance of speciation model WHAM VI and transfer functions (TF2) for free metal ion activity prediction in DMT-soil column experiment

	WHAM Cd	TF2	WHAM Pb	TF2
MAE	0.37	0.41	0.46	0.65
CRM	-0.02	-0.05	0.005	0.08

Table 7. Statistical measures to quantify the performance of transfer functions

	TF1		TF2	
	Cd	**Pb**	**Cd**	**Pb**
MAE	**0.68**	**0.44**	**0.48**	**0.37**
CRM	**-0.07**	**0.04**	**-0.04**	**-0.01**