Running title: Prediction of Cd and Zn concentrations

Soil solution concentration of Cd and Zn can be predicted with a CaCl$_2$ soil extract

F. DEGRYSE, K. BROOS, E. SMOLDERS & R. MERCKX

Laboratory of Soil Fertility and Soil Biology, K.U.Leuven, Kasteelpark Arenberg 20, 3001 Heverlee, Belgium

Correspondence: F. Degryse. E-mail: fien.degryse@agr.kuleuven.ac.be

Summary

Risk assessment of heavy metals in soil requires an estimate of the concentrations in the soil solution. In spite of the numerous studies on the distribution of Cd and Zn in soil, few measurements of the distribution coefficient *in situ*, K_d, have been reported. We determined the K_d of soils contaminated with Cd and Zn by measuring metal concentrations in the soil and in the soil solution and attempted to predict them from other soil variables by regression. Soil pH explained most of the variation in $\log K_d$ ($R^2 = 0.55$ for Cd and 0.70 for Zn). Introducing organic carbon content or CEC as second explanatory variable improved the prediction ($R^2 = 0.67$ for Cd and 0.72 for Zn), but these regression models left, however, more than a factor 10 of uncertainty in the predicted K_d. This large degree of uncertainty may partly be due to the variable degree of metal fixation in contaminated soils. The labile metal content was measured by isotopic dilution (*E* value). The *E* value ranged from 18 to 92% of the total metal content for Cd and from 5 to 68% for Zn. The prediction of K_d improved when metals in solution were assumed to be in equilibrium with the labile metal pool instead of the total metal pool. It seems necessary therefore to discriminate between 'labile' and 'fixed' pools to predict K_d for Cd and Zn in field contaminated soils accurately. Dilute salt extracts (e.g. 0.01 M CaCl$_2$) can mimic soil solution and are unlikely to extract metals from the fixed pool. Concentrations of Cd and Zn in the soil solution were predicted from the concentrations of Cd and Zn in a 0.01 M CaCl$_2$ extract. These predictions were better correlated with the observations for field contaminated soils than the predictions based on the regression equations relating $\log K_d$ to soil properties (pH, CEC and organic C).

Introduction

The mobility of cadmium (Cd) and zinc (Zn) in soils is often expressed by the distribution coefficient between the solid and the solution phase, K_d. Sauvé *et al.* (2000) compiled data from more than 70 studies and found K_d values to cover a range of more than 5 orders of magnitude (0.5 – 192 000 l kg^{-1} for Cd; 1.4 – 320 000 l kg^{-1} for Zn).

Values of K_d for individual sites can be derived with empirical models that relate the K_d of metals to soil properties. Multiple regression analyses of K_d values for Cd have repeatedly shown that the pH is the most important factor explaining the K_d (e.g. Gerritse & van Driel, 1984; Anderson & Christensen, 1988). Sauvé *et al.* (2000) explored the relation between the K_d of heavy metals and the soil's pH, organic matter content and total metal burden. The pH explained most of the variation in logK_d: 47% for Cd (830 data points) and 56% for Zn (298 data points).

Most of the K_d values reported are obtained by measurement of the distribution of Cd or Zn in dilute salt extracts, such as CaCl$_2$ 0.001 M (e.g. Christensen, 1989), CaCl$_2$ 0.01 M (e.g. Boekhold & van der Zee, 1992), Ca(NO$_3$)$_2$ 0.01 M (e.g. Welp & Brümmer, 1999) or mixed electrolytes (e.g. Jopony & Young, 1994). The slopes of the graphs of logK_d against pH for Cd and Zn are only slightly affected by the composition of the contact solution (e.g. Gerritse & van Driel, 1984). However, changes in the electrolytic composition may result in differences in absolute values of K_d. Larger ionic strength and larger concentrations of competing cations (e.g. Ca^{2+}) or complexing anions (e.g. Cl$^-$) lead to less sorption of Cd and Zn (Temminghoff *et al.*, 1995). Also differences in soil:solution ratio may affect the distribution of heavy metals in extracts (see, for example, Jopony & Young, 1994). The influence of electrolyte composition and soil:solution ratio on the solute concentration of Cd and Zn implies that the concentrations in a dilute salt extract are different from the concentrations in soil solution. Therefore, indigenous soil solutions are probably the most

representative to predict metal leaching. Isolation of soil solution is, however, time-consuming and typically yields only small volumes.

Extrapolation of K_ds determined in the laboratory to the field is not only problematic because of this dependency on extractant, but also because the K_d is often estimated from adsorption data of added Cd^{2+} and Zn^{2+} salts. Metals in polluted soils may, however, originate from sparingly soluble components. In addition, ageing might have strengthened the binding of the metals, thereby increasing the K_d compared with that of freshly added metals. The fixation of Cd and Zn in soils is possibly due to slow sorption of metals in oxides. This slow reaction is more pronounced for Zn than for Cd (Bruemmer *et al.*, 1988). Soil pH is probably the most important factor influencing these slow fixation reactions (Brennan, 1990). The presence of insoluble forms of metals in soil and ageing reactions both result in fixed fractions of metals in soils. Fixed metals do not contribute to the immediate solid–solution distribution that occurs between the labile pool on the solid phase and the solution phase. Values of K_d derived from adsorption experiments with soluble Cd and Zn salts may therefore underestimate the *in situ* K_d values in polluted soils in which metals are fixed. The fraction of Cd that is fixed in soil is often only moderate. Smolders *et al.* (1999) found for 10 agricultural soils that the labile Cd pool, measured by isotopic dilution, was between 62 and 90 % of the total Cd content. However, in some cases, more than half of the Cd present in the soil is fixed (e.g. Nakhone & Young, 1993; Young *et al.*, 2000), probably when Cd was introduced in the soil in an insoluble form (e.g. as mine spoil).

Relatively few *in situ* K_d measurements have been reported. Römkens & Salomons (1998) measured *in situ* K_ds of Cd, Cu and Zn in 30 unpolluted soils from The Netherlands. De Groot *et al.* (1998) determined *in situ* K_ds of Cd, Zn and other heavy metals for 46 Dutch soils, both polluted and unpolluted. In both studies, regression equations relating

logK_d to soil properties were derived. These models based on *in situ* K_ds are more representative for field conditions than models derived from adsorption studies, but they do not discriminate between chemically reactive ('labile') and unreactive ('fixed') pools.

An alternative method to estimate the *in situ* K_d is based on the concentrations of Cd and Zn in a dilute salt extract. Houba *et al.* (1996) proposed the use of 0.01 M $CaCl_2$ as extraction agent, as the ionic strength of this extract matches that of many soil solutions. In this extract metals in the solution will be in equilibrium with the same pool of metals as in field conditions, as it is unlikely that this solution extracts metals that are otherwise fixed. The same approach has been successfully adapted in our research group to estimate soil solution ^{137}Cs activity concentration that is often less than the detection limit (Waegeneers *et al.*, 1999).

In this study, the K_d values of Cd and Zn in contaminated soils from the field were determined and correlated with soil properties. The labile pool of Cd and Zn was measured for all soils by isotopic dilution. Our aim was

(1) to compare predictions of *in situ* K_ds of Cd and Zn that are either based on total metal concentrations or on radio-labile metal concentration.

(2) to assess if the concentration of Cd and Zn in a 0.01 M $CaCl_2$ extract can be used to predict the concentration of Cd and Zn in the pore water of contaminated soils in the field.

Materials and methods

Soil sampling

Topsoils (0 - 15 or 20 cm) with large concentrations of Cd and Zn were collected in Belgium (47 soils), France (17), Hungary (4) and UK (6). Table 1 summarizes their important soil characteristics. The samples were from arable land, grassland, industrial sites and residential areas. All contained more than 0.5 mg Cd kg^{-1} and more than 50 mg Zn kg^{-1}. The soils had been contaminated with metals from various sources. Metal salts had been applied in field plots 10 years before sampling to all Hungarian soils and to eight of the French soils. The other French and British soil samples had received sewage sludge. Most of the Belgian soils had been contaminated with emissions from smelters. A few samples were polluted by former mining or by alluvial deposition.

Soil characterisation

The samples of soil were sieved (< 2 mm) and dried in air. The cation-exchange capacity (CEC) was measured at the soil's pH with silverthiourea as index cation (Chhabra *et al.*, 1975). The organic C content was measured by dry combustion (Skalar CA 100). The pH was determined in 0.01 M $CaCl_2$ in a soil:solution ratio of 1:10 after 3 days of equilibration. The total metal content was determined by aqua regia digestion or, for most of the Belgian soils, by microwave digestion with $HNO_3–HBF_4–H_3PO_4–HCl–HF$. Comparison for five soils showed that total metal contents measured by the two methods agree well (within 10% difference). Concentrations of Cd and Zn in the digests were measured by ICP-OES (Perkin Elmer, Optima 3300 DV, dual view). For each digestion, an internal laboratory standard was analysed as quality control. This standard was verified against a soil sample with certified Cd and Zn content (sewage sludge amended soil, CRM 143 from the Central Bureau of Reference of the European Union). Recovery of Cd and

Zn for this standard was always between 90% and 110%. All analyses were done at least in duplicate.

Soil solution was isolated by centrifuging the soils for 1 hour at 3000 g. For most Belgian soils, air-dried samples were rewetted to field capacity with deionized water and incubated for 5 days at 20°C. For the other soils, the soil solution was isolated after plant growth in a pot trial. The soil solution was filtered through a 0.45-µm membrane filter and acidified to pH 1 with HNO_3. The concentrations of Cd, Zn and Ca in the soil solution were measured with ICP-OES. Total carbon and inorganic carbon in the soil solution were determined with a Skalar Formacs[HT] TOC analyser, and the concentration of dissolved organic carbon (DOC) was calculated as the difference between total and inorganic C.

The labile Cd and Zn in soil (E value) was measured by isotopic exchange. Duplicate samples of 2.5 g soil were weighed in polypropylene centrifugation tubes, 25 ml 0.01 M $CaCl_2$ was added, and the suspensions were spiked with between 0.25 and 0.35 ml carrier-free ^{109}Cd (~ 4000 Bq ml^{-1}) and ^{65}Zn (~ 7000 Bq ml^{-1}). The suspensions were shaken end-over-end for 16 hours (most of the Belgian soils) or 3 days (other soils). The effect of equilibration time was studied on four soils. We found that during the equilibration period (16 hours – 3 days), the E values and the concentration of the stable and radioactive Cd and Zn changed less than 10 %. The tubes were centrifuged at 3000 g (10 or 20 minutes) and two 5-ml samples were removed from each tube. The γ-activity of ^{109}Cd (energy window: 15-40 keV) and ^{65}Zn (1000-1200 keV) was measured (Minaxi, 5530 auto Gamma) on one sample. The other sample was acidified to pH 1 with HNO_3, prior to analysis of stable Cd and Zn with ICP-OES. The radio-labile content (E value, mg kg^{-1}) of Cd and Zn was calculated as

$$E = [M] \left(K_d^* + \frac{V}{W} \right), \tag{1}$$

where [*M*] is the Cd or Zn concentration (in mg l^{-1}) in the supernatant, K_d^* is the distribution coefficient of the radioisotope, *V* is the volume of solution (l), and *W* is the mass of soil (kg).

For some of the samples from Hungary and France with large K_d^*, *E* was determined in a solution of 0.01 M CaCl$_2$ and 0.1 mmol l^{-1} Na$_2$EDTA. These samples had high pH and moderate Cd and Zn content, and the Cd and Zn concentrations were therefore less than or near the detection limit of the ICP-OES ($\sim$ 5 µg l^{-1} for Cd and Zn). Addition of EDTA at small concentration (0.1 mmol l^{-1} = 1 mmol kg^{-1}) caused a decrease in the K_d^*, in some cases to less than one hundredth, and the concentrations of Cd and Zn in the extract increased. The *E* values were measured with and without addition of EDTA on 43 soils with detectable concentrations in the CaCl$_2$ extract, to test whether addition of EDTA affected the *E* values. Soil samples of Hungary and France were included with the same soil properties, but with more metal than the samples with solution concentrations less than the detection limits. The *E* measured in the presence of EDTA was for Cd between 0.82 and 1.18 (mean: 1.01) and for Zn between 0.85 and 1.17 (mean: 1.03) of the *E* measured without EDTA. This showed that the presence of EDTA did not affect the *E* significantly in these soils, which is in agreement with the findings of Stanhope *et al.* (2000). They reported that plant-labile Cd (so-called *L* value) was unaffected by addition of EDTA to concentrations of 10 mmol kg^{-1}.

Theory and data treatment

The partitioning of heavy metals between solid and solution phase is expressed in terms of K_d. The *in situ* K_d, hereafter referred to as simply K_d, is calculated as

$$K_d = \frac{M_{tot}}{[M]_{pw}},$$ (2)

where M_{tot} is the total Cd or Zn concentration (mg kg^{-1}) on the solid phase and $[M]_{pw}$ is the concentration in the pore water (mg l^{-1}). The total Cd and Zn content on the solid phase can be estimated by total metal content in soil since the soil:solution ratio is large *in situ*.

Metals are bound with varying binding energy to the solid phase and differ in remobilization kinetics. A labile and a fixed fraction can be defined based on the fraction of metals that is isotopically exchangeable for a defined contact time. The metal fraction that is 'fixed' in the soil, does not contribute to the solid–solution distribution within that certain time. The partitioning between labile metal pool and solution phase *in situ* is expressed by

$$K_d^{lab} = \frac{E}{[M]_{pw}},$$ (3)

where E (mg kg^{-1}) is the radio-labile pool measured by isotopic exchange. The K_d^{lab} differs from the K_d^{*} that expresses the partitioning between labile metal in the solid phase and in the solution phase in a 0.01 M CaCl$_2$ extract, and from the K_d that expresses the distribution between the total metal pool and the solution phase *in situ*. The K_d^{lab} and K_d are related as follows:

$$K_d = K_d^{lab} \frac{M_{tot}}{E}.$$ (4)

Stepwise linear regression was performed for both logK_d and logK_d^{lab} with pH, CEC (cmol$_c$ kg^{-1}), organic C (%), dissolved organic C (DOC, mg l^{-1}), pore water concentration of Ca ($[Ca]_{pw}$, mmol l^{-1}) and $[M]_{pw}$ (mg l^{-1}) as independent variables. All variables were

transformed to their logarithms, except for pH that is already a logarithm. The logarithmic transformation was used to linearize the relationships and to normalize the data. The appropriateness of the model was assessed by studying the normal probability plot of the residuals and the residual plots. Statistical analysis was done using SAS (Release 6.12).

Furthermore, we tested an alternative method to predict the distribution of Cd and Zn in field contaminated soils. Houba *et al.* (1996) proposed the use of a 0.01 M $CaCl_2$ extract to estimate *in situ* K_d of Cd and Zn. They did so because the ionic strength roughly matches that of the soil solution, and Ca^{2+} flocculates the soil suspension. For Cd, half of the Cd present in a 0.01 M $CaCl_2$ extract is present as chloride complex (Lebourg *et al.*, 1998), thereby promoting Cd solubilization. The complexation of Cd with Cl^- can easily be accounted for. The concentrations of Cd and Zn in the $CaCl_2$ extract may also differ from that in pore water because of differences in Ca concentration, concentration of complexing ligands, pH and the different soil:solution ratio, all factors that affect Cd and Zn sorption (see Introduction).

We attempted to refine the prediction of concentration in the pore water by correcting for Cl^- complexation (in the case of Cd) and for the difference in soil:solution ratio. In soil extracts, with small soil:solution ratios, the concentration in solution may become a substantial amount of the total amount of metal, especially in acid soils with small K_d. If the K_d is the same at *in situ* conditions as in a soil extract, then

$$\frac{M_{tot}}{[M]_{pw}} = \frac{M_{tot} - \dfrac{V}{W}[M]_{extr}}{[M]_{extr}}, \tag{5}$$

where $[M]_{extr}$ (mg l^{-1}) is the concentration of Cd or Zn in the extract, V is the volume of solution (l), and W is the mass of soil (kg). Rearranging equation (5) yields for Zn:

$$[Zn]_{pw} = [Zn]_{Ca}\left(\frac{Zn_{tot}}{Zn_{tot} - 10[Zn]_{Ca}}\right), \tag{6}$$

where $[Zn]_{pw}$ is the Zn concentration (mg l^{-1}) in the pore water, $[Zn]_{Ca}$ is the Zn concentration (mg l^{-1}) in a 0.01 M CaCl$_2$ extract at a soil:solution ratio of 1:10 and Zn_{tot} is the total Zn content in the soil (mg kg^{-1}). Complexation by Cl$^-$ in the extract should be considered in the case of Cd. At a chloride concentration of 0.02 M, about 50% of Cd in the solution is present as $CdCl_n^{2-n}$ complexes (mainly $CdCl^+$) that do not adsorb (Temminghoff *et al.*, 1995). Thus, if the Cl$^-$ concentration *in situ* is negligible then a factor 0.5 should be included, and following equation is obtained:

$$[Cd]_{pw} = 0.5[Cd]_{Ca}\left(\frac{Cd_{tot}}{Cd_{tot} - 10[Cd]_{Ca}}\right), \tag{7}$$

where Cd_{tot} is the total Cd content (mg kg^{-1}), $[Cd]_{pw}$ is the concentration (mg l^{-1}) in the pore water and $[Cd]_{Ca}$ is the concentration (mg l^{-1}) in a 0.01 M CaCl$_2$ extract at a soil:solution ratio of 1:10.

Results and discussion

Fixation of Cd and Zn

Figure 1 shows the frequencies of Cd and Zn for varying proportions of labile metal (E/M_{tot}). The proportion labile Cd ranges from 0.18 to 0.92 (median value 0.64) and the proportion labile Zn ranges from 0.05 to 0.68 (median value 0.26). The larger fixation for Zn than for Cd has been observed before by Smolders *et al.* (1999).

We found no correlation between pH and the proportion of labile Cd and only a weak (r=0.48) correlation between pH and the proportion of labile Zn. The different source of contamination and different contact time of the contaminant in the field might explain these results.

These results, as well as the results of Young *et al.* (2000) indicate that the proportions labile Cd and Zn may vary over about one order of magnitude in polluted soils. Models predicting the distribution of Cd and Zn in polluted soils that do not take in account the presence of fixed metal fractions will therefore probably have a level of uncertainty of at least one order of magnitude.

Solid–solution distribution of Cd and Zn

The K_d ranged from 5 to 5800 l kg^{-1} (Cd) and from 3 to 8900 l kg^{-1} (Zn). By regressing it on soil pH we explained most of the variation in logK_d: 55% for Cd and 70% for Zn. Although the residual variation was significantly explained by the organic C content or CEC (see Table 2), the K_d predicted based on pH and CEC or organic C still differed up to a factor of 11 (Cd) or 15 (Zn) from the observed. Linear regression models including soil pH and a capacity factor (CEC, organic C) are commonly used (e.g. Christensen, 1989; Römkens & Salomons, 1998; Sauvé *et al.*, 2000), but they do not account for differences in age and source of the contamination. The role of fixation is clearly illustrated in two

Belgian soils, with almost identical soil properties (pH~6, CEC~5 cmol_c kg^{-1}, organic C~3%), but one with a weak fixation ($E_{Zn}/Zn_{tot} = 0.52$) and the other with a large degree of fixation ($E_{Zn}/Zn_{tot} = 0.05$). The labile K_d is identical for these two soils ($K_d^{lab} = 75$ l kg^{-1}), but the *in situ* K_d of the soil with large percentage labile Zn is only one tenth that of the soil with small percentage labile Zn (K_d respectively 140 and 1400 l kg^{-1}), showing the influence of fixed fractions on the K_d.

Better predictions are therefore expected for K_d^{lab} that describes the equilibrium between the labile pool and solution phase, see Equation (3). Indeed, larger R^2_{adj} were generally obtained for K_d^{lab} than for K_d (Table 2).

Including properties of the soil solution, $[Ca]_{pw}$ and $[M]_{pw}$, further increased the coefficient of determination. For Cd, the largest R^2_{adj} was found for the regression model of $\log K_d^{lab}$ with pH, logCEC, $\log[Cd]_{pw}$ and $\log[Ca]_{pw}$:

$$\log K_d^{lab} = -1.05 + 0.45 \text{ pH} + 0.63 \text{ logCEC} - 0.28\log[Cd]_{pw} - 0.42 \log[Ca]_{pw}. \quad (8)$$

This regression model is similar to an extended Freundlich equation. Elzinga *et al.* (1999) derived the following equation for Cd from sets of sorption data collected from the literature (recalculated to same units as defined above):

$$\log K_d^{ads} = -1.18 + 0.45 \text{ pH} + 0.63 \text{ logCEC} - 0.13 \log[Cd]_{sol} - 0.47 \log[Ca]_{sol},$$

$$n=1125, R^2 = 0.78 \quad (9)$$

in which K_d^{ads} (l kg^{-1}) is the K_d determined in a batch experiment, $[Cd]_{sol}$ (mg l^{-1}) is the Cd concentration in solution and $[Ca]_{sol}$ (mmol l^{-1}) is the Ca concentration of the background electrolyte. The correspondence between Equations (8) and (9) is striking. Regression equations based on batch adsorption experiments appear to predict the solid–solution distribution of labile metal fractions in field samples well. This correspondence is to be expected because adsorption K_ds are equivalent to the labile K_ds. However, such

regression models may fail to predict the total metal partitioning in field soils because the metal can be present in fixed or slowly desorbing fractions. Elzinga *et al.* (1999) found that the regression equations derived from batch experiments in the laboratory for Cd and Zn underestimated the solid–solution distribution in field samples.

For Zn, the best regression model was obtained with pH, log organic C, $\log[\text{Ca}]_{pw}$ and $\log[\text{Zn}]_{pw}$ as independent variables. No larger R^2_{adj} was obtained for $\log K_d^{lab}$ than for $\log K_d$, with all regression variables included which can probably be ascribed to the large number of independent variables. When only pH or pH and log organic C were included in the model, R^2_{adj} was 4 to 6% higher for the regression of $\log K_d^{lab}$ (Table 2).

The regression equations for $\log K_d^{lab}$ can be used to predict the *in situ* K_d by correcting for the labile metal fraction (E/M_{tot}), see Equation (4). Figure 2 shows these predictions based on labile metal fractions and soil properties (pH, CEC or organic C, $[\text{Ca}]_{pw}$ and $[M]_{pw}$). The observed K_d differs maximally by a factor 3 from the predicted K_d, both for Cd and Zn. These regression models adequately predict the observations. They are not practical in the field, however, because the labile metal fraction and the concentration of Ca, Cd and Zn in the soil solution must be known. On the other hand, the more practical regression models that are based on total metal concentration, pH, organic C or CEC, leave more than an order of magnitude of uncertainty for prediction of the *in situ* K_ds, which is not acceptable in risk evaluations.

Estimating concentration of Cd and Zn in pore water from the concentration in a 0.01 M CaCl₂ extract

Concentrations of Cd in the 0.01 M CaCl₂ extract were generally larger than those in the pore water. The concentration in the extract was, on average, 2.4 and maximum 11 times larger than that in the soil solution. The larger concentrations in the CaCl₂ extract can be

ascribed partly to the complexation of Cd by Cl^-. The coefficient of correlation (r) between concentration of Cd in the pore water and in the $CaCl_2$ extract was 0.75. The Zn concentrations in the $CaCl_2$ extract were not systematically larger or smaller than those in the pore water. Differences between the Zn concentration in the extract and in the soil solution were within a factor of 10, except for three soil samples with high pH (pH 6.1, 7 and 7.4) and small Zn concentration (< 50 µg l^{-1}) in the Ca extract. For these samples, concentration of Zn was between 40 and 50 times larger in the pore water than in the Ca extract. Complexation with dissolved organic matter may have caused the large Zn concentration in the soil solution, while this is not the case in the Ca extract, perhaps because of dilution and the coagulation of colloids. The coefficient of correlation between concentration of Zn in the pore water and in the $CaCl_2$ extract was 0.62.

Equations (6) and (7) correct for the difference in Cl^- concentration and soil:solution ratio between the $CaCl_2$ extract and the soil solution. Using these equations, the predicted concentrations of Cd and Zn in the pore water correlated better with those observed ($r=0.77$ for Cd and $r=0.73$ for Zn), but there was still a large degree of uncertainty. This may be ascribed partly to the difference in Ca concentration between the soil solution and the Ca extract, which is not considered in Equations (6) and (7). We studied the effect of the Ca concentration on the solid–liquid distribution of Cd and Zn on several soils at Ca concentrations, as $Ca(NO_3)_2$, between 0.1 and 10 mmol l^{-1}. An increase of the Ca concentration with a factor 10 decreased, on average, the K_d^{lab} with a factor 2.8 ($=10^{0.45}$), both for Cd and Zn, thus

$$K_d^{lab,Ca} = K_d^{lab,10}\left(\frac{10}{[Ca]_{sol}}\right)^{0.45}, \tag{10}$$

where $K_d^{lab,Ca}$ and $K_d^{lab,10}$ are the distribution coefficients between the labile metal pool and the solution phase at Ca concentration $[Ca]_{sol}$ (mmol l^{-1}) and at a Ca concentration of 10

mmol l^{-1} respectively. The theoretical difference between K_d^{lab} in a 10 mmol l^{-1} CaCl$_2$ extract ($K_d^{\text{lab,extr}}$) and in the soil solution (K_d^{lab}) caused by a different Ca concentration, is therefore

$$K_d^{\text{lab}}(\text{Zn}) = K_d^{\text{lab,extr}} \left(\frac{10}{[\text{Ca}]_{\text{pw}}} \right)^{0.45}, \tag{11}$$

and

$$K_d^{\text{lab}}(\text{Cd}) = 2K_d^{\text{lab,extr}} \left(\frac{10}{[\text{Ca}]_{\text{pw}}} \right)^{0.45}. \tag{12}$$

The factor 2 in Equation (12) accounts for the complexation of Cd by Cl$^-$. The *in situ* (large soil:solution ratio) adsorbed labile pool can be approximated by the total labile pool (*E* value), but in the extract – with a smaller (1:10) soil:solution ratio – adjustment should be made for the amount of metal in solution by

$$\frac{K_d^{\text{lab,extr}}}{K_d^{\text{lab}}} = \frac{E - 10[M]_{\text{extr}}}{[M]_{\text{extr}}} \frac{[M]_{\text{pw}}}{E} = \frac{[M]_{\text{pw}}}{[M]_{\text{extr}}} - 10 \frac{[M]_{\text{pw}}}{E},$$

or

$$\frac{[M]_{\text{pw}}}{[M]_{\text{extr}}} = \frac{K_d^{\text{lab,extr}}}{K_d^{\text{lab}}} + \frac{10}{K_d^{\text{lab}}}. \tag{13}$$

Combining Equations (11) and (12) with Equation (13) yields

$$[\text{Zn}]_{\text{pw}} = [\text{Zn}]_{\text{Ca}} \left\{ \left(\frac{[\text{Ca}]_{\text{pw}}}{10} \right)^{0.45} + \frac{10}{K_d^{\text{lab}}} \right\}, \tag{14}$$

and

$$[\text{Cd}]_{\text{pw}} = [\text{Cd}]_{\text{Ca}} \left\{ 0.5 \left(\frac{[\text{Ca}]_{\text{pw}}}{10} \right)^{0.45} + \frac{10}{K_d^{\text{lab}}} \right\}, \tag{15}$$

where [Cd]$_{\text{Ca}}$ and [Zn]$_{\text{Ca}}$ are the metal concentrations in the 0.01 M CaCl$_2$ extract. The concentrations in the pore water predicted with these equations agreed better with the measured concentrations than those from Equations (6) and (7). This is because correction is made for the difference in Ca concentration between the extract and the soil solution and

because the labile metal pool is considered as the buffering pool. Predicted concentrations correlated well with those observed (r=0.97 for Cd and r=0.98 for Zn), and the predicted pore water concentration differed maximum by a factor of 3 from the measured concentration except for three soil samples in the case of Zn (Figure 3). This approach has, however, less practical use, because properties of the soil solution and E values are required for the prediction. It does show, however, that differences between concentrations of Cd and Zn in the soil solution and in a dilute salt extract can be explained satisfactorily.

Comparison between predictions based on the concentration in a CaCl₂ extract and based on regression models

Two 'practical' methods to predict concentration of Cd and Zn in the pore water were compared, either the prediction based on the concentration of Cd and Zn in a CaCl₂ extract, Equations (6) and (7), or the prediction based on total metal content and regression equations for $\log K_d$:

$$[\text{Cd}]_{\text{pw}} = \frac{\text{Cd}_{\text{tot}}}{10^{-0.38 + 0.41\,\text{pH} + 0.58\,\log\text{CEC}}}, \tag{16}$$

and

$$[\text{Zn}]_{\text{pw}} = \frac{\text{Zn}_{\text{tot}}}{10^{-1.16 + 0.58\,\text{pH} + 0.39\,\log\text{OC}}}. \tag{17}$$

Although the more comprehensive regression models (Table 2) give better predictions, we did not consider them because they include properties of the soil solution.

The predictions based on the concentration in a CaCl₂ extract correlated better with the observations than those recalculated from the regression equation (Table 3). However, the CaCl₂ extraction largely underestimated concentrations of Zn for three samples with small Zn concentrations and rather high pH (pH>6), whereas the regression model did perform

better for these samples. When these three samples were excluded, the prediction improved considerably (Table 3).

We tested these two methods to estimate pore water concentrations of Cd and Zn also on an independent data set of de Groot *et al.* (1998). De Groot *et al.* had measured total Cd and Zn content (by aqua regia digestion), concentration in the soil solution (obtained by centrifuging) and in a 0.01 M CaCl$_2$ extract in a 1:10 soil:solution ratio for 49 Dutch soils, both polluted and non-polluted. Again, predictions based on the concentration in the Ca extract were better than when the regression models for logK_d were used. The predictions based on the concentrations in the Ca extract differed maximally a factor 3 from the observed concentrations for Cd and maximally a factor 6 for Zn, except for three soil samples with small Zn concentration (<50 µg l^{-1}) in the CaCl$_2$ extract.

Thus, extraction with a CaCl$_2$ 0.01 M extract provides reasonable estimates of the concentration of Cd and Zn in the pore water of contaminated soils in the field. Also other dilute salt extracts can be used to estimate the pore water concentration of Cd and Zn. Extraction with 0.01 M Ca(NO$_3$)$_2$, for instance, is equivalent, but the correction factor 0.5 for Cd in Equation (7) may be omitted as the complexation of Cd with NO$_3^-$ is negligible. For other soil:solution ratios than 1:10, the factor 10 in Equations (6) and (7) should be adjusted. Predictions can be refined by taking into account differences in ionic strength (mainly Ca) between pore water and salt extract. We found that predictions could be improved by estimating the *in situ* Ca concentration based on the electrical conductivity of a water extract in a 1:1 soil:solution ratio.

Conclusions

The K_d of Cd and Zn *in situ* in polluted soils can be predicted by regression models with soil properties as predictors. However, the residual variance is still large, partly due to the variable degree of metal fixation between soils. Better predictions of the solid–solution distribution were obtained when Cd and Zn in solution were assumed to be in equilibrium with the labile adsorbed metals instead of the total adsorbed metals.

Rather than measuring labile metal fractions in soil, a dilute salt extract can be used to estimate the concentrations of Cd and Zn in the pore water. Concentrations of Cd and Zn in the soil solution of field contaminated soils that were predicted based on the concentration in a 0.01 M $CaCl_2$ extract, were in good agreement with observed values. Differences in ionic strength between the pore water and the soil extract explained most of the differences between the predicted and observed values.

References

Anderson, P.R. & Christensen, T.H. 1988. Distribution coefficients of Cd, Co, Ni, and Zn in soils. *Journal of Soil Science*, **39,** 15-22.

Boekhold, A.E. & van der Zee, S.E.A.T.M. 1992. A scaled sorption model validated at the column scale to predict cadmium contents in a spatially variable field soil. *Soil Science*, **154,** 105-112.

Brennan, R.F. 1990. Reaction of zinc with soil affecting its availability to subterranean clover. II. Effect of soil properties on the relative effectiveness of applied zinc. *Australian Journal of Soil Research,* **28,** 303-310.

Bruemmer, G.W., Gerth, J. & Tiller, K.G. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. 1. Adsorption and diffusion of metals. *Journal of Soil Science*, **39,** 37-52.

Chhabra, R., Pleysier, J. & Cremers, A. 1975. The measurement of the cation exchange capacity and exchangeable cations in soils: a new method. In: *Proceedings of the International Clay Conference* (ed. S.W. Bailey), pp. 439-449. Applied Publishing Ltd., Wilmette, Illinois, USA.

Christensen, T.H. 1989. Cadmium soil sorption at low concentrations. 8. Correlation with soil parameters. *Water, Air and Soil Pollution*, **44,** 71-82.

De Groot, A.C., Peijnenburg, W.J.G.M., van den Hoop, M.A.G.T., Ritsema, R. & van Veen, R.P.M. 1998. *Heavy metals in Dutch field soils: an experimental and theoretical study on equilibrium partitioning.* Report nr 607220 001. National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands.

Elzinga, E.J., van Grinsven, J.J.M. & Swartjes, F.A. 1999. General purpose Freundlich isotherms for cadmium, copper and zinc in soils. *European Journal of Soil Science*, **50,** 139-149.

Gerritse, R.G. & van Driel, W. 1984. The relationschip between adsorption of trace metals, organic matter, and pH in temperate soils. *Journal of Environmental Quality*, **13,** 197-204.

Houba, V.J.G., Lexmond, T.M., Novozamsky, I. & Vanderlee, J.J. 1996. State of the art and future developments in soil analysis for bioavailability assessment. *Science of the Total Environment*, **178,** 21-28.

Jopony, M. & Young, S.D. 1994. The solid–solution equilibria of lead and cadmium in polluted soils. *European Journal of Soil Science*, **45**, 59-70.

Lebourg, A., Sterckeman, T., Ciesielski, H. & Proix, N. 1998. Trace metal speciation in three unbuffered salt solutions used to assess their bioavailability in soil. *Journal of Environmental Quality*, **27,** 584-590.

Nakhone, L.N. & Young, S.D. 1993. The significance of (radio-)labile cadmium pools in soil. *Environmental Pollution*, **82,** 73-77.

Römkens, P.F.A.M. & Salomons, W. 1998. Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. *Soil Science*, **163,** 859-871.

Sauvé, S., Hendershot, W. & Allen, H.E. 2000. Solid–solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology*, 34**,** 1125-1131.

Smolders, E., Brans, K., Földi, A. & Merckx, R. 1999. Cadmium fixation in soils measured by isotopic dilution. *Soil Science Society of America Journal*, **63,** 78-85.

Stanhope, K.G., Young, S.D., Hutchinson, J.J. & Kamath, R. 2000. Use of isotopic dilution techniques to assess the mobilization of non-labile Cd by chelating agents in phytoremediation. *Environmental Science and Technology,* **34**, 4123-4127.

Temminghoff, E.J.M., van der Zee, S.E.A.T.M. & de Haan, F.A.M. 1995. Speciation and calcium competition effects on cadmium sorption by sandy soil at various pHs. *European Journal of Soil Science*, **46,** 649-655.

Waegeneers, N., Smolders E. & Merckx, R. 1999. A $CaCl_2$ 0.01 M extract predicts the soil solution composition and plant availability of ^{137}Cs. In: *Proceedings from the Fifth International Conference on the Biogeochemistry of Trace Metals* (eds W.W. Wenzel, D.C. Adriano, B. Alloway, H.E. Doner, C. Keller, N.W. Lepp, M. Mench, R. Naidu and G.M. Pierzynski.), pp. 48-49. Vienna, Austria.

Welp, G. & Brümmer, G.W. 1999. Adsorption and solubility of ten metals in soil samples of different composition. *Journal of Plant Nutrition and Soil Science*, **162,** 155-161.

Young, S.D., Tye, A., Carstensen, A., Resende, L. & Crout, N. 2000. Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science*, **51,** 129-136.

Table 1 Summary of selected properties of the 74 soil samples. Concentrations of Ca, $[Ca]_{pw}$, and dissolved organic carbon (DOC) were measured in the soil solution.

	pH (in $CaCl_2$)	Organic C / %	CEC /$cmol_c\ kg^{-1}$	Ca_{pw} /mmol l^{-1}	DOC /mg l^{-1}	Cd_{tot} /mg kg^{-1}	Zn_{tot} /mg kg^{-1}
Mean	6.02	6.0	9.7	5.1	71	16.0	1274
St. dev.	1.01	7.8	8.0	3.9	43	21.8	4439
Minimum	3.49	0.9	0.3	0.3	2	0.5	53
Maximum	7.53	38	24.9	18.6	233	118	34 100

Table 2 Summary of linear regression for $\log K_d$ (l kg^{-1}) and $\log K_d^{lab}$ (l kg^{-1}) of Cd and Zn with respect to soil properties. The CEC is expressed in cmol$_c$ kg^{-1}, organic C (OC) in %, [Cd]$_{pw}$ en [Zn]$_{pw}$ in mg l^{-1} and [Ca]$_{pw}$ in mmol l^{-1}. All regression coefficients are significant at α=0.05.

	cadmium							zinc						
				Regression coefficients							Regression coefficients			
Regression for	n [a]	R^2_{adj}	intercept	pH [b]	logCEC	log[Cd]$_{pw}$	log[Ca]$_{pw}$	n [a]	R^2_{adj}	intercept	pH [b]	logOC	log[Zn]$_{pw}$	log[Ca]$_{pw}$
$\log K_d$	59	0.54	-0.76	0.55				56	0.69	-1.43	0.66			
$\log K_d^{lab}$	57	0.59	-1.07	0.57				54	0.75	-1.52	0.58			
$\log K_d$	58	0.66	-0.38	0.41	0.58			56	0.71	-1.16	0.58	0.39		
$\log K_d^{lab}$	56	0.73	-0.66	0.41	0.62			54	0.75	-1.31	0.51	0.30		
$\log K_d$	56	0.81	-0.77	0.44	0.61	-0.29	-0.48	43	0.88	-1.05	0.62	0.65	-0.52	-0.60
$\log K_d^{lab}$	55	0.85	-1.05	0.45	0.63	-0.28	-0.42	42	0.87	-1.26	0.55	0.65	-0.45	-0.52

[a] number of data points   [b] pH measured in 0.01 M CaCl$_2$ in a 1:10 soil:solution ratio

Table 3 Comparison between predictions of porewater concentration ($[M]_{pw}$) of Cd and Zn. Prediction was made with K_d obtained from regression with soil variables, Equations (16) and (17), or based on the concentration in a 0.01 M $CaCl_2$ extract, Equations (6) and (7). Correlation coefficients between measured and predicted concentration (r) and percentiles of the ratio of observed and predicted concentration are given.

Metal	Method	n [a]	r	$\dfrac{\text{Observed}[M]_{pw}}{\text{Predicted}[M]_{pw}}$				
				Minimum	10%	50%	90%	Maximum
Cd	K_d, Equation (16)	58	0.60	0.17	0.31	0.95	2.7	12
	$CaCl_2$, Equation (7)	54	0.77	0.16	0.46	1.0	2.9	3.0
Zn	K_d, Equation (17)	59	0.51	0.12	0.30	1.1	4.8	17
	$CaCl_2$, Equation (6)	51	0.73	0.17	0.50	1.0	7.3	51
		48 [b]	0.73	0.17	0.45	0.97	3.3	10

[a] number of data points

[b] omitting Zn in the Ca extract < 50 µg Zn l^{-1}

Figure Captions

Figure 1 Histograms of the proportion radio-labile metal (E) relative to the total metal content for (a) Cd and (b) Zn.

Figure 2 Comparison between the measured *in situ* K_d values of Cd (n=55) and Zn (n=42) and values predicted based on soil properties and labile metal fractions. Solid line represents the 1:1 line and the dashed lines indicate 3 times over- and under-prediction. Predictions were made using following equations:

$$K_{d,Cd} = \frac{Cd_{tot}}{E_{Cd}} \times 10^{-1.05 + 0.45\,pH + 0.63\,logCEC - 0.28log[Cd]_{pw} - 0.42log[Ca]_{pw}} \,,$$

$$K_{d,Zn} = \frac{Zn_{tot}}{E_{Zn}} \times 10^{-1.26 + 0.55\,pH + 0.65\,log\,organicC - 0.45log[Zn]_{pw} - 0.52log[Ca]_{pw}} \,.$$

Figure 3 Comparison between the concentration of (a) Cd (n=54) and (b) Zn (n=51) in the pore water and the concentrations predicted with Equations (14) and (15). These are based on the concentration in a 0.01 M $CaCl_2$ extract. Solid line represents the 1:1 line and the dashed lines indicate 3 times over- and under-prediction.
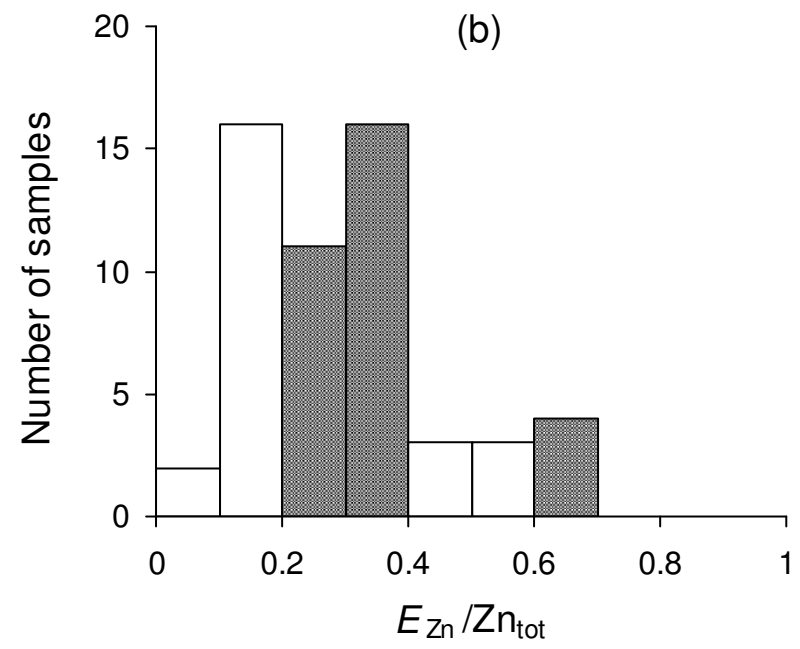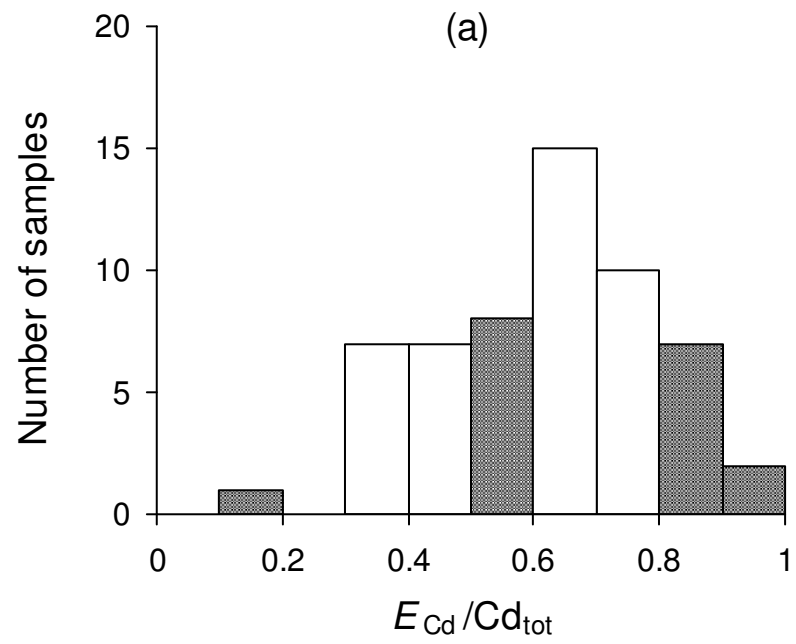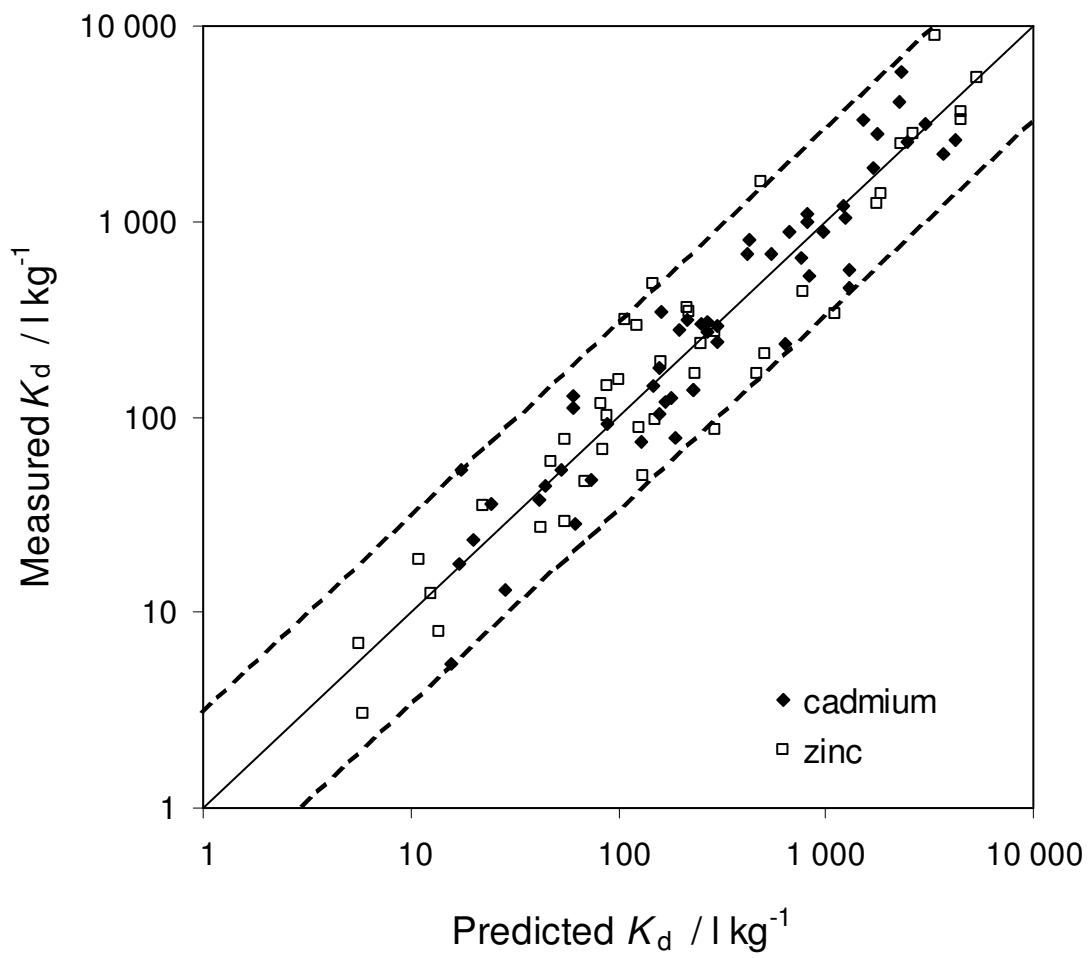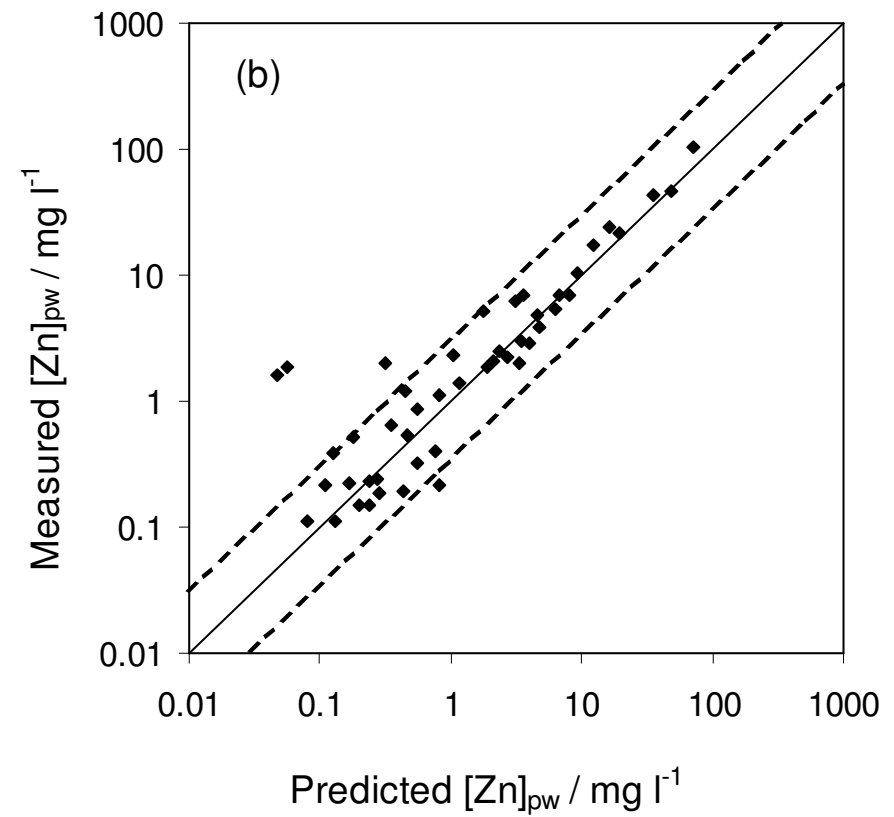
Figure 1

Figure 2

Figure 3