Determination of free heavy metal ion concentrations in soils around a cadmium rich zinc deposit

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The study of heavy metal speciation is of interest for the evaluation of their ecotoxicological risk. Free heavy metal ion concentrations of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} were studied at different soil to soil solution ratio (SSR) to discuss metal bioavailability and toxicity in circumstance. The samples were collected from two farmed soils, impacted by a cadmium rich zinc deposit, Guizhou, China. One is near a bridge (QBT for short), which is 15 km away from smelter and is regarded as polluted by fly ash from smelter, the other is located 300 m away from a smelting factory (BXT for short), and it is polluted badly by waste water from smelter. To determine the free heavy metal ion concentration, Donnan Membrane Technique (DMT) and ECOSAT program were used. The concentrations of free copper and zinc ions in QBT and all studied metal ions in BXT were nearly in direct ratio with the soil to soil solution ratio, and they increased with the increasing of SSR. The variational trends of the concentrations of free nickel and cadmium ions in QBT were contrary to those of copper and zinc ions. The measured and predicted results were compared and they agreed with each other. Individual sorbents contribution to metal binding was also predicted. The results suggest soil organic matter is the most important sorbents in the two soils, and hydrous ferric oxide takes the second place.

Keywords: soil, free heavy metal ion concentration, Donnan Membrane Technique (DMT), ECOSAT program, contribution

INTRODUCTION

During recent several decades soil is polluted more and more serious by heavy metals because of mining, smelting, irrigating with sewerage and some other human activities. These heavy metals may adversely affect soil ecology, agricultural production or product quality, and ground water quality, and will ultimately harm to health of mankind by food chain. These effects are closely related to the biological availability of heavy metals, which in turn are controlled by the metal ion speciation in the soil (Davis *et al.*, 1992; Katbata-Pendias, 1993; Alloway, 1995). Metals exist in a number of different soluble and particulate forms, which influence their mobility and bioavailability (Ge *et al.*, 2005), and free metal activity has been shown to be the key factor in determining metal bioavailability and toxicity in most circumstance (Parker and Pedler, 1996; Weng *et al.*, 2001a; Cancès *et al.*, 2003). Therefore, measuring of free metal ion concentrations in soil solution becomes important.

The free metal ion concentration not only depends on the total metal content in soils, but also on the metal species that exist in the soil. In addition, some environmental conditions (e.g., pH, concentration of competing ions, concentration of complexing ligands in solution, and the soil colloid) and characteristics of organism in soil may play an important role (Temminghoff *et al.*, 2000). Hereto there are a number of methods determining the free metal ion concentration, but each method has its advantages and limitations (Florence, 1986; Apte and Batley, 1995; Mota and Correia dos Santos, 1995). The ion selective electrometry (ISE) is simple and cheap, and can directly measure the free metal ion concentration in solution (Mota and Correia dos Santos, 1995). But its detection limit is high, and other metal ions in solution interferes measurement. The voltammetric methods could measure heavy metal speciation at small concentration (10^{-8} – 10^{-11} mol/L) at first hand (Mota and Correia dos Santos, 1995). But the reaction equilibrium is disturbed by the current applied in the electrolytic cell, and this problem is hardly avoided (Nordstrom, 1996). The method of competitive chelation could achieve free heavy metal ions concentrations directly with good sensitivity, while chelates attain equilibrium with soils very slowly (Norvell and Lindsay, 1969, 1972; Workman and Lindsay, 1990). The cation

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Table 1. Soil characteristics and total metal content extracted with 2 mol/L HNO₃

Sample	pH	CEC–BaCl ₂ (mmol/kg)	OM (%)	Clay (%) (<2 μm)	Fe–ox (g/kg)	Fe–DCB (g/kg)	Total metal content extracted with 2 mol/L HNO ₃ (μmol/kg)			
							Cu	Zn	Ni	Cd
QBT	7.59 ± 0.02	11.89 ± 0.51	4.82 ± 0.07	2.3 ± 0.2	5.05 ± 0.08	19.57 ± 0.41	1153.91 ± 28.36	13137.88 ± 274.06	168.64 ± 1.44	46.15 ± 0.24
BXT	7.51 ± 0.01	13.14 ± 0.39	4.90 ± 0.09	2.5 ± 0.3	5.00 ± 0.06	47.23 ± 0.82	3209.34 ± 34.25	38648.02 ± 768.42	411.28 ± 2.97	538.06 ± 1.87

Table 2. Ion exchange membrane properties

Color	Thickness (mm)	Exchange capacity (mol/kg)	Water content (%)	Surface resistance (μcm ⁻²)	Transference (%)	Demolishment intensity (MPa)
Black	0.11–0.13	≥1.6	≥22	≤8	≥95	≥1.5

exchange resin method can measure several free metal ion concentrations at the same time (Apte and Batley, 1995). But before the method was used, some condition required knowing. It included the adsorption properties of selected resin and the soil solution composition (Fotovat and Naidu, 1997). This make the method complicated.

In recent, a procedure has been developed, named as Donnan membrane technique, which is able to measure several free metal ion concentrations at the same time, moreover, all the metals did not interfere each other, and it minimizes the disturbance of substrate (Temminghoff *et al.*, 2000). It has been successfully used to measured free metal ion concentration in natural waters (Weng *et al.*, 2002; Liesbeth *et al.*, 2006) and soils (Weng *et al.*, 2001a, b; Weng *et al.*, 2002; Cancès *et al.*, 2003) at different pH for assessment of water and soil quality. It was also used for investigating the availability of nutrients in animal slurry for plant uptake (van der Stelt *et al.*, 2005). The objective of this study was to know the heavy metal bioavailability and chemical speciation in the studied soil, and assess the risks posed by contaminated soils. We apply Donnan Membrane Technique to measure the free Cu²⁺, Zn²⁺, Ni²⁺ and Cd²⁺ concentrations in two farmed soils at different SSR, which were compared with those predicted using ECOSAT program. Individual sorbents contribution to metal binding was also predicted. The relative important soil sorbents include soil organic matter, iron hydroxides and clay.

METHODOLOGY

Soil sample

Two farmed soils were collected from the district of a cadmium rich zinc deposit, Guizhou, China. One is near a bridge (QBT for short), which is 15 km away from smelter and is regarded as polluted by fly ash from smelter, the other is located 300 m away from a smelting factory

(BXT for short), and BXT is polluted badly by waste water from smelter (Ye and Liu, 2001; Liu *et al.*, 2004). The samples have been oriented to collect a representative topsoil (0–20 cm) sample of 20 kg in closed plastic bags. After mixed, the samples were dried and sieved at 2 mm. All the experimental studies are done on this fraction (<2 mm). The different bulk soil chemical properties and total metal content extracted with 2 mol/L HNO₃ are given in Table 1.

Donnan membrane technique

Donnan membrane technique is based on theory of Donnan equilibrium. A semipermeable cation exchange membrane separates the reaction cell into two parts: the donor cell and the acceptor cell. The ion exchange membrane properties used were shown in Table 2. Donor solution was composed of background electrolyte and studied soils. Before experiment the solution in the donor cell has reached equilibrium with soil samples. Acceptor solution includes only background electrolyte solution. Peristaltic pumps were used to circle the donor and acceptor solution. The two solutions will diffuse mutually in a subminiature cell through cation exchange membrane, and at last equilibrium will be attained. When Donnan membrane equilibrium is reached, the concentration ratios of the metal ions in the donor solution and in the acceptor solution are equal (Temminghoff *et al.*, 1997).

$$(C_{i,don}/C_{i,acc})^{1/Z_i} = (C_{j,don}/C_{j,acc})^{1/Z_j}, \quad (1)$$

where $C_{i,don}$ and $C_{i,acc}$ are the concentrations of the “free” cation i in the donor and acceptor solution, and Z_i is its charge, and $C_{j,don}$, $C_{j,acc}$ and Z_j are the same for cation j . Assuming that cation j almost can not form complexes with ligands, the total concentration is similar to the “free” cation concentration (Temminghoff *et al.*, 2000; Weng *et al.*, 2001b). Potassium was selected in this study. In the

experiment the total volume of the acceptor solution is 15 ml, whereas that of the donor solution is 250 ml. A large donor volume is used to guarantee that metals diffused to the acceptor solution are very small as compared to the total metal concentration in the donor solution, to ensure that changes in the metal concentration will be negligible. After attaining Donnan membrane equilibrium, the donor solutions were sampled for $[K^+]$, and acceptor solutions for both $[K^+]$ and $[M^{2+}]$. $[K^+]$ was measured by AAS (PE-AA800), and $[M^{2+}]$ were measured by ICP-MS.

Fig. 1. pH measured as function of soil to soil solution ratio.

Modelling

ECOSAT is a computer program which can be used to calculate the chemical equilibrium composition of soil-water systems, depending on speciation and transport (Keizer and Van Riemsdijk, 2002). The multisurface model considers soils as a set of independent sorption surfaces, i.e., organic matter, iron hydroxides, and clay. The metal speciation was predicted using models of adsorption and ion exchange for each sorbent (Weng *et al.*, 2001b).

Humic acid was used as an analogue for the reactive soil organic matter (SOM). The Non Ideal Competitive Adsorption Donnan (NICA-Donnan) model is one of the most advanced models for competitive metal ion binding to humic substances. This model includes site binding heterogeneity, electrostatic effects, competitive binding, and ion specific non-ideality, so it was chosen for metal binding to soil organic matter (Kinniburgh *et al.*, 1999; Koopal *et al.*, 2005). There are two types of iron hydroxides in soil, amorphous and crystalline ferric oxides. In the model they were assumed as hydrous ferric oxide (HFO) and goethite, respectively. Metal binding to HFO was described by a two site surface complexation diffuse double layer (DDL) model. The adsorption of metals to goethite was calculated with the charge distribution multi-site complexation (CD-MUSIC) model (Dzombak and

Fig. 2. Free heavy metal ion concentrations measured as function of soil to soil solution ratio.

Fig. 3. Comparison of measured and modeled free metal ion concentrations. —: one to one line.

Morel, 1990; Hiemstra and Van Riemsdijk, 1996, 1999). X-ray diffraction shows that most clay silicate is illite in the two studied soils (Yi, 2005), so illite was taken as a representative in the model. Its binding metals was model through a Donnan approach (Weng *et al.*, 2001b).

RESULTS AND DISCUSSION

Analytical results

The Cu and Zn transporting through the selected membrane as function of time had been tested, and Donnan equilibrium reached after about 24 h (Yi *et al.*, 2005). The free metal ion concentrations of Cu, Zn, Ni and Cd in two soils were measured using Donnan Membrane Technique (DMT) at different soil to soil solution ratio. We can know pH varieties with SSR from Fig. 1, and Fig. 2 shows the free metal ion concentrations are almost in line with SSR.

The Cu^{2+} concentration measured ranges from 10^{-8} to $10^{-6.7}$ mol/L, Zn^{2+} concentration varies from $10^{-4.9}$ to $10^{-4.2}$ mol/L, Ni^{2+} concentration is between $10^{-7.1}$ to $10^{-6.2}$ mol/L, and Cd^{2+} concentration measured varies from $10^{-8.5}$ to $10^{-6.4}$ mol/L. In general, the free metal ion concentrations increases with increasing SSR, except for the concentrations of free nickel and cadmium ions in QBT. Their variational tendencies are contrary to the oth-

Fig. 4. Calculated metals distributions in soils.

ers. They decrease while SSR increases. With increasing dilution, pH of QBT decreased sharply (Fig. 1). It is widely accepted that pH is one of the key factor in affecting the metal adsorption. Moreover, according to the calculated metals distributions in soils, the contributions to metal binding of soil organic matter reduced with the decreasing SSR. The adverse variational tendencies of free nickel and cadmium ions in QBT were mostly probably the result of Ni^{2+} and Cd^{2+} release from soil organic matter. Among these metals, Cu has the lowest free ion concentration in comparison with total Cu. Less than 0.25% of the total 2 mol/L HNO_3 extractable Cu exists as free Cu^{2+} , whereas for Zn, the soil has much lower affinity for Zn, so it exceeds 4.0%.

Comparison between free heavy metal activity predicted and measured

Not only the free heavy metal ion concentrations in the two soils were measured, but also they were modeled. Prediction was done with the data given in Table 1. In Fig. 3, the predicted free Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} concentrations using ECOSAT program are compared to those measured. They are in good agreement, except for zinc ion. The errors of free Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} concentrations are within 0.2, 0.8, 0.1 and 0.15 log-unit, respectively. Compared to their free concentration ranges, such errors are reasonable, except for Zn^{2+} . Free Zn^{2+} concentration nearly went beyond the detection limit of the ICP-MS, so its error was much higher. But it is still considered succeeding well according to some other results (Weng *et al.*, 2001b).

Individual sorbents contribution to metal binding

Contributions of soil sorbents to the heavy metals adsorptions were modeled through ECOSAT at different SSR. The sorbents in soil included soil organic matter, iron hydroxides, clay and the Donnan gel of soil organic matter.

Figure 4 showed that the contribution bound to clay is very little, and could be neglected. Copper is mainly contributed in soil organic matter, and accounting 80%. With the decreasing of SSR, the contributions of copper bounded to soil organic matter and the Donnan gel of soil organic matter decrease slowly, but the contribution bounded to iron hydroxides increases. Zinc is mainly contributed in soil organic matter and iron hydroxides, and accounting 40% respectively. As SSR decreases, the contribution of zinc bounded to soil organic matter increases little, and the contribution bounded to iron hydroxides is hardly changed, but the Donnan gel of soil organic matter decreases slowly. Nickel is mainly bounded to the soil organic matter and iron hydroxides, and cadmium is almost bounded to the soil organic matter. The contributions of nickel and cadmium are affected little by SSR.

Such results denote soil organic matter is the most important sorbents in the two soils, and hydrous ferric oxide takes second place.

CONCLUSIONS

The free heavy metal ion concentrations of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} were measured with Donnan membrane technique and modeled through ECOSAT at different SSR, and they were consistent with each other. They are usable tool for assessing the risks posed by contaminated soils. In the studied soils free metal ion concentrations increases with increasing SSR, except for the concentrations of free nickel and cadmium ions in QBT. They decrease while SSR increases. Ni^{2+} and Cd^{2+} released from soil organic matter may be response for the result, which was intensified by the modeled contributions of soil sorbents to the heavy metals adsorptions. We concluded that enlarging the quantity of irrigation will reduce the risks posed by the contaminated soils.

According to the modeled contributions of heavy metals, most metals were adsorbed by soil organic matter and hydrous ferric oxide in the two soils, accounting to 80% or more. So the additives comprising much organic matter and hydrous ferric oxide will immobilize the heavy metals contained in the contaminated soils, then the bioavailability of heavy metal in the soil will decrease. This will be a good remediation for the studied soils.

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