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# Pollution, fractionation, and mobility of Pb, Cd, Cu, and Zn in garden and paddy soils from a Pb/Zn mining area

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**Abstract** This study was conducted to investigate the pollution load index, fraction distributions, and mobility of Pb, Cd, Cu, and Zn in garden and paddy soils collected from a Pb/Zn mine in Chenzhou City, China. The samples were analyzed using Leleyter and Probst's sequential extraction procedures. Total metal concentrations including Pb, Cd, Cu, and Zn exceeded the maximum permissible limits for soils set by the Ministry of Environmental Protection of China, and the order of the pollution index was Cd > Zn > Pb > Cu, indicating that the soils from both sites seriously suffered from heavy metal pollution, especially Cd. The sums of metal fractions were in agreement with the total contents of heavy metals. However, there were significant differences in fraction distributions of heavy metals in garden and paddy soils. The residual fractions of heavy metals were the predominant form with 43.0% for Pb, 32.3% for Cd, 33.5% for Cu, and 44.2% for Zn in garden soil, while 51.6% for Pb, 40.4% for Cd, 40.3% for Cu, and 40.9% for Zn in paddy soil. Furthermore, the proportions of water-soluble and exchangeable fractions extracted by the selected analytical methods were the lowest among all fractions. On the basis of the speciation of heavy metals, the mobility factor values of heavy metals have the following order: Cd (25.2–19.8%) > Cu (22.6–6.3%) > Zn (9.6–6.0%) > Pb (6.7–2.5%) in both contaminated soils.

**Keywords** Pollution index · Fractionation distribution · Heavy metal · Leleyter and Probst's sequential extraction · Mobility · Contaminated soils

## Introduction

Soil contamination with heavy metal is a worldwide environmental concern and leads to bioaccumulation of toxic elements in the food chain, destroys the function and balance of ecosystem, and causes human health problems. Both natural

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and anthropogenic activities are releasing heavy metals into soil environment. Solid waste disposal, sludge applications, vehicular exhaust, wastewater irrigation, industrial activities, and metal mining are the major sources of soil contamination with heavy metals (Singh et al. 2005; Khan et al. 2008). Heavy metals such as Pb, Cd, Cu, and Zn are considered the most toxic elements in the environment and included in the US Environment Protection Agency (EPA) list of priority pollutants (Cameron 1992). It is undoubtedly important to know the total metal concentrations for the purpose of evaluating the level of soil contamination. However, many previous studies have shown that the toxicity and mobility of these pollutants depend strongly on their specific forms or binding state (Ahumada et al. 1999; Cornelis 2002; Moćko and Waclawek 2004; Abul Kashem et al. 2007). For this reason, the chemical speciation analysis of heavy metals in soil is increasingly important and attracting more attention. To determine the chemical species of heavy metals in soil, a large number of single and multiple sequential extraction procedures, which use a series of reagents to separate the soil metals into different fractions, have been developed (Tessier et al. 1979; Shuman 1985; Rauret 1998; Leleyter and Probst 1999). Although the sequential extraction methods suffer from non-selectivity and trace element redistribution among phases during extraction, they are still suggested for evaluating the mobility and potentially bioavailable metal fractions in contaminated soils (Gómez Ariza et al. 2000; Kabala and Singh 2001; Abollino et al. 2002; Parat et al. 2003; Pueyo et al. 2003; Banat et al. 2005; Hu et al. 2006). In some research work, consistent correlations between specific metal fractions and plant metal contents were found. Similarly, heavy metals in the water/acid soluble and exchangeable fractions are considered to be the most mobile and available forms present in the soils, followed by the carbonate phase (Tessier et al. 1979; Ahumada et al. 1999; Howari and Banat 2001). The iron and manganese oxide fractions are relatively stable under normal conditions, which are otherwise reduced in acidic conditions (Tessier et al. 1979; Banat et al. 2005). The organic phase is a relatively stable phase in nature, but it can be mobilized under strong oxidizing conditions due to organic matter degradation, leading to a release of the soluble metal (Tessier et al. 1979). The residual fractions are entrapped within the crystal structure of the minerals and represent the least mobile fraction.

The present study was conducted to investigate the pollution load index and properly understand the distributions and mobilities of the selected metals (Pb, Cd, Cu, and Zn) in garden and paddy soils collected from a Pb/Zn mine in Chenzhou, China. The samples of garden and paddy soils were analyzed for total metal concentrations and the pollution load indices were calculated to know the degree of contamination. The fractions of Pb, Cd, Cu, and Zn in both types of soils were determined with Leleyter and Probst's sequential procedure (1999), which is a new, modified method for studying the availability of heavy metals in soils, containing seven fractions such as soluble with water, exchangeable, carbonates, manganese oxides, amorphous iron oxides, crystalline iron oxides, and organic matters, while the residual fraction (eighth fraction) was also added in this study.

## Materials and methods

### Site description

The study area is a Pb/Zn mine site (25°48′N, 113°02′E) located about 10 km east of Chenzhou city in Hunan province, China. In this area, the mining activities of heavy metals have been conducted for 500 years and mine tailings have been piled up around the sites. On 25th August, 1985, the big tailing pool dam of Pb/Zn mine collapsed because of heavy rainfall. In that disaster, 85 persons were killed, and both sides of the Dong river channel were covered with about a 15-cm-thick layer of toxic tailings. After the accident, some emergency soil clean-up measures were quickly carried out in some places, and a major portion of the contaminated soil surface was mechanically removed. Nevertheless, most of the contaminated farmlands are still cultivated presently. There were some previous studies on heavy metal pollution in soils and plants around this area (Liao et al. 2005a, b; Liu et al. 2005; Zeng et al. 2005).

## Soil sampling and analyses

Surface soil samples (0–10 cm) were randomly collected from a garden site contaminated with mine tailings and paddy soil contaminated with mine wastewater around the Pb/Zn mine in Chenzhou City. After transported to the laboratory, these soil samples were air dried, ground to pass through a 2-mm sieve, homogenized, and stored in plastic containers until analysis. The total concentrations of Pb, Cd, Cu, and Zn in the soils were determined using atomic absorption spectrometry (AA-646, Shimadzu, Japan) following acid digestion with $HNO_3/HCl/HClO_4$ (US-EPA 1998). Soil pH was measured with deionized water (1:5 ratio) after shaking for 30 min (Liao et al. 1997). Soil organic matter was determined by the wet oxidation method (Tiessen and Moir 1993), and cation exchange capacity (CEC) was determined by using unbuffered 0.1 M $BaCl_2$ (Hendershot and Duquette 1986). Chemicals used in this study were all analytical grade or super-pure grade. The blank reagent and standard reference soil (geochemical standard reference sample soil, GBW07405) for all the heavy metals were included in each sample to verify the accuracy and precision of the digestion procedure and subsequent analyses. The recoveries of standard reference materials were satisfactory and the ranges were as follows: Pb (97–104%), Cd (94–103%), Cu (93–98%), and Zn (98–110%) for soil. All glass and plastic wares used were previously soaked overnight in $HNO_3$ (10%) and rinsed thoroughly with deionized water before use.

## Sequential extraction procedures

Leleyter and Probst's sequential procedures (1999), which have good repeatability, no pollution problems, good efficiency, and good selectivity for each step, were used to determine fraction distributions of Pb, Cd, Cu, and Zn in both soils, as described in Table 1. According to the procedures, 2 g of each soil sample was placed in a 100-ml centrifuge tube and the extraction reagents were added sequentially. After each extraction step, the tube containing the soil and extractant was centrifuged at 4,000 rpm for 30 min. The supernatant was removed with a pipette and filtered through a 0.45-μm membrane in polyethylene container. The residue, used for the subsequent extraction steps, was rinsed with 40 ml deionized water to wash the extracting solution residues, shaken, centrifuged, and filtered. The liquid supernatant was discarded. At each step of the procedure, the leachate volume was measured in order to prevent the loss of distilled water in the filtration apparatus. Then, all the leachates were kept in polypropylene bottles at 4°C until chemical analysis. All extractions were performed in duplicate and the mean concentrations of heavy metals in extraction solutions were expressed.

## Data analysis

### *Heavy metal pollution assessment for soils*

To evaluate environmental quality of both kinds of soils contaminated by heavy metals, the

**Table 1** Leleyter and Probst's sequential extraction procedures

| ID | Fractions | Reagents | SSR[a] | Conditions |
|---|---|---|---|---|
| FI | Dissolved with water | Deionized water | 1:10 | 20 ± 1°C, 30 min shaking |
| FII | Exchangeable | 1 M $Mg(NO_3)_2$ | 1:10 | 20 ± 1°C, 2 h shaking |
| FIII | Bound to carbonates | 1 M NaOAc, pH 4.5 (HOAc adjust) | 1:10 | 20 ± 1°C, 5 h shaking |
| FIV | Bound to manganese oxides | 0.1 M $NH_2OH{\cdot}HCl$ | 1:10 | 20 ± 1°C, 30 min shaking |
| FV | Bound to amorphous iron oxides | 0.02 M $H_2C_2O_4$–0.2 M $(NH_4)_2C_2O_4$ | 1:10 | 20 ± 1°C, 4 h shaking in the dark |
| FVI | Bound to crystalline iron oxides | 0.2 M $H_2C_2O_4$–0.2 M $(NH_4)_2C_2O_4$–0.1 M ascorbic acid (pH 3) | 1:10 | 80 ± 2°C, 30 min shaking |
| FVII | Bound to organic matter | 1. 0.02 M $HNO_3$, 35% $H_2O_2$<br>2. 3.2 M $NH_4Ac$ (20% (*v*/*v*) $HNO_3$) | 1:3, 1:8<br>1:5 | 1. 85 ± 2°C, 5 h shaking<br>2. 85 ± 2°C, 30 min shaking |
| FVIII | Residual | $HCl + HNO_3 + HClO_4$ | | Microwave digestion |

[a] *SSR* soil solution ratio

pollution index method in accordance with Environmental Quality Standard for Soils (MEP 1995) was employed. Pollution load index ($P_i$) gives information regarding soil quality suitable for agricultural use. The pollution load index expressed as the single index method can be calculated using the following formula (Li et al. 2006):

$$P_i = \frac{C_i}{S_i} \tag{1}$$

where $P_i$ is the pollution load index for heavy metal $i$, $C_i$ is heavy metal concentration in a soil sample (mg kg$^{-1}$), and $S_i$ is the permitted standard of the same metal (mg kg$^{-1}$) (MEP 1995). If $P_i > 1$, the soil sample is classified as polluted, while $P_i \leq 1$ suggests unpolluted soil.

### *Extraction efficiencies of the sequential extraction procedures*

Extraction efficiencies of the sequential extraction procedures expressed as percentage of the total contents, estimated by the following equation:

$$E\,(\%) = \frac{\sum C_{\mathrm{F}i}}{T_{\mathrm{c}}} \times 100\% \tag{2}$$

where $E$ (%) represents the extraction efficiency of heavy metal with Leleyter and Probst's analytical method, $C_{\mathrm{F}i}$ (mg kg$^{-1}$) is the average concentration of each fraction of each heavy metal, and $T_{\mathrm{c}}$ is the total content of each heavy metal in soil (mg kg$^{-1}$).

### *Mobility of heavy metals*

The mobility of metals in contaminated soils can be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a "mobility factor (MF)" (Kabala and Singh 2001; Olajire et al. 2003), and the high MF values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils (Ma and Rao 1997; Ahumada et al. 1999). The MF value was calculated using the following equation:

$$\mathrm{MF} = \frac{(C_{\mathrm{FI}} + C_{\mathrm{FII}} + C_{\mathrm{FIII}})}{\sum C_{\mathrm{F}i}} \times 100\% \tag{3}$$

where $C_{\mathrm{FI}}$, $C_{\mathrm{FII}}$, and $C_{\mathrm{FIII}}$ are the mean concentrations of water-soluble fraction, exchangeable fraction, and carbonates fraction of each heavy metal (mg kg$^{-1}$), respectively.

## Results and discussion

### Heavy metal pollution

Mean total contents of heavy metals such as Pb, Cd, Cu, and Zn in garden and paddy soils are presented in Table 2. The data indicate that the total concentrations of Pb, Cd, Cu, and Zn in both types of soils are significantly higher than Hunan soil background values of heavy metals, and even higher than their respective standard levels set for agricultural soils recommended by the Ministry Environment Protection of China (MEP). These findings are consistent with the results reported by other researchers (Liao et al. 2005a, b; Liu et al. 2005; Zeng et al. 2005). According to Eq. 1, the calculated $P_i$ values of Pb, Cd, Cu, and Zn in both types of soils are presented in Fig. 1. As data indicate, the $P_i$ values of Pb, Cd, Cu, and Zn in all soil samples exceed 1.0 value. As compared to other heavy metals, the highest $P_i$ values for Cd reached 33.3 in the garden soils, while it reached 39.7 in the paddy soils. However, the $P_i$ values of Cu (ranged from 1.0 to 1.9) are the lowest values in all soil samples. In conclusion, the soils of both sites are contaminated with Pb, Cd, Cu, and Zn to some extent. It is therefore recommended that farmers should not grow food crops, particularly leafy vegetables, on these contaminated areas.

### Fraction distributions of heavy metals in contaminated soils

Table 3 summarizes the sum and extraction efficiencies of heavy metals with the selected sequential extraction procedures. Total metal content and the sum of individual chemical fractions deviate from the mean value by no more

**Table 2** Some physico-chemical parameters and total contents of heavy metals in soil samples

| Soils | Soil types | pH | CEC (cmol kg$^{-1}$) | Organic C (g kg$^{-1}$) | Heavy metals (mg kg$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Pb | Cd | Cu | Zn |
| Garden soil | Red soil | 4.8 ± 0.3 | 18.7 ± 0.9 | 15.1 ± 1.2 | 1,268.1 ± 133.7 | 10.0 ± 1.1 | 153.9 ± 13.7 | 1,591.8 ± 172.7 |
| Paddy soil | Yellow red soil | 5.5 ± 0.4 | 16.1 ± 1.3 | 23.3 ± 1.8 | 1,122.8 ± 114.2 | 11.9 ± 1.5 | 93.8 ± 9.1 | 950.5 ± 49.0 |
| HSB | | 4.5–5.5 | 10–20 | 10–20 | 27.0 | 0.098 | 26.0 | 94.0 |
| EQSS | | <6.5 | >5 | nd[a] | 250.0 | 0.3 | 150.0[b] 50.0[c] | 200.0 |

*HSB* Hunan soil background values (Pan and Yang 1988), *EQSS* Environmental Quality Standard for Soils, GB15612-1995 Grade 2 (MEP 1995)

[a] No standard values

[b] For garden soil (MEP 1995)

[c] For paddy soil (MEP 1995)

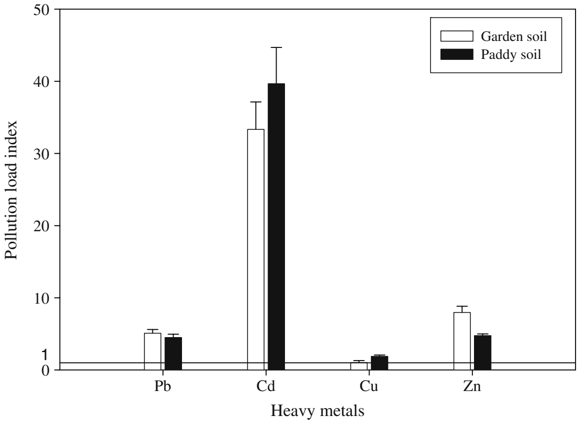

**Fig. 1** Pollution load indices of heavy metals in garden soil and paddy soils

than 8.3%, which means that the fraction distributions of Pb, Cd, Cu, and Zn in soil samples analyzed by Leleyter and Probst's sequential extraction procedures were reasonable. The extraction efficiencies of Pb, Cd, Cu, and Zn from the paddy soils were higher than those from the garden soils due to different soil properties.

According to the Eq. 2, the fraction distributions of Pb, Cd, Cu, and Zn in garden and paddy soils determined by Leleyter and Probst's analytical method are shown in Fig. 2. The different distribution fractions of Pb, Cd, Cu, and Zn are observed in both contaminated soils. Among the studied eight fractions, except Cu in garden soil, the percentages of extractable fractions of Pb, Cd, and Zn associated with FI in both contaminated soils are the smallest, and follow the order: Cu (5.0%) > Cd (1.7%) > Pb (0.7%) > Zn (0.5%) in garden soil and Cd (3.0%) > Cu (1.2%) > Zn (0.4%) > Pb (0.2%) in paddy soil. In general, FI is dissolved with water and can be negligible,

**Table 3** Sum of individual fraction and extraction efficiencies of heavy metals with Leleyter and Probst's analysis procedures in the tested soils

| Heavy metals | Garden soil | | Paddy soil | |
|---|---|---|---|---|
| | Sum (mg kg$^{-1}$) | *E*(%) | Sum (mg kg$^{-}$1) | *E*(%) |
| Pb | 1,247.2 | 98.4 | 1,029.8 | 91.7 |
| Cd | 9.6 | 96.2 | 11.0 | 92.5 |
| Cu | 151.0 | 98.1 | 90.1 | 96.0 |
| Zn | 1,565.8 | 98.4 | 875.1 | 92.1 |

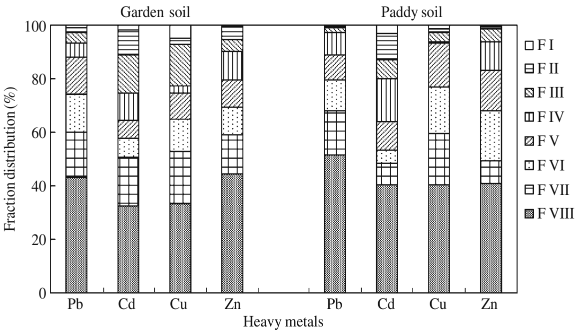

**Fig. 2** Fraction distributions of heavy metals in garden soil and paddy soil analyzed with Leleyter and Probst's method

except if the sample is composed of evaporitic salts (Baldi et al. 1990; Leleyter and Probst 1999). However, they would be released into the environment and become a dangerous fraction and more available for plants (Kabata-Pendias 1993).

As for FII, the aim of this step is to leach cations that are adsorbed onto solid materials due to permanent structural charges. In the second step, to avoid selective problems with $CH_3COO^-$ and $Cl^-$, nitrate magnesium was chosen (Leleyter and Probst 1999). The proportions of FII of Cd with 9.4% and 10.1% are higher than those of other metals in both soils. However, the amount of Pb and Zn bound to FII in paddy soil are the smallest. Elliott et al. (1986) reported that the activity of Cd was strongly associated with exchangeable fraction. Naidu et al. (1994) also reported that the species of exchangeable Cd were probably hydrated $Cd^{2+}$ and adsorbed via outer-sphere surface complexation.

In the case of FIII, 1 M NaOAc–HOAc, pH = 4.50 solution is efficient to dissolve carbonates. High percentages of Cd (14.2%) and Cu (15.4%) are found in garden soil, while it was only 6.7% for Cd and 3.5% for Cu in paddy soil. These compounds are susceptible to changes in pH, and metals can be removed by the application of an acidic solution (Tessier et al. 1979).

According to Leleyter and Probst's procedures, binding to iron and manganese oxides were divided into three fractions as bound to manganese oxides (FIV), bound to amorphous iron oxides (FV), and bound to crystalline iron oxides (FVI). In the comparison of FIV, FV, and FVI, the distribution among the three fractions is less uniform. For example, the proportions of FIV of Cu (0.3% and 2.7%) show the lowest, while more than 10% of Cu is associated with FV. To some extent, the sums of FIV, FV, and FVI for Pb (33.3–29.7%), Cd (24.3–31.7%), Cu (24.5–34.3%), and Zn (31.2–44.4%) become the second largest proportion in both soils.

In the seventh step, hydrogen peroxide was chosen to analyze the binding to organic matter. It can be seen that the percentages of FVII of the four studied metals in garden soils and Pb and Cu in paddy soils are over 14%. High percentages of FVII (19.5–19.2%) for Cu are found and become the next most important fraction in both soils. Copper could easily form complexes with organic matter due to the high stability constant of organic-Cu compounds (Zhou et al. 1998; Ramos et al. 1999).

In Leleyter and Probst's method (1999), there was no residual fraction of element with less than the concentrations of Si and Al. In case of the residue, the residual fractions of heavy metals were investigated in present study. The greatest amounts of fractions of heavy metals were found in FVIII in both soils, which accounted to 43.0% for Pb, 32.3% for Cd, 33.5% for Cu, and 44.2% for Zn in garden soil, while it was 51.6% for Pb, 40.4% for Cd, 40.3% for Cu, and 40.9% for Zn in paddy soil. This fraction composed of detrital silicate minerals, resistant sulfides, and refractory organics is an important carrier of all of the elements studied (Tessier et al. 1979). The higher percentages of FVIII of Pb, Cd, Cu, and Zn in contaminated soils, the lower the degree of pollution.

## Mobility factors of Pb, Cd, Cu, and Zn in soils

The mobility factor (MF) values of heavy metals calculated by the Eq. 3 in the garden and paddy soils are shown in Fig. 3. The results of this study indicate that the MF values of Cd are the highest with 25.2% and 19.8% in the garden soil and paddy soils, respectively, which means that Cd is the most mobile element among the selected metals. However, the MF values of Pb and Zn in both soils are below 10%, suggesting that Pb and Zn are symptoms of high stability in both soils, even if high metal concentrations were contained in soils. The MF value of Cu in garden soil is

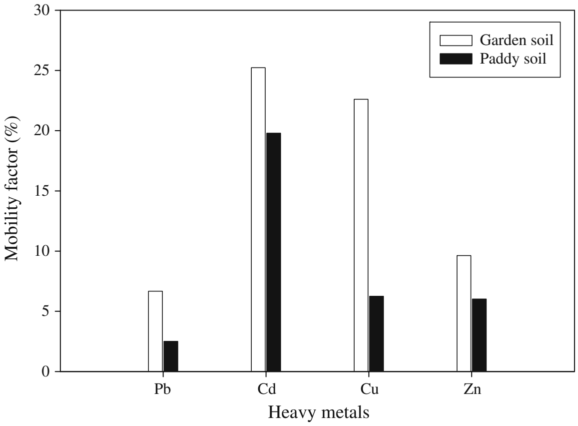

**Fig. 3** Mobility factors of heavy metals in garden soil and paddy soil

22.6%, while it was 6.3% in paddy soils, indicating higher mobility and availability of Cu in garden soil than in paddy soil. Luo and Christie (1991) revealed that plant Cu uptake was particularly correlated with exchangeable Cu. The MF values of heavy metals follow the sequence: Cd > Cu > Zn > Pb in both contaminated soils.

## Conclusions

Heavy metal concentrations and pollution load indices in garden and paddy soils from Pb/Zn area were above Hunan background values and the standard levels, indicating that both soils were severely contaminated with heavy metals. According to Leleyter and Probst's sequential extraction procedures, it was observed that Pb, Cd, Cu, and Zn were mainly controlled by residual fraction, next by binding to organic matter or iron and manganese oxides in both contaminated soils, while the percentages of water-soluble and exchangeable fractions were lowest among all fractions. The proportions of mobility factor for Cd and Cu in garden and paddy soils were higher than those of other metals.

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