

# Speciation and fractionation of heavy metals in soil experimentally contaminated with Pb, Cd, Cu and Zn together and effects on soil negative surface charge

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**Abstract:** Speciation and fractionation of heavy metals in soil subsamples experimentally loaded with Pb, Cd, Cu and Zn in orthogonal design was investigated by sequential extraction, and operationally defined as water-soluble and exchangeable(SE), weakly specific adsorbed(WSA), Fe and Mn oxides-bound(OX) and organic-bound(ORG). The results showed that fractions of heavy metals in the soil subsamples depended on their speciation. About 90% of Cd and 75% of Zn existed in soil subsamples in the SE fraction. Lead and Cu existed in soil subsamples as SE, WSA and OX fractions simultaneously, although SE was still the major fraction. Organic-bound heavy metals were not clearly apparent in all the soil subsamples. The concentration of some heavy metal fractions in soil subsamples showed the good correlation with ionic impulsion of soil, especially for the SE fraction. Continuous saturation of soil subsamples with 0.20 mol/L  $\text{NH}_4\text{Cl}$ , which is the first step for determination of the negative surface charge of soil by the ion retention method, resulted in desorption of certain heavy metals from the soil. It was found that the percentage desorption of heavy metals from soil subsamples depended greatly on pH, the composition and original heavy metal content of the soil subsamples. However, most of the heavy metals in the soil subsamples were still be retained after multiple saturation. Compared with the parent soil, the negative surface charge of soil subsamples loaded with heavy metals did not show difference significantly from that of the parent one by statistical analysis. Heavy metals existed in the soil subsamples mainly as exchangeable and precipitated simultaneously.

**Keywords:** soil; heavy metals; speciation; soil surface charge

## Introduction

Almost all soil physical and chemical processes, for example ionic adsorption, chemical oxidation and reduction reactions, flocculation and dissolution of colloids occurred at the surfaces of soil constituents. On the one hand, these processes are dominated by surface properties of soils directly or indirectly (Yu, 1996). On the other hand, they also influence the surface properties of soils. Thus, study of interaction processes between pollutants and soils can be important for exploring mechanisms of chemical migration and conversion in soils.

Studies on the effects of pollutants on soil surface properties have been reported. It was found that specific adsorbed heavy metals in soil decreased the zero point of charge(ZPC) of the soil(Stoop, 1980). For example, adsorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in hematite decreased the ZPC of hematite markedly, and the effect of  $\text{Pb}^{2+}$  was greater than that of  $\text{Cd}^{2+}$  (Leckie, 1974). The ZPC of  $\gamma\text{-Al}_2\text{O}_3$  decreased by 2 pH units in the presence of  $\text{Pb}^{2+}$  (Xiong, 1990). One possible explanation for these results is that specific adsorbed heavy metals in soils or minerals accumulated in the Stern layers, and correspondingly increased the positive surface charge of the soil. Meanwhile, more  $\text{OH}^-$  ions need to enter this layer to equilibrate the increasing positive surface charge of the soil. Thus, more  $\text{H}^+$  at low pH appeared in the outer Stern layer to keep electron neutrality of the double electric layer. However, most of these studies have concentrated on metal oxides and clay minerals, and not on soils or soil colloids(Breenwsma, 1973; Huang, 1981; James, 1981).

Zhang and Zhao(Zhang, 1988) studied the charge characteristics of variable charge soils as affected by surface properties of the soil and specific adsorption of ions. Treatment of the clay fraction of laterite with phosphate or silica resulted in an increase in negative surface charge and a decrease in positive surface

charge, with a corresponding lowering of  $pH_0$  value and isoelectric point (IEP). Sun (Sun, 1993) studied the change in surface charge of soils by addition of 360 mg/kg Zn. It was found that Zn adsorption in red soil decreased the negative surface charge of soil and increased positive surface charge compared with that in the absence of Zn.

In practice, soils are usually contaminated with more than one pollutant, leading to complicated and potentially serious environment pollution (Chen, 1996; Zhou, 1999). It may therefore be instructive to study multiple pollution rather than single pollutant in order to understand the behavior of pollutants in the field.

The objective of the effects of heavy metals applied to soil on their fractions and soil surface charge was investigated. The relationship between the fractions of heavy metals and their total contents in soil subsamples, reflected by ionic impulsion, was examined.

## 1 Materials and methods

### 1.1 Preparation of soil subsamples spiked with Pb, Cd, Cu and Zn

Brown forest soil sampled from Taian, Shandong Province, was air dried, crushed, and passed through a 20-mesh screen. The main physical and chemical properties were analyzed using routine methods (Agrochemistry Commission, 1983). The total Cu, Zn, Pb and Cd of soil is 19.8 mg/kg, 45.2 mg/kg, 21.5 mg/kg and 0.04 mg/kg, respectively. The CEC of soil is 130.4 mmol/kg. Its organic matter content and pH value is 0.57% and 5.28, respectively.

**Table 1 Concentrations of heavy metals in soil subsamples supplemented with lead, cadmium, copper and zinc in orthogonal design**

Sample No.	Cu, mg/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg
S1	0	0	0	0
S2	0	0	250	10
S3	0	0	500	20
S4	0	300	0	10
S5	0	300	250	20
S6	0	300	500	0
S7	0	600	0	20
S8	0	600	250	0
S9	0	600	500	10
S10	200	0	250	0
S11	200	0	500	10
S12	200	0	0	20
S13	200	300	250	10
S14	200	300	500	20
S15	200	300	0	0
S16	200	600	250	20
S17	200	600	500	0
S18	200	600	0	10
S19	400	0	500	0
S20	400	0	0	10
S21	400	0	250	20
S22	400	300	500	10
S23	400	300	0	20
S24	400	300	250	0
S25	400	600	500	20
S26	400	600	0	0
S27	400	600	250	10

Soil subsamples, artificially amended with Pb, Cd, Cu and Zn, were prepared by the following procedure. Soil (300 g) was weighed into plastic tubes, and then different volumes of Cd, Pb, Cu and Zn stock solutions as metal chloride were added. The soil water was maintained at field capacity. The samples were incubated for 3 months and dried, crushed, passed through a 60-mesh screen, and stored for further use. The concentrations of heavy metals added in these soil subsamples are shown in Table 1.

### 1.2 Reagents and analysis of heavy metals and $NH_4^+$

All chemicals used in the experiments were of analytical grade, and deionized water was used to prepare all solutions. Analysis of heavy metals was carried out using a Hitachi 180 - 80 atomic absorption spectrophotometer.  $NH_4^+$  was determined by distilling the resulting  $NH_4^+$  solution from 4 repeated saturation with 1.0 mol/L  $KNO_3$  in 20% NaOH firstly and then collecting the distillate in a conical flask and titrating using 0.01 mol/L HCl. The standard deviation for soil  $NH_4^+$  determination was 5.41%.

### 1.3 Heavy metal fractions in soil subsamples

Two grams of each soil subsample was placed

in a 100 ml plastic tube and 20 ml of different extractants were added sequentially to extract heavy metals. The method was previously described by Tu (Tu, 2000). When the soil subsamples were extracted initially using 0.5 mol/L  $Mg(NO_3)_2$  (pH 7.0) and shaken continuously for 2h at 25°C, the resulting concentrations of heavy metals in the supernatant were defined as the water soluble and exchangeable (SE) fraction. When the residues were then extracted with 0.5 mol/L NaAc-HAc (pH 5.0) at 25°C and shaken for 2h, the heavy metals in the supernatant was considered to be the weakly specific adsorbed (WSA) fraction after subtracting the residue of the SE fraction. Subsequent extraction with 0.175 mol/L  $(NH_4)_2C_2O_4$  + 0.10 mol/L  $H_2C_2O_4$  at 85°C with UV irradiation for 2h gave the Fe and Mn oxides-bound (OX) fraction after subtracting the residue of the WSA fraction. Finally the organic-bound (ORG) fraction was obtained by extracting the resulting soil residues with 5 ml of 30%  $H_2O_2$  and 3 ml of 0.02 mol/L  $HNO_3$ . The heavy metals remaining in the soil residues were regarded as the residual fraction.

**1.4 Determination of soil negative surface charges**

According to the method described previously (Schofield, 1949), soil subsamples were continuously equilibrated four times using 0.20 mol/L  $NH_4Cl$  with a soil-to-solution ratio of 5:1 at 3 different pH values, until  $NH_4^+$  did not change in the soil solution. After the fourth equilibration with 0.2 mol/L  $NH_4Cl$ , the centrifuge tubes were weighed, and  $NH_4^+$  content in the supernatant was analyzed simultaneously which will be used to subtract the residue of  $NH_4^+$  remaining in the centrifuged soil. The soil subsamples were then equilibrated with 1.0 mol/L  $KNO_3$  four times to replace  $NH_4^+$  adsorbed in the soils. The resulting supernatant was collected in a 250 ml conical flask, and concentrations of  $NH_4^+$  were determined. Negative surface charges of soil subsamples were obtained according to the quantity of  $NH_4^+$  adsorbed in the soil subsamples. All experimental data are the average of two replicates. The concentrations of heavy metals in the centrifuged solutions of Sample No. 25 were determined as example to examine the exchange rate of heavy metals and ammonium.

**2 Results and discussion**

**2.1 Heavy metal fractions in soil subsamples loaded with Pb, Cd, Cu and Zn**

During artificial contamination of Pb, Cd, Cu and Zn into soil, the heavy metals will react with the surfaces of soil solids and be simultaneously retained in the soil by physical and chemical processes (Darmawan, 1999). According to sequential extraction, the results indicate that different initial levels of heavy metals gave different patterns of metal fractions. Moreover, the pattern of fractions was different even at the same initial concentrations. Thus, the pattern of each heavy metal fractions was influenced by the other heavy metals present.

The mean value and standard deviation of each heavy metal speciation in 9 soil subsamples at the same initial concentration was calculated and the percentage content of heavy metal speciation in soil subsamples are shown in Fig.1. These clearly indicate that Cd and Zn existed mainly in the SE fraction. However, besides SE as one of major fractions of Pb and Cu in soil subsamples, their WSA and OX

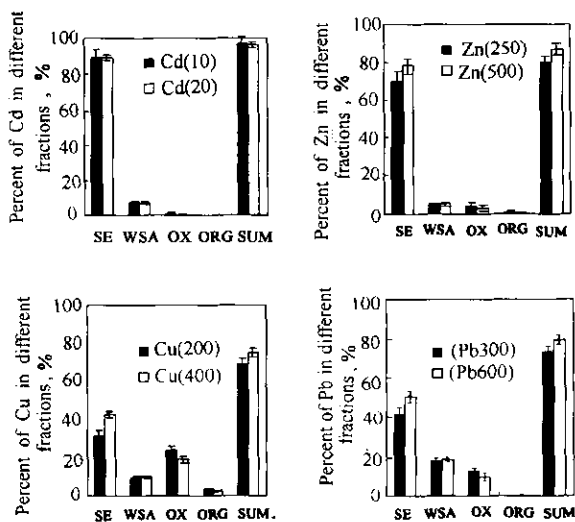


Fig.1 Fractions of heavy metals in soil subsamples (%)

fractions was also very obvious, which was in contract to Cd and Zn. ORG fractions of all four heavy metals was low. This may have been due to the high content of heavy metals added into the soil with only a small soil organic matter content (0.57%). In addition, SE fractions and the sum of SE, WSA and OX one for Zn, Pb and Cu in high initial levels were higher than that in low initial levels in the soil subsamples. This effect was not noted for Cd, perhaps because of its readily mobility in soils.

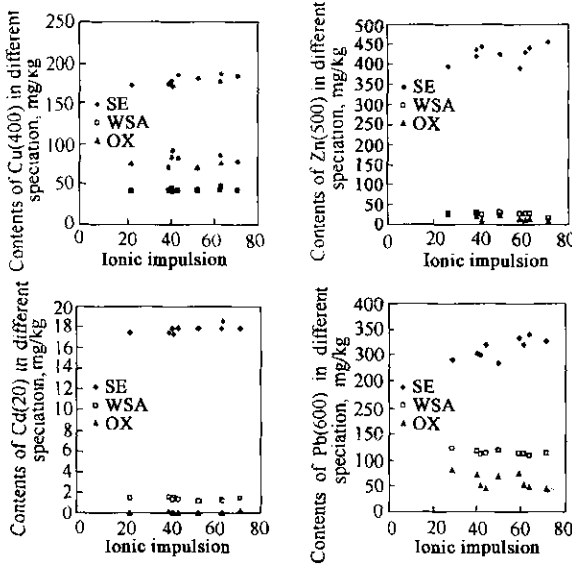


Fig. 2 Dependence of content of heavy metal fractions at the same high initial concentration on ionic impulsion

combined pollution of the soil.

Fig. 2 shows the dependence of content of heavy metal fractions at the same high initial concentration on ionic impulsion as examples. The results indicated that the SE fractions of Cd and Zn in soil increased with increasing ionic impulsion. Thus, ionic impulsion was an important factor influencing the SE fractions of Zn and Cd. However, the changes in the Zn and Cd's WSA and OX fractions with ionic impulsion were less clear. Lead and Cu existed in soil in three clear fractions, namely SE, WSA and OX. Similar to Zn and Cd, their SE fractions also increased with increasing ionic impulsion, and other fractions of Pb and Cu did not show obvious changes with ionic impulsion, even when ionic impulsion was significantly different. It can therefore be concluded that the different treatment mostly influenced the SE fraction of the heavy metals.

The dependence of the heavy metal SE fractions on ionic impulsion were examined by linear regression and correlation as follows:

$$\text{Pb: SE} = 1.0583I + 259.72 \quad n = 9, r = 0.7389, p < 0.02, \quad (1)$$

$$\text{Cd: SE} = 0.0157I + 17.03 \quad n = 9, r = 0.6461, p < 0.05, \quad (2)$$

$$\text{Cu: SE} = 0.2434I + 166.49 \quad n = 9, r = 0.6345, p < 0.05, \quad (3)$$

$$\text{Zn: SE} = 0.7313I + 389.03 \quad n = 9, r = 0.4758, p > 0.1. \quad (4)$$

### 2.3 Effects of heavy metals on soil negative surface charge

Addition of heavy metals to soil may change the soil surface charge (Stoop, 1980; Sun, 1993). In general, these changes occur mainly due to the specific adsorption of heavy metals to soil or soil colloids. For a constant charge soil, the specific adsorption capacity for heavy metals is smaller than that for a constant potential soil (Yu, 1996). However, most natural soils include not only constant charge surfaces

### 2.2 Effect of ionic impulsion on content of each heavy metal fractions in soil subsamples

As shown in Fig. 1, the pattern of heavy metal speciation in the soil subsamples was influenced by other coexisting heavy metals. Romero (Romero, 1987) previously used ionic impulsion using the expression  $I = \sum c_i^{1/n}$  with  $c_i$  being the concentrations in mg/kg and  $n$  being the oxidation number of the relevant considered metals to reflect their environmental behavior.

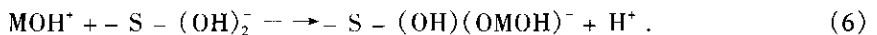
Although the pattern of fractions of each heavy metal among the soil subsamples was different, the dependence of some heavy metal fractions on ionic impulsion gave good correlations, suggesting that ionic impulsion was an important parameter to express the

but also constant potential surfaces. As shown above, heavy metals, especially Pb and Cu, existed in the soil subsamples mostly as WSA and OX fractions. Therefore, it is interesting to examine soil surface charges and correlate them with the speciation of the heavy metals.

The negative surface charge of the parent soil was compared with that of the soil subsamples at three different pH values. The average value of all soil subsamples was almost equal to that of the parent soil as shown in Fig. 3. The coefficient of variation of the negative surface charges among of 27 soil subsamples were 2.57%, 2.70% and 2.88% at pH 3.00, 5.33 and 6.95, respectively, and did not exceed the standard variation of NH<sub>4</sub><sup>+</sup> determination in soils of 5.41%. This indicates that the change in soil negative surface charge was small when the soil subsamples were loaded with heavy metals.

Specific and nonspecific adsorption of heavy metals occurs in soil. Specific adsorption of heavy metals in soil is mainly due to reaction of the first hydrated cations with hydroxyl soil surfaces, and results in an increase in the soil negative surface charge (Yu, 1996). Nonspecific adsorption is usually caused by ionic exchange. No change in negative charge was observed during this process.

Because the negative surface charges of these soil subsamples did not exhibit observable change, the adsorption of heavy metals in soils mainly as ionic exchange can be depicted as follows:



According to experimental results described above, only part of heavy metals SE fractions were desorbed by 0.5 mol/L Mg(NO<sub>3</sub>)<sub>2</sub>, and this is inconsistent with the present results. Thus, the desorption percentage of heavy metals from soil subsamples during their equilibration with 0.2 mol/L NH<sub>4</sub>Cl, the first step to determine surface charge of soil by the ion retention method, was studied in advance to understand the effect of heavy metals on soil negative surface charge. Sample No. 25 (Cu: 400 mg/kg; Pb: 600 mg/kg; Zn: 500 mg/kg; Cd: 20 mg/kg) was chosen as typical subsample to study the percentage desorption of heavy metals from soil by this solution.

Table 2 shows the percentage desorption of heavy metals from soil subsamples at two pH values. Desorption percent of heavy metals from soil decreased continuously from the first occasion to the fourth. Moreover, the extraction percent for the first occasion was far greater than that for the last. Different heavy metals also had their desorption pattern, and the order was Cd > Zn > Pb > Cu. Furthermore, pH also influenced the desorption rate of heavy metals from the soil subsamples, in which increasing pH resulted in a decrease in desorption percent of heavy metals. One plausible explanation is that high pH increased the negative surface charge of the soils and correspondingly increased the adsorption capacity of soils for heavy metals. It is important to note that most heavy metals loaded in soil subsamples were retained in soil after the continuous exchanges with 0.2 mol/L NH<sub>4</sub>Cl.

Previous studies have shown that the precipitation of heavy metals occurred in soil (Farrach, 1979). Thus, with such high levels of heavy metals and high pH values in this experiment, heavy metal precipitation may have been one of the major processes in soil, resulting in an absence of influence on soil negative surface charge. The corresponding reactions included in these soil subsamples may be expressed as follows:

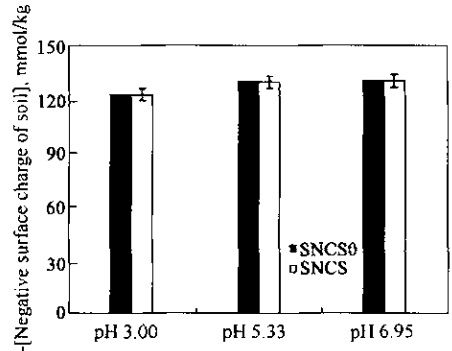
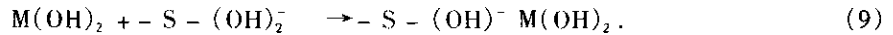


Fig. 3 The negative surface charge of soil subsamples at different pH values  
SNCS0 is the negative surface charge of the parent soil; SNCS is the average negative surface charge of all soil subsamples



**Table 2** Repeated extraction of heavy metals from soil subsamples with 0.20 mol/L  $NH_4Cl$

Heavy metal	pH	The first, %	The second, %	The third, %	The fourth, %	Sum, %
Cd	5.40	90.30	4.10	$\leq 0.01$	$\leq 0.01$	94.40
	6.80	70.60	5.50	$\leq 0.01$	$\leq 0.01$	76.30
Pb	5.40	11.09	5.11	3.12	2.04	21.36
	6.80	2.93	1.06	0.92	0.71	5.62
Cu	5.40	5.05	2.38	1.77	1.10	10.30
	6.80	1.21	0.46	0.64	0.41	2.72
Zn	5.40	38.90	8.43	3.60	1.53	52.46
	6.80	23.10	3.43	0.80	0.32	27.64

### 3 Summary

Each kind of heavy metal showed a different pattern of fraction by the operational definition. The SE fraction was the major form of Zn and Cd, and SE, WSA and OX together were the main forms of Pb and Cu. The relationship between heavy metal fraction and ionic impulsion was satisfactorily described.

Soil subsamples loaded with heavy metals have no clear influence on the negative surface charge of soil, and this is ascribed to the presence of heavy metals mainly in exchangeable and precipitation forms in these soil subsamples.

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