



Time effect on the fractionation of heavy metals in soils

Anxiang Lu, Shuzhen Zhang*, Xiao-quan Shan

Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, 100085, China

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Abstract

Time effect on the fractionation of Cu, Zn, Pb, and Cd in three typical Chinese soils was investigated. A total of 500 mg kg⁻¹ of Cu, Zn, Pb and 2.5 mg kg⁻¹ of Cd were added to soils as nitrates. Metals in the incubated soils were fractionated termly from 3 h to 8 weeks by the sequential extraction procedure, in which the metal fractions were experimentally defined as exchangeable, carbonate-, Fe–Mn oxide-, organic matter-bound and residual fractions. Results showed that the changes of Cu, Pb and Zn in fraction distribution were biphasic by an initial rapid step followed by a slow one. Metals in exchangeable fraction were increased in the first 3 h, and then decreased, such decreases could be simulated by a diffusion equation and the decrease rate followed the order Pb>Cu>Zn>>Cd. Metals bound to Fe–Mn oxides and organic matter increased consistently in the 8-week incubation. There were almost no changes for the metals in the residual fraction. After 3-h incubation most of Cd added to soils presented in the exchangeable fraction. The content of Cd in each fraction changed slightly in the 8-week incubation. Soil pH played an important role in metal fraction distribution patterns. Jiangxi soil, with low soil pH, tended to keep more metals added in exchangeable fraction and the changes of metals in each fraction were not as remarkable as in other two soils. High organic matter content resulted in the increased organic matter-bound fraction. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Soil contamination with anthropogenic heavy metals, which mainly comes from industrial activity, atmospheric deposition and land application of sewage sludge, has received much attention in

recent years. The anthropogenic heavy metals are believed to be easily accumulated in the topsoil (Samsøe-Petersen et al., 2002; Baker, 1990), resulting in potential problems such as toxicity to plants and animals (Ma et al., 2002; Berti and Jacobs, 1996), accumulation in food chain, perturbation of the ecosystem and adverse health effects (Forstner, 1995; Stalikas et al., 1997).

Residence time directly relates to the bioavailability of heavy metals in soils (Pedersen et al.,

* Corresponding author. Tel.: +86 10 62849329; fax: +86 10 62923563.

E-mail address: szzhang@mail.rcees.ac.cn (S. Zhang).

2000; Joner and Leyval, 2001; Alexander, 2000). Generally bioavailability of heavy metals decreases with increasing residence time (McLaughlin, 2001). Such time effect is ascribed to the reactions between metal ions and soils, which mainly include complexation, adsorption, and precipitation of metal ions in the soil particle surface or diffusion into the mesopores and micropores of soil. Although it is often assumed that residence time effect reduced metal mobility and bioavailability, only a few works have been carried out to investigate whether and how time effect influence the metal chemical forms and/or metal fractions in soils (Ma and Uren, 1998; Lim et al., 2002; Bataillard et al., 2003; Davies et al., 2003).

Total elemental contents provide little information on the mobility and bioavailability of the elements of interest. The mobility and bioavailability of heavy metals depend heavily on their physical and chemical forms. Sequential extraction, although operationally defined, can give information about the association of heavy metals with geochemical phases of soil, hence helps to reveal the distribution of heavy metals in fractions and to assess the mobility and toxicity of metals in soils (Tessier et al., 1979; Quevauviller et al., 1993, Ahnstrom and Parker, 1999). Among numerous sequential extraction methods, the method proposed by Tessier et al. (1979) was most widely used. According to this protocol, metals in soil were fractionated into exchangeable, carbonate-, Fe–Mn oxide-, organic matter-bound and residue fractions. Generally, exchangeable form was considered readily mobile and easily bioavailable, while residual form was considered to incorporate into crystalline lattice of soil minerals and appeared to be the most inactive. The carbonate-, Fe–Mn oxide-, and organic matter-bound fractions could be considered relatively active depending on the actual physical and chemical properties of soil.

To fully understand time effect on bioavailability of anthropogenic heavy metals, detailed information is needed on the fractionation of metals after different residence time. The objective of this study was to investigate time effect on the fractionation of Cu, Pb, Zn and Cd added in soils. Differences of the fractionation among the metals and soils and the possible mechanism were discussed.

2. Materials and methods

2.1. Soil samples

Three topsoil samples (0–20 cm) were collected from Beijing, Jiangxi and Heilongjiang Provinces, China. Soil samples were air-dried and passed through a 2.0 mm sieve, homogenized and stored at 4 °C until use. Soil pH was measured with the soil to water ratio of 1:1 (w/v) (Hendershot et al., 1993a), organic matter (OM) was measured by $K_2Cr_2O_7$ digestion method (Nelson and Sommers, 1996), cation exchange capacity (CEC) was determined by using a 0.1 mol l^{-1} $BaCl_2$ displacement method (Hendershot et al., 1993b), the particle size was analyzed by the hydrometer method (Sheldrick and Wang, 1993). Crystal and amorphous Fe oxides were determined by the oxalate-ascorbic acid extraction and ammonium oxalate extraction methods, respectively (Ross and Wang, 1993). These properties are presented in Table 1.

2.2. Incubation

An incubation experiment was conducted with 500 g of each soil in plastic pot. Heavy metals Cu, Zn, Pb and Cd were added as nitrate salts $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$ in aqueous solution and then mixed with soils thoroughly. The amounts of metals added to soils were 500 $mg\ kg^{-1}$ of Cu, Zn and Pb, and 2.5 $mg\ kg^{-1}$ of Cd

Table 1
Selected properties of tested soils

Item	Beijing	Jiangxi	Heilongjiang
pH	6.90	4.56	7.35
OM (%)	4.35	1.53	6.40
CEC (c mol kg^{-1})	15.7	14.2	26.3
Particle-size distribution (%)			
Clay	10.8	42.4	27.4
Silt	51.6	18.7	62.8
Sand	37.6	19.5	9.8
Oxide of Fe (g kg^{-1})			
Crystal	8.87	35.2	15.0
Amorphous	3.22	7.24	4.03
Concentration of metals (mg kg^{-1})			
Cu	21.6	22.8	9.16
Zn	33.6	31.2	28.9
Pb	33.4	19.5	33.0
Cd	0.51	0.32	0.44

(metal/soil), respectively. Samsøe-Petersen et al. (2002) investigated 75 different heavy metal contaminated soils and ranged them into three levels: uncontaminated, medium and heavily contaminated. According to his classification and the level defined by Chinese Environmental Protection Agency (Chinese EPA, 1995), the selected concentrations in this study represented the heavily contaminated soils. Extra pots without addition of heavy metals were simultaneously prepared as control. Soil samples were maintained at about 70% of water holding capacity by periodically weighing the pots and adjusting the weight by addition of distilled water. The soils were incubated for 3 h, 1, 3 days, 1, 2, 3, 4, 6 and 8 weeks, each treatment was repeated in duplicate. After incubation, metals in treated and control soils were fractionated by the sequential extraction procedure of Tessier et al. (1979) in triplicate. The chemical reagents, extraction conditions and corresponding fractions are listed in Table 2. Extractions were conducted in 50 ml polypropylene centrifuge tubes. Between each successive extraction, the supernatant was centrifuged at 6000 rpm for 15 min, and filtered. As a check for the reliability of sequential extraction procedure, ratios of the sum of the metal concentration in individual fractions to the total metal concentration in soils were calculated and were from 81.0% to 101.2%. Lower ratios were considered as the cumulative losses of each extraction procedures (Pueyo et al., 2003).

Table 2
Sequential extraction procedure and the corresponding fractions

Step	Fraction	Extraction procedure
1	Exchangeable (EXC)	1 g of soil sample, 8 ml 1 mol l ⁻¹ MgCl ₂ , pH 7, shake 1 h, room temperature
2	Bound to carbonate (CA)	8 ml 1 mol l ⁻¹ CH ₃ COONa, adjusted pH to 5.0 with CH ₃ COOH, shake 5 h, room temperature
3	Bound to Fe–Mn oxides (Fe–Mn)	20 ml 0.04 mol l ⁻¹ NH ₂ OH · HCl in 25%CH ₃ COOH, pH 2.0, water bath, 96 °C, 6 h, occasional shaking
4	Bound to organic matter (OM)	3 ml 0.02 mol l ⁻¹ HNO ₃ , 30% H ₂ O ₂ (adjusted to pH 2.0), water bath, 85 °C, 5 h, 3.2 mol l ⁻¹ CH ₃ COONH ₄ in 20% (v/v) HNO ₃ , shake 30 min
5	Residual (RES)	3 ml HNO ₃ +HClO ₄ +HF under high pressure, 170 °C

2.3. Metal determination

Metal concentrations in soil fractions were determined by inductively coupled plasma-mass spectrometry (ICP-MS; VG PlasmaQuard 3, Fisons Instruments, UK) under optimized operating conditions. The total metal concentrations in soils were determined after digestion with HNO₃–HF–HClO₄ (1:1:1) mixture under high pressure conditions. The digestion procedure of soil samples and optimization of ICP-MS were detailed in our previous study (Zhang and Shan, 1997).

3. Results and discussion

3.1. Changes of heavy metal concentrations in different fractions

Tables 3, 4 and 5 show the distribution of heavy metals Cu, Zn, Pb and Cd in the five fractions: exchangeable (EXC), carbonate (CA), Fe–Mn oxides (Fe–Mn), organic matter (OM) and residual (RES) fractions in the control and the spiked soils incubated for 3 h, 3 days and 8 weeks. Other values were excluded here otherwise the tables would be too big. In the control soils, the background Cu, Zn, Pb and Cd in each fraction were generally in the order residual>exchangeable>Fe–Mn oxides>organic matter>carbonate fraction. It was observed that after 3 h of incubation metals in exchangeable fraction were predominant in the spiked soils and the increases in the other fractions were also observed except in residual fraction. It may indicate that a fast process of metal distribution among the fractions occurred during the first 3-h incubation. From 3 h to 8 weeks, metals decreased in exchangeable fraction and increased in Fe–Mn oxides and in organic matter bound fractions. The redistribution process happened from 3 h to 8 weeks is much slower comparing with that in hours. At the end of 8-week incubation, the percentages of Cu, Zn, Pb and Cd in exchangeable fraction were still very high, which is consistent with the results obtained by Lim et al. (2002), who studied the adsorption of Pb and Cd on soil clays incubated for over 65 days by using sequential extraction. This observation was possibly due to the slow transformation of metals from loosely bound fractions such as exchangeable fraction to strongly bound

Table 3
Concentration of Cu, Zn, Pb and Cd in each fraction in Beijing soil (mg kg^{-1})

Element	Time	EXC	CA	Fe–Mn	OM	RES	Sum	Total
Cu	Control	5.66	0.273	3.13	1.03	10.7	20.8	21.6
	3 h	260	153	33.6	54.0	11.4	512	530
	3 days	248	139	44.2	67.5	10.3	509	526
	8 weeks	160	118	126	91.5	10.3	506	522
Zn	Control	10.7	1.02	7.45	1.95	12.1	33.2	33.6
	3 h	430	47.3	21.3	1.82	14.2	515	539
	3 days	418	49.8	25.8	1.98	12.2	508	529
	8 weeks	343	70.0	65.0	3.43	13.2	495	526
Pb	Control	8.39	0.551	3.35	4.41	15.1	31.8	33.4
	3 h	398	40.1	47.8	14.6	14.6	515	548
	3 days	379	42.4	59.5	26.0	15.2	522	567
	8 weeks	231	63.0	131	67.5	15.7	508	526
Cd	Control	0.164	0.0236	0.0247	0.0453	0.221	0.479	0.509
	3 h	1.92	0.298	0.0655	0.0298	0.205	2.52	2.74
	3 days	1.88	0.283	0.114	0.0418	0.219	2.54	2.91
	8 weeks	1.80	0.268	0.141	0.0518	0.218	2.48	2.85

fractions such as Fe–Mn oxide and organic matter-bound fractions in the conditions with high metal concentrations in spiked soils and low water contents in soils. No significant differences ($p < 0.01$) in the metal concentrations of the residual fraction were observed between the control and spiked soil samples. After 8-week incubation the added metals were unlikely to enter the crystalline lattice.

Fig. 1 shows the time-dependent changes of Cu concentration in each fraction. Incubation time affected the fraction distribution of Cu significantly. The newly added Cu existed mainly in the surface of

soil particles as exchangeable fraction. After 3-h incubation, Cu in exchangeable fraction was 260, 360 and 332 mg kg^{-1} in Beijing, Jiangxi and Heilongjiang soils, respectively. When the incubation time was prolonged metal concentration of the exchangeable fraction decreased, especially for Beijing and Heilongjiang soils, more than 100 mg kg^{-1} exchangeable Cu was transformed into other fractions. But in Jiangxi soil, the decrease of Cu in exchangeable fraction was only by 26 mg kg^{-1} . From the incubation time of 3 days to 8 weeks, the decreases of Cu in carbonate bound fraction were by 35.0, 59.8,

Table 4
Concentration of Cu, Zn, Pb and Cd in each fraction in Jiangxi soil (mg kg^{-1})

Element	Time	EXC	CA	Fe–Mn	OM	RES	Sum	Total
Cu	Control	3.46	0.282	1.41	1.90	14.8	21.6	22.8
	3 h	360	109	37.2	11.4	15.7	533	554
	3 days	352	74.5	54.5	17.2	15.2	513	541
	8 weeks	334	49.2	78.5	20.1	15.5	497	543
Zn	Control	4.55	0.345	3.65	0.623	20.4	29.6	31.2
	3 h	437	50.5	12.7	0.865	19.2	520	537
	3 days	428	38.8	18.8	1.42	18.9	506	512
	8 weeks	420	34.1	24.7	1.32	21.2	501	565
Pb	Control	2.37	1.15	1.04	0.982	12.2	17.7	19.5
	3 h	389	27.0	25.9	22.5	11.9	476	503
	3 days	374	29.3	39.1	53.0	12.4	508	541
	8 weeks	353	26.4	44.2	69.5	12.6	506	534
Cd	Control	0.0329	0.00638	0.0388	0.0283	0.185	0.291	0.317
	3 h	2.18	0.103	0.0493	0.0227	0.173	2.53	2.84
	3 days	2.16	0.138	0.0385	0.0247	0.176	2.54	2.79
	8 weeks	2.07	0.173	0.0393	0.0388	0.186	2.51	3.04

Table 5
Concentration of Cu, Zn, Pb and Cd in each fraction in Heilongjiang soil (mg kg^{-1})

Element	Time	EXC	CA	Fe–Mn	OM	RES	Sum	Total
Cu	Control	3.61	0.118	0.122	0.604	4.82	9.28	9.16
	3 h	332	118	38.5	19.1	5.01	512	517
	3 days	281	92.5	68.2	57.3	5.34	504	528
	8 weeks	190	61.5	113	126	5.49	496	530
Zn	Control	4.57	0.424	4.81	4.42	12.9	27.1	28.9
	3 h	422	30.6	20.4	1.39	13.4	488	526
	3 days	407	34.0	41.5	2.88	15.2	501	560
	8 weeks	348	55.1	76.5	6.70	11.8	498	558
Pb	Control	2.12	3.17	3.84	5.96	15.4	30.5	33.0
	3 h	395	19.5	59.6	38.9	15.9	529	544
	3 days	321	25.2	87.5	57.5	15.7	507	522
	8 weeks	179	30.0	177	106	16.3	508	521
Cd	Control	0.0962	0.0166	0.0638	0.0440	0.191	0.412	0.435
	3 h	2.01	0.254	0.0171	0.0168	0.181	2.48	2.83
	3 days	1.98	0.240	0.0875	0.0420	0.186	2.54	3.09
	8 weeks	1.94	0.206	0.140	0.0565	0.177	2.52	3.11

and 56.5 mg kg^{-1} in Beijing, Jiangxi and Heilongjiang soils, respectively. The amounts of Cu bounded with Fe–Mn oxides increased consistently with increasing incubation time. After 8 weeks of incubation the concentration of Cu in Fe–Mn oxide-bound fraction reached 126, 78.5, and 113 mg kg^{-1} in

Beijing, Jiangxi and Heilongjiang soils, respectively. In organic matter fraction, Cu concentration increased by 37.5, 8.7, and 107 mg kg^{-1} in Beijing, Jiangxi, and Heilongjiang soils. The increase of Cu in organic matter fraction in Heilongjiang soil was much more than that in other two soils.

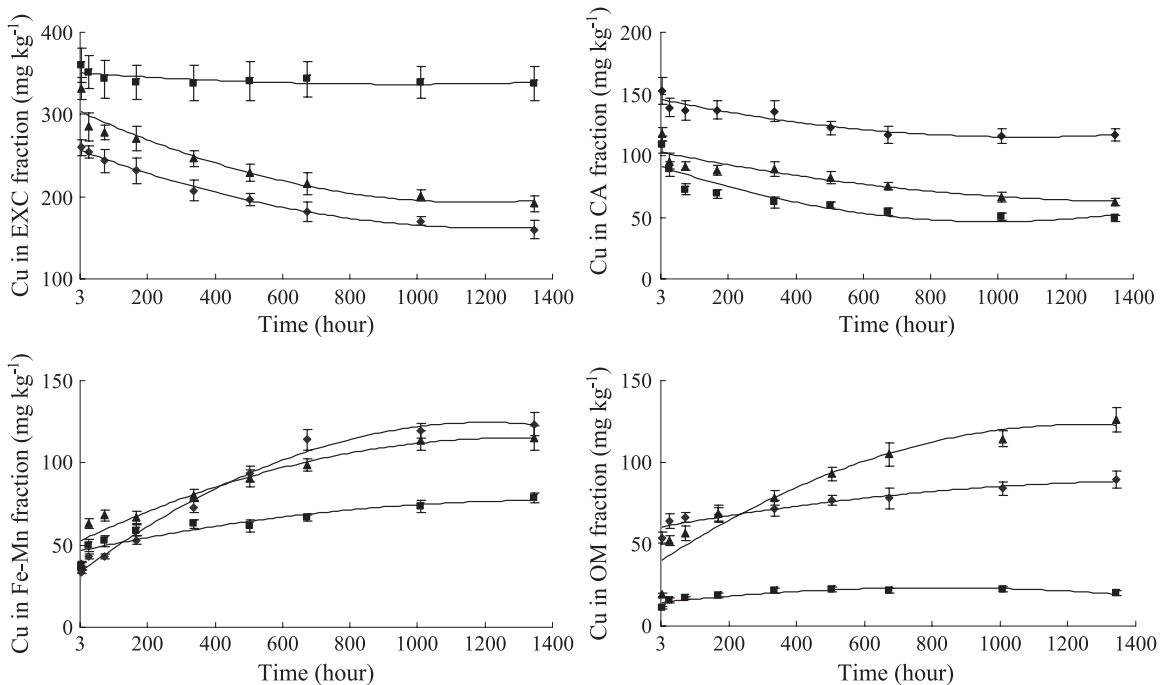


Fig. 1. Concentration of Cu in different fractions (◆ Beijing soil; ■ Jiangxi soil; ▲ Heilongjiang soil).

The changes of Zn in each fraction are shown in Fig. 2. After 3-h incubation, greater content of Zn was observed in exchangeable fraction than that of Cu. From 3 h to 8 weeks, the concentration of Zn in exchangeable fraction decreased by 87 and 74 mg kg⁻¹ in Beijing and Heilongjiang soils, for Jiangxi soil the content of Zn in exchangeable fraction almost remained unchanged. Unlike the decrease of Cu in carbonate fraction, Zn in this fraction increased with increasing incubation time in Beijing and Heilongjiang soils by 22.7 and 24.4 mg kg⁻¹ and there was 16.4 mg kg⁻¹ decreased in Jiangxi soil. Zinc in Fe–Mn oxide fraction also increased by 43.7 and 56.1 mg kg⁻¹ for Beijing and Heilongjiang soils. However, the increase was insignificant for Jiangxi soil.

Fig. 3 gives the change tendency of Pb in the soil fractions, which was similar to that of Cu. From 3 h to 8 weeks, Pb in the exchangeable fraction decreased by 167, 36 and 216 mg kg⁻¹ in Beijing, Jiangxi and Heilongjiang soils, respectively. Changes of Pb in carbonate fraction were not consistent. Lead bound to Fe–Mn oxide and organic matter had the similar change patterns and increased

significantly in Beijing, Heilongjiang soils, but not in Jiangxi soil.

Distribution of Cd among the fractions was different from other three elements (Fig. 4). Most of Cd added to soils appeared in the exchangeable fraction after 3 h and the distribution patterns of Cd among each fraction had no significant change in the incubation time from 3 h to 8 weeks. After 8-week incubation, the exchangeable fraction remained the most dominant fraction in three soils. McGrath and Cegarra (1992) found that the concentration of Cd extracted with 0.1 mol l⁻¹ CaCl₂ was much higher than those of Zn, Cu and Pb in the soil amended with sewage sludge. Naidu et al. (1994) reported that the exchangeable Cd was probably hydrated Cd²⁺ and adsorbed via out-sphere surface complexation, therefore, barricading the transformation from exchangeable fraction. The changes of Cd in carbonate, Fe–Mn oxide and organic matter fractions were insignificant and the experimental variations might have masked the time-dependent transformation among the fractions.

During 8-week incubation, Cu, Zn, Pb in exchangeable fraction decreased and Fe–Mn and organic

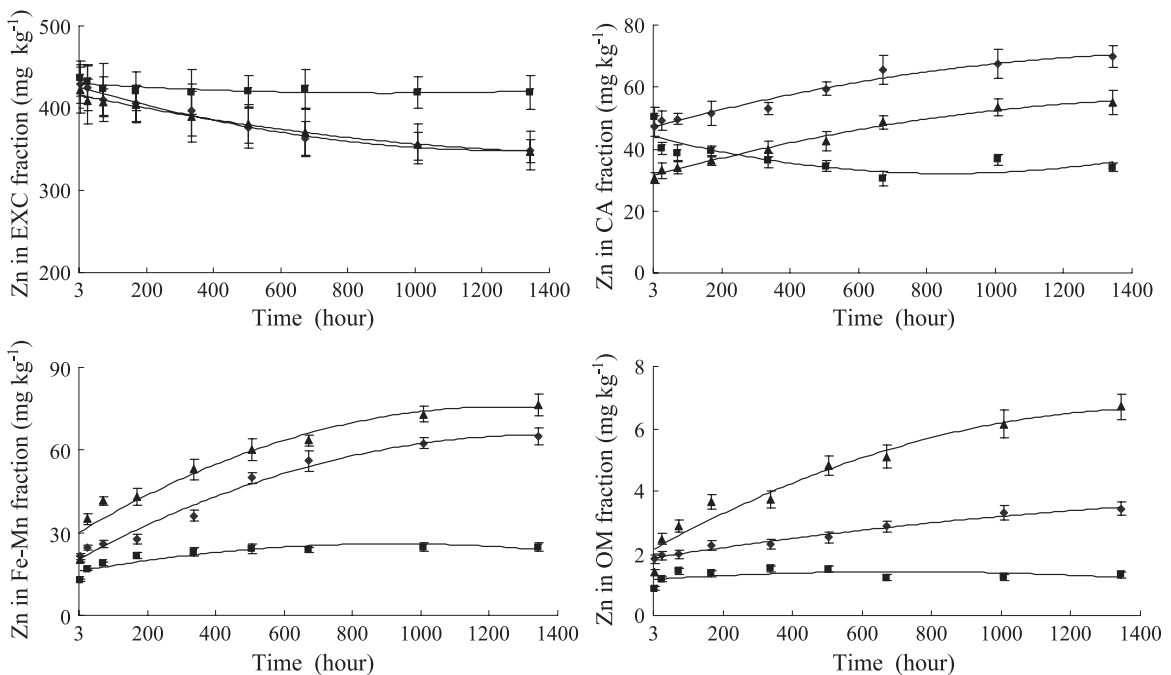


Fig. 2. Concentration of Zn in different fractions (◆ Beijing soil; ■ Jiangxi soil; ▲ Heilongjiang soil).

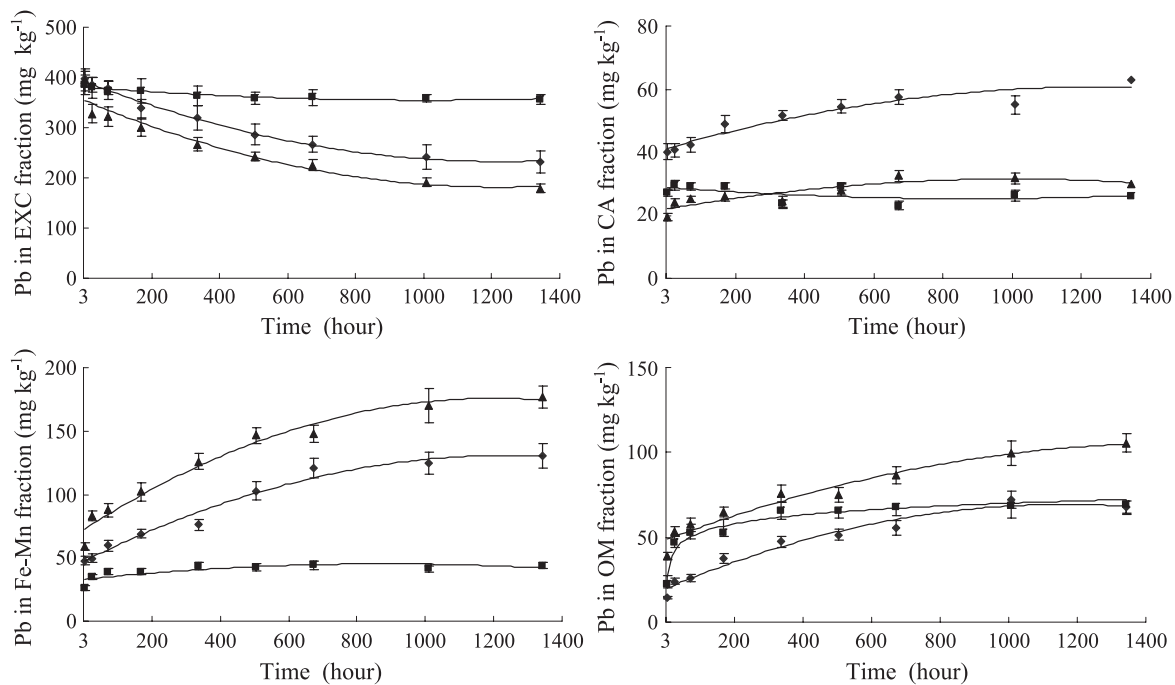


Fig. 3. Concentration of Pb in different fractions (◆ Beijing soil; ■ Jiangxi soil; ▲ Heilongjiang soil).

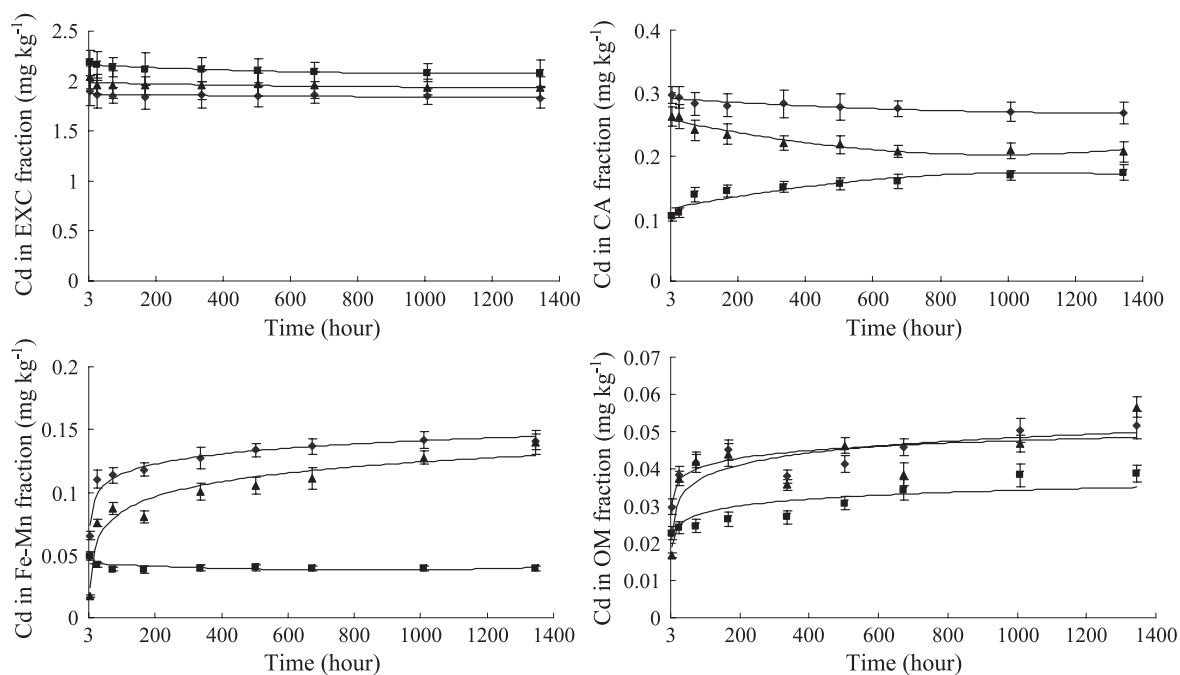


Fig. 4. Concentration of Cd in different fractions (◆ Beijing soil; ■ Jiangxi soil; ▲ Heilongjiang soil).

bound fractions increased, such changes for Cd was not as obvious as for Cu, Zn and Pb. Redistribution of the heavy metals among the fractions did not reach equilibrium in 8 weeks, slower changes among fractions were still observed.

3.2. Comparison of the fractionations among metals and soils

Most of the anthropogenic heavy metals were adsorbed on the soil surfaces as the exchangeable form rapidly and then slowly transformed into stable forms with time (McLaughlin, 2001). The decreases of heavy metals as exchangeable forms could be simulated in a linear relationship with time as the following equation:

$$\log C_m = A + BT \tag{1}$$

Where C_m is the concentration of heavy metals in exchangeable fraction, T is time, A and B are constants, which may have some relationship with the properties of soil and heavy metals. The coefficients were from 0.7713 to 0.9708 ($p < 0.01$),

as illustrated in Fig. 5. This equation can be expressed in another way:

$$C_m = A \exp(BT) \tag{2}$$

It is one of the solutions for the diffusion equation:

$$\frac{\partial C}{\partial T} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \tag{3}$$

where C is the concentration of metals, T is contact time, r is soil particle radius and D is diffusion coefficient. This solution indicated that the decreases of the exchangeable metals were mainly attributed to the diffusive processes of metals, possibly through the mesopores and micropores of soil.

Among the metals investigated, Pb and Cu were easily transformed from the exchangeable fraction to more stable fractions during the incubation period than Zn and Cd. If we defined the constant B in equation as the transformation rate, which were in the order $Pb > Cu > Zn >> Cd$. By using goethite (Forbes et al., 1974) and organic matter (Carmen and Murray, 1999) as adsorbents to investigate the metal

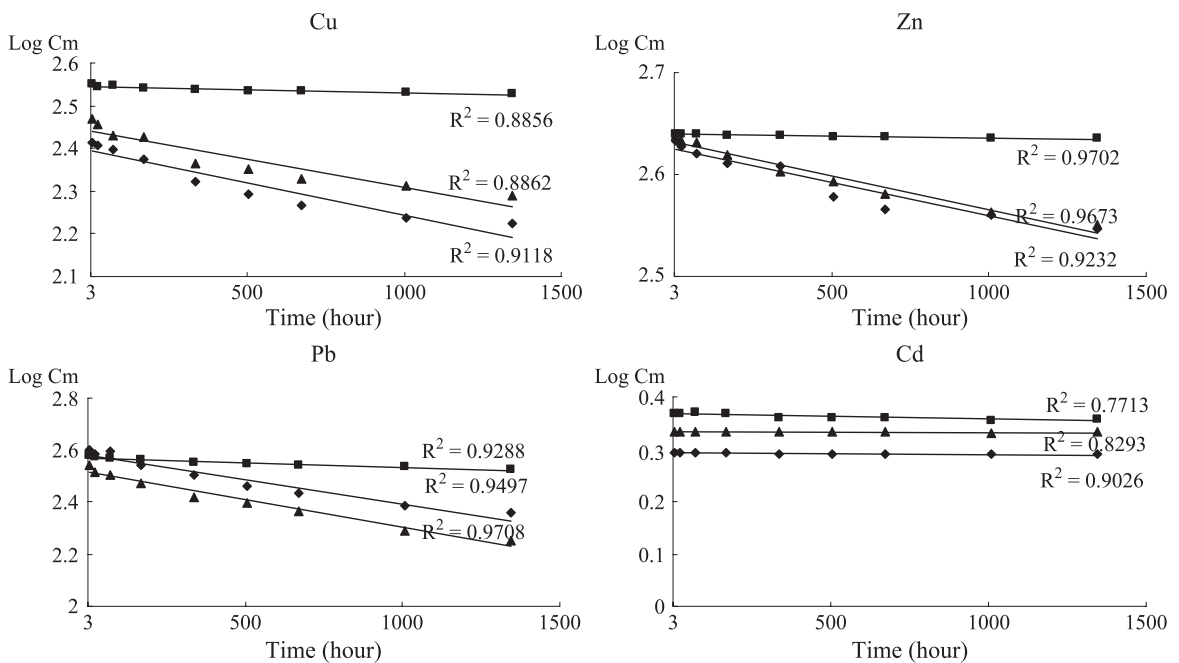


Fig. 5. Decreases of Cu, Zn, Pb and Cd in exchangeable fraction as a function of incubation time (◆ Beijing soil; ■ Jiangxi soil; ▲ Heilongjiang soil).

retention on soil components, the same order of metal affinity was obtained as the transformation rate in this work.

Only three soils were used in this experiment and therefore, correlation analysis between the fractionation and soil properties could not be conducted. However, remarkable differences in fraction distribution could be observed between Jiangxi and other two soils, for Jiangxi soil the changes of all the elements in fractions are not obvious in the test period. Among the soils, Jiangxi soil had the highest metal concentration in exchangeable fraction, and the decreases of the metals in exchangeable fraction were insignificant and the decreases in other fractions were also not as distinct as in other two soils. This phenomenon may contribute to the low soil pH of Jiangxi soil. The pH of Beijing and Heilongjiang soils are 6.90 and 7.35, whereas the pH of Jiangxi soil is 4.56. Acidic soil condition favors the metals added to soil as soluble in soil solution or weakly adsorbed on soil particle, and also restricts the metal ions to diffuse into the micropores of soil or complex with soil minerals or organic matter. Lim et al. (2002) investigated the changes of speciation of Pb and Cd in soil at various pH values with different time and found that the changes of Pb and Cd in exchangeable fraction were pH-dependent. Generally, the change was small under acidic condition and larger decrease occurred at pH 7. By monitoring the process of heavy metals on iron oxide (α -FeOOH), Carmen and Murray (2001) found that either adsorption or coprecipitation of heavy metals with ferrihydrite were pH-dependent. They also found that the increasing pH and incubation time resulted in the increase of adsorption and coprecipitation of heavy metals.

Among the fractions, changes of heavy metals in the carbonate fraction were least and not of uniform in the incubation time from 3 h to 8 weeks. Soil organic matter has been recognized as a critical component in the retention of heavy metals in soils. The increase of organic matter in soil would help to reduce the metal ions from exchangeable sites and acidic conditions (Eillott et al., 1986; Weng et al., 2002). In this experiment, the contents of OM of three soils were in the order: Heilongjiang>Beijing>Jiangxi soil, the heavy metal concentrations in organic matters also followed this order. High content of OM can enhance the binding of metals to this fraction.

4. Conclusion

The fractionation data monitored during 8-week incubation revealed the distribution patterns of Cu, Zn, Pb and Cd in soils. The soluble metals added were transformed from easily extractable fractions to more stable fractions, little change was observed in residual fraction. Among the heavy metals investigated, the transformation rate was in the order Pb>Cu>Zn \gg Cd. No significant decrease of Cd was observed in the exchangeable fraction, indicating most of the anthropogenic Cd entered the mobile fraction and much longer time was needed for Cd to enter the immobilized fraction. Compared among the soils, changes of metal fractions in Jiangxi soil were much slower than in other two soils, which was mainly attributed to the low soil pH. Soil with high OM content could bind more metals in organic matter fraction. Results of this work could be helpful for us to clarify the distribution of anthropogenic heavy metals in soil.

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