

# Speciation of Cadmium, Lead in Soils as Affected by Metal Loading Quantity and Aging Time

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Northeast China has been one of the most important industrial bases and also a main agricultural production area since the People's Republic of China came into existence in 1949. With the rapid development of industrial production in recent decades, anthropogenic activities such as mining, smelting, electroplating, ore refining, the disposal of wastes, and irrigation with sewage have led to increasing heavy-metal contents in soil, and pollution problems induced by heavy metals are becoming prominent in this area. Unlike organic contaminants, most metals in the soil environment do not undergo microbial or chemical degradation, and therefore concentrations of metals persist in soils for a long time (Guo et al., 2006). The direct consequence of heavy-metal accumulation in soil can be ecological risk for plants and other living organisms grown in such soils and a subsequent threat to human health through the food chain (Zhou et al., 2004). Contamination by heavy metals in the soil environment is therefore of great concern because of their toxicity and threat to human health.

Metal speciation is often recognized as an important parameter to assess metal toxicity in soil. It is widely recognized that to assess the environmental impact of

heavy metal in soils, determination of metal speciation gives more information about the potential for release of contaminants and further derived migration and toxicity processes (Navas and Lindhorfer, 2003). Therefore, in ecological risk assessments, it is necessary to determine chemical partitioning among the various soil-chemical phases. The speciation of metals is greatly affected by soil properties, such as pH, redox potential, cation exchange capacity, organic matter and clay content (Singh et al., 1988). However, less is known about the effect of metal loading quantity and aging time. Competitive adsorption of ions occurs in soil (Trivedi et al., 2001), suggesting that metal interactions affect their speciation in soil. In fact, soil is often contaminated with more than one pollutant, so it is interesting to study Cd, Pb speciation in soil when metals are loaded in the soil singly and simultaneously. In this work, we examined Cd, Pb speciation in the soil of northeast China as affected by the level of metal loading, aging time and the interaction between the two metals.

## Materials and Methods

Meadow brown soil samples were collected from the surface layer (0–20 cm) of cultivated soil in our ecological experimental station, Shenyang, Liaoning Province, China. The basic properties of the soil are listed in Table 1. Soil pH (soil/water ratio of 1:2.5), organic matter and cation exchange capacity (CEC) were carried out following the standard methods of chemical analysis (Zhou, 2003). The concentrations of Cd and Pb were analyzed using an atomic absorption spectrophotometer after wet digestion of the air-dried sample with a mixture of HNO<sub>3</sub> and HClO<sub>4</sub> (Guo et al., 2006).

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**Table 1** The basic physical and chemical properties of the tested soil

pH	OM (%)	CEC (cmol kg <sup>-1</sup> )	Clay content <0.002 mm (%)	Total Pb (mg kg <sup>-1</sup> )	Total Cd (mg kg <sup>-1</sup> )
6.50	1.55	15.32	32.10	18.35	0.12

**Table 2** The concentrations (mg kg<sup>-1</sup>) of heavy metals spiked in the soil samples

No.	Cd	Pb	No.	Cd	Pb	No.	Cd	Pb
1	1	0	6	0	500	11	10	300
2	10	0	7	1	100	12	10	500
3	25	0	8	1	300	13	25	100
4	0	100	9	1	500	14	25	300
5	0	300	10	10	100	15	25	500

Soil samples loaded with Cd and Pb were prepared by spiking heavy metals in the form of CdCl<sub>2</sub> · 2.5H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub> into the soil with metal concentrations in an orthogonal design, as shown in Table 2. Each of the soil subsamples weighed 20.000 g, and was mixed thoroughly and aged for different times (2 months, 10 months, 15 months and 20 months, labelled T1, T2, T3 and T4, respectively) in plastic bags at room temperature. Three replicates were used for each treatment. At different aging times, some of the subsamples were air-dried, passed through a 2 mm sieve and preserved for the analysis of metal speciation.

Sequential extraction was developed from that of Tessier et al. (1979) using the same terminology. The defined chemical fractions were as follows: fraction 1, SE (water soluble plus exchangeable); fraction 2, WSA (bound to carbonate or weakly specifically adsorbed); fraction 3, OX (bound to Fe or Mn oxides); fraction 4, OM (bound to organic matter); fraction 5, RES (residual). After each successive extraction, separation was carried out after centrifuging for 30 min. The supernatant was filtered and placed in a tube for measuring. The results are presented as the average of three replicates.

All chemicals used in the experiments were of analytical grade and deionized water was used to prepare all solutions. Analysis of the heavy metals in the supernatants was carried out using a Spectr AA–200 atomic absorption spectrophotometer (AAS, made in Australian). Reference material (GBW07404) was used for quality control of the instrument's performance. The recovery and precision were found to be within 100 ± 10%. Statistic analysis was performed using SPSS11.0 software for Windows.

## Results and Discussion

When external source of heavy metals are spiked into soil, they react with the soil surface and are retained in the soil

(Darmawan and Wada, 1999). In fact, metal toxicity is correlated not only with its concentration in the soil but also its fraction. Intrinsic heavy metals in soil are less mobile (Martinez and Motto, 2000), so metal fractions in soil at zero loading rate are not considered in this work. Metal fractions in artificially contaminated soil were affected by the kind of metals and their interactions. Tables 3 and 4 give the speciation of Cd and Pb at aging time T1. Cadmium in the soil samples existed mainly in the SE (47–76 %), OX (15–23 %) and WSA (6–13 %) fractions. However, compared with Cd, less Pb existed in the SE (1–10 %) fraction, and most of the Pb appeared in the OX (39–52 %) and WSA (7–32 %) fractions. The OM fraction had low content, which is in agreement with the results from Wang and Zhou (2003). This supports the assumption that low amounts of metal exist in the OM fraction in artificially contaminated soil (Morera et al., 2001). 1.5–13.9 % and 13–19 % residual fractions in soil for Cd and Pb, respectively. The relatively high contents of Pb in the residual fraction retained in the soil suggest that Pb entered the internal layer of the mineral crystalline structure and that Cd was more mobile than Pb.

Yarlagadda et al. (1995) characterized heavy metals in contaminated soils by particle size, sequential extraction for metal fraction, scanning electron microscopy for morphology, and energy-dispersive X-ray microanalysis for chemical composition. In artificially contaminated soil, more Pb was found in the SE fraction, whereas for soils from actual hazardous waste sites very little Pb was associated with the SE fraction. The variations of heavy-metal fractions in these soil samples, loaded at the same rate, changed when other metals coexisted with them, suggesting that the fraction of metal was affected by other coexisting metals.

Lim et al. (2001) found that the predominant mode of heavy-metal retention in a soil could be significantly influenced by the level of soil contamination, in addition to geochemical factors and the behavior of the metal itself. As shown in Table 2, soil samples in this experiment were spiked with different total metal loadings. So, it is interesting to examine the effect of coexisting metals on the studied metal fractions in soil. To predict and reflect the environmental behavior of metal in the soil, Romero et al. (1987) developed the concept of ionic impulsion according to the expression  $I = \sum C_i^{1/n}$ , where  $C_i$  is the concentration in mmol L<sup>-1</sup> and  $n$  is the oxidation number of the metals considered. The dependence of the amount of metal in the SE fraction of the soil samples at the same spiking rate on the ionic impulsion is plotted in Fig. 1 and the correlation equations are given in Table 5.

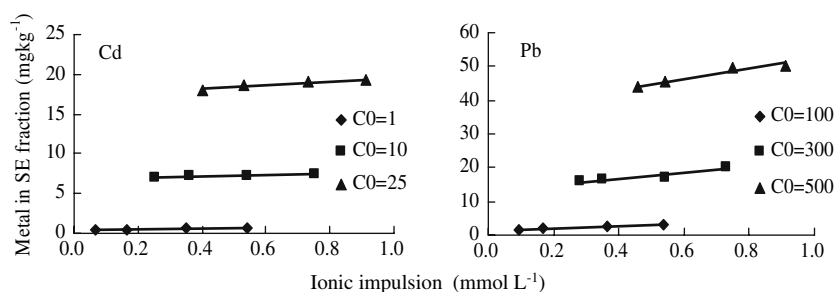
It is obvious that good linear relationships were obtained between the SE fraction content of metals in soil and the ionic impulsion. This also means that, when the

**Table 3** Speciation ( $\text{mg kg}^{-1}$ ) and percentage (%) of each fraction of Cd at aging time T1

No.	SE		WSA		OX		OM		RES		Sum
	Cd	%	Cd	%	Cd	%	Cd	%	Cd	%	
1	0.48	47.52	0.14	13.86	0.20	19.80	0.05	4.95	0.14	13.86	1.01
2	7.02	70.32	0.90	9.01	1.86	18.58	0.02	0.20	0.19	1.89	9.99
3	18.07	72.30	2.48	9.91	3.96	15.86	0.05	0.20	0.43	1.73	25.00
7	0.51	53.13	0.11	11.46	0.21	21.88	0.02	2.08	0.11	11.46	0.96
8	0.56	54.90	0.13	12.75	0.20	19.61	0.04	3.92	0.09	8.82	1.02
9	0.60	56.89	0.09	8.53	0.24	23.20	0.02	1.90	0.10	9.48	1.05
10	7.13	72.15	0.89	9.00	1.65	16.69	0.01	0.14	0.20	2.02	9.89
11	7.34	72.43	0.84	8.29	1.75	17.27	0.03	0.33	0.17	1.68	10.13
12	7.43	74.45	0.73	7.32	1.59	15.98	0.04	0.35	0.19	1.90	9.98
13	18.58	76.03	1.64	6.70	3.74	15.31	0.07	0.28	0.41	1.68	24.44
14	19.13	76.99	1.69	6.79	3.60	14.49	0.06	0.24	0.37	1.49	24.85
15	19.22	76.81	1.68	6.72	3.65	14.58	0.09	0.36	0.38	1.52	25.02

**Table 4** Speciation ( $\text{mg kg}^{-1}$ ) and percentage (%) of each fraction of Pb at aging time T1

No.	SE		WSA		OX		OM		RES		Sum
	Pb	%	Pb	%	Pb	%	Pb	%	Pb	%	
4	1.7	1.70	32.6	32.27	40.7	40.31	9.9	9.82	16.1	15.90	101.0
5	16.0	5.36	23.5	7.86	156.3	52.23	45.8	15.31	576	19.24	299.3
6	43.8	8.73	76.5	15.26	239.3	47.72	68.5	13.66	73.3	14.62	501.5
7	2.0	1.90	33.3	32.15	44.0	42.57	9.4	9.09	14.8	14.29	103.4
8	16.4	5.45	46.4	15.44	148.2	49.33	42.6	14.17	46.9	15.60	300.3
9	45.3	9.07	89.1	17.83	230.4	46.12	66.5	13.32	68.2	13.66	499.5
10	2.6	2.56	32.9	32.37	40.1	39.41	9.3	9.13	16.8	16.53	101.7
11	17.3	5.74	46.0	15.29	148.5	49.34	41.5	13.79	47.7	15.84	300.9
12	49.6	9.93	94.1	18.85	224.9	45.05	63.6	12.73	67.1	13.43	499.2
13	3.1	2.99	33.3	32.13	41.4	40.04	9.3	9.02	16.4	15.82	103.5
14	20.3	6.78	39.1	13.05	150.8	50.25	42.6	14.21	47.2	15.72	300.0
15	50.3	9.96	94.6	18.73	226.8	44.92	64.8	12.83	68.5	13.56	504.9

**Fig. 1** The dependence of the heavy metal content in the SE fraction in soil samples at the same initial concentration at aging time T1 as a function of the ionic impulsion.  $C_0$  is the initial concentration of the metal, in  $\text{mmol L}^{-1}$ 

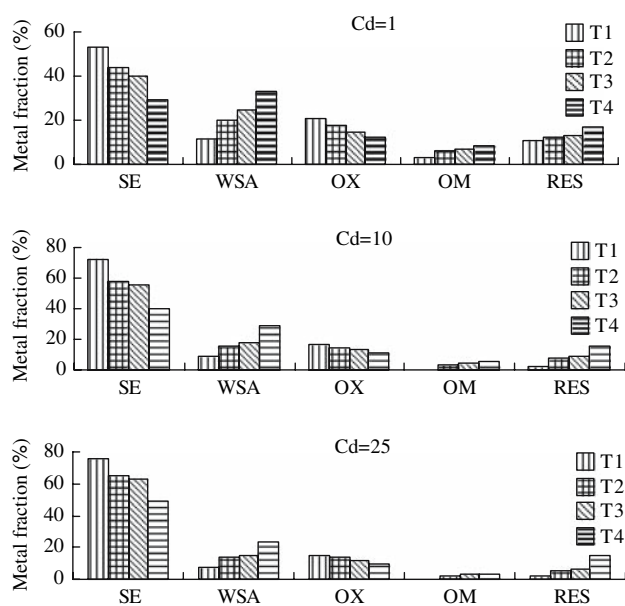
total metal quantity increased, the SE fraction of metals in the soil samples increased correspondingly. The slopes of the corresponding equations are indicative of the influence of ionic impulsion on the metal fraction in each case. When metals were spiked at a high rate, the slope was larger than that obtained at a low loading rate. Meanwhile, when other fractions were plotted similarly, no such good correlations were obtained, suggesting that other fractions were less affected by the amount of metal

loading and their interactions. According to the slopes of the equations in Table 5, the effect was stronger for Pb than for Cd.

According to Fig. 2, at aging time T1 there were higher levels of Cd in the SE, OX and less in the WSA, OM and RES fractions than at the other three aging times. This suggested that for longer aging times there is a movement of Cd from the SE, OX to the WSA, OM and RES fractions.

**Table 5** Relationship between the SE fraction of metals in soil samples and the ionic impulsion (*I*)

Metal (concentration, mg kg <sup>-1</sup> )	Correlation equation	Correlation coefficient
Cd (1)	$SE = 0.25I + 0.47$	$r = 0.996$ ( $p < 0.05$ )
Cd (10)	$SE = 0.84I + 6.83$	$r = 0.981$ ( $p < 0.05$ )
Cd (25)	$SE = 2.28I + 17.29$	$r = 0.955$ ( $p < 0.05$ )
Pb (100)	$SE = 3.13I + 1.44$	$r = 0.999$ ( $p < 0.05$ )
Pb (300)	$SE = 9.25I + 13.12$	$r = 0.957$ ( $p < 0.05$ )
Pb (500)	$SE = 15.21I + 37.13$	$r = 0.973$ ( $p < 0.05$ )

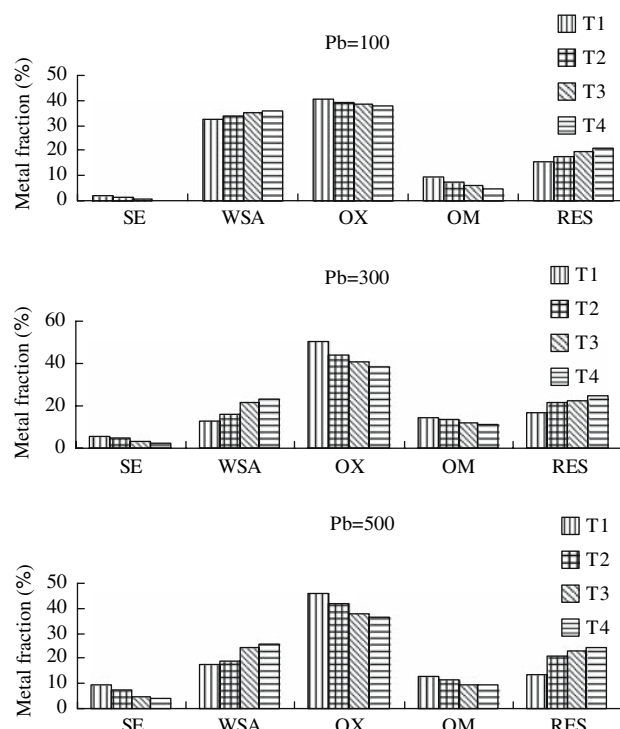
**Fig. 2** Percentages of various fractions of Cd at different aging times

However, in Fig. 3, there were higher SE, OX, OM and less WSA and RES fractions of Pb at aging times T1 than at T2, T3 and T4. This indicates that the Pb content of the SE, OX and OM fraction showed a tendency to move to the WSA and RES fractions during the aging process.

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## References

- Darmawan, Wada SI (1999) Kinetics of fraction of copper, lead and zinc loaded to soils that differ in cation exchange composition at low moisture content. *Commun. Soil Sci Plant Anal* 30: 2363–2375
- Guo GL, Zhou QX, Koval PV, Belogolova GA (2006) Speciation distribution of Cd, Pb, Cu and Zn in contaminated phaeozem in

**Fig. 3** Percentages of various fractions of Pb at different aging times

north-east China using single and sequential extraction procedures. *Aust J Soil Res* 44: 135–142

- Lim TT, Tay JH, The CI (2001) Influence of metal loading on the mode of metal retention in a natural clay. *J Environ Engineer* 127(6):539–545
- Martinez CE, Motto HI (2000) Solubility of lead, zinc and copper added to mineral soil. *Environ Pollut* 107: 153–158
- Morera MT, Echeverria JC, Mazkarian C, Carrido JJ (2001) Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. *Environ Pollut* 113:135–144
- Navas A, Lindhorfer H (2003) Geochemical speciation of heavy metals in semiarid soils of the central Ebro Valley (Spain). *Environ Int* 29:61–68
- Romero F, Elejalde JC, Azpiazu MN (1987) Metal plant and soil pollution indexes. *Water Air Soil Pollut* 34: 347–356
- Singh JP, Karwasra SPS, Singh M (1988) Distribution and forms of copper, iron, manganese and zinc in calcareous soils of India. *Soil Sci* 146:359–366
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51(7): 844–851
- Trivedi P, Axc L, Dyer J (2001) Adsorption of metal ions onto goethite: single-adsorbate and competitive systems. *Colloid Surface A* 191:107–121
- Wang X, Zhou XQ (2003) Distribution of forms for cadmium, lead, copper and zinc in soil and its influences by modifier (in Chinese). *J Agro-Environ Sci* 22(5): 541–545
- Yarlagadda PS, Matsumoto MR, Vanbenschoten JE (1995) Characteristics of heavy metals in contaminated soils. *J Environ Eng* 121(4): 276–285
- Zhou QX (2003) Interaction between heavy metals and nitrogen fertilizers applied in soil-vegetable systems. *Bull Environ Contam Toxicol* 71:338–344
- Zhou QX, Kong FX, Zhu L (2004) *Ecotoxicology* (in Chinese). Science Press, Beijing, China