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Speciation Distribution of Lead and Zinc in Soil Profiles of the Shenyang Smeltery in Northeast China

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Heavy metal contamination commonly results from anthropogenic activities such as mining, smelting, mineral processing, metalliferous electroplating, internal combustion engine operating, energy and fuel production (Kim et al. 2003). Smelting activities generate a great deal of particulate emissions and waste slag enriched with heavy metals which contaminate the surrounding soil, water and air. Such effects are particularly serious and pose a severe ecological and human health risk when smelting works are in the vicinity of urban environment. Recently many smelterys have been moved out of cities in view of the environmental problems, however, the surface of abandoned lands is contaminated by heavy metals and in great need of assessment (Steven, 2003). The studies on metal-contaminated sites around mining or metallurgical sites are numerous and relatively abundant (Dudka and Adriano, 1997), while those seek to evaluate the vertical migration of the contaminants of natural or cultivated soils are scarce (Merrington and Alloway, 1994). Originally, most analytical measurements dealt with the total content of metals in analysed samples. Fewer attempts have been made to evaluate the speciation of metals in particulate forms (i.e. the partitioning among various forms in which they might exist) (Tessier et al., 1979; Guo et al., 2006). The use of total concentration as a criterion to assess potential effects of soil contamination is not sufficient, because fate and toxicity of heavy metals in a contaminated soil is greatly controlled by speciation in the soil (Peakall and Burger, 2003). The profiles examined do not consider the speciation of heavy metals, which is often insufficient to evaluate the potential risk. As it is the speciation of pollutants rather than their total concentrations in soil that determines the potential risk of metal mobilization and transfer to other compartments of the environment (such as plants or groundwater), the data on metal speciation would seem to be essential for any general conclusions.

The Shenyang Smeltery was founded in 1936 and located in Shenyang, a heavy industrial city in northeast China. The main product of the smeltery was lead (Pb) and zinc (Zn). The release of heavy mental dust was about 66.8 ton annually. It was responsible for 98 % lead particulate emissions within this city. Due to pollution problems, the factory was demolished in 2002 and most of the land is badly contaminated with heavy metals. Now the land of the Shenyang Smeltery is

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desolate and waiting for further reclamation. The main objective of the study was to evaluate the vertical-distribution, speciation and downward mobility of Pb and Zn in soils of the Shenyang Smeltery and to determine the main factors influencing mobility. Some conclusions obtained from this work are significant for understanding the mechanism of metal transformation under real field circumstances. Furthermore it would be helpful in predicting the fate of heavy metals in the examined soil.

MATERIALS AND METHODS

The study area is situated in the Shenyang Smeltery, Shenyang, Liaoning Province, China and 3 soil profiles were collected within the smeltery during August 2004. The sampling locations were selected according to different situations in the factory. Site A (42°07.77'N, 123°49.47'E) is located in the center of the smeltery, 10 m north of the workshop of smelter. Site B (42°07.53'N, 123°49.34'E) is located near the gate of the smeltery. This is far away from the smelting workshop and was considered as the least polluted place. Site C (42°07.74'N, 123°49.62'E) is located where the slag heap was, and before the smeltery was demolished and all the slag was carried away. The comparison site D (41°31.05'N, 123°41.23'E) is a reference profile, which is in a park near the smeltery. Surface samples were obtained with a trowel (after removing the top layer contacted with the atmosphere) and stored in plastic bags. In-depth samples were taken from boreholes, to a maximum depth of 120 cm, every 20 cm sampling. The samples were air-dried and ground to pass through a 0.149 mm sieve.

Soil pH of the samples was determined in a soil: water (1: 2.5) suspension by using a pH meter (Ornella et al., 2002). Total organic matter was determined using the dry combustion method (Yu et al., 2005). Total metal contents were determined after strong acid digestion and the acids used for soil samples were HNO_3-$HClO_4$ (HNO_3:$HClO_4$ 3:1) (Guo et al. 2006). Some main properties of the soil samples are listed in Table 1.

The sequential extraction was developed from that of Tessier et al. (1979) and the extraction was carried out progressively on an initial weight of 1.0000 g of the test soil, which was contained in a centrifuge tube (polypropylene, 100 mL) and shaking with variable speed reciprocal shaker (220 strokes min^{-1}). The extractants and operationally 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-Mn oxides); fraction 4, OM (bound to organic matter); fraction 5, RES (residual). The supernatant was filtered and placed in a tube for measuring. The concentrations of heavy metals in stabilized solutions were determined using an atomic absorption spectrophotometer (AAS), model of AAS Hitachi 180-80.

All treatments were replicated three times to minimize experimental errors. The average of the three replicates for each treatment and standard deviation (SD) were calculated and significant differences in heavy metal concentration of the different layers were analyzed statistically by the least significant difference (LSD) for multiple comparisons. The statistical package used throughout this study was SPSS 11.0.

The diagnosis of trace element in soil contamination requires knowledge of the original contents of these elements in soil that is the pedogeochemical background content (Zhou, 2004). This may be sought either by analyzing the corresponding horizon of non-contaminated soils of the same soil type, or by analyzing the deep horizon of surface-contaminated soils (Sterckeman et al., 2000). In this work, the Pb and Zn content in each profile was compared to the deep horizon of the site D, for site D was the same soil type with soil samples in the smeltery and the concentration of heavy metals in deep horizon of site D was nearly consistent.

RESULTS AND DISCUSSION

Soil pH and organic matter content at different soil depths are presented in Table 1. The soil pH of different depth samples had no significant ($p>0.05$) changes in sites A, B and D. As for site C, there was significant ($p<0.01$) positive relationship between soil pH and the depth of soil. In site C, soil pH of profile 0~20 cm was obviously lower than that of other 3 sites, the concentrations of heavy metals in different depth samples of site C were also the highest among all the sites. The lower pH in surface soil of site C was probably caused by the exterior pollution. Site C was used to be slag heap, although the slag heap had been already moved away before sampling, the slag heap was probably the source of exterior pollution. Organic matter of soils had no obvious changes with the increasing depth in B profile. At the same time there existed significant ($p<0.05$) negative relationship between organic matter and the depth of soils in sites A, C and D.

Table 1. Physico-chemical characteristics of soils

Depth	A		B		C		D			
(cm)	pH	OM[a]	pH	OM[a]	pH	OM[a]	pH	OM[a]	Pb[b]	Zn[c]
0	6.61	0.85	6.55	1.22	2.55	4.06	6.67	2.91	15.01	39.12
20	6.67	1.09	6.49	1.09	3.71	3.93	6.71	3.21	11.81	37.05
40	6.86	1.32	6.47	0.91	5.26	1.88	6.65	2.82	11.13	36.17
60	6.83	0.64	6.34	0.62	5.87	1.26	6.63	2.43	12.02	34.97
80	6.97	0.54	6.42	0.87	5.54	0.99	6.58	1.92	12.09	34.84
100	6.98	0.46	6.35	0.83	5.62	0.81	6.64	1.75	11.71	35.98
120	6.8	0.41	6.57	0.81	6.72	0.93	6.66	1.23	11.65	35.04

[a] Organic matter (%); [b] The total Pb in different depth of site D ($mg \cdot kg^{-1}$); [c] The total Zn in different depth of site D ($mg \cdot kg^{-1}$).

Site D was in a park and considered as a reference profile. The concentration of Pb in surface soil of profile D was slightly higher than that of bottom soil (Table 2). The concentrations of Pb from 20 cm to 120 cm in profile D had no difference by the LSD test and the background content of Pb was considered to fluctuate between 11.1~12.1 $mg \cdot kg^{-1}$. Concentrations of Pb were all significantly ($p<0.05$)

decreased with the increase of depth in site A, B or C (Table 2). Different horizon soils of profile A were all polluted by Pb and Pb concentration in surface soil was 139.4 mg·kg^{-1} which was about 12 times higher than the background concentration of Pb. Even 120 cm under the surface of site A, Pb concentration was 43.2 mg·kg^{-1}. Site B was far away from workshop and the slag heap in the Smeltery, and Pb concentration in surface soil was 92.6 mg·kg^{-1} which was the lowest content in surface soil among the three sites of the Smeltery. At 120 cm horizon, Pb content was 15.3 mg·kg^{-1} which was close to the background concentration of Pb. In other words, site B was contaminated which may be caused by a diffuse contamination linking to atmospheric fallout. As for site C, Pb concentration decreased abruptly from the surface to the bottom. Pb concentration in surface soil was about 20 times as much as that of 40 cm depth and about 59 times as much as that of 60 cm depth. Pb concentration from 0 cm to 20 cm in profile C was obviously higher than that of profiles A and B. As profile C was under the slag heap, the above difference was probably induced by the slag heap. There is no international agreement on metal concentrations in soil that constitute significant contamination, but according to the background concentration of Pb we could confer that the 3 sites (A, B and C) were all contaminated with Pb at different degrees. The contamination level in top soil of site C exceeded “3” level for Pb of the environmental quality standard of soil in China.

Speciation of Pb in soil profiles from the sequential extraction experiment was shown in Table 2. In site D the concentration of Pb associated with different fractions was in the sequence: RES > OX > WSA > OM > SE; while for sites A, B and C, the concentration of different fractions of Pb was in the following sequence: OX > WSA > SE > OM > RES. The result was consistent with the results by Wang et al. (2003) who believed that Pb in natural clean soil was mainly existed in the RES fraction, exotic Pb in soil was found predominantly in the OX fraction. In sites A, B and C, no matter which horizon the concentration of the OX fraction was always the maximum. It was showed that Pb preferred to form stable complexes with Fe and Mn oxides which was accordant with the report by Ramos et al. (1994) and other researches also found that most of Pb was present in the Fe-Mn oxide fraction in soil and sediments (Silverira et al., 2006).

From Table 2 we also discovered that in sites A, B and C, the Pb concentration of different fractions was all significantly ($p<0.05$) decreased with the increase of depth in soil. But changes of the percentage (different fractions in total Pb amounts) were not consistent. The percentage of the OX fraction was significantly ($p<0.05$) decreased with the increase of soil depth. While the percentages of WSA and SE fractions were increased with the increase of soil depth, and there was significant ($p<0.05$) positive relationship between the percentage of the SE fraction and the soil depth. There was no obvious change between the percentages of OM, RES fractions and the soil depth. It was possible that there existed a transform from the OX fraction to SE and WSA fractions in the vertical transfer of Pb. In site C, the SE fraction of Pb was high (873.7 mg·kg^{-1}) on top soil, but at 40 cm depth in soil the SE fraction of Pb was significantly ($p<0.05$) lower than that of top soil. Weathering processes were likely to be responsible for the decrease in

Table 2. The variation of the concentration and percentage of Pb in different fractions with soil depth

Depth	Site	SE		WSA		OX		OM		RES		Total
(cm)		mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}
0	A1	18.4	13.2	34.1	24.5	61.2	43.9	15.8	11.4	9.9	7.1	139.4
20	A2	17.4	16.3	26.1	24.5	41.7	39.1	13.3	12.5	8.0	7.5	106.5
40	A3	16.7	18.5	21.4	23.8	32.5	36.0	11.2	12.4	8.4	9.3	90.3
60	A4	16.0	20.6	20.1	24.5	27.5	33.5	10.8	13.2	6.8	8.3	82.3
80	A5	15.4	24.6	16.4	26.2	17.9	28.7	8.3	13.2	4.7	7.5	62.8
100	A6	12.6	24.8	13.3	26.2	13.7	27.0	6.9	13.6	4.3	8.4	50.8
120	A7	10.9	25.1	11.1	25.6	11.4	26.3	5.9	13.6	4.0	9.3	43.2
0	B1	14.7	15.9	21.6	23.3	38.2	41.2	10.4	11.2	7.8	8.4	92.6
20	B2	12.1	16.1	17.6	23.3	31.7	42.0	8.5	11.3	5.5	7.3	75.4
40	B3	11.5	18.3	15.1	24.1	22.3	35.4	7.9	12.5	6.1	9.7	62.9
60	B4	9.1	19.1	11.1	23.1	17.8	37.2	5.4	11.3	4.5	9.3	47.8
80	B5	6.7	21.4	7.5	24.1	10.1	32.3	3.8	12.1	3.2	10.1	31.2
100	B6	5.5	22.4	6.2	25.2	7.0	28.3	3.2	13.0	2.7	11.2	24.6
120	B7	3.5	22.5	3.8	24.6	4.0	25.8	2.2	14.2	2.0	12.8	15.3
0	C1	873.7	15.1	1040.6	17.9	2967.1	51.2	473.9	8.2	438.6	7.6	5793.9
20	C2	827.1	16.5	950.1	18.9	2412.9	48.1	438.4	8.7	393.2	7.8	5021.7
40	C3	49.7	16.8	42.5	14.4	142.6	48.3	39.7	13.4	21.1	10.2	295.5
60	C4	16.9	17.1	17.6	17.8	46.5	47.0	9.7	9.8	8.1	8.2	98.9
80	C5	15.5	17.8	16.3	18.7	40.5	46.4	8.1	9.3	6.9	7.9	87.2
100	C6	13.9	17.8	15.1	19.3	33.9	43.5	8.8	11.3	6.3	8.1	78.0
120	C7	10.3	18.5	13.5	24.3	19.0	34.2	8.2	14.8	4.5	8.1	55.6
120	D7	0.2	1.9	2.0	17.0	3.2	27.0	1.2	10.0	5.1	44.0	11.7

[a] Percentage of different fractions in the total content of heavy metals (%).

Table 3. The variation of the concentration and percentage of Zn in different fractions with soil depth

Depth (cm)	Site	SE		WSA		OX		OM		RES		Total
		mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}	%^{a}	mg·kg^{-1}
0	A1	108.6	10.2	188.6	17.6	412.4	38.6	115.5	10.8	244.1	22.8	1069.2
20	A2	86.5	10.7	153.1	18.9	286.0	35.4	93.1	11.5	188.3	23.3	806.9
40	A3	40.5	10.1	88.0	22.0	129.7	32.4	40.1	10.0	102.1	25.5	400.3
60	A4	12.6	10.2	27.8	22.5	37.6	30.4	12.9	10.4	32.9	26.6	123.9
80	A5	9.0	10.4	20.2	23.5	25.9	30.0	8.6	10.0	22.6	26.2	86.2
100	A6	7.4	10.4	16.8	23.4	21.5	29.9	6.6	9.2	19.4	27.1	71.7
120	A7	6.3	10.7	14.1	24.1	17.2	29.4	6.0	10.3	15.0	25.7	58.5
0	B1	10.2	12.1	15.2	18.1	23.7	28.1	12.3	14.6	22.8	27.1	84.3
20	B2	9.6	14.5	12.1	18.1	17.4	26.2	9.0	13.5	18.5	27.8	66.6
40	B3	7.9	14.8	10.4	19.4	13.8	25.7	6.5	12.0	15.1	28.1	53.8
60	B4	7.9	14.9	10.4	19.5	13.5	25.4	6.2	11.7	15.1	28.4	53.1
80	B5	7.6	14.7	10.1	19.6	13.0	25.2	6.0	11.7	14.9	28.9	51.7
100	B6	6.7	14.6	9.0	19.7	10.7	23.4	5.8	12.8	13.5	29.5	45.7
120	B7	6.3	15.4	8.4	20.5	8.7	21.3	5.2	12.7	12.3	30.1	40.8
0	C1	268.4	14.2	300.3	15.9	677.9	35.8	224.0	11.8	421.6	22.3	1892.2
20	C2	213.3	15.2	226.2	16.1	493.6	35.2	150.5	10.7	320.2	22.8	1403.8
40	C3	82.4	14.3	94.7	16.4	201.6	34.9	65.8	11.4	133.6	23.1	578.1
60	C4	80.2	14.6	96.7	17.6	182.3	33.2	63.3	11.5	127.0	23.1	549.3
80	C5	25.9	15.1	31.4	18.3	55.3	32.2	19.3	11.2	40.0	23.3	171.9
100	C6	20.6	14.7	27.6	19.7	41.6	29.8	16.1	11.5	34.0	24.3	134.0
120	C7	15.2	14.4	21.8	20.6	30.4	28.6	11.9	11.2	26.8	25.2	106.1
120	D7	0.7	2.0	1.8	5.0	5.6	16.0	5.9	17.0	21.0	59.9	35.0

[a] Percentage of different fractions in the total content of heavy metals (%).

the SE fraction and also effectively performed a natural remediation process (Verner et al., 1996).

All horizons of profiles A, B and C were polluted by Zn (Table 3). From the deeper horizon of site D, it was conferred that the background content of Zn fluctuated between 34.8~37.1 mg·kg^{-1}. With the depth increasing for sites A, B and C, Zn concentration was significantly ($p<0.05$) decreased. Site A was in the central of the Shenyang Smeltery and close to the workshop, Zn concentration was 1069.2 mg·kg^{-1} in surface soil and 58.5 mg·kg^{-1} in bottom soil. These values were about 31.0 and 1.7 times as much as that of the background content of Zn. At site B, Zn concentration was 84.3 mg·kg^{-1} in surface soil and 40.8 mg·kg^{-1} in bottom soil, and the latter value approached the background concentration.

Speciation of Zn in soil profiles from the sequential extraction experiment was listed in Table 3. In site D, the concentration of Zn associated with different fractions was in the sequence: RES > OM > OX > WSA > SE. As for sites A, B and C, different fractions of Zn followed the sequence: OX, RES > WSA > OM, SE. The result was consistent with the report by Song et al. (1996) who pointed out that OX, RES and WSA fractions of Zn were the main existing forms in exotic Zn contamination of soil. In addition, Ma and Rao (1997) reported that Zn was mainly associated with Fe-Mn oxides of soils and sediments. Zn adsorption onto these oxides has higher stability constants than onto carbonates. From Table 3, there were significant ($p<0.05$) positive relationships between the percentage of WSA, RES fractions with the depth of soil. At the same time, the percentage of the OX fraction had significant ($p<0.05$) negative relationships with the soil depth, and there were no significant ($p>0.05$) changes in the percentage of SE, OM fractions of Zn. There was a possibility that there existed a transform from the OX fraction to WSA and RES fractions in the vertical transfer of Zn.

The statistical analysis showed that there were significant ($p<0.01$) negative relationships between soil pH in site C and the content of different Pb and Zn fractions, while a significant ($p<0.01$) positive relationship existed between organic matter and the content of different Pb and Zn fractions. In site A there were significant ($p<0.05$) negative relationships between soil pH and the content of WSA, OX and RES fractions of Pb; a significant ($p<0.05$) negative relationship existed between soil pH and all the fractions of Zn. For site B, organic matter had a significant ($p<0.05$) positive relationship with all the fractions of Pb and Zn; pH had no obvious influence on the fractions of Pb and Zn. The above correlation analysis suggested that soil pH and organic matter played an important role in releasing metals to soil. The site nears the source of pollution (i.e. site A) or severely polluted on surface soil (i.e. site C) all could accelerate the vertical transfer of Pb and Zn.

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