



The heavy metal partition in size-fractions of the fine particles in agricultural soils contaminated by waste water and smelter dust

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HIGHLIGHTS

- ▶ A continuous flow ultra-centrifugation method has been developed to obtain fine particles from polluted agricultural soil.
- ▶ Pollution source affected the heavy metal fractionation in size-fractions by changing soil particle properties.
- ▶ The iron oxides affected the distribution of lead species more than other metals in the smelter dust polluted particles.

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ABSTRACT

The partitioning of pollutant in the size-fractions of fine particles is particularly important to its migration and bioavailability in soil environment. However, the impact of pollution sources on the partitioning was seldom addressed in the previous studies. In this study, the method of continuous flow ultra-centrifugation was developed to separate three size fractions ($<1\ \mu\text{m}$, $<0.6\ \mu\text{m}$ and $<0.2\ \mu\text{m}$) of the submicron particles from the soil polluted by wastewater and smelter dust respectively. The mineralogy and physicochemical properties of each size-fraction were characterized by X-ray diffraction, transmission electron microscope etc. Total content of the polluted metals and their chemical speciation were measured. A higher enrichment factor of the metals in the fractions of $<1\ \mu\text{m}$ or less were observed in the soil contaminated by wastewater than by smelter dust. The organic substance in the wastewater and calcite from lime application were assumed to play an important role in the metal accumulation in the fine particles of the wastewater polluted soil. While the metal accumulation in the fine particles of the smelter dust polluted soil is mainly associated with Mn oxides. Cadmium speciation in both soils is dominated by dilute acid soluble form and lead speciation in the smelter dust polluted soil is dominated by reducible form in all particles. This implied that the polluted soils might be a high risk to human health and ecosystem due to the high bioaccessibility of the metals as well as the mobility of the fine particles in soil.

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1. Introduction

Development of small factories have resulted in a severe heavy metals pollution in the surrounding agricultural soils due to the lack of proper treatments for wastewater, exhaust gas and particulate matter in most rural areas of China [1]. Risk from high content of heavy metals usually results from their likelihood to leach to groundwater or to enter the food chain through plant uptake. Many studies have provided the evidence that fine particles mobilized and transported in soils and aquifers can have a profound influence

on contaminant migration [2–4]. Recent evidence indicated that plant could uptake nano-scale particles from solution and pose toxicity to the plant [5,6]. Heavy metal accumulation in soils was known to increase with decreasing particle size. Ajmone-Marsan et al. [7] analyzed heavy metals in particle-size fractions of the soils from five European cities and concluded that all the metals (Cr, Cu, Ni, Pb and Zn) were concentrated in the particle of $<10\ \mu\text{m}$. Besides, Wang et al. [8] and Luo et al. [9] studied the distribution of Pb and Zn in the different size fractions of urban soils in Nanjing and Hong Kong, China, respectively. Both of the results presented the accumulation of metals in fine particles. Although most of the studied metals were enriched in the fine particles, the bioavailability of some metals (Ni, Cu, Pb, etc.) was lower than that in the fine sand fraction with respect to plant uptake [10]. Mineral composition and soil organic matter were assumed to play an important role in

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the accumulation and speciation of heavy metals in the different particle size fractions. Acosta et al. [11] figured out that the high amounts (60–80%) of calcite and dolomite was the main reason of metals accumulation in fine fractions in the soils of urban parks in Murcia City, Spain. Quenea et al. [12] found that Zn seemed to be mainly bounded to soil organic matter associated with clay particles, while Pb seemed to prefer to interact directly with the mineral surfaces versus the organic matter in a soil contaminated by waste water. Tang et al. [13] analyzed organic carbon and heavy metals contents for the separated nanocolloidal particles (five fractions from 250 μm to <0.1 μm) from some mining sites in China and observed a good correlation between Cu, Cd and organic carbon.

Various studies regarding the heavy metals partitioning in different size fraction of soils focused on the size from 2000 μm to <2 μm for the purpose of identifying the contribution of polluted urban soil particles to airborne particulate matter (PM10 and PM2.5) [7–9,11]. The size-fraction of heavy metals in the soil colloid was seldom reported due to the difficulty of separation. Most of studies applied the traditional sieving and centrifugation method to separate different size-fractions [7,11,14], however, the traditional methods are usually low efficient and difficult to obtain fine particles. Although a few studies were concentrated on the very fine particles [1,13], the particle properties and their relationship with metal accumulation were not studied. We hypothesized that different pollution sources would contribute to the size partitioning of heavy metals as well as particle properties. Therefore, the objectives of the study are to develop an efficient separation method to get the fine particles by using polluted soil and to determine the distribution of heavy metals and their speciation as well as particle characteristics in the difference size-fractions based on the two types of polluted soils. The particles within the size range (from <3 μm to <0.2 μm) were assumed to be high mobility with pollutants in soil [3].

2. Materials and methods

2.1. Soil sample and characteristics

Soil samples were taken from a rural area of Fuyang County, Zhejiang Province, in the east of China. The climate of the area is moist monsoon with an annual precipitation of approximately 1425 mm with the maximum during May and June, and a mean temperature of 16 °C. Two typical sites were selected from local area based on previous investigation [1,15]. The first sampling site is a paddy field adjacent to a zinc plating factory which operated in 2005. During the first four years of operation, the wastewater was drained directly from the factory without being any treatments and onto the paddy field by mixture with irrigation water. The surrounding land of the factory has been seriously polluted by zinc, cadmium and copper based on an investigation [15]. The wastewater also caused soil acidification and local farmers have used a lot of lime to naturalize the soil. The paddy soil sample (S-CA) was collected from surface layer (0–20 cm) of the severe polluted sites near the source for the experiment. The second sampling site is an agricultural field adjacent to a small copper smelter plant, which is around 5 miles away from the first sampling site. This site has been influenced by the smelter dust for over 20 years and the severe heavy metal (zinc, copper, lead, cadmium, etc.) pollution has damaged crops growth [1]. Soil sample (S-ZH) was collected from surface layer (0–20 cm) of the site for the experiment. Both soils are Stagnic Anthrosols based on Chinese Soil Taxonomy [16], with loamy soil in texture and a pH around 7.5. The clay minerals of the soils are mainly composed of kaolinite, mica, smectite, vermiculite. However, higher content of calcite was found in the sample of S-CA than in the sample of S-ZH due to the long-term application of agricultural lime.

2.2. Sized fractionation by the method of continuous flow ultra-centrifugation

After air-drying at room temperature and removal of stones and visible plant materials, the soil samples were sieved through a 2 mm nylon mesh. A total of 2.0 kg <2 mm fraction for each sample was weighed and mixed with 20 L pure water in a container. The suspension was mixed thoroughly after stirring of 3 h. Then the soil sample was fractionation based on the particle size of 50–3 μm , <3 μm , <1 μm , <0.6 μm , <0.2 μm . Following is the detail of the physical separation.

- (1) *The fractions of 50–3 μm and <3 μm .* The dispersed sample was sieved through a 0.05 mm mesh and the particle less than 0.05 mm was collected. Drawing 10 ml of the suspension into an aluminum plate to dry at 105 °C for 24 h and particle content of the suspension was calculated. The collected suspension was further mixed with pure water to maintain a soil:water ratio of 1:50 based on the particle contents of the suspension. The fraction of <3 μm was separated by gravity sedimentation based on Stokes' Law. The supernatant was siphoned and collected after a certain time. Pure water was refilled into the container to disperse the particle and the same procedure was repeated twice. The remained suspension was oven dried at 60 °C and collected as fraction of 50–3 μm . All the collected supernatants were mixed for further separation.
- (2) *The fractions of <1 μm , <0.6 μm and 0.2 μm .* These three fractions were separated from the <3 μm suspension by the method of continuous flow ultra-centrifugation (CFUC) as shown in Fig. S1 of the supporting information. Continuous flow centrifugation is a laboratory time-saver whereby large volumes of material can be centrifuged at high centrifugal forces without the tedium of filling and decanting a lot of centrifuge tubes, or frequently starting and stopping the rotor [17]. Maintaining soil particle dispersion thoroughly in the suspension is a key to the separation efficiency. Several methods including addition of hydrogen peroxides, dilution and sonication have been tried prior to the experiment. It turned out that both sonication and 150% of dilution were better than hydrogen peroxides addition with respect to the dispersion of very fine particle (Fig. S2 of the supporting information). The suspension was pumped into the rotor of a high speed refrigerated centrifuge (Hitachi Himac CR22G, rotor R18C) for separation and flow rate was kept at the speed of 250 ml/min. The different size-fraction can be separated by controlling the rotor speed. For the fraction of <1 μm , <0.6 μm and 0.2 μm , the rotor speed was set at 1580 rpm, 2500 rpm and 7500 rpm, respectively. Temperature inside of the rotor was maintained at 25 °C. The supernatant was collected by a container during the process of centrifuge and it was recentrifuged by a high speed rotor (18,000 rpm, rotor R20A2) to collect the solid particle. This collected particle was oven dried at 60 °C. Particle size of each size fraction was verified by a laser particle analyzer (HORIBA, LA -920) and with the result indicated in Fig. 1. The separated soil particle amounts and their ratios were presented in Table S2 of the supporting information. The mass weight of the particle was supposed to meet the requirement of the subsequent physical and chemical analysis.

2.3. Physical and chemical analysis of the soil particle

Bulk soil pH was measured by pH meter after adding 25 ml water into 10.0 g soil. The pH of each size fraction was measured directly by pH meter in suspension. Soil organic carbon (SOC) of the bulk soil and the particle were measured by the method of Nelson and Sommers [18]. Particle composition of the bulk soil was measured by laser particle analyzer. External specific surface area (SSA_e) of

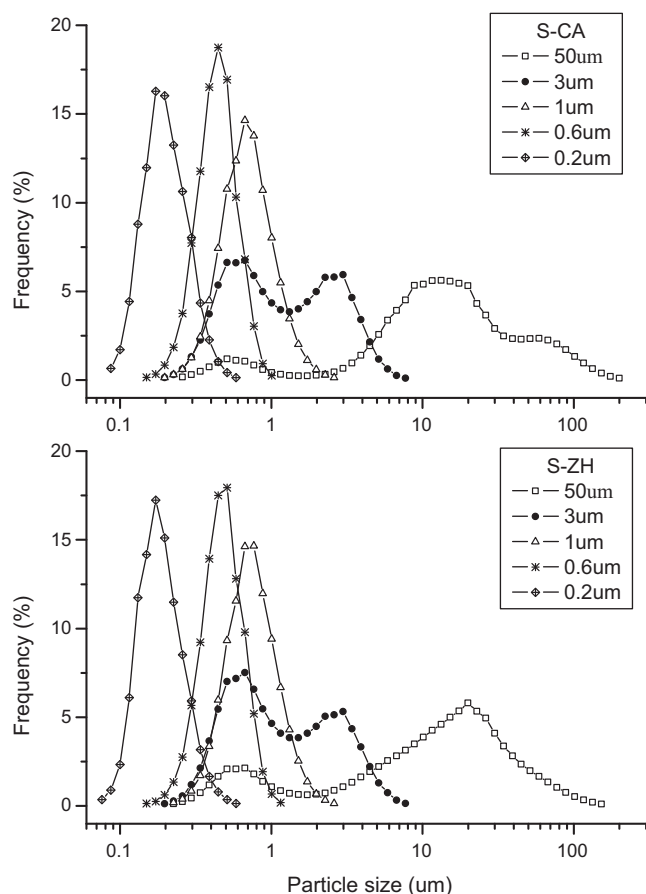


Fig. 1. Validation of the particle size for each separated size-fraction by a laser particle analyzer (HORIBA, LA -920).

the particle was measured with BET- N_2 method (Quantachrome Instruments, AUTOSORB-1). Total specific surface (SSA_t) of the particle was measured with ethylene glycol monoethyl ether (EGME) method. The clay minerals of each size-fraction were identified by X-ray diffraction (XRD) (JEOL, JDX-3530) with Cu K_α radiation after cation saturation by magnesium and potassium, glycerol solvation and heat treatments (330 °C and 550 °C). Transmission electron microscopy (TEM) observations were performed on a H-7650 (Hitachi, Japan) operating at 100 kV.

Total concentration of major and trace elements in the bulk soils and the particles was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian inc., Vista-Pro, USA) after digestion by a mixture of nitric and perchloric acid digestion [19]. Selected and sequential extractions were performed for the elements in addition to the aqua regia digestion. Dithionite–citrate–bicarbonate (DCB) and oxalate buffer (pH 3.0) extraction in dark were selected to evaluate the free and amorphous form of Fe, Al and Mn oxides, respectively. Six-steps sequential extraction was performed according to the method of Makino et al. [20] and Suda et al. [21]. Briefly, 4.0 g soil was extracted sequentially by 1 mol/L ammonium nitrate (pH 7.0) (exchangeable), 0.44 mol/L acetic acid (dilute acid soluble), 0.1 mol/L hydroxylammonium chloride with 0.01 mol/L nitric acid (pH 2.0) (manganese oxide occluded), 0.44 mol/L acetic acid after digestion of 6% hydrogen peroxides (organically bound), 0.2 mol/L ammonium oxalate (pH 3.0) with 4 g of ascorbic acid (iron oxide occluded). The residue soil was digested by a mixture of nitric acid and perchloric acid subsequently. The recovery of metal concentrations of all six fractions compared to metal concentrations extracted by nitric and perchloric acid digestion ranged from 90 to 106% for Cd, from 85 to 109%

for Cu, from 84 to 108% for Pb, from 85 to 109% for Zn, from 88 to 110% for Cr, from 93 to 102% for Ni. For quality assurance of the heavy metals analysis, duplicated samples, blanks, internal check standard and a certified reference material (GBW07401, provided by the Institute of Geophysical and Geochemical Exploration, Langfang, Hebei province, China) were included in the procedure.

3. Results

3.1. Physicochemical properties of the different size-fraction particle

The morphology of the different size-fraction particle is presented by the TEM images (Fig. 2). The large particles are mainly formed to aggregate, however, the aggregate was dispersed with the decrease of particle size. Most of the particle is shown with the shape of hexagon or pseudo-hexagon which is indicative of kaolinite. The clay mineral patterns are shown in Fig. 3. The XRD pattern of the sample with the treatments of Mg^{2+} saturation and glycerol solvation was selected to indicate the difference of clay minerals among the size fractions. Variety was shown between the size fraction of $<0.2 \mu m$ and other fractions in the position of $d = 1.4 nm$ for both samples. In theory, the d -space of smectite shifts from 1.4 nm to 1.8 nm while that of vermiculite does not change in the case of Mg^{2+} saturation followed by glycerol solvation [22]. Therefore, disappearance of 1.4 nm peak in the pattern for the fraction of $<0.2 \mu m$ was an indicative of smectite rather than vermiculite occurrence in the particle. However, both smectite and vermiculite were identified to occur in other three clay fractions. The change of clay minerals with particle size could also be identified by the molar ratio of Fe/Al and Mg/Al [3], which was shown in Fig. 4. The molar ratio of Fe/Al decreased from silt fraction (50–3 μm) to $<0.6 \mu m$ fraction and followed by a slightly increase in $<0.2 \mu m$ fraction for both soils. This implied that the relative enrichment of iron oxides to phyllosilicate decreased with particle size in general although it increased slightly in the finest fraction. The molar ratio of Mg/Al decreased with particle size in the whole size range, which was assumed to be corresponding to the decrease of the relative enrichment of vermiculite to kaolinite or smectite with particle size.

Table 1 shows the quantitative changes of other properties with particle size. The pH is shown a slight increase from silt to clay and submicron clays (all the particle fractions less than 1.0 μm). Content of SOC in bulk soil and its change with particle size were much different between the two samples. Higher content of SOC was measured in S-CA sample than S-ZH sample. The SOC content increased with decrease of the particle size in S-ZH sample. However, such a trend was not observed in S-CA sample, in which, higher SOC content were presented in the fractions of $<0.2 \mu m$ and $<1.0 \mu m$ than other fractions. Higher content of calcium was observed in S-CA sample due to the occurrence of calcite. An inverse change of calcium content from silt fraction to $<0.2 \mu m$ fraction could be founded between S-CA and S-ZH. Total content of iron and manganese oxides in bulk soil and their changes with particle size were much close between the two samples. However, a significant difference was shown in DCB extractable iron and manganese oxides contents. The S-CA sample was shown with higher content of DCB extractable iron and manganese oxides. Higher specific surface area (external and total specific surface areas) was also measured in S-CA bulk sample than in S-ZH bulk sample, which probably as a result of higher content of organic carbon and DCB extracted iron and manganese oxides in S-CA [14,23]. A big difference between the SSA_e and SSA_t as shown in Table 1 was an indicator of swelling clays such as smectites and vermiculites occurrence or small size pore structure in the soils [23]. Both of the external and total specific surface

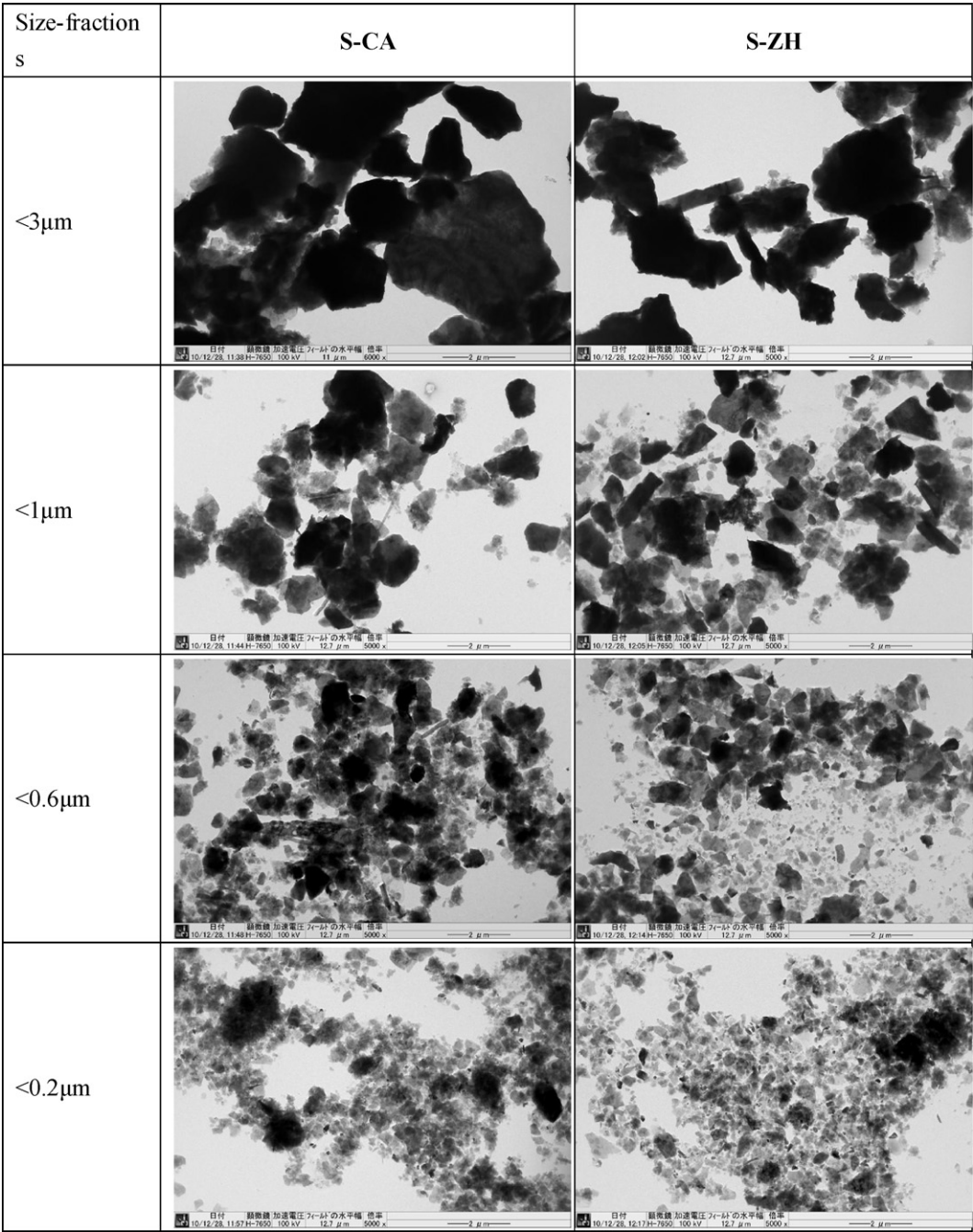


Fig. 2. The morphology of particles in each size-fraction presented by TEM.

areas were shown with a positive relationship with particle size as reported in other studies [14,24].

3.2. Heavy metal concentration of the different size-fraction particle

The content of heavy metal in the bulk soil sample and each size-fraction is shown in Table 2. The polluted heavy metals are much different as indicated in the bulk soils owing to the different anthropogenic sources. The S-CA sample is characterized by severe pollution of Zn, Cd, Ni, Cr and slight pollution of Cu, while the sample of S-ZH is characterized by severe pollution of Zn, Cd, Cu and Pb. The high content of heavy metals in the soils has posed a potential health risk to local residents through consumption of

the rice that cultivated in the polluted lands. Brus et al. [25] and Zhong et al. [15] have found the severe pollution of rice grain by Cd in the S-CA and S-ZH sampling sites, respectively. The highest Cd contents that measured in rice grain were above 10 times of Chinese (and FAO/WHO) standard (0.2 mg/kg). All the metals are found an increase of content with the decrease of particle size, which is similar to the results of other studies [1,7,9,11,13]. However, such a trend is slightly different between cadmium that is severe contaminated metals in both bulk soils and other metals. The highest content of cadmium is found in the fraction of <0.6 μm rather than in <0.2 μm fraction of the sample S-CA. Although the highest cadmium content occurred in <0.2 μm fraction of sample S-ZH, it showed a decrease rather than increase from the fraction of <1.0 μm to <0.6 nm.

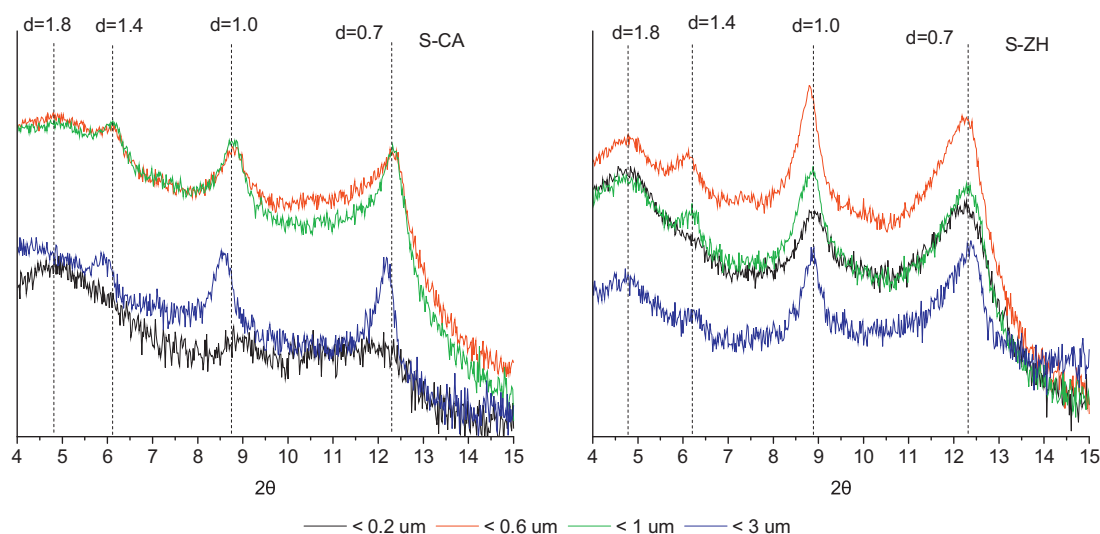


Fig. 3. The clay minerals of each size-fraction, which were identified by X-ray diffraction (XRD) (JEOL, JDX-3530) with Cu K α radiation after cation saturation by magnesium followed by glycerol. It can be applied to distinguish between vermiculite and smectite occurrence in the soil.

Table 1

Physicochemical properties of different size-fraction particles.

Sample No.	Particle size (μm)	pH (H ₂ O)	SOC (g/kg)	CaO (g/kg)	Fe ₂ O ₃ (g/kg)	MnO ₂ (g/kg)	DCB extractable (g/kg)		Acid oxalate extractable (g/kg)		Specific surface area (m ² /g)	
							Fe ₂ O ₃	MnO ₂	Fe ₂ O ₃	MnO ₂	SSA _e	SSA _t
S-CA	Bulk soil	7.6	42.0	132.8	30.4	0.77	12.8	0.54	4.9	0.30	12.4	161.6
	50–3	7.4	29.6	143.0	26.2	0.72	9.7	0.46	3.7	0.28	13.5	137.3
	<3	7.5	32.8	131.4	43.3	0.94	15.7	0.59	5.9	0.33	19.2	240.7
	<1	7.7	49.0	56.2	67.4	1.29	21.5	0.81	9.1	0.75	33.6	369.7
	<0.6	7.8	38.9	30.7	77.8	1.65	23.3	1.11	9.7	1.25	41.3	481.0
	<0.2	7.5	49.8	32.2	81.7	1.59	23.2	0.91	10.7	1.17	42.3	565.7
S-ZH	Bulk soil	7.5	21.8	10.8	27.6	0.52	5.7	0.26	3.8	0.31	6.5	93.3
	50–3	7.0	21.9	11.3	25.6	0.46	5.7	0.25	3.2	0.27	7.0	89.9
	<3	7.2	39.7	9.7	52.3	1.00	13.3	0.53	8.0	0.62	15.9	199.4
	<1	7.3	47.3	12.4	59.1	1.07	16.4	0.71	10.1	0.78	23.5	257.9
	<0.6	7.2	47.7	12.7	61.3	1.15	15.6	0.53	10.6	0.61	29.4	317.8
	<0.2	7.3	49.8	16.3	65.6	1.04	19.0	0.50	13.2	0.57	40.5	428.1

SOC: soil organic carbon; DCB: dithionite–citrate–bicarbonate; SSA_e indicates external surface area measured by BET–N₂ method, SSA_t indicates total surface area measured by ethylene glycol monoethyl ether (EGME) method.

3.3. Six-steps sequential extraction

Chemical speciation of the heavy metals in the bulk soils, clay and submicron clays is shown in Fig. 5. The proportion of exchangeable Cd in S-CA and S-ZH ranges from 1.05% to 1.52% and from 3.41% to 5.28%, respectively, while those of other metals that associated with exchangeable fraction are all lower than 1%. Cadmium

in both soils is predominated by dilute soluble fraction, accounting for about 50% of the total content. Zinc is another severe polluted metal for both soils. The proportion of dilute acid soluble speciation ranges from 41.2% to 65.7% for S-ZH, while it merely ranges from 11.2% to 33.0% for S-CA. For the polluted metals of Cr, Cu, Ni and Zn in S-CA soil, organically bound speciation accounts for a large proportion, from 10.3% to 50%. While for the polluted metals of Cd,

Table 2

Contents of heavy metals in the different size fraction particles (mg/kg).

Sample no.	Particle size (μm)	Cd	Cr	Cu	Ni	Pb	Zn
S-CA	Bulk soil	8.8 \pm 0.66	66.2 \pm 4.15	69.4 \pm 3.91	127 \pm 5.73	35.9 \pm 0.9	2048 \pm 67.9
	50–3	7.3 \pm 0.04	58.0 \pm 2.1	52.5 \pm 0.6	109.4 \pm 0.8	34.7 \pm 0.3	1800 \pm 10
	<3	10.1 \pm 0.07	69.3 \pm 1.2	93.2 \pm 0.5	187.6 \pm 4.3	54.4 \pm 0.3	2857 \pm 15
	<1	12.7 \pm 0.09	133.0 \pm 7.1	151.7 \pm 0.4	327.4 \pm 0.4	82.5 \pm 0.1	4708 \pm 10
	<0.6	13.8 \pm 0.09	146.2 \pm 2.0	165.2 \pm 0.4	394.4 \pm 1.1	86.4 \pm 3.9	5668 \pm 20
	<0.2	12.8 \pm 0.09	173.9 \pm 11.2	198.6 \pm 0.1	397.9 \pm 1.2	94.4 \pm 0.7	5694 \pm 61
S-ZH	Bulk soil	6.0 \pm 0.16	18.5 \pm 4.31	542 \pm 55.2	18.9 \pm 0.89	895 \pm 24.0	4043 \pm 39.8
	50–3	5.1 \pm 0.00	25.1 \pm 0.1	424 \pm 2	20.3 \pm 1.2	829 \pm 3	3767 \pm 4
	<3	11.6 \pm 0.07	37.0 \pm 0.6	886 \pm 6	48.4 \pm 0.1	1673 \pm 13	8348 \pm 136
	<1	13.3 \pm 0.10	43.5 \pm 0.5	1046 \pm 11	56.9 \pm 1.9	1871 \pm 21	9254 \pm 47
	<0.6	12.8 \pm 0.49	43.8 \pm 1.7	1073 \pm 53	60.6 \pm 3.0	2074 \pm 96	10,098 \pm 519
	<0.2	13.7 \pm 0.25	46.3 \pm 4.5	1118 \pm 30	64.3 \pm 2.3	2069 \pm 42	10,630 \pm 121

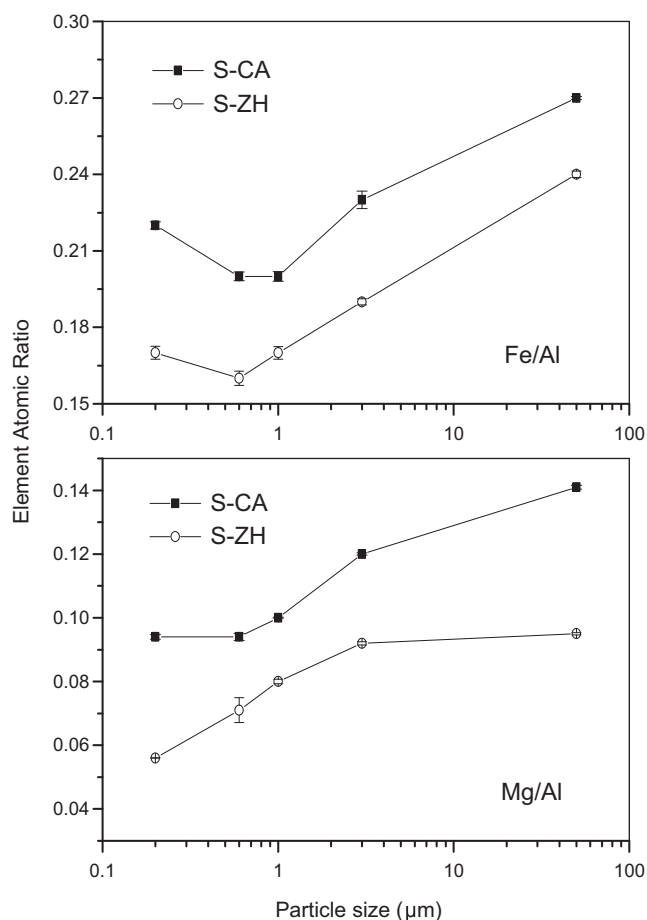


Fig. 4. The element molar ratio (Fe/Al, Mg/Al) changed with particle size, which was applied to indicate the relative enrichment of iron oxides and vermiculite to kaolinite or smectite.

Cu, Pb and Zn, manganese occluded speciation accounts for a large proportion, from 14.3% to 41.7%. For the unpolluted metals of Pb in S-CA soil and Cr, Ni in S-ZH, the residue speciation accounts for a large proportion, from 22.6% to 68.9%.

4. Discussions

4.1. Enrichment of heavy metals in the fine particles as affected by pollution sources

It has been known that anthropogenic heavy metals in soil are sequestered by soil constituents such as clay minerals, metal (hydr)oxides, and soil organic matter through the mechanisms of adsorption and precipitation [26]. Therefore, higher accumulation of heavy metals in the fine fraction was mainly attributed to the increase of the contents of soil organic carbon and oxide minerals as well as the specific surface areas with the particle size decrease. This could be observed from the results of Tables 1 and 2 for both samples and many other studies [7,8,11]. However, the change of heavy metal enrichment in the size-fraction was difficult to compare between the two samples due to a big difference of the heavy metal content in the bulk soils. Therefore, an enrichment factor (EF) was applied based on the method of Acosta et al. [11]. The EF was calculated by heavy metal content in each size-fraction divided by heavy metal content in bulk soil. A substantial difference of EF change with the particle size could be observed from Fig. 6 between the soil of S-CA and S-ZH that was contaminated by wastewater and smelter dust, respectively. For soil of S-CA, a sharp increase of

EF occurred from 3 μm to 0.6 μm, a gradual increase occurred from 50 μm to 3 μm and from 0.6 μm to 0.2 μm for most of metals. In contrast, a dramatic increase of EF occurred from 50 μm to 3 μm and a gradual increase occurred from 3 μm to 0.2 μm in soil of S-ZH. This implied that heavy metals sourced from the wastewater tended to be enriched in more fine soil particles compared with that sourced from the smelter dust. It could be explained that heavy metals from wastewater were usually in a soluble phase or contained in some colloids. These metal speciations tended to be absorbed by the fine particles with larger specific surface area in soil [3,27]. Meanwhile, long-term irrigation of wastewater led to an increase of organic matter and poorly crystalline Fe oxyhydroxides in soil, which increased the adsorption capacity for anthropogenic heavy metals [28,29]. By contrast, size of the smelter dust particles varied considerably from submicroscopic grains to particles with a diameter of several hundred micrometers [30]. Heavy metals in the dust were mainly contained in different kind of minerals and weathered slowly in soil [30,31]. Therefore, the enrichment of heavy metals in the fine soil particles was assumed to be comparatively lower in a similar environment with waste water polluted soil.

Change of the heavy metals enrichment was also in relation to metal speciation in soil. As for the sample of S-CA, a big EF difference occurred between Cd and other metals (Fig. 6). This difference was corresponding to the change of the percentage of organic bound fraction with particle size as shown in the Fig. 5A. The percentage of organically bound Cd in the S-CA sample decreased from the <3 μm to the <1 μm and smaller particles, while the organic bound fractions of other three metals were all shown an increase trend. Another explanation for the big difference between Cd and other metals in EF change with particle size is the change of calcite content. As shown in Fig. 5A, Cd in the S-CA soil tended to be predominated by dilute acid soluble speciation. The acid soluble fraction is a kind of weakly adsorbed fraction that mainly formed as an out-sphere complexes and could be desorbed under acid condition [32]. For S-CA sample, Cd that coprecipitate with carbonate might be involved in this fraction because of high content of calcite (Table 1). However, the calcite content decreases significantly with the decrease of particle size as shown in Table 1, which probably influenced the Cd enrichment in the very fine particles.

4.2. Changes of heavy metal speciation with particle size and associated factors

Heavy metal speciation was essentially a function of soil mineralogy and chemistry. Sequential extraction procedures have been extensively employed to determine the speciation of particulate trace metals in soils, sediments, and other natural particulate phases [32]. However, there are some criticisms regarding the extraction efficiency of speciation for artificial minerals, in which the relatively insoluble form of metals would not be extracted by a sequential extraction [33]. Therefore, chemical extraction methods are usually recommended to be combined with physical instrumental methods (XRD or X-ray adsorption spectroscopies, etc.) to identify the metal species. In this study, a high proportion of extractable forms of anthropogenic metals are presented in the bulk soils and size-fractions, hence the shortcoming of the extraction that mentioned above could be ignored. Difference of the dominant speciation of the polluted heavy metals between the two soils implied effect of the pollution sources. A large proportion of organically bound speciation of the polluted heavy metals in the S-CA soil was mainly related to the organic matter of the wastewater, while a large proportion of manganese oxides occlude speciation of the polluted metals in the S-ZH soil implied that metals sourced from the smelter dust were largely associated with manganese oxide [34].

The different pollution sources further affected enrichment of the anthropogenic heavy metals in the fine particles through influence of the metal speciation. A dramatic increase of organically bounded speciation of Cu, Ni, Cr and Zn from the particle of $<3\ \mu\text{m}$ to $<1\ \mu\text{m}$ in S-CA sample was corresponding well with a sharp increase of EF from the particle of $<3\ \mu\text{m}$ to $<1\ \mu\text{m}$. A decrease of manganese oxides occluded speciation of Cd, Cu, Pb and Zn with particle size decrease was related with flatly change of EF among the different small colloids (Figs. 4 and 5).

Occurrence of exchangeable and high percentage of dilute acid soluble Cd in both soils indicated a high availability of anthropogenic Cd in the soils. This was agreement with the finding that high Cd content was in the rice grain that cultivated in the polluted

land [15,25]. Meanwhile, percentage of the diluted acid soluble Cd increased with particle size decrease, which implied the relative enrichment of bioavailable Cd in the fine particle and potential environmental risk to groundwater by downward migration of colloid [2]. The element of Zn usually has a similar geochemical characteristic to Cd in soil, however, Zn speciation is much different to Cd speciation in S-CA soil (Fig. 5A). Iron and manganese oxides occluded Zn speciation rather than dilute acid soluble speciation account for a large proportion in addition to the organically bound Zn speciation in the bulk soil of S-CA. A dramatic increase of dilute acid soluble Zn speciation proportion occurred from $<3\ \mu\text{m}$ to $<1\ \mu\text{m}$, which was in accordance with the decrease of iron oxides occluded speciation proportion and a sharp increase of the specific

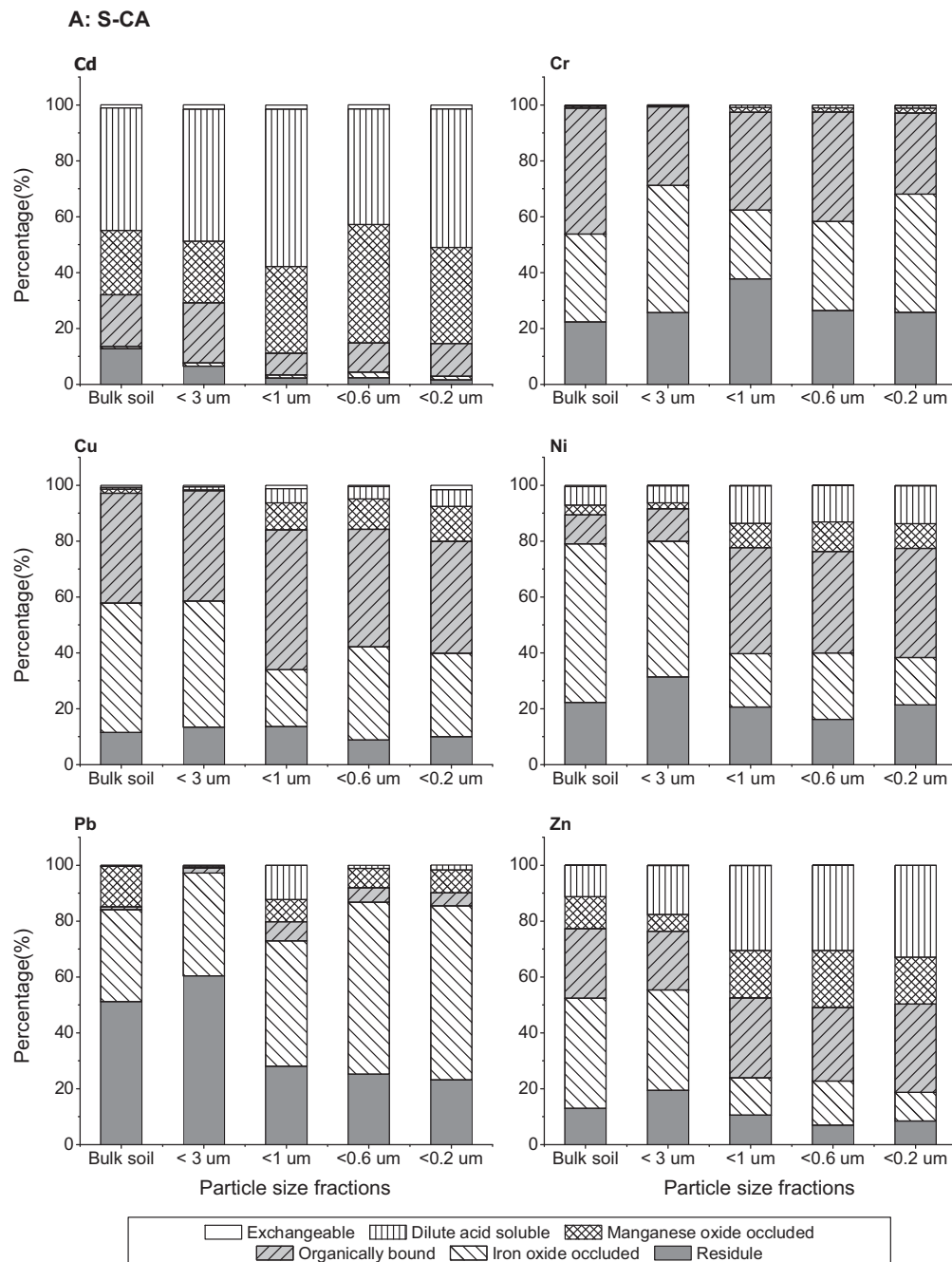


Fig. 5. The chemical speciation of heavy metals in bulk soils and each size-fraction, result of the different speciation was obtained with a six-step sequential extraction as introduced in the paper of Makino et al. [20].

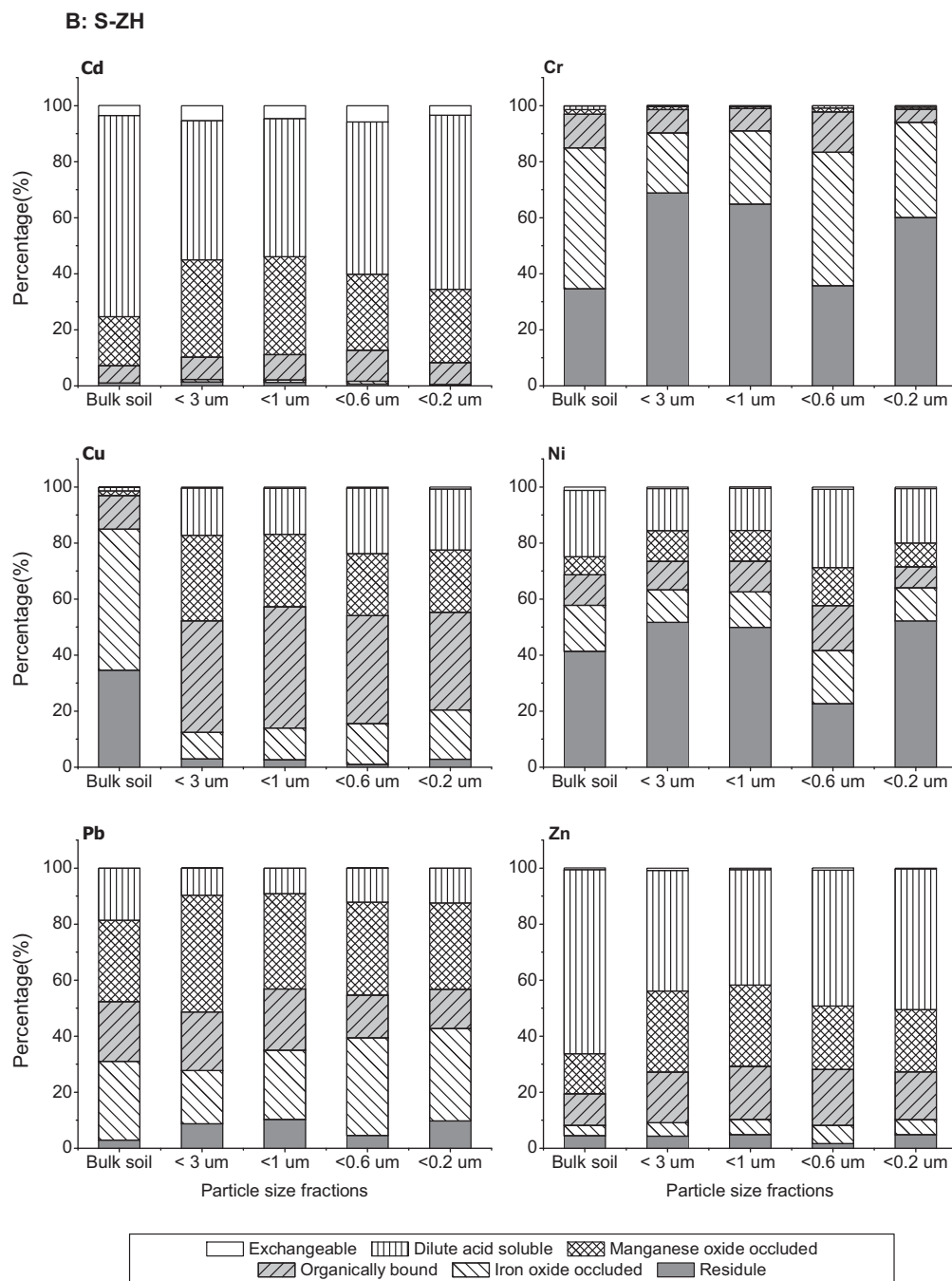


Fig. 5. (Continued)

surface area (Table 1). Other polluted heavy metals like Cr, Cu and Ni were all shown a similar speciation change with particle size. A possible explanation was that the wastewater that contained high content of these metals and reducible agents (surfactants and other organic matters) dissolved the iron oxides into amorphous state in the surface of small particles by reduction and resulted in an increase of specific surface area and sorption sites for the metals [35].

Pb speciation was shown a big difference to other polluted heavy metals (Cd, Cu and Zn) in the soil of S-ZH (Fig. 5A). Speciation that associated with the iron oxide rather than dilute acid soluble form accounts a large proportion in addition to the manganese oxide occluded speciation. Meanwhile, the proportion of iron oxide

occluded Pb speciation increases with the decrease of particle size in the S-ZH soil. Pb was more liable than other metals to be immobilization by iron and manganese oxides in neutral and alkaline soil and it was strong adsorbed by formation of inner-sphere adsorption [36]. This might explain the low proportion of dilute acid soluble fraction of Pb in the soil. The high proportion of reducible Pb that is associated with iron and manganese oxides (from 57.1% to 68.0%) especially in the small colloid might be a potential risk to human health through ingestion or inhalation of the polluted soil [9]. Karadas et al. [37] have reported that the Pb bound to iron and manganese oxides was able to be extracted easily by gastric and intestinal digestion solutions, which means the high bioaccessibility of the reducible speciation of Pb.

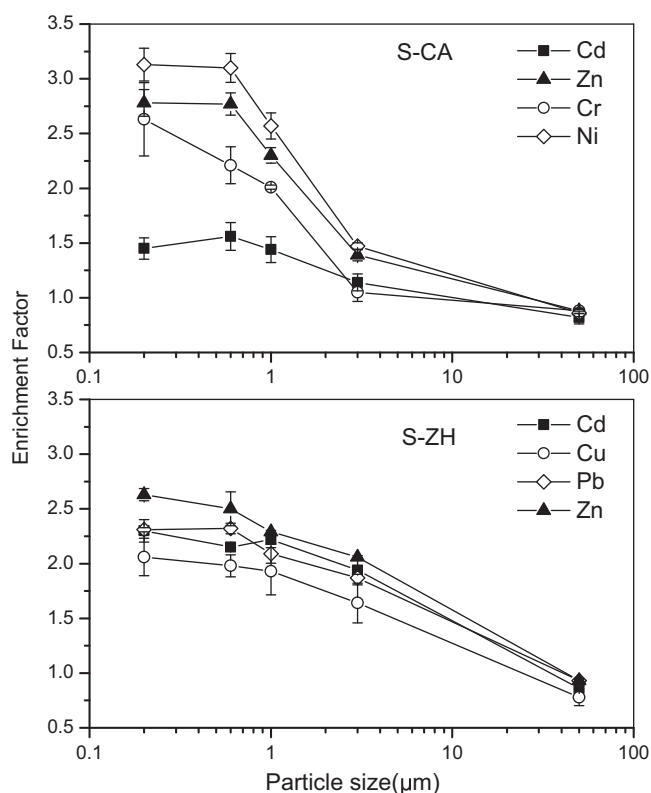


Fig. 6. An enrichment factor (EF) that was calculated by heavy metal content in each size-fraction divided by heavy metal content in bulk soil was used to indicate the degree of metal accumulation in each size-fraction. The difference of heavy metal content between the two samples could be leveled by the enrichment factor.

5. Conclusions

The soil particle properties and enrichment of heavy metals in the size-fraction for the polluted soils were well characterized based on continuous flow ultra-centrifugation method. Heavy metals sourced from electroplating wastewater were more liable to enrich in the submicron particle fractions ($<1\ \mu\text{m}$ or less) than the metals from the smelter emission. The large amount of organic matter in the wastewater was assumed to mainly contribute to the accumulation of the severely polluted metals in the submicron particles of the wastewater polluted soil. In contrast, the manganese oxide occluded fraction accounted for a substantial proportion for the severely polluted metals in the fine particles ($<3\ \mu\text{m}$) of the smelter dust polluted soil. Changes of cadmium speciation and its enrichment in the fine particles were mainly associated with calcite content in the electroplating wastewater polluted soil. While the enrichment of other polluted metals (Cr, Cu, Ni and Zn) in the fine particles is mainly related to the dissolution of iron oxides by the organic substances in the wastewater. Lead speciation that is bound to Fe oxides rather than dilute acid soluble form accounts for a substantial proportion in the smelter dust polluted soil and percentage of the Fe oxide occluded Pb speciation increased with particle size decrease. This is different to other severe polluted metals (Cd, Cu and Zn), which are dominated by the speciation of dilute acid soluble or organically bound in addition to Mn oxides occluded.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.01.019>.

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