

Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine

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Abstract: Heavy metal contamination of soils through anthropogenic activities is a widespread and serious problem confronting scientists and regulators throughout the world. In this study we investigated the distribution, chemical species and availability of lead, zinc, cadmium and copper in nine surface (0 to 20 cm) soils from near an abandoned lead/zinc mine tailings located in Shaoxing, Zhejiang, China. Total heavy metal contents ranged from 5271 to 16369 mg/kg for Pb, 387 to 1221 mg/kg for Zn, 3.0 to 9.3 mg/kg for Cd and 65 to 206 mg/kg for Cu. In general, all heavy metals exceeded China National Standards for Soil Environmental Quality of Heavy Metals by a factor of 3–65 times. Comparison of the heavy metal concentrations (Pb, Zn, Cd and Cu) with clay content revealed a strongly significant relationship while significant relationship ($P < 0.001$) was also obtained between Cd + Zn and Pb + Cu. Solid phase speciation of the soils using Tessier procedure showed that the heavy metals were distributed in the order: residual \gg organically complexed-Fe-Mn oxides occluded $>$ carbonate bound $>$ exchangeable $>$ water soluble. In the organic matter fraction, the ratio of Pb (29.1%) to its total concentration in the soils was higher than those of Zn (4.70%), Cd (3.16%) and Cu (9.50%). The percentages of the water soluble and the exchangeable fractions of Pb (1.80%) and Cd (2.74%) were markedly greater than those of Zn (0.10%) and Cu (0.15%), suggesting that Pb and Cd are relatively more mobile and hence more toxic in the contaminated soils. Strongly significant relationships between H₂O-Pb, H₂O-Zn and H₂O-Cu, strong positive correlations between H₂O-Pb, H₂O-Zn, H₂O-Cu and organic matter in soil were found. The content of H₂O-Pb, H₂O-Zn, H₂O-Cu was negatively correlated with pH values. The similar negative relationships between pH values and exchangeable heavy metals were also recorded. It is suggested that increasing soil pH or liming the soil could decrease bioavailability of heavy metals in the soil.

Keywords: fractionation; heavy metal; mining tailings; risk assessment; soil pollution

Introduction

Heavy metals make a significant contribution to environmental pollution as a result of human activities such as mining, smelting, electroplating, energy and fuel production, power transformation, intensive agriculture, sludge dumping, and military operations. Mining and milling activities, including grinding, concentrating ores and disposal of tailings, along with mine and mill wastewater, can cause heavy metal contamination in the soil environment (Jung, 2001; Kemper, 2002; MacKenzie, 2002; Pagnanelli, 2004; Vega, 2004; Yuksel, 2001). The large heavy metal content of tailings poses threat to nearby agricultural and stream water quality. Indeed, elevated levels of heavy metals have been reported in and around disused metalliferous mines due to discharge and dispersion of mine wastes into nearby agricultural soils, food crops and stream systems (Braun, 2002; David, 2003; Elberling, 2002; Hao, 2003; 2004; Hillier, 2001; Liu, 2003; Sastre, 2004; Xenidis, 2003). Eventually, heavy metals may pose a potential health risk to residents in the vicinity of mining areas.

Many studies have been conducted on heavy metal contamination in soils, plants, waters and sediments from metalliferous mines throughout the world (Akcaay, 2003; Burt, 2003; Giraldez, 2003; Jain, 2004; Kemper, 2002; Lacal, 2003; Liu, 2003; Navas, 2003; Ngiam, 2001; Pagnanelli, 2004; Sastre, 2004; Vega, 2004; Yu, 2004). In China, Pb/Zn mines were distributed over almost all of the country, especially in Southern China and were actively operated since the ancient time. However, some mines were closed, as a result mine waste materials, including tailings, were left without full environmental treatment. Thus, soils,

plants, waters and sediments in the vicinity of the mines have been contaminated by potentially heavy metals from tailings by weathering through wind and water.

Heavy metals may be retained in the soil as exchangeable metals, carbonates, hydroxides, Fe/Mn oxides, or may be bound to organic matter. It is important to know how the heavy metals are held in the contaminated soil before designing a remediation process. In the absence of extended X-ray absorption fine structure (EXAFS), sequential extraction is the most suitable method to investigate solid phase speciation of heavy metals and to evaluate the relative binding strength and hence the solubility, mobility, and toxicity of heavy metals in contaminated soils (Tessier, 1979; Ma, 1997). The retention of heavy metals in any fraction of soil such as exchangeable carbonates, hydroxides, Fe/Mn oxides or organic matter depended on soil solution pH, soil constituents, and the type of heavy metals (Yong, 1993). The metals in water soluble and exchangeable fractions would be readily bioavailable to the environment, whereas the metals in the residual fraction would not be expected to be released under natural conditions.

The procedure of Tessier *et al.* (Tessier, 1979) is one of the most thoroughly researched and widely used procedures to evaluate the efficacy of remediation of contamination sites (Ma, 1997; Yu, 2004). Recently, great attentions have been paid to the studies on fractionation of heavy metals in soils in the literature (Akcaay, 2003; Galan, 2003; Giraldez, 2003; Gismera, 2004; Kaasalainen, 2003; Lacal, 2003; Margu, 2004; McLaren, 2001; Pagnanelli, 2004; Qiao, 2003; Yong, 1993; Zhang, 2004). The objective of the present study was to investigate the solid phase speciation of

heavy metals in nine soil samples around a lead/zinc mine located in Shaoxing, Zhejiang Province, China and based on this information to evaluate the relationship between total metal concentrations on metal partition in relation to soil properties and to assess the environmental risk of heavy metals using China Environmental Quality Standard for Soils (GB15612-1995).

1 Materials and methods

1.1 Soil

The soil (Typentiaqualf) samples (0–20 cm depth) for the present study were collected from near the Pb/Zn mine dump heaps and tailings on the hill slope with varying distances from the center of mine tailings. The soil samples were air-dried and crushed to pass through a 1-mm plastic sieve and stored in plastic containers for routine laboratory studies. The clay mineralogy of the soil was predominantly illitic in nature with kaolin being present in subordinate amounts. The selected properties of the soil are listed in Table 1.

Table 1 Basic properties of the used contaminated soil samples

Soil No.	pH	OM, g/kg	Clay, g/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg	Cu, mg/kg
1	5.72	28.9	330	15956 ± 106 ^{a)}	948 ± 4	8.2 ± 0.3	183 ± 1
2	5.20	48.7	300	14170 ± 193	1221 ± 3	9.1 ± 0.1	168 ± 1
3	5.76	30.9	180	8575 ± 28	628 ± 1	4.3 ± 0.0	95.8 ± 0.1
4	5.72	20.1	280	13858 ± 174	1048 ± 2	8.4 ± 0.1	171 ± 3
5	5.60	35.7	350	16227 ± 208	1065 ± 0	9.3 ± 0.1	205 ± 1
6	5.70	17.7	250	12764 ± 102	966 ± 1	7.7 ± 0.1	151 ± 1
7	5.54	27.6	200	9748 ± 127	703 ± 8	5.4 ± 0.1	115 ± 1
8	5.55	16.1	150	5271 ± 63	387 ± 0	3.0 ± 0.0	65 ± 0.1
9	5.27	42.0	360	16397 ± 261	589 ± 6	4.3 ± 0.1	206 ± 3
Average	5.56	29.7	267	12552	839	6.6	151

Note: ^{a)} Mean concentration ± standard error

1.2 Partitioning method

The selected procedure of Tessier *et al.* (Tessier, 1979) was designed to separate total (T-) heavy metals in soils into six operationally defined fractions: water soluble (H₂O-), exchangeable (Exch-), carbonate bound (Carb-), Fe-Mn oxides bound (Fe/Mn-), organic bound (OM-), and residual fractions (Res-). A summary of the procedure is described as follows:

1.00 g of each soil sample was weighed into a 40 ml polycarbonate centrifuge tube and the following fractions obtained:

Water soluble (H₂O-): Soil sample extracted with 15 ml of deionized water for 2 h.

Exchangeable (Exch-): The residue from water soluble fraction was extracted with 8 ml of 1 mol/L MgCl₂ (pH = 7.0) for 1 h.

Carbonate-bound (Carb-): The residue from exchangeable fraction was extracted with 8 ml of 1 mol/L NaOAc (adjusted to pH 5.0 with HOAc) for 5 h.

Fe-Mn oxide-bound (Fe/Mn-): The residue from carbonate fraction was extracted with 0.04 mol/L NH₂OH · HCl in 25% (v/v) HOAc at 96°C with occasional agitation for 6 h.

Organic-bound (OM-): The residue from Fe-Mn oxide fraction was extracted with 3 ml of 0.02 mol/L HNO₃ and 5

ml of 30% H₂O₂ (adjusted to pH 2 with HNO₃). The mixture was heated to 85°C for 2 h, with occasional agitation. A second 3 ml aliquot of 30% H₂O₂ (pH 2 with HNO₃) was added and the mixture was heated again to 85°C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 mol/L NH₄OAc in 20% (v/v) HNO₃ was added and the samples diluted to 20 ml and agitated continuously for 30 min.

Residual (Res-): The residues from organic fraction were digested using a 3:1 of HCl:HNO₃ dissolution procedure in a microwave digester (Milestone, Microwave Laboratory Systems, Australia).

After each successive extraction, separation was done by centrifuging (Beckman Model J2-21) at 15000 r/min for 30 min. The supernatants were removed with a pipette filtered with 0.2 μm Nucleopore polycarbonate membrane filters, and analyzed for metals. The residue was washed with 8 ml of deionized water followed by vigorous hand shaking, and then followed by 30 min of centrifugation before the next extraction.

1.3 Analytical methods

All extractions of treated samples were conducted in triplicate in acid-washed (5% HNO₃) polycarbonate labware and filtered through a 0.2 μm membrane (Schleicher and Schuell, Germany). All chemicals used in this study were of analytical grade or better. Double deionized water was used. All the elements in the supernatants were measured by ICP-AES (SPECTRO Analytical Instruments, Germany) or by GFAAS (SpectraAA400, Varian) when elemental concentration was lower than ICP detection limit, in CSIRO Land & Water, Adelaide, Australia. Blanks were used for background correction and other sources of error. At least one duplicate and one spike sample were run every 20 samples and the spike recovery was found to be within 100 ± 5%. Solution pH was determined by Orion Mode EA 940 pH meter. Other items of soil properties were measured by conventional methods.

2 Results and discussion

2.1 Total contents of heavy metals

Total concentrations of heavy metals (Pb, Zn, Cd, Cu) in the soil samples varied widely (Table 1), organic matter contents ranged from 16.1 to 48.7 g/kg with a mean value of 29.7 g/kg, pH varied from 5.20 to 5.76 (mean value 5.56), and clay contents (0.02–0.002 mm) ranged from 150 to 360 g/kg (mean value of 267 g/kg).

The soil was contaminated by continuous weathering of tailings from an abandoned Pb/Zn mine for more than 150 years, and thus was severely polluted by lead (5271–16369, averaging 12552 mg/kg) followed by Zn (387–1221, averaging 839 mg/kg). The concentrations of Cd (3.0–9.3 with 6.63 mg/kg on average) and Cu (65–206 with 151 mg/kg on average) were much higher than allowable limits of environmental safety (GB15612-1995, Table 2). The mean concentrations of Pb, Zn, Cd and Cu in the earth's crust are 16, 132, 0.15 and 70 mg/kg (Zhang, 2004).

The hill slope location of the mine site has led to significantly different spatial distribution of heavy metals in the surface soil. Topographic condition influenced redistribution and accumulation of water and products of mineral weathering, leading to different accumulation of

organic matter and clay contents and hence different contents of heavy metals in the same type of soil at the same location. Data from the study were statistically analysed using SPSS program and correlation coefficients illustrating relationship among total content of heavy metals, pH, organic matter and clay are listed in Table 3. Regression coefficients presented in Table 3 show strongly significant relationships between clay contents and Pb ($r = 0.979$, $P < 0.01$), Cu ($r = 0.986$, $P < 0.01$) and clay contents. Strong positive correlation ($P < 0.01$) was also recorded between Cd and Zn, and between Pb and Cu.

Table 2 China national standards (grade 2) for soil environmental quality of heavy metals (GB15612-1995) Unit: mg/kg

Soil pH	As	Hg	Cd	Pb	Cr	Cu	Ni	Zn
< 6.5	40	0.3	0.3	250	150	50	40	200
6.5–7.0	30	0.5	0.3	300	200	100	50	250
> 7.5	25	1	0.6	350	250	100	60	300

Table 3 Correlation coefficients among total content of heavy metals, pH value, organic matter content and clay content in soil

Items	Pb	Zn	Cd	Cu	pH	OM	Clay
Pb	1.000						
Zn	0.666	1.000					
Cd	0.699	0.978**	1.000				
Cu	0.992**	0.631	0.669	1.000			
pH	-0.228	-0.05	0.045	-0.265	1.000		
OM	0.531	0.335	0.248	0.525	-0.733*	1.000	
Clay	0.979**	0.573	0.617	0.986**	-0.329	0.581	1.000

Notes: **Significant different ($P < 0.01$); * $P < 0.05$

2.2 Assessment of soil contamination

Different mine wastes have different constraints for different vegetation. Because this Pb/Zn mine has a long history, through weathering, the heavy metals especially Pb and Cd in the soil exceeded the highest limits of China Environmental Quality Standard for Soils (GB15612-1995, Table 2). The Pb and Cd exceeded permitted standards by 50 and 22 times, respectively. This high total concentrations of Pb and Cd together with the high soluble and exchangeable fraction suggest that these soils are not suitable for agricultural uses.

The suitability of soils for agricultural uses could be further assessed by using pollution index which assesses the environmental risk caused by the contaminated soils. The pollution index can be estimated by using the following formula (Li, 2003):

$$Pi = \frac{Ci}{Si}$$

where Pi is an environmental quality index for heavy metal i ; Ci is the heavy metal content in a soil sample (mg/kg); Si is the permitted standard of the same metal (mg/kg; Table 2). Where $Pi > 1$, the soil sample is classed to be polluted, while $Pi \leq 1$ suggests unpolluted soil.

The environmental quality index (Pi) assessed using single index method are presented in Table 4. The calculated Pi values for all heavy metals under study exceed 1 confirming that the soils are highly polluted. Therefore, it is recommended that farmers should not grow agricultural foods such as edible vegetables, rice, and potato in these soils unless remediated.

Table 4 Environmental quality index (Pi) of heavy metals using single index method

Soil No.	T-Pb	T-Zn	T-Cd	T-Cu
1	63.8	4.7	27.3	3.7
2	56.7	6.1	30.3	3.4
3	34.3	3.1	14.3	1.9
4	55.4	5.2	28.0	3.4
5	64.9	5.3	31.0	4.1
6	51.1	4.8	25.7	3.0
7	39.0	3.5	18.0	2.3
8	21.1	1.9	10.0	1.3
9	65.6	2.9	14.3	4.1

2.3 Contents of different forms of heavy metals

Heavy metals in six operationally defined fractions: water soluble (H_2O -), exchangeable (Exch-), carbonate bound (Carb-), Fe-Mn oxides bound (Fe/Mn-), organic bound (OM-), and residual fractions (Res-) were measured by the procedure of Tessier *et al.* (Tessier, 1979) and the percentages of heavy metals for these 6 fractions are shown in Fig. 1 and Fig. 2. Heavy metals in water soluble and exchangeable fractions are considered more mobile and biotoxic than those in other 4 fractions, especially in the residual fraction (Gismera, 2004; Kaasalainen, 2003; Lal, 2003; Margu, 2004; Yu, 2004; Zhang, 2004). When compared to its total content (Table 1), the percentages of the six fractions for each heavy metal varied greatly in the nine soil samples (Table 5).

Table 5 Concentration (mg/kg) ranges of 6 fractions of heavy metals and their percentages (%) of total concentration in the nine soil samples

Heavy metal	Fraction	Average concentration (range)	Average % of total concentration (% range)
Pb	H_2O -	2.17 (0.05–8.48)	0.02 (0.01–0.06)
	Exch-	223 (37–420)	1.78 (0.70–2.57)
	Carb-	533 (241–860)	4.25 (3.36–6.20)
	Fe/Mn	1893 (701–2433)	15.1 (12.8–18.9)
	OM-	3658 (731–4660)	29.1 (13.9–37.7)
	Res-	6343 (2973–8819)	49.7 (34.7–67.7)
Zn	H_2O -	0.30 (0.01–1.36)	0.03 (0.01–0.11)
	Exch-	0.53 (0.01–2.09)	0.07 (0.01–0.34)
	Carb-	6.3 (2.7–13)	0.79 (0.40–1.70)
	Fe/Mn	86 (19–123)	9.94 (4.96–11.74)
	OM-	42 (8.7–93)	4.70 (2.25–7.62)
	Res-	705 (356–992)	84.5 (80.6–92.1)
Cd	H_2O -	0.01 (0.00–0.02)	0.18 (0.11–0.33)
	Exch-	0.15 (0.08–0.26)	2.56 (1.40–4.82)
	Carb-	0.15 (0.08–0.27)	2.60 (1.16–4.42)
	Fe/Mn	0.54 (0.21–1.18)	7.93 (4.87–11.0)
	OM-	0.21 (0.08–0.38)	3.16 (2.33–4.65)
	Res-	5.58 (2.35–7.61)	83.8 (78.3–88.6)
Cu	H_2O -	0.08 (0.02–0.32)	0.04 (0.02–0.16)
	Exch-	0.18 (0.06–0.47)	0.11 (0.04–0.23)
	Carb-	0.51 (0.21–2.09)	0.34 (0.15–1.02)
	Fe/Mn	10.4 (4.96–22)	6.72 (3.17–10.7)
	OM-	15.3 (2.85–37.9)	9.50 (4.39–18.4)
	Res-	125 (56.7–176)	83.2 (69.5–87.2)

Table 5 shows that Pb in these soils was primarily associated with the residual fraction (34.7%–67.7%, average 49.7%). On average 44.2% of the Pb in these soils was associated with the Fe-Mn oxides and organic matter, while only 1.80% existed in the water soluble and the

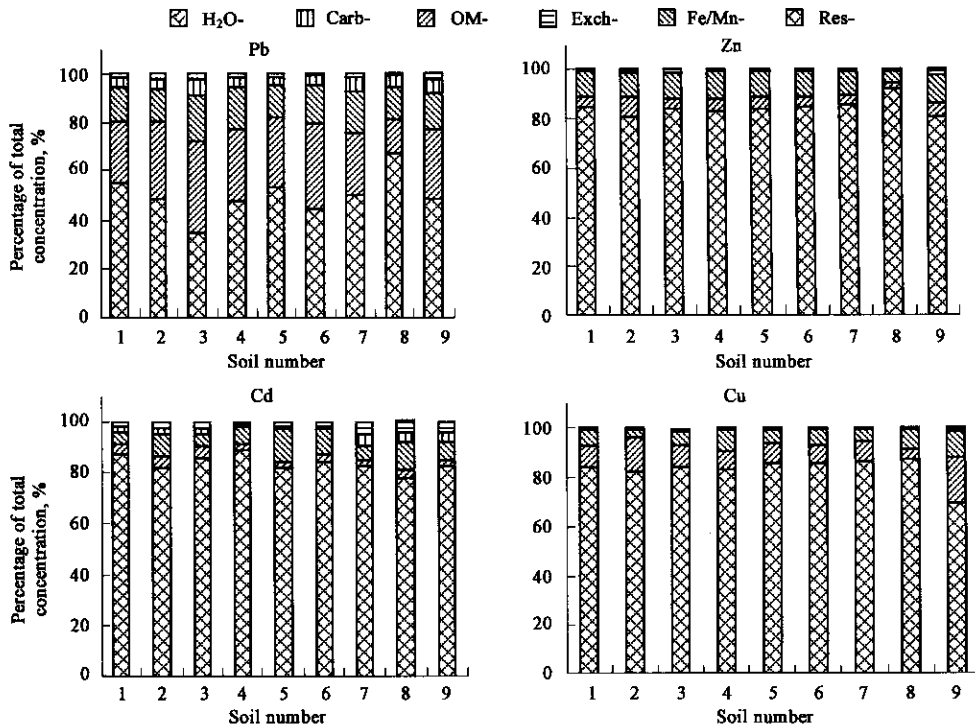


Fig.1 Percentages of 6 different forms of each metal in the nine soil samples

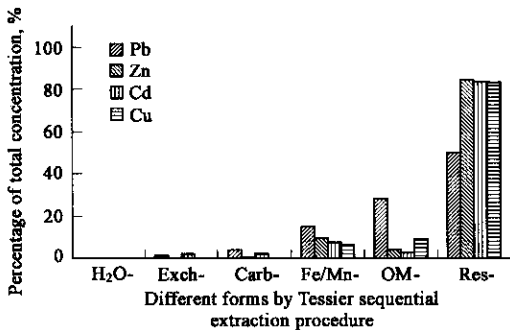


Fig.2 Percentages of 6 different forms of heavy metals in the soils ($n = 9$)

exchangeable fractions. Compared to Pb (49.7%), the average residual fraction of Zn(84.5%), Cd(83.8%) and Cu(83.2%) was much higher, indicating that Pb in these soils was more bioavailable than other 3 metals. The percentages of the water soluble and the exchangeable fractions of Pb(1.80%) and Cd(2.74%) were markedly greater than those of Zn(0.10%) and Cu(0.15%), suggesting that the former 2 metals were more mobile and toxic to biota. As regards to the organic matter fraction, the ratio of Pb(29.1%) to its total concentration in the soils was much greater than that of Zn(4.70%), Cd(3.16%) and Cu(9.50%). The high mean percentages of Zn, Cd and Cu as a residual fraction suggest that they tend to be fixed in solid components such as silicates. Strong adsorption of heavy metals by clay minerals may have also influenced these results (Tiller, 1984). Therefore, Pb had a relatively high mobility and toxicity compared to Zn, Cd and Cu in the present studied soils.

Data from this experiment were statistically analysed using SPSS program and correlation coefficients illustrating relationship among water soluble and exchangeable contents of heavy metals, pH, organic matter and clay are (Table 6 and

7). Regression coefficients presented in Table 6 show strongly significant relationships between H₂O-Pb, H₂O-Zn and H₂O-Cu. Strong positive correlations was also found between H₂O-Pb, H₂O-Zn, H₂O-Cu and organic matter in soil. The content of H₂O-Pb, H₂O-Zn, H₂O-Cu was negatively correlated with pH values at statistically significant levels. The similar relationships between pH values and exchangeable heavy metals are also recorded in Table 7. It is suggested that increasing soil pH or liming the soil could decrease bioavailability of heavy metals in the soil.

Table 6 Correlation coefficients among water soluble content of heavy metals, pH value, organic matter content and clay content in soil

Items	H ₂ O-Pb	H ₂ O-Zn	H ₂ O-Cd	H ₂ O-Cu	pH	OM	Clay
H ₂ O-Pb	1.000						
H ₂ O-Zn	0.913**	1.000					
H ₂ O-Cd	-0.303	-0.214	1.000				
H ₂ O-Cu	0.836**	0.754*	-0.001	1.000			
pH	-0.877**	-0.789*	-0.08	-0.825**	1.000		
OM	0.849**	0.897**	-0.283	0.744*	-0.733*	1.000	
Clay	0.546	0.323	-0.636	0.545	-0.329	0.581	1.000

Table 7 Correlation coefficients among exchangeable content of heavy metals, pH value, organic matter content and clay content in soil

Items	Exch-Pb	Exch-Zn	Exch-Cd	Exch-Cu	pH	OM	Clay
Exch-Pb	1.000						
Exch-Zn	0.583	1.000					
Exch-Cd	0.115	0.367	1.000				
Exch-Cu	0.472	0.911**	0.486	1.000			
pH	-0.408	-0.859**	-0.435	-0.975**	1.000		
OM	0.783*	0.704*	0.085	0.744*	-0.733**	1.000	
Clay	0.318	0.492	-0.447	0.307	-0.329	0.581	1.000

3 Conclusions

The 9 soil samples collected from near the abandoned

tailings from a Pb/Zn mine were heavily contaminated by Pb, Zn, Cd, and Cu. Spatial distribution of heavy metals were found to be influenced by topographic condition. According to statistical analysis, it is obvious that concentrations of Pb, Zn, Cd and Cu were positively correlated with clay contents in the soil, that content of Cd was positively correlated with Zn content and content of Pb was positively correlated with Cu content, respectively. The heavy metal environmental quality index (P_i) estimated using single index method of Li *et al.* (Li, 2003) together with the China National Standards For Soil Environmental Quality of Heavy Metals suggest severe contamination of the area. The high total metal concentration together with the high water soluble fraction suggests that these soils are not suitable for agricultural crop production.

Sequential extraction using the procedure of Tessier *et al.* (Tessier, 1979) demonstrated that Pb in these soils was significantly associated with the residual fraction (49.7%). Up to average 44.2% of the Pb in these soils was associated with the Fe-Mn oxide and organic matter fractions and only 1.80% was associated with the water-soluble and the exchangeable fractions. Compared to Pb, the average residual fraction of Zn (84.5%), Cd (83.8%) and Cu (83.2%) was much higher, indicating that Pb in these soils was more bioavailable. The percentages of the water-soluble and the exchangeable fractions of Pb (1.80%) and Cd (2.74%) were markedly greater than those of Zn (0.10%) and Cu (0.15%). In the organic matter fraction, the ratio of Pb (29.1%) to its total concentration in the soils was extremely higher than those of Zn (4.70%), Cd (3.16%) and Cu (9.50%). The high mean percentages (83.2%–95.4%) of Zn, Cd and Cu as a residual fraction suggest that they tend to be fixed and hence relatively less toxic than Pb (49.7%). Strongly significant relationships among H_2O -Pb, H_2O -Zn and H_2O -Cu, are strong positive correlations among H_2O -Pb, H_2O -Zn, H_2O -Cu and organic matter in soil were found. The contents of H_2O -Pb, H_2O -Zn, H_2O -Cu negatively correlated with pH values. The similar relationships between pH values and exchangeable heavy metals were also recorded. It is suggested that increasing soil pH or liming the soil could decrease bioavailability of heavy metals in the soil.

Acknowledgements: The authors would like to thank senior technical officer Ms. Julie Smith in CSIRO in Adelaide for her ICP run.

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(Received for review February 22, 2005. Accepted April 7, 2005)