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Heavy Metal Contamination of Agricultural Soils and Stream Sediments Near a Copper Mine in Tongling, People's Republic of China

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Metal contamination in mining areas may originate from different sources, such as mining activities together with grinding, concentrating ores and tailings disposal (Adriano 1986). The mechanisms for dispersal of these metals into receiving systems have been the subject of numerous studies. Besides contamination from the weathering and leaching processes of tailings, untreated mine drainage can contribute large amounts of heavy metals to nearby streams. Heavy metals released into aquatic systems are generally bound to particulate matter, which eventually settle and become incorporated into sediments. However, the sediment-bound heavy metals may be remobilized and released back to the water column with a change in environmental conditions such as pH, redox potential or the presence of organic chelators (Förstner 1989), in turn affect the soils through irrigation water. Therefore, accumulation of heavy metals may be found in sediments, soils and plants in and around metalliferous mining sites.

Heavy metals in soils may exist in various chemical forms with different solubilities and bioavailabilities. Thus, it is necessary to identify and quantify the chemical forms of metals in order to gain a better understanding of the potential impacts of elevated heavy metals to the surrounding environment. Several fractionation procedures have been employed to investigate the possible chemical speciation of heavy metals (Tessier et al. 1979; Howard and Vandenbrink 1999; Shiowatana et al. 2001). Based on the sequential extraction procedure, metals can be classified into five operationally defined geochemical forms: (1) exchangeable; (2) bound to carbonate /specifically adsorbed phase; (3) bound to iron-manganese oxides; (4) bound to organic matter/sulphide; and (5) residual phase. Generally, the mobility and bioavailability of metals decrease in the order: exchangeable > carbonate /specifically adsorped > Fe-Mn oxide > organic/sulphide > residual metal phase (Tessier et al. 1979; Ma and Rao 1997).

The Tongling region of Anhui Province contains many different mineral resources in eastern China. Metal mining has been an important economic base in this area from ancient time. The major copper mining operations have been concentrated in a narrow star-shaped basin called Fenghuang Mountain. Past and present mining activities in this area have produced widespread metal contamination. However, there is very little data so far on heavy metal distribution and chemical forms in the

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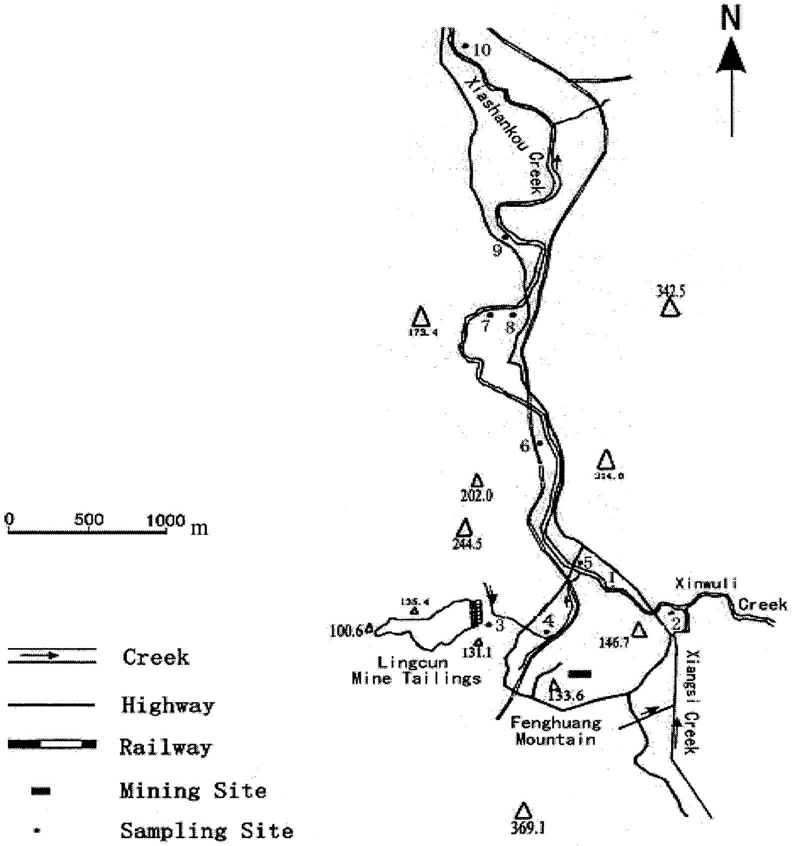

Figure 1. Sampling location map of the Fenghuang Mountain Cu mine area.

soils and stream sediments of the mining area. The present project aims to study the spatial distribution of heavy metals and their chemical partitioning in the soils and sediments in the Tongling mining area.

MATERIALS AND METHODS

The study area is situated near the Fenghuang Mountain copper mine, Tongling, which is one of the largest Cu mines in Anhui Province. Ten composite soil samples were collected with a spade from the 0 to 15 cm surface-ploughed layer in agricultural fields located along the Xiashankou creek (Fig. 1), which flows from south to north. At the same time, sediment samples of the Xiashankou creek were also collected close to the corresponding soil sampling locations. The sampling programs were carried out in the summer of 2000. Soils and sediments were air-dried at room temperature for 7 days. Soils and sediments were analyzed for 'total' Cu, Pb and Zn concentrations by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer *3300 DV*) following a strong acid digestion with a mixture of concentrated $HNO_3/HClO_4$ (Li et al. 1995). The sequential extraction procedure of Tessier et al. (1979) consisted of steps in the following order with associated chemical reagents and conditions: exchangeable fraction (1 M $MgCl_2$, pH 7.0, for 20 min), carbonate/specifically adsorped fraction (1 M NaOAc adjusted to pH 5.0 with acetic acid, for 6 h), Fe-Mn oxide bound fraction (reducible phase) (0.04M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc at 96°C, for 6 h), organic bound/sulphide (oxidizable phase) (5 ml of 30% H_2O_2 and 0.02 M HNO_3 for 2 h, a second 3 ml of 30% H_2O_2 for 3 h, at 85°C), and residual fractions (total digestion with a mixture of concentrated $HNO_3/HClO_4$). Metal concentrations were determined using ICP-AES. The details of the sequential extraction method and ICP analysis were reported by Li et al. (1995). Soil particle-size analysis was carried out by a hydrometric method. The soil pH was measured using a glass electrode in a 2:1 ratio of soil to deionized water suspension. Organic carbon was determined by wet-oxidation by $K_2Cr_2O_7$ of Walkley-Black method. Cation exchange capacity (CEC) was measured by the ammonium acetate method (Sparks et al. 1996).

RESULTS AND DISCUSSION

Selected physical and chemical properties of the soil samples are presented in Table 1. Total metal concentrations in the soils from each location are shown in Figs. 2, 3 and 4. In general, the heavy metal concentrations of the soils were found to decrease in the order Cu > Zn > Pb, reflecting the ore mineral assembly of the Cu mine in this area. The concentrations of Cu were in a wide range of 78-2830 mg/kg, with an average of 618 mg/kg. Lead concentrations in soils also showed a large variability with a mean of 161 mg/kg. The total Zn concentrations varied from 78 to 1280 mg/kg, with an average of 354 mg/kg. Heavy metal concentrations in the soils showed a clear geographical diffusion pattern in the study area (Figs. 2, 3 and 4). The concentrations of all metals decreased with the increasing distance from the mining site. This decrease was most significant for Cu and Zn. The results suggested contamination of the soils with Cu, Pb and Zn emanating from the mining operations at the Fenghuang Mountain in the southern part of this study area. During past and present mining activities, mine waste and mill drainage have been produced and discharged to the Xiashankou creek. Thus, heavy metals can be continuously released downstream along the creek. In turn, these metal pollutants were introduced to the agricultural soils as a result of soil irrigation using the stream water. Heavy metals in mine tailings can be dispersed both downstream and downslope due to the surface runoff and strong leaching processes. The highest concentrations of total Zn and Pb were found in the soil at Site 3, which was located next to the Lingcun mine tailings (Figs. 3 and 4). However, the maximum soil Cu concentration of 2830 mg/kg occurred at Site 4 (Fig. 2). This may be attributed to the direct input of this metal from the mining activities.

The results of sequential chemical extraction of the soils are also showed in Figures 2, 3 and 4. In general, Cu concentrations in the exchangeable, carbonate /specifically adsorbed, Fe-Mn oxide and organic fractions were higher than Pb and Zn. The Cu concentrations in the residual phase were in the range of 28 to 1230 mg/kg, which accounted for 21-64% of the total Cu in the soils (Fig. 2). The residual fraction is the most stable form of metals in soils. More than 50% of the total Cu in the soil samples excluding Site 3 was associated with the non-residual fractions. Among the non-residual fractions, the Fe-Mn oxide fraction contained the greatest amount of Cu in all soil samples except the samples at Sites 8 and 9, in which the organic fraction had the greatest amount of Cu (Fig. 2). In the fractionation scheme, the 1 M NaOAc at pH 5.0 was used to remove the predominantly carbonate-bound metals from the soils. In the soil with low pH from Sites 8, 9 and 10, however, 14.5%, 21.9% and 13.7% of the Cu was associated with the "carbonate/specifically adsorbed" fraction, respectively (Fig. 2). It seems that most of the NaOAc-extractable Cu in these soils could be adsorbed to specific sites under lower pH condition. Acetic acid has been observed to displace greater quantities of Cu than that are present in exchangeable sites (McLaren and Crawford 1973), which is attributed to greater desorption of Cu from organic sites or release from oxide materials. The sum of metals associated with the exchangeable and carbonate fractions is very important because it represents the proportion of heavy metals that can be readily available for plant uptake (Ma and Rao 1997; Planquart et al. 1999). The high percentage of Cu in the exchangeable and carbonate fractions in the present study, accounting for 5.1-24.2% of the total concentration (Fig. 2), indicate that significant amounts of Cu in these soils might be available for plant uptake.

Table 1. Selected physical and chemical properties of soils tested.

Soil sample	Particle size distribution (%)				pH	CEC cmol/kg	Organic Matter (%)
	1-0.05 mm	0.05-0.01 mm	0.01-0.001 mm	<0.001 mm			
1	13.0	34.7	36.7	15.6	8.0	8.7	1.11
2	55.1	20.9	14.6	9.4	8.2	11.1	1.03
3	31.3	22.5	27.5	18.7	7.2	17.8	2.32
4	29.4	65.2	5.1	0.3	7.8	10.0	3.22
5	29.1	26.6	26.6	17.7	7.6	7.3	2.08
6	42.2	22.3	24.5	11.0	6.9	12.7	0.89
7	43.8	24.2	17.5	14.5	8.1	13.0	1.45
8	26.4	28.7	31.4	13.5	5.1	11.7	2.12
9	57.0	16.9	13.7	12.4	5.6	3.9	2.15
10	50.2	18.1	20.6	11.1	6.0	4.4	1.01

The percentage of Cu in the residual fraction was found to be higher in the soil samples collected from the southern part than the northern part of the study area (Fig. 2). In contrast, Cu in the carbonate and organic fractions tended to increase from the southern sites to the northern sites. In the soils of the northern sampling area, the percentages of Cu in the organic, Fe-Mn oxide and carbonate/specifically

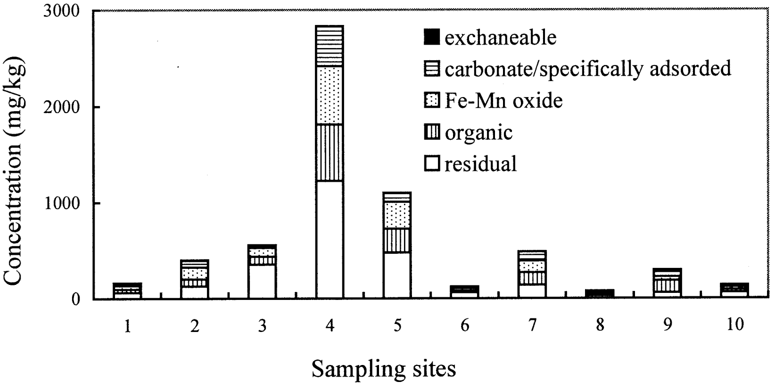

Figure 2. Concentrations of Cu in various fractions of the soils.

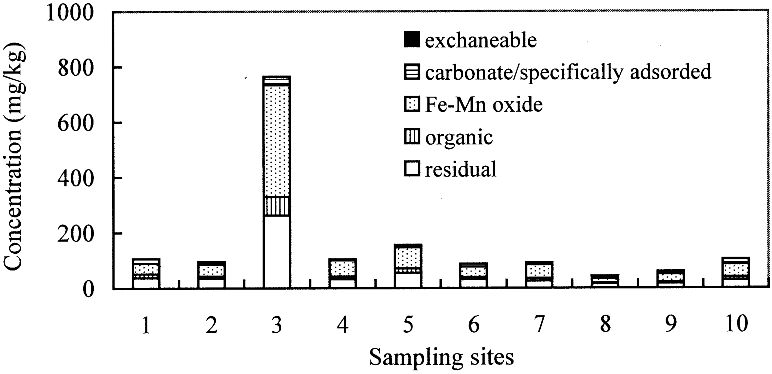

Figure 3. Concentrations of Pb in various fractions of the soils.

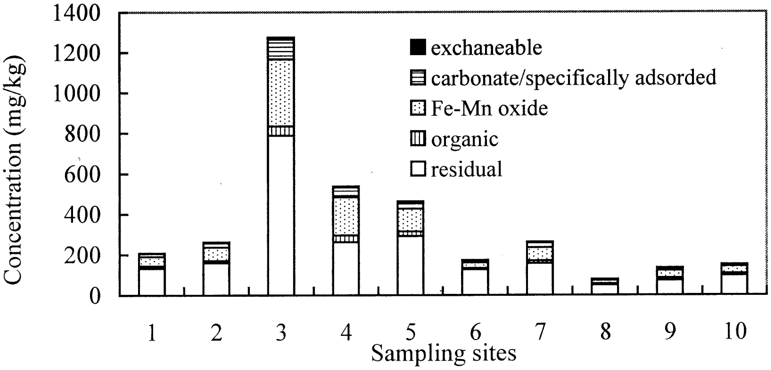

Figure 4. Concentrations of Zn in various fractions of the soils.

adsorbed increased as the total Cu concentrations increased. The result indicated that the increase of total Cu concentration could be attributed to the increase of Cu in non-residual fractions, reflecting that Cu was transported in more mobile forms to the agricultural soils.

Most of the Pb in soils was present in the Fe-Mn oxide (33-56% of the total) fraction (Fig. 3). On average, the percentage of Pb associated with different fractions in all the soil samples was in the order: Fe-Mn oxide (46.3%) > residual (32.6%) > carbonate /specifically adsorped (10.3%), organic (9.6%) > exchangeable (1.2%). Among all the metals studied, Pb had the highest proportion associated with the Fe-Mn oxide fraction and the lowest proportion in the residual fraction. Lead can form stable complexes with Fe-Mn oxide (Ramos et al. 1994). It has been reported that metals adsorbed to hydrous oxide gels of Fe and Al is in the order Pb > Cu > Zn (Kinniburgh et al. 1976). The exchangeable fraction was less than 0.6% of the total Pb in all soils except Sites 8, 9 and 10, in which soil pH was lower than 6.0. The exchangeable, carbonate and Fe-Mn oxide fractions accounted for 52-63% of the total Pb in these soils (Fig. 3), which was greater than those of Cu and Zn. Pb also showed the anthropogenic influence through the decreasing trend in the percentage of the Pb in the Fe-Mn oxide fraction from the mining sites in the south to the agricultural fields in the north.

In all soils, Zn was primarily associated with the residual fraction, ranging from 48% to 74% of the total concentrations (Fig. 4). The Fe-Mn oxide fraction was the next most important fraction for Zn, accounting for 15-35% of the total Zn. The carbonate and organic fractions were also important for Zn, which ranged from 2.3% to 12.1% and 3.6% to 9.2%, respectively. The exchangeable Zn fraction for all sites was low (<3.1%). The percentage of Zn in the exchangeable and carbonate fractions accounted for 5.4-10.2% of the total, being lower than that for Cu and Pb. Several researchers have also reported that Zn could be associated with Fe-Mn oxides in soils and sediments (Fernandes 1997; Ma and Rao 1997; Ramos et al. 1999). The Zn adsorption onto these oxides has higher stability constants than that onto carbonates.

The relationships between Cu, Pb and Zn concentrations in the Fe-Mn oxide fraction and reducible Fe and Mn concentrations in the soils are given in Table 2. The concentrations of Cu, Pb and Zn bound to the Fe-Mn oxide fraction had significant relationships with reducible Fe, reducible Mn and reducible Fe+Mn (Fe-Mn oxides). There were also significant relationships between the total Cu and Zn concentrations with reducible Fe+Mn. This suggested that Fe-Mn oxides may be the main carriers of Cu and Zn during the metal transportation from the mining site to the soils. No significant relationship between the organic bound Pb and the soil organic matter content was observed. These results are in agreement with the fact that non-residual Pb is mostly concentrated in the Fe-Mn oxide fraction, and non-residual Cu is mainly present in the organic and Fe-Mn oxide fractions.

To further investigate dispersion patterns of metal contaminants in this area,

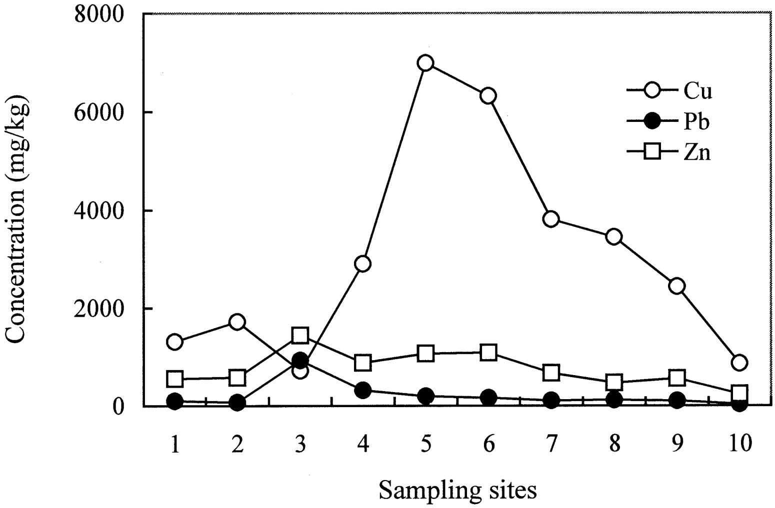

Figure 5. The total heavy metal concentrations in the sediments.

Table 2. Relationships between Cu, Pb and Zn in Fe-Mn oxide and organic fractions, and reducible Fe, reducible Mn and organic matter.

	Reducible Fe	Reducible Mn	Reducible Fe+Mn	Organic matter
Cu bound to Fe-Mn oxide	0.920**	0.758**	0.915**	
Pb bound to Fe-Mn oxide	0.727*	0.804**	0.734*	
Zn bound to Fe-Mn oxide	0.952**	0.931**	0.948**	
Cu bound to organic				0.836**
Pb bound to organic				0.100^{NS}
Zn bound to organic				0.769**
Total Cu	0.887**	0.699*	0.879**	0.792**
Total Pb	0.536^{NS}	0.670*	0.546^{NS}	0.040^{NS}
Total Zn	0.940**	0.889**	0.941**	0.565^{NS}

$P<0.05$; ** $P<0.01$; NS: not significant; (n=10)

sediment samples were also collected, and the total concentrations of heavy metals in these samples are presented in Figure 5. Elevated levels of the metals were found in the sediments, especially of Cu, Zn and Pb. Concentrations of Cu, Zn and Pb at various sampling sites exceeded the ecotox threshold values of 34, 150 and 47 mg/kg for these metals, respectively, developed by the U. S. Environmental Protection Agency (1996). Among elements analysed, the concentrations of Cu were the highest in all sampling sites, followed by Zn. Compared with the metal concentrations in the corresponding soils, the concentrations of Cu and Zn were markedly higher in the sediments. Like the spatial distribution patterns in the soils, the concentrations of metals in the sediments also decreased with increasing distance from the contamination source (the mining site). Sediment from Site 5 had the highest concentration of Cu, which reached 7000 mg/kg. The concentrations of Zn and Pb were the highest at Site 3.

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REFERENCES

Adriano DC (1986) Trace elements in the terrestrial environment. Springer-Verlag, New York

Fernandes HM (1997) Heavy metal distribution in sediments and ecological risk assessment: the role of diagenetic processes in reducing metal toxicity in bottom sediments. Environ Pollut 97: 317-325

Förstner U (1989) Contaminated sediments. In: Bhattacharji S, Friedman GM, Neugebauer HJ, Seilacher A (eds) Lecture Notes in Earth Sciences, Vol. 21. Springer-Verlag, Berlin, pp. 157

Howard JL, Vandenbrink WJ (1999) Sequential extraction analysis of heavy metals in sediments of variable composition using nitrilotriacetic acid to counteract resorption. Environ Pollut 106: 285-292

Kinniburgh DG, Jackson ML, Syers JK (1976) Adsorption of alkaline earth, transition and heavy-metal cations by hydrous oxide gels of iron and aluminum. Soil Sci Soc America J 40: 796-799

Li XD, Ramsey MH, Coles BJ, Thornton I (1995) Sequential extraction of soils for multielement analysis by ICP-AES. Chem Geol 124: 109-123

Ma LQ, Rao GN (1997) Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. J Environ Qual 26: 259-264

McLaren RG, Crawford DV (1973) Studies on soil copper. I. The fractions of copper in soils. J Soil Sci 24: 443-452

Ramos L, Hernandez LM, Gonzalez MJ (1994) Sequential fractionation of copper, lead, cadmium and zinc in soil from or near Donana National Park. J Environ Qual 23: 50-57

Shiowatana J, Tantidanai N, Nookabkaew S, Nacapricha D (2001) A flow system for the determination of metal speciation in soil by sequential extraction. Environ Int 26: 381-387

Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner ME (1996) Methods of Soil Analysis, Part 3, Chemical Methods. Soil Sci Soc Am, Am Soc Agron, Madison, Wisconsin

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of trace metals. Analy Chem 51: 844-851

U S Environmental Protection Agency (1996) ECO update: ecotox thresholds. Intermittent Bulletin Vol 3 (2). Office of Emergency and Remedial Response, EPA, 540/F-95/038