

HEAVY METAL ACCUMULATION FROM ZINC SMELTERS IN A CARBONATE ROCK REGION IN HEZHANG COUNTY, GUIZHOU PROVINCE, CHINA[†]

YUAN-GEN YANG^{1,2,*}, CONG-QIANG LIU¹, WU PAN¹, GUO-PING ZHANG¹ and WEI-HUANG ZHU¹

¹*Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang City, Guizhou Province, 550002, China;* ²*University of Florida, Institute of Food and Agricultural Sciences, Indian River Research and Education Center, 2199 South Rock Road, Fort Pierce, FL34945, USA. extension 156*

(*author for correspondence, e-mail: yangyuangen@hotmail.com, yangyuangen@sohu.com, Tel: 772-468-3922)

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Abstract. In this study, four sites (Sites A, B, C and D, which were associated with varying durations of zinc smelting) namely two slag piles (Profile 1, Profile 2) at Sites B and C and two water channels at Sites A and D in Hezhang County, Guizhou Province, Southwestern China, were investigated.

Significantly elevated mean Pb, Zn and Cd concentrations, 11,192 ($\pm 8,991$), 20,563 ($\pm 16,727$) and 137 (± 112) mg kg⁻¹ in slag Profile 1 ($n = 10$), and 12,535 ($\pm 4,408$), 26,189 ($\pm 6,209$) and 47.9 (± 30.1) mg kg⁻¹ in slag Profile 2 ($n = 12$) were detected, respectively. Both profiles had high pH values (7.72 ± 0.37 in Profile 1 and 8.33 ± 0.49 in Profile 2). In addition, high mean Pb, Zn and Cd in soils (14,945 ($\pm 9,696$), 17,059 ($\pm 12,534$) and 61.9 (± 33.6) mg kg⁻¹) and in stream sediments (11,450 ($\pm 7,097$), 20,768 ($\pm 11,404$) and 66.8 (± 25.5) mg kg⁻¹) were found at Site D. A Composite Pollution Index (CPI) determined for each study Site confirms the anthropogenic origins of the observed Pb, Zn and Cd contamination. Small portions (<3% of the total) of exchangeable Pb and Zn fractions in samples were extracted by using a sequential extraction technique. In contrast, 37.7% ($\pm 7.69\%$), 21.3% ($\pm 7.75\%$) and 22.7% ($\pm 13.2\%$) of total Pb, Zn and Cd was associated with the carbonate bound fraction. This is indicative of the alkaline pH associated with the carbonate based-ores of this region. Further, total metal concentrations were positively and significantly correlated with soil Fe contents. This may in large part be due to the co-precipitation of Pb, Zn and Cd with Fe minerals in the surface weathering environment.

However, a potential threat still exists with regards to the environment release of Pb, Zn and Cd as a result of an alteration of the pH environment, such as in the acidic rhizosphere environment of cultivated crops or acid deposition in this region. It is therefore suggested that immediate remediation measures are implemented to minimize potential risks.

Keywords: zinc smelting slags, heavy metal contamination, chemical speciation, bioavailability, correlation

1. Introduction

Mine exploitation-induced environmental problems, especially toxic substance release such as heavy metal liberation and discharge of acid mine drainage (AMD)

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from sulfide weathering in mine wastes, have received worldwide attention in the past two decades (Moses and Hermamn, 1991; Elberling *et al.*, 1994; Lin and Herbert, 1997; Soucek, *et al.*, 2000; Williams and Smith, 2000; Kumar and Patterson, 2000; Lottermoser *et al.*, 1999).

Toxic substances released from metal smelters and smelting slag heaps are also a world wide environmental problem. Smelting slag heaps usually contain high levels of such metals. Verner *et al.* (1996) detected up to 545 mg kg⁻¹ Pb, 2175 mg kg⁻¹ Zn and 14.8 mg kg⁻¹ Cd in the topsoils around a Pb-Zn smelting center in Bukowno, Poland. Kaasalainen and Yli-Halla (2003) reported increasing concentrations of Cd, Cu and Ni in the topsoils from smelter fallout, and verified that anthropogenic related metals are more mobile than those of geogenic origin. Up to 75–90% of Cd, 49–72% of Cu and 22–52% of Ni existed in a phyto-available form. Ivask *et al.* (2004) found that metal levels were different in soils near two smelters, and variable correlations between Pb, Zn and Cd were linked to the respective history of the smelters and the composition of the smelted ores with regards Pb, Cd and Zn. Kachur *et al.* (2003) applied integrated methods to estimate the negative effects of smelting activities on vegetation, soils, atmospheric environment, and even human bodies (blood lead levels). It is reasonable to conclude that distance from the smelters, prevailing wind direction, history of smelting and composition of smelted ores are main factors controlling offsite pollution (Gzyl, 1995; Van Alphen, 1999; Ivask *et al.*, 2004).

In 1992, as reported by the National Environmental Protection Bureau (NEPB, 1992) China had 618 million tons of solid waste residues of which 23% were mining mullocks and mine wastes. Zhu (1999) indicated that >4000 million tons of waste gangues were produced in total and piled at the rate of several hundred million tons a year. Un-managed this waste poses a significant threat to the ecological environment. However, to date little research has been undertaken with regards heavy metal pollution associated with zinc smelting activities using traditional techniques.

Hezhang County, famous for its lead and zinc ore deposits and coal resources, is located in the northwestern part of Guizhou Province. Zhazichang, Maomaochang and Tianqiao are the three major deposits in the County. In the 18th century zinc smelting practices in Hezhang County were developed to produce coins and the same traditional smelting techniques have prevailed to the present day. By 2000, several thousand smelting furnaces were operating in the County (ECREHC, 2002). This has resulted in barren-vegetated areas in the surrounding mountains and waste dumps and slag heaps scattered along natural drainage channels and hillsides. Increasing attention has focused on the development and implementation of effective ecological remediation measures. However, before this is undertaken detailed research must be undertaken to ensure the applicability and effectiveness of said remediation options.

The aim of this study was to investigate heavy metal accumulation and Pb, Zn and Cd bio-availabilities in soils and sediments at the pre-selected study sites to

assist the effective development of remediation options. The following research questions were taken into consideration namely, Pb, Zn and Cd accumulation in soils and water sediments as compared to background levels, natural attenuation of Pb, Zn and Cd in slags, Pb, Zn and Cd fractionation in slags, soils and water sediments and their bio-availabilities and, soil characteristics influencing Pb, Zn and Cd bioavailability.

2. Methodology

Four study sites were evaluated in this study located at Haozichong (Site A), Xing-guanzai (Site B), Hejiachong (Site C) and Zhazichang (Site D) in Hezhang County (Table I). Sites A and B were associated with active zinc smelting in 2001 at time of sampling whilst Sites C and D had been abandoned for 20 and more than 10 years, respectively. The region of study has an elevation ranging from 1800–2000 m above sea level, mean annual temperature of 12°C and annual rainfall ranging from 900 to 1200 mm yr⁻¹. At Sites B and C, Profile 1 and Profile 2 slag profiles were sampled at 20 cm intervals to a depth of 190 and 210 cm, respectively. At all sites, 10 point (within 1 m²) composite top soils (0–20 cm depth) were taken from 20–30 randomly selected sampling locations. Under the USDA Taxonomy, the yellow brown soils of the area are classified as Alfisols (USDA, 1992). Sediment samples (0–30 cm depth) were collected at 10 m intervals along the mine waste channel and at 100 m intervals along the stream associated with Sites A and D, respectively (Figure 1).

TABLE I
Basic descriptions of studied sites

Location	Years of zinc smelting	Smelting activity when sampling	Pollutants released routes	Pollutant receiver	Sampling objects
Site A (Haozichong)	2	Operating	Atmospheric deposition; waste slags; waste water	Soils; Leakage lake	Soils; Water Sediments
Site B (Xinguanzai)	10	Operating	Atmospheric deposition; waste slags	Soils	Soils; Waste slags (Profile 1)
Site C (Hejiachong)	30	Ceased	Waste slags	Soils	Soils; Waste slags (Profile 2)
Site D (Zhazichang)	>50	Ceased	Scattered waste slags	Soils; Stream	Soils; Water Sediments

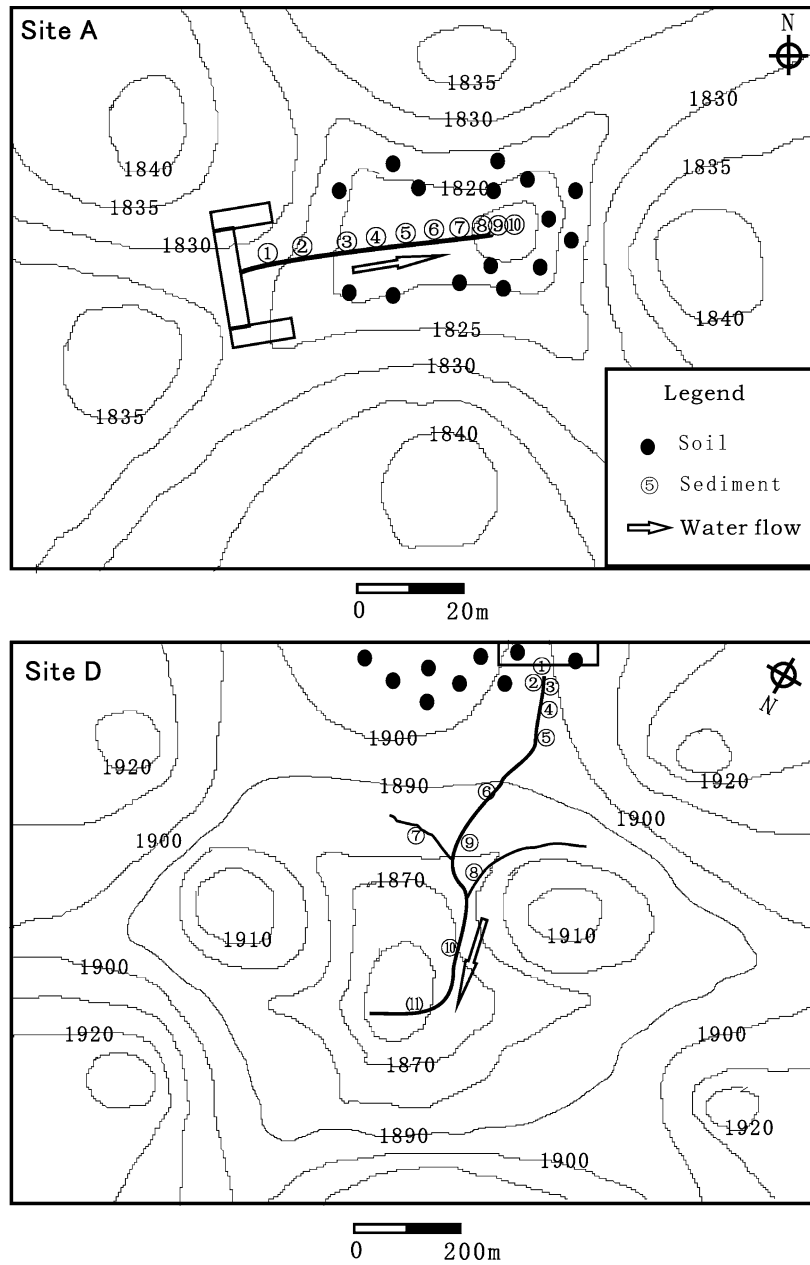


Figure 1. A sketch map showing sampling location of soils and water sediments at studied sites.

All soil and sediment samples were air-dried and ground to <0.125 mm using an agate miller prior to chemical analysis.

Soil pH was determined in de-ionized water at a water to sample ratio of 2.5:1 following the method of NISS (1980). Total Pb, Zn and Cd were determined following the mixed acid (HNO₃, HClO₄ and HF) digestion method of Tessier *et al.* (1979). Iron (Fe₂O₃) and aluminium oxides (Al₂O₃) were determined following Tessier *et al.* (1979). Fractionation of Pb, Zn and Cd into exchangeable, carbonate bound, Fe-Mn oxide bound, organic matter bound and residual fractions was achieved following Tessier *et al.* (1979) and Li *et al.* (1995). Quality control was evaluated through the use of the US EPA Mag#1 Standard Reference Material (SRM). The recovery rates of SRM in this study were 90–112% for Pb, 98–103% for Zn and 105–116% for Cd, respectively.

Total and extractable forms of Pb, Zn, Cd and Fe were determined on an Atomic Adsorption Spectrophotometer (Model PE5100PC, PERKIN ELMER, USA). Total and extractable forms of Al were determined by Graphite Furnace Atomic Adsorption Spectrometry (GFAAS) (Model PE5100PC, PERKIN ELMER, USA). The measuring wavelengths are 283.3, 213.9, 228.8 nm for Pb, Zn, Cd, and 248.3, 309.3 nm for Fe and Al, respectively. Total Fe₂O₃ and Al₂O₃ were subsequently calculated.

3. Results

3.1. DISTRIBUTION OF HEAVY METALS IN SLAG PILES

Slag Profile 1: Significantly higher Pb levels were observed in the top 10 cm of the profile as compared to the 30 cm sampling depth with values of 31,631 and 7,320 mg kg⁻¹, respectively (Figure 2). Thereafter, from 70–150 cm Pb concentrations remained relatively constant with a mean ($n = 5$) Pb concentration of 7,325 ($\pm 2,038$) mg kg⁻¹. In Profile 1 the lowest Pb concentrations are found at depth (170–190 cm) and are associated with the basal soil. However, the Pb level in basal soil of 105–155 mg Pb kg⁻¹ is still elevated above the background level of Pb in soils of Guizhou Province of 35 mg Pb kg⁻¹ (CEMS, 1990).

In contrast, the highest Zn concentration in Profile 1 is observed at 50 cm depth with a concentration of 57,178 mg kg⁻¹. Similarly to Pb, Zn concentrations remain relatively constant 11,884 mg kg⁻¹ ($\pm 3,749$) from 70–150 cm depth. Again, although elevated above background levels, the lowest profile Zn concentrations are associated with the basal soils (Figure 2). High Cd concentrations are observed in the top 10–50 cm of Profile 1 with a sharp decline at 90–130 cm depth to a relatively constant value of 20.75 mg kg⁻¹ (± 2.30). However, in contrast to Pb and Zn a subsequent increase in Cd is observed in the basal soil (Figure 2). Zn/Pb, Pb/Cd and Zn/Cd ratios in Profile 1 vary significantly with depth. This may in large part be due to the relative concentration of Pb, Zn and Cd in the zinc ore smelted over

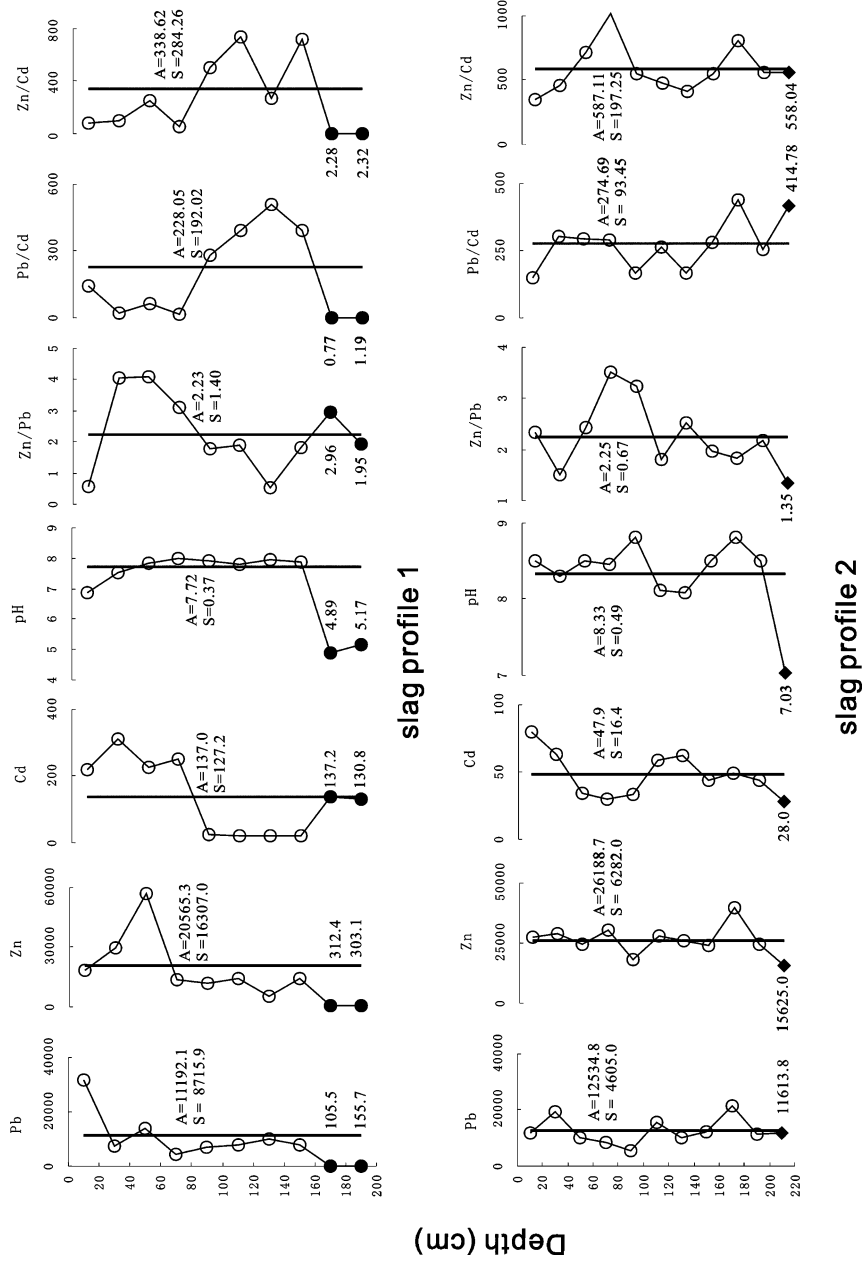


Figure 2. Profile distribution of Pb, Cd and Zn (mg kg⁻¹) as related to soil pH and Zn:Pb, Pb: Cd and Cd:Zn ratios. A represents average value; S standard deviation. ○ represents slag samples; ● basal soils; ◆ basal sediments.

time and variations in weathering environment over time. However, as indicated in Figure 2, pH is relatively constant throughout Profile 1.

Slag Profile 2: Significantly higher Pb levels were found at the depths of 30 and 170 cm with values of 19,238 and 21,555 mg Pb kg⁻¹, respectively as compared with other sampling depths that varied close to the grand mean average value of 12,535 mg kg⁻¹ (Figure 2). The basal sediment had a Pb level of 11,614 close to the grand mean average of Profile 2.

The highest Zn concentration in Profile 2 is observed at 170 cm depth with a concentration of 39,616 mg kg⁻¹. Apart from this, Zn concentrations fluctuated around the average concentration of Profile 2 (26,189 mg kg⁻¹, $n = 11$), with the lowest Zn concentration in Profile 2 associated with its basal sediment (Figure 2). However, the highest Cd concentration in Profile 2 was observed in the top layer of 10 cm depth. Thereafter, Cd concentration sharply decreased down to 50 cm depth, remained relatively stable at intervals of 50–90 cm depth, increased between 110–130 cm depth and then decreased again at 150–190 cm depth. Similarly to Zn, its lowest concentration is associated with the basal sediment. Zn/Pb, Pb/Cd and Zn/Cd ratios in Profile 2 vary greatly with depth as in Profile 1. In contrast to Profile 1, the pH in Profile 2 is relatively high, usually over 8.3 except for the 110–130 cm depth, and the lowest pH of 7.03 is associated with the basal sediment.

Comparing the two profiles, higher mean Pb and Zn concentrations with smaller variations were observed in Profile 2 ($12,535 \pm 4,605$, $26,189 \pm 6,282$, respectively) compared with Profile 1 ($11,192 \pm 8,716$, $20,563 \pm 16,307$, respectively). However, a higher mean Cd concentration with larger variations was found in Profile 1 (137 ± 127) than in Profile 2 (47.9 ± 16.4).

As with Profile 1, Zn/Pb, Pb/Cd and Zn/Cd ratios varied significantly with depth in Profile 2, presumably due to changes with time in the relative concentrations of Pb, Zn and Cd in the zinc ores smelted. However, there were no significant differences between the mean Zn/Pb, Pb/Cd or Zn/Cd ratios between the two profiles.

Although mean Zn/Pb ratios in the two profiles were very similar (around 2.2), and still no significant differences of Pb/Cd and Zn/Cd ratios can be found using Two-sample Tests ($p = 0.175$ and 0.018 , respectively), different smelted ore substance might mainly be responsible for the different Pb, Zn and Cd levels in the two Profiles due to the evident information of obviously different pH values, and higher Cd concentrations with relatively lower pH in Profile 1 than in Profile 2 (Figure 2).

3.2. DISTRIBUTION OF HEAVY METALS IN SOILS AND SEDIMENTS

Highly variable Pb, Zn and Cd concentrations in soil and sediment were observed at all study sites (Table II). The lowest metal concentrations were found at Site A with average concentrations of 104, 260 and 9.7 mg kg⁻¹ for Pb, Zn and Cd, respectively in soils, and 560, 1627 and 24.5 mg kg⁻¹ for Pb, Zn and Cd, respectively in sediments. This may be attributed to the comparatively short smelting history at Site A

TABLE II
Concentrations of Pb, Cd and Zn (mg kg^{-1}) in soils and sediments at the studied sites

Location	Soil			Water sediment		
	Pb	Zn	Cd	Pb	Zn	Cd
Site A (Haozichong)	104 \pm 28 (20)	260 \pm 133	9.7 \pm 3.8	560 \pm 225 (10)	1627 \pm 394	24.5 \pm 3.7
Site B (Xinguanzai)	133 \pm 91 (30)	510 \pm 187 ^a	7.4 \pm 4.5			
Site C (Hejiachong)	1962 \pm 1598 ^{a,b} (20)	5148 \pm 3891 ^{a,b}	25.2 \pm 8.8 ^{a,b}			
Site D (Zhazichang)	14945 \pm 9696 ^{a,b,c} (30)	17059 \pm 12534 ^{a,b,c}	61.9 \pm 33.6 ^{a,b,c}	11450 \pm 7097 ^x (11)	20768 \pm 11404 ^x	66.8 \pm 25.5 ^x
Background levels in Guizhou	35 (CEMS, 1990)	100	0.20	29.4 (He, 1998)	89.9	0.31

Data are expressed as Mean \pm 1 STDEV, in parenthesis are sample numbers. Superscript a refers to a significant difference with a probability level of $p < 0.001$ between soil metal concentrations at Sites B, C and D compared with Site A by using Two-sample *t*-test; b refers to a significant difference ($p < 0.001$) compared with Site B; and c refers to a significant difference ($p < 0.001$) compared with Site C. Superscript x refers to a significant difference with a probability level of $p < 0.001$ between sediment metal concentration at Site D compared with Site A.

of 2 years with Pb, Zn and Cd accumulating in soils mainly through atmospheric deposition, and in sediments via discharge and occasional runoff. Surface runoff and uncontrolled discharge are the main mechanisms transporting Pb, Cd and Zn from smelting slags with subsequent precipitation in sediments even though the discharge was not utilized for agricultural irrigation.

Significantly higher levels of soil Zn ($p < 0.001$) were found at Site B as compared to Site A. However, Pb and Cd levels were not significantly different. During smelting metal Zn is more readily volatilized than Pb and is correspondingly more readily released to soils in the vicinity of the smelter through atmospheric deposition. The long-term (10 of years) accumulation from atmospheric deposition is the most likely factor controlling Pb, Zn and Cd levels in soils at Site B.

It is postulated here that waste slags might be the main source releasing Pb, Zn and Cd into soils at Site C since the long-term abandonment of smelting activities. Long-term weathering of waste slags was responsible for the significantly higher levels ($p < 0.001$) of Pb, Zn and Cd with averages of 1962, 5148 and 25.2 mg kg⁻¹, respectively, in soils compared with Sites A and B.

The spatial distribution of Pb, Zn and Cd at Site D is different from Sites A, B and C. Although smelting operations have been abandoned at Site D for 10 years no smelting slag piles or dumps are visible, with smelting slags noticeably scattered randomly within soils. It is suggested therefore that Pb, Zn and Cd release is primarily due to leaching from sub-surface slags or historical distribution through surface erosion.

Furthermore, a stream receiving upstream drainage is the only water channel at Site D (Figure 1), and would serve as the main carrier of smelting slags during and after the cessation of smelting operations. The long smelting history associated with Site D and exposure of smelting slags to pro-longed surface erosion processes has resulted in the extremely high Pb, Zn and Cd levels in soils and sediments (Table II).

As indicated in Figure 3, Pb, Zn and Cd concentrations varied significantly along the length of the water courses at Sites A and D. At Site A, Pb, Zn and Cd levels in sediment increase with increasing distance from the smelter with concentrations of 231 to 912, 985 to 2,346 and 18 to 29, respectively. At Site D Pb, Zn and Cd concentrations decreased with increasing distance down stream with concentrations of 21,850 to 4,375, 30,425 to 7,275 and 95 to 42 mg kg⁻¹, respectively (Figure 3). In contrast, at sampling points 7 and 8 Pb, Zn and Cd concentrations were significantly lower with values of 1575 and 1150, 2175 and 1450, 25 and 30, respectively. However, Pb, Zn and Cd concentrations at points 7 and 8 were much higher than their sediment background values (Table II). This may partly be explained by surface runoff input from soils randomly scattered with smelting slags.

The significantly higher Pb, Zn and Cd levels in sediment at Site D are primarily attributed to the long smelting history and associated off-site contamination through scouring of slag heaps. Field observations indicated small (<2 mm) black smelting

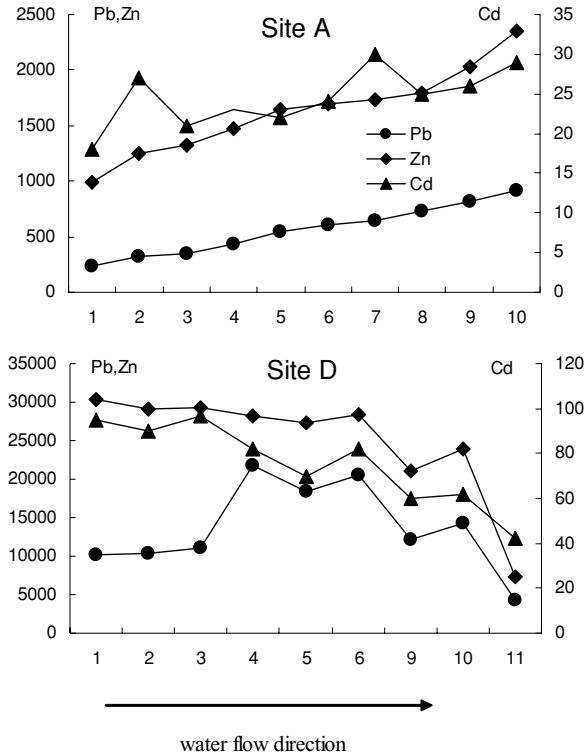


Figure 3. Pb, Zn and Cd concentrations (mg kg^{-1}) in stream sediments in relation to distance from pollution source. Site A (Haozichong), Site D (Zhazichang). Sampling numbers are same as shown in Figure 1. At Site D, number 7 and 8 are samples of branch stream sediments.

slag particles within the sediments in the upstream sections of the Site D drainage channel.

3.3. POLLUTION INDEX IN SOILS AND SEDIMENTS

In order to quantify the severity of Pb, Zn and Cd contamination derived from anthropogenic origins as compared with background levels, the Composite Pollution Index (CPI) developed by Yang *et al.* (2004) was determined at all sites for both soils and sediments.

$$\text{CPI} = \sum \left[\frac{(C_i * P_i)}{C_o} \right]$$

where C_i represents concentrations of Pb, Zn or Cd in soils or sediments; P_i represents the Pb, Zn and Cd as proportions of the total metal concentrations in the soils or sediments; C_o refers to background Pb, Zn and Cd levels in soils or sediments in Guizhou Province.

At all sites, CPIs were positively correlated with soil and sediment Pb, Zn and Cd concentrations. Further, significantly ($p < 0.001$) higher CPI values were observed at Sites C and D as compared with Sites A and B (Table III). Therefore, the anthropogenic contamination severity for the sites evaluated is in the order of Site D > Site C > Sites B and A, which is probably linked to the long smelting histories associated with Sites C and D as compared with A and B.

3.4. FRACTIONATION OF HEAVY METALS

The recovery rates (cumulative metal fractionation total concentration/metal total concentration $\times 100$) for metals Pb, Zn and Cd were 108.3 (± 8.62), 104.9 (± 9.04), 112.1 (± 8.84), respectively. The fractionation results for Pb, Zn and Cd in the soil and sediment samples evaluated in this study are illustrated in Figure 4. As expected in slag, soil and sediment samples, the percentage of Pb in the exchangeable fractions is negligible. In slag samples, Pb occurs primarily in the carbonate and iron and manganese bound fractions. In contrast, in soil and sediment samples taken from Site D, Pb was comparatively evenly distributed between the carbonate, iron (Fe) and manganese (Mn) bound and residual fractions. In soils and sediments this may in part be explained by the existence of stable mineral phases such as pyromorphite (Davis *et al.*, 1994; Cotterhowell *et al.*, 1994). Furthermore, a decreasing trend of carbonate bound and iron and manganese bound Pb, however, an increasing trend of residual Pb, can be observed from slags to sediments and soils, probably indicating a more mobile environment for Pb in slags than in sediments and soils. In the slag samples, the comparatively large Fe and Mn oxide bound fractions of Pb can be attributed to the formation of Fe-oxide minerals namely goethite during weathering of smelting slags (Wu *et al.*, 2002). In addition, Isaure *et al.* (2002)

TABLE III

Soil and sediment CPI values and their correlation coefficients with total metal (Pb, Zn and Cd) concentrations at the studied sites

Location	Soil	$r_{\text{soil metal-CPI}}$	Sediment	$r_{\text{sediment metal-CPI}}$
Site A	4.4 \pm 1.5	0.90**	19.1 \pm 5.1	0.99**
Site B	6.1 \pm 2.4	0.99**		
Site C	62.0 \pm 45.0 ^{a,b}	0.99**		
Site D	304.3 \pm 217.8 ^{a,b,c}	0.99**	294.4 \pm 166.2 ^x	0.96**

Data are expressed as Mean \pm 1STDEV. Superscript a refers to a significant difference with a probability level of $p < 0.001$ for soil CPI values at Sites C and D compared with Site A by using Two-sample *t*-test; b refers to a significant difference ($p < 0.001$) compared with Site B; and c refers to a significant difference ($p < 0.001$) compared with Site C. Superscript x refers to a significant difference with a probability level of $p < 0.001$ for sediment CPI at Site D compared with Site A. Superscript ** represents a positive relationship at $\alpha = 0.01$ significant level with total metal concentrations (in mmol kg^{-1}).

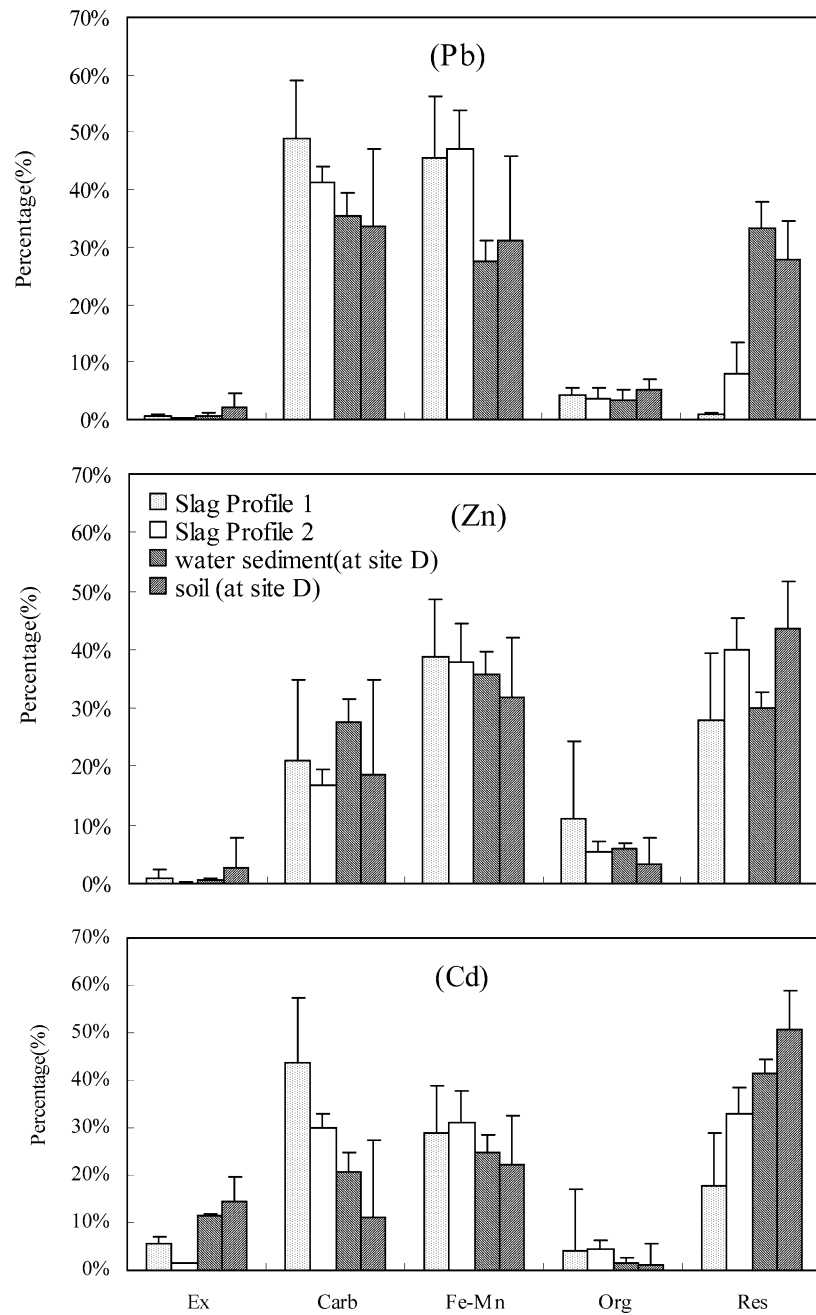


Figure 4. Chemical fractions of metals Pb, Zn and Cd in slags, soils and sediments at the studied sites. Data expressed as average plus standard deviation (error bar). Ex: exchangeable fraction; Carb: Carbonate bound fraction; Fe-Mn: iron and manganese oxide bound fraction; Org: organic (sulfide) bound fraction; Res: residual fraction.

also reported Zn-containing Fe (oxyhydr) oxides as one of the major Zn forms in smelting slags.

In slag samples as compared with Pb, Zn occurred primarily in the Fe and Mn oxide bound fractions and residual fractions with significantly lower percentages associated with the carbonate fraction. Further for the slag, soil and sediment samples as for Pb, low levels of exchangeable and organically bound Zn were observed. Lower levels of organic carbon in slag, sediment and soil (0.08–0.23%, 0.17–0.46% and 1.5–3.5%, respectively) may in part explain the low percentage of metals in organic fractions. The fractionation results observed for Zn may in large part be attributed to the formation of sparingly soluble zinc silicate minerals namely willemite ($Zn_2[SiO_4]$), fraiponite ($Zn_8Al_4[OH]_8(SiO_4)_5 \cdot 7H_2O$) during smelting (Wu *et al.*, 2002). Wu *et al.* (2002) confirmed the existence of these minerals in these slags by Transmission Electron Microscope/Scanning Electron Microscope with Energy Dispersive X-ray Detection (TEM/SEM-EDX). Isaure *et al.* (2002) also demonstrated the existence of smelter-derived willemite, Zn-containing Fe oxides and zincite in slags. Further, the alkaline conditions associated with the study sites investigated would facilitate the formation of secondary carbonate minerals including smithsonite (Hudson-Edwards *et al.*, 1997) which may in part explain the partitioning of Zn, Pb and Cd in the carbonate fraction.

In contrast to Pb and Zn, large proportions of exchangeable Cd, >1% in slags and >10% in sediments and soils, could be measured (Figure 4). This may indicate a greater mobilization of Cd than Pb and Zn in the samples. Larger portions of exchangeable Cd in slag Profile 1 ($5.68 \pm 3.23\%$) than in slag Profile 2 ($1.32 \pm 0.48\%$) were observed with a probability level of $F < 0.01$ as determined by ANOVA analysis. This could be related to leaching-induced removal of Cd during weathering as evidenced by difference in the Cd concentration of the two slag Profiles (Figure 2).

Verner *et al.* (1996) stated that the weathering process is responsible for the decrease of exchangeable fractions of Pb; however, their observation of increasing exchangeable fractions of Cd contradicts our result. The difference might be attributed to variations in Cd sources, weathering and geological settings. The formation of carbonate secondary minerals of Cd at high pH might serve as a depleting mechanism of exchangeable Cd, a possibility supported by the large proportions of carbonate bound Cd in slags ($8.33 \text{ mg kg}^{-1} \pm 0.49$ in slag2, $7.72 \text{ mg kg}^{-1} \pm 0.37$ in slag1). Secondary cadmium carbonate minerals, such as octavite ($CdCO_3$) can exist under such alkaline environments (Brenann and Lindsay, 1996; Eary, 1999).

Concentrations of Pb, Zn in different chemical fractionation were not significantly different between the two slags as determined by using the two-sample Tests. However, significant differences (with a Probability level of $p < 0.001$) of carbonate bound Cd and iron and manganese bound Cd between the two slags were found due to the differences in pH (Figure 2) and weathering duration (Table I).

Furthermore, correlation analyses revealed significantly negative correlations (at significant levels of <0.01) between slag pH and exchangeable fractions of Cd and Zn (Table IV). This suggests that high pH environments might be beneficial for reducing Cd and Zn bio-availability.

At site D, exchangeable + carbonate bound fractions of Pb, Zn and Cd accounted for on average 35%, 28% and 32% in water sediments, and 36%, 21% and 25.5% in soils, respectively. This demonstrates that large fractions of zinc smelting-derived metals in soil and sediment could be remobilized, for example, low pH from acid deposition could dissolve carbonate minerals so as to activate these metals, and therefore, could increase their bioavailability. As reported by Zhao *et al.* (1988), heavy industrialization in south-western China from 1980's resulted in much acid precipitation due to high sulphur coal consumption. A concentration of SO_2 as high as $159 \mu\text{g SO}_2 \text{ L}^{-1}$ was measured in rainwater in the ambient of Guiyang, Capital city of Guizhou Province, China (Tanner *et al.*, 1997). Seasonal surface runoff could carry metal-polluted soils into agricultural fields and might produce Cd contaminated rice so as to affect human health through the food chain. Therefore, urgent remediation action should be taken immediately in the region.

3.5. CORRELATION ANALYSES

Fe oxides/hydroxides/oxyhydroxides and Fe oxyhydroxysulphates are thought to be the most common contaminant metal-bearing minerals in the surface weathering environment (Hudson-Edwards *et al.*, 1999). To validate the observation of Hudson-Edwards *et al.* (1999) correlative analysis between Pb, Zn and Cd concentrations and Fe, Al contents in soils and sediments at study Sites A-D was undertaken (Table V).

Significant positive relationships (with confidence levels of $\alpha = 0.01$) between soil Fe_2O_3 contents and total metal concentrations can be observed except for soils at site A; much higher coefficient values were found at site D (Table V). This might be attributed to the strong specific adsorption of metals on iron minerals in soils, such as goethite, amorphous iron and iron hydroxides. Ladonin (2003)

TABLE IV
Correlation of pH with percentages of Pb, Zn and Cd fractionation in smelting slags

	Ex	Carb	Fe-Mn	Org	Res
Pb	-0.692**	-0.717**	0.504	-0.061	0.367
Zn	-0.753**	-0.523*	0.380	-0.503	0.705**
Cd	-0.791**	-0.640**	0.426	0.135	0.821**

Ex: exchangeable fraction; Carb: Carbonate bound fraction; Fe-Mn: iron and manganese oxide bound fraction; Org: organic (sulfide) bound fraction; Res: residual fraction. Superscripts *, ** represent $\alpha = 0.05$ and 0.01 significantly correlative levels on 15 sample basis, respectively.

TABLE V

Correlations showing total metal concentrations (mmol kg^{-1}) as related with soil and sediment Fe_2O_3 and Al_2O_3 contents (%) at different sites

	Site A			Site D
		Sediments		
Fe_2O_3 (%)	0.99 (10)**			0.89 (11)**
Al_2O_3 (%)	0.52 (10)			0.02 (11)
		Soils		
Fe_2O_3 (%)	0.51 (20)*	0.81 (30)**	0.60 (20)**	0.92 (30)**
Al_2O_3 (%)	0.46 (20)*	0.29 (30)	0.58 (20)**	-0.95 (30)**

In parenthesis are sample numbers. Superscripts *, ** represent $\alpha = 0.05$ and 0.01 significantly levels of correlation, respectively.

found Cd and Pb exhibit high affinity to iron minerals. It is of interest to note that the greater the duration of zinc smelter-derived metal inputs in soils, the higher the correlations between metal concentrations and soil Fe_2O_3 contents were. This demonstrated that prolonged chemical reactions of soil iron minerals with input metals might immobilize toxic metals in a cumulative effect. A natural attenuation of bioavailability of metals Pb, Zn and Cd in soils of carbonate geological setting could result due to the formation of metal carbonate minerals such as octavite, smithsonite or calamine.

Positive relationships between soil Al_2O_3 contents and total metal concentrations can be observed at site A, B and C (Table V), However, an extremely negative relationship (with confidence levels of $\alpha = 0.01$) existed at site D. That might be related to the amphoteric behavior of Al^+ under different conditions. At low metal concentrations, soil Al minerals, such as clay minerals can adsorb metals Pb, Zn and Cd, therefore, positive correlations can be observed; however, at high metal concentrations, aluminate may release H^+ through hydrolysis, and thus prohibit Pb, Zn and Cd being adsorbed onto soil.

In water sediments, good relationships between metal inputs and sediment Fe_2O_3 contents were still evident (Table V). Better relationships were found at site A than at site D, which implied that metal input was more readily fixed by water sediment at the site with the shorter smelting history. This relationship is different from that in soils, which might indicate that, in soils, the longer-term reaction of metals is with iron minerals. However, longer-term washing by stream water might induce more metals to be removed from sediment.

4. Discussion

Concentrations of Pb, Zn and Cd in slag, soil and sediment samples at study Sites A-D and the associated CPIs demonstrate significant anthropogenic contamination

of these elements as associated with Zn-smelting activities. However, Pb, Zn and Cd concentrations varied significantly between study sites. Study Sites C and D were associated with pro-longed Zn-smelting as compared with Sites A and B which in large part explains the significantly high levels of Pb, Zn and Cd at Sites C and D as compared with Sites A and B. Boulet and Iaroque (1998) suggested that time is one of the important factors controlling pollutant accumulation after they compared two abandoned skarn-type Cu-Zn mines with a 50y time difference.

Meanwhile, different discharge pathway of pollutants from smelters may also attribute to the varying accumulation levels of pollutants. At Sites A and B, atmospheric deposition of pollutants dominated, however, at Sites C and D, both atmospheric deposition and release from smelting slags were responsible for pollutant accumulations even though the atmospheric deposition-derived source was cut off after smelting ceased.

Even though prevailing wind direction is another important factor controlling metal accumulation in soils and sediments (Van Alphen, 1999), it was impossible to consider the importance of this factor due to the random sampling around the smelting furnaces; therefore, less consideration of this factor could be taken into account in this study.

Mineral components of stream sediments and water media conditions (such as pH) have an important impact on heavy metal retention. For example, adsorption and co-precipitation of soluble metals with non-metals at elevated media pH were observed by Domenico and Schwartz (1998) and Lottermoser *et al.* (1999). As theoretically estimated from the relationship showing the influence of water pH on metal adsorption on ferric hydroxide (Domenico and Schwartz, 1998), ferric hydroxides in the stream sediments could absorb 100% Pb, and as much as 70% Zn and 30% Cd under the alkaline conditions of stream water at Site D (where the stream water pH ranged from 7.38 to 8.14, and the Fe₂O₃ contents of stream sediment varied between 10 and 20%, Yang *et al.*, 2003). Subsequently, large proportions of iron and manganese oxide bound fractions of Pb and Zn could be reasonably expected in stream sediment samples at Site D (as shown in Figure 4).

Large proportions of carbonate bound Pb, Zn and Cd were noticeable at the studied sites, especially at Site D, however, under lower pH conditions, such as in the rhizosphere environment, carbonate minerals are more readily dissolved compared with pyrite and silicate minerals (Banwart and Malmstrom, 2001). At the studied sites, acid rain occurred frequently due to the daily coal combustion of local residents (Hong *et al.*, 1994). Furthermore, owing to shortage of farmlands, local residents also planted crops, such as potatoes, maize and vegetables on the soils scattered with smelting slags. Official statistics in 2000 (Wang *et al.*, 2000) showed that total crop production in Hezhang County reached 123580 tons, of which maize and potatoes accounted for 50.2 and 22.5%, respectively. As previously reported, metals Pb, Zn and Cd in carbonate minerals could be remobilized and released in the acidic environment in the rhizosphere and be uptaken up by crops (Jauert *et al.*, 2002; Hammer and Keller, 2002), and therefore, could harm human health

through the soil (sediment)-plant (drinking water)-human body chain. Nevertheless the carbonate rock geological setting at the sites studied could lessen this adverse effect to some degree.

5. Conclusions

It can be concluded that as compared with regional background levels, the metals Pb, Zn and Cd show heavy accumulation in soils and water sediments at the four studied sites. Prolonged smelting activities and different metal release patterns are mainly responsible for the great difference in metal levels between the four studied sites. The carbonate background induces high media pH and the chemical composition of soil and sediment in part contribute to the high metal accumulations. Large quantities of the metals Pb, Zn and Cd still remain in the two slag piles in spite of the losses due to the weathering process. Natural attenuation of bioavailability of metals can be observed; the formation of secondary metal carbonate minerals and the strong fixation ability of iron oxide and hydroxide minerals may contribute to this attenuation process.

However, potential impairment still persists due to the ready remobilization of carbonate bound metals under altered environments, resulting from regional acid deposition or rhizosphere activity, and this may have adverse effects on human health through the food chain. Therefore, it is suggested that remediation steps are taken immediately in the studied region.

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