

# Lead, Zn, and Cd in slags, stream sediments, and soils in an abandoned Zn smelting region, southwest of China, and Pb and S isotopes as source tracers

Yuangen Yang · Sun Li · Xiangyang Bi · Pan Wu ·  
Taozhe Liu · Feili Li · Congqiang Liu

Received: 1 September 2009 / Accepted: 7 May 2010 / Published online: 29 May 2010  
© Springer-Verlag 2010

## Abstract

**Purpose** Smelting activity produced tons of slags with large quantities of highly toxic metals, resulting in contamination in adjacent soils and sediments as well. This study investigated the fractionation and sources of metals Pb, Zn, and Cd in polluted soils and sediments in a region with once prosperous Zn smelting activities in southwestern China. Soils with varying land uses were of a special concern due to their connection to the food chain. Obtained data would offer a valuable reference to the development of land-use management strategy in this region.

**Materials and methods** In total, 130 soils and 22 stream sediments were sampled in the studied region. After air-dried and passed through a 2 mm sieve, soils and sediments were subjected to a three-step sequential extraction for the fractionation of Pb, Zn, and Cd. Besides, 66 slags were sampled, and acid-digested for the determination of total Pb, Zn, and Cd. Soils/sediments with extremely high Pb, Zn, and Cd concentrations were selected for observation and analysis using a scanning electron microscopy equipped with energy dispersive X-ray spectroscopy. Stable lead and sulphur isotope techniques were applied for source tracing of metals in soils and sediments. Data were pooled for analysis of variance together with a post-hoc multiple comparison procedure.

**Results and discussion** High concentrations of Pb (~46,219 mg kg<sup>-1</sup> with medians of 846 mg kg<sup>-1</sup> in soil, 7,415 mg kg<sup>-1</sup> in sediment, and 8,543 mg kg<sup>-1</sup> in slag), Zn

(~57, 178 mg kg<sup>-1</sup> with medians of 1,085 mg kg<sup>-1</sup> in soil, 15,678 mg kg<sup>-1</sup> in sediment, and 14,548 mg kg<sup>-1</sup> in slag), and Cd (~312 mg kg<sup>-1</sup> with medians of 29.6 mg kg<sup>-1</sup> in soil, 47.1 mg kg<sup>-1</sup> in sediment, and 47.9 mg kg<sup>-1</sup> in slag) were measured. Soils with no cultivation had greater concentrations of Pb (16,686 mg kg<sup>-1</sup> in median), Zn (13,587 mg kg<sup>-1</sup> in median), and Cd (44.1 mg kg<sup>-1</sup> in median) than those with cultivation. Al-normalized enrichment factors for Pb, Zn, and Cd were in 40.6–1,066, 11.6–382, and 128–647 in sediments, and in 58.0–1,771, 10.1–450, and 88.6–1,035 in soils. Greater Pb/Cd and Zn/Cd ratios in slags (241 and 386 in median) than in soils (uncultivated (187 and 267 in median) > cultivated) or sediments (106 and 260 in median) were observed, indicating extra atmospheric borne Cd in soils and sediments from smelting dust emission. Pb, Zn, and Cd were mainly associated with Fe/Mn oxides/hydroxides in soils and sediments, with their mobile fractions varying with land use in soils that had a close relation to pH ( $r=-0.569$ ,  $p<0.01$ ). In <sup>206</sup>Pb/<sup>207</sup>Pb~<sup>208</sup>Pb/<sup>206</sup>Pb diagram, plots of soils and sediments constructed a satisfactory linear model ( $p<0.01$ ) with wall rock, coal, and ore samples. Four different domains can be identified in the  $\delta^{34}\text{S}$ -<sup>206</sup>Pb/<sup>207</sup>Pb diagram, in which soils and sediments formed a domain with middle  $\delta^{34}\text{S}$  (-2.79~+10.3‰) and <sup>206</sup>Pb/<sup>207</sup>Pb ratios (1.1823~1.1853). **Conclusions** Smelting activities result in great enrichments of Pb, Zn, and Cd in surveyed soils and sediment. Mobile fraction of these metals was controlled by land use type as well as soil pH, which is informative for land use management to prevent toxic substance from potentially menacing human health. Bean cultivation and low pH can result in more Cd of mobile fraction in soils, therefore, alternative cultivation and pH elevation are recommended for the studied region. This would help reduce the remobilization and uptake of Cd from the polluted soils.

Responsible editor: Willie Peijnenburg

Y. Yang (✉) · S. Li · X. Bi · P. Wu · T. Liu · F. Li · C. Liu  
Institute of Geochemistry, Chinese Academy of Sciences,  
Guiyang City, Guizhou Province 550002,  
People's Republic of China  
e-mail: yangyuangen@hotmail.com

**Keywords** Chemical fractionation · Isotope tracing · Land use · SEM-EDS

## 1 Introduction

Besides atmospheric diffusion, smelting slags contained a large amount of residues from smelting activities. Nowadays, some may be processed as construction materials (Ettler et al. 2003), however, large amounts of slags were still piled and scattered in smelting regions, such as in southwestern China (Yang et al. 2006). These slags may re-enter soils or water/sediments through surface runoff flushing, weathering, or by human activities, resulting in an accumulation of toxic substances in soils and sediments. The releases of toxic substances from slags are chemically and mineralogically dependent on smelting techniques and ore components (Ettler et al. 2009). Therefore, there existed apparent differences in releases of heavy metals Pb, Cu, Zn, Cd, and As from slags resulting from processing of carbonate/oxide ores and sulphide ores (Ettler et al. 2009). Morrison and Gulson (2007) discovered particle size was reversely related to bioavailability of Pb with especially available part in slags at size <20  $\mu\text{m}$ .

Previous studies reported high accumulations of heavy metals in soils around metal smelters (Little and Martin 1972; Farago and O'Connell 1983; Verner et al. 1996; Ullrich et al. 1999; Basta and Gradwohl 2000; Li and Thornton 2001; Kaasalainen and Yli-Halla 2003; Förstner et al. 2004), possibly causing further accumulation in crops through plant uptake (Douay et al. 2008; Zhuang et al. 2009). River/lake sediment was another victim of heavy metal accumulations by such activities in recent studies (Förstner et al. 2004; Telmer et al. 2006; Boughriet et al. 2007; Aleksander-Kwaterczak and Helios-Rybicka 2009). Atmospheric deposition of chimney dust from smelting and release from slags under weathering were considered as two main contributions (Rolfe and Jennett 1975; Rieuwerts and Farago 1996).

However, toxicity of heavy metals is highly dependent on their bioavailability. Even though it is difficult to directly evaluate the bioavailability of heavy metals in the environment, sequential extraction techniques or single extraction methods were commonly served for such purposes (Tessier et al. 1979; Ure et al. 1993; Li et al. 1995; Houba et al. 1996; Figueiro et al. 2002; Prokop et al. 2003). Maiz's three-step sequential extraction (Maiz et al. 1997) is one among these extractions, which is simple to follow and time saving compared with other sequential extractions and has the advantage of reasonably estimating the amounts of available metals (Bi et al. 2006a).

Lead and zinc smelting activities in Guizhou province can be traced back to the Tang and Song dynasties, ca.

300 years ago. Such practices were described in ancient books such as "Pretty Brook, Laughing Cluster" and "Book of Guizhou-Lead in Kaili". Zinc smelting in Hezhang County was one among the most productive activities in Guizhou province in the past century. It produced 4,540 tons of coarse zinc and no refined zinc in 1985 surging up to 61,800 tons of coarse zinc and 46,400 tons of refined zinc by 2000, resulting in huge amounts of slags (more than 20 million tons) piling along the steep hill or scattering in the surrounding soils. Previous studies reported severe heavy metal pollution in soils in the vicinity of the zinc smelters in Hezhang County (Yang et al. 2006), even mosses accumulated great amounts of Pb, Zn, and Cd near these zinc smelters (Bi et al. 2006b), resulting in high concentrations of these metals in crops growing nearby (Bi et al. 2009).

This study was one attempt to thoroughly survey the region that once had the most smelting activities in China. The objectives were (1) to survey levels of Pb, Zn, and Cd in slags, soils, and stream sediments, and their enrichments in soils and sediments with respect to local soil and sediment backgrounds; (2) to estimate their bioavailabilities in soils and sediments; (3) to investigate their relations to Zn smelting activity using lead and sulphur isotope tracers. Based on these, the obtained results were designed to offer a reasonable strategy for land use management in this region.

## 2 Sampling and analytical methods

### 2.1 Field sampling

Soils, stream sediments, and smelting slags were sampled in a Zn smelting region in Guizhou province, southwest China (Latitude: 26°56'–27°01'N; Longitude: 104°31'–104°34'E). The region of this study has an elevation of 2,000–2,400 m above sea level, with a mean annual temperature of 12°C and annual rainfall of 900–1,200 mm year<sup>-1</sup>. Smelting furnaces were normally installed on the top of flat hills or the open platform of hillside. Even though smelting activities ceased, a large amount of slags piled along hillside, and were readily subjected to surface runoff, flushing into downhill agricultural fields and stream sediments. In total, 130 surface yellow brown soil samples (each sample is a composite of five points in each 1 m<sup>2</sup> area) were randomly collected in eight sampling locations at a depth of ~30 cm using a stainless spade. Black slag particles were occasionally visible in soils, especially in the uncultivated soils on slope hillsides. Under the USDA Taxonomy, the yellow brown soils of this area are classified as Alfisols (USDA 1992). A total of 23 stream sediments (each sample is a composite of three points in each 1 m<sup>2</sup>

area) were collected in three sampling locations at a depth of ~15 cm in three streams in the smelting region. Sixty-six slags in eight different slag piles (each sample is a composite of two points in each depth layer) were also vertically sampled in seven sampling locations for this study after the surface layer was exploited until the non-weathered slags were revealed. Most slag piles were 1–2 m in height and 2–3 m in diameter, consisting of particles from ~5 cm blocks to <1 mm powdery substance. Sampling locations are presented in Fig. 1.

After air-dried, samples were allowed to pass through a 2-mm stainless steel sieve to remove visible plant debris (for soil samples) and large stones. After mixing well, subsamples of soils and sediments were subjected to sequential extraction, while slags were ground to less than 0.125 mm for determination of total Pb, Zn, and Cd.

## 2.2 Fractionation of Pb, Zn, and Cd in soil and sediment and total Pb, Zn, and Cd in slag

A three-step sequential extraction method (Maiz et al. 1997) was applied for fractionation of Pb, Zn, and Cd in soils and sediments. Simply, 3 g of samples were first extracted in 30 ml 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution for 2 h (named as F1 in this study). After decanting the supernatant

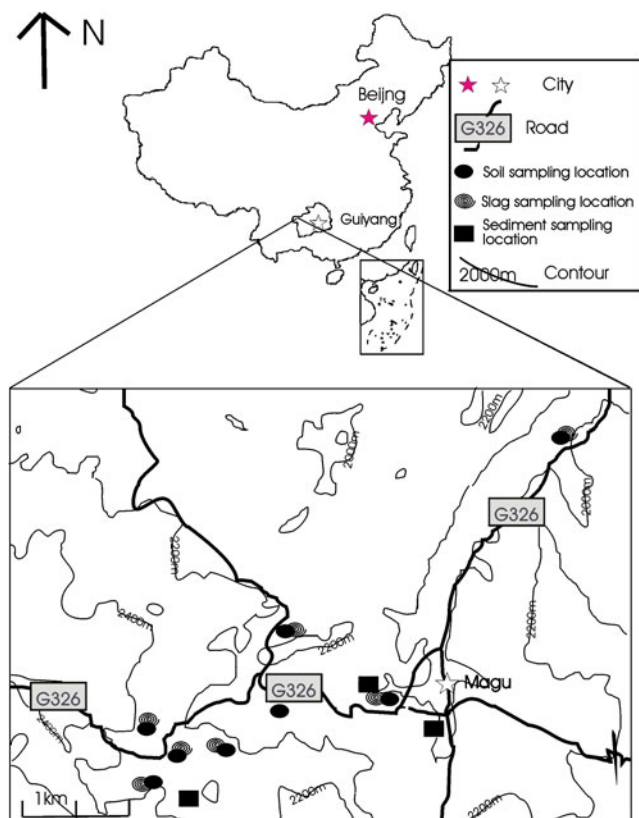
and washing twice using deionized H<sub>2</sub>O, the residue was then extracted in a complex of 6 ml 0.005 mol L<sup>-1</sup> DTPA, 0.1 mol L<sup>-1</sup> TEA, and 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution (pH≈7.3) for 4 h (named as F2). The final residue was then digested in mixed acids HNO<sub>3</sub> and HF for Pb, Zn, and Cd analysis (named as F3). Total Pb, Zn, and Cd in slags were determined following the mixed acid (HNO<sub>3</sub>, HClO<sub>4</sub>, and HF) digestion method of Tessier et al. (1979). The concentrations of Pb, Zn and Cd in the extracts/digestions were determined using an atomic absorption spectrometry with a graphite furnace (model PE5100PC). A standard soil sample SRM 2710 from the National Institute of Standards and Technology (NIST, USA) was used as a reference of quality control in this study. Duplicate analyses were performed every ten samples, and the recoveries of Pb, Zn, and Cd for SRM2710 were 90–110%, 95–105%, and 105–115%, respectively (Bi et al. 2006b).

## 2.3 SEM-EDS analysis

Samples of soil and sediment with extremely high Zn concentration (>20,000 mg kg<sup>-1</sup>) were selected for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis. For this purpose, these samples were first dispersed on a sheet of paper and amounts were reduced till about 20 g using a quartation method. The obtained samples were allowed to pass a 1 mm sieve and detained on a 0.125 mm sieve. Such portion of the samples (sand particles) were fixed onto a supporting plate using a double face tape, and then subjected to surface imaging and EDS determination after the surface was coated with carbon using an Amray KYKY-1000B SEM-EDS instrument at 25KV accelerating voltage with magnifications ranging from 20 to 12,000 (Lei 2000).

## 2.4 Pb and S isotopes

Pb isotopic composition analysis was performed using an ICP-MS (Perkin-Elmer ELAN 6000). For this, samples (soil and stream sediment) were first digested with a mixture of ultra pure acids (HCl, HNO<sub>3</sub>, and HF) until a bright yellow color developed. Then the digestion was extracted with a mixture containing 1 M HBr and 2 N HCl with a ratio of 1:2, and Pb was then eluted into a Teflon flask using 6 N HCl after being rinsed onto an AG-1X8 resin column. After evaporation, the Teflon flask containing purified Pb was preserved for Pb isotopic composition determination. A common Pb isotopic standard (NIST SRM 981) was used as Pb isotope quality control. Results of 1.0938±0.0011 and 2.3710±0.0030 for <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>207</sup>Pb in SRM 981 were comparable with their recommend values of 1.0933, and 2.3704, respectively, with an analytical error <0.046% (Bi et al. 2006b). Relative



**Fig. 1** A map showing sampling locations in this study

standard deviations of analytical samples were in 0.031–0.093%.

A method, suggested by Yanagisawa and Sakai (1983), was applied for sulphur isotope determination in this study. Briefly, sulphur in samples was first converted to BaSO<sub>4</sub>, which was then reduced to SO<sub>2</sub> by V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>-Cu at 900°C. Produced SO<sub>2</sub> was then quantified using a mass spectrometry (MAT-252) to obtain a <sup>34</sup>S/<sup>32</sup>S ratio, δ<sup>34</sup>S value of samples was then calculated. Sulphur isotope result was expressed as CDT (Canyon Diablo Troilite, <sup>34</sup>S/<sup>32</sup>S = 0.0450045 ± 93) standard value. Laboratory prepared BaSO<sub>4</sub> standard and two international S isotope reference samples (No. 220 seawater sulfate, NBS127; No. 253 silver sulfide, IAEA-S-1) were used for calibration with an analysis error <±0.1‰ (Zhang et al. 2004).

## 2.5 Data process

Analysis of variance together with a post-hoc multiple comparison procedure was used to compare results among soils, sediments, and slag (SPSS 10.0; SPSS Inc., Richmond, CA). Figures were computed using Sigma Plot 10.0 software (SPSS Inc., Richmond, CA, USA) and Corel Draw 9.0 software (Corel Corporation, Mountain View, CA, USA).

## 3 Results and discussion

### 3.1 Accumulation of Pb, Zn, and Cd in slag, soil, and stream sediment

Great variances of Pb (20.0–46,219 mg kg<sup>-1</sup>), Zn (37.2–57,178 mg kg<sup>-1</sup>), and Cd (<DL–312 mg kg<sup>-1</sup>) in slags, soils, and stream sediments were observed in the Zn smelting region (Table 1). Large amounts of Pb (averaging 10,679 mg kg<sup>-1</sup>), Zn (averaging 16,004 mg kg<sup>-1</sup>), and Cd (averaging 62.8 mg kg<sup>-1</sup>) remained in slag samples, and similar amounts of Pb (averaging 8,340 mg kg<sup>-1</sup>), Zn (averaging 15,463 mg kg<sup>-1</sup>), and Cd (averaging 57.6 mg kg<sup>-1</sup>) were also detected in sediment samples, however, smaller amounts of Pb (averaging 6,578 mg kg<sup>-1</sup>), Zn (averaging 6,141 mg kg<sup>-1</sup>), and Cd (averaging 34.9 mg kg<sup>-1</sup>) were in the soil samples (Table 1). These results are comparable to the extremely high concentrations of Pb (9,700–184,000 mg kg<sup>-1</sup>), Zn (28,200–120,900 mg kg<sup>-1</sup>), and Cd (12–6,940 mg kg<sup>-1</sup>) in smelting slags previously reported in Namibia (Ettler et al. 2009), and up to 25,000 mg kg<sup>-1</sup> of Pb in slags from a Pb–Zn smelter in Australia (Morrison and Gulson 2007). Even though there were no apparent differences in Pb, Zn, and Cd concentrations between the slag and sediment samples, the ratios of Pb/Cd and Zn/Cd were apparently higher (655 and 690,

**Table 1** Concentrations of Pb, Zn, and Cd (mg kg<sup>-1</sup>) and ratios of Pb/Cd and Zn/Cd in soils, sediments, and slags in the Zn smelting region

Item	Sample type	No of samples	Mean	Standard deviation	Median	95% confidence interval for mean		Minimum	Maximum
						Lower bound	Upper bound		
Pb	Soil	130	6,578b	9658	846	4902	8,254	27.9	37,770
	Sediment	22	8,340a,b	7,057	7,415	5,211	11,469	20.0	21,850
	Slag	66	10,679a	9,075	8,543	8,448	12,909	621	46,219
Zn	Soil	130	6,141b	8,430	1,085	4,678	7,604	37.2	31,625
	Sediment	22	15,463a	11,691	15,678	10,280	20,647	120	30,425
	Slag	66	16,004a	9,269	14,548	13,725	18,283	1,780	57,178
Cd	Soil	130	34.9b	30.5	23.7	29.6	40.2	<DL	131
	Sediment	22	57.6a	23.5	53.6	47.1	68.0	25.0	97.0
	Slag	66	62.8a	60.5	43.8	47.9	77.6	1.00	312
Pb/Cd	Soil	127	244b	482	54.9	160	329	0.299	3,637
	Sediment	22	123b	86.7	106	84.2	161	0.714	266
	Slag	66	655a	1,403	241	310	1,000	7.69	8,373
Zn/Cd	Soil	127	234b	469	86.6	151	316	3.47	3,848
	Sediment	22	225b	131	260	167	284	4.28	390
	Slag	66	690a	1,167	386	403	977	32.6	7,994

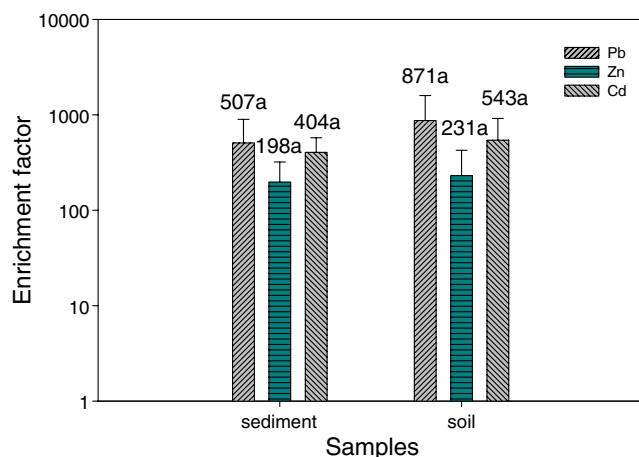
Means/ratios with different lowercase letters are statistically different at a significance level of  $p < 0.05$

DL detection limit



respectively) in slag samples than in sediments (123 and 225, respectively,  $p < 0.05$ ) and soils (244 and 234, respectively,  $p < 0.05$ ) (Table 1). Much smaller Pb/Cd and Zn/Cd ratios can be an indicator of extra atmospheric borne Cd in sediments and in soils from dust emission during Zn smelting (Bi et al. 2006b), indicating dust emission during Zn smelting can be an important metal source for soils and sediments. However, soils receiving dust emission from a Zn smelter near the sampling region had concentrations up to 300, 1,000, and 15 mg kg<sup>-1</sup> for Pb, Zn, and Cd, respectively (Yang et al. 2009). Considering the geographical locations of Zn smelting furnaces in the sampling region, slags can be another important source for the receiving stream sediments and agricultural soils down the mountains due to flushing of surface runoff.

Enrichment factors normalized by crustal Al (EF) (Ketterer et al. 2001) in the studied sediments were in 40.6–1066, 11.6–382, and 128–647 for Pb, Zn, and Cd with their averages of 507±389 (mean±SD), 198±122, and 404±170, respectively; whereas, EFs were in 58.0–1771(871±720), 10.1–450 (231±194), and 88.6–1035 (543±374) for Pb, Zn, and Cd in soils, respectively (Fig. 2). Apparently, Pb and Cd had greater EFs than Zn both in sediments and soils. This could be attributed to the more mobile property of Cd and Pb than Zn in the environment (Podlesakova et al. 2001), especially those affected by Zn smelting. Leaching experiments of air-pollution-control residues from smelting also indicated a more mobile feature of Cd than Pb and Zn (Ettler et al. 2008). Even though enrichment factors of Pb and Zn varied, a very close correlation between Pb and Zn in samples can be computed ( $R^2=0.805$ ,  $p < 0.01$ ). However,



**Fig. 2** Aluminum-normalized enrichment factor (EF) of Pb, Zn, Cd in soils and sediments in the Zn smelting region.  $EF_x = (X/REF)/(X_{crust}/REF_{crust})$  (Ketterer et al., 2001), where  $X$  represent Pb, Zn, and Cd in soils and sediments, here Al was chosen as crustal original REF. Crustal data of Al, Pb, Zn, and Cd referred from Wedepohl (1995). Data are presented as mean±1 SD. Means with same letters are not statistically different ( $p > 0.05$ )

such relationship between Pb and Cd was poor (Fig. 3). This suggested that even though Pb, Zn, and Cd are classified as the same group of chalcophile elements, they behaved differently in the smelting process at around 1,000°C (the boiling point for Pb, Zn, and Cd is 1,525°C, 906°C, and 767°C, respectively).

Significantly higher concentrations of Pb, Zn, and Cd ( $p < 0.05$ ) were observed in uncultivated soils than any cultivated soils, and soils cultivated with potato had higher Pb than soils with bean (Fig. 4). However, the differences in Zn and Cd were not apparent among soils cultivated with potato, maize, and bean (Fig. 4). Types of land use may not be decisive for Pb, Zn, and Cd accumulation in soils in the Zn smelting region; however, uptake of Pb, Zn, and Cd by different vegetations might affect the metal levels in soils in the long term. Another possible explanation could lie in more slag originated metals in uncultivated soils than those cropped with beans, since Pb/Cd and Zn/Cd ratios were much smaller in bean-cultivated soils (35.9 and 53.6 in average, respectively) than in other soils (>190 for Pb/Cd, with the highest of 439 in uncultivated soils and >110 for Zn/Cd, with the greatest of 461 in uncultivated soils).

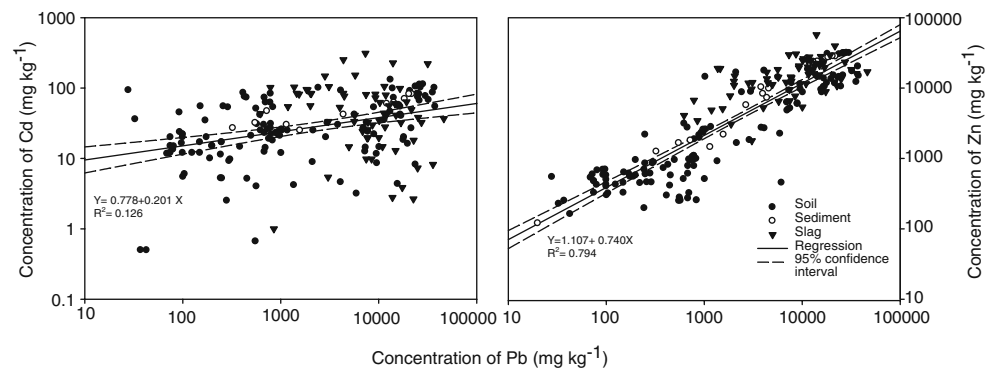
No apparent evidence can prove a crop type influencing soil metal levels, even though cropping can influence soil aggregation and organic matter under no tillage (Martins et al. 2009). Soil pH varied with crop types, lower pH ( $p < 0.05$ ) was measured in the bean cultivated soils ( $5.6 \pm 0.71$ ) than in noncultivated soils ( $6.5 \pm 0.79$ ). Metal migration in soils is highly pH dependent (Elzahabi and Yong, 2001), therefore, crop type may indirectly affect metal mobilization in soils through affecting soil pH. Such mechanism may suggest cropping management to be an important strategy in reducing soil metal availability in this region.

### 3.2 Fractionation of Pb, Zn, and Cd

A three-step sequential extraction was applied for the fractionation of Pb, Zn, and Cd in sediments and soils. Fraction one (F1, extracted by 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>) is readily mobile part in environment; F2 (extracted by DTPA) is regarded as mobilisable part, while F3 represents a relatively stable portion of metals (Maiz et al. 1997).

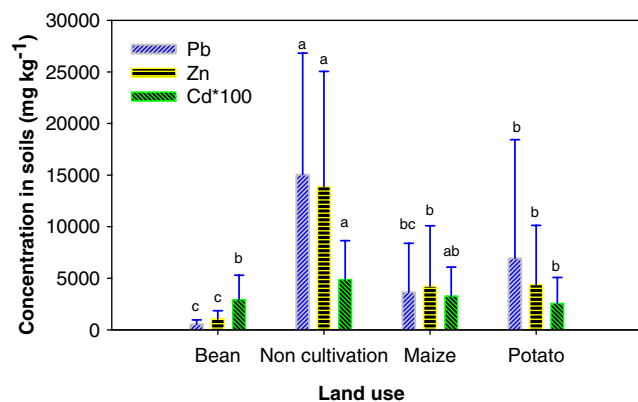
In this study, F3 was the dominant fraction, averagely made up to 7,606, 14,710, and 39.6 mg kg<sup>-1</sup> for Pb, Zn, and Cd in sediment and 8,436, 6,779, and 35.2 mg kg<sup>-1</sup> for Pb, Zn, and Cd in soils, respectively (Fig. 5). This suggests a large amount of Pb and Zn might remain relatively stable in the sediments and soils, which is similar to previous studies (Du et al. 2008; Udovic and Lestan 2009). F2 of Pb, Zn, and Cd were 673, 679, and 11.4 mg kg<sup>-1</sup> in average in sediments, and 352, 252, and 4.12 mg kg<sup>-1</sup> in soils, respectively (Fig. 5). Even though, F1 was the lowest of all three fractions, it made up to 62.0, 74.1, and

**Fig. 3** Relationships between Pb and Zn or Cd in soils, sediments, and slags in the Zn smelting region



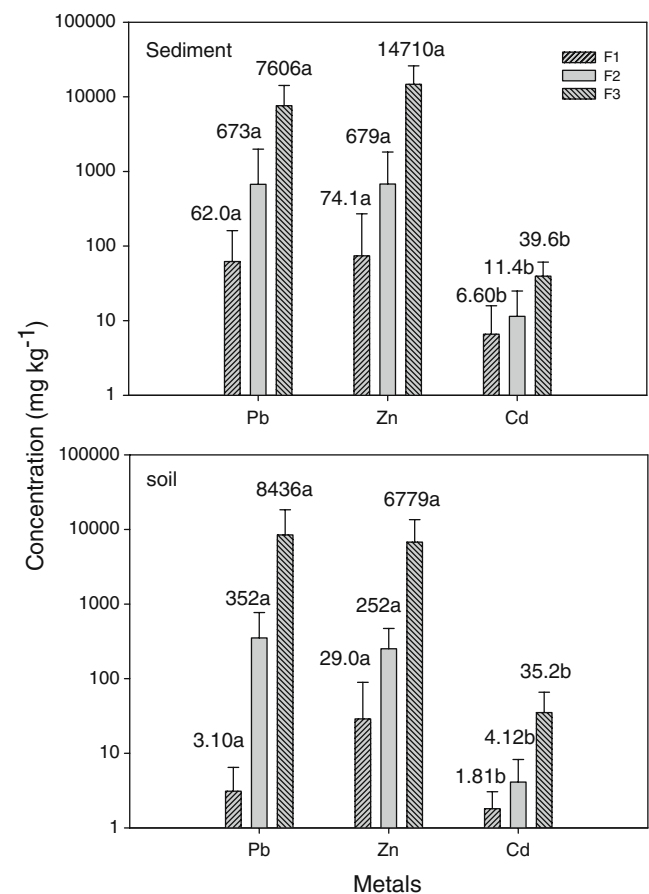
6.60 mg kg<sup>-1</sup> for Pb, Zn, and Cd in sediments, and 3.10, 29.0, and 1.81 mg kg<sup>-1</sup> in soils, respectively (Fig. 5). F2 of Pb, Zn, and Cd in the studied sediments were ~23, ~8, and ~128 times over their respective backgrounds (29.4, 89.9, and 0.31 mg kg<sup>-1</sup> for Pb, Zn, and Cd, respectively) in the sediment in Guizhou province (He 1998); whereas F1 of Pb, Zn, and Cd were ~2, ~1, and ~21 times over. This indicated highly mobile portions of metals (especially Cd) in the sediments that exceeded local background, which might be potentially toxic to water-sediment system. In soils, F2 of Pb, Zn, and Cd were ~10, ~2.5, and ~20 times exceeding their respective soil backgrounds in Guizhou (35, 100, and 0.20 mg kg<sup>-1</sup> for Pb, Zn, and Cd, respectively, EMS, 1990). F1 of Pb and Zn were below their respective backgrounds; however, F1 of Cd was ~9 times over its background. This result suggested Cd is greatly mobile in the studied soils, and could be potentially toxic to the cropping system. Such concern was also given by Du et al. (2008) and Udovic and Lestan (2009).

Fractions of Pb, Zn, and Cd in the studied soils varied with land uses. Potato cultivated soils had the highest Pb in F2 (1,022 mg kg<sup>-1</sup>) and F3 (23,786 mg kg<sup>-1</sup>), whereas, soils with bean cropping had the lowest (71.3 mg kg<sup>-1</sup> for F2 and 408 mg kg<sup>-1</sup> for F3) (Fig. 6). However, land uses



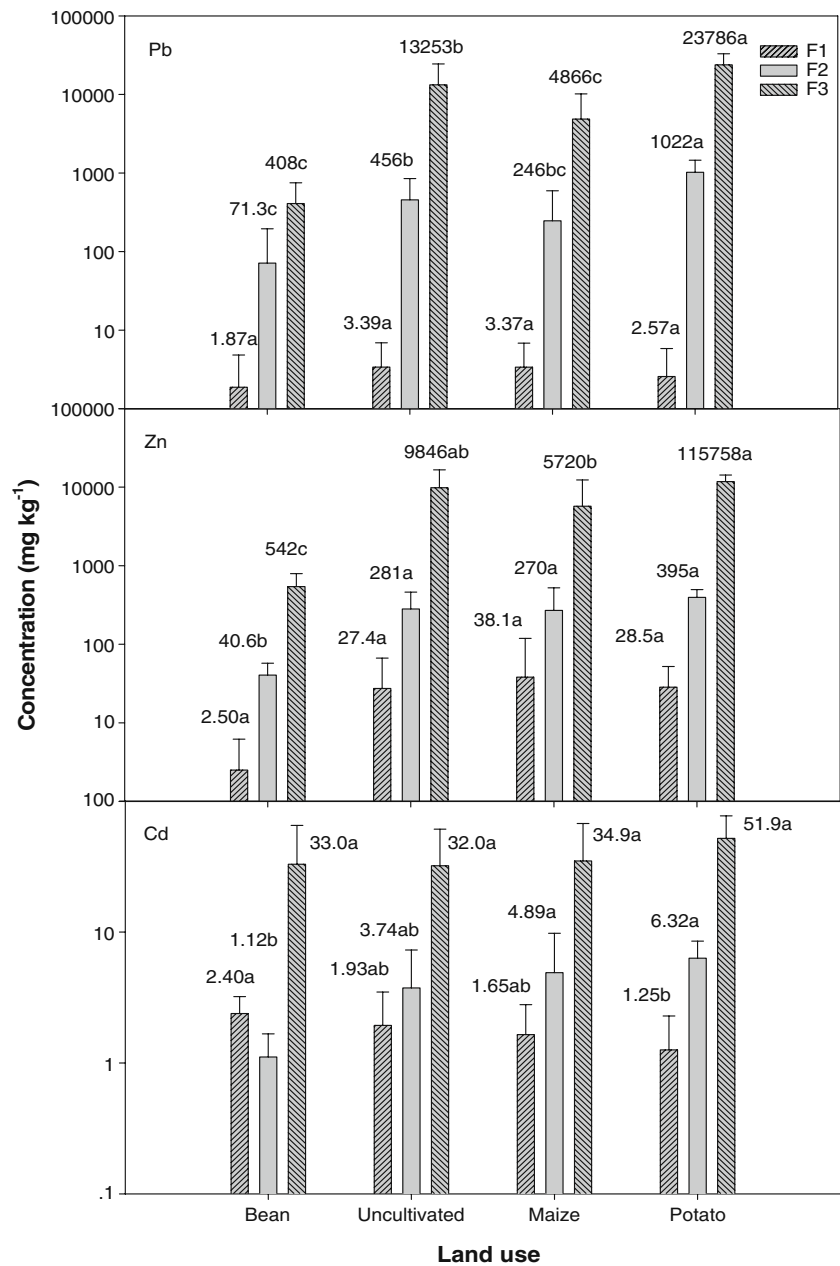
**Fig. 4** Concentrations of Pb, Zn, and Cd in soils in the Zn smelting area in relation to their land use types. Data are presented as mean ± 1 SD. Means with varying letters are statistically different among varying land uses ( $p < 0.05$ )

did not result in any differences in Pb in F1 (1.87–3.39 mg kg<sup>-1</sup>), which suggest mobile fraction of Pb might not be altered under varying land uses. Fractions of Zn demonstrated a comparable tendency among varying land uses with those of Pb, in which bean cultivated soils had extremely lower Zn fractions of F2 (40.6 mg kg<sup>-1</sup> in average) and F3 (542 mg kg<sup>-1</sup> in average) compared with soils under other land uses (Fig. 6).



**Fig. 5** Fractionations of Pb, Zn, and Cd in soils and sediments in the Zn smelting region. Data are presented as mean ± 1 SD. Means with varying letters are statistically different among varying land uses ( $p < 0.05$ )

**Fig. 6** Fractionations of Pb, Zn, and Cd in soils with different land uses. Data are presented as mean±1 SD. Means with varying letters are statistically different among varying land uses ( $p<0.05$ )



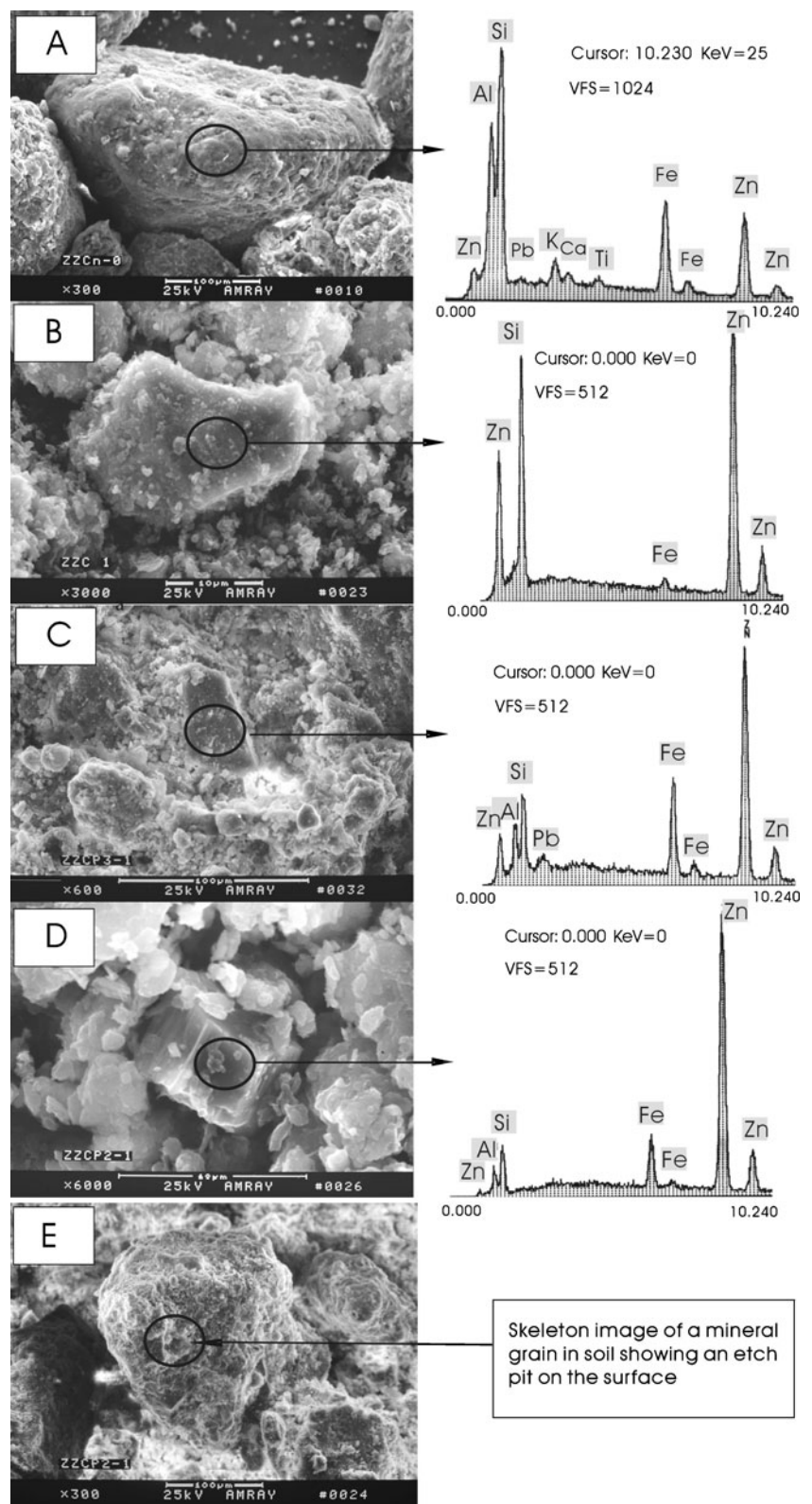
For Cd, the fraction of F3 did not vary among land uses, whereas, the greatest fraction of F2 was measured in potato (6.32 mg kg<sup>-1</sup>) and maize (4.89 mg kg<sup>-1</sup>) cultivated soils, and the lowest (1.12 mg kg<sup>-1</sup>) in soils with bean cultivation. However, the great fraction of F1 (2.40 mg kg<sup>-1</sup>) was observed in bean-cultivated soils (Fig. 6). Exudates of organic acids from plant roots, such as acetic acid, malic acid, and citric acid (Hinsinger 1999), can produce a low pH environment in rhizosphere, which could enhance the release of Cd. In the studied soils, bean cultivation resulted in a much lower pH (5.64±0.706,  $p<0.05$ ) than those cultivated with Maize (6.17±0.958) and potato (6.62±0.319), and uncultivated soil (6.52±

0.787). In addition, soil pH demonstrated a strong correlation with Cd in F1 ( $r=-0.569$ ,  $N=71$ ,  $p<0.01$ ), which could explain that a large part of Cd in F1 was measured in bean-cultivated soils that had a lower pH. Such information could drive the development of soil management, as well as cropping selection as an important strategy to immobilize metals, especially Cd so as to reduce its potential toxic to the food chain.

### 3.3 SEM observation

Slags usually had very complicated phase compositions (Ettler et al. 2005). In the studied slags, quartz minerals

**Fig. 7** Images showing that Pb and Zn were observed as carbonate minerals or strongly correlated to silicate minerals and Fe/Mn oxides in soil and sediment samples as revealed by SEM-EDS. Right are the EDS spectra for the center part of the relevant left images. **a** Pb and Zn were probably adsorbed onto silicate minerals or Fe and Mn oxides in sediments. Spectra at its right showing energy peaks of Si, Al, Fe, and K/Ca. **b** Zn minerals likely adhered to quartz grain and Fe oxides in sediments. Apparent spectra of Si (Fe) were detected (*right side* of image B). **c** Pb and Zn were observed to coexist with Fe oxides or silicate minerals in soils (*right side* showing spectra of Fe and Si). **d** Smithsonite grain was observed in soils (*diamond-shaped* grain in the center of image D) associated with silicate mineral or Fe oxides (spectra of Fe, Si, and Al observed in the right side of image D). **e** Round-shaped particle in soil showing etch pits



(such as quartz,  $\alpha$ -cristobalite), aluminum silicates, iron phases, and some amorphous phases (such as silicate glass) were the commonly observed phases. Smelting techniques and ore compositions are the two responsible factors for

such complicated phases in slags (Ettler et al. 2009), but supergene weathering action is also important for the occurrence of secondary phases (such as gibbsite, goethite, clay minerals), further influencing the phases of metals Pb,

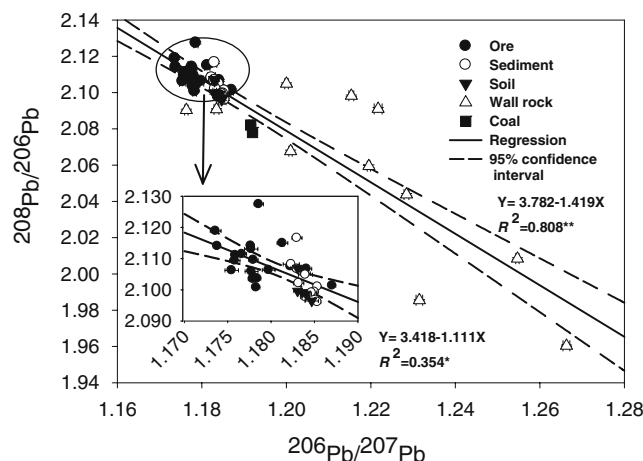


Zn, and Cd in slag piles. Pb mainly existed as Pb metal in the studied slags or adsorbed on the surface of Fe minerals. Zn can form as varying aluminum silicates, such as  $Zn_2SiO_4$ ,  $(Zn,Mn)_2SiO_4$ , and fibrous fraiponite  $(Zn_8Al_4(OH)_8(SiO_4)_5 \cdot 7H_2O)$ , or even Zn melting bead (Wu et al. 2002).

In soil and sediment, Pb and Zn were observed as carbonate minerals or strongly correlated to silicate minerals or Fe/Mn oxides (Homlstrom et al. 1999; Madrid 1999; Wolfgang 2000; Dinelli and Tateo 2001; Gutierrez et al. 2004). In this study, most of them were adsorbed by or adhered onto Fe/Mn oxides/hydroxides or Al silicates (Fig. 7). Exposed to surface flushing, round shapes and erosion pits were observed for most Pb and Zn contained particles (Fig. 7a). However, particles in the upstream sediment were angularly shaped, mainly as silicates with high Zn concentration (Fig. 7b). High concentrations of Pb and Zn in soils were mainly associated with Fe oxides and Al silicates in irregular shapes (Fig. 7c). These results agreed with the observations that Pb normally existed as  $Pb^{2+}$  and strongly adsorbed onto the surface of Al, Fe, and Mn oxides (Gesser et al. 1996), and Zn also showed strong binding ability to oxides under the surface environment (Kuo et al. 1983). Singh et al. (1999) noticed as well that large grains were difficult to move and easy to form oxide coatings on the surface to detain heavy metals. Rhombohedron-shaped smithsonite grains were occasionally found in soils (Fig. 7d), probably due to the carbonate rock background in the smelting region. This could be supported by positive correlations of soil pH with concentrations of metals Pb ( $r=0.427, N=71, p<0.01$ ), Zn ( $r=0.749, N=71, p<0.01$ ), and Cd ( $r=0.264, N=71, p<0.05$ ) in the studied soils. Subjected to reactions with soil solution, Pb/Zn-contained minerals were observed with etching pits on their surface (Fig. 7e). With the elevation of pH, Fe and Al oxides/hydroxides can increase the binding ability to metals Pb, Zn, and Cd (Gasser et al. 1996). Consequently, increment of soil pH could be one effective management measure in reducing mobilization of metals in the studied region. Due to the relatively low concentration of Cd compared with Pb or Zn in samples, no response spectra of Cd were detected by SEM-EDS (Fig. 7).

### 3.4 Lead and sulphur isotope features

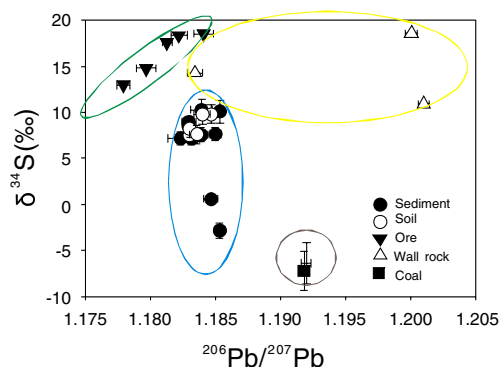
Lead stable isotope tracer has been widely applied in environmental pollution research, serving as a source tracer for contaminants and their migrating routes, or as an indicator for discrimination of anthropogenic contamination in atmosphere, sediments and soils (Sturges and Barrie 1989; Munksgaard 1998; Polissar et al. 1999; Cloquet et al. 2006). For examples, Ketterer et al. (2001) proved zinc smelting as a source for Pb and Zn pollution in Pennsylvania soils, USA with the adoption of stable lead isotopes,



**Fig. 8** Pb isotopes in soils and sediments in the Zn smelting region and their relations with wall rock, ore, and coal. Data are presented as mean±1 SD; \* $p<0.05$  and \*\* $p<0.01$  denote correlation significance levels

Sonke et al. (2002) reported as well a heavy metal contamination in a sediment core that was associated with mining activities by application of this stable lead isotope technique.

In this study, the  $^{206}Pb/^{207}Pb$  ratios of soils and sediments varied in 1.1823–1.1853 with an average of 1.1839, which is within the range of ore samples (1.1736–1.1870) and wall rocks (1.1763–1.2663) (Fig. 8). The  $^{208}Pb/^{206}Pb$  ratios of soils and sediments were in 2.0961–2.1166 with an average of 2.1022, which is also within the scope of ore samples (2.1008–2.1274) (Liao 1984), but is partially overlapped by wall rocks (1.9603–2.1049) (Wang et al. 1996) (Fig. 8). These results are comparable with the lead isotopic compositions from Pb smelter slags and heavy metal polluted sediments in the study of Aberg et al. (2001). In the  $^{206}Pb/^{207}Pb \sim ^{208}Pb/^{206}Pb$  diagram, plots of soils and sediments were clustered together, and had an excellent linear fitting model with plots of ore, wall rock, and coal samples ( $R^2=0.808, p<0.01$ ), however, they were more closely



**Fig. 9** Sulfur and Pb isotopes in soils and sediments in relation to those in ores, wall rocks, and coals. Data are presented as mean±1 SD

related to ores (Fig. 8). This suggested that there existed a two-end member mixing model for Pb in soils and sediments: ore made one end member, whereas coal and wall rock the another, however, zinc-smelting source was more apparently affecting the Pb isotope features in soils and sediments.

Low  $\delta^{34}\text{S}$  values were noticed in sediment samples (<0.00‰), however, most soils and sediments had a very narrow range of  $\delta^{34}\text{S}$ , from +7.13 to +10.30‰, which was smaller than ore and wall rock samples. The latter normally had  $\delta^{34}\text{S}$  values larger than 10.0‰ to up to 18.6‰ (Fig. 9). The sulphur isotope value of mine pit water in this region was +7.80‰, very similar to those of the soils and sediments, suggesting a close relationship of sulphur in soils and sediments with that in ores. Four different domains can be discriminated in the  $\delta^{34}\text{S}$  -  $^{206}\text{Pb}/^{207}\text{Pb}$  diagram (Fig. 9). Ores were clustered at the top left with the lowest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and highest  $\delta^{34}\text{S}$  values, and wall rock samples were clustered at the top right with the highest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, however, soils and sediments had the low  $\delta^{34}\text{S}$  values and median  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, whereas coals made a domain with the lowest  $\delta^{34}\text{S}$  and high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (Fig. 9). This may suggest a sulphur isotope fractionation in sulfide ores during zinc smelting activities (Thode 1991), when light sulphur ( $^{32}\text{S}$ ) mainly released with evaporation and probably precipitated into soils and sediments. Another possibility is that part of the sulphur was from coal combustion, since coals in this region had much lower  $\delta^{34}\text{S}$  values ( $\sim -6.39\%$ , Hong et al. 1993) and were used as both combustion and a catalyst during zinc smelting.

Both lead and sulphur stable isotopes proved that Zn smelting had severely polluted soils and sediments in the

studied region, therefore, since smelting activity ceased, afterwards measures to immobilize metals is an essential to prevent them from entering the food-chain.

#### 4 Conclusions

Extremely high concentrations of Pb, Zn and Cd were measured in soils and sediments in the studied region. Peak concentration of Pb in soils overwhelmed the highest report value (8,714 mg kg<sup>-1</sup> from Lastenia, Argentina, Friesl-Hanl et al. 2009) in the soils worldwide affected by Pb/Zn smelters (Table 2). Zinc was comparable to 31,175 mg kg<sup>-1</sup> from Aubry, France (Sterckeman et al. 2000), and Cd had one comparable partner from Pribram, Czech Republic (129 mg kg<sup>-1</sup>, Boruvka and Vacha 2006), but was less than from Oklahoma, USA (Basta et al. 2001) and Aubry, France (Sterckeman et al. 2000, Table 2). Therefore, severe enrichments of these metals in soils and sediments were observed comparing with their respective regional background levels. However, the enrichments in soils varied with land uses. Sequential extraction and SEM-EDS observation revealed that Pb, Zn, and Cd in soils and sediments were either adsorbed onto the surface of Fe, Mn oxides/hydroxides, or involved in Al silicates or formed as carbonate minerals. In sediments, mobile fractions of Pb and Cd exceeded their respective local background, whereas in soils, mobile fraction of Cd was nine times over its local soil background. Lead and S isotope combination proved that Zn smelting was responsible for metal enrichments in the adjacent soils and sediments.

**Table 2** Comparison of peak Pb, Zn, and Cd concentrations in soils and sediments affected by Pb/Zn smelter with referenced studies

Region	Pb (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Source
Soil				
Lastenia, Argentina	8,714	1,637	30.7	Friesl-Hanl et al. (2009)
Pribram, Czech Republic	8,445	11,739	129	Boruvka and Vacha (2006)
Avonmouth, UK	4,210	3,970	79.0	Gary et al. (2006)
Kremikovtzi Plovdiv, Bulgaria	4,196	5,231	87.0	Bacon and Dinev (2005)
Oklahoma, USA	2,450	19,510	296	Basta et al. (2001)
Noyelles-Godault Aubry, France	5,410	31,175	305	Sterckeman et al. (2000)
Landskrona, Sweden	2,100	1,160	7.80	Farago et al. (1999)
Bukowno, Poland	3,570	12,400	73.2	Verner et al. (1996)
Guizhou, China	37,770	31,625	131	This study
Sediment				
Fendrod Lake, South Wales, UK	1,289	34,855		Blake et al. (2007)
Deule, France	10,079	12,895	1,399	Boughriet et al. (2007)
Kempen region, Belgium	47,000	11,000	1,000	Sonke et al. (2002)
Guizhou, China	21,850	30,425	97.0	This study

## 5 Recommendations and perspectives

Source, release mechanism, and migration route are important for heavy metal contaminated soil management and pollution prevention. Obtained results suggested mobile fraction of Cd in soils should be of most concern, and relevant measures to prevent the pollutants from entering the food chain are of an urgent necessity. Since smelting activities have ceased, best land use management practices to prohibit remobilization and translocation of Cd are recommended. Alternative cultivation (for example, replacement of bean cropping) and pH elevation of soils could be suitable strategies in the studied region.

**Acknowledgments** This study was supported in part by One Hundred Talents Program of CAS, the Science Innovation Program of the Chinese Academy of Sciences (CAS) (No. KZCX2-105), and the Western Light of CAS. Anonymous reviewers are appreciated for their key suggestions in improving the manuscript.

## References

- Aberg G, Charalampides G, Fosse G, Hjelmseth H (2001) The use of Pb isotopes to differentiate between contemporary and ancient sources of pollution in Greece. *Atmos Environ* 35: 4609–4615
- Aleksander-Kwaterczak U, Helios-Rybicka E (2009) Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of South Poland. *J Soils Sediments* 9:13–22
- Bacon JR, Dinev NS (2005) Isotopic characterisation of lead in contaminated soils from the vicinity of a non-ferrous metal smelter near Plovdiv, Bulgaria. *Environ Pollut* 134:247–255
- Basta NT, Gradwohl R (2000) Estimation of Cd, Pb, and Zn bioavailability in smelting-contaminated soils by a sequential extraction procedure. *J Soil Contam* 9:149–164
- Basta NT, Gradwohl R, Snethen KL, Schroder JL (2001) Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. *J Environ Qual* 30:1222–1230
- Bi XY, Yang YG, Feng XB (2006a) Evaluation of phytoavailability of zinc and cadmium in contaminated soils by a short sequential extraction procedure. *Environ Sci* 27(4):770–774
- Bi X, Feng X, Yang Y, Qiu G, Li G, Li F, Liu T, Fu Z, Jin Z (2006b) Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China. *Environ Int* 32(7):883–890
- Bi X, Feng X, Yang Y, Li X, Shin G, Li F, Qiu G, Li G, Liu T, Fu Z (2009) Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions. *Environ Pollut* 157:834–839
- Blake WH, Walsh RPD, Reed JM, Barnsley MJ, Smith J (2007) Impacts of landscape remediation on the heavy metal pollution dynamics of a lake surrounded by non-ferrous smelter waste. *Environ Pollut* 148:268–280
- Boruvka L, Vacha R (2006) Litavka river alluvium as a model area heavily polluted with potentially risk elements. In: Morel JL (ed) *Phytoremediation of metal-contaminated soils*. Springer, Dordrecht, Netherland, pp 267–298
- Boughriet A, Proix N, Billon G, Recourt P, Ouddane B (2007) Environmental impacts of heavy metal discharges from a smelter in Deule-canal sediments (Northern France): concentration levels and chemical fractionation. *Water Air Soil Pollut* 180(1–4):83–95
- Cloquet C, Carignan J, Libourel G, Sterckeman T, Perdrix E (2006) Tracing source pollution in soils using cadmium and lead isotopes. *Environ Sci Technol* 40(8):2525–2530
- Dinelli E, Tateo F (2001) Factors controlling heavy metal dispersion in mining areas: the case of Vigonzano (northern Italy), a Fe–Cu sulfide deposit associated with ophiolitic rock. *Environ Geol* 40(9):1138–1150
- Douay F, Roussel H, Pruvot C, Waterlot C (2008) Impact of a smelter closedown on metal contents of wheat cultivated in the neighborhood. *Environ Sci Pollut Res* 15:162–169
- Du P, Xue ND, Liu L, Li FS (2008) Distribution of Cd, Pb, Zn, and Cu and their chemical speciation in soils from a peri-smelter area in northeast China. *Environ Geol* 55:205–213
- Elzhabi M, Yong RN (2001) pH influence on sorption characteristics of heavy metal in the vadose zone. *Eng Geol* 60(1–4):61–68
- Ettler V, Piantone P, Touray JC (2003) Mineralogical control on inorganic contaminant mobility in leachate from lead–zinc metallurgical slag: experimental approach and long-term assessment. *Mineral Mag* 67:1269–1283
- Ettler V, Johan Z, Baronnet A, Jankovsky F, Gilles C, Mihaljevic M, Sebek O, Strnad L, Bezdzicka P (2005) Mineralogy of air-pollution-control residues from a secondary lead smelter: environmental implications. *Environ Sci Technol* 39(23):9309–9316
- Ettler V, Sebek O, Grygar T, Klementova M, Bezdzicka P, Slavikova H (2008) Controls on metal leaching from secondary Pb smelter air-pollution-control residues. *Environ Sci Technol* 42(21):7878–7884
- Ettler V, Johan Z, Kribek B, Sebek O, Mihaljevic M (2009) Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. *Appl Geochem* 24(1):1–15
- Fangueiro D, Bermond A, Santos E, Carapuca H, Duarte A (2002) Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA extractions: search for optimal experimental conditions. *Anal Chim Acta* 459:245–256
- Farago ME, O'Connell JT (1983) Soil and plant concentrations of cadmium and zinc in the vicinity of a smelter. *Miner Environ* 5:71–78
- Farago ME, Thornton I, White ND, Tell I, Martensson MB (1999) Environmental impacts of a secondary lead smelter in LANDSKRONA, southern Sweden. *Environ Geochem Health* 21:67–82
- Förstner U, Heise S, Schwartz R, Westrich B, Ahlf W (2004) Historical contaminated sediments and soils at the River basin scale. Examples from the Elbe River catchment area. *J Soils Sediments* 4(4):247–260
- Friessl-Hanl W, Platzer K, Horak O, Gerzabek MH (2009) Immobilising of Cd, Pb, and Zn contaminated arable soils close to a former Pb/Zn smelter: a field study in Austria over 5 years. *Environ Geochem Health* 31:581–594
- Gesser UG, Walker WJ, Dahlgren RA, Borch RS, Burau RG (1996) Lead release from smelter and mine waste impacted materials under simulated gastric conditions and relation to speciation. *Environ Sci Technol* 30(3):761–769
- Gutierrez M, Neill H, Grand RV (2004) Metals in sediments of springs and cave streams as environmental indicators in karst areas. *Environ Geol* 46(8):1079–1085
- He SL (1998) Geochemical background of supergene sediments in Guizhou. *Guizhou Geol* 15(2):149–156
- Hinsinger P (1999) Bioavailability of trace elements as related to root-induced chemical changes in the rhizosphere. In: Wenzel WW, Adriano DC, Alloway B, Doner HE, Keller C, Lepp NW, Mench M, Naidu R, Pierzynski GM (eds) *Proceedings of Extended*

- Abstracts of 5th International Conference on the Biogeochemistry of Trace Elements, Vienna, pp 152–153
- Homlstrom H, Ljungberg J, Ohlander B (1999) Role of carbonates in mitigation of metal release from mining waste. Evidence from humidity cells tests. *Environ Geol* 37(4):267–280
- Hong YT, Zhang HB, Zhu YX (1993) Sulfur isotopic characteristics of coal in China and sulfur isotopic fractionation during the coal-burning process. *Chinese Journal of Geochemistry* 12(1):51–59
- Houba VJG, Lexmond ThM, Novozamsky I, Van der Lee JJ (1996) State of the art and future developments in soil analysis for bioavailability assessment. *Sci Total Environ* 178:21–28
- Kaasalainen M, Yli-Halla M (2003) Use of sequential extraction to assess metal partitioning. *Environ Pollut* 126:225–233
- Ketterer ME, Lowry JH, Simon J, Humphries K, Novotnak MP (2001) Lead isotopic and chalcophile element compositions in the environment near a zinc smelting-secondary zinc recovery facility, Palmerton, Pennsylvania, USA. *Appl Geochem* 16:207–229
- Kuo S, Heilman PE, Baker AS (1983) Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. *Soil Sci* 135:101–109
- Lei P (2000) Application of SEM and EDS for indentifying judicial evidence. *Phys Test Chem Anal, Part A: Phys Anal (In Chinese)* 36(11):505–507
- Li X, Thornton I (2001) Chemical partitioning of trace and major elements in soils contaminated mining and smelting activities. *Appl Geochem* 16:1693–1706
- Li X, Coles BJ, Ramsay MH, Thornton I (1995) Sequential extraction of soils for multi element analysis by ICP-AES. *Chem Geol* 124:109–123
- Liao W (1984) Sulfur and Lead isotope features in lead and zinc ore deposits in the region of eastern Yunnan province and western Guizhou province. *Geol Explor* 1:1–6 (in Chinese with English abstract)
- Little P, Martin MH (1972) A survey of zinc, lead and cadmium in soil and natural vegetation around a smelting complex. *Environ Pollut* 3:241–254
- Madrid L (1999) Metal retention and mobility as influenced by some organic residues added to soils: a case study. In: Selim HM, Iskandar IK (eds) *Fate and transport of heavy metals in the vadose zone*. CRC Press, Boca Raton, pp 201–223
- Maiz I, Esnaola MV, Millin E (1997) Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. *Sci Total Environ* 206(2–3):107–115
- Martins MD, Cora JE, Jorge RF, Marcelo AV (2009) Crop type influences soil aggregation and organic matter under no-tillage. *Soil Tillage Res* 104(1):22–29
- Morrison AL, Gulson BL (2007) Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. *Sci Total Environ* 382(1):30–42
- Munksgaard NC, Parry DL (1998) Lead isotope ratios determined by ICP-MS: monitoring of mining-derived metal particulates in atmospheric fallout, Northern Territory, Australia. *Sci Total Environ* 217:113–125
- Podlesakova E, Nemecek J, Vacha R (2001) Mobility and bioavailability of trace elements in soils. In: Iskandar IK, Kirkham MB (eds) *Trace elements in soil: bioavailability, flux and transfer*. CRC Press, Florida, pp 21–42
- Polissar AV, Hopke PK, Paatero P, Kaufmann YJ, Hall DK, Bodhaine BA, Dutton EG, Harris JM (1999) The aerosol at Barrow, Alaska: long-term trends and source locations. *Atmos Environ* 33:2441–2458
- Prokop Z, Cupr P, Zlevorova-Zlamalikova V, Komarek J, Dusek L, Holoubek I (2003) Mobility, bioavailability, and toxic effects of cadmium in soil samples. *Environ Res* 91:119–126
- Rieuwerts J, Farago M (1996) Heavy metal pollution in the vicinity of a secondary lead smelter in the Czech Republic. *Appl Geochem* 11:17–23
- Rolfé GL, Jennett JC (1975) Environmental lead distribution in relation to automobile and mine and smelter sources. In: Krenkel PA (ed) *Heavy metals in the aquatic environment*. Pergamon Press, Oxford, pp 231–241
- Singh AK, Hasnain SI, Banerjee DK (1999) Grain size and geochemical partitioning of heavy metals in sediments of the Damodar River—a tributary of the lower Ganga, India. *Environ Geol* 39(1):90–98
- Sonke JE, Hoogewerff JA, Van der Laan SR, Vangronsveld J (2002) A chemical and mineralogical reconstruction of Zn-smelter emissions in the Kempen region (Belgium), based on organic pool sediment cores. *Sci Total Environ* 292:101–119
- Sterckeman T, Douay F, Proix N, Fourrier H (2000) Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. *Environ Pollut* 107:377–389
- Sturges WT, Barrie LA (1989) Stable lead isotope ratios in Arctic aerosols: evidence for the origin of air pollution. *Atmos Environ* 23(11):2513–2519
- Telmer KH, Daneshfar B, Sanborn MS, Kliza-Petelle D, Rancourt DG (2006) The role of smelter emissions and element remobilization in the sediment chemistry. *Geochem* 6:187–202
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51(7):844–851
- Thode HG (1991) Sulphur isotopes in nature and the environment: an overview. In: Krouse HR, Grinenko VA (eds) *Stable isotopes in the assessment of nature and anthropogenic sulphur in the environment*. Wiley, Indianapolis, pp 1–26
- Udovic M, Lestan D (2009) Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching. *Chemosphere* 74(10):1367–1373
- Ullrich SM, Ramsey MH, Helios-Rybicka E (1999) Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland. *Appl Geochem* 14:187–196
- United States Department of Agriculture (USDA) (1992) *Soil taxonomy—a basic system of soil classification for making and interpreting soil surveys*. Government Printing Office, Washington, DC, p 863
- Ure A, Quevauviller Ph, Muntau H, Griepink B (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int J Environ Anal Chem* 51:135–151
- Verner JF, Ramsey MH, Helios-Rybicka E, Jedrzejczyk B (1996) Heavy metal contamination of soils around a Pb–Zn smelter in Bukowno, Poland. *Appl Geochem* 11(1–2):11–16
- Wang H, Liang F, Zeng D, Wang H (1996) *Guizhou Lead and Zinc ore deposit Geology*. Guizhou Science and Technology Publish House, Guiyang, pp 126–141
- Wedepohl KH (1995) The composition of the continental crust. *Geochim Cosmochim Acta* 59:1217–1232
- Wolfgang W (2000) Small-scale variability of metal concentrations in soil leachates. *Soil Sci Soc Am J* 64:138–143
- Wu P, Liu CQ, Yang YG, Zhang GP (2002) The mineralogical characteristics of heavy metals (Pb, Zn) in historical Zn smelting wastes. *Acta Mineral Sinica* 22(1):65–70
- Yanagisawa F, Sakai H (1983) Thermal decomposition of barium sulfate-vanadium pentoxide-silica glass mixtures for preparation



- of sulfur dioxide in sulfur isotope ratio measurements. *Anal Chem* 55:985–987
- Yang YG, Liu CQ, Pan W, Zhang GP, Zhu WH (2006) Heavy metal accumulation from zinc smelters in a carbonate rock region in Hezhang County, Guizhou Province, China. *Water Air Soil Poll* 174(1–4):321–339
- Yang YG, Jin ZS, Bi XY, Li FL, Sun L, Liu J, Fu ZY (2009) Atmospheric deposition-carried Pb, Zn, and Cd from a zinc smelter and their effect on soil microorganisms. *Pedosphere* 19(4):422–433
- Zhang GP, Liu CQ, Yang YG, Wu P (2004) Characterization of heavy metals and sulfur isotope in water and sediments of a mine-tailing rich in carbonate. *Water Air Soil Poll* 155(1–4):51–62
- Zhuang P, McBride MB, Xia H, Li N, Li Z (2009) Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Sci Total Environ* 407:1551–1561