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Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China

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Abstract

Total heavy metal (Cd, Cr, Cu, Pb and Zn) concentrations were evaluated in smelting waste, soil, crop and moss samples collected from the Hezhang artisanal zinc smelting areas, Guizhou, China. Soil samples from the cornfield near the smelting sites contained extremely high Cd (5.8–74 mg kg^{-1}), Pb (60–14,000 mg kg^{-1}) and Zn (260–16,000 mg kg^{-1}) concentrations. Elevated heavy metal concentrations were also found in corn plants and total Pb (0.80–1.5 mg kg^{-1}) and Cd (0.05–0.76 mg kg^{-1}) concentrations in corn grain have totally or partially exceeded the national guidance limits for foodstuff. Thus, the soil-to-crop transfer of heavy metals might pose a potential health risk to the local residents. Similar to the high heavy metal levels in soil and corn, Cd, Cr, Cu, Pb and Zn concentrations in moss samples collected from the smelting sites ranged from 10 to 110, 10 to 55, 26 to 51, 400 to 1200 and 330 to 1100 mg kg^{-1}, respectively, exhibiting a local spatial pattern of metals deposition from the atmosphere. Based on examination of Zn/Cd and Pb/Cd ratios of the analyzed samples, we have distinguished between the flue gas dust derived and smelting waste derived metals in different environmental compartments.

Keywords: Zinc smelting activity; Heavy metal; Soil; Crop; Moss; Source attribution; Hezhang; China

1. Introduction

Nonferrous metals smelting is considered as one of the most important anthropogenic sources of heavy metal pollution to the environment worldwide (Rieuwerts and Farago, 1996; Sterckeman et al., 2000; Barcan, 2002; Cui et al., 2004; Bacon and Dinev, 2005). Such pollutants have been attributed to emissions from both smelter stacks and fugitive sources such as stockpiles and waste heaps (Rieuwerts and Farago, 1996). Smelting emitted metals are transferred to environmental compartments, such as water, soil and plant, and can eventually enter the human bodies through food chains or direct ingestion, which will pose a threat to human health. Many studies have reported the high levels of Pb and Cd in the blood and urine of people, particularly children living close to nonferrous metal smelters (Silvany-Neto et al., 1989; Ariane et al., 2001; Fischer et al., 2003; Cui et al., 2005).

Since the 17th century, artisanal zinc smelting using indigenous methods had been widely applied in Hezhang County located at western Guizhou Province, SW China. The zinc smelting activities were completely ceased in 2004 due to the concern of environmental pollution. During the long-term zinc smelting activities in Hezhang, huge quantities of exhaust gases containing many kinds of heavy metals had been released into air, and significant quantities of smelting wastes had been produced into piles and spoil heaps. Feng et al. (2004) and Bi et al. (in press) estimated that approximately 50 ton of Hg and 450 ton of Cd were released into the atmosphere from the zinc smelting activities in Hezhang, from 1989 to 2001. Previous studies related to metal contamination to the local environment were conducted at Hezhang district, and data shown that the local surface water, air and soil compartments were seriously contaminated with heavy metals (Shen et al., 1991; Yang et al.,

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2003; Wu et al., 2002; Feng et al., 2004, in press). However, these researches focused only on limited individual samples, and the impacts of metal contamination on the ecosystem have not been fully discussed.

In this study, we for the first time systemically measured heavy metal (Cd, Cr, Cu, Pb and Zn) concentrations in smelting waste, soil, crop and moss compartments at zinc smelting areas in Hezhang for the following purposes: (1) delineate the extents of heavy metal contamination and assess their potential health risk to the local residents related to the zinc smelting activities; (2) distinguish heavy metal origin of different sample compartments by using Zn/Cd and Pb/Cd ratios.

2. Methods

2.1. Study area

Hezhang County (104°10′–105°03′E, 26°46′–27°28′N) is situated at about 340 km west of Guiyang, the capital of Guizhou Province. It lies on the Yunnan-Guizhou Plateau with altitudes varying from 1230 to 2900 m above sea level. Its climate represents a typical subtropical humid monsoon with an average temperature of 13.4 °C and an average annual rainfall of 854 mm. The main soil types are ultisol and limestone soil, and the main crop is corn plant with planting area up to 80%.

All artisanal zinc smelting furnaces were distributed along rivers and valleys in an area <150 km^2 around Magu in Hezhang county. Five smelting areas including Xinguanzhai-Dapingzi, Heinizhai, Haozidong, Zhaizichang and Tianqiao were selected in this study (Fig. 1 and Table 1). Xinguanzhai-Dapingzi site is relatively open, and about 180 zinc smelting furnaces were distributed along rivers in 2002. This site has a relatively long history of artisanal zinc smelting activities since 1980s. At Heinizhai, about 430 artisanal zinc smelting furnaces were densely distributed along a narrow valley in 400 m distance with downwind direction open in 2002. The zinc smelting activities initiated at this site in 1996. Haozidong is a close and narrow valley in which about 240 zinc smelting furnaces were densely distributed in 2002. Zinc smelting activities started at this site from early 1990s. Zhaizichang located in a relatively open valley has a long history of zinc smelting activities since 1950s. Only a few zinc smelting furnaces were found here in 2002. Tianqiao, a relatively open area, has the longest history of zinc smelting activities since the 17th century. Only a few zinc smelting furnaces were distributed along a river in 2002.

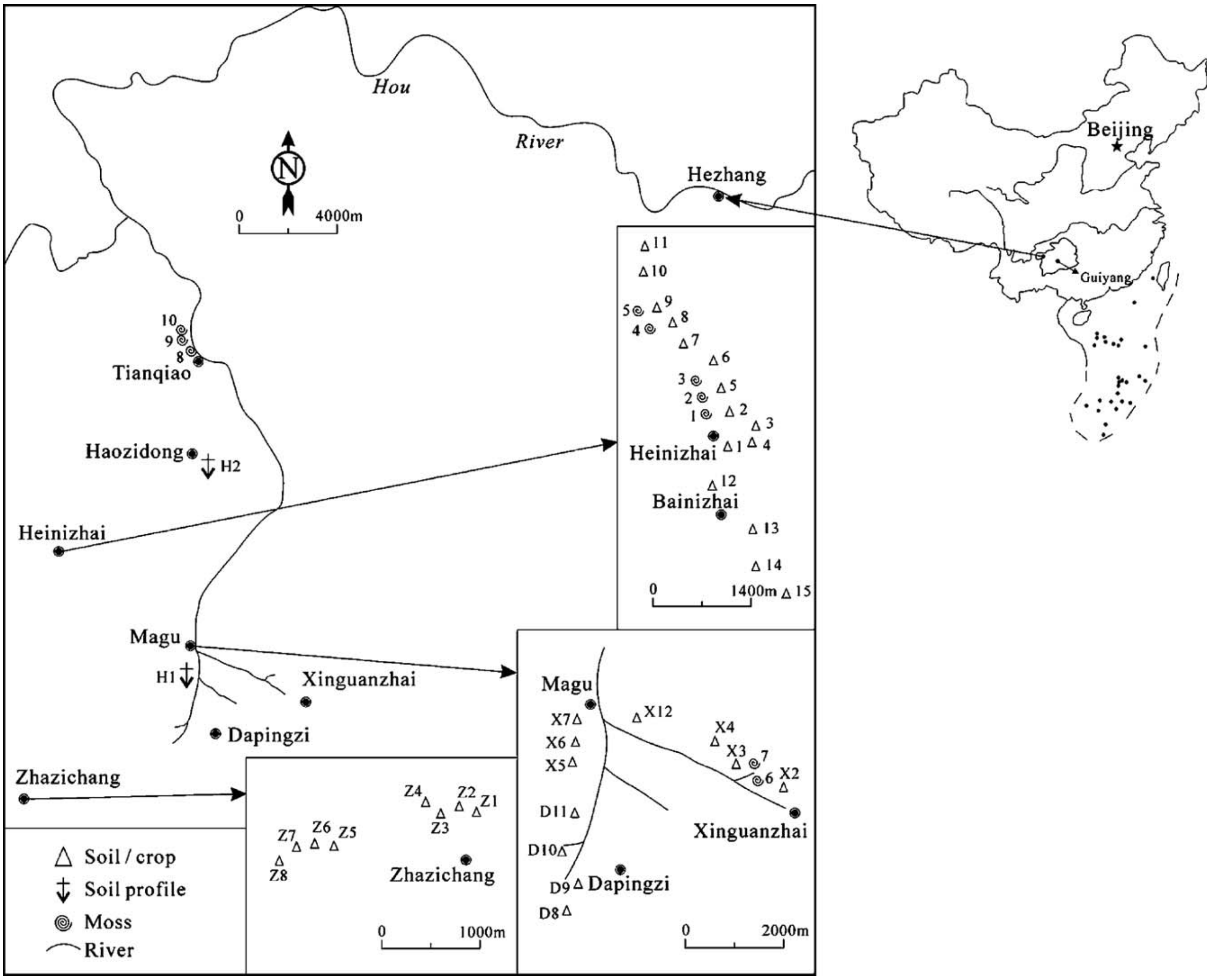

Fig. 1. Sampling locations in the study area.

Table 1
Description of sampling sites in the study areas

Sampling sites/ smelting sites	Smelting history/ beginning of the smelting activity	Smelting scale/ the amount of the smelting furnace	Sample type
Xinguanzhai-Dapingzi	1980s	180	Smelting waste; zinc ore; soil; soil profile; corn; moss
Heinizhai	1996	430	Smelting waste; zinc ore; soil; corn; moss
Haozidong	1990s	240	Smelting waste; zinc ore; soil profile
Zhaizichang	1950s	Few	Smelting waste; zinc ore; soil
Tianqiao	17th century	Few	Smelting waste; zinc ore; moss

2.2. Sampling procedure

Smelting waste, zinc ore, soil, crop and moss samples were systematically collected from the zinc smelting districts in Hezhang in September 2002 and September 2004 (Table 1). Smelting wastes were collected as grab samples from discarded heaps. Two depth profiles of natural soil nearby smelting sites were used to exhibit vertical soil heavy metal distributions. Surface soil (0–10 cm) from cornfields and corn plant (*Zea mays* L.) samples were collected to show heavy metal impacts on the agroecosystem. In order to better understand atmospheric deposition of heavy metals from the zinc smelting sites, naturally growing moss samples (*Hypnum revolutum*) were also collected. Each sample consisted of 5–10 sub-samples from 1 m^2 area.

2.3. Sample preparation and analytical methods

After homogenization, the smelting waste and zinc ore samples were milled and ground to <100 mesh prior to the chemical analysis. A total of 250 mg sample was oxidized with 5 ml of aqua regia in a Teflon vessel in a microwave digestion system (MDS 2000, CEM Inc.) for 50 min. The digested solution was then made up to 100 ml by adding Milli-Q water. Soil samples were air dried at the room temperature and ground to <100 mesh. About 250 mg of sample was digested with 6 ml of HCl (30%, v/v), 2 ml of HNO_3 (65%, v/v) and 2 ml of HF (40%, v/v) in microwave digestion system for 26 min and the digested solution was diluted to 25 ml with Milli-Q water. After being thoroughly cleaned with tap water and Milli-Q water, individual corn samples were separated into root, stalk, leaf and grain sub-samples. All sub-samples were air-dried, and ground to powder. For moss samples, the green and yellowish green parts were selected, and were carefully washed with tap water and Milli-Q water to remove plant remains, epiphytic organisms and dust (Fernández and Carballeira, 2001; Carballeira et al., 2002). After being dried in an oven at 60 °C to a constant weight, the moss samples were subsequently ground to powder. Both corn and moss samples (500 mg) were digested with 6 ml of HNO_3 (65%, v/v) and 2 ml of H_2O_2 (30%, v/v) in a microwave digestion system for 30 min and the digested solution was diluted to 25 ml with Milli-Q water. The soil pH and organic matter were determined using standard methods recommended by the Chinese Society of Soil Science (Lu, 1999), whose values ranged from 4.2 to 6.4 and 2.3% to 5.9%, respectively.

Heavy metal (Cd, Cr, Cu, Pb and Zn) concentrations in all prepared solutions were determined using atomic absorption spectrometry (AAS 5100, Perkin-Elmer Inc.). For some samples, graphite furnace was used due to their relatively low heavy metal concentrations. Quality assurance and quality control of metal analysis were assessed using duplicates, method blanks and standard reference materials (SRM 2710, GBW 07404 and GBW07602). The recoveries ((Measured value/Certified value) × 100%) for the metals in standard reference materials were in the range of 87–114%, and the relatively percentage difference of sample duplicates was <13%.

3. Results and discussion

3.1. Heavy metals in soil

Total heavy metal concentrations in soil samples collected from Hezhang zinc smelting areas and the controlled sites are listed in Table 2. Soil samples collected from the controlled sites contained 0.20–0.31 mg kg^{-1} of Cd, 69–72 mg kg^{-1} of Cr, 25–27 mg kg^{-1} of Cu, 49–51 mg kg^{-1} of Pb and 79–96 mg kg^{-1} of Zn, respectively. These results were comparable to their corresponding concentrations in worldwide uncontaminated soils (Kabata-Pendias and Pendias, 1992), and therefore can represent regional baseline concentrations. However, total heavy metal concentrations in soil from the smelting areas were highly elevated compared to the baseline values. The most seriously contaminated metals in soil were Cd, Pb and Zn, whose concentrations were 18–240, 1.2–270 and 2.7–170 times above the baseline values, respectively.

Obviously, the extent of heavy metal contamination to the local soil compartment depended strongly on the zinc smelting history. At Zhazichang, though there were only a few zinc smelting furnaces during sampling period, the zinc smelting history in this site is much longer than Heinizhai and Xinguanzhai-Dapingzi (Table 1). We can see that Cd, Pb and Zn concentrations in soil samples at Zhazichang are the highest with mean values greater than 40, 9000 and 10,000 mg kg^{-1}, respectively (Table 2).

At Heinizhai, surface soil samples were collected along the valley from the up wind to down wind direction. The peaks of heavy metal concentrations in surface soil were found within a distance of 500 m from the smelting area, and then the concentrations (except Cr) decreased significantly with the distance away from the zinc smelting area at downwind direction. Simultaneously, heavy metal concentrations in surface soil samples dropped more rapidly at upwind direction than at downwind direction (Fig. 2). The observed trend of metal

Table 2
Total heavy metal concentrations in soil collected from different sampling areas (in mg kg^{-1}, dry weight)

Location	n	Cd	Cr	Cu	Pb	Zn
Zinc smelting site						
Zhazichang	8	43 (11–58)[a]	130 (93–170)	120 (61–190)	9000 (2000–14,000)	11,000 (6000–16,000)
Xinguangzhai-Dapingzi	11	24 (13–74)	140 (71–200)	150 (40–260)	260 (100–570)	1400 (530–5500)
Heinizhai	17	18 (5.8–55)	150 (95–240)	52 (9.3–180)	520 (60–2300)	1300 (260–4200)
Controlled site	2	0.26 (0.20–0.31)	71 (69–72)	26 (25–27)	50 (49–51)	88 (79–96)

[a] Metal concentrations are presented in mean and range values (in parenthesis); *n* = number of analyzed samples.

dispersions in soil could be mainly related to the presence of atmospheric metals source.

The extent of heavy metal contamination to soil was also well presented by two typically vertical undisturbed soil profiles collected from Xinguanzhai-Dapingzi and Haozidong (Fig. 1). These two soil profiles exhibited the similar trends of vertical metal distribution pattern as showed in Fig. 3. The majority of Pb contamination generally remained within the surface layer (0–20 cm) of the soil. With increase of the depth, the total Pb concentrations decreased abruptly and reached the regional background levels at a depth of about 30 cm. Similarly, the Zn profile also exhibited an obviously decreasing trend, but the downward migration of Zn can reach a depth of at least 50 cm, indicating its stronger mobility than Pb. However, the reducing trend of Cd in soil profile was unclear. Even at a depth of >1 m, total Cd concentrations were still as high as 6.0–10 mg kg^{-1}, reflecting its very strong mobility in soil. Based on these results, we can classify the mobility of these three metals in the following order: Cd ≫ Zn ≥ Pb. A similar result was obtained from Lille Zn–Pb smelting regions, north France, in which the mobility of metals in soil profiles was classified by Cd ≫ Pb ≥ Zn (Sterckeman et al., 2000). It can be seen that Zn mobility in our study area seems to be stronger. On the other hand, the Cr and Cu concentrations appeared to be uniformly distributed in the soil profiles and were very close to their baseline values, probably indicating their geogenic origin.

3.2. Heavy metals in corn plant

Corn plant (*Z. mays* L.) cultivated in the contaminated soil was not free from the heavy metal contamination (Table 3). The correlation analyses showed that heavy metal concentrations in corn plant especially in root tissue were, to a certain extent, positively correlated with their corresponding concentrations in soil samples (Table 4), suggesting that heavy metals in soil could be readily transferred into the plant. The root tissue generally contained the highest heavy metal concentrations, followed by leaf, stalk and grain (Table 3). But the highest mean total Zn (350 mg kg^{-1}) and Pb (62 mg kg^{-1}) concentrations were found in leaf tissue, indicating that the dry deposition of Zn and Pb to the leaf of corn is an important route of these metals accumulation in this plant. A previous study demonstrated that the absorption of atmospheric mercury by leaf of corn is a major route of mercury accumulation in the plant in the studied areas (Feng et al., in press). Total heavy metal concentrations (0.05–0.76, 0.28–1.7, 1.2–6.4, 0.80–1.5 and 27–68 mg kg^{-1} for Cd, Cr, Cu, Pb and Zn, respectively) in corn grain tissue were the lowest in all tissues of the corn plant (Table 3). Results were comparable to the metal concentrations in similar samples collected from a Zn–Pb mining area in Chenzhou, China, which were 0.03–0.47 mg kg^{-1} for Cd, 2.43–10.10 mg kg^{-1} for Cu, 0.18–1.91 mg kg^{-1} for Pb and 41.73–88.79 mg kg^{-1} for Zn (Liu et al., 2005). However, compared to data from Zhang et al. (1998) for corn grain grown in north-eastern China, which were 0.002–0.006 mg kg^{-1} of Cd and 0.007–0.616 mg kg^{-1} of Pb, respectively, the concentrations of these metals in the corn grain in our study areas were significantly elevated.

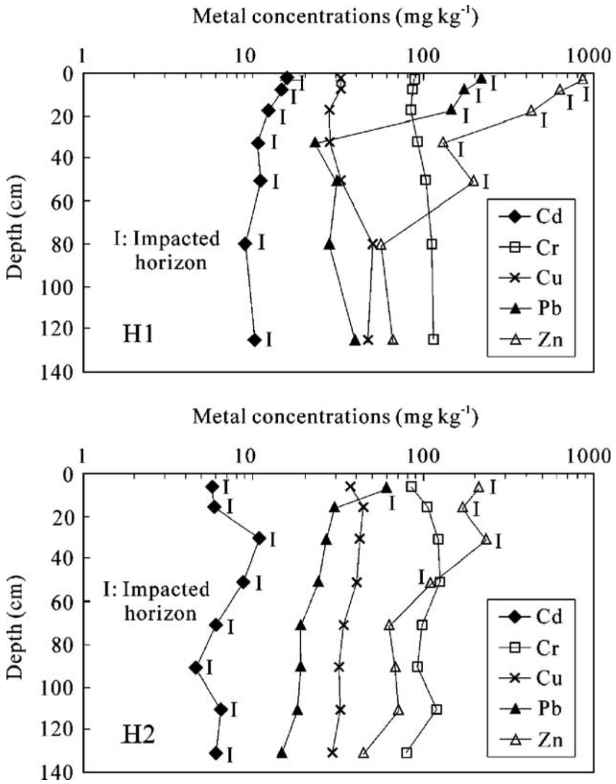

Fig. 3. Heavy metal distribution patterns in soil profiles collected at Xinguangzhai-Dapingzi (H1) and Haozidong (H2).

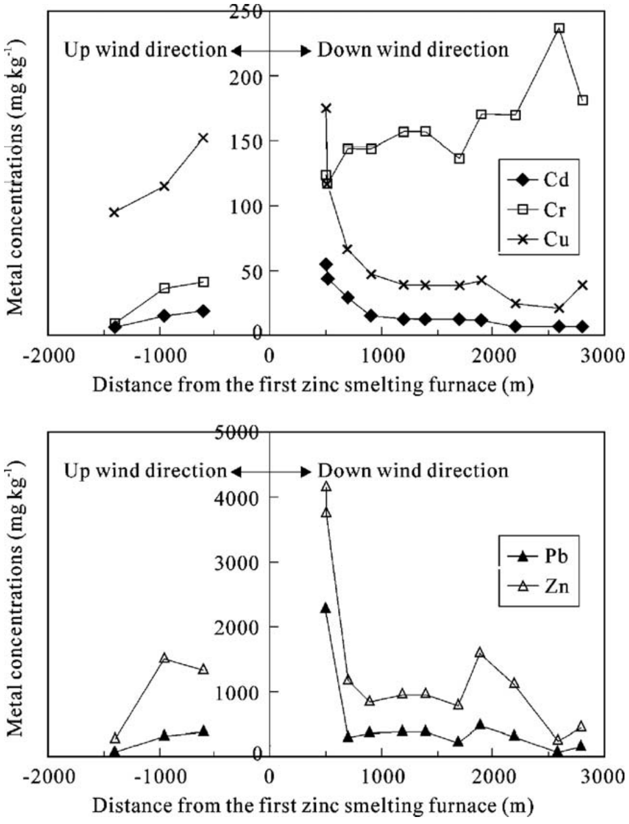

Fig. 2. Distribution of heavy metal concentrations in soil on transect from up wind direction to down wind direction of Heinizhai zinc smelting site.

The accumulation of heavy metals by agricultural crops is a public health concern (Türkdoðan et al., 2002; Alam et al., 2003; Cui et al., 2004, 2005; Yang et al., 2004). Considering that corn is the basic food for the local people, the highly elevated Pb and Cd concentrations in corn grain, which totally or partially exceeded the national guidance limit of 0.4 mg kg^{-1} for Pb and 0.2 mg kg^{-1} for Cd for foodstuff, respectively (Chinese National Standard Agency, 1994a,b) (Fig. 4), may have posed a threat to the health of the local inhabitants. If we

Table 3
Total heavy metal concentrations in different tissues of corn plant (*Zea mays* L.) (in mg kg^{-1}, dry weight)

Tissue	n	Cd	Cr	Cu	Pb	Zn
Grain	27	0.2 (0.05–0.76)[a]	0.72 (0.28–1.7)	2.3 (1.2–6.4)	1.1 (0.80–1.5)	42 (27–68)
Stalk	27	1.2 (0.04–6.7)	0.97 (0.05–2.6)	6.7 (1.5–27)	2.6 (1.4–5.0)	150 (4.6–630)
Leaf	24	12 (2.9–31)	3.0 (1.3–5.0)	14 (7.7–23)	62 (14–170)	350 (81–1000)
Root	27	13 (0.71–40)	8.4 (2.4–32)	24 (5.7–48)	31 (2.5–220)	190 (16–700)

[a] Metal concentrations are presented in mean and range values (in parenthesis); n = number of analyzed samples.

assume that the average daily dietary intake of corn by local residents is 52 g (Zhang et al., 1997), the average daily intake of Pb and Cd from corn by local residents is calculated to be 57.2 μg day^{-1} (1.1 mg kg^{-1} × 52 g day^{-1}) and 10.4 μg day^{-1} (0.2 mg kg^{-1} × 52 g day^{-1}), respectively, which reached 27% and 17% of the provisional allowable intake of Pb (210 μg day^{-1}) and Cd (60 μg day^{-1}) (for 60 kg body weight) recommended by the FAO/WHO (1993, 2003), respectively. However, it should be noted that the leaf tissue of corn is used as the food for livestock by the local people. Since heavy metal concentrations in leaf were extremely high (62 mg kg^{-1} for Pb and 12 mg kg^{-1} for Cd), these metals will probably enter human body through food chain. Hence, the daily metal intakes in local residents through dietary route may exceed the recommended values mentioned above. Previous research conducted by Guizhou Research Institute of Environmental Protection (1995) showed that the Pb concentrations in the blood of children living in Hezhang zinc smelting areas were highly elevated, and exceeded its concentrations in normal children blood by 5.3 times. According to the above study, we concluded that the pathway of soil-to-crop transfer of heavy metals may play an important role in the elevated blood Pb concentrations in children living in Hezhang district.

3.3. Heavy metals in moss

The analytical results of total heavy metal concentrations in moss (*Hypnum revolutum*) samples and their locations are shown in Table 5 and Fig. 1. Samples collected from the controlled sites generally exhibited lower heavy metal concentrations. However, the moss samples collected near the smelting sites contained highly elevated heavy metal concentrations. The most seriously contaminated metals in moss were Cd, Pb and Zn and their values exceed those in the controlled samples by 6–69, 17–46 and 4–13 times, respectively. The highest concentrations of Cd (110 mg kg^{-1}), Cr (55 mg kg^{-1}), Cu (51 mg kg^{-1}) and Zn (1100 mg kg^{-1}) in moss were found in Heinizhai and the highest Pb (1200 mg kg^{-1}) and Zn (1100 mg kg^{-1}) samples were obtained from Xinguanzhai-Dapingzi.

In this study, the moss samples were all collected with a distance away from the smelting waste piles and they were, therefore, less impacted by the wastes. The heavy metals in the moss samples were expected to be mainly derived from the deposition of the smelting flue gas dusts. The spatial distribution patterns of the heavy metal concentrations in moss samples among different zinc smelting sites well proved this hypothesis. There were much more zinc smelting furnaces in Heinizhai and Xinguanzhai-Dapingzi than Tianqiao (Table 1). As a result, the deposition rates of heavy metals associated with the flue gas dusts should be much heavier at Heinizhai and Xinguanzhai-Dapingzi than Tianqiao during the sampling period. Moss samples collected in the former two sites correspondingly exhibited higher heavy metal concentrations. Moreover, the decreasing trend of heavy metal concentrations in moss samples with distance away from the smelting sites as shown in Table 5 further demonstrated their atmospheric deposition origin of heavy metals in the moss.

Table 4
Correlations between heavy metal concentrations in soil and different tissues of the corn plant

	Root	Leaf	stalk	Grain
Soil				
Cd	0.667**	0.695**	0.787**	0.767**
Cr	0.430*	0.238	0.325	−0.241
Cu	0.468*	0.165	0.011	−0.301
Pb	0.546**	0.449*	0.400	0.143
Zn	0.791**	0.554**	0.537**	0.010

* Significant level at $p < 0.05$.
** $p < 0.01$ (two-tailed).

In general, naturally growing mosses have been recognized as an effective biomonitor of air pollution, particularly for heavy metals (Fernández and Carballeira, 2001; Carballeira et al., 2002; Migaszewski et al., 2002; Qiu et al., 2005). Therefore, the high heavy metal concentrations in moss samples indicated that the ambient air were heavily contaminated with these metals, which agreed with a previous study, which showed that total Cd and Pb concentrations in ambient air from the zinc smelting areas in Hezhang were up to 480 ng m^{-3} and 11.9 μg m^{-3}, respectively (Shen et al., 1991). In addition, these data also suggested that atmospheric deposition of heavy metals may be the main pathway of heavy metal contamination to the local environment of the smelting areas in Hezhang.

3.4. Source attribution of heavy metal contamination

The smelting flue gas dusts and the abandoned smelting wastes were the two main heavy metal contamination sources to the local environment in Hezhang. In this study, we also measured heavy metal concentrations in the zinc smelting wastes and the feeding ores (Table 6). Smelting waste is characterized by relatively much lower Cd concentrations compared to the zinc ores, suggesting that most Cd in the original ores might be evaporated and entered the gas-phase during the high temperature smelting process due to its low boiling point (765 °C) (Bi et al., in press). On the contrary, the high boiling point metals such as Pb and Zn prefer to retain in the smelting wastes. These different behaviors of metals during zinc smelting processes will result in higher Zn/Cd and Pb/Cd ratios in the smelting wastes than those in the flue gas dusts. Therefore, it should be theoretically possible to distinguish between the flue gas dusts derived and the smelting wastes derived metals in different sample compartments in the smelting impacted areas using Zn/Cd and Pb/Cd ratios.

Ratios of Zn/Cd against Pb/Cd in different samples are plotted in Fig. 5. The concentrations of Cd, Pb and Zn in soil and moss samples used here are the margins of the measured metal values in these considered samples minus their baseline concentrations (see Tables 2 and 5), hence they can be roughly estimated as the smelting derived metals. It is showed that the smelting wastes expectantly contained

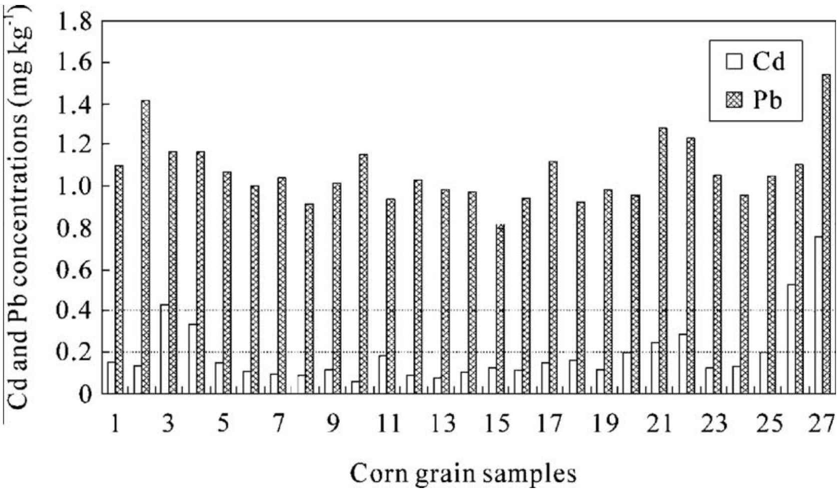

Fig. 4. Cd and Pb concentrations in corn grain in the Hezhang zinc smelting areas. The dashed lines are the national guidance limit of 0.4 mg kg^{-1} for Pb and 0.2 mg kg^{-1} for Cd for foodstuff, respectively.

high ratios of Zn/Cd (200–2800) and Pb/Cd (130–6700). On the contrary, moss samples exhibited much lower Zn/Cd (9.0–34) and Pb/Cd (7.8–59) ratios, which confirmed that metals in the moss were mainly derived form the smelting flue gas dusts. The relatively high Zn/Cd (140–1600) and Pb/Cd (130–290) ratios in soil collected from Zhazichang were much close to the values obtained in the smelting wastes, indicating their main origin of these metals in soil was the smelting wastes. However, ratios of Zn/Cd (23–180) and Pb/Cd (1.9–51) in soil collected from Heinizhai and Xinguangzhai-Dapingzi were similar to those in the moss, suggesting that metals in these samples may be derived predominantly from atmospheric deposition of the smelting flue gas dusts. Moreover, the Pb/Cd ratios in these soil and moss samples matched closely with the values obtained in airborne particulate matter samples collected in the same areas previously as shown in Fig. 5 (Shen et al., 1991), which were 18–26, further supporting this statement.

Table 5
Total heavy metal concentrations in moss (*Hypnum revolutum*) (in mg kg^{-1}, dry weigh)

Sampling site	Description	Cd	Cr	Cu	Pb	Zn
1	500 m from smelting site at Heinizhai	110	21	38	1100	1100
2	800 m from smelting site at Heinizhai	88	55	51	700	910
3	900 m from smelting site at Heinizhai	79	36	27	660	780
4	2000 m from smelting site at Heinizhai	13	16	31	510	330
5	2200 m from smelting site at Heinizhai	10	12	29	520	330
6	800 m from smelting site at Xinguanzhai-Dapingzi	81	15	41	1200	1100
7	1000 m from smelting site at Xinguanzhai-Dapingzi	49	10	26	630	940
8	700 m from smelting site at Tianqiao	29	12	46	740	860
9	800 m from smelting site at Tianqiao	27	19	46	580	950
10	1000 m from smelting site at Tianqiao	21	20	42	400	490
11	Controlled site	1.9	4.8	11	35	76
12	Controlled site	0.89	16	14	12	55
13	Controlled site	2.0	14	13	24	120

Using elemental ratios to distinguish metals origin is a simple and useful approach and has been applied in other researches (Eckel et al., 2002). Our study demonstrated that the application of Zn/Cd and Pb/Cd ratios could effectively identify metals origin between that from zinc smelting wastes and from flue gas dusts in the zinc smelting impacted areas. Since artisanal zinc smelting activities using indigenous methods were widely applied in the southwestern China, the present study may supply a useful tool for the future study on identifying metals origin in the similar zinc smelting contaminated areas. In addition, it is expected that this approach could also be used to delineate the impact extent of different originated metals. Of course more work is needed to test this hypothesis.

4. Conclusions

Artisanal zinc smelting activities in Hezhang have resulted in serious environmental heavy metal contamination. Both soil and corn plant from the smelting sites contained highly elevated heavy metal concentrations and total Pb and Cd concentrations in corn grain totally or partially exceeded the national guidance limit for foodstuff. Moss samples collected from the smelting sites also exhibited high heavy metal concentrations compared to the samples collected in the controlled sites. The high Zn/Cd and Pb/Cd ratios in soil collected from Zhaizichang were close to those in the smelting wastes, probably indicating their smelting waste origin. However, the much lower Zn/Cd and Pb/Cd ratios in soil collected from Heinizhai and Xinguanzhai-Dapingzi and in moss suggested that metals in these samples

Table 6
Total heavy metal concentrations in zinc smelting waste and zinc ore

Sample type	*n*	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Pb (%)	Zn (%)
Smelting waste	15	4.0–70	20–118	190–2200	0.17–6.8	0.29–5.6
Zinc ore	36	54–1400	2.0–154	36–2500	0.13–8.7	16–66

n = number of analyzed samples.

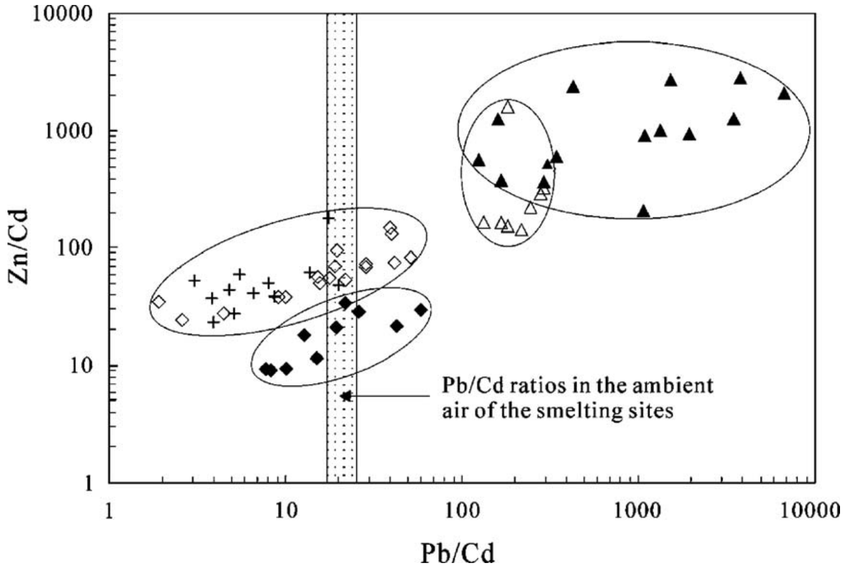

Fig. 5. A plot of Zn/Cd against Pb/Cd for the analyzed samples. The five groups of samples are smelting waste (▲), soil from Zhaizichang (△), soil from Heinizhai (◇), soil from Xinguanzhai-Dapingzi (+) and moss (◆). The ellipses have been added manually to indicate the groupings. The rectangular area shows the Pb/Cd ratios in ambient air of the smelting sites ($n=4$) (Shen et al., 1991).

may be derived predominantly from the atmospheric deposition of the smelting flue gas dusts.

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