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Short communication

Quantitative assessment of cadmium emission from zinc smelting and its influences on the surface soils and mosses in Hezhang County, Southwestern China

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Abstract

Using a mass balance method, we estimated the average Cd emission factors from artisanal zinc smelting using indigenous method in Hezhang, Guizhou, China, to be 1460 and 1240 g Cd t^{-1} of Zn produced from sulfide ore and oxide ore, respectively. These emission factors are much higher than the literature value used to estimate Cd emission from zinc smelting using pyrometallurgical method in developed countries, which is 50 g Cd t^{-1} of Zn produced. Based on the average Cd emission factors obtained in the study, annual Cd emission rates from artisanal zinc smelting in this area were calculated from 1989 to 2001. And up to 2003, approximately 450 t of Cd have been released to the ambient air from zinc smelting in a small area ($<150\,km^2$) in Hezhang district. Owing to a huge quantity of Cd atmospheric deposition, surface soils and mosses collected around the smelting areas were heavily contaminated. The highest total Cd concentrations in surface soils and naturally growing mosses were found to be 74 and 110 mg kg^{-1}, respectively, exhibiting a local spatial pattern of Cd deposition from atmosphere.

Keywords: Cadmium; Emission; Zinc smelting; Soil; Moss; Hezhang; Guizhou; China

1. Introduction

As a highly toxic and mobile metal, cadmium attracts most environmental attention worldwide. Cd emission from the smelting of nonferrous metals especially the zinc metal is considered as one of the major anthropogenic sources of Cd contamination in the environment. Cd emission from nonferrous metal industries in 1996 for UK, for instance, accounts for 37% of the total Cd emissions from the whole country (Goodwin et al., 1999). Generally, Cd emissions from zinc smelting vary widely and always depend on the ore used, smelting methods and the abatement measures applied. Previous study showed that the pyrometallurgical smelting has a much larger Cd emission factor than the electrolytic refining, but the later dominates the world production of zinc from zinc ore (Jackson and MacGillivray, 1995).

Hezhang County located at western Guizhou Province, SW China, is a region of high zinc smelting activities. Artisanal zinc smelting using indigenous methods had been widely applied in this

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area since the 17th century. Till recent years (up to 2004), artisanal zinc smelting activities could be completely ceased due to the concern of environmental protection. Previous studies on local environments have been focused on the potential hazard related to Cd, Cu, Hg, Pb and Zn resulted from zinc smelting activities in water, air and soils, and data have shown that the local water, air and soils are seriously contaminated with these metals (Shen et al., 1991; Yang et al., 2003; Feng et al., 2006). Recently, Feng et al. (2004) estimated that Hg emission factors from artisanal zinc smelting in Hezhang are 79 and 155 g Hg t^{-1} of Zn produced from oxide zinc ores and sulfide zinc ores, respectively. From 1989 to 2001, approximately 50 t of Hg had been released into the atmosphere from the zinc smelting activities. However, little attention was paid to the toxic element Cd emission, an even more important by-product of zinc smelting, from the artisanal zinc smelting and its influence on the local environments. The objectives of this study were to (1) assess Cd emissions from the artisanal zinc smelting by using a mass balance method and (2) delineate the extent of Cd contaminations in surface soils and naturally growing mosses.

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 (Fig. 1). All artisanal zinc smelting furnaces are distributed along rivers and valleys in an area $<150\,km^2$ around Magu in Hezhang County. In this study, four smelting areas including Heinizhai (HNZ), Xinguanzhai-Dapingzi (XGZ-DPZ), Zhaizichang (ZZC) and Tianqiao (TQ) were selected for investigation (detailed description see Table 1 and Fig. 1).

2.2. Sampling and analysis

The sampling was carried out in September 2002. We used a mass balance method to calculate Cd emission factor from the zinc smelting process. In this case, zinc ore (sulfide, oxide and desulfurized ore), smelting residue and primary zinc metal samples were collected. Cd emissions from coal burning have not been taken into account due to their negligible contribution compared to those from zinc ores smelting. To monitor atmospheric deposition of Cd, surface soils (0–10 cm) and naturally growing mosses (*Hypnum revolutum*) were sampled from the vicinities of the smelting sites and from control sites.

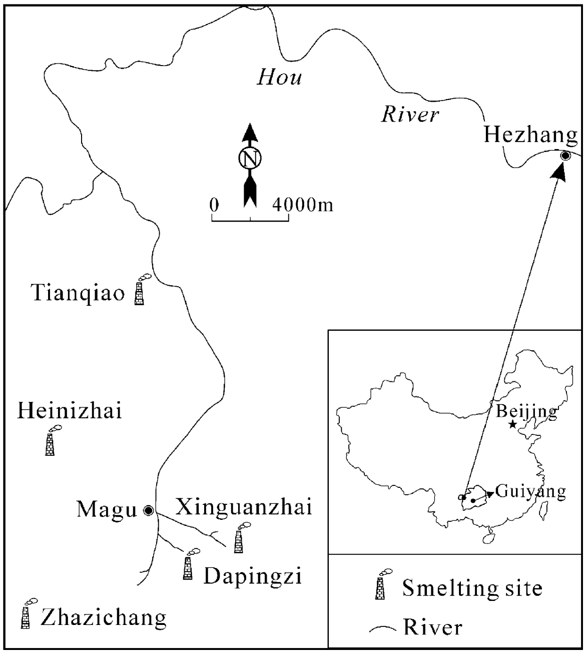

Fig. 1. Sampling locations in the study area.

After homogenization, milling and riffling, samples related to zinc smelting activities except primary zinc metal were digested by aqua regia, soil samples by mixture of HCl–HNO_3–HF, and moss samples (only green and yellowish-green parts which are being washed) by HNO_3 and H_2O_2. All the digested processes were carried out with assistance of a microwave digestion system. Zinc metal samples were dissolved with concentrated HCl. Zn and Cd concentrations in obtained solutions were determined using flame or flameless atomic absorption spectrometry (AAS). For quality control, standard reference materials SRM 2710 and GBW 07602 were used. The recoveries for the metals in standard reference materials were in the range of 98–114%, and the relative percentage difference of sample duplicates was <10%.

3. Results and discussion

3.1. Cd emission from artisanal zinc smelting in Hezhang

In Hezhang, zinc ores are divided into two major categories, one is sulfide ore as sphalerite (ZnS) and

Table 1
Description of sampling sites and total Cd concentrations in surface soils from different sampling locations (mg kg^{-1}, dry weight)

Sampling sites	Smelting history/beginning of the smelting activity	Smelting scale/the amount of the smelting furnace	Cd concentration	*n*
Smelting site				
HNZ	1996	430	18 (5.8–55)	17
XGZ-DPZ	1980s	180	24 (13–74)	11
ZZC	1950s	few	43 (11–58)	8
TQ	17th century	few		
Control site			0.26 (0.22–0.31)	5

Note: Cd concentrations are presented in mean and range values (in parenthesis); n = number of analyzed samples.

the other is oxide ore mainly as calamine ($ZnCO_3$) (detail description of the smelting processes see our previous paper; Feng et al., 2004). Cd emissions from Zn smelting using sulfide ores come from two kinds of sources. The first is from desulfurization process, the second is from the final smelting process. According to the mass balance method, Cd emission factor of zinc smelting from sulfide ores could be calculated from

$$F_s = [A - (1-\alpha)B]/(D\gamma) + [B - (1-\beta)C]/[E - (1-\beta)F] - M, \quad (1)$$

where F_s is Cd emission factor in g Cd t^{-1} of Zn produced; A, B, C and M are Cd concentrations in sulfide ore, desulfurized ore, smelting residue and primary zinc metal in g t^{-1} (mg kg^{-1}), respectively; D, E and F are Zn concentrations in sulfide ore, desulfurized ore and smelting residue in t t^{-1}, respectively; α and β are mass loss ratio during desulfurization and zinc production processes, respectively; γ is the recovery of Zn from the final smelting process. It is noted that Zn concentrations in desulfurized ore are generally higher than those obtained in sulfide ores resulting from mass loss during desulfurization process. Therefore, the mass loss ratio during desulfurization process could be estimated from

$$\alpha = 1 - D/E. \quad (2)$$

Using measurement data from Table 2, α is calculated to be 0.17. Assuming that the only mass loss from zinc production process is the removal of zinc from the ore, whose value is equal to the output of metal Zn from per tonne of zinc ore (t Zn t^{-1} zinc ore), the mass loss ratio β could be therefore calculated from

$$\beta = E - F, \quad (3)$$

Table 2
Zn and Cd concentrations in different types of samples related to zinc smelting

Sample type	*n*	Cd (mg kg^{-1})	Zn (t t^{-1})
Sulfide ore	7	950 (430–1500)	0.45 (0.28–0.58)
Oxide ore	25	440 (54–1400)	0.24 (0.16–0.44)
Desulfurized ore	11	800 (390–1300)	0.54 (0.34–0.66)
Smelting residue	15	23 (4.0–70)	0.02 (0.003–0.06)
Primary zinc metal	10	690 (200–1300)	

Note: Cd and Zn concentrations are presented in mean and range values (in parenthesis); n = number of analyzed samples.

β is estimated to be 0.52. Subsequently, γ can be computed from

$$\gamma = [E - (1-\beta)F]/E, \quad (4)$$

γ is calculated to be 0.98. According to Eq. (1), the average Cd emission factor of Zn smelting using sulfide ores F_s is 1460 g Cd t^{-1} of Zn produced.

Cd emission factor from smelting zinc using oxide ores (F_o) could be calculated from the mass balance method as

$$F_o = [G - (1-\beta')C]/[H - (1-\beta')F] - M, \quad (5)$$

where G, C and M are Cd concentrations in oxide zinc ores, smelting residues and primary zinc metal in g t^{-1}, respectively; H and F are Zn concentrations in oxide zinc ores and smelting residues in t t^{-1}, respectively; β' is mass loss ratio during zinc smelting using oxide zinc ores, whose value could be calculated from Eq. (6) assuming that the only mass loss from zinc production process is the removal of zinc from the ore:

$$\beta' = H - F, \quad (6)$$

β' is estimated to be 0.22. According to Eq. (6), the average Cd emission factor of Zn smelting using oxide ores F_o is 1240 g Cd t^{-1} of Zn produced.

It is obvious that Cd emission factors of artisanal zinc smelting both using sulfide ores and oxide ores in Hezhang are significantly higher than the literature value used to estimate Cd emission from zinc smelting using pyrometallurgical method in developed countries, which is 50 g Cd t^{-1} of Zn produced (Jackson and MacGillivray, 1995). These high Cd emission factors should be resulted from the indigenous smelting method applied and the absence of pollution control devices. In Hezhang district, the ratio of primary zinc produced from sulfide ore and oxide ore is 9:1. Therefore, using the above estimated Cd emission factors and the annual primary zinc productions from artisanal zinc smelting (Table 3; Feng et al., 2004), Cd emissions from artisanal zinc smelting in Hezhang from 1989 to 2001 are calculated and listed in Table 3. It is showed that Cd emission from the artisanal zinc smelting within a small area ($<150\,km^2$) in Hezhang reached hundreds of tonnes in these years. The maximum annual Cd emission was up to 69 t in 2000, which is equal to the annual Cd emission (69 t) from the whole industrial processes in EU 15 in 1990 (Entec, 2001).

China is one of the largest zinc producers in the world and a substantial proportion of zinc production is derived from these artisanal zinc smelting workshops. Based on above study, it is reasonable to believe that huge quantity of Cd will be emitted to the air as a by-product of smelting zinc ores in China. Since smelting-emitted metals can undergo long-range atmospheric transport and contaminate remote areas (Steinnes, 1997), particularly Cd, Hg and Pb, which are of significance regarding a proposed protocol for "heavy metals" under the United Nations Economic Commission for Europe convention on Long-Range Transboundary Air Pollutants (Skeaff and Dubreuil, 1997), Cd emissions from the artisanal zinc smelting not only poses a threat to the local eco-environment, but also contributes to the global cycle of this element in the atmosphere.

Table 3
Annual zinc production and Cd emission from artisanal zinc smelting in Hezhang

Year	Primary zinc production (t)	Cd emission (kg)
1989	7610.5	10912
1990	11289	16186
1991	11639	16688
1992	11989	17190
1993	17403	24952
1994	23453	33627
1995	26731	38327
1996	23038	33032
1997	22700	32547
1998	31100	44591
1999	45200	64808
2000	48098	68963
2001	32700	46885

3.2. Cd in surface soils

Compared to control site samples, significantly elevated concentrations of Cd (5.8–74 mg kg^{-1}) in surface soils were found around the smelting areas (Table 1). The extent of Cd contamination to local soil depends strongly on zinc smelting history. At ZZC, though there were only a few zinc smelting furnaces, the history of zinc smelting in this area is the longest among the three considered smelting areas in terms of Cd distribution in surface soils (Table 1). The mean total Cd concentration in soils is the highest. Similarly, XGZ-DPZ has a longer history of zinc smelting activities than HNZ; total Cd concentrations in soil from XGZ-DPZ are, therefore, higher than that from HNZ.

At HNZ, surface soils were sampled along the valley from the upwind to downwind direction. Total Cd concentrations decrease exponentially with the distance away from the zinc smelting area at downwind direction. Simultaneously, Cd concentrations in surface soils dropped more rapidly at upwind direction than at downwind direction (Fig. 2). This decreasing trend of Cd dispersions in soil must be mainly related to the presence of atmospheric Cd depositions.

3.3. Cd in mosses

Moss samples collected around the smelting areas also contained high total Cd concentrations compared to those from control site, ranging from 10 to 110 mg kg^{-1} (Table 4). The highest total Cd concentration in moss was found in HNZ. In the other two sampled areas, total Cd concentrations in mosses collected from XGZ-DPZ are to an extent higher than those from TQ. Moreover, similar to the surface soils, total Cd concentrations in mosses decrease significantly with distance away from the zinc smelting sites (Table 4).

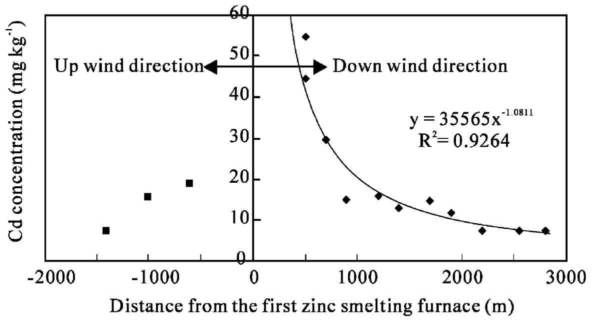

Fig. 2. Distribution of total Cd concentrations in surface soils on transect from upwind direction to downwind direction of HNZ zinc smelting site.

Table 4
Total Cd concentrations in mosses ($mg\,kg^{-1}$, dry weight)

Sampling site	Description	Cd concentration
1	500 m from smelting site at HNZ	110
2	800 m from smelting site at HNZ	88
3	900 m from smelting site at HNZ	79
4	2000 m from smelting site at HNZ	13
5	2200 m from smelting site at HNZ	10
6	800 m from smelting site at XGZ-DPZ	81
7	1000 m from smelting site at XGZ-DPZ	49
8	700 m from smelting site at TQ	29
9	800 m from smelting site at TQ	27
10	1000 m from smelting site at TQ	21
11	Distant area from the smelting sites	1.9
12	Similar to 11	0.89
13	Similar to 11	2.0

The spatial distribution patterns of Cd in mosses are well consistent with the characteristics of atmospheric Cd depositions. Considering that HNZ has the most smelting furnaces (Table 1), atmospheric Cd depositions around this site must be the heaviest during the sampling period. Mosses (1, 2 and 3) collected close to this smelting site correspondingly exhibit the relatively high Cd concentrations. Furthermore, the finding that total Cd concentrations in mosses collected from XGZ-DPZ are higher than those from TQ should also attribute to that XGZ-DPZ has more smelting furnaces than TQ. Since Cd in mosses should be mainly or solely derived from deposition of atmospheric sources (Aceto et al, 2003), the elevated moss Cd concentrations imply that the atmosphere in the smelting area may contain a high level of Cd, which is quite in agreement with the previous study, which shows that total Cd concentration in ambient air from smelting area in Hezhang was up to $480\,ng\,m^{-3}$ (Shen et al., 1991).

4. Conclusions

According to mass balance studies, the average Cd emission factors from the artisanal zinc smelting using an indigenous method in Hezhang, Guizhou, China, were estimated to be 1460 and $1240\,g\,Cd\,t^{-1}$ of Zn produced from sulfide ore and oxide ore, respectively. Based on these results, annual Cd emission rates from artisanal zinc smelting in this area were calculated from 1989 to 2001. Up to 2003, approximately 450 t of Cd are estimated to have been released to the ambient air from zinc smelting in a small area ($<150\,km^2$) in Hezhang district, posing a threat to the local environment. Significantly high levels of Cd in the surface soils and mosses collected around the smelting areas were found, exhibiting a local spatial pattern of Cd deposition from the atmosphere, which highlight the main source of Cd that was emitted from the zinc smelting processes. It is urgently needed to evaluate Cd contaminations to the food chains in terrestrial system and to scrutinize the human health impact of Cd contamination to the local environment due to artisanal zinc smelting activities in this area.

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