

Environmental mercury contamination of an artisanal zinc smelting area in Weining County, Guizhou, China

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Artisanal zinc smelting caused serious mercury contamination in Weining, Guizhou, China.

Abstract

To investigate the extent of Hg contamination due to artisanal Zn smelting activities in Weining County, northwestern Guizhou, China, total Hg and methyl mercury (MeHg) concentrations in soil and surface water were determined. Samples of corn plants growing in the study area were also collected for total Hg analysis. A high geometric mean Hg emission factor of $75 \text{ g Hg t}^{-1} \text{ Zn}$ was estimated and significantly elevated total gaseous mercury (TGM) concentrations were found in the atmosphere adjacent to the Zn smelting sites, ranging from 30 to 3814 ng m^{-3} . Total Hg and MeHg concentrations in topsoil samples ranged from 62 to $355 \text{ } \mu\text{g kg}^{-1}$ and from 0.20 to $1.1 \text{ } \mu\text{g kg}^{-1}$, respectively. Total Hg Concentrations in corn plant tissues increased in the order of grains < stalks < roots < leaves. This study revealed a significant Hg pollution to the local environment resulted from the artisanal Zn smelting activities.

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Keywords: Artisanal Zn smelting; Hg emission factor; Total gaseous mercury (TGM); Total mercury; MeHg; Weining County

1. Introduction

Mercury (Hg) is a highly toxic and persistent pollutant of considerable concern due to its strong accumulation in organisms. Emissions of Hg into the atmosphere are both from natural and anthropogenic sources. Natural sources usually include volcanic eruptions, geothermal activities, forest fires, and soil and water surface evaporation, whereas anthropogenic sources include fossil fuel combustion, waste incineration, chlor-alkali plants, and metallurgical processes (Nriagu, 1989; Pirrone et al., 1996; Schroeder and Munthe, 1998). Non-ferrous metal processing, which mainly refers to primary Zn production, is currently regarded as an important

atmospheric Hg emission source. Since both Hg and Zn belong to sulphophile elements, Hg is an important associate element in Zn ores, especially in Zn sulfide ore. Hg concentrations in zinc ores varied largely depending on the ore types, the origins or geneses, and locations. Hg in Zn ore will inevitably emit to atmosphere during the smelting processes when a high temperature ($\sim 1000^\circ\text{C}$) is employed in Zn metal smelters. Nriagu and Pacyna (1988) estimated that the Hg emission factor generated from Zn production is from 8 to 45 g t^{-1} . Recently, Streets et al. (2005) reported that the Hg emission factor for Zn smelting in China varied from 13.8 to 156.4 g t^{-1} , with an average value of 86.6 g t^{-1} . To date, emission factors of $7.5\text{--}8.0 \text{ g t}^{-1}$ for Europe, North America and Australia, and of 20 or 25 g t^{-1} for Africa, Asia and South America are widely accepted by researchers (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Prasad et al.,

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2000; Pacyna and Pacyna, 2002; Pacyna et al., 2003, 2006; Streets et al., 2005). Generally, Hg emissions from Zn smelting processes are primarily Hg^0 (80%), divalent reactive gaseous mercury (RGM; 15%), and particulate Hg (5%) (Pacyna et al., 2001; Pacyna and Pacyna, 2002). It is usually accepted that Hg^0 has a long lifetime between 0.5 and 2 years allowing for its global circulation, while RGM and particulate Hg are expected to deposit efficiently on a local or regional scale near the sources because of their short lifetime on the order of a day to several weeks (Schroeder and Munthe, 1998; Weiss-Penzias et al., 2003). Hence, atmospheric deposition adjacent to the Zn smelting areas may be largely attributed to the particulate Hg and RGM forms that are directly emitted to the atmosphere.

Artisanal Zn smelting activities using indigenous methods are still in operation in remote areas of China, such as Guizhou province. The total Zn produced by the artisanal method accounts for less than 3% of the total Zn production in China, and most of the artisanal Zn smelting activities are distributed in northwest Guizhou, especially in Hezhang and Weining Counties. In Hezhang County, previous studies have been focused on the potential hazards related to Cd, Cu, Hg, Pb and Zn resulting from Zn smelting activities. Studies have shown that water, air and soils in the Hezhang area were highly contaminated with these metals (Shen et al., 1991; Yang et al., 2003; Feng et al., 2006a; Bi et al., 2006a). More recently, results for Hg and Cd emission factors from artisanal Zn smelting activities in the Hezhang area were estimated to be from 79 to 155 $\text{g Hg t}^{-1} \text{Zn}$ and from 1240 to 1460 $\text{g Cd t}^{-1} \text{Zn}$, respectively, with approximately 46 t of Hg and 450 t of Cd released into the atmosphere from 1989 to 2001 (Feng et al., 2004; Bi et al., 2006b). However, documentation of heavy metals contamination to local environments caused by Zn smelting in the Weining County, which has a long history of artisanal Zn smelting activities, is still lacking.

This paper presents a more comprehensive investigation on Hg emission from artisanal Zn smelting activities and on Hg contamination to the local environment in the Weining area. The Hg emission factor during the Zn smelting process was estimated. Concentrations of TGM in the ambient air, total Hg and MeHg in topsoil and surface water samples, and total Hg in corn plants tissues were systematically investigated.

2. Materials and methods

2.1. Study area

Weining County ($103^{\circ}36' - 104^{\circ}45' \text{E}$, $26^{\circ}30' - 27^{\circ}25' \text{N}$) is located in northwest Guizhou province, southwestern China, covering an area of approximately 6295 km^2 . It lies on the Yunnan–Guizhou Plateau with an average altitude of 2200 m above sea level. Weining County is mountainous and its climate is typical subtropical and humid with an average temperature of 10.4°C and annual precipitation of 960–1100 mm. The agricultural soil type in the study area is mainly the yellow-brown earth. Several streams flow across Weining County and then merge into the Dahe river (Fig. 1).

Artisanal Zn smelting activities in Weining County are mainly distributed in Jinzhong (J), Lushan (L), Dongfeng (D), and Ertang (E) areas (Fig. 1). A large number of artisanal Zn workshops is scattered in those narrow valleys along the rivers. Zn ingot production from these workshops has reached

more than 20,000 t since 1995. More than 90% of total Zn production in Guizhou is from artisanal Zn smelting.

2.2. Artisanal Zn smelting process

Zn ores used in the artisanal smelting in Guizhou are always divided into two major categories: sulfide ore as sphalerite (ZnS) and carbonate Zn ore as smithsonite (ZnCO_3). Most of these Zn ores came from adjacent regions (e.g. Yunnan Province and Sichuan Province) because there are no lead–zinc mines in Weining County. The carbonate Zn ores, mainly ZnCO_3 , are mixed with coal with low sulphur content as a reducing agent, is simply roasted using coal to generate the heat to produce Zn in small workshops. The reactions are shown by Eq. (1). Zn in smithsonite may be entirely reduced to liquid metallic Zn by carbon when heated at a high temperature using coal. Sulfide ores have been seldom used in artisanal Zn smelting in the study area since 2004 mainly due to the concern of SO_2 pollution to ambient air, and hence, only carbonate Zn ores were collected for the emission factor evaluation in this study. Artisanal Zn smelting is a pyrometallurgical process, which will generate a significant quantity of dust. In addition, the slag created by the pyrometallurgical process is randomly distributed along the rivers. Hg both in coal and Zn ore is released to the air during Zn smelting process.



2.3. Sample collection

Total gaseous mercury (TGM) in ambient air was monitored at 1.5 m above the ground at the J, L, D, and E Zn smelting areas using a Lumex RA-915+ Hg detector at a time resolution of 30 s. The instrument is a real time Hg detector, which is based on the Zeeman cold vapor absorption spectrometry technique with a time resolution of 1 s. The instrument is calibrated with an internal Hg vapor source. The detection limit of the instrument is 0.3 ng m^{-3} (Feng et al., 2006a). TGM was monitored at 89 sites, 24 at the Zn smelting sites, 18 at smelting residual sites, 25 in the cornfields, and 22 in residential areas. At each sampling site, an average value was obtained from 10 to 20 measurements.

Twenty-three soil samples and corresponding corn plants (*Zea mays* L.) were collected in cornfields from the study area (Fig. 1, Table 1). The soil samples were collected with a steel shovel at a depth of 10 cm, without encountering the mineral soil, and gravel and coarse fragments were removed. At each sampling site, a final sample was composited from 3 to 5 subsamples collected from several locations. All samples were stored in sealed polyethylene bags to avoid contamination. Corn plant samples were collected simultaneously with cornfield soil samples. At each sampling site, three individual corn plants were collected within a 1 m^2 area. The corn plant samples were cleaned with water, and then separated into root, stalk, leaf, and grain subsamples.

Twenty-nine carbonate Zn ore samples and 19 smelting residue samples were collected during the sampling campaign. Each sample was a mixture of at least 10 subsamples collected from different artisanal Zn workshops to make sure that they are representative. All samples were stored in polyethylene bags.

Filtered and unfiltered stream water samples were also collected in September 2004. At each sampling site, a 500-ml sample was filtered in situ through a $0.45\text{-}\mu\text{m}$ acid-cleaned membrane filter (Millipore Durapore Membrane Filters) with a pre-cleaned apparatus. Filtered water was then collected in pre-cleaned 100-ml borosilicate glass bottles. Before sample collection, bottles were rinsed three times with the sampled water prior to filling. Unfiltered water samples for total Hg and MeHg analysis were directly collected into pre-cleaned borosilicate glass bottles. All collected samples were preserved by adding 0.4% (v/v) of sub-boiling distilled ultra-pure HCl within 48 h. The sampled bottles were tightly capped and placed in double bags to be stored in clean coolers ($+4^{\circ} \text{C}$) until processing and analysis.

2.4. Sample preparation and analysis

In the laboratory, solid and Zn ore samples were air-dried, homogenized, and ground. For each sample, no less than 100 g was sieved through 0.074 mm pore size screen and stored in plastic containers for analysis. For total Hg in soil, all samples were digested with aqua regia in a microwave

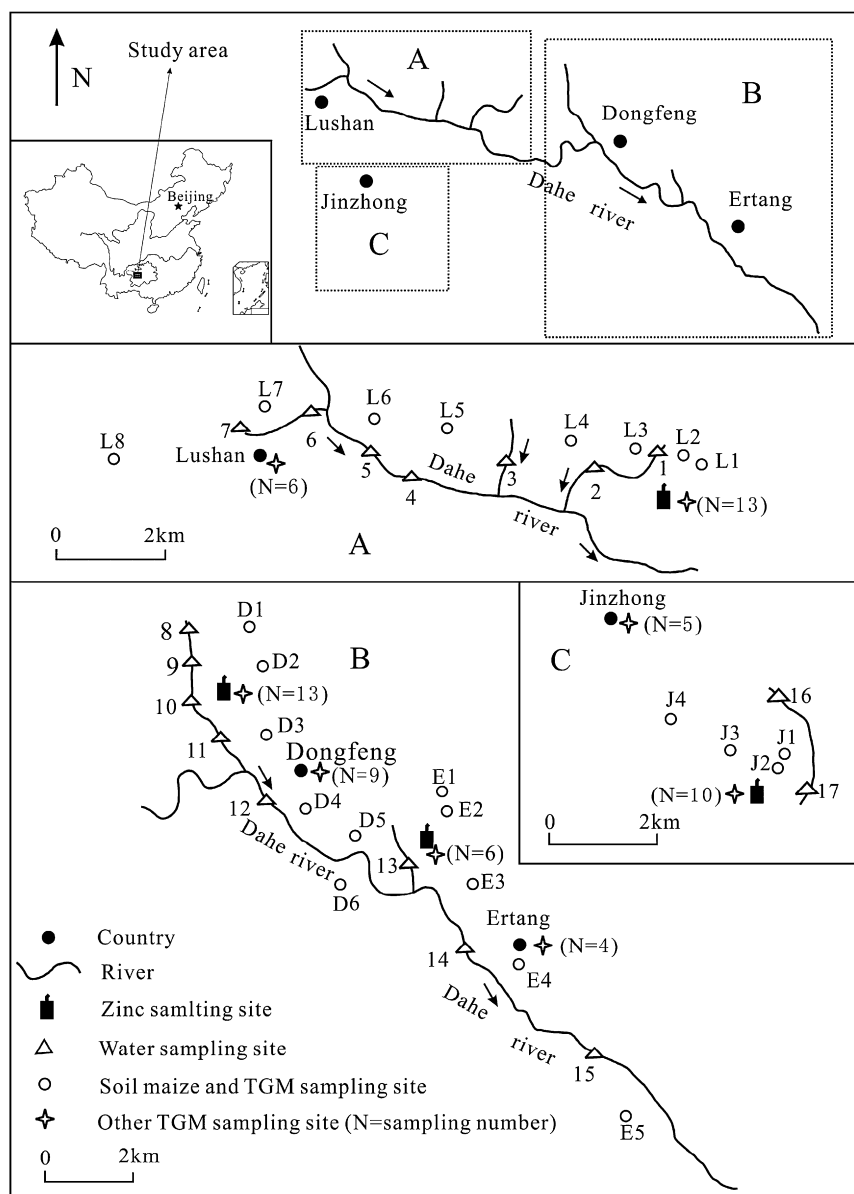


Fig. 1. Map of sampling sites in Weining County.

oven. Then an aliquot of digested sample solution was measured using cold vapor atomic absorption spectrometry (CVAAS), with a detection limit of $0.01 \mu\text{g L}^{-1}$. Zn concentrations in Zn ores were determined by Method GB/T8151.1-2000 (Meng and Sun, 2004). Smelting residue was tested for Hg by cold vapor atom fluorescence spectrometry (CVAFS). MeHg in soil was determined by GC–CVAFS (Glas-Col TM568; Tekran Model 2500) with a solvent extraction technique (Liang et al., 1994, 1996) following Method 1630 (US EPA, 2001). The pH of soil was determined at a water:soil ratio of 1:2.5 (v/v) using an Orion pH-meter model 818 (Wang et al., 2006a). Soil organic carbon was determined by digesting the sample with a strong acid/oxidizing solution, according to Method GB9834-88 (Yang and Jin, 1999).

All corn subsamples were air-dried, ground to a fine powder in a pre-cleaned food blender, and stored in polyethylene bags. Samples for total Hg analysis in different parts of corn were digested with nitric acid in boiling water bath for 3 h and measured by CVAFS.

Analyses of Hg species in water samples were completed within 28 days after sampling. Total Hg (THg) and dissolved Hg (Hg_D) were analyzed using Method 1631 (US EPA, 1999). Particulate Hg (Hg_P) was calculated as $\text{THg} - \text{Hg}_\text{D}$. MeHg in water samples was analyzed using distillation and

ethylation processes and GC–CVAFS detection according to US EPA Method 1630 (US EPA, 2001).

2.5. Quality control

Quality control for total Hg and MeHg analysis was shown in Table 2. Results were in excellent agreement with the certified values. The relative percentage difference of sample duplicates was <5%. Spike recovery from water samples was made for each batch of analysis and the recoveries ranged from 88.2 to 108.4%. The average relative standard deviation was less than 5%. The detection limit of MeHg was 0.04 ng l^{-1} for water sample.

3. Results and discussion

3.1. TGM in ambient air

The TGM distribution in the smelting areas is shown in Fig. 2. TGM concentrations were highly elevated at the

Table 1
Hg in Weining County (TGM concentrations in ambient air, THg and MeHg concentrations in soil, and THg concentrations in corn plants)

ID	Description	Soil ($\mu\text{g kg}^{-1}$ dry weight)				Corn ($\mu\text{g kg}^{-1}$ dry weight)				TGM ^a (ng m^{-3})
		THg	MeHg	OC (%)	pH	Root	Leaf	Stalk	Grain	
Soil and corn from a narrow valley at Lushan (L) with winds blowing west and a mountain with steep slopes										
L1	Cornfield near a smelting area in a hill	259	0.80	4.0	4.8	143	238	13	10	35
L2	Cornfield 200 m west of L1	176	0.25	1.7	5.3	100	157	12	4.8	24
L3	Cornfield 1000 m west of L1	303	0.41	2.8	5.5	88	149	12	5.7	18
L4	Cornfield 1000 m from L3	186	0.20	2.9	6.3	37	108	14	5.6	13
L5	Cornfield 2200 m from L4	102	0.46	5.1	4.7	55	104	7	4.7	17
L6	Cornfield near one residential area	76	0.36	2.9	6	39	92	11	4.7	15
L7	Different cornfield near the same residential area	62	0.34	5.5	5.4	44	78	12	5.0	15
L8	Cornfield 3000 m from L7 as reference site	121	0.30	5.1	5.4	59	66	11	4.9	17
Soil and corn from Dongfeng (D)										
D1	Cornfield a valley near the smelting area	250	1.10	7.1	5.9	89	255	12	4.6	35
D2	Cornfield 1000 m south of D1	282	0.49	9.4	6	83	451	13	6.2	37
D3	Cornfield 1800 m south of D2	72	0.47	1.5	5.3	51	162	10	5.4	31
D4	Cornfield near one residential area	96	0.45	4.5	5.8	53	178	13	4.9	32
D5	Cornfield near another smelting area	204	0.66	1.5	4.9	196	837	21	5.5	48
D6	Cornfield near the river	84	0.77	7.1	5.9	89	255	12	4.6	27
Soil and corn from Ertang (E)										
E1	Cornfield on a hill near the smelting area	188	0.82	4.1	4.4	113	349	18	10	39
E2	Cornfield 500 m south of E1 on the ridge	355	0.77	5.4	5	164	312	75	13	32
E3	Cornfield near the river	219	0.66	4.1	5.8	48	82	10	5.6	21
E4	Cornfield 2200 m from E3	176	0.72	4.5	6	79	90	12	4.9	23
E5	Cornfield 4000 m from E4 as reference site	119	0.75	7.9	6.1	63	121	13	4.5	27
Soil and corn in a valley that extends north at Jinzhong (J)										
J1	Cornfield near a waste pile	179	1.0	3.2	6.2	88	115	12	5.6	28
J2	Cornfield 200 m from J1	224	0.58	4.1	5.6	116	71	10	8.2	21
J3	Cornfield 1000 m northwest of the smelting area	183	0.30	4.4	6.3	67	54	11	6.0	16
J4	Cornfield 1300 m northwest of J3	183	0.48	4.3	6.7	39	92	14	6.4	13

^a TGM concentrations in ambient air in the cornfield.

smelting sites and sharply decreased away from the smelting sites. A previous study showed that >98% of the Hg in Zn ore was emitted to the atmosphere due to the high smelting temperature of $\sim 1000^\circ\text{C}$ (Feng et al., 2004).

TGM concentrations in the atmosphere in Weining County are presented in Table 2. As expected, high TGM concentrations were observed at smelting sites, with the highest geometric mean value of 124 ng m^{-3} (Table 3), similar to those values found in the air impacted by a chlor-alkali plant in Sweden and a thermometer plant in Chongqing, China. (Wängberg et al., 2003; Wang et al., 2003). However, the average concentration value is much lower than the value ($18,047 \text{ ng m}^{-3}$) in ambient air caused by an operating gold mill using Hg technology in

Tongguan, China (Dai et al., 2004). These data indicated that workers employed in those smelting workshops might be exposed to high levels of Hg through inhalation.

TGM concentrations near residue piles were much lower compared to those in workshops, with a geometric mean value of 36 ng m^{-3} . The geometric mean TGM concentration in the residential area was 20 ng m^{-3} , which is still much higher than the mean concentration obtained in urban areas in China, such as Guiyang, Beijing, Chongqing, and other areas as shown in Table 3 (Liu et al., 2002; Feng et al., 2003; Li et al., 2005; Wang et al., 2006b). TGM concentrations at a site far distance away from the smelting sites (e.g. Jinzhong) were always less than 10 ng m^{-3} (Fig. 2). Compared to TGM concentrations

Table 2
Summary of measured and certified values of THg and MeHg concentrations in some standard reference materials ($\mu\text{g g}^{-1}$)

Name	Standard material	Certified value \pm SD	Measured mean value \pm SD	Recovery (%)
GBW07165	Rich Pb and Zn ore rock	114 ± 20	110 ± 2	96.5
GBW07168	Zn concentrate	540 ± 80	533 ± 7	98.7
GBW07405	Soil reference material	0.29 ± 0.04	0.30 ± 0.01	103.4
GBW07604	Foliage of polar	26.0 ± 3.0	25.6 ± 1.5	98.5
IAEA 405 ^a	Sediment reference material	5.49 ± 0.53	5.67 ± 0.25	103.3

Recovery (%) = (mean measured value/mean certified value) \times 100%.

^a Concentration for MeHg.

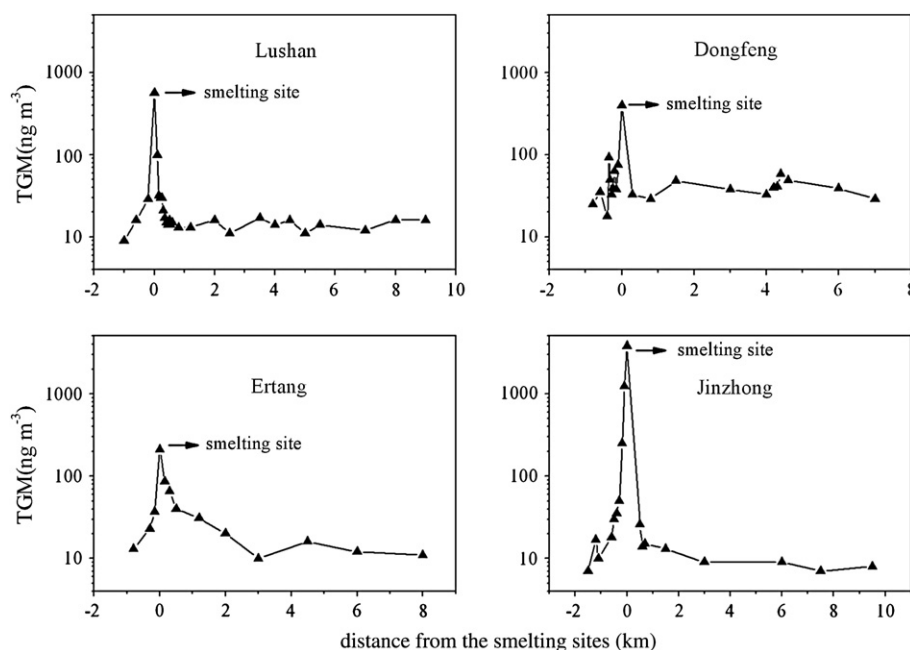


Fig. 2. Total gaseous Hg concentrations with distance from different smelting sites.

observed at background sites in the northern hemisphere ($\sim 1.5\text{--}2.0\text{ ng m}^{-3}$; Lindberg et al., 2007), the average TGM concentrations observed at the control sites in Weining County were significantly elevated.

3.2. The Hg emission factor from the artisanal Zn smelting process

We used a simple mass balance to estimate the Hg emission factor from the Zn smelting process. The range and average

concentrations of Hg and Zn in carbonate Zn ores and smelting residues in the study area are presented in Table 4. Hg emissions during the Zn smelting process come from the ore itself, due to the high temperature smelting process, as well as coal combustion. In order to estimate the Hg emission factor, one assumption was made: no mercury in the final Zn ingots (Feng et al., 2004). The Hg emission factor from Zn smelting using carbonate Zn ore is calculated from Eq. (2),

$$Fo = [A - (1 - \beta)B] / \{[C - (1 - \beta)D]\gamma\} \quad (2)$$

Table 3

Statistical results of TGM concentrations in ambient air measured in Weining County and other cities in China (ng m^{-3})

City	Site	Season	Geometric mean TGM	<i>n</i>	SD
Weining ^a	Category 1 workshops	Autumn	124 (30–3814)	24	895
	Category 2 waste residue pile	Autumn	36 (25–63)	18	10
	Category 3 farmland	Autumn	25 (13–48)	25	8
	Category 4 residential area	Autumn	20 (7–50)	22	11
Chongqing ^b	Jinyun mountain	Autumn	9.9 (7.3–13.0)		
	Beibei district (contaminated)	Spring	24.8 (5.0–139.3)		
Beijing ^c	Three suburban sites	Winter	8.6; 10.7; 6.2		
	Two urban sites	Winter	24.7; 8.3		
		Summer	10; 12.7		
	Rural	Summer	3.1–5.3; 4.1–7.7		
Guiyang ^{d,e}	Urban	Spring	7.09		
	Urban	Year-round	7.39		
Huangshi ^f	Urban factory		34–1257	5	
	Urban		5–341	4	
	Suburban		4–9	4	

^a This study.

^b Wang et al. (2006b).

^c Liu et al. (2002).

^d Shang et al. (2003).

^e Feng et al. (2004).

^f Li et al. (2005).

Table 4
Mercury and zinc concentrations in carbonate Zn ores and smelting residues

Sample type	Hg concentration (g t^{-1} of ore or smelting residue)					Zn concentration (t t^{-1} of ore or smelting residue)				
	Min	Max	Geometric mean	SD	<i>n</i>	Min	Max	Geometric mean	SD	<i>n</i>
Carbonate Zn ores	1.06	87.1	13.4	25	29	0.097	0.32	0.20	0.066	29
Smelting residue	0.016	0.19	0.08	0.038	18	0.0021	0.039	0.015	0.011	18

where F_o is the Hg emission factor from Zn smelting using carbonate Zn ores in g Hg t^{-1} of Zn produced; A and B are Hg concentrations in carbonate Zn ores and in smelting residues in g t^{-1} , respectively; C and D are Zn concentrations in carbonate Zn ores and smelting residues in t t^{-1} , respectively; β is mass loss ratio during Zn smelting, which is calculated from Eq. (3) assuming that mass loss from the Zn production process is due to the removal of Zn from the ore,

$$\beta = C - D \quad (3)$$

and γ is the recovery of Zn from the artisanal smelting process and varies from 0.85 to 0.90 (Wang et al., 2000). A value of 0.90 was selected for γ in this study.

According to Eq. (2), the Hg emission factor of Zn smelting using carbonate Zn ores varies from 11 to 330 g Hg t^{-1} (average 75) of Zn produced, similar to that obtained in Hezhang County using the same Zn smelting method (Feng et al., 2004), but is much higher than the value of 20 g Hg t^{-1} of Zn produced for industrial Zn smelting in developing countries reported by Pacyna and Pacyna (2002). A high Hg emission factor in this study suggests that artisanal Zn smelting activity in Weining is an important Hg emission source to the ambient air.

3.3. Hg in soils

Total Hg and MeHg concentrations in cornfield soils are shown in Table 4. Overall data for samples collected from the study areas were affected to some degree by the local Zn smelting activities. Concentrations of total Hg in cornfield soils were more contaminated within or near smelting sites compared to those in cornfields at the residential and the reference sites (far from smelting sites, e.g. L8 and E5). Total Hg in soil samples collected from near the smelting sites ranged from 72 to 355 $\mu\text{g kg}^{-1}$, with a geometrical mean value of $186 \pm 73 \mu\text{g kg}^{-1}$, similar to concentrations in contaminated cornfield soil irrigated historically with sewage effluent in suburban Beijing (Rothenberg et al., 2007). Soil samples in L8 and E5 collected within $\sim 9 \text{ km}$ of the nearest Zn smelter also had relatively high total Hg concentrations of 119 and 121 $\mu\text{g kg}^{-1}$, respectively (Table 1). Total Hg concentrations in soil decreased exponentially with increasing distance from the smelting sites (Fig. 3). Since no Hg mineralization was discovered in the study area, the elevated Hg in soil is believed to be a result of Hg emission and subsequent deposition from the Zn smelting process. The pattern of total Hg distribution in soils from those sites may, therefore, be explained by the

particulate Hg and RGM emitted from the pyrometallurgical process, as well as Hg adhered to dust carried in the wind from smelting slag piles, all of which can rapidly deposit within or near the smelting area (Ragaini et al., 1977; Sterckeman et al., 2002). Total Hg concentrations in cornfield soils near the residential areas varied from 62 to 96 $\mu\text{g kg}^{-1}$, with a geometrical mean value of $76 \pm 17 \mu\text{g kg}^{-1}$, suggesting that these soils represent the regional background soil with respect to total Hg content in Weining County.

Similarly, more contaminated soils near the Zn smelting sites exhibit MeHg concentrations ranging from 0.20 to 1.1 $\mu\text{g kg}^{-1}$, with a geometrical mean concentration of 0.52 $\mu\text{g kg}^{-1}$ (Table 1). The soil samples with the highest MeHg concentrations were found within or near the smelting sites, such as samples J1, D1, and E1. As shown in Fig. 3, we do not observe any trends in soil MeHg concentrations with respect to the distance from the smelting site. The percentages of MeHg to total Hg range from 0.08 to 0.92%, which is well in agreement with the literature data (Horvat et al., 2003; Qiu et al., 2005). In general, there is no significant correlation

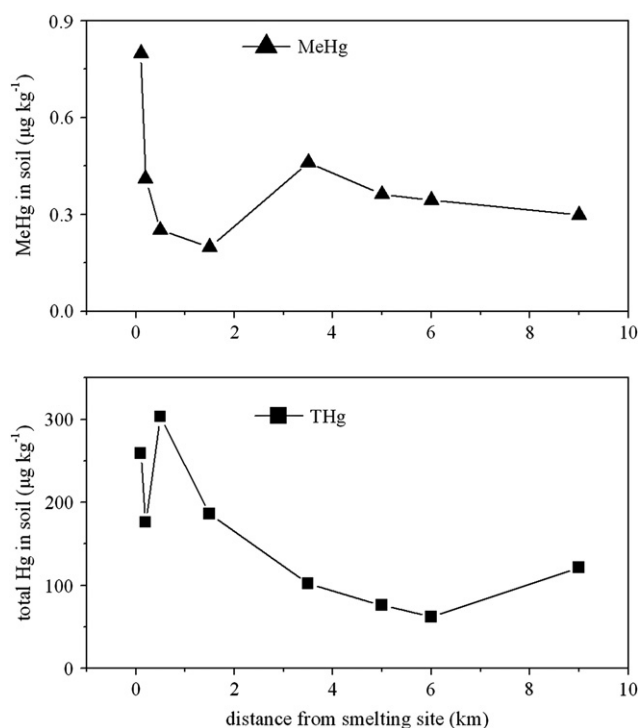


Fig. 3. Total Hg and MeHg concentrations in soil samples at various distances from zinc smelting area.

between the concentrations of total Hg and MeHg in soil reflecting the fact that the total Hg concentration is not the only factor influencing the transformation mechanisms of Hg in different environmental conditions (Fig. 4) (Qiu et al., 2005). Moreover, the concentrations of MeHg in soil do not seem to be influenced by soil organic carbon (OC) content, and there is no correlation between MeHg and soil %OC in our study (Fig. 5) (Feng et al., 2006a).

THg concentrations in soil samples collected from Hezhang were higher than those from Weining (Table 5). Li and Thornton (1993) found that the geochemical associations accompanying the mineralization of ore fields affected Hg concentration in the topsoil in Pb or Zn mining area. Sterckeman et al. (2002) found the technological methods of producing Zn might be the major factor controlling Hg concentration in topsoil around two Zn plants in the north of France. No Zn mineralization was observed in the Zn smelting areas both in Hezhang and Weining Counties, and the ores used came primarily from the adjacent provinces such as Yunnan and Sichuan. Moreover, the same Zn smelting technology was utilized in both areas. It is obvious that the extent of Hg contamination to the local environment is also related to the scale and history of Zn smelting activities. Hezhang has a longer Zn smelting history than Weining, so that total Hg concentrations in soil samples collected from Hezhang are higher than those from Weining. As expected, Hg concentrations in soil near the artisanal smelting workshops were much lower than those near the larger Zhuzhou and Huludao Zn smelters (Table 5) (Wang and Stuanes, 2003; Feng et al., 2006b; Zheng et al., 2007; Li, 2007).

3.4. Hg in surface waters

Concentrations of different Hg species in surface water samples collected from the Weining Zn smelting area are listed in Table 6. Concentrations of THg and Hg_D ranged from 95 to 278 ng l⁻¹ and from 87 to 117 ng l⁻¹, respectively. These values are much higher than those in spring water in the

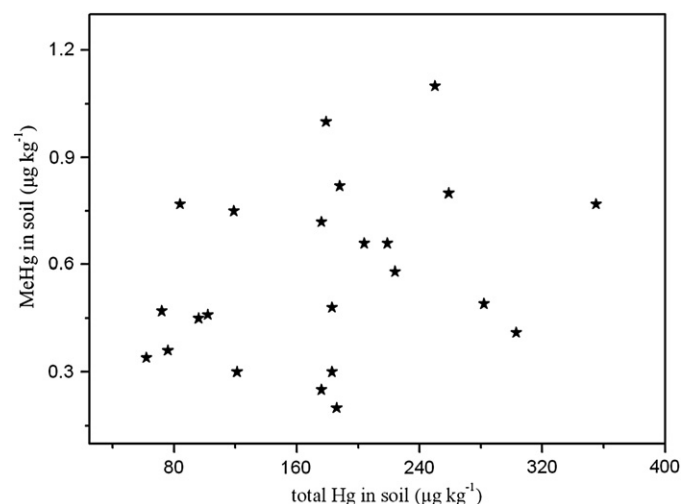


Fig. 4. Total Hg with respect to MeHg in soil samples.

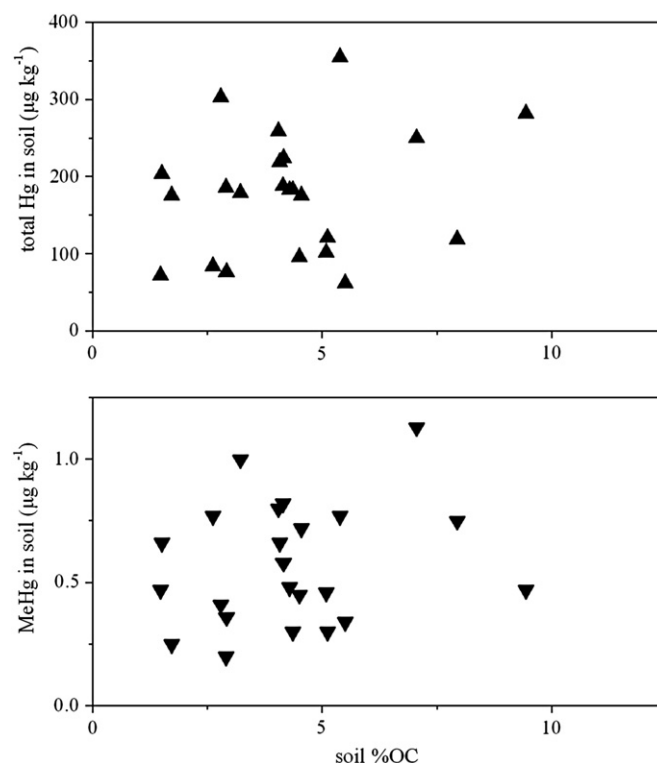


Fig. 5. Total Hg and MeHg with respect to TOC in soil samples.

artisanal zinc smelting area which are 13 ng l⁻¹ for THg (Feng et al., 2004), and also higher than those in Aha lake, a background site for THg (2.1–19.1 ng l⁻¹) in the same region (Bai et al., 2006). The highest THg concentration of 278 ng l⁻¹ was observed at sampling station 13 in the Ertang area, where surface water flows through the smelting residue piles. THg concentrations in the main river at a distance of ~3.5 km from Dongfeng smelting area decreased gradually (e.g. samples 14 and 15, Table 6) compared with the station 13. Hg_D includes soluble Hg as well as Hg in the colloidal fraction because we used a 0.45-µm filter to separate particulate from dissolved Hg. Several studies have indicated that a significant fraction of Hg leaving mining sites is found in the colloidal fraction (Sarkar et al., 2000; Kim et al., 2004a,b; Slowey et al., 2005). This may explain the high proportions of dissolved Hg to total Hg, which varied from 34 to 95% with an average value of 74%, found in our study.

Concentrations of total MeHg (TMeHg) and dissolved MeHg (MeHg_D) in the surface water samples varied from 0.23 to 6.1 ng l⁻¹ and from 0.19 to 2.2 ng l⁻¹, respectively (Table 6). The total MeHg/THg ratios in surface water samples ranged from 0.1 to 4.4%. The highest total MeHg concentration and TMeHg/THg ratio were measured in water samples near the smelting site (samples 1, 8, and 11). The MeHg_D/Hg_D ratios ranged from 0.21 to 2.6%.

3.5. Hg concentrations in corn plants

The Hg concentrations in different tissues of corn plants (*Z. mays* L.) are listed in Table 1. Total Hg concentrations

Table 5
Mercury concentrations in topsoils collected from lead or zinc mines and smelting areas worldwide (dry weight)

Location		Total Hg (mg kg ⁻¹)	Pollution source
Weining, China ^a	Reference sites	0.119, 0.121	Zn smelting
	Residential sites	0.076 (0.062–0.096)	
	as regional background		
	Contaminated sites	0.186 (0.072–0.355)	
Hezhang, China, PR China ^b		0.38 (0.14–0.58)	Zn smelting
Huludao, China, PR China ^c		1.28 (0.128–3.79)	Zn smelting
Zhuzhou, China, PR China ^d		0.08–1.5	Zn smelting
Zn smelting area, PR China ^e		0.27 (0.16–0.35)	Zn smelting
		1.03 (0.26–2.99)	
		0.150 (0.090–0.280)	
Douai, north of France ^f		0.240 (0.060–0.550)	Zn smelting
		0.18–0.80	
Derbyshire, UK and Shiphams, UK ^g		1.9–5.8	Pb smelting and mining Zn mining

^a This study.

^b Feng et al. (2006b).

^c Zheng et al. (2007).

^d Wang and Stuanes (2003).

^e Li (2007).

^f Sterckeman et al. (2002).

^g Li and Thornton (1993).

ranged from 45 to 837 $\mu\text{g kg}^{-1}$ in leaf tissue, from 30 to 196 $\mu\text{g kg}^{-1}$ in root tissue, from 7 to 75 $\mu\text{g kg}^{-1}$ in stalk tissue, and from 4.6 to 13 $\mu\text{g kg}^{-1}$ in grain. Total Hg concentrations in leaf tissues were significantly higher than those in other parts and usually decreased in the order leaves > roots > stalks > grains (Fig. 6). Total Hg concentrations in different tissues of corn plants gradually decreased with distance from the smelting sites, which is in agreement with results for total Hg in corn grown in the artisanal Zn smelting area in Hezhang (Feng et al., 2006b).

In our study the Hg level in stalk is similar to that in the agricultural fields irrigated historically with sewage effluent and groundwater in suburban Beijing, but the Hg level in roots is higher than that in soil in suburban Beijing, which may be due to different soil factors and Hg sources (Rothenberg et al., 2007). The highest concentration of Hg in corn grain was 13 $\mu\text{g kg}^{-1}$, lower than the maximum limit for foodstuff in China (20 $\mu\text{g kg}^{-1}$). This value is higher than those in sewage-irrigated cornfields in China (Xiao et al., 1997) and in the Rwamagasa artisanal gold mining area, northwest Tanzania (Taylor et al., 2006), which mainly were below the detection limit of 4 $\mu\text{g kg}^{-1}$. In this study considerably higher Hg concentrations in leaf tissue were found compared to other tissues of the corn plants (Fig. 6). Hg in leaves would inevitably enter the human food chain and pose health concerns since the leaf tissues of corn are usually used as important foodstuffs for local livestock in Weining.

Mosbæk et al. (1988) found that airborne Hg may directly contribute more than 90% of the Hg content in green parts of plants, suggesting that Hg accumulation in the foliage of green plants takes place predominantly via uptake of atmospheric Hg. This observation has been corroborated by several other studies (Bargagli et al., 1986; Rea et al., 2002; Ericksen et al., 2003; Ericksen and Gustin, 2004). Highly elevated

Table 6

Concentrations (ng l⁻¹) of different mercury species in surface water samples collected from Weining County zinc smelting area

Sample ID	Description	THg	Hg _D	Hg _P	TMeHg	MeHg _D
<i>Water samples from the town of Lushan</i>						
1	Lower reach of a stream	126	103	23	5.6	0.99
2	Under a bridge	157	117	39	0.23	0.19
3	Lower reach of another stream	175	111	64	1.0	0.38
4	Mainstream	191	117	73	0.37	0.24
5	A nearby residential area	107	93	14	3.2	0.89
6	Water from a small waterfall	120	107	13	0.31	0.19
7	Spring water at bottom of hill	95	87	8.3	0.58	0.29
<i>Water samples from the town of Dongfeng</i>						
8	Middle reach of a stream near smelting site	116	96	20	3.8	0.37
9	Lower reach of the same stream	115	— ^a	— ^a	0.48	— ^a
10	Near a bridge in residential area	99	— ^a	— ^a	0.28	— ^a
11	Main stream near another smelting site	141	100	42	2.6	1.4
12	Main stream	176	— ^a	— ^a	0.24	— ^a
<i>Water samples from the town of Ertang</i>						
13	Lower reach of a stream	278	99	179	1.8	1.1
14	After the confluence of a tributary and the main stream	256	87	168	0.47	2.2
15	Main stream	220	— ^a	— ^a	6.1	— ^a
<i>Water samples from the town of Jinzhong</i>						
16	Spring water in a small pool	104	99	5.4	0.77	0.49
17	Middle reach of a stream before it disappears underground	111	103	7.8	0.70	0.35

^a Not detected.

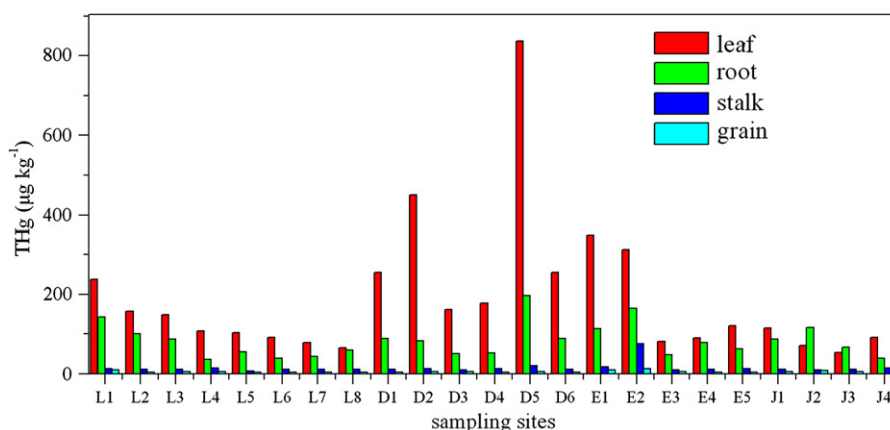


Fig. 6. The distribution of total Hg in different parts of the corn plant.

TGM concentrations, ranging from 13 to 48 ng m⁻³, were observed in the ambient air in the cornfield. There was a positive correlation to soil levels ($y = 0.0775x + 12.2$; $r^2 = 0.672$) (Fig. 7). This linear relationship suggests that *Z. mays* L. absorbs Hg from ambient air.

Table 7 shows that there is no statistical correlation between soil vs. stalk ($r^2 = 0.057$, $p = 0.27$), but that there is a significant positive correlation ($r^2 = 0.32$, $p < 0.01$) between stalk and leaf and root vs. stalk ($r^2 = 0.22$, $p = 0.023$). However, the correlation between stalk and leaf is more significant than that between root and stalk. This may suggest that the source of Hg in the stalk is more likely to be from the leaf, which primarily gets its Hg from the atmosphere. Total Hg concentrations in root tissues positively correlated with THg in the corresponding soil samples, with $r^2 = 0.39$ ($p < 0.01$). Moreover, THg concentrations in root tissues also correlated significantly with TGM in the ambient air ($r^2 = 0.53$, $p < 0.01$). Apparently, this indicated the Hg concentration in roots was dependent on Hg concentration in soil and TGM in ambient air.

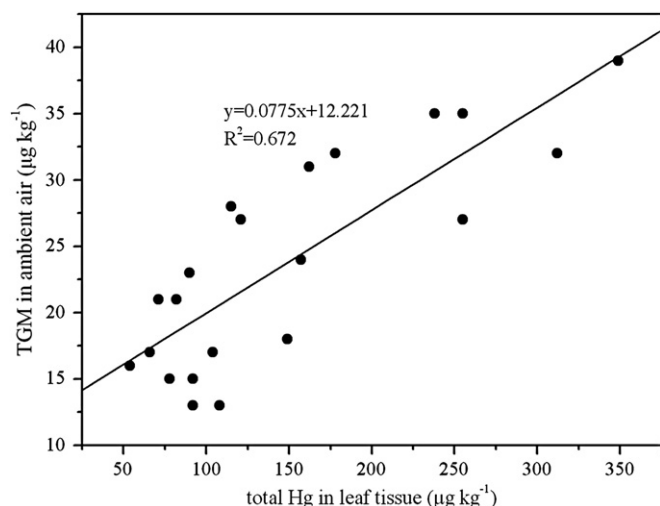


Fig. 7. Total Hg in leaf tissue with respect to TGM in ambient air in cornfields.

4. Conclusions

Our study revealed significant Hg contamination in the local environment due to artisanal Zn smelting activities in Weining County, Guizhou Province. Artisanal Zn smelting workshops are clearly an important Hg emission source in this area. The geometrical mean Hg emission factor of Zn smelting using carbonate Zn ores is 75 g Hg t⁻¹ of Zn produced. High TGM concentrations in ambient air in the Zn smelting workshop areas were observed, which may eventually pose a potential risk to the health of the Zn smelting workers. The cornfield soil and corn plants in the vicinity of the Zn smelters were also contaminated with mercury. In the vicinity of the smelters, high total Hg concentrations in soils may be a result of the deposition of Hg combined by dust and RGM emitted from Zn smelting processes. In the study area, surface waters were also heavily contaminated with Hg due to Zn smelting activities, suggesting that Hg methylation processes were enhanced near the smelting sites. Hg concentrations in corn plant tissues increased in the order of grains < stalks < roots < leaves. Our data indicate that uptake

Table 7

Huber's robust regression results for mercury concentrations in soil, TGM in the ambient air and Hg concentrations in different tissues of corn plants ($n = 25$)

Plot	Potential outliers	Robust regression results	
		r^2	p
Grain vs. root	E2, D5	0.34**	<0.01
Stalk vs. root	E2, D5	0.22**	0.023
Grain vs. soil	E2	0.30**	<0.01
Stalk vs. soil	E2	0.057*	0.27
Grain vs. leaf	D5, E2	0.022**	0.50
Stalk vs. leaf	E2, D5	0.32*	<0.01
Air vs. grain		0.053*	0.29
Air vs. stalk	E2	0.15*	0.071
Soil vs. root		0.39*	<0.01
Air vs. root	D5	0.53*	<0.01

*Not correlated ($p > 0.05$).

**Significantly correlated ($p < 0.05$).

of atmospheric Hg by leaves is the predominant pathway for Hg accumulation in plants.

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