



## Mercury emission to atmosphere from primary Zn production in China

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### ABSTRACT

Emissions of mercury (Hg) to air have regional and global impacts through long range transport in the atmosphere. Primary Zn production is regarded as an important anthropogenic Hg source in China, but research on its Hg emission is limited. To gain a better understanding of Hg emissions from Zn production activities in China, field investigations at four industrial-scale Zn production plants using electrostatic process with Hg removal (HP-WR), electrostatic process without Hg removal (HP-WOR), retort Zn production (RZ), imperial smelting process (ISP), and one artisanal Zn smelting process (AZ) were carried out. In the investigation, Hg emission factors are defined as how much Hg was emitted to the atmosphere per ton Zn produced during various Zn production methods and were estimated by using mass balance method. The results showed that the estimated Hg emission factors of Zn production were  $5.7 \pm 4.0$  g Hg t<sup>-1</sup> Zn for HP-WR,  $31 \pm 22$  g Hg t<sup>-1</sup> Zn for HP-WOR,  $34 \pm 71$  g Hg t<sup>-1</sup> Zn for RZ,  $122 \pm 122$  g Hg t<sup>-1</sup> Zn for ISP, and  $75 \pm 115$  g Hg t<sup>-1</sup> Zn for AZ. Approximately 80.7–104.2 t year<sup>-1</sup> of Hg was emitted to atmosphere from primary Zn production during the period of 2002–2006 in China.

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### 1. Introduction

Mercury (Hg) is a ubiquitous element in the environment, which can be released and mobilized through both natural processes and anthropogenic activities. Contrary to natural Hg emission, the anthropogenic Hg emission to the atmosphere is well documented (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Prasad et al., 2000; Seigneur et al., 2004; Feng et al., 2006; Wang et al., 2006; Pacyna et al., 2006; Zheng et al., 2007). Observations of atmospheric Hg concentrations during the last decade indicated that Hg emission rates from anthropogenic activities decreased in Europe and North America (Slemr and Scheel, 1998; Slemr et al., 1995, 2003; Han et al., 2008; Pacyna et al., 2009). However, there are still large uncertainties on the estimate of Hg emission from certain source categories (e.g. non-ferrous metal production) in developing countries (Jaffe et al., 2005; Pacyna et al., 2006; Pan et al., 2007).

Primary Zn production is currently regarded as an important atmospheric Hg emission source. Both Hg and Zn belong to the sulphophile elements. Hg is an important associate element in Zn ores, especially in Zn sulfide ores. Therefore, Hg concentrations in Zn ores are highly variable, depending on ore types, origins or geneses, and locations. Given an average Hg concentration of 100–300 mg kg<sup>-1</sup> in sulfide ores, the high temperatures (~1000 °C) employed in Zn

smelters could result in more than 100 mg m<sup>-3</sup> (at 273 K and 10 1325 Pa) Hg in the flue gas (Habashi, 1978). Nriagu and Pacyna (1988) estimated that the Hg emission factor generated from Zn production was of 8–45 g Hg t<sup>-1</sup> Zn. Recently, Streets et al. (2005) reported that Hg emission factors for Zn production in China varied from 13.8 to 156.4 g Hg t<sup>-1</sup> Zn, with an average value of 86.6 g Hg t<sup>-1</sup> Zn. To date, emission factors of 7.5–8.0 g Hg t<sup>-1</sup> Zn for Europe, North America, and Australia, and of 20 or 25 g Hg t<sup>-1</sup> Zn for Africa, Asia, and South America are widely accepted by researchers (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Streets et al., 2005; Pacyna et al., 2006).

China is rich in Zn mines and the reserve of Zn ranks second in the world. However, the Zn ingots production, which accounted for more than 25% of the global production in 2006, ranks first in the world (ECCNMY, 2003–2007). Basically, there are two types of Zn production in China. One is the hydrometallurgical process (HP), which accounts for more than 90% production of Zn metal in the world (<http://www.iza.com/production.html>). The other is the pyrometallurgical process (PP), which consists of four sub-types: retort Zn production (RZ), the imperial smelting process (ISP), the electric furnace (EFF), and the artisanal Zn smelting process (AZ). The major difference of the HP and PP is that the first produces very pure Zn directly whereas the latter produces lower grade Zn that still contains significant impurities that have to be removed by thermal refining in the Zn refinery. Apart from Zn, ZC also contains some 25–30% or more sulfur as well as different amounts of Fe, Pb, Ag and other minerals. At present before metallic Zn can be recovered by using either HP or PP in China, sulfur in the concentrate must be removed. This is done by

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roasting or sintering. The ZC is processed at a temperature of 700–1100 °C according to different Zn production methods where ZnS is converted into the more active Zn oxide (ZnO). At the same time sulfur reacts with oxygen giving out sulfur dioxide (SO<sub>2</sub>) (Hylander and Herbert, 2008). When SO<sub>2</sub> and Hg<sup>0</sup> vapor are carried through a series of air pollution control devices (APCDs), a fraction of Hg vapor is retained by APCDs, while the rest is emitted into the atmosphere. In our study Hg emission from primary Zn production includes Hg emission during roasting or sintering processes.

The total Zn production in China in 2004 reached 2.7 million tons. It was estimated that 71.8% used HP, while 7.7%, 13%, 5.9%, and 1.6% used ISP, RZ, EFF, and AZ, respectively (ECCNMY, 2003–2007). Feng et al. (2004) and Li et al. (2008) estimated that Hg emission factors from artisanal Zn smelting activities in Hezhang and Weining in Guizhou province, China, were from 79 to 155 g Hg t<sup>-1</sup> Zn and 75 g Hg t<sup>-1</sup> Zn, respectively. However, in China data for Hg emission factors from industrial-scale Zn production plants are adopted from the studies conducted in Europe and North America.

In this paper, we present a comprehensive investigation on Hg emissions from four industrial-scale Zn production plants and one artisanal Zn smelting area in China, named as A, B, C, D and E in Fig. 1, which cover various Zn production methods (e.g. HP, ISP, RZ, and AZ). The Hg emission factors for those Zn production methods were estimated based on the mass balance method. An inventory of Hg emissions from industrial-scale Zn production plants in China was consequently compiled.

## 2. Materials and methods

### 2.1. Zn production plants description

Four industrial-scale Zn production plants, named as A, B, C and D in Fig. 1, are located in different provinces in China. Plant A located in

Hunan province is the largest Zn smelter in China. It has produced Zn metal using electrostatic process since 1950s and reclaimed Hg from flue gas during Zn production process. The ZC used by plant A comes from more than fifty Zn mines in China. Plant B is located in Liaoning province and has produced Zn since the 1930s using RZ process, which was developed from AZ process. The source of ZC in plant B is similar to that of the plant A. Plant C is located in Guangdong province and has produced Zn metal using the ISP since the 1970 s. It has its own Zn mine. Plant D is located in Guizhou province and is a middle-scale Zn smelter with 20 kilotons Zn production per year. ZC used in plant D came from Guizhou, Sichuan and Hunan provinces. The Zn production method adopted by plant D is the electrostatic process without Hg removal.

An artisanal Zn smelting area, named E, is located in Guizhou province in southwestern China. The smelting process used at E is the AZ method. Although small artisanal Zn smelting activities have been banned by the government since 2000, they still exist in the laggard and remote areas. Because of poor technology and the lack of air pollution control devices, artisanal smelting using AZ process generally emitted more Hg than other processes. The details of the AZ technique were recently described by Feng et al. (2004) and Li et al. (2008).

The main differences in the five plants are (1) the roasting temperature, (2) the type of gas cleaning devices, and (3) the method of Zn production. The Zn production from these five plants contributed nearly 30% of the total national production in 2005.

### 2.2. Sample collections

Twelve and thirty-five Zn concentrates (ZC), which came from different Zn mines in China, were collected from A and B smelters in 2005 and 2006, respectively. Other samples, e.g. feed ZC for A, B and D smelters, mixed Pb–Zn concentrate for C smelter, calcine, dust

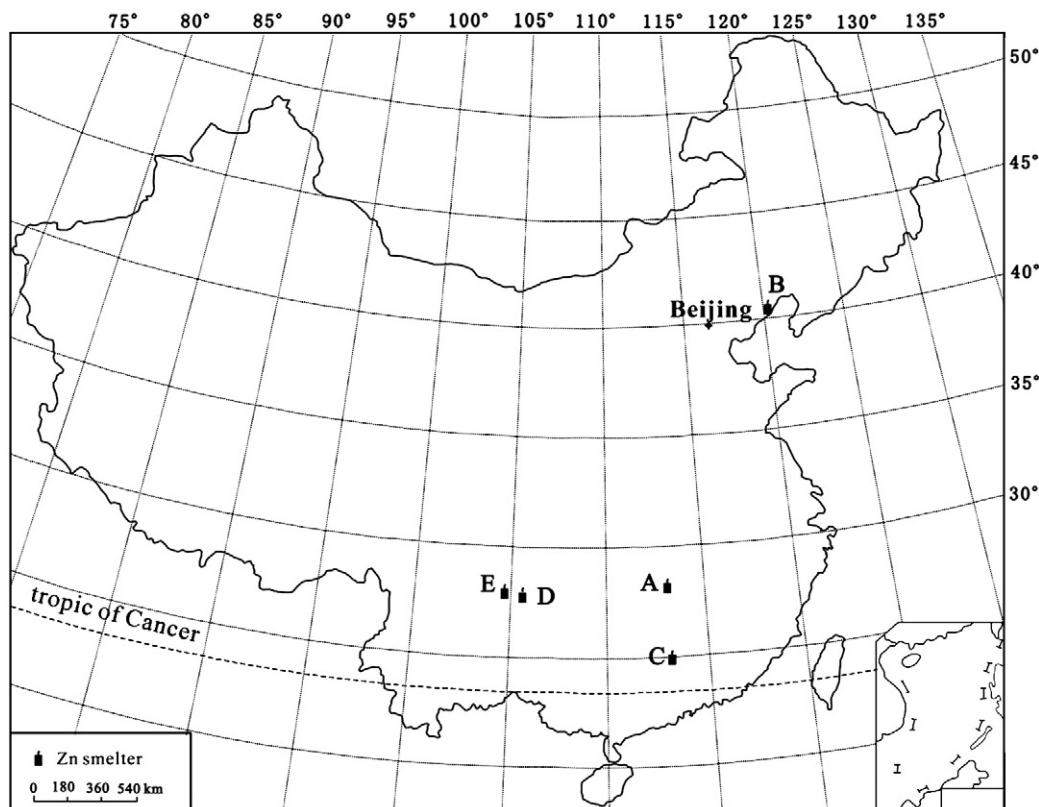


Fig. 1. The location of Zn plants in our study.

captured by waste heat boiler, cyclone collector and electrostatic precipitator (ESP), waste gas cleaning water, sillage, which was the mixture of dust captured by gas cleaning and liquid Hg from condensation of Hg vapor to liquid Hg due to vast change of flue gas temperature (from 300 °C to 40 °C), in the bottom of recycled water tank and sulfuric acid, were collected in the production line from A, B, C and D smelters. The information on the number of samples for different types of samples is listed in Table 1. The details of the sampling of E area using AZ process were recently described by Li et al. (2008). Each sample was a mixture of at least 3 sub-samples collected from the production line for 15 min to make sure that they were representative. Solid samples were stored in polyethylene bags; waste gas cleaning water was stored in polyethylene containers; and sulfuric acid was stored in brown borosilicate glass bottles.

### 2.3. Sample preparation and analysis

Solid samples were air dried after homogenization, then milled and grounded to <100 mesh for chemical analysis. For total Hg in solid samples, 200 mg samples were digested using aqua regia at a temperature of 95 °C in a water bath. Waste gas cleaning water and sulfuric acid were digested using US EPA method 7471A. Then a suitable aliquot of digested sample solution except calcine was measured using cold-vapor atomic absorption spectrometry with a detection limit of 0.01 µg kg<sup>-1</sup> (Feng and Hong, 1999). The digested solution of calcine was detected by cold vapor atom fluorescence

spectrometry. Zn concentrations in ZC were determined by the chemical method GB/T8151.1-2000.

### 2.4. Quality control

Certified Reference Materials, Zn ore sample GBW07165, and ZC sample GBW-07168 from Chinese National Research Centre, were used to accomplish the QA/QC for Hg. The average total Hg concentration in GBW07165 and GBW07168 were 110 ± 2 mg kg<sup>-1</sup> (n = 5) and 533 ± 7 mg kg<sup>-1</sup> (n = 5) respectively, which were in good agreement with the standard reference values of 114 ± 20 mg kg<sup>-1</sup> and 540 ± 80 mg kg<sup>-1</sup>, respectively. The relative difference of sample duplicates was <5%.

## 3. Results and discussion

### 3.1. Hg in Zn (mixed Pb–Zn) concentrates

Results of Hg and Zn concentrations in Zn (mixed Pb–Zn) concentrates and by-product are shown in Table 1. The concentrations of Hg in ZC in China varied widely and ranged from 2.10 to 701 mg kg<sup>-1</sup> and 1.98 to 1120 mg kg<sup>-1</sup> in A and B, respectively. The Hg contents in feed ZC from plant A, which were 106 ± 14.7 mg kg<sup>-1</sup> in the samples collected in June 2006 and 44.6 ± 1.2 mg kg<sup>-1</sup> in the samples collected in July 2006, respectively. This showed a significant variation of mercury concentrations in feed ZC, probably due to different sources of ZC.

**Table 1**  
Statistical results of Hg in the ZC and by-product in our study (N is the number of samples).

Sample	Plant/Site	Sampling time	Hg (mg kg <sup>-1</sup> )	Zn (%)	N
			Geomean ± SD	Geomean ± SD	
Zn concentrate	A	2006	31.3 ± 218 (2.10–701)	48.5 ± 4.53 (42.5–56.1)	12
	B	2005	21.5 ± 278 (1.98–1120)	46.5 ± 3.54 (38.1–57.2)	35
Feed Zn concentrate	A	06/2006	106 ± 14.7 (85.1–121)	47.8 ± 4.53 (42.2–53.0)	6
		07/2006	44.6 ± 0.65 (43.9–45.2)		3
	B	Line 1	26.1 ± 34.7 (14.7–96.7)	49.2 ± 5.23 (44.4–56.1)	9
		Line 2	37.4 ± 57.9 (11.1–148)		6
Mixed Pb–Zn concentrate	D	2007	57.9 ± 7.42 (47.2–67.0)	49.6 ± 2.90 (48.2–56.8)	6
	C	2005	190 ± 6 (183–193)	32.5 ± 2.19 (30.9–34.0)	3
Calcine	A	06/2006	0.20 ± 0.13 (0.12–0.29)		6
		07/2006	0.059 ± 0.012 (0.052–0.073)		3
Dust (captured by waste heat boiler)	B	Line 1	0.12 ± 0.13 (0.029–0.44)		9
		Line 2	0.25 ± 0.20 (0.055–0.52)		6
	D	2007	0.020 ± 0.0080 (0.013–0.035)		6
	A	06/2006	0.20 ± 0.13 (0.12–0.29)		6
Dust (captured by cyclone collector)		07/2006	0.11 ± 0.017 (0.097–0.13)		3
	B	Line 1	2.22 ± 1.43 (0.48–5.65)		8
		Line 2	2.41 ± 2.21 (0.48–6.79)		6
	D	2007	3.21 ± 1.61 (0.22–4.96)		6
	A	06/2006	0.43 ± 0.12 (0.36–0.49)		6
		07/2006	0.99 ± 0.046 (0.97–1.05)		3
	B	Line 1	3.38 ± 1.55 (0.72–5.70)		8
		Line 2	3.21 ± 1.61 (0.22–4.96)		6
Dust (captured by electrostatic precipitator)	D	2007	5.40 ± 2.20 (4.20–6.02)		6
	A	06/2006	15.6 ± 5.90 (9.84–21.3)		6
		07/2006	9.98 ± 5.59 (5.12–16.2)		3
	B	Line 1	16.9 ± 9.18 (10.1–37.7)		9
		Line 2	5.15 ± 4.10 (2.91–13.9)		6
	D	2007	6.90 ± 2.42 (4.69–10.91)		6
Waste gas cleaning water	A	06/2006	7.12 ± 3.20 (3.40–11.3)		9
		07/2006	7.26 ± 1.10 (6.73–7.79)		6
	B	Line 1	1.53 ± 0.83 (0.35–3.08)		9
		Line 2	2.83 ± 1.89 (1.20–5.08)		6
Sillage (× 10 <sup>4</sup> )	D	2007	28.9 ± 8.12 (20.5–35.6)		6
	B		5.06 ± 0.55 (4.55–5.75)		5
Sulfuric acid	A	06/2006	3.50 ± 2.30 (1.02–8.30)		9
		07/2006	2.48 ± 0.80 (2.30–2.67)		6
	B	Line 1	6.25 ± 7.04 (4.12–22.0)		6
		Line 2	12.9 ± 6.56 (7.90–30.0)		9
	D	2007	33.8 ± 7.21 (32.9–42.7)		6

Similarly, a wide range of Hg in feed ZC, 11.1–148 mg kg<sup>-1</sup>, was found in the plant B. However, the average Hg content of 57.9 mg kg<sup>-1</sup> in feed ZC used by the D smelter was equivalent to that in ZC reported by Hylander and Herbert (2008) in the world, but is lower than that in feed ZC from Finland and Sweden (Mukherjee et al., 2000; Kemi Report, 2004; Hylander and Herbert, 2008). The geometrical mean of Hg concentration in the mixed Pb–Zn concentrate of the plant C was 190 ± 25 mg kg<sup>-1</sup>.

In general, Zn contents in feed ZC varied from 40 to 60%. However, average Zn content in mixed Pb–Zn concentrate in plant C was 32.5%, which is lower than that in feed ZC in plants of A, B and D.

### 3.2. Hg removal efficiencies by APCDs

The amounts of Hg ( $F_i$ ) retained by APCDs  $i$  could be calculated from

$$F_i = [\text{Hg}]_{\text{by-products}} M_{\text{by-products}} \quad (1)$$

where  $[\text{Hg}]_{\text{by-products}}$  represents Hg concentration in by-products in Zn smelters (calcine, dust, waste gas cleaning water, and sulfuric acid);  $M_{\text{by-products}}$  stands for the amounts of by-products produced. The amounts of Hg removed by the Hg reclaiming tower were obtained from the plants' record data.

According to the mass balance, the amount of Hg emitted into atmosphere ( $Hg_{\text{emission}}$ ) from the Zn smelter was estimated as follows:

$$Hg_{\text{emission}} = [\text{Hg}] M_{\text{feed}} - \sum_{i=1}^n F_i \quad (2)$$

where  $[\text{Hg}]$  represents Hg concentration in the feed ZC in Zn smelters,  $M_{\text{feed}}$  means the amounts of the feed ZC in Zn smelters.

The Hg removal efficiency ( $\omega_i$ ) which is defined as the fraction Hg retained by APCDs can be calculated from

$$\begin{aligned} \omega_i &= 100 \frac{[\text{Hg}]_{\text{device-inlet}} - [\text{Hg}]_{\text{device-outlet}}}{[\text{Hg}]_{\text{device-inlet}}} \quad (3) \\ &= 100 \frac{F_i}{[\text{Hg}] M_{\text{feed}} - \sum_{i=2}^{i-1} F_{i-1}} \quad (i = 2, 3, 4, 5) \end{aligned}$$

On the basis of the data in Table 1, Hg removal efficiencies from the Zn production process were calculated according to Eqs. (1) to (3) and shown in Fig. 2. More than 99% Hg was evaporated from the feed ZC

during the high temperature roasting stage in plants of A, B and D. The result was similar to that of the artisanal Zn smelting reported by Feng et al. (2004) and Li et al. (2008).

Hg in flue gas exists at least in three forms, Hg<sup>0</sup>, reactive gaseous mercury (RGM), and particulate Hg (Pacyna et al., 2006; Tang et al., 2007). The dry processes, including waste heat boiler, cyclone collector and ESP, had low Hg removal efficiencies, ranging from 0.5 to 4.7% in plants A, B and D as shown in Fig. 2. Because RGM is highly water-soluble, the gas cleaning process can effectively remove RGM from the flue gas. Our data showed that approximately 3.5–5.9% and 9.2–9.8% of Hg were removed by gas cleaning process in plants A and B, respectively. During the investigations, we found that the Hg reclaiming tower had high Hg removal efficiencies, which reached to 89.2% and 93.5% in plant A in June and July 2006, respectively. However, up to 29.6–65.3% of Hg could be removed by the sulfuric acid plant. There might be two mechanisms on Hg adsorbed by sulfuric acid, (1) the sulfuric acid can oxidize Hg in situ (Habashi, 1978), and (2) Hg can be oxidized by the vanadium pentoxide catalyst bed in acid plant, which was utilized for conversion of SO<sub>2</sub> to SO<sub>3</sub> (Straube et al., 2008).

In the study, the Hg removal efficiency shown in Fig. 2 by the ESP during Zn production process is much lower than that of coal combustion power plants with ESP (Wang et al., 2000; Streets et al., 2005). This might be due to higher dust content in coal flue gas, especially if pulverized coal was burnt, the high dust surface can efficiently adsorb reactive gaseous mercury only to be later retained efficiently by the ESP. Previous studies also found that Hg removal efficiency by ESP was related to temperature and Hg concentration in flue gas (Meij and Winkel, 2006). Usually, after the ESP the temperature of flue gas was about 300 °C in Zn plants, but lower temperature of about 140 °C was found in the coal-fired power plants. In addition, the concentrations of Hg in flue gas in Zn plants were two to three orders of magnitudes higher than that in coal-fired power plants (Habashi, 1978; Tang et al., 2007). All these factors attributed to the low Hg removal efficiency by ESP in Zn plants.

### 3.3. Hg emission factors in Zn smelters

The Hg emission factor ( $F_{\text{emission}}$ ) is defined as how much Hg is emitted to atmosphere per ton Zn produced during Zn production process. The  $F_{\text{emission}}$  can be estimated as follows:

$$F_{\text{emission}} = \frac{Hg_{\text{emission}}}{M_{\text{Zn-production}}} \quad (4)$$

where  $Hg_{\text{emission}}$  represents the total amounts of Hg emission to atmosphere from Zn plants and  $M_{\text{Zn-production}}$  represents Zn production that is calculated from

$$M_{\text{Zn-production}} = M_{\text{feed}} [\text{Zn}]_{\text{feed}} \phi \quad (5)$$

where  $M_{\text{feed}}$  represents the total amount of feed ZC in Zn smelters;  $[\text{Zn}]_{\text{feed}}$  means Zn concentrations in the feed ZC;  $\phi$  represents the overall recovery of Zn during Zn production, which varied from 95.0% to 96.7% in Zn smelters (data from the plants' reports).

The results showed that the Hg emission factors were 5.0 ± 1.0 g Hg t<sup>-1</sup> Zn for June 2006 and 6.5 ± 4.8 g Hg t<sup>-1</sup> Zn for July 2006 in plant A, 30 ± 43 g Hg t<sup>-1</sup> Zn in the line 1 and 38 ± 97 g Hg t<sup>-1</sup> Zn in the line 2 of plant B, 122 ± 122 g Hg t<sup>-1</sup> Zn in the C smelter. Our previous studies found that emission factors were 31 ± 22 g Hg t<sup>-1</sup> Zn in plant D and 75 ± 115 g Hg t<sup>-1</sup> Zn in AZ process (Li et al., 2008). From the definition of the Hg emission factor from Zn production, Zn content in Zn (mixed Pb–Zn) concentrate or Zn oxide ores directly affects the emission factor. High Hg concentrations in mixed Pb–Zn concentrate from plant C resulted in a high Hg emission factor from plant C. Even though Hg concentrations in Zn oxide ores were low at

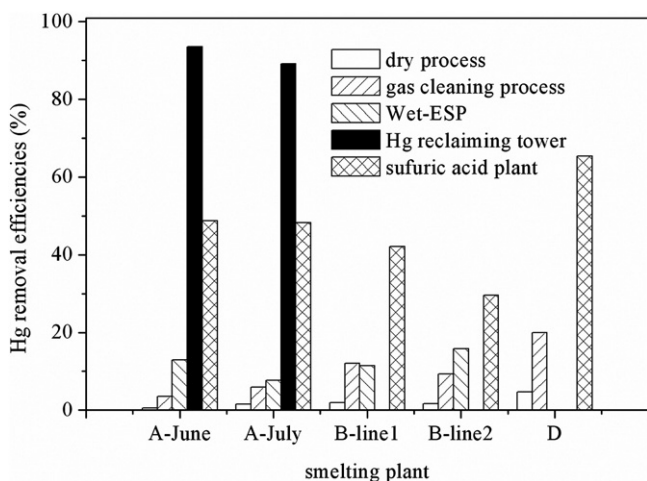


Fig. 2. Hg removal efficiencies by air pollution control devices in Zn production plants.

**Table 2**  
Statistical results of Hg emission factors in Zn production from our study and other studies.

Place	Methods	Emission factors g Hg t <sup>-1</sup> Zn	References	
China	HP <sup>a</sup>	WR <sup>b</sup>	5.7 ± 4.0	This study
		WOR <sup>c</sup>	31 ± 22	
	PP <sup>d</sup>	AZ <sup>e</sup>	75 ± 115	Li et al. (2008)
		RZ <sup>f</sup>	34 ± 71	This study
		ISP <sup>g</sup>	122 ± 122	
		AZ	79	Feng et al. (2004)
World		155		
		88.6 (13.8–156.4)	Streets et al., 2005; Wu et al., 2006	
		8–45	Nriagu and Pacyna (1988)	
Australia, Europe, Canada, USA		25	Pirrone et al. (1996)	
		7.5–8.0	Pacyna et al. (2006)	
	PP	12.09	Hylander and Herbert (2008)	
World (excl. Australia, Europe, Canada, USA)	PP	16.61		

<sup>a</sup> HP electrostatic process.

<sup>b</sup> HP-WR electrostatic process with Hg removal.

<sup>c</sup> HP-WOR electrostatic process without Hg removal.

<sup>d</sup> PP pyrometallurgical process.

<sup>e</sup> AZ the artisanal Zn smelting process.

<sup>f</sup> RZ retort Zn production.

<sup>g</sup> ISP the imperial smelting process.

plant E, it had a high Hg emission factor due to the absence of APCDs.

Our data for Hg emission factors were different than that reported by other researchers as shown in Table 2 (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Streets et al., 2005; Pacyna et al., 2006; Hylander and Herbert, 2008). The Hg emission factor of 7.5–8.0 g Hg t<sup>-1</sup> Zn adopted by Pacyna and Pacyna et al. (2006) was based on the statistical data for the production of industrial goods and/or the consumption of raw materials. An average Hg emission factor of 86.6 g Hg t<sup>-1</sup> Zn reported by Streets et al. (2005) was according to the average Hg concentration of 150 g t<sup>-1</sup> in ZC. Hylander and Herbert (2008) gave 16.61 g Hg t<sup>-1</sup> Zn of Hg emission factor in Asia from the PP method based on Hg removal efficiencies where 30% were retained by ESP and 95% retained by acid plant. The wide variations of the Hg emission factors of Zn production in the literatures might be contributed by the following reasons: (1) the concentrations of Hg in ZC or in mixed Pb–Zn concentrate; (2) Zn production methods, (3) the type and efficiency of the control equipments that can remove Hg from the flue gases, especially the Hg removal efficiencies of ESP and sulfuric acid plant, and (4) Hg reclaiming tower.

### 3.4. Hg emission from primary Zn production in China

The Zn plants we selected are from different geographic locations in China, the methods of Zn production used by these plants covered all methods used in China, and Zn concentrates used by these plants are from the major Zn ore production areas in China. In addition, as we mentioned in Section 2.1, the Zn production from these five plants contributed nearly 30% of the total national production in 2005. Therefore, we can use Hg emission factors from this study to estimate Hg emission from primary Zn production in China. Of course more study is needed to investigate Hg emission from Zn smelting in China in the future to reduce the uncertainty of Hg emission inventory from this source category.

Based on our study, we applied the Hg emission factors, which were 5.7 ± 4.0, 31 ± 22, 34 ± 71, 122 ± 122 and 75 ± 115 g Hg t<sup>-1</sup> Zn for HP-WR, HP-WOR, RZ (EFF), ISP, and AZ processes, to estimate Hg emission from the corresponding Zn production methods, respectively. The Zn production method of EFF is similar to that of RZ; hence for both EFF and RZ we used the same emission factor to estimate Hg emission in our study.

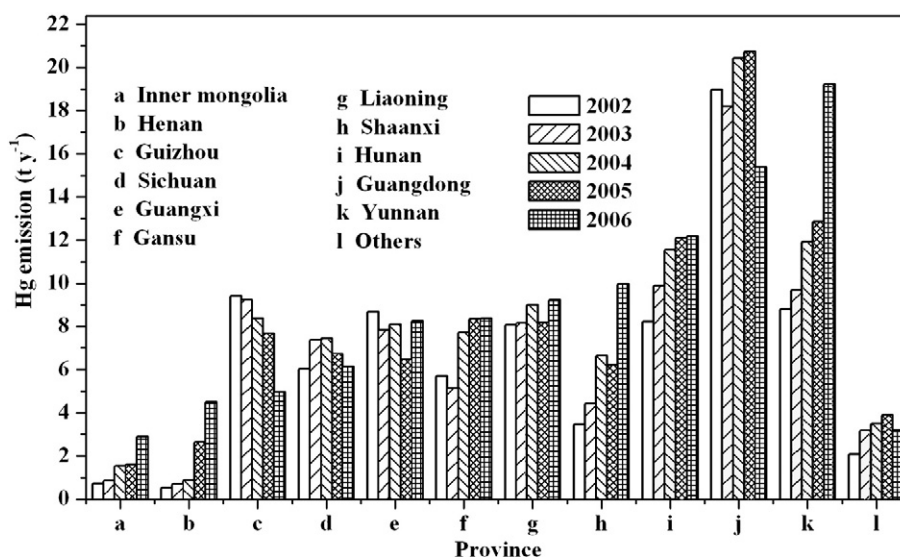


Fig. 3. Hg emission from different provinces in China.

The annual Zn production in China is increasing dramatically, reaching from 2.16 million tons in 2002 to 3.15 million tons in 2006 with an average annual increase rate of 8.9%. According to the Zn production using different sub-types Zn production methods and above Hg emission factors, Hg emissions from the Zn plants were 80.7, 84.6, 97.1, 97.4, and 104.2 t from 2002 to 2006 in China, respectively, with an average annual increasing rate of 6.1% (ECCNMY, 2003–2007). Total Hg emissions by province for 2002 and 2006 are shown in Fig. 3. The following provinces, Yunnan, Guangdong, Hunan, Shaanxi, Liaoning, Gansu, Guangxi, Sichuan, Guizhou, Henan and Inner Mongolia, contributed more than 95% of total Hg emission per year.

At the provincial level, the temporal trends of total Hg emissions show significant differences. Some provinces (e.g. Inner Mongolia, Yunnan and Henan) showed much higher Hg emission growth during the past decade; however, other provinces (e.g. Guizhou) presented reduced Hg emissions over this period. In general, the total amount of Hg emissions depended on amounts of Zn production when using the same Zn production method; however, Hg emissions for some provinces are strongly affected by the Zn production methods. Guangdong province was the largest Hg emitter among the above provinces except in 2006. This might be attributed to high Hg emission factor. More than 85% Zn produced in the province came from plant C used ISP. The Hg emission from Zn production in Guizhou province decreased sharply because up to 90% of the Zn production came from artisanal Zn smelting in the province before 2004, and then after 2004 AZ activities were completely phased out (Feng et al., 2004, Li et al., 2008). Hunan Zn production contributed 21.9–23.8% of the total Zn emissions from 2002 to 2006; however, Hg emission only contributed 10.2–12.4% of total Hg emission in China due to the employment of the Hg removal technology. It was estimated that up to 8 tons of Hg was obtained in 2005 from the plant A using Hg removal technology (personal communications with the manager of the plant).

#### 4. Conclusions

We present the first detailed estimation of Hg emissions from primary Zn production using different methods in China. Hg emission factors from Zn production using HP-WR, HP-WOR, RZ (EFF), ISP and AZ were estimated to be  $5.7 \pm 4.0$ ,  $31 \pm 22$ ,  $34 \pm 71$ ,  $122 \pm 122$ , and  $75 \pm 115$  g Hg t<sup>-1</sup> Zn, respectively. Hg reclaiming towers have the highest Hg removal efficiencies, which may play the most important role to reduce Hg emissions in China. Hg emission from Zn production was 80.7–104.2 t year<sup>-1</sup> in China from 2002 to 2006. We find that emissions are concentrated in Guangzhou, Sichuan, and Hunan provinces. However, some uncertainties remain in our knowledge of anthropogenic Hg emission from primary Zn production in China due to lack of data from analyses of gases in the stacks. In addition, we could not provide Hg speciation emission data from Zn smelters in China. To improve our understanding of mercury emission from Zn production in China, the information on speciation of mercury in the flue gas of Zn smelters is urgently needed.

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