

1    **Update of mercury emissions from China's primary zinc,**  
2    **lead and copper smelters, 2000-2010**

3    *Submitted to ACP for Special Issue titled "Atmospheric Mercury Processes: Papers*  
4    *from the 10<sup>th</sup> ICMGP"*

5    **Q. R. Wu<sup>1</sup>, S. X. Wang<sup>1</sup>, L. Zhang<sup>1</sup>, J. X. Song<sup>1</sup>, H. Yang<sup>1</sup> and Y. Meng<sup>1</sup>**

6    <sup>1</sup>School of Environment, and State Key Joint Laboratory of Environment Simulation and  
7    Pollution Control, Tsinghua University, Beijing 100084, China

8    *Correspondence to:* S. X. Wang ([shxwang@tsinghua.edu.cn](mailto:shxwang@tsinghua.edu.cn))

## 1    **Abstract**

2        China is the largest anthropogenic mercury emitter in the world, where primary  
3    nonferrous metal smelting is regarded as one of the most significant emission sources. In this  
4    study, atmospheric mercury emissions from primary zinc, lead and copper smelters in China  
5    between 2000-2010 were estimated using a technology-based methodology with  
6    comprehensive consideration of mercury concentration in concentrates, smelting processes,  
7    mercury removal efficiencies of air pollution control devices (APCDs) and the application  
8    percentage of a certain type of APCD combinations. Our study indicated that atmospheric  
9    mercury emissions from nonferrous metal smelters in 2000, 2003, 2005, 2007 and 2010 was  
10   67.6, 100.1, 86.7, 80.6 and 72.5 t, respectively. In 2010, the amounts of mercury emitted into  
11   atmosphere were  $39.4 \pm 31.5$ ,  $30.6 \pm 29.1$ ,  $2.5 \pm 1.1$  t from primary zinc, lead and copper smelters,  
12   respectively. The largest amount of mercury was emitted from the Gansu province, followed  
13   by Henan, Yunnan, Hunan, Inner Mongolia and Shaanxi provinces.  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^p$   
14   emissions from zinc smelters were 25.6, 11.8 and 1.97 t, respectively. The emissions  
15   percentage of  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  were almost the same from lead and copper smelters. The average  
16   mercury removal efficiency was  $90.5 \pm 52.5\%$ ,  $71.2 \pm 63.7\%$  and  $91.8 \pm 40.7\%$  in zinc, lead, and  
17   copper smelters, respectively.

## 1        **1    Introduction**

2        Studies on atmospheric mercury emissions from major sources have been intensively  
3 carried out in the past several years due to the worldwide concern about mercury  
4 contamination (Strode et al, 2009; Li et al, 2009; Lin et al., 2010; Wu et al, 2010; Li et al,  
5 2010; Tian et al., 2010, Kocman et al, 2011; Fukuda et al, 2011;). Nonferrous metal smelting  
6 is believed to be one of the most significant anthropogenic mercury emission sources. Global  
7 atmospheric mercury emissions from nonferrous metal smelters in 2007 reached 310 t, of  
8 which about 203 t was emitted from China. Atmospheric mercury emission from Chinese  
9 nonferrous metal smelters was estimated to be 9% of the total global anthropogenic emissions  
10 (Streets et al., 2005; Wu et al., 2006; Hylander and Herbert, 2008; Pirrone et al., 2010; Wang  
11 et al., 2010).

12        The main factors affecting atmospheric mercury emissions from nonferrous metal  
13 smelters include the mercury concentration in ore concentrate, smelting technology, the type  
14 of APCD combination applied and the application percentage of a certain type of APCD  
15 combinations. Current inventories reflecting atmospheric mercury emissions from China's  
16 zinc, lead and copper smelters are subject to high uncertainty due to the following reasons:

17        First, the range of mercury content of global ore concentrates was reported too vague  
18 and there are little data about mercury concentration in Chinese concentrates. Global results  
19 concerning mercury content in concentrates from Brook Hunt and Associates Ltd indicated  
20 that the maximum concentrations are 6000, 325 and 1500 g t<sup>-1</sup> for zinc, lead and copper  
21 concentrates, respectively, while the minima are all less than 1 g t<sup>-1</sup> (Hylander and Herbert,  
22 2008). However, no data about China's mines were noted in this report. Streets et al. (2005)  
23 reported that mercury concentration in Chinese zinc concentrates varied from less than 1 g t<sup>-1</sup>  
24 to more than 1000 g t<sup>-1</sup>. Yin et al. (2012) pointed out that such a wide range depended on the  
25 ore types and their geneses. Data about mercury concentration in Chinese lead and copper  
26 concentrates are scarce.

27        Secondly, in most previous studies, an average emission factor was used to estimate  
28 emissions, which did not consider the removal effect of APCDs. Hylander and Herbert (2008)

1 pointed out the synergic effect of APCDs but the mercury removal efficiencies in their paper  
2 were estimated on the basis of sulfur abatement technology. About 95% of gaseous mercury  
3 was removed from flue gas in zinc/lead smelters with sulfuric acid plants and no mercury  
4 removal tower (Hylander and Herbert, 2008). However, such kind of assumption neglected  
5 the different removal efficiencies of various types of sulfuric acid plant. Field measurements  
6 conducted in China's zinc, lead and copper smelters indicated the total mercury removal  
7 efficiency for zinc/lead smelters with double-contact sulfuric acid plants and no mercury  
8 removal tower is over 99% while mercury removal efficiency is only 89% for Zn/Pb smelters  
9 with single-contact sulfuric acid plants (Li et al., 2010; Wang et al., 2010; Zhang et al., 2012).  
10 In this study, these updated removal efficiencies of APCDs will be used for emission  
11 estimation.

12 Thirdly, various smelting processes and APCDs are used in China's smelters and they  
13 have been improved in the past decade because of the stringent regulations for environmental  
14 protection. Therefore, the emission factors used in previous studies will not apply to the  
15 current situation since the application percentage of the types of APCD combinations in  
16 smelters have been undergoing change. Streets et al. (2005) adopted the average mercury  
17 emission factors of 86.6, 43.6 and 9.6 g t<sup>-1</sup> for zinc, lead and copper, respectively, mainly  
18 based on the average mercury concentration in concentrates without consideration of APCDs.  
19 Hylander and Herbert (2008) estimated the emission factors of 16.61, 14.91 and 6.72 g t<sup>-1</sup> for  
20 zinc, lead and copper smelters, respectively, in the global inventory of 2005 for China's  
21 nonferrous metal smelters. However, the increased application percentage of acid plants after  
22 2005 indicates that these emission factors are not presently applicable to China.

23 In this paper, nationwide as well as imported concentrates have been sampled and  
24 analyzed for mercury content. Up-to-date mercury removal efficiencies in the existing  
25 literature have been summarized and applied. Moreover, information on smelting technologies  
26 as well as APCDs has been investigated throughout China. A technology-based method with  
27 comprehensive consideration of the above factors is used to estimate atmospheric mercury  
28 emissions from primary zinc, lead and copper smelters in China between 2000-2010.

## 2 Methodology

Various smelting processes are used in China's nonferrous metal smelters. Zinc smelting processes include oxygen pressure leaching process (OPLP), electrolytic process (EP), imperial smelting process (ISP), retort zinc smelting process (RZSP), electric zinc furnace (EZF), and artisanal zinc smelting process (AZSP). There is no atmospheric mercury emission from OPLP since it is a hydrometallurgical process and mercury in ore concentrates are released into water or solid waste. Lead smelting processes can be divided into four major types, namely rich-oxygen pool smelting process (RPSP), imperial sinter process (ISP), sinter machine process (SMP), and sinter pan or pot process (SPP). Copper smelting processes include flash furnace smelting process (FFSP), rich-oxygen pool smelting process (RPSP), imperial furnace smelting process (IFSP), roasting-leaching-electrolyzing process (RLEP) as well as the outdated technologies that were forbidden by the Chinese government such as electric furnace smelting process (EF) and the revelatory furnace smelting process (RF).

In all the above processes, although additives, such as quartz stone, limestone, also contain limited mercury, ore concentrate is the main source of mercury input. Mercury input  $Q$  for smelters with  $j$  technology in  $i$  province can be calculated using the following equations.

$$Q_{ij} = [Hg]_{com,ij} C_{com,ij} \quad (E1)$$

$$[Hg]_{com,ij} = \frac{\sum_k [Hg]_{su,k \rightarrow ij} C_{su,k \rightarrow ij}}{\sum_k C_{su,k \rightarrow ij}} \quad (E2)$$

$$C_{com,ij} = \sum_k C_{su,k \rightarrow ij} \quad (E3)$$

where  $[Hg]_{com,ij}$  and  $C_{com,ij}$  are mercury content and amount of the ore concentrates consumed by  $j$  technology in  $i$  province.  $[Hg]_{com,ij}$  is calculated based on mercury content in the concentrates supplied by  $k$  province and concentrates trade between provinces (See E2).

1 In equation E2,  $[Hg]_{su,k \rightarrow ij}$  and  $C_{su,k \rightarrow ij}$  are mercury content and supply of ore concentrates  
2 produced in  $k$  province which are transported to  $j$  technology in  $i$  province for smelting. The  
3 value of  $[Hg]_{su,k \rightarrow ij}$  is from our own survey results. The survey was conducted in China's  
4 main ore mineral and smelting plants. The number of sampling mines (see **Table S1**), and  
5 sampling, preparation and analysis methods are described in supporting information.  
6 Geometric mean of all mines was used to represent national mercury content since the  
7 distribution of mercury content meets the skewed distribution (see **Table 1** and **Fig. S1**). Most  
8 concentrates have low mercury content, typically less than 10 g mercury  $t^{-1}$  copper  
9 concentrates, or 20 g mercury  $t^{-1}$  zinc / lead concentrates (see **Table 1** and **Fig. S1**). The  
10 transportation data  $C_{su,k \rightarrow ij}$  between provinces were based on the trade between ore mineral  
11 plants and 244 smelters in our investigation (See **Table S2, S3, S4**). The value of  $[Hg]_{com,ij}$  is  
12 listed in **Table 1** and **Fig. 1**.  $C_{com,ij}$  is calculated according to equation E3. The value of  
13  $C_{com,ij}$  is shown in **Table S2, S3, S4**.

14 Based on the mercury content and amount of concentrates consumed in each province,  
15 the weighted national average of mercury content of zinc, lead and copper concentrates  
16 consumed by China's smelters in 2010 was 40.27, 20.03 and 2.25 g  $t^{-1}$ , respectively, according  
17 to equation(E4), while the corresponding results are 47.02, 16.81 and 2.82 g  $t^{-1}$ , respectively,  
18 in 2005.

$$[Hg] = \frac{\sum_i \sum_j [Hg]_{com,ij} C_{com,ij}}{\sum_i \sum_j C_{com,ij}} \quad (E4)$$

19 Mercury in ore concentrates is released in the form of gaseous mercury during  
20 pyrometallurgical extraction processing and a portion is captured by APCDs and transferred  
21 to waste water, acid or fly ash. Usually, pyrometallurgical extraction of nonferrous metals  
22 from concentrate requires dehydration, smelting/roasting, extraction and reclaiming/refining  
23 (**Fig. 2**). Total atmospheric mercury emissions from one smelter includes the sum of  
24 emissions from the above four procedures. Mercury emission from smelting flue gas,  
25 excluding overflow flue gas, is termed as the primary flue gas emission ( $E_p$ ). Mercury  
26 emission from dehydration, overflow, extraction and refining/reclaiming flue gas is regarded

as other emissions ( $E_o$ ). The atmospheric mercury emissions for smelters with  $j$  technology in  $i$  province can be calculated with the following equation.

$$E_{ij} = E_{p,ij} + E_{o,ij} \quad (E5)$$

The mercury removal effect of APCDs has been proved in previous studies (Wang et al., 2010; Li et al., 2010; Zhang et al., 2012). Generally, APCDs for primary flue gas in most nonferrous metal smelters consist of dust collectors (DC) including cyclone dust collector, waste heat boiler, electrostatic precipitator and fabric filter (or their combination), flue gas scrubber (FGS), electrostatic demister (ESD), mercury reclaiming tower (MRT), and conversion and absorption tower (CAT). The CAT may be a double conversion double absorption (DCDA) tower or a single conversion single absorption tower (SCSA). Usually, the above APCDs combined into 7 types used in smelters (**Table 2**). The information about the type APCD combinations in most smelters is based on our investigation of 244 nonferrous metal smelters. For smelters without APCD combinations information but with acid making, we assumed that the type 1 of APCD combinations (DC+FGS+ESD+DCDA) was adapted. For smelters without any information about acid production or APCDs, type 7 (None APCDs) were adapted. The proportion of metal production from smelters with different types of APCDs is given in **Table 2**. Combining the effect of APCDs and the mercury flow diagram in smelters (**Fig. 2**), atmospheric mercury emissions from primary flue gas is calculated with the following equation.

$$E_{p,ij} = \sum_l \theta_{l,ij} Q_{ij} (1 - \gamma_{d,j}) \gamma_{s,j} (1 - \xi_{of,j}) (1 - \eta_l) \quad (E4)$$

Where  $E$  is atmospheric Hg emission (kg);  $p$  refers to primary smelting flue gas;  $i$  refers to province;  $j$  refers to technology.  $\theta$  is the application percentage of a certain type of APCD combinations; information about  $\theta$  is obtained from our investigation of 244 smelters and China's Nonferrous Metal Industry Association (**Table S3**).  $l$  is the type of APCD combinations (**Table 2**).  $Q$  is mercury input (kg).  $\gamma$  is the mercury release rate; the value of  $\gamma$  was based on our field experiments in Chinese smelters (Li et al., 2007; Wang et al., 2010; Zhang et al., 2012). For technology without field experiment, the median value of the results

from other technologies was applied. Mercury release rates in various smelting process,  $\gamma_{ss}$ , are at the range of 97.7% - 99.4% (**Table S6**).  $d$  refers to dehydration sector;  $of$  refers to overflow flue gas.  $\xi$  is called as distribution coefficient (**Table S6**).  $\xi_{of}$  refers to the proportion of gaseous mercury emitted into atmosphere as overflow flue gas. The value of distribution coefficient was calculated from the mercury mass balance of field experiment result (Li et al., 2007; Wang et al., 2010; Zhang et al., 2012). Mercury distribution rate for dehydration is 0.1% - 1.0% (**Table S6**).  $\eta$  is mercury removal efficiency of APCD, the value of which was based on field experiment (Li et al., 2007; Wang et al., 2010; Zhang et al., 2012). The value of  $\eta$  is shown in **Table 3**.

Atmospheric mercury emissions from other flue gas are calculated with the following equation.

$$\begin{aligned}
 E_{o,ij} &= E_{d,ij} + E_{of,ij} + E_{e,ij} + E_{r,ij} \\
 &= Q_{ij} \gamma_{d,j} (1 - \eta_{o,j}) \\
 &\quad + Q_{ij} (1 - \gamma_{d,j}) \gamma_{s,j} \xi_{of,j} (1 - \eta_{o,j}) \\
 &\quad + Q_{ij} (1 - \gamma_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) \gamma_{e,j} (1 - \eta_{o,j}) \\
 &\quad + Q_{ij} (1 - \gamma_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) (1 - \gamma_{e,j} - \xi_{se,j}) \gamma_{r,j} (1 - \eta_{o,j})
 \end{aligned} \tag{E5}$$

Where  $o$  refers to other flue gas;  $d$ ,  $s$ ,  $e$ ,  $r$  refers to dehydration, smelting/roasting, extraction and refining/reclaiming, respectively.  $\xi_{ss}$  and  $\xi_{se}$  here refer to the proportion of mercury entering into the solid waste in the smelting and extraction sector, respectively. The value of  $\xi_{ss}$  and  $\xi_{se}$  is 0.02%-20.6%, and 2.4%-14.4%, respectively (**Table S6**).  $\gamma_d$ ,  $\gamma_e$ ,  $\gamma_r$  is mercury release rate in hydration, extraction and refining/reclaiming process. The value of these three parameters is shown in **Table S6**.  $\eta_o$  is the mercury removal efficiency for other flue gases (**Table S6**). For most processes, dust collectors are widely installed for dehydration, overflow, extraction and refining/reclaiming flue gas. In several large smelters with advanced smelting processes, flue gas desulfurization (FGD) devices are installed. No APCDs are installed for the flue gas from the out-of-date processes such as AZSP, RZSP and EF/RF. Therefore mercury removal efficiencies for other flue gas depend on the APCD applied. The mercury removal efficiencies of dust collector and FGD were 12.5% and 34.7%, respectively. (**Table S6**).



1 Atmospheric mercury emissions from  $i$  province is calculated by

$$E_i = \sum_j E_{ij} \quad (E6)$$

2

3 Atmospheric mercury emissions from  $j$  process is calculated by

$$E_j = \sum_i E_{ij} = EF_j \times M_j = EF_j \times \sum_i C_{com.,ij} \times \alpha_j \times \varphi_j \quad (E7)$$

4

5 Thus, the average emission factor for  $j$  process is

$$\begin{aligned} EF_j = & \frac{1}{\sum_i C_{com.,ij} \times \alpha_j \times \varphi_j} \times [\sum_i \sum_l Q_{ij} (1 - \gamma_{d,j}) \gamma_{s,j} (1 - \xi_{of,j}) \theta_{l,ij} (1 - \eta_l) \\ & + \sum_i Q_{ij} \gamma_{d,j} (1 - \eta_{o,j}) + \sum_i Q_{ij} (1 - \gamma_{d,j}) \gamma_{s,j} \xi_{of,j} (1 - \eta_{o,j}) \\ & + \sum_i Q_{ij} (1 - \gamma_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) \gamma_{e,j} (1 - \eta_{o,j}) + \\ & \sum_i Q_{ij} (1 - \gamma_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) (1 - \gamma_{e,j} - \xi_{se,j}) \gamma_{r,j} (1 - \eta_{o,j})] \end{aligned} \quad (E8)$$

6 Where  $\alpha$  is metal concentration and the values for zinc, lead and copper concentrates  
7 were 50.5%, 62.85 and 21.7%, respectively (**Table S6**)(CNMIA, 2011).  $\varphi$  is metal recovery  
8 rate of smelting process. For most zinc smelting process, the metal recovery rate was 95.5%  
9 while for EP it was 94%. For the lead and copper smelting processes, the metal recovery rate  
10 was 96.8% and 97.8%, respectively (**Table S6**).

### 11 **3 Results and Discussion**

#### 12 **3.1 Regional atmospheric mercury emissions from primary smelters in 2010**

13 In 2010, total mercury input into China's primary nonferrous metal smelters with the  
14 consumption of ore concentrates in 2010 was 543 t, of which 74.8%, 19.5% and 5.7% was  
15 input into zinc, lead and copper smelters, respectively. However, mercury emitted into the  
16 atmosphere was about 72.5 t from China's primary nonferrous metal smelters. Emissions

1 from primary zinc, lead and copper smelters were 39.4, 30.6 and 2.5 t, respectively. The  
2 largest mercury emitter was the Gansu province, followed by Henan, Yunnan, Hunan, Inner  
3 Mongolia and Shaanxi provinces. Summation of the emissions from these six provinces  
4 accounted for 87.9% of the national emissions (**Fig. 3**).

5 China's zinc smelters emitted 39.4 t of mercury into atmosphere in 2010. Gansu, Yunnan,  
6 Shaanxi and Henan provinces were the top four emitters. For zinc smelters, summation of  
7 mercury emissions from these four provinces accounted for 80.5% of national amount. The  
8 high mercury content of the zinc concentrate consumed was the main reason for the elevated  
9 mercury emissions in Gansu and Shaanxi province. For example, the mercury concentration  
10 in the concentrates consumed by zinc smelters in the Gansu province was as high as 403.4 g  
11  $\text{t}^{-1}$ , which is about 10 times higher than the national average. Thus, the total mercury input  
12 into zinc smelters reached 181 t in the Gansu province. If the national average was used, this  
13 value would be only 18 t. High mercury emissions in Yunnan and Henan is caused by the low  
14 application percentage of acid plants, which is only 79.3% and 48.5%, respectively

15 Atmospheric mercury emission from lead smelters was about 30.6 t. Mercury emissions  
16 from China's lead smelters came mainly from Henan, Hunan, Yunnan and Inner Mongolia.  
17 The emissions of these four provinces accounted for 89.6% of total emissions from lead  
18 smelters. Huge consumption of concentrates, more than 60% of national consumption, was  
19 the most important factor for the high mercury emissions from lead smelters in Hunan and  
20 Henan. High mercury concentration in the concentrates consumed in Inner Mongolia  
21 contributed to its high emissions while low mercury removal efficiency led to the elevated  
22 emissions in Yunnan's lead smelters.

23 Copper smelters emitted 2.5 t of mercury in 2010 and nearly half was emitted in the  
24 Yunnan province. High mercury content of copper concentrates consumed in local smelters  
25 was the main reason for the large mercury emissions in this province. Mercury content in the  
26 ore concentrates consumed by smelters in the Yunnan province was 8.7 g  $\text{t}^{-1}$ , about four times  
27 of the national average (2.3 g  $\text{t}^{-1}$ ).

28 The mercury speciation profile was assumed to be 80%  $\text{Hg}^0$ , 15%  $\text{Hg}^{2+}$  and 5%  $\text{Hg}^{\text{p}}$  for  
29 nonferrous metal smelting in previous estimate (Pacyna et al., 2002). The field experiments in

Chinese nonferrous smelters provided a very different speciation profile (Wang et al., 2010; Zhang et al., 2012). In this study, the median of the results from field experiments was used to estimate mercury speciation emissions. For zinc smelters, the percentage of  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^{\text{p}}$  in emitted flue gas emitted to the atmosphere was 65%, 30% and 5%, respectively. The  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^{\text{p}}$  emissions from zinc smelters were 25.6, 11.8 and 1.97 t, respectively. Using the same speciation profile, the  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^{\text{p}}$  emissions from lead smelters were 11.5, 17.6 and 1.53 t, respectively, and those for copper smelters were 1.19, 1.16 and 0.12 t, respectively.

### 3.2 Atmospheric mercury emissions from various smelting processes in 2010

In 2010, China's production of zinc, lead and copper from primary smelters reached 5033, 2794 and 2921 kt, respectively. For primary zinc smelters, about 2.5% of refined zinc is produced by hydrometallurgical process. The rest were produced by EP, ISP, RZSP, EZF and others, accounted for 78.7%, 7.1%, 7.9%, 1.3% and 2.5% of total zinc production, respectively. For primary lead smelters, the percentages of lead produced by RPSP, ISP, SMP and SPP were 47.3%, 5.1%, 20.2% and 27.4%, respectively. Refined copper produced by FFSP, RPSP, IFSP, RLEP and EF/RF, accounted for 34.2%, 52.4%, 9.8%, 0.2% and 3.4%, respectively.

For zinc smelters, most of mercury is emitted from smelters with EP. Mercury emissions from RZSP, EZF, ISP and AZSP were 6.3%, 2.4%, 5.4% and 14.4%, respectively. For lead and copper smelters, more than half of the mercury was emitted from smelters with out-of-date technologies (**Fig. 4**). The average mercury removal efficiency of air pollution control devices in the zinc, lead and copper smelters was  $90.5 \pm 52.5\%$ ,  $71.2 \pm 63.7\%$  and  $91.8 \pm 40.7\%$ . The mercury emissions can be further reduced by improving the mercury removal efficiencies of current APCDs or by installing mercury reclaiming tower.

### 3.3 Uncertainty analysis

The uncertainty of this inventory was estimated by combining the coefficients of variation (CV, or the standard deviation divided by the mean) of the contributing factors

1 according to the detailed methodology for uncertainty analysis described in Streets et al.  
2 (2003a). The relative 95% confidence intervals for emissions are calculated as 1.96 times CV.  
3 Thus, atmospheric mercury emission from zinc, lead and copper smelters was  $39.4 \pm 31.5$ ,  
4  $30.6 \pm 29.1$ ,  $2.5 \pm 1.1$  t in 95% relative confidence and the uncertainty is  $\pm 80\%$ ,  $\pm 95\%$  and  
5  $\pm 45\%$ , respectively. In previous studies, the uncertainty for these three sources reached 100%,  
6 200% and 100%, respectively. The improvement in this study was contributed by better  
7 knowledge on the mercury content of ore concentrates and mercury removal efficiency of  
8 APCDs. However, more field experiments are still important to better understand the mercury  
9 fate in smelters. Besides, high uncertainties exist for the emissions from small-scale smelters.

### 10 **3.4 Historical changes of mercury emissions from primary nonferrous metal** 11 **smelters**

12 According to our estimation, atmospheric mercury emissions from nonferrous metal  
13 smelters in 2000, 2003, 2005, 2007 and 2010 were 67.6, 100.1, 86.7, 80.6, and 72.5 t,  
14 respectively. At the same time, the refined metal production from primary smelters increased  
15 from 3909 kt to 4958, 6460, 8190 and 10749 kt, respectively (see **Fig. 5**). The increased  
16 application percentage of acid plants was the main reason for the atmospheric mercury  
17 abatement in the past decade. Broadly speaking, the suitability of flue gas for making acid  
18 depends on its  $\text{SO}_2$  concentration determined by the smelting process. Flue gas from process  
19 such as IFSP or SMP has a  $\text{SO}_2$  concentration lower than 3.5% and cannot be used to produce  
20 sulfuric acid. In that case, other flue gas desulfurization technologies such as ammonia  
21 absorption are applied. Flue gas produced from pool smelting processes, such as RPSP,  
22 usually has a  $\text{SO}_2$  concentration higher than 3.5% and can be used to produce sulfuric acid.

23 Mercury emissions will be further reduced after 2010 because of “the 12<sup>th</sup> five year  
24 national plan for comprehensive prevention and control of heavy metal pollution”. In this plan,  
25 China has set a target that by 2015, the mercury emissions in certain key areas will be reduced  
26 by 15% on the basis of the 2007 emission level while mercury emissions in other areas will be  
27 maintained at the emission level of 2007.

### 3.5 Comparison with previous studies

In previous mercury emission inventory studies, the emission factor method was used and the difference in mercury emissions was mainly caused by the uncertainty of the emission factors (Table 4, Table 5). In earlier estimates, the mercury emission factors for China's nonferrous metal smelters were regarded as same as those for other countries (Nriagu et al., 1988; Pacyna et al., 1996). Pirrone et al. (1996) assumed the mercury emission factors for zinc and lead smelters in developing continents to be 25 and 3 g t<sup>-1</sup> metal produced, respectively. But there were no data for developing countries including China. Wu et al. (2006) and Wang et al. (2006) analyzed the mercury content in concentrates and estimated the mercury emission factor to be 13.8-156.4, 43.6 and 9.6 g t<sup>-1</sup> for zinc, lead and copper smelters, respectively. However, these values were proven to be overestimated since the synergic mercury removal effect of APCDs was not considered (Feng et al., 2004; Li et al., 2010; Wang et al., 2010; Zhang et al., 2012). Feng et al. (2009) summarized previous studies and pointed out that the average emission factors were 5.4-155 g t<sup>-1</sup> Zn, 43.6 g t<sup>-1</sup> Pb, 9.6 g t<sup>-1</sup> Cu, respectively. If these three emission factors were adopted for emission estimation as that in Pirrone et al. (2010), the atmospheric mercury emission from nonferrous metal smelters in 2010 will reach 558 t. This indicated that atmospheric mercury emissions in China in 2010 will be overestimated by 400 t.

Hylander and Herbert (2008) considered mercury removal efficiencies in their study and total atmospheric mercury emission from China's zinc, lead and copper smelters reached 83 t in 2005, which is similar to our estimation. However, such similar results are coincidental due to their lower estimated ore mercury concentrations but also lower application percentages for acid plants. The weighted national average of mercury content in zinc, lead and copper concentrates consumed by smelters reached 47.02, 16.81 and 2.82 g t<sup>-1</sup>, respectively. However, global mercury concentration of 10, 9 and 3.5 g t<sup>-1</sup> for zinc, lead and copper concentrates was used in the former study. Thus, if we assumed concentrate consumption was the same in these two studies, the mercury input into Chinese nonferrous metal smelters was estimated to be higher than Hylander and Herbert's (2008) estimation. However, the application percentage

of acid plants in 2005 was about 76.3%, 43.7% and 70.5% for zinc, lead and copper smelters, which was also higher than their estimation. According to E4, atmospheric mercury emissions from nonferrous metal smelters increased with the raise of mercury input and the descend of application percentage of acid plants. This indicates that the lower estimation of mercury input in Hylander and Herbert's study, was offset by their lower estimation of application percentage of acid plants.

#### 4 Conclusion

In this paper, we have presented an updated estimate of mercury emissions from nonferrous metal smelters using a detailed technology-based methodology specifically for China. We estimate that the mercury emissions from zinc, lead and copper smelters in China increased by 48.1%, from 67.6 t in 2000 to 100.1 t in 2003. After 2003, the mercury emissions decreased 27.6%, from 100.1 t in 2003 to 72.5 t in 2010 although the production of zinc, lead and copper increased 116.7% in the same period. The mercury reduction is mainly due to the improvement of the smelting process and the increase of the application percentage of acid plants, from 60.9%, 30.7% and 61.0% in 2003 to 87.8%, 65.5% and 95.6% in 2010 for zinc, lead and copper smelters, respectively.

In 2010, atmospheric mercury emissions from zinc, lead and copper smelters was  $39.4 \pm 31.5$ ,  $30.6 \pm 29.1$ ,  $2.5 \pm 1.1$  tat relative 95% confidence and the uncertainty is  $\pm 80\%$ ,  $\pm 95\%$  and  $\pm 45\%$ , respectively.  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^p$  emitted from zinc smelters was 25.6, 11.8 and 1.97 t, respectively.  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$  and  $\text{Hg}^p$  emissions were 11.64, 17.74 and 1.53 t for lead smelters, respectively, while it was 1.19, 1.16 and 0.12 t for copper smelters, respectively. The average mercury removal efficiency of air pollution control devices in zinc, lead and copper smelters was  $90.5 \pm 52.5\%$ ,  $71.2 \pm 63.7\%$  and  $91.8 \pm 40.7\%$ , respectively.

With better understanding of mercury fate in nonferrous metal smelters, atmospheric mercury emission estimates based on smelting processes and mercury abatement devices lower the estimation uncertainty. However, mercury removal efficiency estimates from current studies covers a broad range and the mercury removal mechanism of APCDs is still unclear.

1    ***Acknowledgment.*** This work was financially supported by the Natural Science Foundation of  
2    China (No. 20 937 002), MEP's Special Funds for Research on Public Welfares (201209015),  
3    and Government of Norway.

## References

- CNMIA(Chinese Nonferrous Metal Industry Association): The yearbook of nonferrous metals industry of China (2011), Chinese nonferrous metal industry association publications, Beijing, China, 2011.
- Dong, S. L.: Review of nonferrous metallurgy and off-gas acid production during the tenth five-year period and prospect for development trend during the eleventh five-year period, *Sulphur. Acid Indus.*, 1, 1-7, 2007.
- Feng, X. B., Li, G. H. ,and Qiu, G. L.: A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China - Part 1: Mercury emission from zinc smelting and its influences on the surface waters, *Atmos. Environ.*, 38, 6223-6230, 2004.
- Feng, X., Streets, D., Hao, J., Wu, Y., and Li, G.: Mercury emissions from industrial sources in China, Springer, New York, USA, chap. 3, 67–79, 2009.
- Fukuda, N., Takaoka, M., Doumoto, S., Oshita, K., Morisawa, S., and Mizuno, T.: Mercury emission and behavior in primary ferrous metal production, *Atmos. Environ.*, 45, 3685-3691, 2011.
- Guo, Z. S. and Huang, W. H.: Present situation and development prospect of metallurgical acid production technologies, *Sulphur. Acid Indus.*, 2, 13-21, 2007.
- Lin, H. C.: Production of sulfuric acid with flue from nonferrous metal smelters, *Min. & Metal.*, 10(4), 58-61, 2001.
- Hylander, L. D. and Herbert, R. B.: Global emission and production of mercury during the pyrometallurgical extraction of nonferrous sulfide ores, *Environ. Sci. and Technol.*, 42, 5971-5977, 2008.
- Kocman, D.and Horvat, M.: Non-point source mercury emission from the Idrija Hg-mine province: Gis mercury emission model, *J Environ. Manage.*, 92, 2038-2046, 2011.
- Li, G. H., Feng, X. B., Li, Z. G., Qiu, G. L., Shang, L. H., Liang, P., Wang, D. Y., and Yang, Y. K.: Mercury emission to atmosphere from primary Zn production in China, *Sci. Total Environ.*, 408, 4607-4612, 2010.



- Li, G. H.: Preliminary studies on zinc smelting emission Hg to atmosphere and its effect to the environment in China, Ph.D. thesis, Institute of Geochemistry, Chinese Academy of Sciences, China, 154 pp, 2007.
- Li, P., Feng, X. B., Qiu, G. L., Shang, L. H., and Li, Z. G.: Mercury pollution in Asia: A review of the contaminated sites, *J. Hazard. Mater.*, 168, 591-601, 2009.
- Lin, C. J., Pan, L., Streets, D. G., Shetty, S. K., Jang, C., Feng, X., Chu, H. W., and Ho, T. C.: Estimating mercury emission outflow from East Asia using CMAQ-Hg, *Atmos. Chem. Phys.*, 10, 1853-1864, 2010.
- NDRC (National Development and Reform Commission): Requirements for new smelters construction in copper industry. Online available at: [http://www.ndrc.gov.cn/zcfb/zcfbgg/gg2006/t20060721\\_77236.htm](http://www.ndrc.gov.cn/zcfb/zcfbgg/gg2006/t20060721_77236.htm), 2006.
- NDRC: Requirements for new smelters construction in lead/zinc industry. Online available at: [http://www.ndrc.gov.cn/zcfb/zcfbgg/2007gonggao/t20070316\\_121733.htm](http://www.ndrc.gov.cn/zcfb/zcfbgg/2007gonggao/t20070316_121733.htm), 2007.
- Nriagu, J. O. and Pacyna, J. M.: Quantitative assessment of worldwide contamination of air, water and soils by trace-metals, *Nature*, 333, 134-139, 1988.
- Pacyna, E. G. and Pacyna, J. M.: Global emission of mercury from anthropogenic sources in 1995, *Water Air Soil Pollut.*, 137, 149-165, 2002.
- Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., and Wilson, S.: Global anthropogenic mercury emission inventory for 2000, *Atmos. Environ.*, 40, 4048-4063, 2006.
- Pirrone, N., Chinirella, S., Feng, X., Finkelman, R. B., Friedli, H. R., Leaner, J., Mason, R., Mukherjee, A. B., Stracher, G. B., Streets, D. G., and Telmer, K.: Global mercury emissions to the atmosphere from anthropogenic and natural sources, *Atmos. Chem. Phys.*, 10, 5951-5964, 2010.
- Pirrone, N., Keeler, G. J., and Nriagu, J. O.: Regional differences in worldwide emissions of mercury to the atmosphere, *Atmos. Environ.*, 30, 2981-2987, 1996.
- Streets, D. G., Bond, T. C., Carmichael, G. R., Feamdes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J. -H., and Yarber K. F.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, *J. Geophys. Res.*, 108, 8809-8831, 2003.

- Streets, D. G., Hao, J. M., Wu, Y., Jiang, J. K., Chan, M., Tian, H. Z., and Feng, X. B.: Anthropogenic mercury emissions in China, *Atmos. Environ.*, 39, 7789-7806, 2005.
- Strode, S., Jaegle, L. and Selin, N. E.: Impact of mercury emissions from historic gold and silver mining: global modeling, *Atmos. Environ.*, 43, 2012-2017, 2009.
- The State Council of the People's Republic of China: Notice on further strengthening the work of eliminating out-of-date production capacity. 2010. Online available at: [http://www.gov.cn/zwgk/2010-04/06/content\\_1573880.htm](http://www.gov.cn/zwgk/2010-04/06/content_1573880.htm).
- Tian, H. Z., Wang, Y., Xue, Z. G., Cheng, K., Qu, Y. P., Chai, F. H., and Hao, J. M.: Trends and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980-2007, *Atmos. Chem. Phys.*, 10, 11905-11919, 2010.
- Wang, S. X., Liu, M., Jiang, J. K., Hao, J. M., Wu, Y., and Streets, D. G.: Estimate the mercury emissions from non-coal sources in china, *Chinese Environ. Sci.*, 27, 2401-2406, 2006.
- Wang, S. X., Song, J. X., Li, G. H., Wu, Y., Zhang, L., Wan, Q., Streets, D. G., Chin, C. K. and Hao, J. M.: Estimating mercury emissions from a Zinc smelter in relation to China's mercury control polices, *Environ. Pollut.*, 158, 3347-3353, 2010.
- Wu, C. L., Cao, Y., Dong, Z. B., Cheng, C. M., Li, H. X., and Pan, W. P.: Evaluation of mercury speciation and removal through air pollution control devices of a 190 MW boiler, *J. Environ. Sci.*, 22, 277-282, 2010.
- Wu, Y., Wang, S. X., Streets, D. G., Hao, J. M., Chan, M., and Jiang, J. K.: Trends in anthropogenic mercury emissions in China from 1995 to 2003, *Environ. Sci. and Technol.*, 40, 5312-5318, 2006.
- Yin, R. S., Feng, X. B., Li, Z. G., Zhang, Q., Bi, X. W., Li, G. H., Liu, J. L., Zhu, J. J., and Wang, J. X.: Metallogeny and environmental impact of Hg in Zn deposits in China, *Appli. Geochem.*, 27, 151-160, 2012.
- Zhang, C.: Technology progress in domestic sulphuric acid industry during the ninth five-year plan, *Liaoning Chem. Indus.*, 30(12), 526-530, 2001.
- Zhang, L., Wang, S. X., Meng, Y., and Hao, J. M.: Influence of mercury and chlorine content of coal on mercury emissions from coal-fired power plants in China. *Environ. Sci.*

&Technol. 46(11), 6385-6392, 2012.

Zhang, L., Wang, S. X., Wu, Q. R., Meng Y., Yang H., Wang F. Y., and Hao J. M.: Were mercury emission factors for Chinese non-ferrous metal smelters overestimated? Evidence from onsite measurements in six smelters, Environ. Pollut., 171C, 109-117, 2012.

## Tables

**Table 1.** Mercury content in ore concentrates supplied and consumed by province in 2010

Province	Mercury content in ore concentrates supplied by $k$ province $[Hg]_{su,k \rightarrow ij}$ ,			Mercury content in ore concentrates consumed by $i$ province $[Hg]_{com.,ij}$ ,		
	(g t <sup>-1</sup> )			(g t <sup>-1</sup> )		
	Zinc	Lead	Copper	Zinc	Lead	Copper
Anhui	4.10	14.66	0.34	4.10	5.13	13.03
Chongqing		114.91				
Fujian	0.54	12.63		0.54		
Gansu	499.91	10.77	2.86	403.39	10.77	5.06
Guangdong	72.16	43.75	0.05	33.15	39.91	
Guangxi	9.34	10.13	0.62	10.43	6.92	25.56
Guizhou		25.67		9.74		
Hebei	4.96	2.25				9.11
Henan		6.86	0.99	16.06	19.78	10.22
Hubei	4.72	1.31				16.91
Hunan	2.16	62.21	1.84	8.98	14.33	2.20
Inner Mongolia	13.29	18.61	0.06	12.09	62.21	22.18
Jiangxi	1.47	19.51	4.66	1.47	22.06	9.81
Jilin		55.58				55.58
Liaoning		61.04		8.07	42.47	37.85
Ningxia		0.6	1.77		62.21	
Qinghai	240.77	45.14		8.44	0.60	
Shaanxi		4.92	1.5	73.61	45.26	45.14
Shandong						3.16
Shanxi		52.17	0.14	9.04		24.06

Sichuan	45.55	26.46	2.15	58.35		26.46
Xinjiang	16.86		2.02	16.86		
Xizang	0.23	0.02				10.29
Yunnan	10.98	21.54	13.68	17.66	15.21	14.38
Zhejiang	0.88	20.96		0.88		9.26
National	9.74	10.29	2.87	40.27	20.03	2.25
Other countries	9.04	3.16	0.88			

**Table 2.** The proportion of metal production from smelters with different types of APCDs

APCDs	Type of APCDs combination ( <i>l</i> )	Zinc		Lead		Copper	
		Production (kt)	Percentage (%)	Production (kt)	Percentage (%)	Production (kt)	Percentage (%)
DC+FGS+ESD+DCDA	1	3841.05	76.31	1720.57	61.58	2721.28	93.15
DC+FGS+ESD+MRT+DCDA	2	508.04	10.09	0.00	0.00	0.00	0.00
DC+FGS+ESD+SCSA	3	69.52	1.38	108.35	3.88	81.40	2.79
DC+FGS	4	37.24	0.74	179.67	6.43	18.09	0.62
DC	5	172.07	3.42	37.52	1.34	2.44	0.08
FGS	6	1.68	0.03	3.16	0.11	0.00	0.00
None <sup>a</sup>	7	275.10	5.47	744.68	26.65	98.12	3.36

a. Smelters without detailed APCDs' information are treated as having no APCDs

**Table 3.** Mercury removal efficiency of APCD

Reference APCD	Zhang et al., 2012 $\eta(\%)$						Wang et al., 2010 $\eta(\%)$	Li et al., 2010 $\eta(\%)$	This study	
	Smelter 1	Smelter 2	Smelter 3	Smelter 4	Smelter 5	Smelter 6			Geometric mean $\eta(\%)$	Standard deviation
DC	20.0	13.9	13.8	-	2.4	-	-	-	12.5	7.3
FGS	66.6	-	-	-	-	-	17.4	-	42.0	34.8
ESD	32.2	-	-	-	-	-	30.3	-	31.3	1.3
FGS+ESD	88.2	99.0	99.3	80.5	76.2	97.5			90.1	10.1
RT	-	-	-	-	-	-	87.5	91.4	89.5	2.8
DCDA	99.2	80.0	30.4	90.9		28.0	97.4	-	71.0	33.1
SCDA	-	-	-	-	52.3	-	-	-	52.3	-

**Table 4.** Atmospheric mercury emission estimation from China's zinc, lead and copper smelters between 2000-2010

Estimation year	Atmospheric mercury emissions (t)				Reference
	Zinc	Lead	Copper	Total	
2000	161.4	48.0	12.7	222.1	Wu et al., 2006
2000	44.23	17.99	5.40	67.63	This study
2001	173.0	54.3	13.7	241.0	Wu et al., 2006
2002	178.5	57.8	14.8	251.1	Wu et al., 2006
2002	80.7	-	-	-	Li et al., 2010
2003	187.6	70.7	17.6	275.9	Wu et al., 2006
2003	84.6	-	-	-	Li et al., 2010
2003	73.08	20.88	6.11	100.08	This study
2004	97.1	-	-	-	Li et al., 2010
2005	37.59	29.75	15.84	83.19	Hylander and Herbert, 2008
2005	97.4	-	-	-	Li et al., 2010
2005	56.98	25.14	4.57	86.69	This study
2006	104.2	-	-	-	Li et al., 2010
2006	107.7	-	-	-	Yin et al., 2012
2007	-	-	-	203	Pirrone., 2010
2007	46.17	30.53	3.93	80.63	This study
2010	39.4	30.6	2.5	72.5	This study



**Table 5.** Comparison of mercury emission factors for China's primary zinc, lead and copper smelters

Metal	Smelting Process	Mercury emission factor (g t <sup>-1</sup> )												
		A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>	D <sup>a</sup>	E <sup>a</sup>	F <sup>a</sup>	G <sup>a</sup>	H <sup>a</sup>	I <sup>a</sup>	J <sup>a</sup>	K <sup>a</sup>	L <sup>a</sup>	M <sup>a</sup>
Zinc	- <sup>b</sup>	8-45	25	20		13.8-156.4	7.5-8	16.61	5.4-155	7				7.82
	EP with MRT										5.7	0.5		0.59
	EP without MRT										31		0.57	9.75
	RZSP										34			6.16
	EZF													13.80
	ISP										122		2.98	6.02
	AZSP				79/155						75			45.75
Lead	- <sup>b</sup>	2-4	3	3		43.6	3	14.91	43.6	3				10.97
	RPSP												1.00	1.19
	SMP												0.49	10.16
	SPP													29.35
	ISP													6.07
Copper	- <sup>b</sup>			10		9.6	5-6	6.72	9.6	5				0.85
	FFSP												0.23	7.91
	RPSP												0.09	0.28
	IFSP													1.07
	EF/RF													14.96
	RLEP													0.38

a. A. Nriagu et al., 1988; B. Pirrone et al., 1996; C. Pacyna et al., 2002; D. Feng et al., 2004; E. Streets et al., 2005; Wu et al., 2006; F. Pacyna et al., 2006; G. Hylander and Herbert., 2008; H. Pacyna et al., 2010; I. Feng et al., 2009; Li et al., 2010; K. Wang et al., 2010; L. Zhang et al., 2012; M. This study

b. Not specific value for each process

### **Figure Caption**

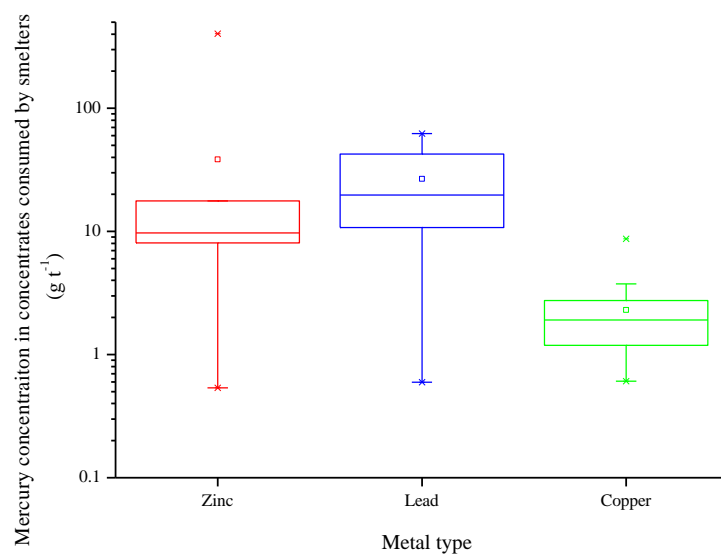
**Fig. 1.** Mercury concentration in concentrates consumed by smelters

**Fig. 2.** Flow diagram for nonferrous metal smelters

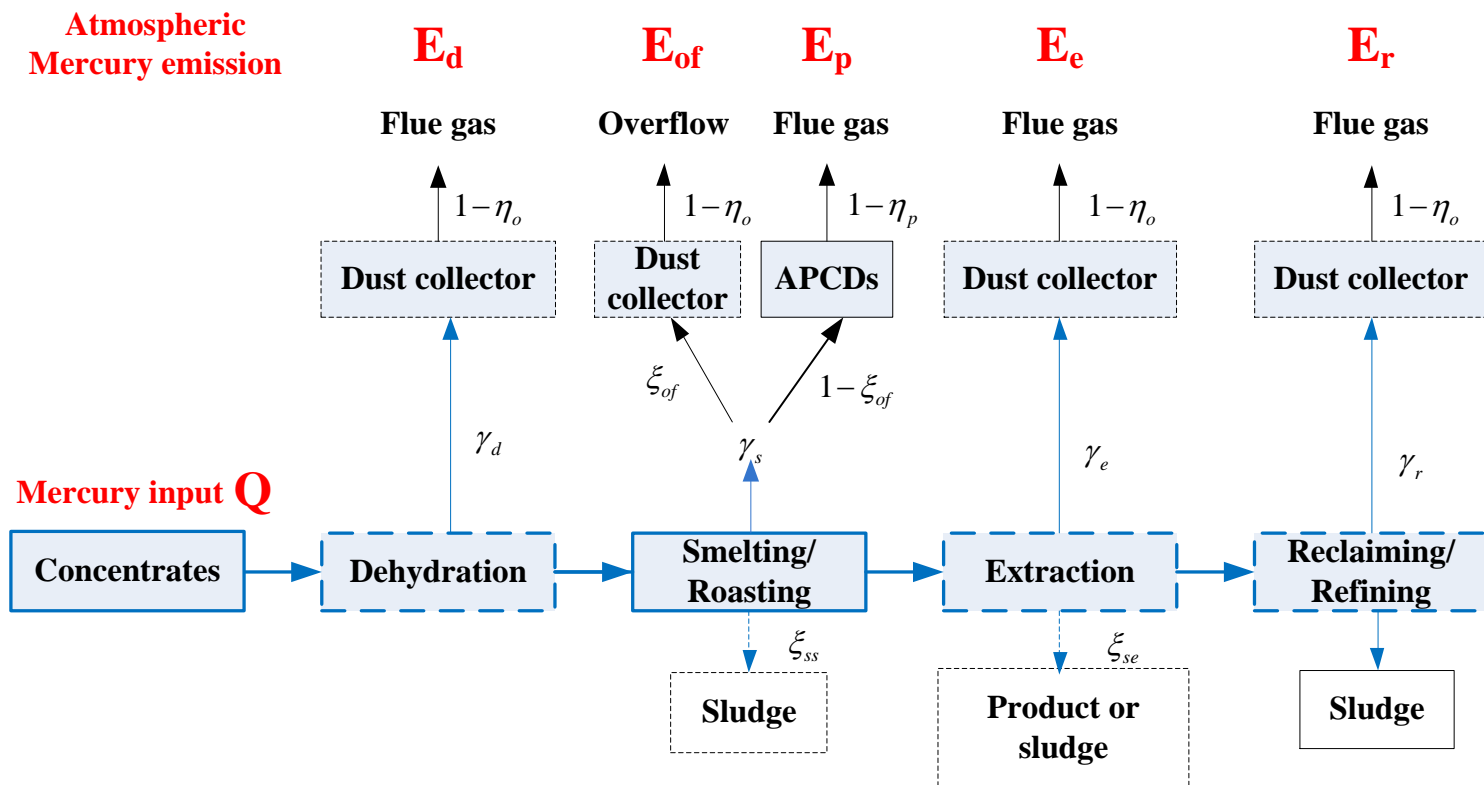
**Fig. 3.** Atmospheric mercury emissions from zinc, lead and copper smelters by province, 2010

**Fig. 4.** Atmospheric mercury emissions from zinc, lead and copper smelters by process, 2010

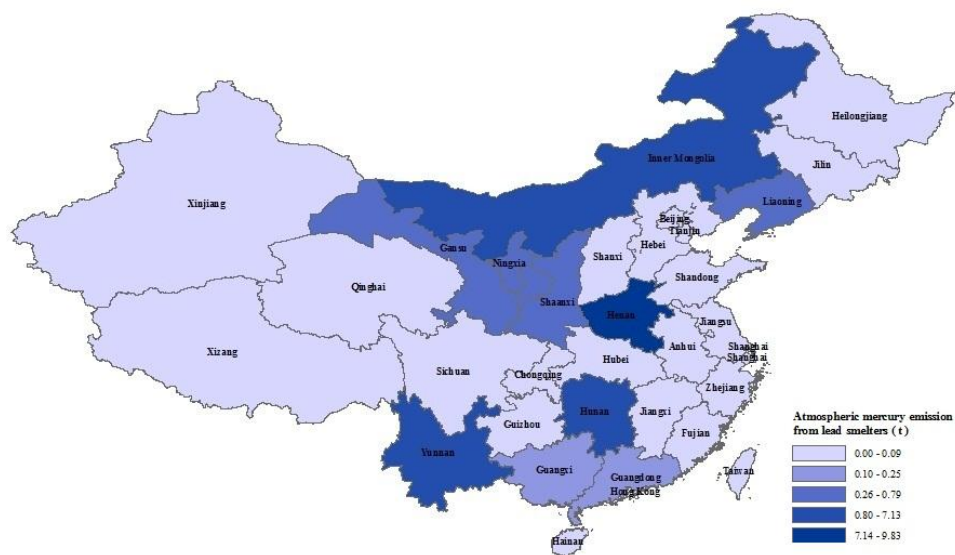
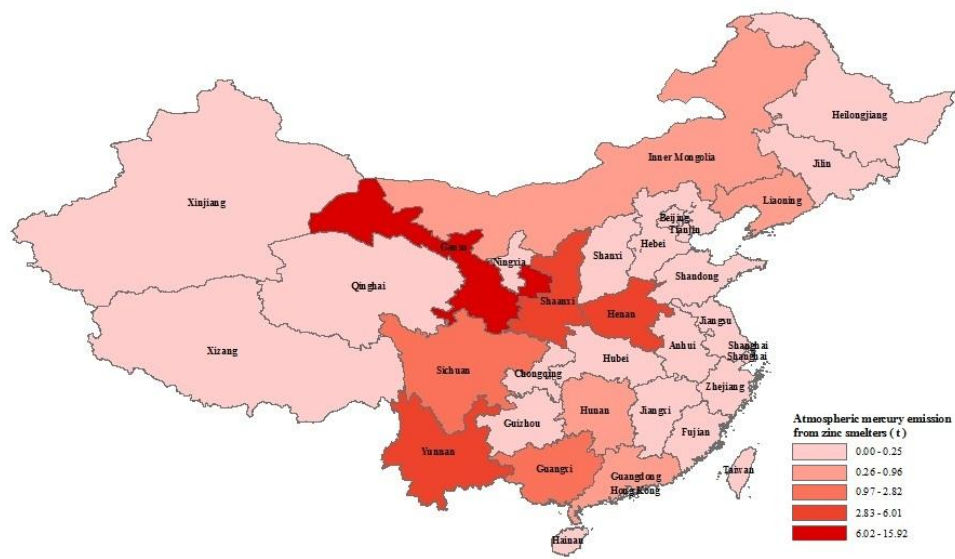
**Fig. 5.** Historic changes of atmospheric mercury emissions and metal production from nonferrous metal smelters in China, 2000-2010



**Fig. 1.** Mercury concentration in concentrates consumed by smelters

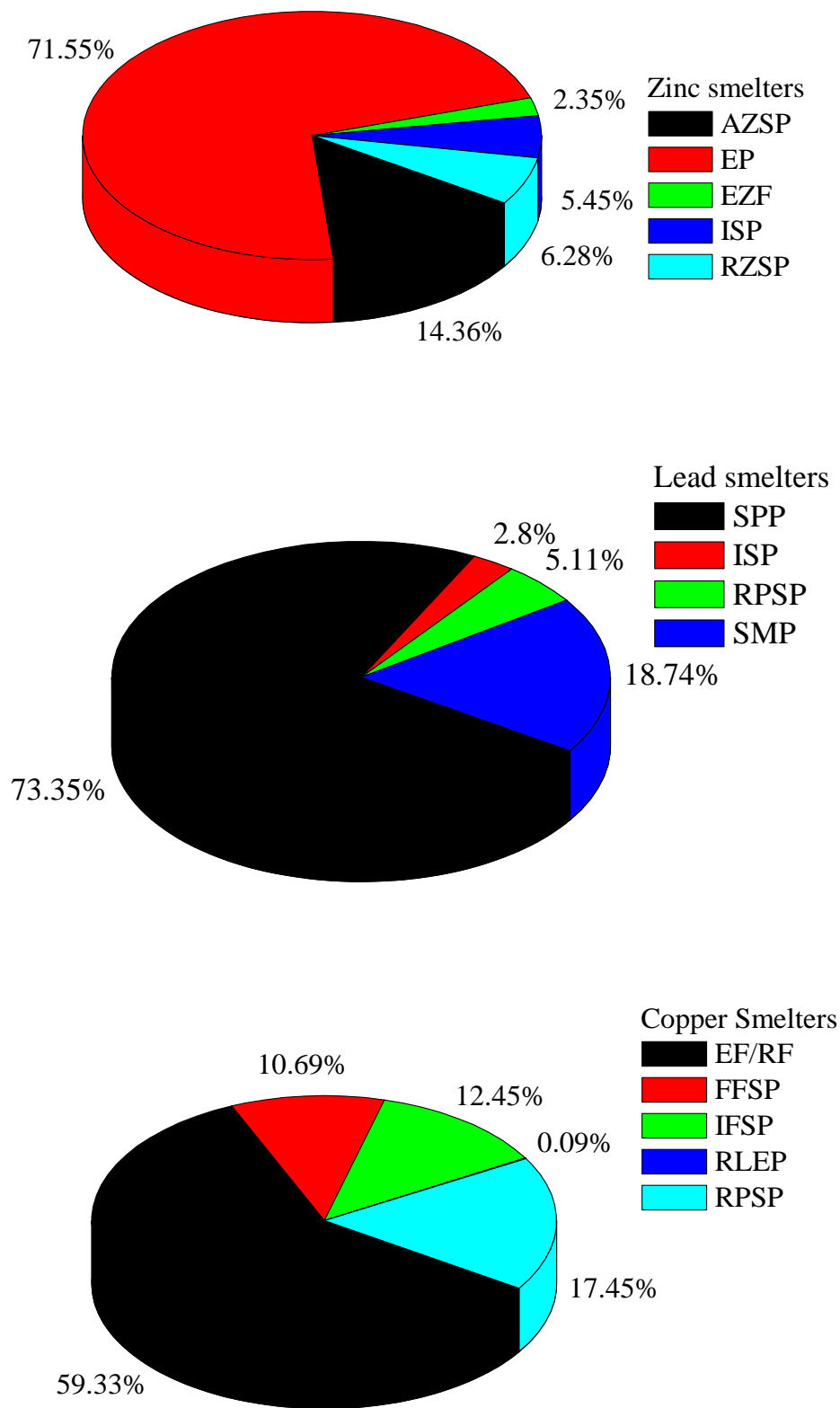


**Fig. 2.** Flow diagram for nonferrous metal smelters

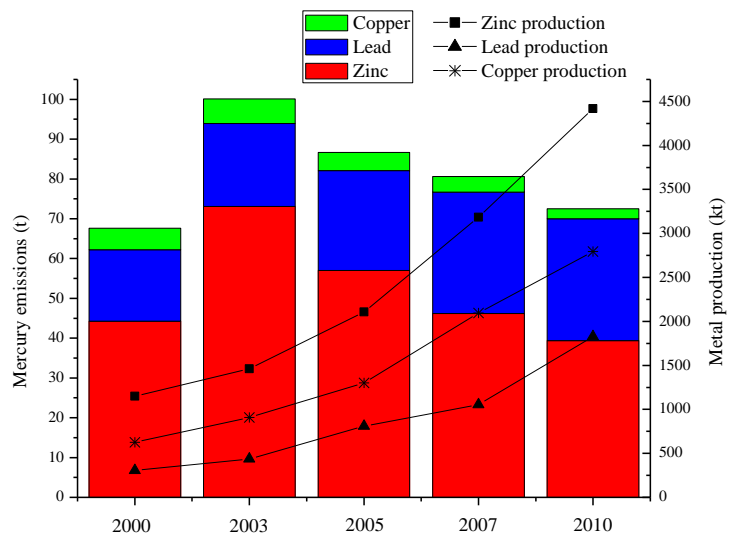




**Fig. 3.** Atmospheric mercury emissions from zinc, lead and copper smelters by province, 2010



**Fig. 4.** Atmospheric mercury emissions from zinc, lead and copper smelters by process, 2010



**Fig. 5.** Historic changes of atmospheric mercury emissions and metal production from nonferrous metal smelters in China, 2000-2010