Atmospheric Environment 43 (2009) 2247–2251

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric mercury emission from artisanal mercury mining in Guizhou Province, Southwestern China

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ARTICLE INFO

Article history:
Received 29 October 2008
Received in revised form
22 January 2009
Accepted 27 January 2009

Keywords:
Artisanal mercury mining
Emission factor
Atmospheric mercury emission
Guizhou
China

ABSTRACT

Mercury (Hg) mining is an important anthropogenic source of atmospheric Hg emissions. The Guizhou Province in Southwestern China is a region with extensive artisanal mercury mining (AMM), but little Hg emission data from this area is available. Using a mass balance method, we estimated emission factors from artisanal mercury mining in Wuchuan mercury mining area (WMMA) and Gouxi area (GX). Average emission factors were 18.2% in WMMA (ranging from 6.9% to 32.1%) and 9.8% in GX (ranging from 6.6% to 14.5%), respectively, which were 2.2–36.4 times higher than the literature values used to estimate Hg emission from Hg mining. Furthermore, the average Hg emission factor of AMM in WMMA was much higher than that in GX, indicating that double condensation processes practiced in GX resulted in higher recoveries and lower emission factors compared to single condensation process applied in WMMA. Atmospheric Hg emission was estimated to be 3.7–9.6 metric tons in 2004 for WMMA and 1.3–2.7 metric tons in 2006 for GX, indicating artisanal Hg mining was an important atmospheric Hg emission source in the study area.

1. Introduction

Mercury (Hg) is considered as a global pollutant (Lindqvist, 1991), because of its long residence time in the atmosphere (from 0.5 to 2 years, Schroeder and Munthe, 1998). Long-range transport of atmospheric Hg, its deposition, bioaccumulation and the enrichment of highly toxic methylmercury compounds in the aquatic food chain pose a serious environmental problem to the global environment even in remote areas (Lucotte et al., 1995; Schuster et al., 2002; Miller et al., 2005). Hg is released to the atmosphere from natural and anthropogenic sources. Coal combustion, waste incineration, chlorine–akali production as well as metal mining, refining and manufacturing form the currently major source categories in the industrialized world (Schroeder and Munthe, 1998; Pacyna and Pacyna, 2002; Pacyna et al., 2003; Feng, 2004; Streets et al., 2005; Wu et al., 2006).

Among Asian countries, China is now regarded as the largest anthropogenic Hg emission source. The annual mercury emission from China reaches 604.7 t of Hg, which contributes about 28% to the global emissions of mercury (Pacyna and Pacyna, 2002). Feng, (2004) calculated about 402 t of total Hg (including Hg^0, Hg^{2+} and particulate Hg) were emitted in 1995; Streets et al. (2005) estimated China's emissions were 536 (±236) t of total Hg in 1999; Wu et al. (2006) speculated that total Hg emissions from all anthropogenic sources in China increased at an average annual rate of 2.9% during the period 1995–2003, reaching 696 (±307) t in 2003. These studies indicate that there are great differences and uncertainties in estimating anthropogenic Hg emissions from China. This may be due to very limited data on Hg emission factors from different source categories in China. Typically, emission factors are adopted from studies in western developed countries with similar sources, but the processes and pollution-control techniques used in China may differ dramatically from those in developed countries. Therefore, Hg emission factors in China could significantly differ from those currently utilized. Hence there is tremendous need to investigate Hg emissions from different source categories in China, for more accurate modeling of the global atmospheric Hg cycling.

Emission from Hg mining is one of the most important anthropogenic sources. Global emissions to the atmosphere from Hg mining are estimated as 10–30 t per year currently and probably exceeded 10,000 t historically (Hylander and Meili, 2003). In previous Hg emission inventory studies, an emission factor of 45 kg Hg per 1 t Hg produced was calculated (Qi, 1997) and total Hg emission in China from Hg mining was estimated to be 8.8 t in 1999 (Streets et al., 2005). Large scale Hg mining activities in Guizhou Province ceased after 2003, mainly due to economic reasons and

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doi:10.1016/j.atmosenv.2009.01.050

environmental pollution concerns (Feng and Qiu, 2008). However, demands of Hg, which is mainly utilized as a catalyst for the manufacturing of polyvinyl chloride (PVC) (NRDC, 2007), have steadily increased since China restricted Hg imports. Hence, Hg prices have increased sharply, which in return stimulated revivals of artisanal or small scale mercury mining (AMM) in Guizhou Province, China (Li et al., 2008a,b).

Most of AMM took place in and/or nearby Hg mines, such as Yinqiangou and Luoxi in Wuchuan area, and Gouxi area in Tongren City. Previous studies showed that AMM activities have resulted in serious Hg pollution to local environment (Qu, 2004; Qiu et al., 2006; Li et al., 2008c), and mining workers were seriously exposed to Hg vapor through inhalation of Hg polluted air (Iwata et al., 2007; Li et al., 2008a).

This study was designed to establish Hg emission factors and Hg emissions from AMM in Guizhou Province by a mass balance method. These results will address critical uncertainties in Guizhou's Hg emission inventory to better estimate Hg emissions from this region.

2. Material and method

2.1. Study areas

AMM in Wuchuan Hg mining area (WMMA) and Gouxi area (GX), Tongren City (Fig. 1) were selected for the study. Wuchuan County is in the northeast of Guizhou Province. The terrain is hilly and karstic with an average altitude of 1034 m above sea level. The land area is about 45 km^2 with a population of 8500 inhabitants. Wuchuan Hg mine is one of the largest Hg mines in China with an Hg reserve of 23,320 t. Mining activity has spanned at least 400 years and more than 4070 t of elemental Hg had been produced.

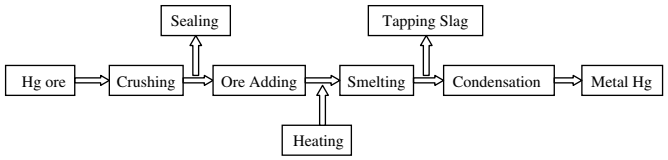

Fig. 2. The sketch map of the process of artisanal mercury mining in Guizhou Province, China.

Large-scale Hg mining began in 1949 and ceased in 2003. In WMMA, AMM activities were distributed throughout three villages, including Yinqiangou, Luoxi and Taiba (Fig. 1). Hg ores for AMM in Yinqiangou and Luoxi were supplied from Wuchuan Hg mine by illegal exploitation, while those in Taiba were provided by a local small Hg mine.

GX is situated in Tongren City (Fig. 1), located in the eastern part of Guizhou Province. Tongren is also hilly and karstic, with elevation ranging from 205 to 1149 m above sea level. The region has a sub-tropical humid climate, characterized by abundant rainfall and mild temperature. There are many small-scale Hg mines located in GX, which provided Hg ore for AMM.

2.2. Processes of artisanal mercury mining

Artisanal mercury mining is a small-scale mercury smelting activity with indigenous method, which is forbidden by State Environmental Protection Agency. The cinnabar is crushed and then roasted at 700–800 °C to produce Hg vapor that is condensed in a wooden barrel and cooled by water (Fig. 2).

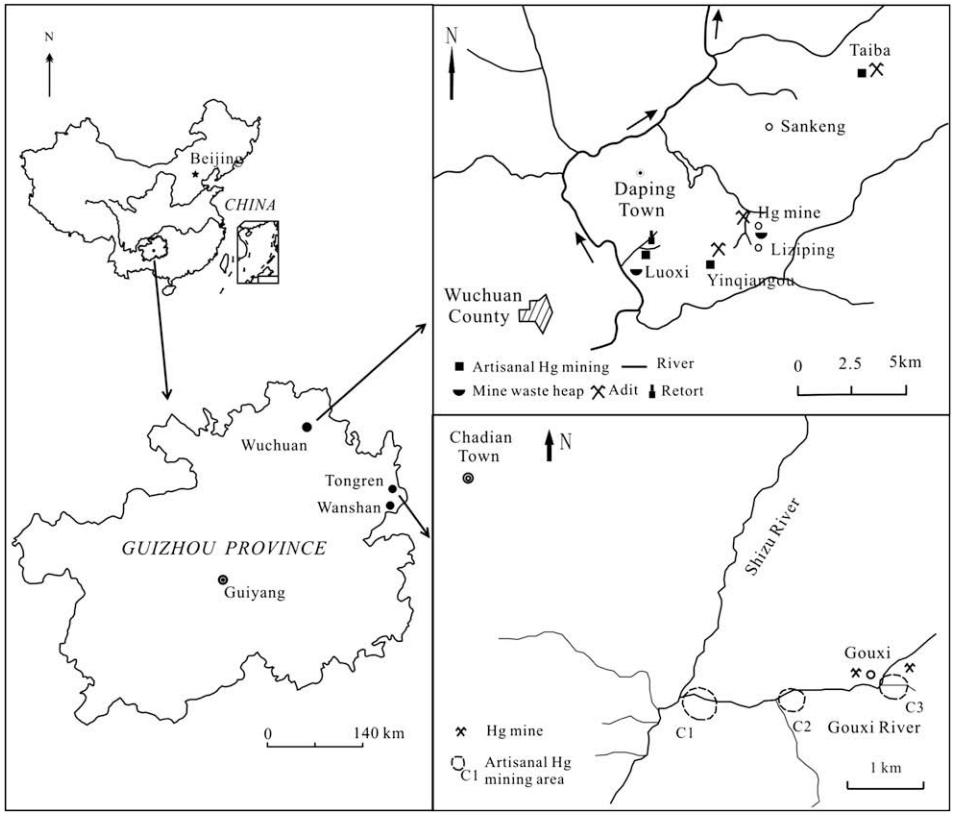

Fig. 1. Location of the study area in Guizhou Province, China.

Fig. 3. The photographic comparison of different condensation technologies of AMM in WMMA and GX.

The major difference of the processes between AMM in WMMA and GX was in the condensation procedure. Double condensation processes used in AMM in GX were a little more advanced compared to that in WMMA, where single condensation technology was used. A photographic comparison is given in Fig. 3.

2.3. Sampling and analysis

To calculate Hg emission factors, a mass balance method was employed utilizing Hg concentrations analyzed in Hg ore and mine waste. All samples were a composite of at least 4 sub-samples, for increased spatial resolution. The Hg ore and mine waste samples of AMM in WMMA and GX were collected in December 2004 and October 2006, respectively.

After homogenization, milling and riffling, the samples were ground to minus 150 mesh (106 μm) prior to Hg analysis. Then appropriate amounts of samples were digested with 5 ml concentrated $HNO_3 + HCl$ (1:3 v/v) in a water bath (95 °C). Hg concentration was determined using BrCl oxidation and $SnCl_2$ reduction coupled with cold vapor atomic absorption spectrometry (Feng and Hong, 1999). Soil sample GBW-07405 (GSS-5) was used to verify QA/QC, and results showed that the pretreatment procedures can quantitatively recover of Hg from the standard samples.

Table 1
Hg concentration in Hg ores and mine wastes of AMM in the study area.

Area	Site/Furnace	Hg concentration Mean ± SD (*n*, min–max)		Distribution pattern (Hg ore, mine waste)
		Hg ore %	Mine waste mg kg^{-1}	
WMMA	Yinqiangou	0.614 ± 0.202 (*11*, 0.395–0.927)	11[a] (*11*, 3.4–58)	a, b
	Luoxi	0.367 ± 0.131 (*6*, 0.095–0.443)	120[a] (*6*, 6.6–810)	a, b
	Taiba	0.167 ± 0.098 (*6*, 0.047–0.339)	7.2[a] (*6*, 3.3–55)	a, b
	Total	0.432 ± 0.288 (*23*, 0.047–0.927)	17[a] (*23*, 3.3–810)	a, b
GX	A	0.270[a] (*5*, 0.092–0.610)	170[a] (*5*, 24–750)	b, b
	B	5.67[a] (*4*, 1.92–23.0)	48[a] (*4*, 21–100)	b, b
	C	1.11[a] (*4*, 0.152–5.06)	25[a] (*4*, 12–48)	b, b
	D	1.90[a] (*5*, 0.615–8.03)	82[a] (*5*, 22–180)	b, b
	E	0.752[a] (*7*, 0.145–2.66)	56[a] (*7*, 14–150)	b, b
	F	0.971[a] (*5*, 0.282–5.82)	110[a] (*5*, 32–250)	b, b
	Total	1.06[a] (*30*, 0.092–23.0)	47[a] (*30*, 12–750)	b, b

[a] Geometric mean; a, normal; b, log-normal.

3. Results and discussion

3.1. Hg emission from AMM in WMMA

Table 1 summarizes the measurement results of Hg concentrations in Hg ores and mine wastes of AMM in WMMA. The average Hg concentration in Hg ores is 0.432%. However, regional variations were observed, which indicated as Yinqiangou (0.614%) >Luoxi (0.367%) >Taiba (0.167%). The geometric mean of Hg concentration in mine wastes was 17 mg kg^{-1} and the mine wastes collected from Luoxi exhibited the highest Hg concentrations. The majority of Hg in the ores was volatilized and condensed in the collection barrel during the retort process; a part was released to the ambient air through the exhaust gas; the remainder was in mine wastes.

Consequently, the Hg emission factor of AMM could be calculated from

$$F = \frac{\left(O \times 10^{-4} - S\right) \times W \times 10^{-6} - P}{P} \times 100\% \quad (1)$$

Where F is the Hg emission factor, defined as the amount of Hg (t) released to the ambient air during 1 t Hg produced; O is Hg concentration in the ore (%); S is Hg concentration in the mine waste (mg kg^{-1}); W is the amount of consumed ores (kg), determined to be an average of 270 kg per furnace; P is the production of Hg (kg) per furnace.

The recovery (R) of AMM could be calculated from

$$R = \frac{P}{O \times W} \times 100\% \quad (2)$$

Table 2
Hg emission factor and recovery of AMM in the study area.

Area	Site/Furnace	O %	S mg kg^{-1}	W kg	P kg	F %	R %
WMMA	Yinqiangou	0.614	11	270	1.25–1.50	10.1–32.1	75.7–90.8
	Luoxi	0.367	120	270	0.75–0.85	6.9–21.1	82.6–93.6
	Taiba	0.167	7.2	270	0.35–0.40	11.6–27.6	78.4–89.6
	Average	0.432	17			18.2	85.1
GX	A	0.270	170	2000	4.9	8.2	92.5
	B	5.67	48	750	38.0	11.8	89.4
	C	1.11	25	1500	15.5	7.1	93.3
	D	1.90	82	3500	60.2	10.3	90.7
	E	0.752	56	5000	35.1	6.6	93.9
	F	0.971	110	3000	25.2	14.5	87.3
	Average	1.06	47			9.8	91.2

Table 3
Hg production and atmospheric Hg emission from AMM in WMMA in 2004.

Site	Furnace numbers	Hg production metric tons	Atmospheric Hg emission metric tons
Yinqiangou	70	26.3–31.5	3.2–8.4
Luoxi	10	2.3–2.6	0.2–0.5
Taiba	25	2.6–3.0	0.3–0.7
Total	105	31.2–37.1	3.7–9.6

Using the measurement data in Table 1, the Hg emission factors of AMM were 10.1–32.1%, 6.9–21.1%, and 11.6–27.6% in Yinqiangou, Luoxi, and Taiba, respectively. The results were listed in Table 2.

The annual Hg production (*TP*, t) of AMM in WMMA is calculated from

$$TP = \sum TP_i \quad TP_i = P_i \times D \times N_i \times 10^{-3} \tag{3}$$

Where P_i is the daily Hg production of a furnace (kg); N_i is the number of the furnace in an area; D is the annual running days for a furnace and estimated as 300 d.

The annual Hg emission (E) of AMM in WMMA could be calculated from

$$E_i = TP_i \times F_i \quad E = \sum E_i \tag{4}$$

The results of Hg production and Hg emission from AMM in WMMA are given in Table 3. The AMM in WMMA is mainly located in Yinqiangou, where 26.3–31.5 t Hg was produced and 3.2–8.4 t Hg was released into the ambient air. The atmospheric Hg emission from AMM in WMMA ranged from 3.7 t to 9.6 t in 2004.

3.2. Hg emission from AMM in GX

The geometric mean of Hg concentration in Hg ores is 1.06%, and the results of Hg concentrations in Hg ores and mine wastes of AMM in GX were also given in Table 1. Hg concentrations in Hg ores collected from GX vary widely from 0.092 to 23.0%. The geometric mean of Hg concentrations in mine wastes of different furnaces in GX ranged from 25 to 170 mg kg^{-1}.

The Hg emission factor of AMM in GX ranged from 6.6 to 14.5%, with an average of 9.8%; the recovery varied from 87.3 to 93.9%, with an average of 91.2%. The results are listed in Table 2.

The annual Hg output of AMM in GX could be calculated from

$$TP = O \times Y \times R \tag{5}$$

Where O is the average Hg concentration in Hg ores; Y is the annual ore output of the GX mine; R is the recovery of the AMM.

The results of Hg production and atmospheric Hg emission from AMM in GX are given in Table 4. The atmospheric Hg emission ranged from 1.3 to 2.7 t during the AMM activities in GX in 2006.

3.3. The comparison of emission factor and Hg emission between different studies

The Hg emission factor of AMM in WMMA ranged from 6.9 to 32.1%, with an average of 18.2%, while the Hg emission factor in GX varied from 6.6 to 14.5%, with an average of 9.8%. The Hg emission factor of AMM in WMMA was much higher than that in GX, indicating that double condensation processes practiced in GX resulted in higher recoveries and low emission factors (Fig. 3).

Table 4
Hg production and atmospheric Hg emission from AMM in GX in 2006.

Ore production metric tons	Average Hg concentration in ores %	Hg production metric tons	Atmospheric Hg emission metric tons
2000	1.06	18.6–20.0	1.3–2.7

Table 5
Comparison of Hg emission factors and annual Hg emission between different studies.

Emission source	Period	Emission factor	Atmospheric Hg emissions metric tons	Reference
China anthropogenic activity			400–600/year	Pacyna et al. (2003); Feng (2004); Streets et al. (2005)
China Hg mining	1999	4.5%	8.78	Streets et al. (2005)
Guizhou anthropogenic activity	1999		39.0	Streets et al. (2005)
Almadén Hg mine	Operation period	0.5–1%	10/year	Ferrara et al. (1998)
Idrija Hg mine	1960-1995	0.61%	1.7/year	Kotnik et al. (2005)
Five main Hg mines in Guizhou Province	1983	1.69%	11	Tan et al. (1997)
Wuchuan Hg mine	2000	1.69%	0.4	Qu (2004)
AMM in WMMA	2004	18.2% (6.9–32.1%)	3.7–9.6	This study
AMM in GX	2006	9.8% (6.6–14.5%)	1.3–2.7	This study

Measurements and estimates at Almadén Hg mine, Spain (Ferrara et al., 1998) suggested that up to 10 t of Hg per year may be lost to the atmosphere during roasting operations at a production of up to 1500 t of Hg per year. This yields a direct emission factor on the order of 0.5–1%. In Idrija Hg mine, Slovenia, 9777 t of commercial Hg was produced and 60 t was emitted into the atmosphere by flue gases during the period between 1960 and 1995 (Kotnik et al., 2005). This indicated the average emission factor was 0.61%. The total amount of Hg emitted to the air was estimated be about 11 t with a production of 828 t for the five main Hg mines of Guizhou Province in 1983 and the emission factor was 1.69% (Tan et al., 1997). Tan et al. (1997) also estimated the emission factor is about 7% for the AMM in Guizhou Province. Streets et al. (2005) reported the emission factor was 4.5% for the Hg mining in China. Our results were much higher than the estimations from previous studies, which reflected the poor recovery processes of AMM in WMMA and GX.

Comparisons of estimation factor and Hg emissions from different studies are given in Table 5. Among all countries in the world, China has the largest Hg emissions, and the annual total Hg emission rate to the air was estimated to range from 400 to 600 t (Pacyna et al., 2003; Feng, 2004; Streets et al., 2005). The atmospheric Hg emission from Hg mining for China was estimated to 8.78 t in 1999 and the anthropogenic Hg emission was estimated to 39.0 t for Guizhou Province in 1999 (Streets et al., 2005). This study indicates that AMM is a significant source to the atmosphere, which not only poses a threat to local eco-environment, but also contributes to the global cycle of Hg in the atmosphere.

4. Conclusions

The average Hg emission factor was 18.2% (6.9–32.1%) for the AMM activities in WMMA and the atmospheric Hg emission was 3.7–9.6 metric tons in 2004. The average Hg emission factor was 9.8% (6.6–14.5%) for the AMM activities in GX and the atmospheric Hg emission was 1.3–2.7 metric tons in 2006. The Hg emission factor of AMM in WMMA was much higher than that in GX,

indicating that double condensation processes practiced in GX resulted in higher recoveries and low emission factors. These emission factors are much higher than those reported for other Hg mining regions. The results of this study confirm that artisanal Hg mining activities are significant anthropogenic atmospheric Hg emission sources in the study area.

Acknowledgements

This research was financed by the Chinese Academy of Sciences through an innovation project (KZCX3-SW-443), and by the National Natural Science Foundation of China (40532014, 40703024 and 40773067). We would like to gratefully thank Dr. Sarah Rothenberg and Dr. Jonas Sommar for editing our previous manuscript, which significantly improved the quality of our manuscript.

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