Mercury pollution in Wuchuan mercury mining area, Guizhou, Southwestern China: The impacts from large scale and artisanal mercury mining

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ABSTRACT

To evaluate the environmental impacts from large scale mercury mining (LSMM) and artisanal mercury mining (AMM), total mercury (THg) and methyl mercury (MeHg) were determined in mine waste, ambient air, stream water and soil samples collected from Wuchuan mercury (Hg) mining area, Guizhou, Southwestern China. Mine wastes from both LSMM and AMM contained high THg concentrations, which are important Hg contamination sources to the local environment. Total gaseous mercury (TGM) concentrations in the ambient air near AMM furnaces were highly elevated, which indicated that AMM retorting is a major source of Hg emission. THg concentrations in the stream water varied from 43 to 2100 ng/L, where the elevated values were mainly found in the vicinity of AMM and mine waste heaps of LSMM. Surface soils were seriously contaminated with Hg, and land using types and organic matter played an important role in accumulation and transportation of Hg in soil. The results indicated heavy Hg contaminations in the study area, which were resulted from both LSMM and AMM. The areas impacted by LSMM were concentrated in the historical mining and smelting facilities, while Hg pollution resulted from AMM can be distributed anywhere in the Hg mining area.

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1. Introduction

Mercury (Hg) has been considered as a global pollutant (Lindqvist, 1991) due to its long range transport in the atmosphere. Gaseous elemental mercury (GEM) (Hg⁰) is very stable with a residence time between 0.5 and 2 years (Schroeder and Munthe, 1998). Its transport and deposition pose a serious environmental problem to the global environment, because the deposited Hg can be readily transformed into methyl mercury (MeHg) as a highly toxic form.

Mercury mining areas are considered as hot spots of Hg pollution, and the biogeochemical cycle of Hg has been widely studied worldwide in Hg mining areas: Almadén (Berzas Nevado et al., 2003; Gray et al., 2004; Higueras et al., 2003; Millán et al., 2006) and Asturias (Loredo et al., 2005, 2006) in Spain; Idrija (Biester et al., 1999, 2000; Gosar et al., 1997) in Slovenia; Amiata (Ferrara et al., 1998a) in Italy; Nevada (Bonzongo et al., 1996; Gray et al., 2002), Alaska (Bailey et al., 2002; Gray et al., 2000) and California Coast Range (Domagalski, 2001; Domagalski et al., 2004; Ganguli et al., 2000; Kim et al., 2004) in U.S.; Palawan (Gray et al., 2003) in Philippines; Wanshan (Horvat et al., 2003; Qiu et al., 2005; Zhang et al., 2010a, b), Wuchuan (Qiu et al., 2006a; Wang et al., 2007a), Tongren (Li et al., 2008a) in Guizhou

Province and Xunyang (Zhang et al., 2009) in Shaanxi Province in China. The cinnabar ore roasting generally generates huge quantities of mine waste, which contain lots of fine-grained secondary Hg phases (Rytuba, 2003) and are dominant Hg sources to the local environment (Gray et al., 2003; Li et al., 2008a; Loredo et al., 2005). Local air, surface water and soil can be seriously polluted by the emission and leaching of Hg from the mine waste calcines. The occupational exposures to Hg vapor (Bellander et al., 1998; Gómez et al., 2007; Kobal et al., 2004; Li et al., 2008b) as well as MeHg bio-accumulation in the food chain and related human health risk assessments (Feng et al., 2008; Li et al., 2008c; Williams and Apostol, 2000) in those Hg mining areas gained much concerns.

China has abundant Hg resources and Guizhou Province is the most important Hg production center (Feng and Qiu, 2008). Wuchuan Hg mine is one of the largest Hg mines in Guizhou Province. More than 4070 tons of metal Hg had been produced during the period of large scale mercury mining (LSMM), which began in 1949 and ceased in 2003. Although Hg productions in China decreased temporarily in early 2000s with the closure of several largest mines, the internal demand has increased steadily, being estimated to be 700 tons in 2004 (NRDC, National Resource Defense Council, 2007). The largest user of Hg is the manufacturing of polyvinyl chloride (PVC) plastic from coal (NRDC, National Resource Defense Council, 2007; Hao et al., 2005; Jian et al., 2009). The increased demand stimulates the revival of artisanal mercury mining (AMM) in Hg mining areas in Guizhou

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Province. The annual Hg production of AMM was estimated to be 200 tons in whole China (NRDC, National Resource Defense Council, 2007) and 40 tons in Wuchuan mercury mining area (WMMA) (Li et al., 2009).

A number of studies have been conducted in WMMA to investigate the influence by LSMM on the local Hg contamination (Qiu et al., 2006a; Qu, 2004; Wang et al., 2007a). Concerning AMM, Li et al. (2009) estimated the annual Hg emission to the atmosphere to be 3.7–9.6 tonnes in 2004 and Li et al. (2008b) evaluated the health aspects related to Hg vapor exposure for the artisanal mining workers.

Recent researches highlighted that rice cultivated in Hg contaminated areas can accumulate MeHg (Qiu et al., 2008) and the main route of human exposure to MeHg is related to frequent rice consumption (Feng et al., 2008). Zhang et al. (2010c) demonstrated that rice preferentially bio-accumulate MeHg than inorganic Hg. Meng et al. (2010, 2011) found that paddy soil is a potential source for MeHg in tissues of rice plant, where newly deposited Hg from AMM appear to be more susceptible to methylation than the bulk of old Hg in soil. This suggested the significant impact of AMM on MeHg accumulation in rice, which finally can pose a health risk to humans.

AMM is known for its low recovery efficiency, high environmental costs, and poor health and safety measures (Li et al., 2009). It's periodically operated by the local peasants seasonally or according to the market price development. It can be widely distributed in the Hg mining area as a non-point pollution source to the local environment. This article is designed to investigate the extent and degree of Hg pollution to the local environment and to evaluate the contribution from LSMM and AMM in the study area.

2. Material and methods

2.1. Study area

Wuchuan is located in the northeast part of Guizhou Province and its detailed information has been given in previous studies (Li et al., 2008b; Li et al., 2008c; Li et al., 2009; Qiu et al., 2006a). The total area of Wuchuan County is approximately 2778 km² and the Hg mining area is about 45 km². The main Hg mines and adits were located in Yinqiangou and Jixiuchang. The mineral processing plant was located in Laohugou, and the ore roasting ovens and distillation plants were distributed in Luoxi (Fig. 1). The mine waste calcines have been stockpiled into two collection dams located at Luoxi and Laohugou, respectively.

AMM in the study area was principally occurring around three villages of Yinqiangou, Luoxi and Taiba (Fig. 1). The supply of Hg ore for AMM in Yinqiangou and Luoxi was from the Hg mine by illegal exploitation; while in Taiba a local small Hg mine was the supplier. The procedures utilized in AMM have previously been described by Li et al. (2009).

WMMA has an estimated population of 8500, of which agricultural population constitutes up to 85%. About 1000 people lived in the mine center, and most of them are laid-off workers in Wuchuan Hg mine. Other residents live in the surrounding villages, which are within 5 km of the mine center. Majority of the young people went out to do labor work in big cities. Some residents were involved in AMM activities in order to get rid of extreme poverty and landlessness. In addition to the laid-off workers in the mine center, the local inhabitants live on the foods they produce from their own land. They rarely eat fish, and rice and vegetables are the staple foods. The
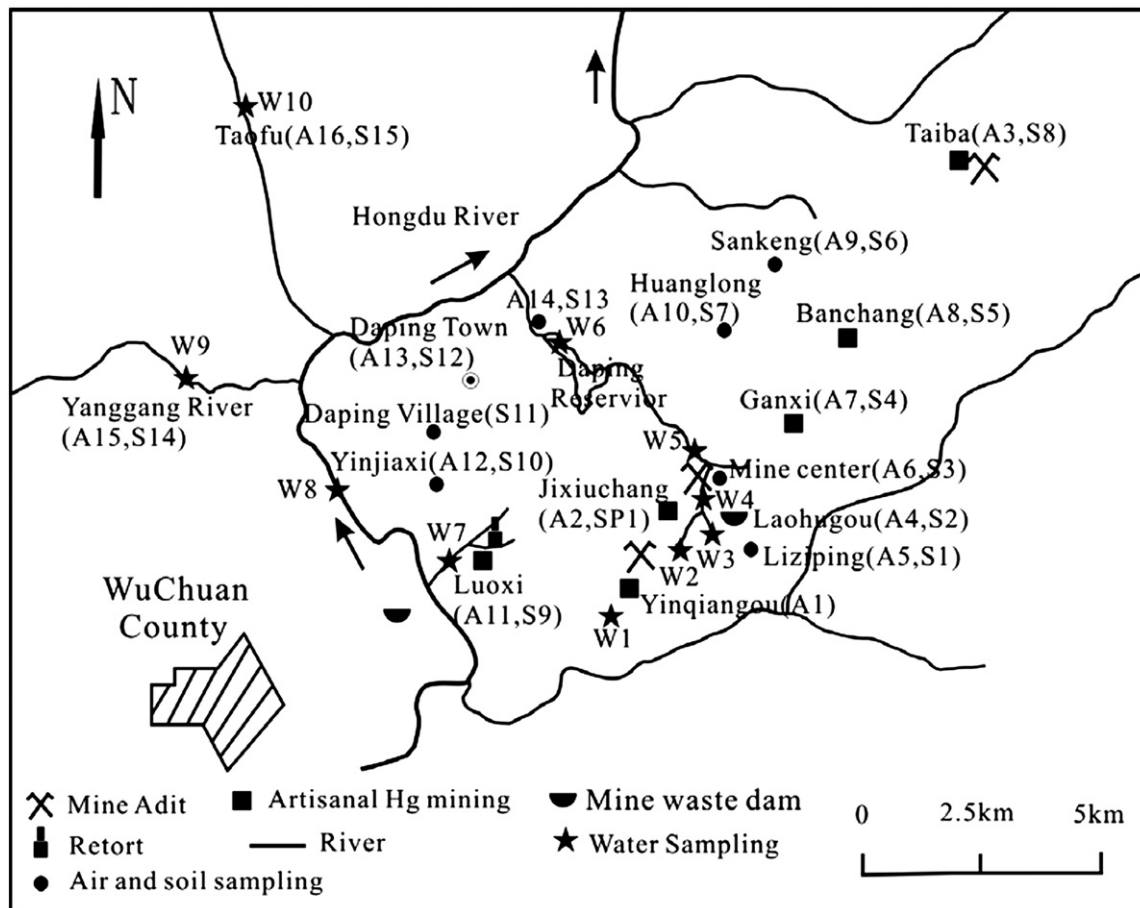

Fig. 1. Location of sampling sites in the study area.

drinking water source for residents in mine center is from tap water, and for other residents is from local streams and ponds.

2.2. Sample collection

The environmental samples were collected in June 2005. Two control sites, Yanggang River and Taofu, were selected for the comparison with the polluted sites as shown in Fig. 1.

Mine waste calcines were collected from Yinqiangou, Luoxi and Taiba as representative of AMM, and from Luoxi and Laohugou dam as representative of LSMM.

The total gaseous mercury (TGM) concentrations were measured in situ (Fig. 1) with a portable atomic absorption spectrometer operating on the Zeeman principle (Lumex RA-915+, Russia). The detection limit of the instrument is 2 ng/m³. A single concentration data represents an average value of a time interval of 30 s and the measurements at each site were carried out at least 10 min.

Filtered and unfiltered water samples were collected in the study area (Fig. 1). Each sample site was selected at the point of the former large scale/artisanal Hg mining or at the fluvial system confluence with its tributaries. Water samples were filtered in situ through a 0.45 μm polyvinylidene fluoride filter (Millipore). Prior to sampling, the borosilicate glass bottles were pre-cleaned by heating for 1 h in a muffle furnace at 500 °C. Water samples were preserved by adding 0.4% (v/v) of ultra-pure HCl within 24 h. Collection, storage, and preservation techniques of water samples strictly followed the USEPA Method 1631 (USEPA, United States Environmental Protection Agency, 1999).

Surface soil samples were collected at different villages to reveal spatial distribution of Hg pollution in the study area, which also include the two control sites. Moreover, a soil profile was collected at Jixiuchang to display vertical Hg distribution (Fig. 1).

2.3. Analytical method

In the laboratory, the mine waste calcine and soil samples were air dried, ground, and sieved to minus 100 meshes particle sizes. For THg analysis, soil and mine waste samples were digested with fresh aqua regia (HCl + HNO₃, v/v 3:1) in water bath at 95 °C and determined by cold vapor atomic absorption spectrometry (CVAAS).

Soil pH was measured using an electrode with a solid:water ratio of 1:2.5. Organic matter (OM) contents in the soil samples were determined by a potassium dichromate volumetric method coupled with water heating technique (Lu, 2000).

Total Hg (unfiltered) and dissolved Hg (filtered) in stream water samples were determined by BrCl oxidation, SnCl₂ reduction, purge, gold trap and cold vapor atomic fluorescence spectrometry (CVAFS) detection (USEPA, United States Environmental Protection Agency, 1999; Yan et al., 2003). Reactive Hg (RHg) was determined by addition of 20% SnCl₂ to unfiltered samples, followed by the purge, trap and CVAFS detection. The total MeHg (TMeHg) and dissolved MeHg (DMeHg) concentrations in the stream water samples were determined using distillation, NaBEt₄ ethylation, and GC-CVAFS detection according to USEPA Method 1630 (USEPA, United States Environmental Protection Agency, 2001). The particulate Hg (PHg) and particulate MeHg (PMeHg) concentrations were obtained by subtracting dissolved fraction from THg and TMeHg, respectively.

2.4. Quality control

Quality control for THg and MeHg analysis was implemented by method blanks, blank spikes, matrix spikes, certified reference materials (GBW07405) as well as blind duplicates. The detection limits were 0.02 mg/kg for THg in mine waste and soil samples, whereas the detection limits for THg and MeHg in water sample were 0.02 ng/L and 0.009 ng/L, respectively. The average of THg

Table 1
THg concentrations in the mine waste in the study area.

Site	Source	n	THg/mg·kg^{-1}		
			Geomean	Min	Max
Yinqiangou	AMM	10	13	3.4	58
Jixiuchang	AMM	2	6.1	4.4	8.5
Luoxi	AMM	6	120	6.6	810
Taiba	AMM	6	7.2	3.3	55
Luoxi Dam	LSMM	1	150	–	–
Laohugou Dam	LSMM	2	110	95	130
Total	–	27	22	3.3	810

concentrations in the geological standard GBW07405 was determined to be 0.30 ± 0.01 mg/kg ($n = 5$), which was comparable with the certified concentration of 0.29 ± 0.04 mg/kg. Recoveries on matrix spikes of MeHg in water samples were in the range of 93 to 106%. The relative standard deviation was <5% for THg in soil, mine waste and water duplicate samples and was <10% for MeHg in water duplicate samples.

3. Results and discussions

3.1. Mine wastes

THg concentrations in the mine waste calcines in the study area varied widely from 3.3 to 810 mg/kg (Table 1). THg concentrations in the mine waste calcines in Luoxi and Laohugou dam from LSMM and in Luoxi from AMM were generally very high (>100 mg/kg). Highly elevated THg concentrations in the mine waste indicated that the retorting was not totally efficient (Rytuba, 2003). The results are similar to those found at Hg mines worldwide, e.g., Almadén, Spain and California and western Nevada, USA (Gray et al., 2002, 2004; Kim et al., 2004).

Generally, the mine waste calcines contain large quantities of secondary Hg phases, such as metacinnabar (a polymorph of HgS), corderoite, Hg chloride, Hg sulfates, Hg oxides, and elemental Hg (Biester et al., 1999; Kim et al., 2000, 2004), which was the by-product during the distillation and condensation processes. These secondary Hg phases are more soluble than cinnabar and can cause a greater extent of Hg contamination to the surrounding environment. It may also result in a favorable condition for methylation of Hg in the surroundings. Previous studies indicated that mine waste calcines were important sources of MeHg to the downstream environment (Zhang et al., 2010b). The waste waters used for agricultural irrigation can provide abundant source of inorganic Hg and MeHg to the rice paddy field in the study area. The bio-accumulation of MeHg in rice and its consumption can cause a health threat to the local residents (Zhang et al., 2010a).

Approximately 2 million tons of mine waste calcines had been dispersed into the adjacent ecosystems by LSMM. Meanwhile, 8500 tons of calcines were estimated to be discarded along the stream banks and flood plain by AMM (Li et al., 2009). Therefore, the huge quantities of calcines are potential threat to the local environment in the study area.

Table 2
Total gaseous mercury (TGM) concentrations in the study area.

| No	Site	Description	TGM/ng·m^{-3}
A1	Yinqiangou	Smelting site, at distance of 0, 100, 500, 800 m	47–40,000
A2	Jixiuchang	Smelting site, at distance of 0 and 300 m	720–30,000
A3	Taiba	Smelting site, at distance of 0, 100, and 500 m	41–1200
A4	Laohugou	Mine waste dam from large scale Hg mining	4500
A5	Liziping	A village close to the Hg mine	380
A6	Mine Center	Former mine center of the Hg mine	190
A7	Ganxi	A village with some artisanal Hg mining	76
A8	Banchang	A village with some artisanal Hg mining	170
A9	Sankeng	A village in Hg mining area	20
A10	Huanglong	A village in Hg mining area	10
A11	Luoxi	Former retort, with some artisanal Hg mining	28–230
A12	Yinjiaxi	A village close to Luoxi retort	9.3
A13	Daping Town	The only town in Hg mining area	29
A14	Daping Reservoir	A reservoir used for agricultural irrigation	76
A15	Yanggang River	Control site	18
A16	Taofu	Control site	28
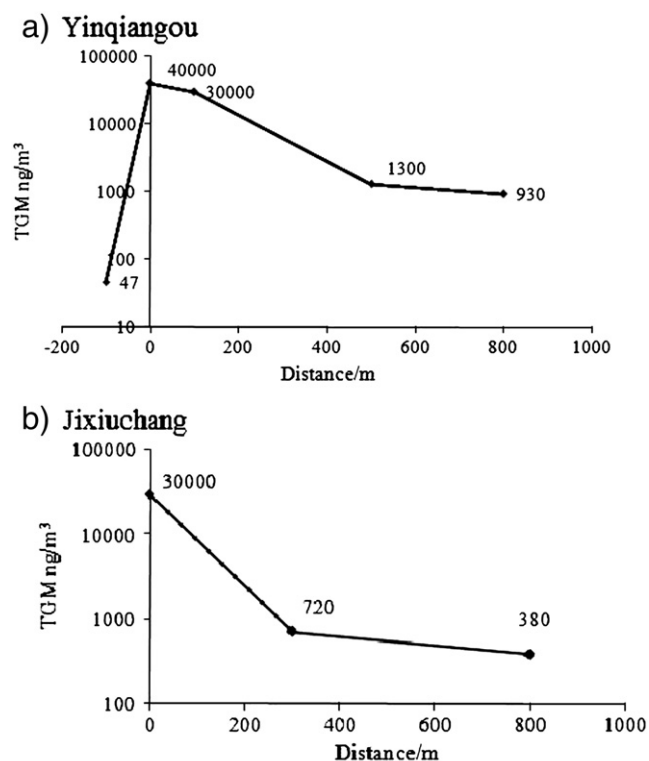
Fig. 2. Total gaseous mercury (TGM) concentrations at different distances from AMM sites (Y-axis in log scale; a, Yinqiangou; b, Jixiuchang).

3.2. Ambient air

TGM concentrations in ambient air in the study area were shown in Table 2. TGM concentrations were highly elevated at the sites of AMM. TGM concentrations near the smelting furnace in Yinqiangou, Jixiuchang, and Taiba were measured in $\mu g/m^3$ range with an average of 40, 30 and 1.2 $\mu g/m^3$, respectively. Air Hg concentrations near the smelting furnace were elevated by 3–4 orders of magnitude compared to that in the control sites. TGM concentrations near the smelting furnace in Yinqiangou and Jixiuchang exceeded the maximum allowable occupational standard in China (10 $\mu g/m^3$). Previous study indicated that the artisanal mining workers in the study area were seriously exposed to Hg vapor (Li et al., 2008b).

As expected, the TGM concentrations decreased gradually with increasing distances from the smelting sites. In Fig. 2, the dispersion of TGM in air around the Yinqiangou and Jixiuchang sites was shown. For instance, in Yinqiangou, TGM concentrations decreased to 30 $\mu g/m^3$, 1.3 $\mu g/m^3$ and 0.93 $\mu g/m^3$ at distances of 200 m, 500 m and 800 m away from the smelting sites in the downwind direction, respectively. However, TGM concentration sharply decreased to a value of 47 ng/m^3 at a distance of 100 m in the upwind direction. Hence, AMM activities represent the most important Hg emission source to the atmosphere in a regional scale. The annual atmospheric Hg emission from AMM was estimated to be 3.7–9.6 metric tons in 2004 in the study area (Li et al., 2009).

Highly elevated TGM concentrations were also found proximate to the abandoned facilities of LSMM. For instance, the average of TGM concentration near the Laohugou dam was 4500 ng/m^3, whereas that close to the former Luoxi smelting plant was 230 ng/m^3. The results indicated that the mine waste and abandoned smelting facilities are also important Hg emission sources to the atmosphere. The annual Hg emissions from the mine waste heaps in whole Wanshan Hg mining area ranged from 0.96 to 3.0 kg (Qiu, 2005).

TGM concentrations in ambient air at the two control sites were 18 and 28 ng/m^3, respectively, which were comparable in magnitude to that of urban areas such as Guiyang City (Feng et al., 2004). Even though highly elevated compared to the global background values (Ebinghaus et al., 2002), the results basically represented the regional background levels in the study area.

TGM concentrations in the study area are compared with those of other studies from Hg mines over the world as shown in Table 3. Our results were comparable with the observations reported during the Hg mine production period from Almadén Hg mine, Spain (Ferrara et al., 1998b), and with those reported for Wanshan and Wuchuan Hg mining impacted from AMM (Qiu, 2005; Wang et al., 2007a,b). Bellander et al. (1998) observed highly elevated TGM concentrations in the breathing air of the plant in Abbadia San Salvatore Hg mine, Italy with a maximum value of 234 $\mu g/m^3$. However, in comparison with the typical air concentrations reported for abandoned Hg mines, the highly elevated data in this study indicated a significant impact of the AMM.

3.3. Stream water

Hg speciation and other parameters in the stream water in the study area are listed in Table 4. Low Hg levels were found in the control sites, due to a long distance to the Hg mining area and to a less impact from Hg mining activities. THg concentrations in the surface water at two control sites were 13 and 18 ng/L, respectively, which are comparable to the range (0.1–20 ng/L) of natural fluvial systems (Louis and Chamberland, 1995).

THg concentrations in the stream water in the polluted area (with a range of 43–2100 ng/L) were highly elevated compared to the control sites. Local maxima at sites 1, 2, and 7 possibly reflected the impact of atmospheric deposition and water leaching from the calcines both of which are related to the AMM. The Hg pollution at site 3 was derived from LSMM activities, since the influx flowed through the calcine pile in Laohugou dam. These results indicated that the mine wastes are significant Hg pollution sources to the local aquatic system.

The particulate Hg concentrations ranged from 28 to 2000 ng/L and constituted a large portion (65–96%) of the THg concentrations in the stream water. The reactive and dissolved Hg concentrations varied from 2.5 to 13 ng/L and from 8.7 to 95 ng/L, respectively. A significant correlation ($r = 0.999$, $n = 8$, $p < 0.001$; Fig. 3a) was observed

Table 3
The comparison of TGM concentrations in Hg mining areas over the world.

Location	Description	Sampling period	Method	TGM/ng·m^{-3}	Reference
Almadén Hg mine, Spain	Mine production period	Sep. 1993, Feb. 1994	Gold trap, AAS and LIDAR	100–50,000	Ferrara et al., 1998b
California Coast Range, U.S.	Abandoned Hg mine	–	Tekran 2537A	2.7–720	Gustin et al., 2003
Abbadia S. Salvatore Hg mine, Italy	Abandoned Hg mine	–	Gold trap, AAS and LIDAR	2–1000	Edner et al., 1993
Three Hg mines in Mt. Amiata area, Italy	Abandoned Hg mine	Sep. 1994, July 1995	Gold trap, AAS and LIDAR	2–6000	Ferrara et al., 1998a
Palawan Hg mine, Philippines	Abandoned Hg mine	2002	Solid Sorbent trap, CVAAS	0.88–65	Maramba et al., 2006
Munon Cimero Hg mine, Asturias, Spain	Abandoned Hg mine	2003–2004	Mercury Tracker-3000	170–46,000	Loredo et al., 2006
Abbadia S. Salvatore Hg mine, Italy	Mine production period	Jan.–July, 1982	AAS	8000–234,000	Bellander et al., 1998
Idrija Hg mine, Slovenia	Abandoned Hg mine	Nov. 2003	Lumex RA-915+	2.5–2000	Kotnik et al., 2005
Wuchuan Hg mining area, China	Abandoned Hg mine, artisanal Hg mining	Dec. 2003, Dec. 2004	Tekran 2537A	12–12,000	Wang et al., 2007a
Wanshan Hg mining area, China	Abandoned Hg mine, artisanal Hg mining	Nov. 2002, Aug. 2004, Dec. 2004	Tekran 2537A and Lumex RA-915+	6.7–16,000	Qiu, 2005; Wang et al., 2007b
Lanmuchang Hg mining area, China	Abandoned Hg mine	Dec.2002, May 2003	Tekran 2537A	7.9–470	Wang et al., 2005
Dazhai Hg mining area, China	Hg mine active period	Aug.–Oct. 1993	Gold trap, CVAAS	16–250	Feng et al., 1996
Wuchuan Hg mining area, China	Abandoned Hg mine, artisanal Hg mining	June 2005	Lumex RA-915+	9.3–40,000	This study

AAS: atomic absorption spectrometry; LIDAR: light detection and ranging.

Table 4
Mercury concentrations and other parameters in the stream water in the study area.

Type	No	pH	DO/ mg·L^{-1}	DOC/ mg·L^{-1}	THg/ ng·L^{-1}	DHg/ ng·L^{-1}	PHg/ ng·L^{-1}	RHg/ ng·L^{-1}	TMeHg/ ng·L^{-1}	DMeHg/ ng·L^{-1}	PMeHg/ ng·L^{-1}	TMeHg/THg (%)
Polluted area	W1	8.5	7.54	3.04	2100	95	2000	13	0.38	0.28	0.10	0.02
	W2	8.6	7.56	1.19	960	40	920	7.6	0.45	0.44	0.017	0.05
	W3	8.5	7.10	0.66	280	24	260	10	0.59	0.41	0.18	0.21
	W4	8.6	7.23	2.29	510	77	430	6.0	0.41	0.35	0.063	0.08
	W5	8.3	7.53	2.51	180	19	160	4.1	0.31	0.26	0.057	0.17
	W6	8.4	6.42	8.36	43	15	28	6.5	0.43	0.31	0.12	1.00
	W7	8.6	7.64	2.13	670	32	640	11	1.1	1.0	0.10	0.16
	W8	8.6	8.42	0.40	190	8.7	180	2.5	0.43	0.29	0.14	0.23
Control site	W9	8.7	8.80	0.56	13	8.6	4.6	6.4	0.093	0.073	0.020	0.68
	W10	8.6	9.73	1.98	18	8.3	9.2	4.7	0.26	0.12	0.14	1.49

THg: total mercury; DHg: dissolved mercury; PHg (particulate mercury) = THg − DHg; RHg: reactive mercury; TMeHg: total methyl mercury; DMeHg: dissolved methyl mercury; PMeHg (particulate MeHg) = TMeHg − DMeHg.

between THg and particulate Hg concentration in the stream water. The results confirmed that Hg tends to be bound to particulate matters. Previous studies confirmed the increase of THg concentration with decreasing particle size in mine waste of Hg mine (Kim et al., 2004). The suspended particles would present as a primarily transport pathway from mine waste to the aquatic system. With the deposition of suspended particles in downstream, therefore, the particulate Hg concentration decreased sharply as well.

Total and dissolved MeHg in water samples in the polluted area ranged from 0.31 to 1.1 ng/L and from 0.26 to 1.0 ng/L, respectively (Table 4). Considering the fraction of MeHg in the water samples, dissolved form is the primary species. On average, dissolved MeHg accounted for 80.1% of total MeHg in the water samples, with a range of 67.4–97.8%. A significant correlation ($r = 0.976$, $n = 8$, $p < 0.001$; Fig. 3b) was observed between total and dissolved MeHg concentrations in the stream water samples. Total

MeHg concentrations in water samples in the polluted area were significantly higher than those in the control sites (0.093 and 0.26 ng/L). The highest MeHg concentration was found at Luoxi (site 7), where the former ore processing and retorting plant is located, and the long history of LSMM activities have resulted in serious Hg pollution to the local environment.

The proportion of THg present as MeHg in stream water was generally <1%. However, a high ratio (1.49%) was found at the control site 10. However, no significant correlation between total MeHg and THg concentrations was observed in the water samples.

The range of THg concentrations in the stream waters in the study area was comparable to that obtained from other Hg mining areas (Table 5), while the MeHg concentrations were comparatively much lower. The results indicated the non-optimum conditions of Hg methylation in the karstic environment. Alkalinity may significantly affect MeHg distribution in water body (Ullrich et al., 2001). In the study area, the dominant mineral in Hg ore is cinnabar, which lacks other sulfide minerals. The host rocks are mainly carbonates, which contribute to the alkaline environment present in the calcines (Zhang et al., 2004). The alkalinized stream water (pH 8.3–8.7) thus appears to inactivate bio-methylation processes in the environment.

Many studies suggested that dissolved organic carbon (DOC) may have mitigating effects on the production and/or bioaccumulation of MeHg in natural waters (Ullrich et al., 2001). In this study, DOC contents in the water were comparatively low compared to that reported in relevant studies in North America and Europe (Gorski et al., 2003; Watras et al., 1998). High concentrations of inorganic carbon and low levels of complexing organic carbon may indirectly be responsible for the low levels of MeHg in the stream water.

3.4. Soils

THg concentrations in different types of arable soils are listed in Table 6. The data indicated that the surface soils were seriously contaminated with Hg (1.3–360 mg/kg) compared to that in the control sites (0.22–0.33 mg/kg). The latter represented the
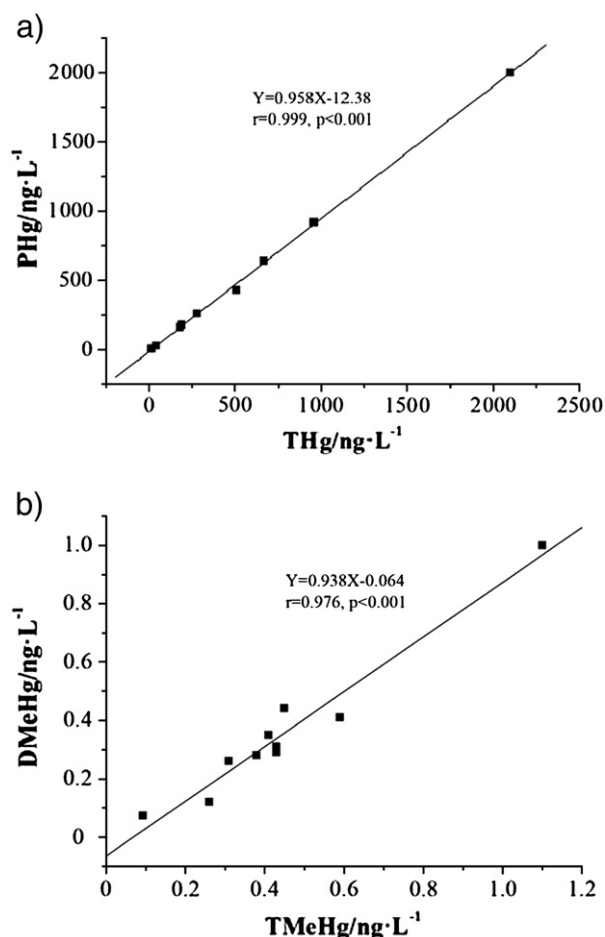

a)
Y=0.958X−12.38
r=0.999, p<0.001

b)
Y=0.938X−0.064
r=0.976, p<0.001

Fig. 3. The relationship between different Hg speciations in surface water in the study area.

Table 5
THg and MeHg concentrations in the stream water in Hg mines over the world/ng·L^{-1}.

Location	THg	MeHg	Reference
Wuchuan Hg mines, Guizhou, China	22–360	0.21–5.7	Qiu et al., 2006a
Wanshan Hg mines, Guizhou, China	17.3–12,000	0.012–25	Feng et al., 2003; Horvat et al., 2003; Qiu et al., 2009; Zhang et al., 2010a,b
Lanmuchang Hg–Tl mines, Guizhou, China	25–7020	–	Qiu et al., 2006b
Nevada Hg mines, USA	3.1–2000	–	Gray et al., 2002
Almadén Hg mines, Spain	7.6–13,000	0.41–30	Gray et al., 2004
Idrija Hg mine, Slovenia	2.8–322	0.01–0.6	Hines et al., 2000
Palawan Hg mines, Philippines	8–31,000	<0.02–3.1	Gray et al., 2003
California Hg mines, USA	2–450,000	0.003–47	Ganguli et al., 2000; Thomas et al., 2002
Alaska Hg mines, USA	1.0–2500	0.01–1.2	Gray et al., 2000
Tongren Hg mines, Guizhou, China	92–2300	2.6–7.9	Li et al., 2008a
Xunyang Hg mines, Shaanxi, China	120–21,000	–	Zhang et al., 2009
Wuchuan Hg mines, Guizhou, China	13–2100	0.093–1.1	This study

Table 6
THg concentrations in different types of arable soils in the study area/mg·kg^{-1}.

No	Location	Rice field	Vegetable field	Corn field	No	Location	Rice field	Vegetable field	Corn field
S1	Liziping	–	90	15	S9	Luoxi	220	3.6	12
S2	Laohugou	360	–	18	S10	Yinjiaxi	3.1	1.6	–
S3	Mine center	–	10	39	S11	Daping Village	6.4	4.4	–
S4	Ganxi	220	–	–	S12	Daping Town	18	1.3	–
S5	Banchang	260	300	280	S13	Daping Reservoir	27	–	–
S6	Sankeng	27	2.9	–	S14	Yanggang River	0.22	–	–
S7	Huanglong	8.9	–	3.2	S15	Taofu	–	–	0.33
S8	Taiba	–	–	4.9	–	–	–	–	–

local geochemical baseline being in the range of 0.01–0.5 mg/kg present in worldwide uncontaminated soils (Senesi et al., 1999).

Concerning co-located arable soils vegetated by various crops, generally the paddy field had higher THg concentrations than the vegetable and corn field. This may be due to the fact that the paddy fields were irrigated with highly Hg polluted stream water, and that the soils of paddy field contain abundant organic matters to complex and bind Hg (Biester et al., 2002; Lindqvist et al., 1991). The water sources of vegetable and corn fields were mainly derived from rainfall and then atmospheric Hg deposition was the main Hg pollution source.

Highly elevated THg concentrations in the surface soil were mainly found in the areas seriously impacted by Hg mining activities, such as the vicinity of mine waste heaps, ore processing plant and retorting plant, and the sites of AMM. For instance, THg concentrations in the paddy field located at flood plains downstream of Laohugou dam and Luoxi were 360 and 220 mg/kg, respectively. These may have resulted from Hg rich particles transported from the upstream polluted areas during the flooding season. High THg concentrations were also found in the surface soil in Banchang and Ganxi, which may be impacted from the AMM.

The vertical distribution of THg in the soil profile from Jixiuchang exhibited a maximum near the surface (Fig. 4). With an increase of depth, the THg concentration decreased sharply and reached a stable value at the depth of 60–70 cm (12.8–14.6 mg/kg, Fig. 4). THg concentrations at the bottom of the soil profiles were significantly higher than the local baseline (0.22–0.33 mg/kg), possibly explained by Hg mineralization in the bedrock. The trend of THg concentrations in the soil profile indicated that Hg contamination in top soil was primarily derived from the atmospheric deposition of Hg emitted from AMM.

No significant correlation was observed between soil pH and THg concentrations, however high THg concentrations were essentially related to high pH values (Fig. 5a). A significant correlation ($r = 0.53$, $p < 0.01$) was found between soil THg and OM concentrations (Fig. 5b). Organic matter has a strong capacity to complex and bind Hg (Biester et al., 2002; Lindqvist et al., 1991). Positive correlations between soil organic carbon and THg concentrations have previously been reported (Hissler and Probst, 2006; Tomiyasu et al., 2003). Hissler and Probst (2006) concluded that most of atmospheric Hg deposition was trapped by OM contained in soil. The amount and quality of OM and its partition between aqueous and solid phases might play a major role in distribution and transportation of Hg through soil profiles (Semu et al., 1987). Lin et al. (2010) reported that rice paddy soil contained a small portion, but significant amount of organically-bound Hg in Wanshan Hg mine. The accumulation of Hg in the organic-rich upper soil layers may be related to atmospheric Hg deposition.
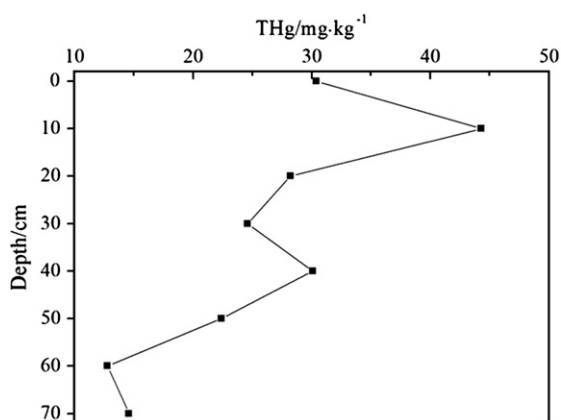
4. Conclusions

This study revealed a significant Hg contamination in mine waste calcines, ambient air, stream water and soils in the study area, which was concluded as a combined impact of LSMM and AMM. The areas impacted by LSMM were essentially confined to the historical remains of Hg mining activities. However, AMM has a characteristic of non-point source pollution and the mercury pollution caused by AMM can be distributed widely over the Hg mining area. The mine waste calcines from AMM were important Hg contamination sources to the surface water and rice paddy fields. Therefore, the calcines must be appropriately disposed of and AMM should be strictly banned by the local government. More feasible remedial techniques should be
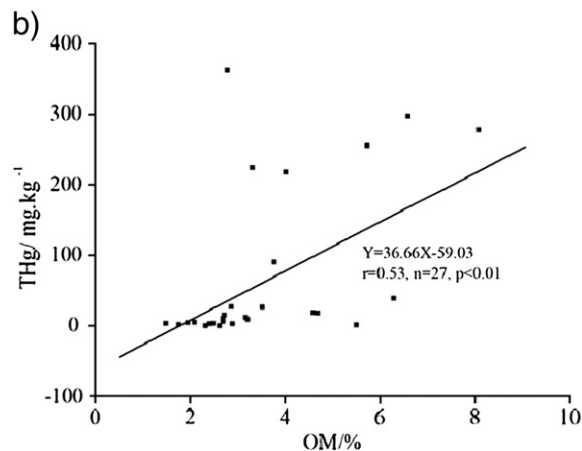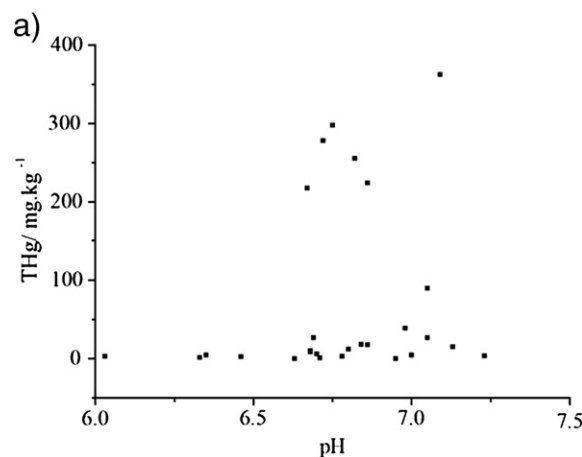
Fig. 4. Total mercury (THg) distribution pattern in the soil profile at Jixiuchang in the study area.

Fig. 5. The relationship between total mercury (THg) concentration and pH, organic matter (OM) in soil samples.

utilized to reduce Hg pollution and human exposure risks in the study area.

Acknowledgments

References

Bailey EA, Gray JE, Theodorakos PM. Mercury in vegetation and soils at abandoned mercury mines in southwestern Alaska, USA. Geochem Explor Environ Anal 2002;2:275–85.
Bellander T, Merler E, Ceccarelli F, Boffetta P. Historical exposure to inorganic mercury at the smelter works of Abbadia San Salvatore, Italy. Ann Occup Hyg 1998;42:81–90.
Berzas Nevado JJ, Garcia Bermejo LF, Rodriguez Martin-Doimeadios RC. Distribution of mercury in the aquatic environment at Almadén, Spain. Environ Pollut 2003;122: 261–71.
Biester H, Gosar M, Muller G. Mercury speciation in tailings of the Idrija mercury mine. J Geochem Explor 1999;65:195–204.
Biester H, Gosar M, Covelli S. Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. Environ Sci Technol 2000;34:3330–6.
Biester H, Muller G, Scholer HF. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. Sci Total Environ 2002;284:191–203.
Bonzongo JC, Heim KJ, Warwick JJ, Lyons WB. Mercury levels in surface waters of the Carson River-Lahontan Reservoir system, Nevada: influence of historic mining activities. Environ Pollut 1996;92:193–201.
Domagalski J. Mercury and methylmercury in water and sediment of the Sacramento River Basin, California. Appl Geochem 2001;16:1677–91.
Domagalski J, Alpers C, Slotton D, Suchanek T, Ayers S. Mercury and methylmercury concentrations and loads in the Cache Creek watershed, California. Sci Total Environ 2004;327:215–37.
Ebinghaus R, Kock HH, Coggins AM, Spain TG, Jennings SG, Temme Ch. Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. Atmos Environ 2002;36:5267–76.
Edner H, Ragnarson P, Svanberg S, Wallinder E, Ferrara R, Maserti BE, et al. Atmospheric mercury mapping in a cinnabar mining area. Sci Total Environ 1993;133:1-15.
Feng X, Chen Y, Zhu W. The fluxes of volatile mercury over soil surface in Guizhou Province. Environ Sci 1996;17:20–5 (In Chinese with English abstract).
Feng X, Qiu G, Wang S, Shang L. Distribution and speciation of mercury in surface waters in mercury mining areas in Wanshan, Southwestern China. J Phys IV 2003;107:455–8.
Feng X, Shang L, Wang S, Tang S, Zheng W. Temporal variation of total gaseous mercury in the air of Guiyang, China. J Geophys Res 2004;109:D03303, doi:10.1029/2003JD004159.
Feng X, Li P, Qiu G, Wang S, Li G, et al. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou province, China. Environ Sci Technol 2008;42:326–32.
Feng X, Qiu G. Mercury pollution in Guizhou, China — an overview. Sci Total Environ 2008;400:227–37.
Ferrara R, Mazzolai B, Edner H, Svanberg S, Wallinder E. Atmospheric mercury sources in the Mt. Amiata area, Italy. Sci Total Environ 1998a;213:13–23.
Ferrara R, Maserti BE, Andersson M, Edner H, Ragnarson P, Svanberg S, Hernandez A. Atmospheric mercury concentrations and fluxes in the Almadén district (Spain). Atmos Environ 1998b;22:3897–904.
Ganguli PM, Mason RP, Abu-Saba KE, Anderson RS, Flegal AR. Mercury speciation in drainage from the New Idria mercury mine, California. Environ Sci Technol 2000;34:4773–9.
Gómez M, Klink J, Boffetta P, Español S, Sällsten G, Quintana J. Exposure to mercury in the mine of Almadén. Occup Environ Med 2007;64:389–95.
Gorski PR, Cleckner LB, Hurley JP, Sierszen ME, Armstrong DE. Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. Sci Total Environ 2003;304:327–48.
Gosar M, Pirc S, Bidovec M. Mercury in the Idrija river sediments as a reflection of mining and smelting activities of the Idrija mercury mine. J Geochem Explor 1997;58:125–31.
Gray JE, Peter U, Theodorakos M, Bailey EA, Turner RR. Distribution, speciation, and transport of mercury in stream sediment, stream water, and fish collected near abandoned mercury mines in southwestern Alaska, USA. Sci Total Environ 2000;260:21–33.
Gray JE, Crock JG, Fey DL. Environmental geochemistry of abandoned mercury mines in West-Central Nevada, USA. Appl Geochem 2002;17:1069–79.
Gray JE, Greaves IA, Bustos DM, Krabbenhoft DP. Mercury and methylmercury contents in mine-waste calcine, water, and sediment collected from the Palawan Quicksilver Mine, Philippines. Environ Geol 2003;43:298–307.
Gray JE, Hines ME, Higueras PL, Adatto I, Lasorsa BK. Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the Almadén mining district, Spain. Environ Sci Technol 2004;38:4285–92.
Gustin MS, Coolbaugh M, Engle M, Fitzgerald BC, Keislar RE, et al. Atmospheric mercury emissions from mine wastes and surrounding geologically enriched terrains. Environ Geol 2003;43:339–51.

Hao C, Shen Y, Zhang Y. Study on mercury consumption reduction plans for PVC resin industry in China. Res Environ Sci 2005;18:112–5 (In Chinese with English abstract).
Higueras P, Oyarzun R, Biester H, Lillo J, Lorenzo S. A first insight into mercury distribution and speciation in soils from the Almadén mining district, Spain. J Geochem Explor 2003;80:95-104.
Hines ME, Horvat M, Faganeli J, Bonzongo JC, Barkay T, et al. Mercury biogeochemistry in the Idrija river, Slovenia, from above the mine into the Gulf of Trieste. Environ Res 2000;83:129–39.
Hissler C, Probst J. Impact of mercury atmospheric deposition on soils and streams in a mountainous catchment (Vosges, France) polluted by chlor-alkali industrial activity: the important trapping role of the organic matter. Sci Total Environ 2006;361:163–78.
Horvat M, Nolde N, Fajon V, Jereb V, Logar M, et al. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. Sci Total Environ 2003;304:231–56.
Jian X, Shen Y, Yao W, Wang Y, Zhang X. Status analysis and reduction countermeasures of China's mercury supply and demand. Res Environ Sci 2009;22:788–92 (In Chinese with English abstract).
Kim CS, Brown-Jr G, Rytuba JJ. Characterization and speciation of mercury-bearing mine waste using X-ray adsorption spectroscopy. Sci Total Environ 2000;261:157–68.
Kim CS, Rytuba J, Brown-Jr G. Geological and anthropogenic factors influencing mercury speciation in mine wastes: an EXAFS spectroscopy study. Appl Geochem 2004;19: 379–93.
Kobal A, Horvat M, Prezelj M, Briski SA, Krsnik M, et al. The impact of long-term past exposure to elemental mercury on antioxidative capacity and lipid peroxidation in mercury miners. J Trace Elem Med Biol 2004;17:261–74.
Kotnik J, Horvat M, Dizdarevic T. Current and past mercury distribution in air over the Idrija Hg mine region, Slovenia. Atmos Environ 2005;39:7570–9.
Li P, Feng X, Shang L, Qiu G, Meng B, Liang P, Zhang H. Mercury pollution from artisanal mercury mining in Tongren. Guizhou China Appl Geochem 2008a;23:2055–64.
Li P, Feng X, Qiu G, Li Z, Fu X, et al. Mercury exposures and symptoms in smelting workers of artisanal mercury mines in Wuchuan, Guizhou, China. Environ Res 2008b;107:108–14.
Li P, Feng X, Qiu G, Shang L, Wang S. Mercury exposure in the population from Wuchuan mercury mining area, Guizhou, China. Sci Total Environ 2008c;395:72–9.
Li P, Feng X, Qiu G, Shang L, Wang S, Meng B. Atmospheric mercury emission from artisanal mercury mining in Guizhou Province, Southwestern China. Atmos Environ 2009;43:2247–51.
Lin Y, Larssen T, Vogt R, Feng X. Identification of fractions of mercury in water, soil and sediment from a typical Hg mining area in Wanshan, Guizhou province, China. Appl Geochem 2010;25:60–8.
Lindqvist O, Johansson K, Aastrup M, Anderson A, Bringmark L, Hovsenius G. Mercury in the Swedish environment-recent research on causes, consequences and corrective methods. Water Air Soil Pollut 1991;55:1-261.
Lindqvist O. Special issue of first international on mercury as a global pollutant. Water Air Soil Poll 1991;56:1.
Loredo J, Alvarez R, Ordonez A. Release of toxic metals and metalloids from Los Rueldos mercury mine (Asturias, Spain). Sci Total Environ 2005;340:247–60.
Loredo J, Ordonez A, Alvarez R. Environmental impact of toxic metals and metalloids from the Munon Cimero mercury-mining area (Asturias, Spain). J Hazard Mater 2006;136:455–67.
Louis L, Chamberlain A. Field sampling and analytical intercomparison for mercury and methylmercury determination in natural water. Water Air Soil Poll 1995;80:1247–56.
Lu R. Chemical analysis method of agricultural soil. Beijing: China Agricultural Science Press; 2000. p. 106–7. (in Chinese).
Maramba N, Reyes J, Francisco-Rivera A, Panganiban L, Dioquino C, et al. Environmental and human exposure assessment monitoring of communities near an abandoned mercury mine in the Philippines: A toxic legacy. J Environ Manage 2006;81:135–45.
Meng B, Feng X, Qiu G, Cai Y, Wang D, et al. Distribution patterns of inorganic mercury and methylmercury in tissues of rice (Oryza sativa L.) plants and possible bioaccumulation pathways. J Agric Food Chem 2010;58:4951–8.
Meng B, Feng XB, Qiu GL, Liang P, Li P, Chen CX, Shang LH. The process of methylmercury accumulation in rice (Oryza sativa L.). Environ Sci Technol 2011;45:2711–7.
Millán R, Gamarra R, Schmid T, Sierra MJ, Quejido AJ, et al. Mercury content in vegetation and soils of the Almadén mining area (Spain). Sci Total Environ 2006;368:79–87.
NRDC (National Resource Defense Council). NRDC fights to stop mercury pollution in China: China is cornerstone in solving global mercury problem; 2007. Website: http://www.nrdc.org/international/china/mercury.pdf.
Qiu, G, 2005. Environmental geochemistry of mercury in typical Hg-mined areas, Guizhou Province. Ph.D. Thesis, Graduate University, Chinese Academy of Sciences. Beijing.
Qiu G, Feng X, Wang S, Shang L. Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China. Appl Geochem 2005;20:627–38.
Qiu G, Feng X, Wang S, Shang L. Environmental contamination of mercury from Hg-mining areas in Wuchuan, northeastern Guizhou, China. Environ Pollut 2006a;142:549–58.
Qiu G, Feng X, Wang S, Xiao T. Mercury contaminations from historic mining to water, soil and vegetation in Lanmuchang, Guizhou, southwestern, China. Sci Total Environ 2006b;368:56–68.
Qiu G, Feng X, Li P, Wang S, Li G, Shang L, Fu X. Methylmercury accumulation in rice (Oryza sativa L.) grown at abandoned mercury mines in Guizhou, China. J Agric Food Chem 2008;56:2465–8.
Qiu G, Feng X, Wang S, Fu X, Shang L. Mercury distribution and speciation in water and fish from abandoned Hg mines in Wanshan, Guizhou province, China. Sci Total Environ 2009;407:5162–8.

Qu L. A study on prevention and remedy of Hg contamination in Guizhou. Guiyang: Guizhou Press; 2004. pp. 1–251.

Rytuba JJ. Mercury from mineral deposits and potential environmental impact. Environ Geol 2003;43:326–38.

Schroeder WH, Munthe J. Atmospheric mercury—an overview. Atmos Environ 1998;32: 809–22.

Semu E, Singh BR, Selmer-Olsen AR. Adsorption of mercury compounds by tropical soils. II. Effects of soil: solution ration, ionic strength, pH and organic matter. Water Air Soil Pollut 1987;32:1-10.

Senesi GS, Baldassarre G, Senesi N, Radina B. Trace element inputs into soils by anthropogenic activities and implications for human health. Chemosphere 1999;39:343–77.

Thomas MA, Conaway CH, Steding DJ, Marvin-DiPasquale M, Abu-Saba KE, Flegal RA. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. Geochem Explor Environ Anal 2002;2:1–7.

Tomiyasu T, Okada M, Imura R, Sakamoto H. Vertical variations in the concentration of mercury in soils around Sakurajima Volcano, Southern Kyushu, Japan. Sci Total Environ 2003;304:221–30.

Ullrich SM, Tanton TW, Abdrashitova SA. Mercury in the aquatic environment: a review of factors affecting methylation. Crit Rev Env Sci Tec 2001;31:241–93.

USEPA (United States Environmental Protection Agency). Method 1631, revision B: mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. Washington: USEPA; 1999. pp. 1–33.

USEPA (United States Environmental Protection Agency). Method 1630: methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS. Washington: USEPA; 2001. pp. 1–41.

Wang S, Feng X, Qiu G, Wei Z, Xiao T. Mercury emission to atmosphere from Lanmuchang Hg–Tl mining area, Southwestern Guizhou, China. Atmos Environ 2005;39:7459–73.

Wang S, Feng X, Qiu G, Shang L, Li P, Wei Z. Mercury concentrations and air/soil fluxes in Wuchuan mercury mining district, Guizhou province, China. Atmos Environ 2007a;41:5984–93.

Wang S, Feng X, Qiu G, Fu X, Wei Z. Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China. Atmos Environ 2007b;41:5584–94.

Watras CJ, Back RC, Halvorsen S, Hudson RJM, Morrison KA, Wente SP. Bioaccumulation of mercury in pelagic freshwater food webs. Sci Total Environ 1998;219:183–208.

Williams TM, Apostol Jr AN, Miranda CR. Assessment by hair analysis of mercury exposure among mining impacted communities of Mindanao and Palawan, the Philippines. Environ Geochem Hlth 2000;22:19–31.

Yan H, Feng X, Shang L, Tang S, Qiu G. Speciation analysis of ultratrace levels of mercury in natural waters. J Instrum Anal 2003;22:10–3 (in Chinese with English abstract).

Zhang G, Liu C, Wu P, Yang Y. The geochemical characteristics of mine-waste calcines and runoff from the Wanshan mercury mine, Guizhou, China. Appl Geochem 2004;19:1735–44.

Zhang H, Feng X, Larssen T, Shang L, Vogt RD, et al. Fractionation, distribution and transport of mercury in rivers and tributaries around Wanshan Hg mining district, Guizhou Province, Southwestern China: part 1—total mercury. Appl Geochem 2010a;25:633–41.

Zhang H, Feng X, Larssen T, Shang L, Vogt RD, et al. Fractionation, distribution and transport of mercury in rivers and tributaries around Wanshan Hg mining district, Guizhou Province, Southwestern China: Part 2 methyl mercury. Appl Geochem 2010b;25:642–9.

Zhang H, Feng X, Larssen T, Shang L, Li P. Bio-accumulation of methylmercury versus inorganic mercury in rice (Oryza sativa L.) grain. Environ Sci Technol 2010c;44: 4499–504.

Zhang L, Jin Y, Lu J, Zhang C. Concentration, distribution and bioaccumulation of mercury in the Xunyang mercury mining area, Shaanxi Province, China. Appl Geochem 2009;24:950–6.