Environmental geochemistry of an abandoned mercury mine in Yanwuping, Guizhou Province, China

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ABSTRACT

The distribution of mercury (Hg) and methylmercury (MeHg) in paddy soil and rice grain (polished), and Hg in surface waters and gaseous elemental Hg (GEM) in atmosphere at the Yanwuping Hg mining district (YMM), Guizhou Province, China was investigated. Results exhibited high total Hg (Hg^T) and MeHg concentrations in soil at sites adjacent to calcine pile and tailings, and ranged from 5.6 to 240 mg kg^{-1} and 0.66 to 7.3 µg kg^{-1}, respectively. Concentrations of Hg^T in rice ranged from 10 to 45 µg kg^{-1}, and high MeHg concentrations were also observed ranging from 3.2 to 39 µg kg^{-1}. The elevated Hg^T and MeHg concentrations in soil in the vicinity of calcine pile and tailings reflected in high MeHg concentrations in rice. Those data were significantly correlated with MeHg concentration in soil confirming that soil is the major source of MeHg in rice. The highest Hg concentrations in water, otherwise rather low, ranging from 3.8 to 51 ng l^{-1} for Hg^T and of 0.14 to 2.7 ng l^{-1} for $MeHg^T$, were found at the proximity of calcine pile suggesting that untreated mine wastes are the principal source of Hg in the nearby area. Huge emissions of GEM were also detected from calcines affecting the whole area, ranging from 12 to 180 ng m^{-3} with an average of 46 ± 35 ng m^{-3}. The distribution patterns of Hg and MeHg observed in the environmental compartments suggest an elevated contamination of Hg in the region. Elevated high MeHg concentrations in rice might pose a potential health risk to local populations.

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1. Introduction

Mercury is a highly toxic substance to human beings (Clarkson, 1998). Most of the large Hg mines in China abandoned in early 2000 due to shortages of cinnabar resources and increasing environmental issues. The primary environmental concern on abandoned Hg mines is MeHg, which is highly toxic and can be bio-accumulated into the livings. The retorted cinnabar ores (termed calcine) produced by inefficient roasting of Hg ore generally contain abundant soluble Hg compounds, such as elemental Hg and Hg salts (Kim et al., 2000, 2004; Li et al., in preparation). Those water-soluble Hg compounds are readily released into the environmental compartments, such as water, soil and sediments, hereafter can be converted into MeHg and enter the food chain.

The Yanwuping Hg mine (YMM) was one of the large Hg mines of Wanshan, the largest center of metal Hg produced in China. The Hg mining history of the YMM was approximately 700 year dated back to the mid-14th century of the Ming Dynasty. The industrial mining activity of the YMM stared in 1951 and stopped in 1994. Approximately 200 t of metal Hg was produced and 283,000 m^3 of calcine were introduced into the local surroundings. To date Hg distribution

in ambient air and Hg speciation, especially MeHg in the local environmental compartments, such as soil, water, and plants affected by the abandoned Hg mine is still lacking.

In this study, gaseous elemental Hg (GEM) concentrations in ambient air were examined. Concentrations of Hg^T and MeHg in riparian soil and rice as well as Hg speciation in surface water were also determined. The objectives are to evaluate (1) distribution of GEM in the ambient air; (2) transport of Hg^T and MeHg in soil and rice as well as Hg speciation in surface water, and (3) extent of MeHg contaminations to the local ecosystems. This study of the Yanwuping mine is one in a series of studies related to Hg mining in China in our research group including published studies of the Xunyang mine (Qiu et al., 2012a, 2012b), Wanshan mine (Lin et al., 2011, 2010; Zhang et al., 2010a, 2010b; Li et al., 2009; Qiu et al., 2005), Tongren mine (Li et al., 2008a), Wuchuan mine (Li et al., 2008b; Qiu et al., 2006a), and Lanmuchang mine (Qiu et al., 2006b).

2. Experimental and materials

2.1. Study area

The Yanwuping mine is located 15 km northeastern of the Wanshan town, covering approximate 1.0 km^2 (Fig. 1). The region is hilly and karsitic and has a sub-tropical humid climate characterized by abundant precipitation and mild temperatures. The annual average temperature is 15 °C, with the highest concentration of
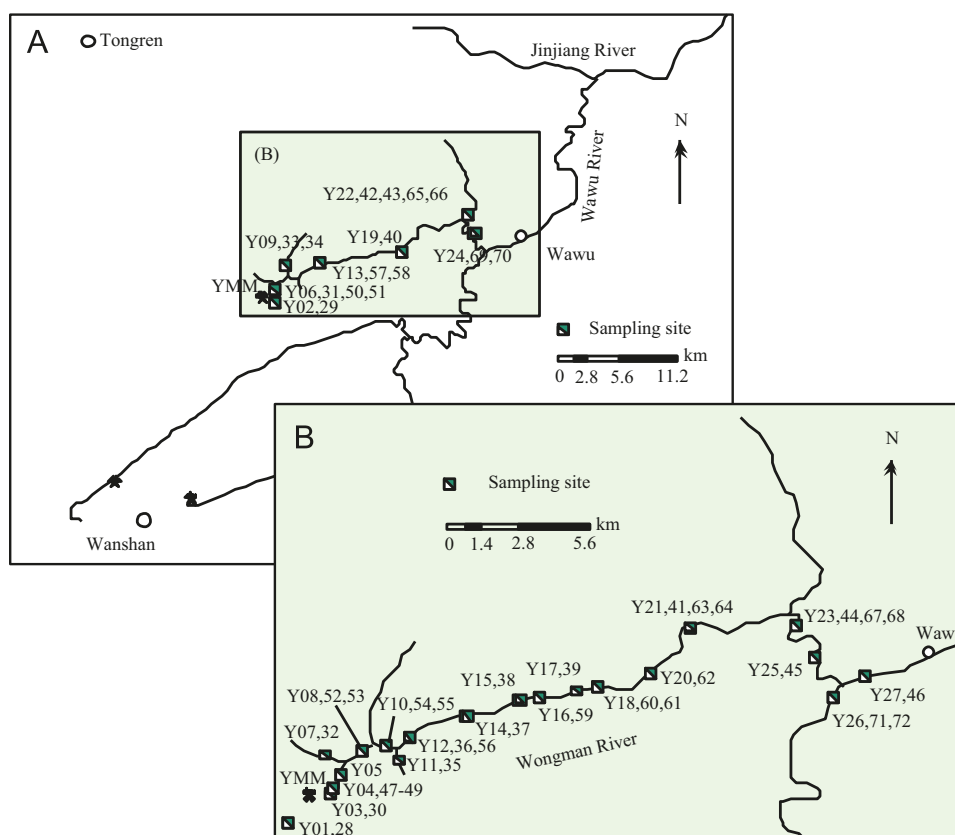
Fig. 1. The study area and location of the sampling sites.

33.5 °C occurring in July. Average yearly rainfall is of 1200–1400 mm. The dominant ore mineral of the YMM is cinnabar and the associated element is selenium (Hua and Cui, 1995). The Wongman River, a tributary of the Wawu River, is directly impacted by the historic Hg mining activity and flows through the YMM district. The Wawu River is a tributary of the Jinjiang River, which flows into Hunan Province.

The historic Hg retorting facility of the YMM and quantities of calcines and waste rocks were located at the upstream of Wongman River. A huge calcines pile and a big dam full of waste rocks combined with calcines can be observed. The drainages and runoff through the calcines pile and the tailings' dam directly flows into the Wongman River without any treatments. However, an ongoing treatment of the cements' covering on the calcines pile has been started since July 2011.

2.2. Sampling and preparation

The concentrations of GEM in ambient air ($n=27$) were measured using the Lumex RA-915+ Portable Mercury Vapor Analyzer (Lumex Ltd., Russia). The Lumex RA-915+ is a multifunctional atomic absorption spectrometer with Zeeman background correction. The detection limit of Hg in ambient air is 0.5 ng m^{-3} at a flow rate of 10 l min^{-1}.

Surface water samples ($n=19$), including the unfiltered for Hg^T and total methylmercury (MeHg^T) analyses, and the filtered for dissolved Hg (Hg^D) and dissolved methylmercury (MeHg^D) analyses, were collected from the Wongman River and its tributaries not directly affected by the YMM. For the unfiltered samples, 100 ml volume of water was collected with polyethylene-gloved hands into a 100 ml borosilicate-glass bottle pre-cleaned by heating at 550 °C for 1.5 h. For the filtered samples, 1000 ml volume of water was in situ filtered with 0.45 μm membrane filters (Millipore) using pre-cleaned borosilicate-glass filtration apparatus, then 100 ml volume of the filtered water was collected. Both unfiltered and filtered samples were acidified with ultra-pure HCl using a final acid concentration of 0.4% (v/v) within 24 h of the collection.

Paddy soil samples ($n=26$) were collected at sites nearby the Wongman River as well as its tributaries. Samples were collected from 2 to 5 cm surface-layer following the removal of covering organic materials (e.g. leaves, litter). At each sampling site, a final sample was composed of 3–5 sub-samples from several localities within an area of 1 m^2 following the diagonal sampling technique. All samples for Hg^T and MeHg analysis were stored in double-sealed polyethylene bags to avoid cross contaminations and were frozen until analysis. In the laboratory, soil samples were air dried, ground in a ceramic disc mill, and sieved to 200 meshes prior to analysis.

Rice samples (Oryza sativa L., $n=26$) corresponding to soil sampling sites were collected along the Wongman River as well as its tributaries during the harvest season.

Each sample was composed of at least five sub-samples within an area of about 5–10 m^2 in the same paddy field. Rice samples were in situ cleaned using drinking water followed by de-ionized water rinses after being brought back to the laboratory, and finally air-dried. Then the polished rice was separated using a pestle and mortar, and ground to 200 meshes (IKA-A11 basic, IKA, Germany) prior to analysis. The GEM concentrations in ambient air of the corresponding rice sampling sites were also measured.

2.3. Measurements

2.3.1. Water

The Hg^T and Hg^D in samples were determined by SnCl$_2$ reduction and BrCl oxidation following CVAFS detection (Bloom and Crecelius, 1983; Horvat et al., 1987, 1991), and the MeHg^T and MeHg^D were analyzed by NaBEt$_4$ ethylation following distillation, Tenax trapping, and GC-CVAFS detection (Horvat et al., 1993; Liang et al., 1994, 1996). Measurements of total Hg in samples followed Method 1631E (USEPA, 1999) and of MeHg in samples followed Method 1630 (USEPA, 2001). The particulate fractions of both HgT and MeHg in the following discussion were defined as the difference between the total and the dissolved.

2.3.2. Soil

For Hg^T analysis, approximate 0.1–0.3 g of dry sample was digested at 95 °C in a water bath with a fresh mixture of HCl and HNO$_3$ (3:1, v/v). Then a suitable aliquot of digested sample solution was measured using cold-vapor atomic absorption spectrometry (CV-AAS), with a detection limit of 0.01 μg kg^{-1}. For MeHg analysis, approximate 0.2–0.5 g of dry sample was extracted with CH$_2$Cl$_2$ after HNO$_3$ leaching (Liang et al., 1994, 1996). Then a suitable aliquot of digested sample solution was determined by GC-CVAFS following Method 1630 (USEPA, 2001). Soil organic matter (SOM) and humic acid (HA) contents were determined followed the National Standard Method GB 7857-87 and Method GB 7858-87, respectively (NSA, 1987a, 1987b).

2.3.3. Rice

For Hg^T analysis, approximate 0.5–1.0 g of dry sample was digested using a fresh mixture of HNO$_3$ and H$_2$SO$_4$ (8:2, v/v) in an oven at 95–140 °C for 2 h, then following CVAFS detection similar to the water sample analyses. For MeHg analysis, approximate 0.2–0.5 g of dry sample was digested using 25% KOH-methanol in an oven at 75–80 °C for 3 h. MeHg in samples was then extracted with methylene

chloride and back-extracted into water for measurement following Method 1630 (USEPA, 2001; Liang et al., 1996).

2.3.4. QA/QC

Quality assurance and quality control of Hg^T and MeHg in samples analysis were determined using duplicates, method blanks, matrix spikes, and certified reference materials (GBW07405; BCR 580; TORT-2).

The relative percent difference in soil sample duplicates was < 10% for Hg^T and < 8.6% for MeHg. For the geological standard of GBW07405 analyzed in this study, an average Hg^T concentration of 0.30 ± 0.01 mg kg^{-1} ($n=5$) was observed and is comparable with the certified concentration of 0.29 ± 0.04 mg kg^{-1}. For MeHg in soil analysis, BCR 580 was analyzed and the MeHg concentration of 76 ± 6 µg kg^{-1} ($n=5$) obtained is comparable with the certified concentration of 75 ± 4 µg kg^{-1}. Limits of determination were 0.01 µg kg^{-1} for Hg^T and 0.002 µg kg^{-1} for MeHg.

The relative percentage difference was < 6.3% for Hg^T and < 9.1% for MeHg in rice duplicate samples. Recoveries on matrix spikes in rice were 89–106% for Hg^T and 90–118% for MeHg. For MeHg, TORT-2 was also analyzed and an average MeHg concentration of 151 ± 7.1 µg kg^{-1} ($n=5$) was obtained comparable with the certified concentration of 152 ± 13 µg kg^{-1}. Limits of determination were 0.013 µg kg^{-1} for Hg^T and 0.003 µg kg^{-1} for MeHg.

The relative percentage difference was < 10% for Hg^T and < 8.5% for MeHg in water duplicates. Recoveries on matrix spikes in water were 91–108% for Hg^T and 87–113% for MeHg. Limits of determination were 0.02 ng l^{-1} for Hg^T and 0.009 ng l^{-1} for MeHg. The method blank was lower than the detection limits. The field blank was 0.16 ± 0.05 ng l^{-1} for Hg^T and 0.012 ng l^{-1} for MeHg in water samples.

3. Results and discussion

3.1. Air

The concentrations of GEM ranged from 12 to 180 ng m^{-3}, with an average of 46 ± 35 ng m^{-3}. The GEM spatial distribution pattern was characterized by a significant variability and some extremely high concentrations. The highest concentration of GEM was detected at site Y03, approximately 0.5 km downwind site of the upstream calcines pile, which suggested the Hg^0 emission from those abandoned tailings. Fig. 2 exhibits a trend that GEM concentrations dropped sharply from the highest concentration to 12 ng m^{-3} within a distance approximately 0.5 km, and then increased to from 15 ng m^{-3} at distance 1.5 km of the calcines pile to a peak concentration of 90 ng m^{-3} at distance 4.0 km of the calcines pile. The increase of GEM concentrations in ambient air far distances from the YMM might indicate a strong nearby active human-made Hg emission source.

Levels of ambient air GEM concentrations in the YMM district were significantly elevated compared to the concentrations reported for urban areas and remote sites in China. For urban areas of China, relatively low GEM concentrations were reported in Shanghai and Ningbo, which were 2.7 ± 1.7 ng m^{-3} and

3.8 ± 1.3 ng m^{-3}, respectively (Friedli et al., 2011; Nguyen et al., 2011), while elevated concentrations were reported in the range of 6.7–18 ng m^{-3} in inland cities, such as Changchun, Chongqing, and Guiyang, which were usually co-located with large point sources and residential coal burning (Fang et al., 2004; Feng et al., 2004; Yang et al., 2009; Fu et al., 2011; Liu et al., 2011). Published data for GEM concentrations observed at remote sites were usually in the range of 1.6–4.0 ng m^{-3}, such as at Mt. Gonga, Mt. Changbai, Mt. Leigong, and Mt. Waliguan, (Wan et al., 2009; Fu et al., 2009, 2012). The average GEM concentration of 46 ± 35 ng m^{-3} detected in our study was about 2.5–17 folds higher compared to those reported concentrations observed at urban inland cities. It is close to the current ambient air quality standard for type II (50 ng m^{-3}: represents residential, commercial, industrial, and rural areas) proposed by the Ministry of Environmental Protection of China (MEP).

3.2. Water

The water affected by the YMM exhibited a wide range of 3.8–51 ng l^{-1} for Hg^T, of 2.7–27 ng l^{-1} for Hg^D, and of 0.24–24 ng l^{-1} for Hg^P, respectively. Peak concentrations of Hg^T, Hg^D, and Hg^P were all found in the sample Y29, which is adjacent to the calcines pile and was directly affected by its drainage. This suggested that the calcine, which generally contains abundant water-soluble Hg compounds, such as elemental Hg, metacinnabar, and Hg sulfate and chlorides (Zhang et al., 2004; Li et al., in preparation), is the primary source of Hg contamination to surface water. Samples collected from sites at tributaries, which were not directly affected by the calcines, contained low concentrations of Hg, with ranges from 3.8 to 17 ng l^{-1} for Hg^T, from 0.85 to 4.5 ng l^{-1} for Hg^D, and from 2.2 to 16 ng l^{-1} for Hg^P, respectively. These constant low concentrations of Hg speciation in tributaries might represent the baseline Hg concentrations in surface water in the study area.

The concentration of Hg^T in stream water was much lower than the limit set by the Chinese national standard for type V (1000 ng l^{-1}: represents water bodies for agricultural purposes). Comparison with the 770 ng l^{-1} aquatic wildlife standard for Hg^T as recommended by the USEPA (2009), all concentrations of Hg^T in samples were lower.

Concentrations of $MeHg^T$ varied from 0.14 to 2.7 ng l^{-1}, $MeHg^D$ from 0.038 to 0.38 ng l^{-1}, and $MeHg^P$ from 0.0055 to 2.6 ng l^{-1}, respectively. Samples collected from the Wongman River exhibited higher concentrations of $MeHg^T$ than those in its tributaries. Peak concentrations of both $MeHg^T$ and $MeHg^P$ were, however, not found at sites proximal to the calcines pile (Y29, Y30), but at sites approximate 1.0 km or at even far distances downstream, such as Y31, Y33, Y37, Y39, and Y43, probably suggesting an in situ favorable environment conditions for Hg methylation. Previous studies showed that water pH may affect MeHg distribution in water body (Ullrich et al., 2001). In the present study, inputs of water discharges from the calcines pile usually resulted in strong alkaline conditions (pH=8.3–11), thus might reduce the MeHg productions in the surrounding water.

There seems to be insignificant correlation between $MeHg^T$ and Hg^T, whereas, Hg^T and $MeHg^T$ were both significantly correlated with their particulate fractions (Table 1). In the present study, Hg^D fraction constituted high portions of Hg^T (averaged 57%) in samples affected by the YMM, reflecting impacts of water-soluble Hg compounds released from the upstream calcines. For MeHg fractions, however, the $MeHg^P$ constituted large portions (averaged 64%) in the Wongman River but low portions in its tributaries. The high portions of $MeHg^P$ in the Wongman River might indicate that MeHg produced in the water affected by the YMM was readily combined onto particles.
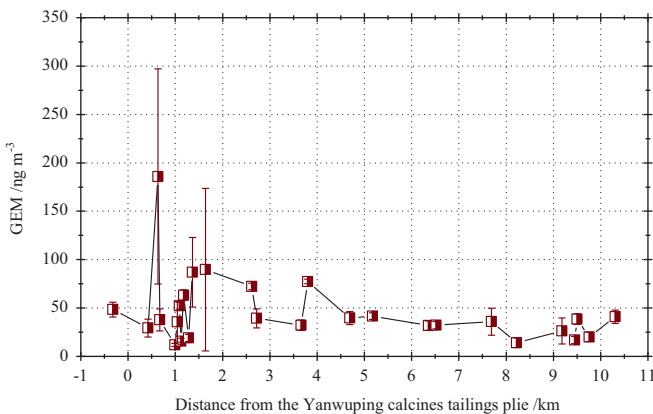

Fig. 2. The distribution of GEM concentrations in ambient air in the Yanwuping Hg mining district, Guizhou, China (Vertical bar means average ± s.d.).

Table 1
Correlations among Hg speciation, pH in water and other parameters collected from the Yanwuping Hg mining district, Guizhou, China (Dis – the distance downstream away from the upstream calcines pile).

	Hg^T	Hg^P	Hg^D	$MeHg^T$	$MeHg^P$	$MeHg^D$	pH	Dis	GEM
Hg^T	1								
Hg^P	0.92[b]	1							
Hg^D	0.83[b]	0.55[a]	1						
$MeHg^T$	0.001	−0.088	0.13	1					
$MeHg^P$	−0.032	−0.12	0.099	0.99[b]	1				
$MeHg^D$	0.25	0.22	0.22	0.024	−0.11	1			
pH	0.63[b]	0.34	0.87[b]	0.047	0.031	0.11	1		
Dis	−0.67[b]	−0.77[b]	−0.34	−0.12	−0.079	−0.33	−0.16	1	
GEM	0.23	0.38	−0.050	−0.13	−0.14	0.11	−0.008	−0.44	1

[a] Correlation is significant at the 0.05 level (2-tailed).
[b] Correlation is significant at the 0.01 level (2-tailed).

Table 2
Concentrations of Hg^T and MeHg in surface water and soil collected from Hg mining areas worldwide.

Location	Unfiltered water		Filtered water		Soil		Reference
	Hg^T/ng l^{-1}	$MeHg^T$/ng l^{-1}	Hg^D/ng l^{-1}	$MeHg^D$/ng l^{-1}	Hg^T/mg kg^{-1}	MeHg/µg kg^{-1}	
Yanwuping Hg mine, China	3.8–51	0.20–2.7	0.85–27	0.038–0.38	0.24–240	0.34–7.3	This study
Xunyang Hg mine, China	6.2–23,500	0.022–3.7	0.21–3500	0.015–0.52	1.3–750	1.2–11	Zhang et al. (2009), Qiu et al. (2012a)
Wanshan Hg mine, China	3.3–10,580	0.012–25	1.1–655	< 0.005–6.0	0.10–790	0.10–23	Horvat et al. (2003), Qiu et al. (2005, 2009), Zhang et al. (2010a, 2010b), Søvik et al. (2011), Lin et al. (2010, 2011)
Almadén Hg mine, Spain	< DL–20,300	0.04–30	2.5–136		3.4–8889		Higueras et al. (2003), Berzas Nevado et al. (2003, 2009), Gray et al. (2004), Millán et al. (2006), Bueno et al. (2009)
Idrija Hg mine, Slovenia	0.20–708	0.01–0.6	0.03–134	0.10–0.27	0.18–2759	0.32–80	Hines et al. (2000), Gnamuš et al. (2000), Horvat et al. (2002), Gosar et al. (2006), Kocman et al. (2004, 2011)
Palawan Hg mine, Philippines	1.0–31,000	< 0.02–3.1	8.0–30,000		0.012–566		Gray et al. (2003), Maramba et al. (2006)
Hg mines, California, USA	0.65–45,000	0.017–47	0.2–140	0.017–1.2	0.6–1500		Ganguli et al. (2000), Rytuba (2000), Domagalski (2001), Thomas et al. (2002), Nacht et al. (2004), Suchanek et al. (2009)
Hg mines, Alaska, USA	0.1–2500	0.01–1.2	1.3–50		0.03–5326	0.02–41	Gray et al. (2000), Bailey et al. (2002)

Data for both Hg^T and MeHg in waters in this study were lower compared to the results of waters from other Hg mining areas (Table 2). Stream waters impacted by the calcines in Coast Range Hg mines, California, and in Palawan Quicksilver Hg mine, Philippines, exhibited as much as 45,000 and 31,000 ng l^{-1} in Hg^T, respectively (Rytuba, 2000; Gray et al., 2003). MeHg concentrations as high as 47 ng l^{-1}, 30 ng l^{-1}, and 25 ng l^{-1} in stream waters collected from California, Almadén, and Wanshan, respectively, were observed (Rytuba, 2000; Gray et al., 2004; Qiu et al., 2005). Results both from the present study and from other investigations worldwide prove that the creek waters impacted by drainages of calcines usually contain high concentrations of Hg.

3.3. Soil

Concentrations of Hg^T in soil samples varied widely from 0.24 to 240 mg kg^{-1}. Most of samples at sites adjacent to the upstream tailings contained levels higher than 10 mg kg^{-1}. The highest concentration of Hg^T was observed at site Y51 adjacent to the tailings' dam. Elevated concentrations of Hg^T were also found nearby sites, such as Y49, Y50, Y52, and Y53. The high concentrations of Hg^T demonstrated heavy impacts of those untreated tailings (Fig. 3). Because all sampling sites investigated in the present study are paddy soil and located on flood plains along the Wongman River and its tributaries, high concentrations of Hg^T found in surface soil collected along the Wongman River might result from the runoff contaminated with Hg during flooded seasons and air depositions.

The concentration of Hg^T found in all soil was higher than the limit of 0.20 mg kg^{-1} concentration for Hg^T in agricultural soils (type II at pH ≤ 5.5) set by the Chinese national standard. Compared with the probable effect concentration (PEC) of 1.06 mg kg^{-1} for Hg^T (MacDonald et al., 2000), appropriately 85% of all paddy soil samples exceeded the PEC, which indicates possible harmful effects to dwelling organisms.

Concentrations of MeHg in the samples were also elevated, ranging from 0.34 to 7.3 µg kg^{-1}. Similar to Hg^T data, most of elevated concentrations of MeHg were observed at sites proximal to the upstream tailings, such as samples of Y47, Y49, Y52, Y53, and Y55, which contained MeHg concentrations of 5.5 µg kg^{-1}, 5.3 µg kg^{-1}, 7.3 µg kg^{-1}, 6.1 µg kg^{-1}, and 4.4 µg kg^{-1}, respectively.

Table 3
Correlations among rice Hg^T (Hg$_R^T$), rice MeHg (MeHg$_R$), soil Hg^T (Hg$_S^T$), soil MeHg (MeHg$_S$), and other parameters in soil collected from the Yanwuping Hg mining district, Guizhou, China.

	Hg$_S^T$	MeHg$_S$	Hg$_R^T$	MeHg$_R$	SOM	HA	pH	GEM
Hg$_S^T$	1							
MeHg$_S$	0.55[b]	1						
Hg$_R^T$	0.49[a]	0.86[b]	1					
MeHg$_R$	0.23	0.66[b]	0.74[b]	1				
SOM	0.39	0.60[b]	0.48[a]	0.24	1			
HA	0.32	0.65[b]	0.61[b]	0.20	0.68[b]	1		
pH	0.56[b]	0.29	0.23	−0.038	0.22	0.18	1	
GEM	−0.052	−0.15	0.027	−0.098	−0.084	−0.16	0.29	1

[a] Correlation is significant at the 0.05 level (2-tailed).
[b] Correlation is significant at the 0.01 level (2-tailed).

Those elevated MeHg concentrations in soil indicated that calcines are also a potential source of MeHg (Fig. 3). Compared to Hg^T data, levels of MeHg in soil is lower, but of more concern because it is readily bio-available (cf. Section 3.4). The potential MeHg source of the calcines should be paid more attention and the runoff and drainages must be properly treated.

Soil pH was positively correlated with Hg^T concentrations (Table 3). High concentrations of pH lead to Hg^T increases in soil prove that the calcine is an important source, which was also expected since it contains quantities of water soluble alkaline compounds (Zhang et al., 2004). In addition, both the SOM and HA were significantly positively correlated with MeHg. Previous studies reported that the increasing levels of organic carbon have been attributed to a stimulating effect of organic nutrients on microbial methylation activities (Ullrich et al., 2001), and as a result increasing in MeHg production, which is in agreement with our results.

Concentrations of Hg^T were highly elevated and variable in soil samples collected from other Hg mines, such as Almadén, Spain, Alaska, USA, and Wanshan, China (Table 2). At Almadén and in Alaska, Hg^T in soil samples could reach as much as 8889 mg kg^{-1} (Higueras et al., 2003) and 5300 mg kg^{-1} (Bailey et al., 2002), respectively. Similarly, MeHg in soil samples varied widely from 0.04 to 41 µg kg^{-1} (Bailey et al., 2002) at Hg mines in Alaska, and from 1.3 to 78 µg kg^{-1} at the Idrija mine in Slovenia (Gnamuš et al., 2000), respectively. Though the soils collected from the YMM district have slightly lower concentrations of Hg^T and MeHg compared to other Hg mines worldwide, they are still seriously contaminated with Hg^T and MeHg.

3.4. Rice

Concentrations of Hg^T in rice samples ranged from 10 to 45 µg kg^{-1}. The average concentration of 22 ± 9.5 µg kg^{-1} slightly exceeded the Chinese national permitted limit of 20 µg kg^{-1} in foods (NSA, 1994). Compared to data for the samples from other abandoned Hg mines (Qiu et al., 2008; Feng et al., 2008; Meng et al., 2010), the concentrations of Hg^T in rice of the YMM district were lower. Unlikely, MeHg concentrations in samples were high, ranging from 3.2 to 39 µg kg^{-1} with an average of 11 ± 7.6 µg kg^{-1}. Previous studies indicated that the inorganic Hg (Hg^{Ino}), defined as the difference between the Hg^T and MeHg in plants (Lin et al., 2008), largely depends on levels of atmospheric Hg and above-ground parts accumulate Hg from the air (Fay and Gustin, 2007; Meng et al., 2011). This might suggest that the major source for Hg^{Ino} in plants is the ambient air Hg. Slightly lower Hg^T in the rice of the YMM probably attribute to lower GEM concentrations compared to those observed at active Hg mines (Meng et al., 2010; Qiu et al., 2012b).

Daily intake (DI) of Hg^{Ino} and MeHg for adults' consuming rice was calculated. It was assumed that routine consumption of rice
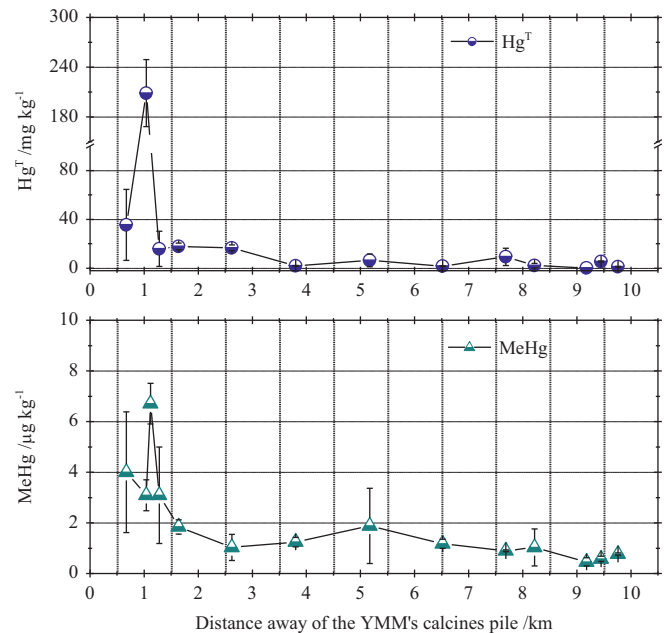

Fig. 3. The distribution of Hg^T and MeHg concentrations in paddy soil collected from the Yanwuping Hg mining district, Guizhou, China (Vertical bar means average ± s.d.).

was 400 g per day and body weight was 60 kg per person. The estimated DI varied widely between 0.013 and 0.17 µg kg^{-1} (average: 0.072 µg kg^{-1}) for Hg^{Ino} and between 0.021 and 0.26 µg kg^{-1} (average: 0.076 µg kg^{-1}) for MeHg. This wide range reflects the large range in rice concentrations of Hg observed in this study. The DI of 0.26 µg kg^{-1} for MeHg may indicate that consumption of rice is an effective way of entry of MeHg, which represents a threat to human health. This value is slightly higher than the new dietary reference dose (RfD) of 0.23 µg kg^{-1} body weight per day for MeHg recommended by the UN Committee (WHO, 2003), but much higher than the RfD of 0.1 µg kg^{-1} body weight per day for MeHg exposure recommended by the USEPA (1997).

Comparison of MeHg concentrations in rice with other Hg mines as well as the control site exhibited that high MeHg concentrations were observed in both the active Hg mining districts and abandoned Hg mining districts (Fig. 4). MeHg concentrations in samples in the YMM district were about 4 folds higher than 2.9 µg kg^{-1} concentration for MeHg observed at a control site (Meng et al., 2010). A significantly positive correlation between rice MeHg and soil MeHg (r=0.66, $p < 0.01$) was observed (Table 3), suggesting the rice MeHg is associated with soil MeHg (Meng et al., 2010, 2011; Qiu et al., 2012b). Generally, activities of Hg mining result in elevated atmospheric Hg concentrations and as a result increasing Hg deposition. Those newly deposited Hg were proven to be much more easily bioaccumulated in soil and be responsible for the elevation of MeHg in rice (Meng et al., 2011).

4. Implications for risk assessment

Exposure to MeHg is of great concern due to its potential impact to organisms' neurodevelopment. Results from this environmental study exhibit a relatively low percentage of MeHg in water and soil; however, it represents a relatively high concentration in rice grains. This result indicates that there is an uptake of MeHg from soil by rice and subsequent translocation of MeHg to grains. Estimated potential risks for human exposure on MeHg suggests pathway of dietary rice intaking. The pool of MeHg must not be overlooked since rice is a staple food for local habitants.
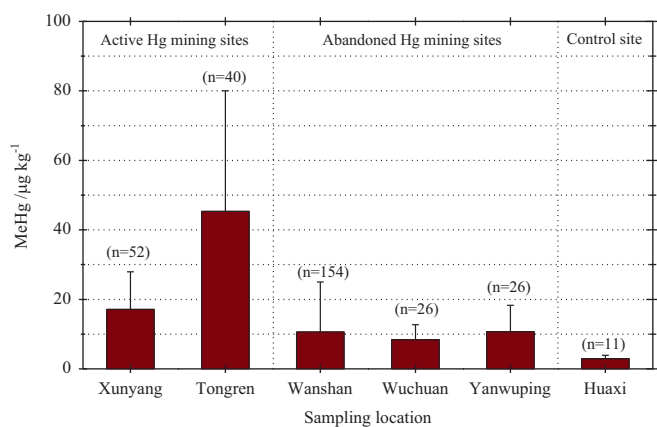
Fig. 4. Plots of MeHg concentrations in the rice seed collected from active and abandoned Hg mining districts in China (Horvat et al., 2003; Qiu et al., 2006, 2008; Zhang et al., 2010c; Meng et al., 2011; Li et al., 2008a, 2009; this study; vertical bar means average ± s.d.).

Despite the quality criteria for Hg^T in foodstuff as proposed by the Chinese national standard (1994) and which is 20 μg kg^{-1} for Hg^T in cereals, currently no limits for MeHg are available for comparison. Since rice is of poor nutritional quality and lacks specific micronutrients identified as having health benefits, such as n-3 long chain polyunsaturated fatty acid, essential amino acids, and selenium comparing to fish (Li et al., 2010), it should be given more emphasis on assessing the health effects of low level MeHg exposure in the rice-consumption population. Also, limits of MeHg in rice should be set in the future.

Previous studies indicated that Hg^{Ino} and MeHg have different uptake and accumulation mechanisms in rice (Zhang et al., 2010d; Meng et al., 2010, 2012) and atmospheric Hg deposition is known to be playing an important role of MeHg accumulation (Meng et al., 2011). It is necessary to further understand the methylation of newly deposited Hg as well as its potential affecting factors in paddies. There is still however little information about the transformation of newly deposited Hg to MeHg as well as on subsequent translocation of MeHg to rice, although rice roots can to a certain extent transport MeHg to above ground plant parts.

5. Conclusions

Our study revealed a significant contamination of Hg^T in soil and MeHg in rice in the Yanwuping Hg mining district. High concentrations of Hg^T in soil form sites adjacent to the upstream calcines pile and tailings' dam were expected. Those soil samples also exhibited elevated MeHg concentrations. Though concentrations of Hg^{Ino} in rice were lower compared to those from other Hg mines of China, significantly high concentrations of MeHg were found, and MeHg concentrations in rice were positively correlated with soil MeHg. Correlations indicated that soil MeHg is the major source of MeHg in rice. The surface water in the study region contains low concentrations of Hg, but a peak concentration of Hg^T was observed at site proximal to the calcines pile, suggesting those untreated mine-wastes is a dominant Hg source to the nearby surroundings. GEM concentrations in ambient air exhibited a local spatial pattern, indicating a huge Hg^0 emission from the calcines as well as unknown active anthropogenic Hg emission. The upstream calcines and tailings must be appropriately disposed of and runoff should be properly treated and not be used as irrigating water. In the future, limits for MeHg in rice grains for human consumption should be set for food safety.

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