ORIGINAL ARTICLE



# The influence of atmospheric Hg on Hg contaminations in rice and paddy soil in the Xunyang Hg mining district, China

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Abstract To date, the Xunyang mercury (Hg) mining district is the only ongoing large-scale Hg mining district in China. To understand the influence of Hg contamination mode from the Hg mining and smelting activities, 27 sampling sites in the Xunyang Hg mining district were chosen in this study. Total gaseous mercury (TGM) in ambient air was measured using a Lumex-RA915 automatic Hg analyzer in 2011. Rice samples and soil samples from rhizosphere were collected systematically and simultaneously. Total Hg (THg) and methylmercury (MeHg) concentrations in rice grain and soil samples and Hg speciation with modified sequential selective extractions were measured. The local environment was seriously polluted with Hg. The TGM  $(302 \pm 376 \text{ ng} \cdot \text{m}^{-3})$ , ranging from 24 to 2220  $\text{ng} \cdot \text{m}^{-3}$ ) in the local ambient air, THg (28  $\pm$  30 mg·kg<sup>-1</sup>, ranging from 0.31 to 121 mg·kg<sup>-1</sup>) and MeHg (2.3  $\pm$  1.9  $\mu$ g·kg<sup>-1</sup>, ranging from 0.24 to 8.9  $\mu g \cdot kg^{-1}$ ) in soil samples were at the sample level with Hg contaminated area. The THg concentration (26  $\pm$  16  $\mu$ g·kg<sup>-1</sup> ranging from 4.5 to 71  $\mu$ g·kg<sup>-1</sup>) in most of the rice grain samples clearly exceeds the threshold level (20  $\mu$ g·kg<sup>-1</sup>) in the Chinese national guidelines for cereals (NY 861-2004). The inorganic mercury (IHg)  $(9.1 \pm 5.6 \ \mu g \cdot kg^{-1})$ , ranging from 1.2 to 24  $\ \mu g \cdot kg^{-1}$ ) and MeHg (14  $\pm$  9.8 µg·kg<sup>-1</sup>, ranging from 2.1 to 59 µg·kg<sup>-1</sup>) concentration in rice grain samples were at the same level

with Hg contaminated area. The main species of Hg in paddy soils reveal strong complex Hg and residue Hg. According to the correlation analysis, a Hg pollution mode from local Hg mining and smelting was hypothesized, including Hg emission, transportation, methylation, and uptake process.

**Keywords** Xunyang · Total gaseous mercury · Mercury speciation · Methylmercury · Rice

# **1** Introduction

Mercury (Hg) is a toxic element. The total gaseous mercury (TGM) is a global pollutant capable of long-range transport in the atmosphere, and the residence time of TGM in the atmosphere is about 0.5–2 years (Lindqvist et al. 1991; Schroeder and Munthe 1998). TGM in the air can be deposited into the terrestrial and aquatic ecosystems through dry and wet deposition (Lucotte et al. 1995; Swain et al. 1992). According to the global atmospheric Hg cycle model, about 50% of anthropogenic emissions of Hg are involved in atmospheric circulation while the remaining part quickly deposits around the emission sources (Bullock et al. 1998).

Methylmercury (MeHg) can bioaccumulate and biomagnify in the food chain with a bioaccumulation factor as high as  $10^4$  to  $10^7$  in top-trophic-level predatory fish (Stein et al. 1996). Rice is one of the main food staples of Asian residents. MeHg in rice grain grown in the Wanshan Hg mining area can reach upwards of 174 µg·kg<sup>-1</sup> (Qiu et al. 2008). Consumption of rice has become the most important pathway of MeHg exposure for people in inland China (Li et al. 2008; Meng et al. 2011; Zhang et al. 2010).

The transportation and transformation mechanism of Hg in terrestrial ecosystems is quite complex. In particular,

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there are few reports about the effect of newly deposited Hg on Hg speciation in soil and its influence on plants. Therefore, it is important to examine the Hg speciation in soil and understand its influence on Hg in rice, and this study undertakes this important task.

As the only active Hg mining and smelting district, the Xunyang Hg mining district in Shaanxi Province, China, was selected to study the Hg contamination in air, soil and rice. The primary objectives of this study were to elucidate the Hg contamination status in the air, paddy soil and rice and to address the Hg contamination process that Hg smelting activities have on soil and rice.

## 2 Material and method

# 2.1 Study areas

The Xunyang Hg mining district (N:33°01'-33°05', E:109°24'-109°39') is located in Southeast Shaanxi Province, covering approximately 1000 km<sup>2</sup>. The study area is characterized as a northern, sub-tropical humid climate with an average yearly rainfall of 851 mm. The annual average temperature is 15.4 °C, and the altitude is between 185 and 2358 m. The historical Hg mining activities in Xunyang can be dated back to the Spring Autumn period and the Warring States period (770-221 B.C.). The total reserves of Hg deposits in the Xunyang Hg mine have reached 14000 t of Hg. Presently, there are four Hg ores and two Hg smelting factories in Xunyang. The mining activities in the Wanshan, Wuchuan Hg mine in Guizhou were ceased in the 2000s, leaving Xunyang as the only active, large-scale Hg-producing mine in China. In the process of mining and smelting Hg ore, large quantities of waste rocks were piled along the banks of the Zhutong River without any control. Wastewater and waste gas is discharged into the surrounding environment without any treatment, causing severe Hg pollution in the surrounding atmosphere, river, and soil.

## 2.2 Sample collection

The soil and rice samples were collected along the Zhutong River in the Hg mine area in October 2011. In total, 27 sampling sites were selected to collect soil and rice samples. The sampling sites are shown in Fig. 1. Each rice sample was comprised of at least five sub-samples of the rice plants within an area of about 5–10 m<sup>2</sup> in the same paddy field. Soil samples were also collected at the same site as the rice samples. Each sample collected was about 0.5 kg of rhizosphere soil. All samples were stored in polyethylene bags to avoid cross-contamination. The rice samples were first cleaned using drinking water on site and

then using double deionized water in laboratory, and finally, they were freeze-dried. Then the processed and polished rice was separated using a pestle and mortar, and it grounded to 200 meshes per inch. The soil samples were sealed and double-bagged, then kept in a -18 °C refrigerator in the laboratory. Subsequently, the freeze-dried soil samples were homogenized to a size of 200 meshes per inch with a mortar before chemical analysis.

The corresponding TGM concentrations in ambient air to the rice and soil samples were also measured. The concentrations of TGM in ambient air were measured using the Lumex RA-915+ Portable Mercury Vapor Analyzer (Lumex Ltd., Russia). This instrument is based on the Zeeman cold vapor atomic absorption spectrometry technique with a detection limit for Hg in ambient air of  $0.5 \text{ ng} \cdot \text{m}^{-3}$  at a rate of  $10 \text{ L} \cdot \text{min}^{-1}$ . Average TGM concentrations during a 20 s interval were retrieved and stored in a portable computer, and measurements at each sampling site were continuously carried out for at least 20 min.

# 2.3 Analytical methods

#### 2.3.1 THg

Soil: Approximately 0.1–0.2 g of dry sample was digested with freshly prepared aqua regia HCl/HNO<sub>3</sub> (v/v, 3:1) in a water bath (95 °C) for 0.5 h. An aliquot of digested sample solution and 0.4 mL 20% SnCl<sub>2</sub>·2H<sub>2</sub>O was added into the bubbler, then determined by a F732-V, and the detection limit for THg in sample is 0.05  $\mu$ g·L<sup>-1</sup>.

Rice: Approximately 0.2-0.3 g of dry sample was digested using HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (v/v, 4:1) in a water bath (95 °C) for 3 h. BrCl was added into the digested solution 24 h before determination. An appropriate aliquot was added into the bubbler for SnCl<sub>2</sub> reduction, purging and gold-trap collection. Finally, Hg onto gold-trap was measured by cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500, Canada) (US EPA 2001b).

## 2.3.2 MeHg

Soil: For MeHg analysis, approximately 0.2–0.3 g of a dry soil sample was leached with 2 mol·L<sup>-1</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O and 25%HNO<sub>3</sub>. Then, MeHg in samples was extracted with CH<sub>2</sub>Cl<sub>2</sub> as well as back-extracted from the solvent phase into water and aqueous phase ethylation. MeHg was separated from the digested solution by purging with N<sub>2</sub> onto a Tenax trap. Then, a suitable aliquot of digested sample solution was determined by GC-CVAFS (Liang et al. 2004).

Rice: About 0.2–0.5 g of dry sample was digested using 25% KOH–methanol in a water bath (75–80 °C) for 3 h. Then, MeHg in the samples was extracted with  $CH_2Cl_2$  as



Fig. 1 The study area and location of the sampling sites

well as back-extracted from the solvent phase into water. MeHg was separated from digestive solution by purging with  $N_2$  onto a Tenax trap. An aliquot of digested sample solution was then determined by GC-CVAFS (Liang et al. 1996; US EPA 2001a).

In this study, the concentration of inorganic Hg (IHg) in rice was calculated by the difference between the concentration of THg and MeHg in rice. The calculation formula is:

IHg = THg - MeHg

#### 2.3.3 Sequential extraction of Hg speciation in soil

The sequential extraction procedure of Hg speciation in soil followed the method developed by Bloom et al. (2003), with some modifications.

(1) Water soluble Hg (F1): Approximately 1.0 g of a soil sample was weighed. Then, 40 mL of reagentgrade double deionized water was added. After shaking for 24 h, the sample was centrifuged, and the supernatant was collected for analysis.

- (2) 'Human stomach acid' soluble Hg (F2): The residue of F1 was digested with 40 mL of 0.1 M CH<sub>3</sub>COOH+ 0.01 M HCl. After shaking for 24 h, the sample was centrifuged, and the supernatant was collected for analysis.
- (3) Organo-chelated Hg (F3): The residue of F2 was digested using 40 mL 1 M KOH and was shaken for 24 h to homogenize. After shaking for 24 h, the sample was centrifuged, and the supernatant was collected for analysis.
- (4) Strong complex Hg (F4): The residue of F3 was digested with 40 mL 12 M HNO<sub>3</sub> and was shaken for 24 h. After shaking for 24 h, the sample was centrifuged, and the supernatant was collected for analysis.
- (5) Residue Hg (F5): Residue Hg was calculated as the difference of THg and the sum of F1, F2, F3 and F4. The calculation formula is:

$$F_5 = THg - F_1 - F_2 - F_3 - F_4$$

The different forms of Hg in soil were determined by SnCl<sub>2</sub> reduction and BrCl oxidation followed by CVAFS detection (US EPA 2001b).

Soil pH was measured following the addition of 10 g of the sample to 25 mL of double distilled water (China agriculture industry standard 2007).

# 2.4 Quality control

Quality control of THg and MeHg determination in samples was performed using duplicates, method blanks, matrix spikes and certified reference materials (BCR 580; GBW 10020; TORT-3). The method detection limits were 10  $ng \cdot kg^{-1}$  for THg and 2  $ng \cdot kg^{-1}$  for MeHg in rice and soil samples. Analytical accuracy for THg and MeHg in soil was estimated from an analysis of the sediment quality standard of BCR 580, with obtained values of  $133 \pm 3.0 \text{ mg} \cdot \text{kg}^{-1}$  and  $75.2 \pm 2.9 \text{ } \mu\text{g} \cdot \text{kg}^{-1}$  respectively, which are comparable with the certified values of  $132 \pm 3.0 \text{ mg} \cdot \text{kg}^{-1}$  and  $75.5 \pm 4.0 \text{ }\mu\text{g} \cdot \text{kg}^{-1}$  respectively. Analytical accuracy for THg in rice was estimated from an analysis of the plant standard substance of GBW10020, with obtained values of 148  $\pm$  3.0  $\mu g \cdot k g^{-1}$  and a certified value of  $150 \pm 20 \ \mu g \cdot kg^{-1}$  used as reference. MeHg concentrations measured in rice were estimated from analyses of the biological standards of TORT-3, with obtained values of  $136 \pm 4.0 \ \mu g \cdot kg^{-1}$ , whose reference value is  $137 \pm 12 \ \mu g \cdot k g^{-1}$ .

# **3** Results

# 3.1 Atmosphere

The concentration of TGM in the Xunyang Hg mining district was  $302 \pm 376 \text{ ng} \cdot \text{m}^{-3}$  (ranging from 24 to 2220 ng·m<sup>-3</sup>) (Table 1). High values of TGM were found near the smelting plant (Fig. 2). TGM concentrations in the sampling sites far from the smelter and the Hg mine decreased rapidly with the increase in distance but still remained higher than those in background areas (Fu et al. 2008; Wan et al. 2009), suggesting the TGM in the ambient air mainly came from the smelting plant.

The TGM concentrations in Wanshan and the Wuchuan Hg mining area were reported as 12-1652 and  $10-40,000 \text{ ng} \cdot \text{m}^{-3}$ , respectively (Li et al. 2012; Wang et al. 2007). The TGM concentrations in Xunyang Hg mining area were higher than that of Wanshan, but slightly lower than that of Wuchuan, indicating that the ambient air in Xunyang Hg mining area is suffering from serious Hg contamination. Compared to the TGM observed at remote sites in China, the TGM concentrations in the Xunyang Hg mining district are 75 times that of Gongga Mountain (Fu et al. 2008), which is far beyond the remote mountainous areas unaffected by Hg pollution. The high TGM contamination indicates that the emitted waste gas and

discharged waste residue of Hg mining and smelting resulted in serious Hg pollution.

## **3.2 Rice**

IHg and MeHg concentrations in the rice were  $9.1 \pm 5.6 \ \mu g \cdot kg^{-1}$  (ranging from 1.2 to  $24 \ \mu g \cdot kg^{-1}$ ) and  $14 \pm 9.8 \ \mu g \cdot kg^{-1}$  (ranging from 2.1 to  $59 \ \mu g \cdot kg^{-1}$ ), respectively (Table 1). THg concentrations in the rice (mean:  $26 \pm 16 \ \mu g \cdot kg^{-1}$  with a range of  $4.5-71 \ \mu g \cdot kg^{-1}$ ) clearly exceeded the threshold level ( $20 \ \mu g \cdot kg^{-1}$ ) in the Chinese national guidelines for cereals (China agriculture industry standard 2004). The MeHg constituted a large proportion of the THg in the rice grain, with an average of  $58\% \pm 18\%$  (ranging from 14% to 95%). The highest MeHg level in rice was in XY-01, with the average value as high as  $41 \ \mu g \ kg^{-1}$ . The highest IHg concentration was present in XY-12, with average values of  $24 \ \mu g \cdot kg^{-1}$ . The THg and MeHg in rice of this study were similar to the result of Qiu et al. (2012).

The THg and MeHg in rice from polluted and unpolluted areas are listed in Table 2. The THg and MeHg in rice in Xunyang were significantly higher than that in areas without Hg contamination (Cheng et al. 2013; Meng et al. 2010; Rolfhus et al. 2003; Rothenberg et al. 2011; Silva et al. 2012). The THg and MeHg in rice were basically the same level as in other Hg polluted areas (Appleton et al. 2006; Cheng et al. 2013; Li et al. 2008; Morishita et al. 1982; Windham-Myers et al. 2014), but lower than some of most extremely Hg polluted areas (Krisnayanti et al. 2012; Lenka et al. 1992; Pataranawat et al. 2007; Qiu et al. 2008). This suggests that the rice in the Xunyang Hg mining area has suffered serious Hg and MeHg contamination. The variation of Hg can related to the source of Hg, the existence of Hg species, and the physical and chemical properties of soil.

#### 3.3 Soil

The mean THg and MeHg concentrations in soil were  $28 \pm 30 \text{ mg} \cdot \text{kg}^{-1}$  (ranging from 0.31 to 121 mg \cdot \text{kg}^{-1}) and  $2.3 \pm 1.9 \ \mu\text{g} \cdot \text{kg}^{-1}$  (ranging from 0.24 to 8.9  $\ \mu\text{g} \cdot \text{kg}^{-1}$ ), respectively (Table 1). The THg and MeHg concentrations in soils far from the smelter and the Hg mine decreased rapidly with the increase in distance (Fig. 3). The average concentration of THg in paddy soil is far beyond the THg threshold level (0.50 mg \cdot \text{kg}^{-1}, \text{pH} = 6.5-7.5) for agricultural paddy soil (2nd level) and the environment quality guidelines (National Standard of China 1995), showing that the paddy soil of Xunyang Hg mining area has been seriously polluted by Hg (Table 3).

It was reported that THg concentrations in soils in the Xunyang Hg mining area ranged from 1.3 to 750 mg·kg<sup>-1</sup> (Zhang et al. 2009) while Qiu et al. (2012) reported

Table 1	TGM in ambient	air and Hg in s	soil and rice sar	nples								
Site	TGM	Rice		Soil								
	ng·m <sup>-3</sup>	IHg (μg·kg <sup>-1</sup> )	MeHg (µg·kg <sup>-1</sup> )	THg (mg·kg <sup>-1</sup> )	MeHg (µg·kg <sup>-1</sup> )	$\frac{F1}{(\mu g \cdot k g^{-1})}$	$\begin{array}{c} F2 \\ (\mu g \cdot k g^{-1}) \end{array}$	F3 (mg·kg <sup>-1</sup> )	F4 (mg·kg <sup>-1</sup> )	F5 (mg·kg <sup>-1</sup> )	TOC %	Hq
XY-01	1157 ± 99	$12 \pm 2.1$	$41 \pm 12$	$99 \pm 16$	$6.2 \pm 0.82$	418	148	1.2	44	54	0.95	7.1
XY-02	$1810\pm312$	$20 \pm 3.6$	$14 \pm 3.6$	$118\pm5.9$	$6.8\pm1.5$	309	118	1.6	49	66	1.2	7.6
XY-03	$373 \pm 14$	$9.1\pm1.1$	$28\pm0.51$	$15\pm0.89$	$1.2 \pm 0.14$	181	116	3.1	5.5	11	0.88	4.8
XY-04	$251 \pm 44$	$12 \pm 2.5$	$19 \pm 0.52$	$16\pm0.25$	$5.7\pm0.95$	114	218	1.8	14	0.93	1.0	5.9
XY-05	$277 \pm 19$	$11 \pm 2.6$	$12 \pm 0.19$	$29 \pm 0.76$	$3.6\pm0.05$	55	95	2.2	5.9	16	1.1	8.1
30-YX	$349 \pm 15$	$9.3\pm1.6$	$22 \pm 1.1$	$7.1\pm0.56$	$5.4 \pm 0.94$	104	117	1.2	0.4	ς.	0.48	7.5
70-YX	$228 \pm 42$	$1.2 \pm 0.18$	$25 \pm 1.4$	$9.1\pm0.54$	$1.7\pm0.2$	57	118	1.9	0.21	6.7	0.82	5.5
XY-08	$136 \pm 2.0$	$9.6\pm1.6$	$8.7\pm0.04$	$39 \pm 2.6$	$3.6\pm1.4$	230	354	3.2	7.9	42	1.2	7.2
60-YX	$313 \pm 15$	$14 \pm 3.9$	$29 \pm 4.8$	$25 \pm 0.42$	$2.2 \pm 0.43$	99	140	1.9	1.6	6.7	0.75	7.2
XY-10	$133 \pm 9.1$	$7.0 \pm 2.2$	$13 \pm 0.69$	$20 \pm 0.17$	$1.9\pm0.74$	44	74	1.7	0.88	13	0.57	6.3
XY-11	$859 \pm 43$	$13 \pm 2.5$	$35 \pm 4.3$	$41 \pm 10$	$1.5\pm0.18$	96	97	2	4.9	34	0.62	7.9
XY-12	$240 \pm 14$	$24 \pm 3.7$	$14 \pm 0.02$	$43\pm4.3$	$1.8\pm0.08$	134	341	0.85	8.2	34	0.56	8.0
XY-13	$151 \pm 11$	$8.6 \pm 2.0$	$5.1 \pm 0.49$	$36 \pm 4.5$	$1.0 \pm 0.09$	125	163	1.3	7.8	27	0.92	7.9
XY-14	$319 \pm 53$	$10 \pm 3.9$	$14 \pm 2.9$	$4.1\pm0.69$	$2.3\pm0.13$	54	17	0.64	0.35	3.3	0.98	7.8
XY-15	$268\pm18$	$6.3\pm1.6$	$5.0\pm0.36$	$88 \pm 2.4$	$1.4\pm0.38$	181	214	1.4	5.3	81	1.3	T.T
XY-16	$226\pm 6.2$	$8.4\pm0.94$	$4.6\pm0.47$	$36 \pm 0.86$	$1.1 \pm 0.17$	101	240	1.3	6.1	28	0.72	T.T
XY-17	$130 \pm 3.2$	$4.4\pm1.4$	$9.1\pm0.97$	$54 \pm 11$	$1.3 \pm 0.21$	120	2476	0.84	10	40	0.77	8.0
XY-18	$48\pm3.6$	$4.7 \pm 0.98$	$7.9\pm0.89$	$17 \pm 0.68$	$1.2 \pm 0.19$	63	443	1.8	3.4	11	1	7.8
XY-19	$102 \pm 5.6$	$8.7\pm1.8$	$8.2\pm0.59$	$2.6\pm0.60$	$2.9 \pm 0.80$	15	113	0.54	0.4	1.9	0.89	5.7
XY-20	$75 \pm 2.4$	$6.9\pm1.8$	$8.4 \pm 2.7$	$5.4 \pm 2.3$	$0.52\pm0.07$	22	36	0.69	0.39	4.3	0.99	5.7
XY-21	$146\pm8.4$	$4.3\pm0.34$	$5.9\pm0.19$	$6.8 \pm 3.9$	$0.94\pm0.14$	20	42	1.3	0.81	4.6	1.0	T.T
XY-22	$116 \pm 3.0$	$7.8\pm0.69$	$15 \pm 0.24$	$1.0 \pm 0.11$	$1.6\pm0.50$	14	18	0.37	0.5	0.09	0.68	8.0
XY-23	$65 \pm 2.5$	$4.9\pm1.0$	$5.0 \pm 0.73$	$3.0\pm0.37$	$1.1 \pm 0.03$	14	12	0.13	0.06	2.8	0.95	7.8
XY-24	$82 \pm 2.6$	$20 \pm 2.4$	$3.3\pm0.36$	$19 \pm 0.41$	$1.3 \pm 0.28$	64	179	0.76	1.5	6.8	0.66	8.0
XY-25	$57 \pm 2.7$	$3.1 \pm 0.53$	$3.7\pm0.38$	$11 \pm 0.14$	$0.47\pm0.13$	19	76	0.44	0.87	7.1	0.79	7.9
XY-26	$55 \pm 2.4$	$3.4 \pm 1.2$	$11 \pm 1.3$	$2.3\pm0.63$	$0.44\pm0.11$	23	14	0.27	0.22	1.7	0.49	8.0
XY-27	$45 \pm 2.1$	$1.4\pm0.54$	$9.4\pm1.3$	$0.71\pm0.19$	$0.46\pm0.07$	14	12	0.1	0.02	0.57	0.61	7.0
Mean	$302 \pm 376$	$9.1 \pm 5.6$	$14 \pm 9.8$	$28 \pm 30$	$2.3 \pm 1.9$	98	222	1.3	6.7	19	0.85	7.3
Range	24–2220	1.2–24	2.1–59	0.31-121	0.24-8.9	14-418	12–2476	0.10 - 3.2	0.02-49	0.09 - 81	0.49 - 1.3	4.8-8.1
F1: water	soluble Hg, F2:	'human stomac	h acid' soluble	Hg, F3: organo-c	helated Hg, F4:	strong complex	x Hg, F5: resid	lue Hg				



Fig. 2 The distribution of TGM in ambient air and MeHg and IHg in rice versus the distance from the Hg smelting

5.4–120 mg·kg<sup>-1</sup> for THg concentrations and 1.2–11  $\mu$ g·kg<sup>-1</sup> for MeHg concentrations. The characteristics of the soils and sample site locations may have contributed to these different results. The sampling sites of Zhang et al. (2009) were dry land located around the Qingtonggou Hg mine while the sampling sites of Qiu et al. (2012) were paddy soils located along the banks of river. The dry land soil mixed with large amounts of waste rock with high Hg concentration, while the paddy soil was relatively far from the Hg mine, so the Hg mainly comes from the dry and wet deposition and irrigation water.



Fig. 3 The distribution of THg and MeHg in paddy soil versus the distance from the Hg smelting activity

Compared to the THg and MeHg results in Hg mining area, such as Wanshan (THg:  $5.1-790 \text{ mg}\cdot\text{kg}^{-1}$ , MeHg:  $0.13-15 \text{ µg}\cdot\text{kg}^{-1}$ ), Wuchuan (THg:  $0.33-320 \text{ mg}\cdot\text{kg}^{-1}$ , MeHg:  $0.69-20 \text{ µg}\cdot\text{kg}^{-1}$ ) and Lanmuchang (THg:  $0.41-610 \text{ mg}\cdot\text{kg}^{-1}$ , MeHg:  $0.41-8.8 \text{ µg}\cdot\text{kg}^{-1}$ ) (Qiu et al. 2005, 2006a, 2006b), the THg and MeHg concentration in soils of the Xunyang Hg mining area are slightly lower than these areas, but Hg contamination could be more serious with the soil from the Xunyang Hg mining district was also lower than that from the Almadén Hg mining district (THg:  $6.0-8889 \text{ mg}\cdot\text{kg}^{-1}$ ) and the Alaska Hg-mine region (THg:  $0.05-5326 \text{ mg}\cdot\text{kg}^{-1}$ ) (Bailey et al. 2002; Higueras et al. 2003).

The water soluble Hg (F1), 'Human stomach acid' soluble Hg (F2), organo-chelated Hg (F3), strong complex Hg

Table 2 Comparison of THg and MeHg in rice from other Hg contaminated sites

Sampling site	Polluted site	Polished rice grain?	Sample size	$THg (\mu g \cdot kg^{-1})$	MeHg (µg·kg <sup>-1</sup> )	Method	References
Guizhou Province, China	Hg mining	Yes	17	27 (6.0–113)	7.8 (3.8–12)	CV-AFS	Li et al. (2008)
Shannxi Province, China	Hg mining	Yes	10	103 (51-200)	22 (8.2-80)	CV-AFS	Qiu et al. (2012)
Hunan Province, China	Hg mining	No	26	29 (11-58)	11 (6.5–24)	CV-AFS	
Zhejiang Province, China	E-waste	Yes	13	22 (16-68)	NA	Hydride generation-AFS	Fu et al. (2008)
Mindanao, Philippines	Hg mining	Yes	NA	18 (8-50)	NA	Flame-AAS	Appleton et al. (2006)
Indonesia	Hg mining	No	6	NA	58 (11–115)	CV-AFS	Krisnayanti et al. (2012)
California, USA	Hg mining	No	14	50 (50-51)	4.6 (4.1–5.0)	CV-AFS	Windham-myers et al. (2014)
Kratie, Cambodia	Gold mining	Yes	6	13 (9.9–17)	1.5 (1.1–2.3)	AAS(THg), CVAFS(MeHg)	Cheng et al. (2013)
Phichit Province, Thailand	Gold mining	Yes	4	212 (172–268)	NA	CV-AFS	Pataranawat et al. (2007)
Ganjam, India	Chloralkili facility	No	6	510 (470–530)	NA	CV-AFS	Lenka et al. (1992)
Mie prefecture, Japan	Chloralkili facility	No	25	23 (3.0-60)	NA	AAS	Morishita et al. (1982)
This study	Hg mining	Yes	54	26 (4.5–71)	14 (2.1–59)	CV-AFS	

 Table 3 Correlations between Hg species of paddy soil and TGM concentrations in ambient air

TGM	F1	F2	F3	F4	F5
1					
0.71**	1				
-0.09	0.15	1			
0.28	0.49**	0.04	1		
0.89**	0.80**	0.07	0.2	1	
0.59**	0.72**	0.27	0.22	0.62**	1
	TGM 1 0.71** -0.09 0.28 0.89** 0.59**	TGM         F1           1	TGM         F1         F2           1	TGM         F1         F2         F3           1	TGM         F1         F2         F3         F4           1

\* P < 0.05; \*\* P < 0.01

(F4) and residue Hg (F5) concentrations in paddy soils were 0.098, 0.22, 1.3, 6.7 and 19 mg·kg<sup>-1</sup>, respectively, accounting for 0.21%-2.3%, 0.10%-7.2%, 1.2%-58%, 3.1%-88% and 5.5%-93% of the THg, respectively. The main species of Hg in paddy soils were residue Hg and strong complex Hg, with proportions of 68% and 20%, respectively. Compared with the previous research, the Hg species in soil in the Hg mining area were dominated by residue Hg and mercuric sulfide Hg, with the proportion of more than 95% (Bao et al. 2011). In this study, the proportion of residue Hg in the paddy soil was significantly lower than in the results that were previously reported. The strong complex Hg in the paddy soil of XY-1 and XY-2 were as high as 44 and 49 mg·kg<sup>-1</sup>, respectively. And the Hg smelting activity is close to the sampling site XY-2.

# 4 Discussion

#### 4.1 Effect of TGM on Hg in soil

Significant positive correlation was observed between TGM and THg ( $R^2 = 0.57, P < 0.01$ ) (Fig. 4a) which may suggest that the Hg in paddy soil mainly comes from Hg deposition



Fig. 4 Correlation between TGM and THg and MeHg concentrations of soil



Fig. 5 Correlation between TGM and IHg and MeHg concentrations of rice

after the Hg emission during the processes of Hg ore mining and smelting production. Additionally, a significant positive relationship was also found between TGM and MeHg  $(R^2 = 0.45, P < 0.01)$  (Fig. 4b) in soil, which may suggest that methylated Hg in the soil was significantly related with the newly deposited Hg in the soil. The research results in Lake 239 in America by enriched stable Hg isotope addition show that the MeHg was mainly formed from the newly deposited Hg and was even bioaccumulated by fish and invertebrates (Paterson et al. 2006). Further statistical analysis showed a significant positive correlation between TGM and water soluble Hg ( $R^2 = 0.71, P < 0.01$ ) and strong complex Hg ( $R^2 = 0.89, P < 0.01$ ). It demonstrated that the Hg occurrence and transformation process in soil happened after Hg deposited in paddy soil.

## 4.2 Effect of TGM on Hg in rice

There was a significant positive correlation between TGM and rice IHg ( $R^2 = 0.22$ , P < 0.01) (Fig. 5a). It shows that the uptake of IHg by rice from soil was related to TGM. The newly deposited Hg in the soil has a high bio-availability and mobility and is easily absorbed by rice through its roots (Paterson et al. 2006). Thus, the process of emission of Hg from Hg smelting process, TGM transportation and deposition, and Hg uptake by rice from soil can be hypothesized. IHg in rice had a significant positive correlation with water soluble Hg ( $R^2 = 0.45$ , P < 0.05) and strong complex Hg ( $R^2 = 0.47$ , P < 0.05) in soil. Hence, it implied that the water soluble Hg and strong complex Hg in paddy soil were more easily absorbed by rice while the 'Human stomach acid' soluble Hg and residual Hg were not as easily to be absorbed by rice.

There was a significant positive correlation between TGM and MeHg in rice ( $R^2 = 0.25$ , P < 0.01) (Fig. 5b), showing that TGM plays an essential role in Hg

biogeochemical cycles and that newly deposited Hg in soil is a potential source of Hg methylation to produce MeHg. The newly deposited Hg in the soil was found to show a high Hg methylation potential, and the new generation of MeHg was also easily absorbed by organisms (Meng et al. 2010; Orihel et al. 2008; Paterson et al. 2006).

# **5** Conclusions

Serious Hg pollution was found in the environment of the Xunyang Hg mining area, including the air, soil and rice. TGM played an essential role in the Hg transportation from the Hg mining and smelting activities to the greater environment in this region. The main species of Hg in paddy soils were strong complex Hg and residue Hg, while the newly deposited Hg in soil mainly existed as water soluble Hg and strong complex Hg. The IHg and MeHg in rice were correlated with TGM. These results indicate that TGM plays an essential role in Hg biogeochemical cycles, and newly deposited Hg in soil is a potential source of Hg methylation, which produces MeHg. A Hg emission, transportation, methylation, and uptake process were hypothesized. In order to further verify the conclusion of this study, further research is required to get more evidence.

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