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ORIGINAL ARTICLE

Mercury speciation, bioavailability and risk assessment on soil–rice systems from a watershed impacted by abandoned Hg mine-waste tailings

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Abstract Mercury (Hg) is a global pollutant and can be accumulated in the food chain, posing exposure risks to humans. In this study, rice plants and corresponding rhizosphere soil samples were collected from a watershed of the Wawu River Basin that is heavily impacted by historic Hg mining and retorting activities. Total mercury (THg) and methylmercury (MeHg) in rice grains, as well as other tissues and soil samples, were measured. Five soil Hg fractions, as well as soil parameters, were also determined. The results show that the average concentrations of THg and MeHg in rice grains were 14 ± 7.0 μg kg^{-1} and 7.2 ± 4.0 μg kg^{-1}. Soil organic-bound (Hg-o) and strong complex-bound (Hg-s) were the main Hg fractions, accounting for 44% of the total. To estimate the Hg–ligand interaction in the soils, soil -N/Hg ($R = 0.451$, $p < 0.05$), -S/Hg ($R = 0.372$, $p < 0.1$), and -OM/Hg ratio ($R = 0.320$, $p < 0.5$) with MeHg$_{\text{soil}}$ were observed with significant positive correlations, indicating that the formation of Hg–OM, Hg–N–OM or Hg–S–OM complexes could prevent Hg(II) from methylation in soils. The significant positive correlations of the -N/Hg ratio, -S/Hg ratio and -OM/Hg ratio with MeHg in rice tissues suggested that Hg methylation and MeHg demethylation occurred throughout the rice paddy ecosystem. The estimated MeHg daily intake (EDI) was 0.075 ± 0.041 μg kg^{-1} bw d^{-1} and was lower than the RfD level of 0.1 μg kg^{-1} bw d^{-1} recommended by the US EPA. However, approximately 29% of the hazardous index (HI) of MeHg in grain exceeded 1, posing a potential threat to local populations, particularly pregnant women and children.

Keywords Mercury and methylmercury · Rice · Mercury speciation and bioavailability · Paddy soil · Risk assessment

1 Introduction

Mercury (Hg) is a global pollutant (Lindqvist et al. 1991), and its mobility, bioavailability and toxicological effects are highly dependent on Hg chemical forms (Ullrich et al. 2001). Methylmercury (MeHg), an organic Hg form, has been considered one of the most toxic Hg forms (Mergler et al. 2007). Under certain environmental conditions, inorganic mercury (IHg) can be converted into MeHg by anaerobic bacteria (Ullrich et al. 2001). Owing to the fat-solubility and long half-life period, MeHg can be bioaccumulated and biomagnified in the food chain (Qiu et al. 2008). As a consequence, up to 95% of total Hg (THg) can be bioaccumulated in organisms like fish, posing health risks to biota (WHO 1990; Clarkson 2002). MeHg concentrations in fish can be more than 10^6 times greater than in ambient water (Stein et al. 1996). Fish consumption is currently considered the dominant pathway of MeHg exposed to humans (Mergler et al. 2007).

China has one of the world's greatest Hg deposits in the form of cinnabar ores, most of which are allocated in the Guizhou Province (Feng et al. 2008). Guizhou is located in the center of the circum-Pacific mercuriferous belt and the total reserves of metal Hg have reached 80,000 tons (Qu 2004; Qiu et al. 2005a, b). An approximately 600-year history of intensive mining and retorting activities have

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generated huge quantities of Hg-containing waste residue, wastewater and exhausts in the local ecosystem, causing heavily Hg-contaminated soil, water, air and biota (Tan et al. 1997; Feng et al. 2008). In Hg mining areas, rice paddies have been heavily contaminated with Hg and have caused accumulation of MeHg in rice (Qiu et al. 2008; Meng et al. 2010; Zhang et al. 2010a, b, c). Elevated MeHg concentrations, as high as 174 μg kg^{-1} in edible parts of rice, were first reported in the Wanshan Hg mining area (Qiu et al. 2008). Recently, studies suggest that rice consumption can be the main pathway of MeHg exposure to populations dwelling in abandoned Hg mining areas (Feng et al. 2008; Qiu et al. 2008; Zhang et al. 2010a, b).

Rice plantations are the most prevalent use of land in South and East Asia, where rice is the dominant foodstuff, and approximately 70% of the daily dietary energy of more than 2 billion people comes from rice and its byproducts (FAO 2002, 2006). China is the largest producer of rice, generating 29% of the global rice supply in 2009 (IRRI 2012). Rice paddies, as typical wetland environments, have usually been kept as flooded reduction environments during the rice growing period. This has resulted in favorable conditions for Hg methylation for microorganisms, which is considered an important source of MeHg in the terrestrial ecosystem (Meng et al. 2010, 2011). The mobility and methylation of Hg in temporarily flooded paddies are determined by a range of factors, such as pH, dissolved organic matter (OM), sulfur, iron, redox potential, and dissolved Hg concentration (Liu et al. 2014; Zhao et al. 2016). Previous studies have indicated that Hg methylation is largely facilitated by a subset of sulfate-reducing bacteria (SRB) or iron-reducing bacteria (IRB) in anoxic conditions (Gilmour et al. 1992; Fleming et al. 2006). Particularly, the OM, which contains various O-, N-, and S-bearing ligands, not only serves as an important electron donor for SRB, but also as a direct binder to Hg(II) (Skyllberg and Drott 2010; Graham et al. 2012).

Although paddy soil has been confirmed to be the primary MeHg source to rice, no significant positive correlation between soil THg and MeHg and rice THg has been reported (Gnamuš et al. 2000; Meng et al. 2010, 2011; Rothenberg et al. 2011; Zhang et al. 2012). Water soluble and organo-chelated Hg in soil is readily available to biota (Schuster 1991; Wallschläger et al. 1998; Boszke et al. 2006; Covelli et al. 2009), while Hg in paddy soil, particularly in Hg mining regions, can be bound to different matrices, resulting in various capabilities of mobility, bioavailability and potential toxicity (Issaro et al. 2009). Hence, the paddy soil Hg species and their interconversions play important roles in the Hg accumulation of rice. However, the transfer of different Hg species from soil to rice still remains far from being well understood. Few studies have focused on the relationships between different Hg species in soils and Hg in rice in watershed impacted by abandoned Hg mine-waste tailings.

In this study, rice plants and corresponding rhizosphere soils were collected from a watershed that has been strongly impacted by historic Hg retorting activities. The main objectives are (1) to reveal the distribution and accumulation of THg and MeHg in rice plants and rhizosphere soils, (2) to characterize the influence of soil Hg speciation on Hg bioaccumulation in rice, (3) to elucidate key factors of soil parameters that determine the production and bioaccumulation of MeHg in rice and, (4) to assess the health exposure risk of both IHg and MeHg via rice consumption.

2 Materials and methods

2.1 Study area

The study region of the Wawu River watershed (E: 109°23′–109°43′, N: 27°53′–27°70′) covers an area of approximately 343 km^2 in Wanshan, Guizhou Province, Southwest China. The Wawu River flows into the Jinjiang River at the confluence of Yangtou Town. The main tributaries of the Wengman, Aozhai and Xiaxi originate from the Yanwuping (YWP), Meizixi (MZX) and Dashuixi (DSX), which are located at 8.3 km northeast, 2.5 km southwest and 2.5 km east of Wanshan Town, respectively.

The region is characterized by a subtropical monsoon humid climate with an average annual rainfall of 1400 mm and a mean temperature of 13.4 °C. Large quantities of mine-waste calcines have been deposited adjacent to the sites of the MZX, DSX and YWP. The calcines nearby the MZX and DSX sites were approximately 2.83 million m^3 and 44.5 million m^3, respectively, and there were approximately 3337 tons of mine tailings near the YWP. The historic intensive Hg smelting activities have resulted in serious Hg contaminations to the ambient air, water, soil and biota (Qiu et al. 2005a, b; Li et al. 2008a, b, 2009).

2.2 Sampling and preparation

Whole rice plants and corresponding rhizosphere paddy soil samples were collected within the Wawu River watershed during the harvest season of September 2015 (Fig. 1). Briefly, at each sampling site, approximately 2–3 clusters of whole rice plants within a plot area of 50 m × 50 m were randomly collected and pooled as one final sample. After the separation of grains, the whole plant was thoroughly washed in situ, with water from the adjacent rivers. At each site, approximately 1.5 kg of rhizosphere composited soils were collected simultaneously. Soil from the roots of 2–3 clusters was mixed and

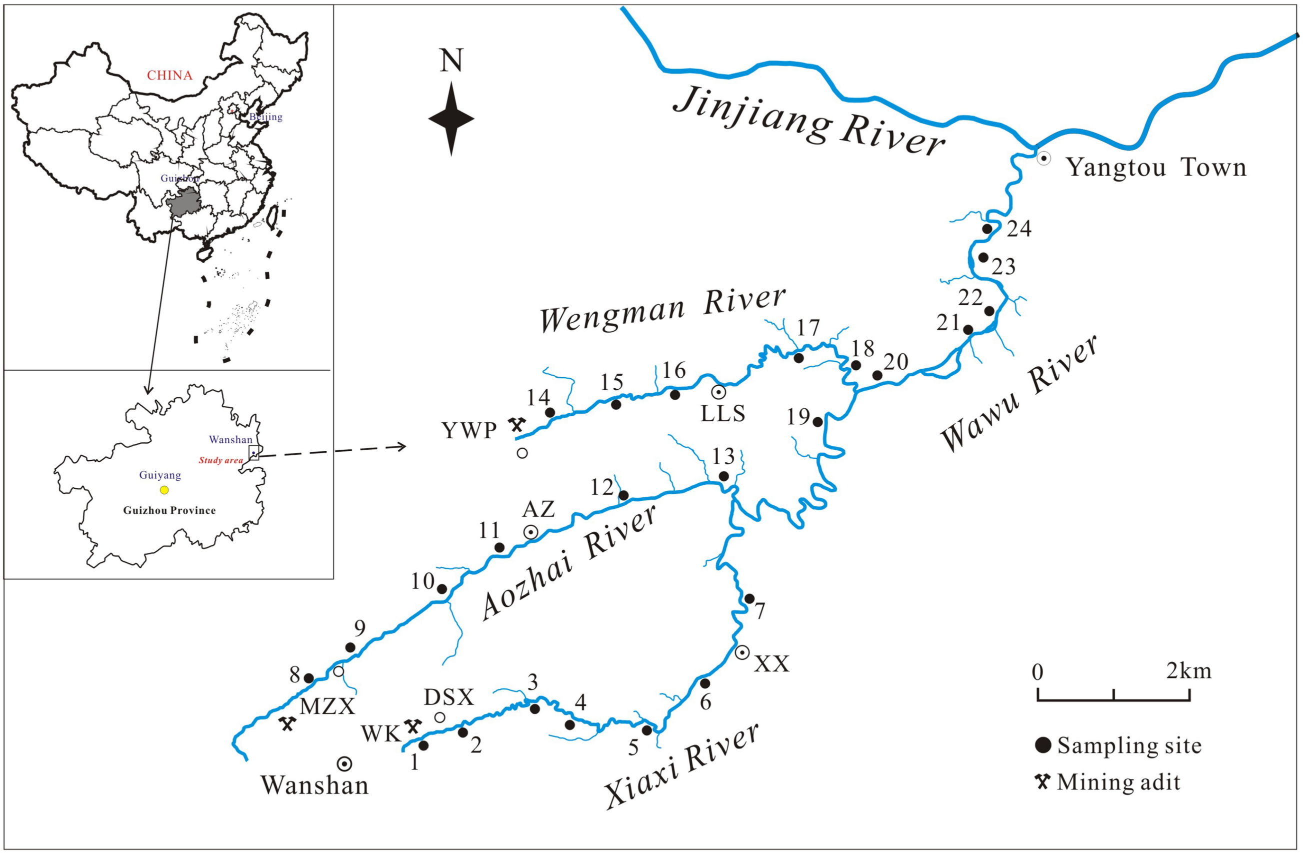

Fig. 1 Map of sampling sites (*WK* Wukeng, *DSX* Dashuixi, *XX* Xiaxi, *MZX* Meizixi, *AZ* Aozhai, *YWP* Yanwuping, *LLS* Liulongshan)

represented a final sample. All samples were kept in Ziplock bags to prevent cross-contamination. Then, all samples were stored in coolers (+ 4 °C) and transported to the laboratory for further processing prior to speciation analysis.

In the laboratory, the whole rice plants were thoroughly washed with tap water, then with Milli-Q water three times. After rinsing, the rice plants were separated into leaf, stem, and root with ceramic scissors. All samples were dried with a Freeze Dryer (FDU-1100, Japan). For grain, polished rice was obtained by shelling and removing the hull and bran. Then, all samples were ground with a Micro Plant Grinding Machine (IKA-A11, Germany). The soil samples were ground with a mortar and passed through a 200 µm mesh size sieve and packed in Ziplock bags. During the sample preparation processes, the tools (such as scissors) and machines (such as FDU-1100 and IKA-A11) were rinsed three times with ethanol, to avoid cross-contamination.

2.3 Analytical methods

2.3.1 *THg*

For rice, approximately 0.05–0.2 g sample was added to 5 ml Milli-Q water and a 5 ml fresh mixture of HNO_3/H_2SO_4 (v/v 4:1) and was digested in a water bath at 95 °C for 3 h (Zhang et al. 2010a, b, c). THg was determined by the dual-stage gold amalgamation method and cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500, Tekran Inc, Canada), preceded by BrCl oxidation, $SnCl_2$ reduction, preconcentration, and thermoreduction to Hg^0 (US EPA 2002).

For soil, approximately 0.2 g sample was weighed into plastic tubes, then 5 ml Milli-Q water and 5 ml fresh aqua regia were added for digestion in a water bath at 95 °C for 3 h. THg was determined by using a F732 V Atomic Absorption Spectrometry Mercury Analyzer (AAS, F732-V; Shanghai Huaguang, China).

2.3.2 *MeHg*

For rice, approximately 0.1–0.2 g sample was diluted with 5 ml 25% KOH–methanol solution and heated in 75 °C water for 3 h (Liang et al. 1996). MeHg in the sample was extracted with CH_2Cl_2, then back-extracted from the solvent phase into an aqueous ethyl phase. The sample extraction was followed by distillation, addition of 2 M acetate buffer, ethylation with 1% sodium tetraethylborate and purging and trapping of MeHg onto Tenax (US EPA 2001). MeHg was determined using gas chromatography-cold vapor atomic fluorescence spectrometry (GC-CVAFS, Brooks Rand Model III, Brooks Rand Laboratories, Seattle, WA), following US EPA Method 1630.

For soil, approximately 0.05–0.1 g sample was prepared using 1.5 ml $CuSO_4$-methanol solvent and 7.5 ml 25% HNO_3, heated in 75 °C water for 3 h (Liang et al. 1994). The following steps were similar to the processing of rice, and the MeHg analysis was also according to the US EPA Method 1630.

2.3.3 *Soil Hg fractions*

Sequential extraction of the Hg fractions in soil referred to Bloom et al. (2003), with a modification. Five operational Hg fractions: water-soluble-bound (Hg-w), simulated gastric acid-bound (Hg-g), fulvic acid-bound (Hg-f), humic acid-bound (Hg-h) and strong complex-bound (Hg-s) fractions were extracted. All Hg species were analyzed by CVAFS. Detailed information on the extraction steps is listed in Table 1.

2.3.4 *Soil parameters*

To determine pH, approximately 10 g of a soil sample was added to 25 ml Milli-Q water, shaken for 5 min at room temperature and allowed to stand for 1–3 h. The clear solution was used to measure the pH value by PHS-3C pH meter (NY-T, 1377-2007). For organic matter (OM), approximately 0.25 g of a soil sample was mixed with 0.05 g $HgSO_4$, 2.5 ml $K_2Cr_2O_7$, and 3.75 ml H_2SO_4. The mixed solution was digested for 30 min at 135 °C and diluted with Milli-Q water to 50 ml. The absorbance was measured at 585 nm by using a 72 UV–Vis spectroscope (HJ, 615-2011). To measure total nitrogen (TN) and total sulfur (TS), approximately 0.1 g of a soil sample was weighed in aluminum tin cups and determined by Vario MACRO Cube Elemental analyzer (Elementar analysensysteme, Hanau; Germany).

2.3.5 *QA/QC*

Method blanks, the standards curve, certified reference material (CRM), and relative standard deviation (RSD) were employed for quality assurance and quality control for THg and MeHg analyses in rice and soil (Table 2).

For soil, the THg in the estimated value of estuarine sediments (ERM CC580) was 130 ± 0.005 mg kg^{-1}, which is comparable with the certified value of 132 ± 0.003 mg kg^{-1}. The estimated value of MeHg was 0.075 ± 0.006 mg kg^{-1}, which is comparable with the certified value of 0.076 ± 0.004 mg kg^{-1}. The method detection limits were 0.1 μg kg^{-1} for THg and 0.003 μg kg^{-1} for MeHg. The method blank was below the limit for THg and MeHg.

For rice, the method detection limits for THg and MeHg were the same as in the soil samples. The average THg concentration of citrus leaves (GBW 10020) was 0.140 ± 0.005 mg kg^{-1}, whereas the certified value was 0.152 ± 0.020 mg kg^{-1}. An average MeHg concentration of Lobster hepatopancreas (TORT-2) was 0.140 ± 0.006 mg kg^{-1}, with a certified value of 0.152 ± 0.013 mg kg^{-1}. The method blank was below the limit for THg and MeHg.

2.4 Statistical analysis

Statistical analysis of the data was performed using the SPSS Statistics 22.0 software (IBM, International Business Machines Corporation, America, 2013) and Origin Pro 8.5 software (Origin Lab, America, 2011). The correlation

Table 1 The specific extraction steps of Hg fractions in soil

Hg fractions	Reagent	Extraction conditions
Hg-w	Milli-Q water	Shaking 24 h at 25 °C, centrifuged 20 min at 3500 rpm, rinsed twice
Hg-g	0.1 M CH_3COOH + 0.01 M HCl	Shaking 24 h at 25 °C, centrifuged 20 min at 3500 rpm, rinsed twice
Hg-f	1 M KOH	Shaking 12 h at 25 °C, centrifuged 20 min at 3500 rpm, rinsed twice, adjusted supernatant pH to 1
Hg-h	1 M KOH	Adjusted pH to approximately 8
Hg-s	12 M HNO_3	Shaking 12 h at 25 °C, centrifuged 20 min at 3500 rpm, rinsed twice

Table 2 Information on QA/QC of measurement data

Item	Soil		Rice	
	THg	MeHg	THg	MeHg
CRM	ERM CC580	ERM CC580	GBW 10020	TORT-2
Certified value (mg kg^{-1})	132 ± 0.003	0.076 ± 0.004	0.15 ± 0.02	0.152 ± 0.013
Estimated value (mg kg^{-1})	130 ± 0.005	0.075 ± 0.006	0.14 ± 0.005	0.140 ± 0.006
Detection limit (μg kg^{-1})	0.1	0.003	0.1	0.003
Method blank (μg kg^{-1})	< 0.1	0	< 0.1	0
R^2	0.9990	0.990	0.9991	0.990
RSD (%)	< 10	< 10	< 10	< 10

coefficients (R) and significance probabilities (*p*) were adopted among the data.

3 Results and discussion

3.1 Soil

3.1.1 THg and MeHg

As shown in Fig. 2, the THg (THg_{soil}) concentrations of soils, obtained from different areas, ranged from 0.43 to 110 mg kg^{-1}, with an average value of 23 ± 28 mg kg^{-1}. Most of the paddy soil samples exhibited rather high THg values, exceeding the Chinese national standard limit of 1.5 mg kg^{-1} for paddy soils (GB15618, 1995). The soil sample collected from XX showed the highest THg value, which is 36 ± 39 mg kg^{-1} on average, followed by AZ, with 28 ± 24 mg kg^{-1}; and WM, with 23 ± 29 mg kg^{-1}. The lowest value of 6.9 ± 2.8 mg kg^{-1}, on average, was observed in WW (Fig. 2a). The high THg concentrations observed in XX and AZ suggested that the historically intensive Hg mining and retorting activities might be responsible for this high THg value.

The average MeHg concentration in the soil samples was 1.3 ± 1.0 μg kg^{-1}, with values ranged from 0.3 to 4.2 μg kg^{-1}. The proportion of MeHg to THg in the soil was 0.018%, with a range of 0.00084%–0.072%, suggesting that soil Hg was the main source in IHg forms (Qiu et al. 2005a, b). The highest MeHg concentration of 2.0 ± 1.2 μg kg^{-1} on average was recorded in samples from AZ, followed by XX, with 1.4 ± 1.3 μg kg^{-1} on average; WM, with 0.87 ± 0.39 μg kg^{-1} and WW, with 0.87 ± 0.39 μg kg^{-1} (Fig. 2b). The average MeHg concentrations were at a similar level between the Wengman River and Wawu River, which were 2.3 times lower than those observed in the Aozhai River. A large amount of Hg^0 that was released into the atmosphere during Hg retorting activities may eventually be deposited into its surroundings, causing in situ MeHg production (Zhao et al. 2016).

To estimate the Hg–ligand interaction in soils, the soil -N/Hg ratio, -S/Hg ratio and -OM/Hg ratios were calculated (Yin et al. 2018). Significant positive correlations of soil -N/Hg ratio (R = 0.451, $p < 0.05$), -S/Hg ratio (R = 0.372, $p < 0.1$), and -OM/Hg ratio (R = 0.320) with $MeHg_{soil}$ were observed (Fig. 3a–c), indicating that the elevated N/Hg ratio, S/Hg ratio and OM/Hg ratio in the soils inhibited the production of MeHg, possibly due to the formation of Hg–OM, Hg–N–OM or Hg–S–OM

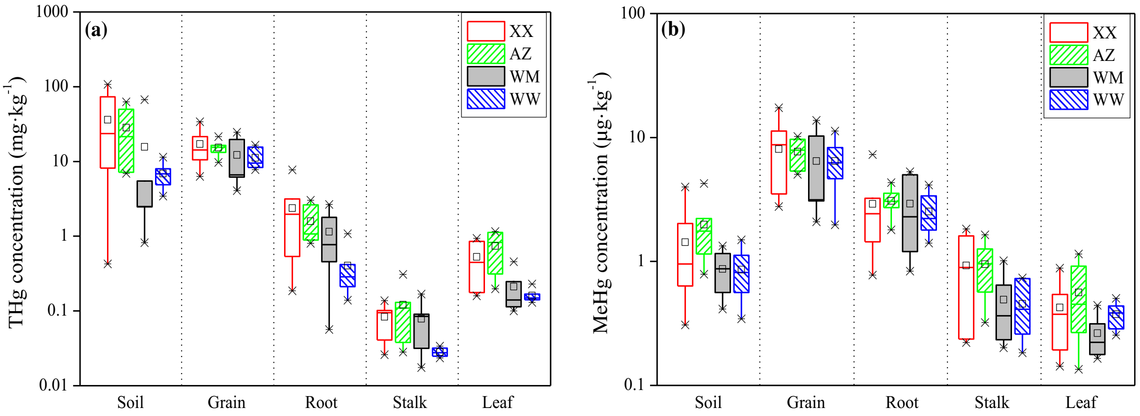

Fig. 2 The distribution of THg (**a**) and MeHg (**b**) concentrations in rhizosphere soil and rice tissues for samples from four tributaries (*XX* Xiaxi River, *AZ* Aozhai River, *WM* Wengman River, *WW* Wawu River) (units of THg_{grain}: μg kg^{-1})

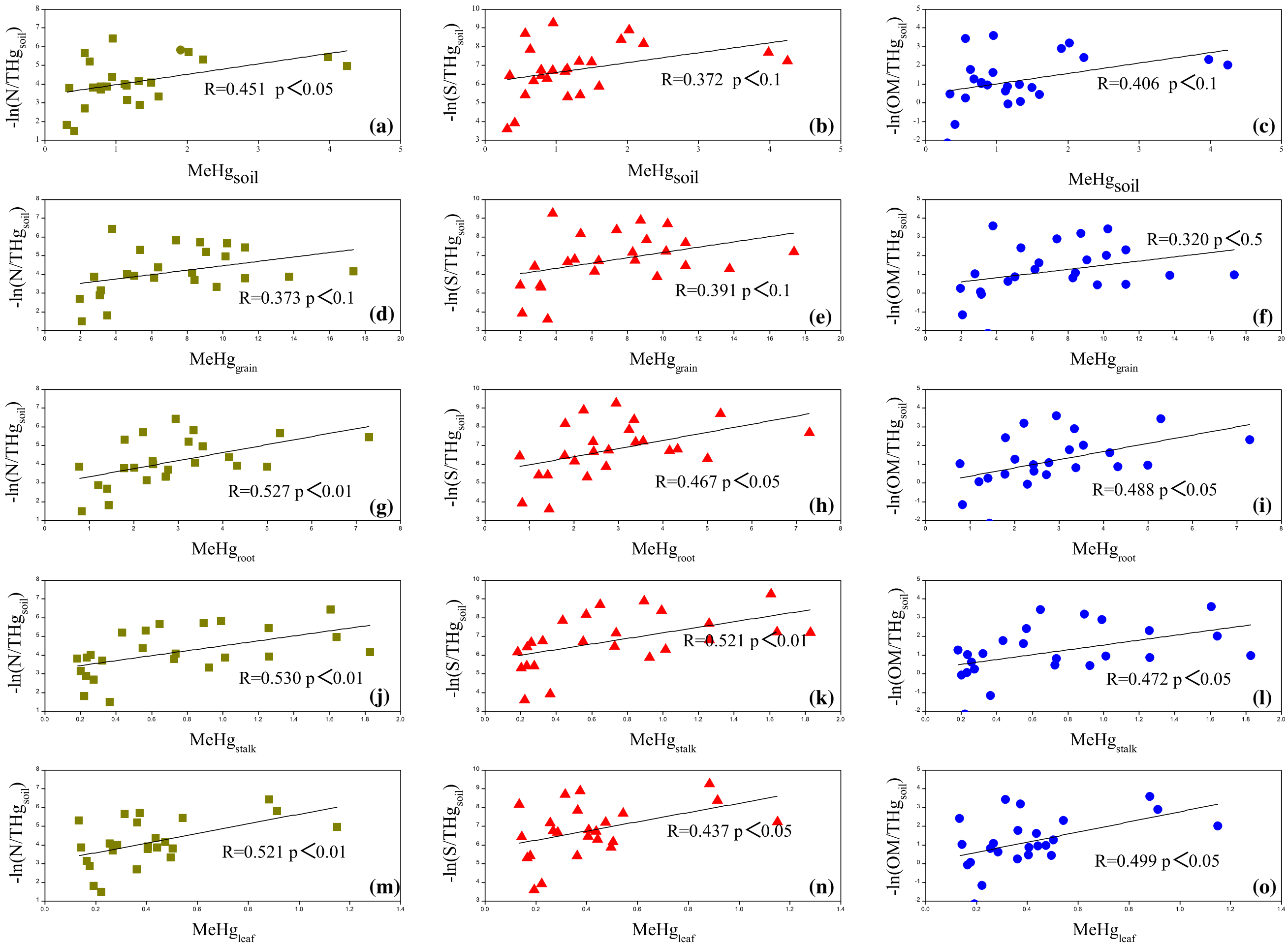

Fig. 3 The correlations of MeHg in soil and rice with soil -N/Hg ratio, -S/Hg ratio and -OM/Hg ratio [$\text{MeHg}_{\text{soil}}$ (**a**–**c**), $\text{MeHg}_{\text{grain}}$ (**d**–**f**), $\text{MeHg}_{\text{root}}$ (**g**–**i**), $\text{MeHg}_{\text{stalk}}$ (**j**–**l**), and $\text{MeHg}_{\text{leaf}}$ (**m**–**o**)]

complexes, which prevented Hg(II) from methylation in the soils (Skyllberg et al. 2006).

3.1.2 Soil Hg fractions

Soil Hg fraction concentrations indicated that organic-bound Hg (Hg-o: Hg-f and Hg-h) and strong complex-bound (Hg-s) were the main forms, accounting for approximately 44% of the total amount. The bioavailable bound Hg fraction (Hg-b: Hg-w and Hg-g) in the soil samples, which was considered to be dominated by active Hg^{2+} and contributed to Hg methylation or was directly absorbed by plants (Boszke et al. 2006; Covelli et al. 2009), generally accounted for 0.029% of the total. Soil samples from XX, AZ, and WM exhibited the highest concentrations of Hg-s, followed by Hg-o, and the lowest of Hg-b, while soils from WW showed the highest values of Hg-o (Fig. 4a, b). The reason for the high Hg-o in WW could be the large biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the water (Li et al. 2012), which can readily absorb Hg released from upstream mine-waste tailings.

Both Hg-b (R = 0.687, $p < 0.01$) and Hg-s (R = 0.917, $p < 0.01$) were significantly correlated to THg_{soil}, as well as to each other (R = 0.428, $p < 0.05$) (Table 3). The positive collection between Hg-b and Hg-s might indicate that Hg-s can be transformed to Hg-b. A recent study proposed that the nonbioavailable fraction in soil could be transformed to more toxic or potentially bioavailable fractions, hence promoting MeHg production during rice cultivation (Wu et al. 2018). The transformation between Hg-s and Hg-b has been a great concern to scientists. The increased Hg-b in paddy soil might be a hint of readily accumulated Hg in biota that could eventually enter and biomagnify in the food chain.

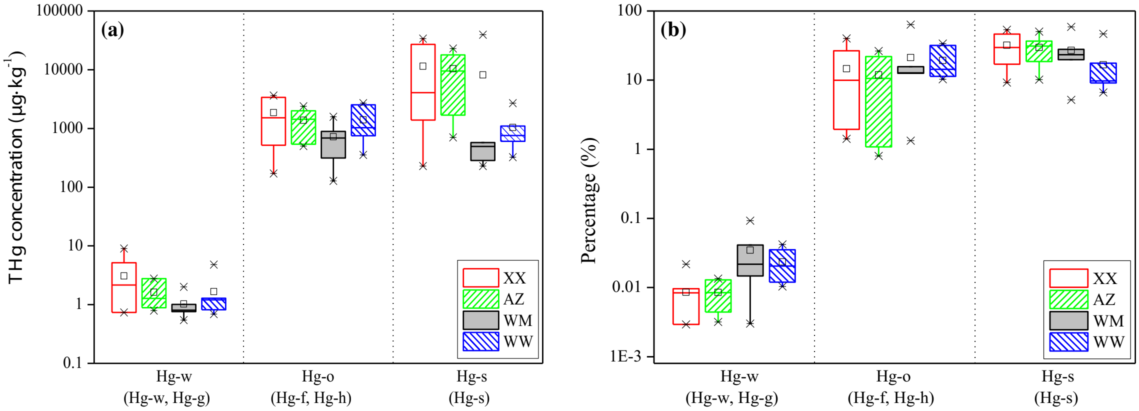

Fig. 4 The distribution of Hg fractions concentration in rhizosphere soil (**a**), the percentage of Hg fractions in soil THg (**b**) from four tributaries (*XX* Xiaxi River, *AZ* Aozhai River, *WM* Wengman River, *WW* Wawu River) (Hg-w: water-soluble; Hg-g: simulated gastric acid bound; Hg-f: fulvic acid bound; Hg-h: humic acid bound and Hg-s: strong complex bound)

3.2 Rice

3.2.1 THg and MeHg in grain

The THg concentration (THg_{grain}) was 14 ± 7.0 μg kg^{-1} on average, ranging from 4.1 to 34 μg kg^{-1}. The XX exhibited the highest THg concentration of 17 ± 9.1 μg kg^{-1} on average, followed by AZ at a concentration of 15 ± 3.9 μg kg^{-1}, WM at 13 ± 4.3 μg kg^{-1}, and the lowest of 11 ± 3.9 μg kg^{-1}, observed in WW (Fig. 2a). Samples collected from sites 2 and 7 from XX, site 11 from AZ, and site 14 from WM exhibited high values, exceeding the maximum Hg level of 20 μg kg^{-1} recommended by the Ministry of Health Standardization Administration of China (2017) (Fig. 5). Among those four sites, both site 7 and site 11 are adjacent to abandoned artisanal Hg retorting facilities and were strongly impacted by atmospheric Hg deposition. This newly deposited Hg is considered to be highly bioavailable and is readily transformed into MeHg, resulting in high THg_{grain} levels (Meng et al. 2011).

The MeHg concentration ($MeHg_{grain}$) was 7.2 ± 4.0 μg kg^{-1} on average, ranging from 2.0 to 17 μg kg^{-1}. Similar to THg_{grain}, the highest average MeHg concentration of 8.1 ± 5.3 μg kg^{-1} was recorded in XX, followed by AZ at concentrations of 7.7 ± 2.2 μg kg^{-1}, WM at 6.5 ± 5.2 μg kg^{-1}, and WW at 6.5 ± 3.2 μg kg^{-1} (Fig. 2b). High $MeHg_{grain}$ levels were found near the abandoned Hg mining sites and artisanal Hg smelters, which was consistent with the distribution of THg_{grain}. Moreover, $MeHg_{grain}$ contributed to a large portion of Hg in rice ($FMeHg_{grain}$), reaching an average of 51%, with a range of 25%–79%. The high MeHg ratios in grain certainly bring a great risk to the health of local residents, since MeHg is readily bioavailable (Li et al. 2008a, b).

3.2.2 THg and MeHg in roots, stalks and leaves

THg concentrations in tissues exhibited the highest values in roots, followed by leaves, with the lowest in stalks, ranging from 0.06 to 7.7, 0.10 to 1.2, and 0.02 to 0.31 mg kg^{-1}, respectively. The XX exhibited the highest value of 2.4 ± 2.6 mg kg^{-1} in roots, indicating that the heavily Hg-contaminated soils for root Hg levels was directly associated with soil Hg levels (Fay and Gustin 2007). Both the leaves and stalks from AZ exhibited the highest values of 0.74 ± 0.44 mg kg^{-1} and 0.12 ± 0.10 mg kg^{-1}, respectively. Since plants can absorb Hg^0 from the air into the leaves and stalks (Meng et al. 2012), the high values of THg_{stalk} and THg_{leaf} found in AZ likely suggest a high level of atmospheric Hg in ambient air.

The average MeHg concentration in roots ($MeHg_{root}$) was 2.9 ± 1.5 μg kg^{-1}, with a range of 0.78–7.3 μg kg^{-1}. The AZ exhibited the highest $MeHg_{root}$ of 3.1 ± 0.86 μg kg^{-1}, followed by XX at 3.0 ± 2.1 μg kg^{-1}, WM at 2.9 ± 2.1 μg kg^{-1}, and WW at 2.5 ± 1.0 μg kg^{-1}. In contrast, the lowest MeHg concentration ($MeHg_{stalk}$) of 0.72 ± 0.50 μg kg^{-1} on average was observed in stalks, with a range of 0.18–1.8 μg kg^{-1}. The XX exhibited the highest $MeHg_{stalk}$ of 1.0 ± 0.66 μg kg^{-1}, and the lowest of 0.46 ± 0.25 μg kg^{-1} was observed at WW (Fig. 2b). Among the different tissues, the leaf tissue exhibited the lowest average MeHg concentration ($MeHg_{leaf}$) of 0.41 ± 0.25 μg kg^{-1} with a range of 0.13–1.2 μg kg^{-1}. Similarly, the AZ exhibited the highest $MeHg_{leaf}$ of 0.56 ± 0.39 μg kg^{-1}, followed by XX at 0.42 ± 0.25 μg kg^{-1}, WW at 0.37 ± 0.094 μg kg^{-1}, and WM at 0.26 ± 0.12 μg kg^{-1} (Fig. 2b).

The proportion of MeHg to THg in stalks ($FMeHg_{stalk}$) is 1.25%, with a range of 0.28%–4.5%. Then, the proportion of MeHg to THg in roots ($FMeHg_{root}$) is 0.47%, with a range of 0.038%–12%. $MeHg_{leaf}$ contributed the smallest

Table 3 Pearson's correlation matrix, the linear correlation coefficients among the Hg levels (THg, MeHg and soil Hg fractions) in rice-soil system

	THg_{Root}	THg_{Stalk}	THg_{Leaf}	THg_{Grain}	THg_{Soil}	Hg-b	Hg-o	Hg-s	$MeHg_{Root}$	$MeHg_{Stalk}$	$MeHg_{Leaf}$	$MeHg_{Grain}$	$MeHg_{Soil}$
THg_{Root}	1												
THg_{Stalk}	0.317	1											
THg_{Leaf}	0.470*	0.714**	1										
THg_{Grain}	0.27	0.536**	0.518**	1									
THg_{Soil}	0.860**	0.413*	0.561**	0.265	1								
Hg-b					0.687**	1							
Hg-o					0.151	0.095	1						
Hg-s					0.917**	0.428*	0.124	1					
$MeHg_{Root}$									1				
$MeHg_{Stalk}$									0.482*	1			
$MeHg_{Leaf}$									0.361	0.711**	1		
$MeHg_{Grain}$									0.525**	0.612**	0.318	1	
$MeHg_{Soil}$									0.454*	0.536**	0.525**	0.296	1

**Correlation is significant at the 0.01 level; *correlation is significant at the 0.05 level

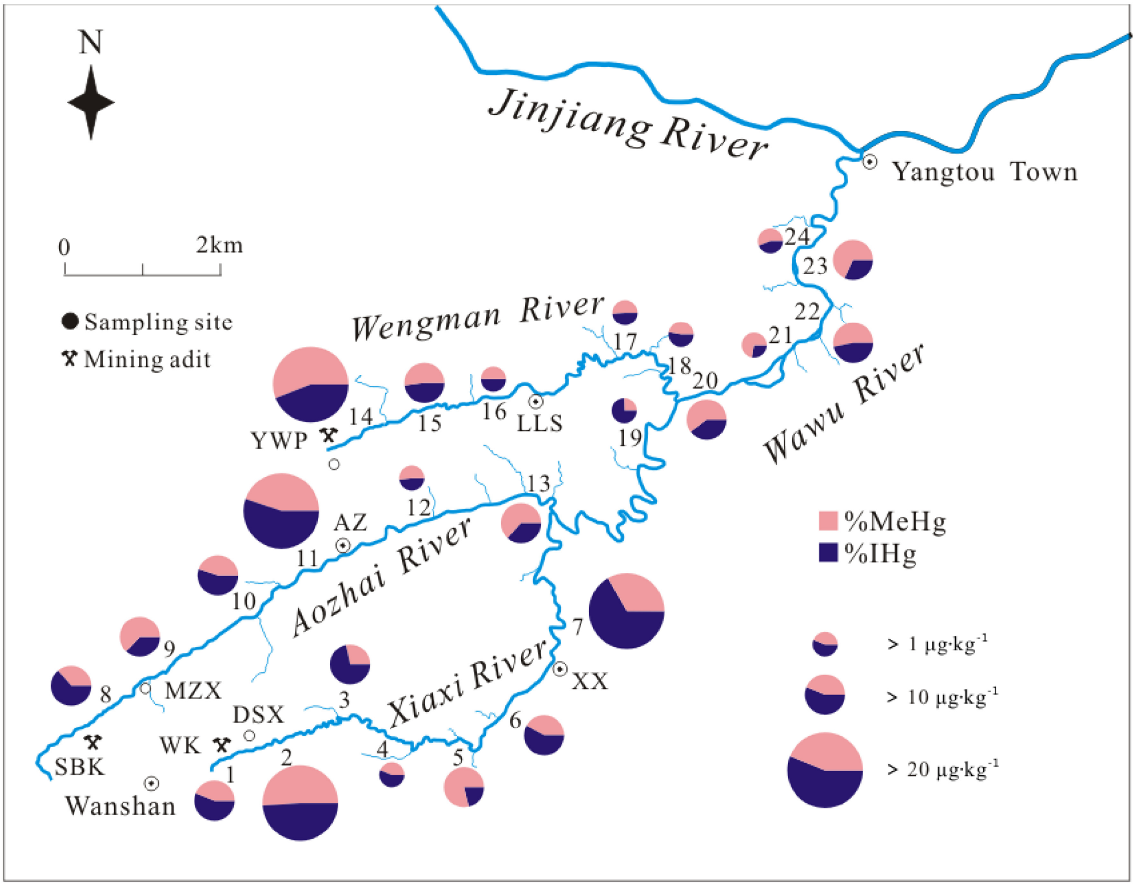

Fig. 5 THg and MeHg concentrations in grain of rice grown in the Wawu River Basin (*WK* Wukeng, *DSX* Dashuixi, *XX* Xiaxi, *MZX* Meizixi, *AZ* Aozhai, *YWP* Yanwuping, *LLS* Liulongshan)

proportion of Hg in rice ($FMeHg_{leaf}$), only reaching 0.14%, on average, with a range of 0.025%–0.33%.

3.3 Factors affecting Hg levels in rice

3.3.1 Soil THg and MeHg

The THg_{soil} significantly correlated to THg_{root} (R = 0.860, $p < 0.01$), followed by THg_{leaf} (R = 0.561, $p < 0.01$), THg_{stalk} (R = 0.413, $p < 0.05$), and THg_{grain} (R = 0.265) (Table 3). Among rice tissues, THg_{grain} was significantly positively correlated with THg_{stalk} (R = 0.536, $p < 0.01$) and THg_{leaf} (R = 0.518, $p < 0.01$), indicating that atmospheric Hg may be one of the Hg sources in the aerial parts of rice (Meng et al. 2012).

$MeHg_{grain}$ exhibited significant positive correlations with $MeHg_{root}$ (R = 0.525, $p < 0.01$), $MeHg_{stalk}$ (R = 0.612, $p < 0.01$) and $MeHg_{soil}$ (R = 0.296). $MeHg_{root}$ was also positively correlated with $MeHg_{soil}$ (R = 0.454, $p < 0.05$). These results indicated that MeHg in soil is a potential source of MeHg in rice roots and rice grains (Meng et al. 2014).

3.3.2 Soil Hg speciation

There was a significant negative correlation between $FMeHg_{grain}$ and Hg-s (%) (R = – 0.408, $p < 0.05$) (Fig. 6). A significant positive correlation between $FMeHg_{grain}$ and Hg-o (%) (R = 0.336) was observed (Fig. 6). No significant relationship of Hg-b (%) (R = 0.094) with $FMeHg_{grain}$ can be obtained (Fig. 6). This could be mostly attributed to the fact that the Hg fraction was not a direct factor in $MeHg_{grain}$ distribution (Zhao et al. 2016).

Hg-b (%) was significantly positively correlated with $FMeHg_{leaf}$ (R = 0.595, $p < 0.01$) and $FMeHg_{root}$ (R = 0.399, $p < 0.1$) (Fig. 6). This is likely because the bioavailable bound Hg might be a major substrate for the methylation process of IHg (Covelli et al. 2009). Hg-o (%) was significantly correlated with $FMeHg_{root}$ (R = 0.169), $FMeHg_{stalk}$ (R = 0.186) and $FMeHg_{leaf}$ (R = 0.340), suggesting that organic-bound Hg in rice can promote the production of the more toxic MeHg (Zhou et al. 2015). Negative correlations of $FMeHg_{root}$ (R = – 0.149), $FMeHg_{stalk}$ (R = – 0.152) and $FMeHg_{leaf}$ (R = – 0.256,

$p < 0.1$) with strong complex-bound Hg were observed (Fig. 6). However, the MeHg accumulation in rice may be influenced by many factors. More studies are needed to further investigate the process of the methylation of the Hg fraction.

3.3.3 Other soil parameters (OM, TN and TS)

Soil -N/Hg ratio (R = 0.373, $p < 0.1$), -S/Hg ratio (R = 0.391, $p < 0.1$), and -OM/Hg ratio (R = 0.320, $p < 0.5$) with $\text{MeHg}_{\text{grain}}$ (Fig. 3d–f) showed significant positive relationships, indicating the distribution of $\text{MeHg}_{\text{grain}}$ was largely controlled by the OM (N, S)-Hg interactions in the soils (Yin et al. 2018).

Significant positive relationships of $\text{MeHg}_{\text{root}}$ (R = 0.527, $p < 0.01$), $\text{MeHg}_{\text{stalk}}$ (R = 0.530, $p < 0.01$) and $\text{MeHg}_{\text{leaf}}$ (R = 0.521, $p < 0.01$) with -N/Hg ratio (Fig. 3g, j, m) were observed. In addition, -S/Hg ratio was significantly correlated with $\text{MeHg}_{\text{root}}$ (R = 0.467, $p < 0.05$), $\text{MeHg}_{\text{stalk}}$ (R = 0.521, $p < 0.01$) and $\text{MeHg}_{\text{leaf}}$ (R = 0.437, $p < 0.05$) (Fig. 3h, k, n). There were significant correlations between -OM/Hg ratio and $\text{MeHg}_{\text{root}}$ (R = 0.488, $p < 0.05$), $\text{MeHg}_{\text{stalk}}$ (R = 0.472, $p < 0.05$) and $\text{MeHg}_{\text{leaf}}$ (R = 0.499, $p < 0.05$) (Fig. 3i, l, o). These results suggest that Hg methylation and MeHg demethylation occurred throughout the rice paddy ecosystem (Zhao et al. 2016).

3.4 Risk assessment

Estimated daily intake (EDI) and hazard index (HI) via rice consumption of residents were assessed based on data for both IHg and MeHg in the grain obtained in the present study. According to a report by Lin et al. (2008), IHg was defined as the difference between THg and MeHg. The RfD referred to the Hg daily safe intake recommended by JECFA (2010) and the US EPA (1998), and the corresponding values of IHg and MeHg were 0.57, 0.23 μg kg^{-1} bw d^{-1} and 0.30, 0.10 μg kg^{-1} bw d^{-1}, respectively. An HI value lower than 1 means that the level of Hg will not cause noncarcinogenic Hg exposure risk to humans (Cao et al. 2010). In contrast, when the HI value is greater than 1, potential health risks arising from carcinogenic Hg exposure should be of concern (Qiu et al. 2005a, b). Assuming MeHg absorption in the body was 100%, the calculations were as follows:

$$\text{EDI} = \text{CM} \times \text{IR}/\text{BW} \tag{1}$$

$$\text{HI} = \sum \text{EDI}/\text{RfD} \tag{2}$$

where *EDI* is the estimated daily intake, μg kg^{-1} bw d^{-1}; *CM* is the concentration of Hg (IHg and MeHg) in rice grain, μg kg^{-1}; *IR* is the daily intake rate, 0.625 kg d^{-1} (Feng et al. 2013); *BW* is the average body weight, 60 kg; *HI* is the hazard index.

The results for EDI and HI of both IHg and MeHg are shown in Table 4. The IHg average value of EDI in rice was 0.072 ± 0.040 μg kg^{-1} bw d^{-1}, ranging from 0.021 to 0.170 μg kg^{-1} bw d^{-1}. The MeHg average value of EDI was 0.075 ± 0.041 μg kg^{-1} bw d^{-1}, ranging from 0.021 to 0.180 μg kg^{-1} bw d^{-1}. According to the evaluation method recommended by JECFA, the average HI of IHg and MeHg were 0.13, with a range of 0.04–0.30 and 0.33, with a range of 0.09–0.79. The average HIs of IHg and MeHg were 0.24, with a range of 0.07–0.58, and 0.75, with a range of 0.21–1.80, as recommended by the US EPA.

Approximately 29% EDI of MeHg in white rice samples exceeded the maximum dose of 0.1 μg kg^{-1} bw d^{-1} MeHg developed by the United States Environmental Protection Agency (US EPA 1997). Among all samples, the EDI and HI of IHg in Wawu River Basin were slightly lower than the values shown in the previous study (Zhang et al. 2010a, b, c). The EDI of MeHg in the present study was consistent with the results reported by Zhang et al. (2010a, b, c), but much lower than the results reported by Qiu et al. (2008).

According to the daily safe intake evaluation method recommended by JECFA, the HI of IHg and MeHg were less than 1. According to the US EPA, the HI of IHg does not exceed 1, but approximately 29% HI of MeHg exceeded 1, which is a potential threat to the health of local residents who consume the rice on regular basis. It is urgent to adopt corresponding ecological restoration measures to debase soil Hg and atmospheric Hg in Hg mining areas and reduce Hg exposure risks for local residents, especially sensitive groups, such as pregnant women and children.

4 Conclusions

In summary, we have measured the THg and MeHg values of rice plants, and the corresponding rhizosphere soil samples were collected from a watershed of the Wawu River Basin. Soil Hg fractions of Hg-w, Hg-g, Hg-f, Hg-h, and Hg-s and other important parameters (e.g., pH, OM, TN and TS) were evaluated systematically. Our results revealed that rice plants and the corresponding rhizosphere soil samples collected from the Wawu River Basin contain significant Hg-contaminations. Soil Hg fractions of Hg-o and Hg-s are the main Hg forms and reached 44% in total. Significant correlations of MeHg in rice and soil with soil parameters (N, S and OM) were observed, mainly caused by demethylation activities in soil throughout the rice paddy ecosystem. The distribution of $\text{MeHg}_{\text{grain}}$ was largely controlled by the OM (N, S)-Hg interactions in the soil. The EDI value of MeHg was measured to be

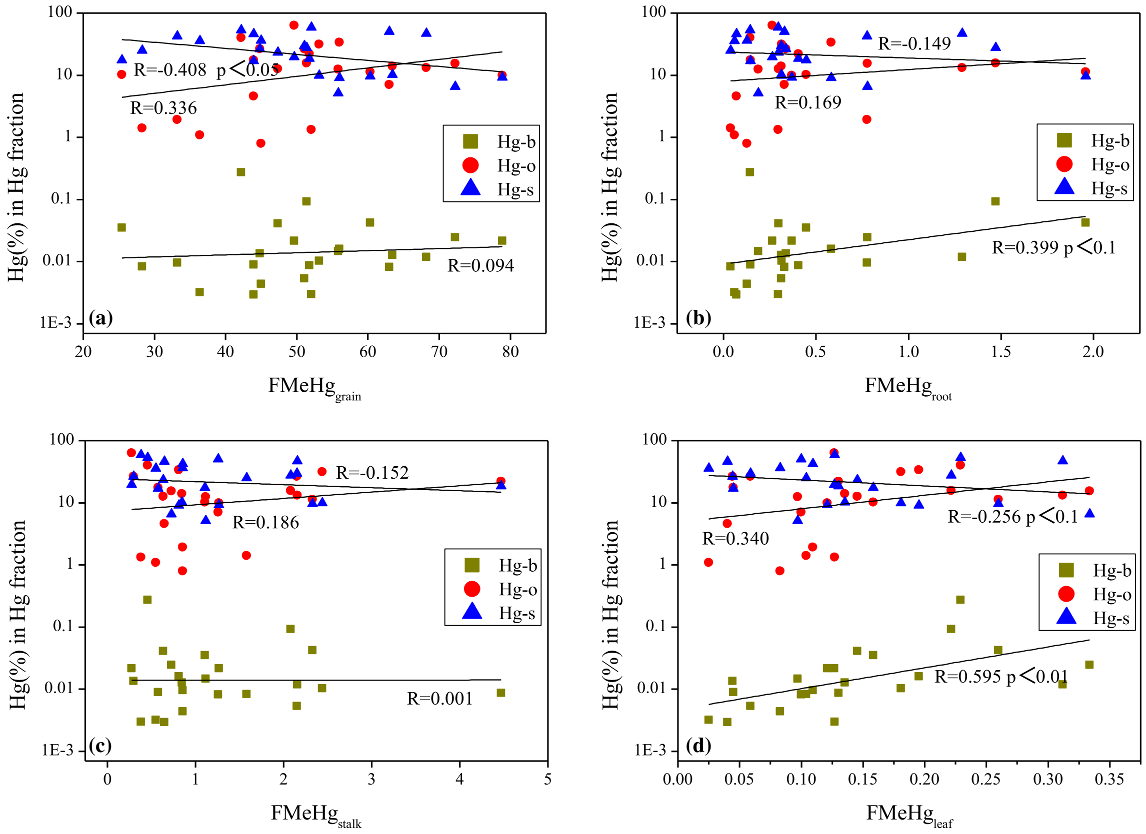

Fig. 6 The correlations of Hg (%) in Hg fraction with FMeHg$_{grain}$ (**a**), FMeHg$_{root}$ (**b**), FMeHg$_{stalk}$ (**c**) and FMeHg$_{leaf}$ (**d**) (FMeHg$_{grain}$, FMeHg$_{root}$, FMeHg$_{stalk}$ and FMeHg$_{leaf}$ were the proportion of MeHg to THg in grain, root, stalk and leaf)

Table 4 The EDI and HI of IHg and MeHg for human exposures in Wawu River Basin

Forms	RfD	EDI			HI		
		Mean ± SD	Min	Max	Mean ± SD	Min	Max
IHg	0.57[a]	0.072 ± 0.040	0.021	0.17	0.13 ± 0.07	0.04	0.30
	0.30[b]				0.24 ± 0.13	0.07	0.58
MeHg	0.23[a]	0.075 ± 0.041	0.021	0.18	0.33 ± 0.18	0.09	0.79
	0.10[b]				0.75 ± 0.41	0.21	1.80
∑ (IHg, MeHg)	0.80	0.150 ± 0.081	0.042	0.35	0.46 ± 0.25	0.13	1.10
	0.40				0.99 ± 0.54	0.28	2.38

[a] From JECFA

[b] From US EPA

0.075 ± 0.041 μg kg^{-1} bw d^{-1}, which was lower than the RfD level 0.1 μg kg^{-1} bw d^{-1} recommended by the US EPA. However, it is worth noting that 29% of HIs of MeHg exceeded 1, indicating the potential MeHg exposure risks to local residents, particularly to sensitive populations, e.g., pregnant women and children. Ongoing research is focused on understanding the possible processes of Hg methylation in rice paddies and developing ecological restoration measurements to reduce Hg concentrations in the paddy soil and Hg mining areas.

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