Biogeosciences Discuss., doi:10.5194/bg-2015-638, 2016
Manuscript under review for journal Biogeosciences
Published: 27 January 2016

Biogeosciences
Discussions
Open Access

Mercury Methylation in paddy soil: Source and distribution of mercury species at a Hg mining area, Guizhou Province, China

L. Zhao[1,2], C. W. N. Anderson[3], G. L. Qiu[2], B. Meng[2], D. Y. Wang[1], and X. B. Feng[2]

[1]College of Resources Environment, Southwest University, Chongqing 400716, P. R. China

[2]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, P.R. China

[3]Soil and Earth Sciences, Institute of Agriculture and Environment, Massey University, Palmerston North, New Zealand

Correspondence to: X. B. Feng (fengxinbin@vip.skleg.cn) and B. Meng (mengbo@vip.skleg.cn)

Abstract.

Rice paddy plantation for human consumption is dominant land uses throughout Asia. Rice paddy fields have been identified as important sites for methylmerucry (MeHg) production in the terrestrial ecosystem, and a primary pathway of MeHg exposure to human in mercury (Hg) mining areas. We compared the source and distribution of Hg species in different compartments of the rice paddy during a complete rice-growing season at two different typical Hg-contaminated mining sites: an abandoned site with high Hg concentration in soil but low concentration in atmosphere, and a current-day artisanal site with low concentration in soil but high concentration in atmosphere. The contribution of new Hg to the ecosystem from irrigation and atmospheric deposition was insignificant relative to the pool of old Hg; the dominant source of MeHg to paddy soil is in situ methylation of inorganic Hg. Elevated MeHg

concentrations jointly with the high proportion of Hg as MeHg in paddy water and the surface soil layer at the artisanal site demonstrated active Hg methylation at this site only. We propose that the in situ production of MeHg is dependent on elevated IHg in the atmosphere, and the deposition of new Hg into a low pH anoxic geochemical system. In contrast, the absence of depth-dependent variability in the MeHg concentration in soil cores collected from abandoned Hg mining site, consistent with the low concentration of Hg in atmospheric deposition and high pH of the paddy water/irrigation water, suggested that the net production of MeHg was limited. We also propose that the concentration of Hg in ambient air is an indicator for the risk of MeHg accumulation in paddy rice.

1 Introduction

Reports that rice (*Oryza sativa*) is a bioaccumulator species of MeHg have recently focussed scientific attention on this important agricultural crop (Qiu et al., 2008; Zhang et al., 2010a; Meng et al., 2010, 2011, 2014). Numerous studies have reported high MeHg concentrations in rice grain collected from Indonesia (Krisnayanti et al., 2012) and different parts of China (Qiu et al., 2008; Horvat et al., 2003; Meng et al., 2014) and the MeHg concentrations in rice grain can be enhanced even in cases where soil is not significantly elevated in Hg (Zhang et al., 2010a; Horvat et al., 2003). A common theme to these studies is a high flux of Hg into the environment through mining or other industrial contamination that discharges into the atmosphere.

Rice paddy plantation is one of the most prevalent land uses in South and East Asia where rice is the dominant foodstuff (FAO, 2002). Rice throughout Asia is generally cultivated in paddy soil and this land use represents an ephemeral wetland, which is known to be a significant environment for Hg methylation. MeHg accumulated throughout a rice plant during the growing season can be readily translocated to grain during rice-seed ripening (Meng et al., 2011). Rice paddy fields have therefore been identified as important sources of MeHg in the terrestrial ecosystem (Meng et al., 2010, 2011), and a primary vector for human exposure to MeHg in Hg mining areas (Feng et al., 2008; Zhang et al., 2010b).

The general consensus among Hg researchers is that soil is the principle source of MeHg in rice plants, whereas Hg from the ambient air is the principal source of IHg in rice grain (Meng et al., 2010, 2011, 2012, 2014). Recently, Meng et al. (2010, 2011) suggested that newly deposited Hg is more readily transformed to MeHg and accumulated in rice plants than Hg forms with an extended residence time in mining-contaminated soil. Meng et al. (2010) focused on the Wanshan area of China, a region of both historical large scale and current small-scale mercury mining. The concentration of MeHg in rice grain collected from artisanal Hg mining areas was shown to be significantly higher than that in rice grain collected from abandoned Hg mining areas (Meng et al., 2010). Despite these reported observations, the biochemical processes that control the cycling of Hg in paddy soils impacted by Hg mining are poorly understood.

All reports on MeHg and rice emphasize that the concentration and distribution of Hg in ambient air, wet/dry deposition, irrigation water, and solid and liquid phases of soil are important factors that control the biochemical cycling of Hg within rice paddy ecosystems impacting by mining activities. These factors in turn impact the absorption, transportation, and accumulation of Hg in rice plants (Meng et al., 2010, 2011, 2012, 2014; Rothenberg and Feng, 2012; Liu et al., 2012; Wang et al., 2014; Peng et al., 2012). Past studies have focused on the source, distribution, and accumulation of IHg and MeHg in rice plant, but, no study has presented results from a systemic survey of the concentration of Hg fractions in the rice paddy ecosystem. Such a study is necessary to mitigate against the risk for MeHg formation in paddy soil where a rice crop is being grown in a Hg contaminated area. Better understanding of the distribution of Hg species in paddy soils within a Hg mining area is necessary to underpin more reliable risk assessment and appropriate strategies to remediate contaminated soil.

To expand our knowledge of the biochemical processes that affect Hg we assessed the status of Hg species in different compartments of the rice paddy ecosystem. We measured the concentration of Hg species in ambient air, atmospheric deposition, irrigation water, paddy water, and soil cores at two contrasting Hg mining sites during a complete rice-growing season to quantify the distribution and origin of Hg species in the rice paddy. The relative contribution of different Hg vectors to the surface pool of soil Hg was subsequently estimated. The primary objectives of our study were to 1) investigate the speciation and distribution of Hg in the paddy soil, and 2) to assess the primary source and mechanism for transformation of Hg species within paddy soil at a Hg mining area. Documenting Hg cycling in rice paddy ecosystems within Hg mining areas is an important step towards better assessing potential health threats that may be associated with the cultivation of rice in a Hg-contaminated environment.

2 Materials and methods

2.1 Site description

This study was conducted in the Wanshan Hg mining district, Guizhou province, Southwest China, where historical large-scale Hg smelting combined with current artisanal Hg smelting activities have resulted in Hg contamination of ambient air, water, soil, sediment, and biota (Qiu et al., 2005; Li et al., 2008, 2009). Two Hg contaminated sites within the Wanshan Hg mining district were selected for this study: an artisanal Hg mining site (Gouxi); and an abandoned Hg mining site (Wukeng) (Fig. 1). The sampling sites of Gouxi and Wukeng are situated within the Wanshan district which experiences subtropical monsoon-type weather with an average annual rainfall of 1200-1400 mm and a perennial mean temperature of 17 ^{o}C. Historical Hg mining activities in the Wanshan area can be dated back to the Qin Dynasty (221 B.C.) but large-scale mining activities officially ceased in 2001. Mining activity across Wanshan generated an estimated cumulative 1.0×10^{8} tons of calcine and waste rock between 1949 and the 1990s. Recently, illegal artisanal Hg and small-scale mining activities have been revived due to an increase in the global Hg price and domestic demand.

The Gouxi artisanal Hg mining site is located to the north of Wanshan town (Fig. 1). Small-scale artisanal smelting was ongoing during the rice growing seasons of 2012 when the samples for the current study were collected. Mercury is released into the atmosphere during artisanal smelting and is subsequently deposited onto nearby rice paddy fields through wet and dry deposition. The Wukeng sampling site is located north east of Wanshan town at an abandoned Hg mining area where large quantities of calcines were deposited along the river.

Paddy field rice is the primary agricultural land use at both Gouxi and Wukeng. Field sampling for the current research focused on two 10×10 m plots (one at each site) within rice paddies that were established according to the following methodology: The rice paddies were flooded on 10th May; rice seedlings (hybrid rice) widely grown throughout Guizhou province were transplanted into the submerged soil 20 days after flooding (1 plant each 25×25 cm area on 1st June, defined as Day 0). Thereafter, the two experimental plots were cultivated during the period 1st June through 10th September (100 days) 2012. Standing water (2-8 cm) was maintained above the soil surface (flooded condition) throughout the growing period, from Day 0 to Day 80. The paddy fields were thereafter drained from Day 80, prior to harvest between Days 90 to 100. During the 10 days draining period, approximately 2-4 cm depth of water was maintained above the soil surface. The paddy plots received water through precipitation and stream water irrigation, while evaporation and seepage were the primary vectors for water loss. There was no outflow from either paddy.

2.2 Sample collection and preparation

Five consecutive sampling campaigns were conducted during the rice growing season (1st June-10th September, 2012). The first sampling was initiated 20 days after the plants were planted out (20th June, 2012; Day 20), and thereafter samples were collected on Days 40, 60, 80, and 100 (Day 100 was 10th September, 2012; final harvest). The Hg concentration in ambient air was measured at each sampling time, and a sample of cumulative precipitation, irrigation water, paddy water, and soil cores were collected at each time. The paddy fields were dry from Day 90, and therefore irrigation water, paddy water, and soil pore water samples were not collected on Day 100.

2.2.1 Mercury in ambient air and wet/dry deposition

The concentration of total gaseous mercury (TGM, Hg^0) in ambient air at both Gouxi and Wukeng was measured in the field at each sampling time using an automated Hg vapor analyzer (LUMEX, RA-915$^+$, Ohio Lumex Co., Twinsburg, OH) with detection limit of 2 ng m^{-3}. The average Hg^0 concentration during a 10 s interval was quantified and stored in a portable computer. At each sampling time, measurements were carried out continuously for at least one hour period; therefore, 360 data points (10 s reading) were collected at each location at each sampling time.

An integrated bulk precipitation sampler based on the design of Guo et al. (2008) was used in the field to quantify the concentration of Hg in cumulative precipitation (Oslo and Paris, 1998). Both dry and wet atmospheric deposition were collected concurrently with the TGM measurement once every 20 days using this sampling method. Samples collected at each site were poured into two 100 mL pre-cleaned borosilicate glass bottles for direct and unfiltered total Hg (HgT_{unf}) and total MeHg ($MeHg_{unf}$) analysis.

2.2.2 Irrigation water and paddy water

Samples of irrigation water at both Gouxi and Wukeng were collected at rice paddy inlets on Days 20, 40, 60, and 80. All water samples were collected by hand using ultra-clean handling protocols and stored in acid-cleaned borosilicate glass bottles. Each bottle was rinsed three times with irrigation water on site before sample collection. Filtered samples were collected on site using a 0.45 μm disposable polycarbonate filter unit (Millipore), and subsequently analyzed for dissolved total Hg concentrations (HgT_f) and dissolved MeHg concentration ($MeHg_f$). In addition, unfiltered irrigation water samples were siphoned into pre-cleaned borosilicate glass bottles using a disposable syringe and analyzed for total Hg (HgT_{unf}) and MeHg ($MeHg_{unf}$).

Paddy water (overlying water) and corresponding soil pore water samples at both Wukeng and Gouxi were collected at the centre of the two plots on Days 20, 40, 60, and 80, simultaneously with the irrigation water collection. Firstly, an undisturbed soil core was collected at each sampling site by pushing a pre-cleaned 6-cm diameter polycarbonate core tube into the soil to approximately 20 cm depth. The paddy water (0-8 cm above the soil surface) in the core tube was siphoned into a 200 ml pre-cleaned borosilicate glass bottles. One aliquot of the paddy water was then filtered into a 100 ml pre-cleaned borosilicate glass bottle using a 0.45 μm disposable polycarbonate filter unit (Millipore), and subsequently analyzed for HgT_f and $MeHg_f$. A second aliquot of paddy water for HgT_{unf} and $MeHg_{unf}$ analysis was immediately transferred into another 100 ml pre-cleaned borosilicate glass bottle.

General Water Quality Characteristics of irrigation water and paddy water including pH, dissolved oxygen (DO) concentration, and temperature (T) were measured *in situ* using a portable analyzer. All water samples were promptly acidified on site to 0.5% (v/v) using adequate volumes of ultra-pure concentrated hydrochloric acid (HCl). The sample bottles were then capped, sealed with Parafilm®, double-bagged, transported to the laboratory in an ice-cooled container to the lab within 24 h. Prior to Hg analysis, samples were stored in a refrigerator at +4 ºC in the dark.

2.2.3 Soil pore water (liquid phase) and soil core (liquid phase+solid phase)

The soil cores were immediately sliced on site into 2 cm intervals using a plastic cutter in an oxygen-free glove box under argon. The soil samples were placed in acid-cleaned 50-ml plastic centrifuge tubes, capped and sealed with Parafilm®. All samples were transported in an ice-cooled container to the lab within 24 h and stored at 3-4 °C for further laboratory processes. Following centrifugation (30 min, 3000 r min^{-1}, and 5 °C), the samples were returned to the glove box where the pore water was then filtered through 0.45 μm disposable nitrocellulose filter unit. The filtrate was stored in borosilicate glass bottles and divided for HgT_f and MeHg_f analysis. The water content of soil cores was estimated by weight loss.

.At each sampling site and at each sampling time a second soil core was collected, and immediately placed into liquid nitrogen. This second set of soil cores was transported in a liquid nitrogen-iced container to the lab within 24 h and then sliced at 2 cm intervals. The sliced soil cores were then freeze-dried, prior to homogenisation to 200 mesh with a mortar and pestle for analysis of total Hg (THg) and MeHg. The concentration of each Hg species in this second set of soil cores is therefore the sum of both liquid and solid phase. Precautions were taken to avoid cross-contamination during sample processing; the mortar and pestle were thoroughly cleaned after each sample with drinking water followed by deionized water rinses. The powdered samples were subsequently packed into plastic dishes, sealed in polyethylene bags and stored in a refrigerator within desiccators for subsequent laboratory analysis.

2.3 Sample analysis

All reagents used in this study were of guaranteed quality purchased from Shanghai Chemicals Co. (Shanghai, China).

2.3.1 Total Hg and MeHg in soil samples

For THg analysis, a soil sample (0.1-0.2 g) was digested using a fresh mixture of HCl and HNO_3 (1:3, *v/v*). THg was determined by cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500, Tekran Instruments) preceded by BrCl oxidation, $SnCl_2$ reduction, pre-concentration, and thermo-reduction to Hg^0 (U.S. EPA, 2002).

For MeHg analysis, a soil sample (0.3-0.4 g) was prepared using the $CuSO_4$-methanol/solvent extraction (Liang et al., 1996). MeHg in samples was extracted with methylene chloride, then back-extracted from the solvent phase into an aqueous ethyl phase. The ethyl analog of MeHg, methylethylHg ($CH_3CH_3CH_2Hg$), was separated from solution by purging with N_2 onto a Tenax trap. The trapped $CH_3CH_3CH_2Hg$ was then thermally desorbed, separated from other Hg species by an isothermal gas chromatography (GC) column, decomposed to Hg^0 in a pyrolytic decomposition column (800°C), and analyzed by CVAFS (Brooks Rand Model III, Brooks Rand Labs, U.S.A.) following method 1630 (U.S. EPA, 2001).

2.3.2 Total Hg and MeHg in water samples

The analysis of Hg species in water samples was conducted within three weeks of sampling. The HgT_{unf} and HgT_f concentration in water samples was quantified using dual amalgamation CVAFS (Tekran 2500, Tekran Inc., Toronto, Ontario, Canada) following approved methodology (U.S. EPA, 2002). Samples for HgT_{unf} and HgT_f analysis were oxidized with 0.5% (*v/v*) BrCl (bromine chloride). Excess BrCl was reduced with hydroxyl-ammonium chloride before adding $SnCl_2$ (stannous chloride) to convert Hg^{2+} to volatile Hg^0. The Hg^0 was trapped by gold amalgamation (U.S. EPA, 2002). Water samples were analyzed for MeHg using CVAFS (Brooks Rand Model III, Brooks Rand Labs, Seattle, WA, USA) following distillation, aqueous phase ethylation, and isothermal GC separation (U.S. EPA, 2001).

2.4 Quality control

Quantification for THg and MeHg in soil and water samples was conducted using daily calibration curves with the coefficient of variation (r^2) ≥ 0.99. Quality control and assurance measurements for all analytes were performed using triplicates, method detection limits, field blanks, matrix spike recoveries, and certified reference materials. Field blanks of water samples were 0.12 ng L^{-1} and 0.011 ng L^{-1} for THg and MeHg. The method detection limits ($3\times\sigma$) were 0.02 μg kg^{-1} for THg and 0.002 μg kg^{-1} for

MeHg in soil samples; 0.02 ng L^{-1} for THg and 0.01 ng L^{-1} for MeHg in water samples. The precision and bias for triplicate samples were less than 7.5% for THg and MeHg analysis for both water and soil samples. Recoveries for matrix spikes in water samples ranged from 88 to 108 % for THg analysis, and from 86 to 113% for MeHg. The following certified reference materials were employed: Montana soil (SRM-2710, National Institute of Standards and Technology), Loamy Sand 1 (CRM024-050, Resource Technology Corporation), Sandy Loam 3 (CRM021-100, Resource Technology Corporation), and Sediment (BCR-580, Institute for Reference Materials and Measurements). The results of the certified reference material analysis are shown in Table 1.

Statistical analysis was performed using SPSS 13.0 software (SPSS). Mercury concentrations in samples are described by the analysed mean ± standard deviation (SD) unless otherwise stated. Relationships between covariant sets of data were subjected to regression analysis. Correlation coefficients (r) and significance probabilities (p) were computed for the linear regression fits. Differences are declared as significant for $p< 0.05$. Kolmogorov-Smirnov test (K-S) and Kruskal-Wallis test (K-W) were processed for comparing the significant difference between the two or more independent datasets.

3 Results and Discussion

3.1 Mercury in ambient air and precipitation

The average TGM concentration in ambient air over the 100 days rice season at Gouxi (403±399 ng m^{-3}) was significantly higher than that at Wukeng (28±13 ng m^{-3}) and the regional background (6.2±3.0 ng m^{-3}) (Table 2). Serious Hg contamination of air was therefore observed at Gouxi during the monitoring period. The elevated TGM concentration in ambient air at Gouxi compared to Wukeng and the regional background area (Huaxi) is attributed to the emission of TGM from nearby artisanal Hg smelters (Meng et al., 2010; Li et al., 2008, 2009).

During the rice growing season, the HgT_{unf} concentration in precipitation at Gouxi was highly elevated (mean=2599±1874 ng L^{-1}), and 1-3 orders of magnitude higher than that recorded for Wukeng (mean=445±296 ng L^{-1}) and the regional background concentration at Huaxi (mean=27±17 ng L^{-1}) (Table 2). The relative concentration of Hg in precipitation between the three sites was comparable to the concentration of Hg in the ambient air suggesting that elevated Hg in precipitation at Gouxi can be linked to the ongoing Hg smelting activities. Mercury in precipitation is therefore a function of the enhanced flux of both dry and wet deposition of Hg from the atmosphere.

The $MeHg_{unf}$ concentration in precipitation collected from the two sites (Gouxi; 0.48±0.20 ng L^{-1}; Wukeng: 0.30±0.15 ng L^{-1}) was similar to the regional background concentration of MeHg (0.28±0.14 ng L^{-1}) in these compartments (Table 2). Furthermore, there was no difference in $MeHg_{unf}$ concentration between the two sampling sites during the rice growing season (*K-S*, test, $p>0.05$). These results confirm previous suggestions that atmospheric deposition is responsible for the flux of inorganic Hg but not MeHg to mining areas where artisanal Hg mining is ongoing (Meng et al., 2011).

3.2 Mercury in irrigation water and paddy water

The concentration of Hg in irrigation water and paddy water across the two sampling sites is presented in Table 2. Paddy fields selected in this study were irrigated with local stream water with a high concentration of Hg due to the contaminated of the streams with calcines and tailings. During the rice growing season, irrigation water at Wukeng had a significantly higher HgT_{unf} (mean=513±215 ng L^{-1}) and $MeHg_{unf}$ (1.1±1.7 ng L^{-1}) concentration than at Gouxi (mean HgT_{unf}=159±67 ng L^{-1}; mean $MeHg_{unf}$=0.75±0.65 ng L^{-1}). Mercury concentrations in irrigation water at both sites were significantly higher than the regional background ($p<0.05$).

Clear differences were observed between the two sites with regard to MeHg concentration and the ratio of $MeHg_{unf}/HgT_{unf}$ in paddy water. The highest values of $MeHg_{unf}$ in paddy water were all observed at Gouxi (mean=5.9±4.4), whereas sampling at Wukeng (mean=0.48±0.63) maintained a relatively low MeHg concentration in paddy water throughout the rice growing season when compared with the corresponding data from Gouxi. The ratio of MeHg to total Hg is recognized as a measure of Hg methylation efficiency (Sunderland et al., 2006). In our study, the $MeHg_{unf}/HgT_{unf}$ ratio was up to 11 % ($MeHg_{unf}/HgT_{unf}$) for paddy water at Gouxi and the mean $MeHg_{unf}/HgT_{unf}$ ratio for this water compartment was significantly higher than the corresponding data for irrigation water (mean=0.71±0.93) and precipitation (mean=0.031±0.028) (Table 2). However, there was no significant difference between the $MeHg_{unf}/HgT_{unf}$ ratios for the various water compartments at Wukeng (K-W test, $p>0.05$). These results imply active net Hg methylation paddy fields at Gouxi but not at Wukeng.

3.3 Mercury in soil profiles

3.3.1 Hg in soil pore water

The vertical distribution of HgT_f and $MeHg_f$ in pore water was monitored over four successive time intervals during the rice growing season (Fig. 2). The distribution of pore water HgT_f as a function of depth was different to pore water $MeHg_f$ at both sampling sites. The mean concentration of HgT_f in pore water samples over the 100 days rice growing season was 142±111 ng L^{-1} (range: 15-460 ng L^{-1}) at Gouxi and 180±160 ng L^{-1} (range: 38-916 ng L^{-1}) at Wukeng. The highest concentration of HgT_f in pore water was observed at the soil surface layer (top 2cm), and decreased with depth at both sampling sites. The HgT_f concentration in pore water at Gouxi was consistent with respect to time, and showed no significant difference between the different sampling dates (K-W test, $p>0.05$). However, the concentration of HgT_f in pore water at Wukeng was time dependent, with the highest concentration in surface layer recorded at Day 20, and the lowest at Day 80.

The maximum concentration of $MeHg_f$ in soil pore water (15 ng L^{-1}) was observed at sampling site of Gouxi, which was approximately 2.3 times higher than the corresponding data (6.6 ng L^{-1}) at Wukeng. The MeHg concentration in soil pore water collected from Gouxi was significantly higher than that for Wukeng throughout the 100 days monitoring (K-S test, $p<0.01$) suggesting different rates of net Hg methylation between the Gouxi and Wukeng sites. The concentration of $MeHg_f$ in pore water was general highest in the surface soil at Gouxi, and then sharply declined from a depth of 4 cm. However, the vertical distributions of $MeHgT_f$ in soil pore water of Wukeng showed little variation, with the exception of small (unexplained) peaks at 10 cm for ay 20 and at 6 cm for Day 60. The proportion of pore water HgT_f that was $MeHg_f$ ($MeHg_f/HgT_f$) ranged from 0.50 to 8.7 % (mean value of 2.6±1.7%) and from 0.089 to 4.8 % (mean value of 1.6±1.1%) at Gouxi and Wukeng respectively. Regression analysis revealed a significant and positive correlation between HgT_f and $MeHg_f$ at Gouxi ($r=0.75$, $p<0.001$, n=40) but not for Wukeng ($r=0.22$, $p=0.17$, n=40) (Fig. 3), suggesting a mechanistic relationship between these two Hg species at the artisanal mining site only.

Biogeosciences Discuss., doi:10.5194/bg-2015-638, 2016
Manuscript under review for journal Biogeosciences
Published: 27 January 2016

3.3.2 Mercury in soil cores

The concentration and distribution of THg as a function of depth in soil cores at Gouxi and Wukeng is shown in Fig. 4. Over the rice growing season, the mean concentrations of THg in soil was 3.2±0.75 mg kg^{-1} (0.88~4.4 mg kg^{-1}) and 38±4.8 mg kg^{-1} (27~48 mg kg^{-1}) at Gouxi and Wukeng, respectively. The THg concentration in paddy soil collected from both Wukeng and Gouxi was higher than the domestic environmental quality standard for paddy fields in China (0.5 mg kg^{-1}) (GB15618-2008), and considered non-suitable for agricultural or residential use according to the level III criterion (1.5 mg kg^{-1}) in the Chinese national standard for soil environmental quality. The THg concentration in soil cores showed no significant difference with depth although there was a nominal trend towards decreasing concentration at Gouxi. For all depths the THg concentration in soil was elevated at Wukeng relative to Gouxi, indicating a greater degree of historic contamination at Wukeng as a function of a long period of commercial mining activities.

In contrast, the MeHg concentration in soil cores showed significant variation with depth and time (Fig. 4). The MeHg concentration in soil cores at Gouxi showed a maximum value at the water-soil interface and decreased with depth for sampling from Day 20 to Day 80. For Day 100, however, there was no recorded increase in surface MeHg concentration. We believe this observation reflects active net Hg methylation in the soil surface layer at Gouxi throughout the flooded period (from Day 20 to Day 80). The MeHg concentration in Wukeng soil cores showed very little variation with depth, and the MeHg concentration at this site, for all depths, was significantly lower than at Gouxi (K-S test, $p<0.001$). Recorded MeHg concentrations at the top of the Gouxi soil profile varied from 0.76 ng g^{-1} to 6.2 ng g^{-1}, but remained relatively stable at Wukeng (range: 0.80~3.8 ng g^{-1}). Comparison of the MeHg concentration and distribution patterns between the two sites supports the hypothesis of active Hg methylation in the Gouxi soil only.

Changing redox parameters over the rice growing season may affect the process of Hg methylation. Previous studies have observed that in artificially Hg-polluted soil, the bioavailability of Hg to methylation can be significantly affected by the level of water saturation (Rothenberg and Feng, 2012; Wang et al., 2014; Peng et al., 2012). Peng et al. (2012) specified that intermittent flooding, as opposed to continuous flooding, could reduce soluble Hg concentrations and inhibit Hg methylation in the rice rhizosphere, subsequently decreasing the accumulation of MeHg in rice grain. Flooded conditions enhance anaerobic microbial activities and increase MeHg yields. Drying of a paddy field is an important cultivation step to control rice plant tillering and increase yield. Therefore, one possible reason for the considerably elevated MeHg concentrations in soil at Gouxi between Day 20 and Day 80 relative to Day 100 is an enhancement of Hg bioavailability under flooded conditions that stimulated Hg methylation, and increased the soil MeHg concentration (Wang et al., 2014). As the paddy field dried from Day 80, some degree of net MeHg degradation may have occurred. This likely contributed to a decreasing trend in soil MeHg concentration during the harvest period.

The profile of MeHg concentration with depth for the Wukeng site indicates limited MeHg production in this soil despite a significantly higher THg concentration when compared with Gouxi. The average concentration of THg in soil cores collected from Gouxi was 1 order of magnitude lower that at Wukeng, whereas the MeHg concentration in soil cores at Gouxi was significantly higher than at Wukeng (K-S test, $p<0.001$) during the rice growing season. Further comparison reveals that the average MeHg concentration in the surface soil layer (2 cm) at Gouxi was approximately 3 times higher than that at Wukeng. To explain this apparent anomaly, differences in the source and pool of Hg at each site need to be considered.

3.4 The relative contribution of different vectors to the surface pool of soil Hg

Using enriched stable isotopes, Hintelmann et al. (2002) examined the fate and relative importance of newly deposited Hg in a forest ecosystem. They showed that newly deposited Hg was mainly stored in the uppermost soil layer (<3 cm) after three months of simulative deposition, suggesting that a large fraction of newly deposited Hg is not immediately mobile. Munthe et al. (2001) observed that Hg deposited in the dissolved form is incorporated into the uppermost soil layer and is retained there. Citing this evidence we propose that Hg derived from atmospheric deposition and irrigation water (with a greater flux for Gouxi) was restricted to the surface soil layer throughout the rice growing season.

In order to access the proportional input of the various sources of Hg to paddy fields, we estimated the relative contribution of different Hg vectors (atmospheric- and irrigation-derived Hg, and native Hg) to the surface soil. We chose to select the uppermost 2 cm as the principle sink for new soil Hg (Hintelmann et al., 2002; Munthe et al., 2001). To avoid confusion in the naming of the various Hg pools, we refer to deposited Hg as 'new Hg'. Mercury already present in the soil is termed 'old Hg', which can be either of geogenic and anthropogenic origin. The current study did not attempt to distinguish between these two sources of old Hg.

We assume 1) that during the flooded period of the rice growing season, the depth of overlying water remained the same, i.e. that an equilibrium existed between irrigation and water loss; and 2) that all Hg species derived from deposition or irrigation entered into the surface layer of paddy soil and there was no loss. Using these assumptions we derived the following equations to quantify the relative contribution of different sources of Hg to the surface soil layer based on the measured Hg concentration in atmospheric deposition, irrigation water, and soil:

$$\mathrm{R_p} = \frac{\mathrm{M_p \times A \times C_p \times 10^{-3}}}{\mathrm{C_S \times W}} \quad (1)$$

$$\mathrm{R_w} = \frac{\mathrm{M_W \times A \times C_w \times 10^{-3}}}{\mathrm{C_s \times W}} \quad (2)$$

$$\mathrm{R_n} = 1 - \mathrm{R_p} + \mathrm{R_w} \quad (3)$$

where, R_p, R_w, and R_n are the relative contribution of deposition, irrigation, and native sources to the Hg content of the surface soil layer, respectively; M_p is cumulative rainfall during the rice growing season (17.76 cm); M_w is the amount of irrigation water during the rice growing season (cm); C_p and C_w are the concentration of Hg (e.g. HgT_{unf} and $MeHg_{unf}$) in deposition and irrigation water (ng L^{-1}); C_s is the concentration of Hg species (e.g. THg and MeHg) in the surface soil layer (ng g^{-1}); W is the mass of the specific surface soil layer (g); and A is the cross-sectional area of the soil core (cm^2).

The amount of the irrigation water during the rice growing season can be calculated using the following equation (Lan et al., 2010):

$$\mathrm{M_w} + \mathrm{M_p} = \mathrm{M_d} + \mathrm{M_e} + \mathrm{M_i} + \mathrm{M_t} + \mathrm{M_o} \quad (4)$$

where, M_d is water demand by rice during the rice growing season; M_e is amount of water lost by evaporation; M_i is amount of water lost by infiltration; M_t is amount of water lost water by transpiration; M_o is amount of water lost by other pathways. According to published literature, values for M_d, M_e, M_i, M_t, and M_o specific to the study area are 34 cm, 40 cm, 0.45 cm, 1.4 cm, and 0.38 cm, respectively (Lan et al., 2010).

Using equations 1-3, the relative contribution of the different sources of Hg in the soil surface layer were calculated and are presented in Table 3. The MeHg content of the surface soil attributable to atmospheric deposition (Gouxi=3.32 mg ha^{-1}; Wukeng=2.07 mg ha^{-1}) and irrigation (Gouxi=1.33 mg ha^{-1}; Wukeng=3.02 mg ha^{-1}) was orders of magnitude smaller than the amount of native MeHg already present in the paddy soil (Gouxi=508 mg ha^{-1}, Wukeng=382 mg ha^{-1}). Only 0.65% of total MeHg in the surface soil layer at Gouxi and 0.54% at Wukeng was assessed as being from atmospheric deposition, while 0.79 % of total MeHg at Wukeng and 0.26 % at Gouxi was attributed to irrigation. A similar low contribution of atmospheric deposition at irrigation water was apparent for THg. Our calculations therefore show that despite the highly elevated Hg concentration in atmospheric deposition and irrigation water, the contribution of new Hg (MeHg and THg) from external sources was small because of the relatively large pool of old Hg in soil (Dai et al., 2013). Therefore, we propose that the dominant source of MeHg to the surface soil layer is *in situ* methylation of inorganic Hg.

3.5 Source and mechanism for Hg transformation in paddy field soils

The mean concentration of HgT_{unf} in paddy water at Wukeng was 1-2 orders of magnitude higher than that at Gouxi, whereas the $MeHg_{unf}$ concentration in paddy water at Gouxi was approximately 12 times higher than that at Wukeng. Furthermore, the concentration of MeHg in paddy water at Wukeng was significantly higher than that in precipitation, but slightly lower than in irrigation water. The sampling site for the Wukeng paddy was located next to calcine piles and the proximity of this waste had a major impact on water chemistry. Both the irrigation water (pH=11±0.45) and paddy water (pH=8.6±1.3) were alkaline during the rice growing season (Table 4). We propose that the alkaline conditions of the irrigation and paddy water at Wukeng could restrain Hg methylation and/or stimulate MeHg demethylation (Rothenberg and Feng, 2012; Ullrich et al., 2001). The concentration of $MeHg_{unf}$ in paddy water at Gouxi was significantly higher than the concentration in either the precipitation or the irrigation water and this implies active Hg methylation within the Gouxi rice paddy. Both paddy water and irrigation water at Gouxi exhibit a pH that can be considered optimal for Hg methylation (Table 4), favouring net methylation in the paddy fields (Ullrich et al., 2001).

During the rice growing season, HgT_{unf} in paddy water exceeded the EPA water-quality criterion of 50 ng L^{-1} (U.S. EPA, 2000). No regulatory criterion for MeHg exists, but Rudd (1995) suggested that MeHg above a concentration of 0.1 ng L^{-1} is elevated and is likely to lead to significant MeHg bioaccumulation. During the rice growing season, photo demethylation can reduce paddy water MeHg. However, the MeHg concentration in both filtered and unfiltered paddy water samples at both sites exceeded 0.1 ng L^{-1} (Table 2), confirming that rice paddies across the Hg mining area are an exposure pathway for MeHg and may have direct implications for human and wildlife health. Previous studies have indicated that vertebrates and fish cultivated in flooded rice paddies will accumulate MeHg to critical threshold levels within 30 days (Ackerman et al., 2010a, 2010b). In rice paddy fields that combine rice and fish cultivation, potential co-exposure of MeHg through rice and fish consumption should receive more attention (Qiu et al., 2008; Feng et al., 2008; Lansing and Kremer, 2011).

Our finding that MeHg concentrations in surface soil at Gouxi were much higher than those at Wukeng indicate that newly deposited mercury can be expected to rapidly methylate after deposition. The peak concentration of MeHg in paddy soil at Gouxi, was at the soil-water interface and decreased with depth. We believe that restricted supply of newly deposited Hg to depths below the soil-water interface is a plausible explanation for the sharply reducing concentration of MeHg with depth at Gouxi; newly deposited Hg is constrained to surface soil and cannot be transferred to lower depth. However, stimulated MeHg production due to favorable geochemical conditions (pH) at Gouxi, while likely of lesser importance, cannot be excluded.

The Wukeng site has received significant historic Hg deposition as a function of large scale mining, but is not currently receiving significant inputs of fresh Hg. Atmosphere-derived mercury is physically unstable and bioavailable when it first enters the rice paddy (Hintelmann et al., 2002; Schuster, 2011). Immediate reactions of this new Hg with soil constituents are governed by adsorption-desorption interactions with soil surfaces (Schuster, 1991) which favour the retention of Hg in the surface layers of the soil profile. Over time this newly deposited Hg will be transformed into more stable, less available forms (Schuster, 1991), and the net methylation potential of this Hg will consequently decrease. The relatively low MeHg concentration in soil at Wukeng is indicative of old Hg which has become tightly bound to soil complexes over time, and is unavailable for methylation (Hintelmann et al., 2002). Our data indicates that the concentration of THg in soil is not a reliable indicator of Hg methylation potential in soil. Instead the concentration of bioavailable or new Hg must be considered, in agreement with the findings of Meng et al. (2010, 2011)

3.6 Implications of this work to environmental risk assessment

Elevated MeHg concentrations combined with an elevated MeHg% in surface soil in this work infer active Hg methylation processes are occurring in Gouxi rice paddy soil. The rate of Hg methylation is a function of an elevated concentration of Hg in atmosphere and the low pH of irrigation water/paddy water. The absence of depth-dependent variability in the MeHg concentration in soil cores at Wukeng is consistent with the low concentration of Hg in ambient air and corresponding atmospheric deposition, and high pH of the paddy water/irrigation water. The *in situ* production of MeHg in Wukeng soil, despite the elevated concentration of THg, is low. Our results demonstrate that soil is the primary source of MeHg for paddy rice, and elevated MeHg in rice pose a potential threat to wildlife and local residents. Mercury in surface soil that has been derived from atmospheric deposition is susceptible to methylation in the rice paddy ecosystem immediately after deposition. Consequently, net MeHg production is principally governed by the supply of fresh deposited Hg to soil and the pH conditions therein. The relationship between MeHg and fresh deposited Hg implies that the concentration of Hg in ambient air could be used as a monitoring tool to assess the relative risk of MeHg production in the rice paddy environment, and the possible risk to human health that may be associated with the accumulation of this MeHg in rice grain.

Acknowledgements

This research was financed by the National Key Basic Research Program of China (973 Program 2013CB430004), financed by natural science foundation of China (41173126, 41573135, 41203091, and 41473123), and also financed by natural science foundation of Guizhou (2012-2333).

References

Columbus, C.: How I Discovered America. Hispanic Press, Barcelona, 1492.

Green, R. J., Fred, U. P., and Norbert, W. P.: Things that go bump in the night, Psych. Today, 46, 345-678, 1900.

James, K., Harris, Jr., G., and Wollops, W.: American independence and magnetism, Revol. Tracts, 32, 34-55, 1776.

Phillips, T. P.: Possible influence of the magnetosphere on American history, www.sma-london.ac.uk/~phillips/magnet_infl.htm, 1999.

Smith, J. G. and Weston, H. K.: Nothing particular in this year's history, J. Oddball Res., 2, 14-15, 1954.

Ackerman, J. T. and Eagles-Smith, C. A.: Agricultural wetlands as potential hotspots for bioaccumulation: experimental evidence using caged fish, Environ. Sci. Technol., 44, 1451-1457, 2010a.

Ackerman, J. T., Miles, A. K., and Eagles-Smith, C. A.: Invertebrate mercury bioaccumulation in permanent, seasonal, and flooded rice wetlands within California's Central Valley, Sci. Total Environ., 408, 666-671, 2010b.

Dai, Z. H., Feng, X. B., Zhang, C., Wang, J. F., Jiang, T. M., Xiao, H. J., Li, Y., Wang, X., and Qiu, G. L.: Assessing anthropogenic sources of mercury in soil in Wanshan Hg mining area, Guizhou, China, Environ. Sci. Pollut. Res., 20, 7560-7569, 2013.

Feng, X. B., Li, P., Qiu, G. L., Wang, S., Li, G. H., Shang, L. H., Meng, B., Jiang, H. M., Bai, W. Y., Li, Z. G., and Fu, X. W.: Human exposure to methylmercury through rice intake in mercury mining areas, guizhou province, china, Environ. Sci. Technol., 42, 326-332, 2008.

Guo, Y. N., Feng, X. B., Li, Z. G., He, T. R., Yan, H. Y., Meng, B., Zhang, J. F., and Qiu, G. L.: Distribution and wet deposition fluxes of total and methyl mercury in Wujiang River Basin, Guizhou, China, Atmos. Environ., 42, 7096-7103, 2008.

Hintelmann, H., Harris, R., Heyes, A., Hurley, J. P., Kelly, C. A., Krabbenhoft, D. P., Lindberg, S., Rudd, J. W. M., Scott, K. J., and St. Louris, V. L.: Reactivity and Mobility of New and Old Mercury Deposition in a Boreal Forest Ecosystem during the First Year of the METAALICUS Study, Environ. Sci. Technol., 36, 5034-5040, 2002.

Horvat, M., Nolde, N., Fajon, V., Jereb, V., Logar, M., Lojen, S., Jacimovic, R., Falnoga, I., Qu, L. Y., Faganeli, J., and Drobne, D.: Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China, Sci. Total Environ., 304, 231-256, 2003.

Krisnayanti, B. D., Anderson, C. W. N., Utomo, W. H., Feng, X. B., Handayanto, E., Mudarisna, N., Ikram, H., and Khususiah.: Assessment of environmental mercury discharge at a four-year-old artisanal gold mining area on Lombok Island, Indonesia. J. Environ. Monitor., 14, 2598-2670, 2012.

Lan, X. S., Li, O., and Wu, S. Z.: Research on the balance of water demanding retion in rice field and irrigation system in central Guizhou Karst Area, Guizhou Science, 28, 76-79, 2010. (In Chinese with English abstract).

Lansing, J. S. and Kremer, J. N.: Rice, fish, and the planet. PNAS., 108, 19841-19842, 2011.

Li, P., Feng, X. B., Qiu, G. L., Shang, L. H., Wang, S. F., and Meng, B.: Atmospheric mercury emission from artisanal mercury mining in Guizhou Province, Southwestern China, Atmos. Environ., 43, 2247-2251, 2009.

Li, P., Feng, X.B., Shang, L. H., Qiu, G. L., Meng, B., Liang, P., and Zhang, H.: Mercury pollution from artisanal mercury mining in Tongren, Guizhou, China, Appl. Geochem., 23, 2055-2064, 2008.

Liang, L., Horvat, M., Cernichiari, E., Gelein, B., and Balogh, S.: Simple solvent extraction technique for elimination of matrix interferences in the determination of methylmercury in environmental and biological samples by ethylation gas chromatography cold vapor atomic fluorescence spectrometry. Talanta., 43, 1883-1888, 1996.

Liu, J. L., Feng, X. B., Qiu, G. L.; Anderson, C. W. N., and Yao, H.: Prediction of Methyl Mercury Uptake by Rice Plants (Oryza sativa L.) Using the Diffusive Gradient in Thin Films Technique, Environ. Sci. Technol., 46, 11013-11020, 2012.

Meng, B., Feng, X. B., Qiu, G. L., Cai, Y., Wang, D. Y., Li, P., Shang, L. H., Sommar, J.: Distribution patterns of inorganic mercury and methylmercury in tissues of rice (Oryza sativa L.) plants and possible bioaccumulation pathways, J. Agric. Food Chem., 58, 4951-4958, 2010.

Meng, B.: Biogeochemistry Process of Mercury in Sensitive Ecosystem and Health Risk Assessment, Southwest China. Ph.D. Dissertation, The Graduate School of the Chinese Academy of Sciences (in Chinese with English abstract), Beijing, China, 2011.

Meng, B., Feng, X. B., Qiu G. L., Liang, P., Li, P., Chen, C. X., Shang, L. H. The process of methylmercury accumulation in rice (Oryza sativa L.), Environ. Sci. Technol., 45, 2711-2717, 2011.

Meng, B., Feng, X. B.; Qiu, G. L., Anderson, C. W. N., Wang, J. X., and Zhao, L.: Localization and Speciation of Mercury in Brown Rice with Implications for Pan-Asian Public Health, Environ. Sci. Technol., 48, 7974-7981, 2014.

Meng, B., Feng, X. B., Qiu, G. L., Wang, D. Y., Liang, P., Li, P., and Shang, L. H.: Inorganic mercury accumulation in rice (Oryza sativa L.), Environ. Toxicol. Chem., 31, 2093-2098, 2012.

Meng, M., Li, B., Shao, J. J., Wang, T., He, B., Shi, J. B., Ye, Z. H., and Jiang, G. B. Accumulation of total mercury and methylmercury in rice plants collected from different mining areas in China, Environ. Pollut., 184, 179-186, 2014.

Munthe, J., Lyven, B., Parkman, H., Lee, Y. H., Iverfeldt, A., Haraldsson, C., Verta, M., and Porvari, P.: Mobility and Methylation of Mercury in Forest Soils Development of an In-Situ Stable Isotope Tracer Technique and Initial Results, Water Air Soil Pollut., 1, 385-393, 2001.

Oslo and Paris C.: JAMP guidelines for the sampling and analysis of mercury in air and precipitation; Joint Assessment and Monitoring Programme, 1-20, 1998.

Peng, X. Y., Liu, F. J., Wang, W. X., and Ye, Z. H.: Reducing total mercury and methylmercury accumulation in rice grains through water management and deliberate selection of rice cultivars, Environ. Pollut., 162, 202-208, 2012.

Qiu, G. L., Feng, X. B., Li, P., Wang, S. F., Li, G. H., Shang, L. H., and Fu, X. W.: Methylmercury accumulation in rice (Oryza sativa L.) grown at abandoned mercury mines in Guizhou, China, J. Agric. Food Chem., 56, 2465-2468, 2008.

Qiu, G. L., Feng, X. B., Wang, S. F., and Shang, L. H.: Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China, Appl. Geochem., 20, 627-638, 2005.

FAO.: Rice Information, Rome, Italy, 2002.

Rothenberg, S. E. and Feng, X. B.: Mercury cycling in a flooded rice paddy, J. Geophys. Res., 117, 2012.

Rudd, J. W. M.: Source of methyl mercury to fresh-water ecosystems- a review, Water air soil Pollut., 80, 697-713, 1995.

Schuster, E.: The behavior of mercury in the soil with special emphasis on complexation and adsorption processes - A review of the literature, Water air soil pollut., 56, 667-680, 1991.

Sunderland, E. M., Gobas, F. A. P. C., Branfireun, B. A., and Heyes, A.: Environmental controls on the speciation and distribution of mercury in coastal sediments, Mar. Chem., 102, 111-123, 2006.

U.S. EPA.: Water quality standards - establishment of numeric criteria for priority toxic pollutants for the State of California, 40 CFR part 131. http://www.epa.gov/fedrgstr/EPA-WATER/2000/May/Day-18/w11106.pdf. 2000.

U.S. EPA.: Method 1630: Methylmercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS, EPA-821-R-01-020, Washington, DC, 2001.

U.S. EPA.: Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (Revision E), EPA-821-R-02-019. Washington, DC, 2002.

Ullrich, S. M., Tanton, T. W., and Abdrashitova, S. A.: Mercury in the aquatic environment: A review of factors affecting methylation, Crit. Rev. Environ. Sci. Technol., 31, 241-293, 2001.

Wang, X., Ye, Z. H., Li, B., Huang, L. A., Meng, M., Shi, J. B., and Jiang, G. B.: Growing Rice Aerobically Markedly Decreases Mercury Accumulation by Reducing Both Hg Bioavailability and the Production of MeHg, Environ. Sci. Technol., 48, 1878-1885, 2014.

Zhang, H., Feng, X. B., Larssen, T., Shang, L. H., Li, P. Bioaccumulation of methylmercury versus inorganic mercury in rice (Oryza sativa L.) grain, Environ. Sci. Technol., 44, 4499-4504, 2010a.

Zhang, H., Feng, X. B., Larssen, T., Qiu, G. L., and Vogt, R. D.: In inland China, rice, rather than fish is the major pathway for methylmercury exposure, Environ. Health Perspect., 118, 1183-1188, 2010b.

Zheng, W.: Mercury Species in the urban air of Guiyang. Ph.D. Dissertation, The Graduate School of the Chinese Academy of Sciences (in Chinese with English abstract), Beijing, China, 2007.

Table 1. List of certified reference materials used in the present study and corresponding analytical result.

Producer	CRM	*n*	Hg speciation	Obtained value	Certified value
NIST	SRM-2710	10	THg (mg kg^{-1})	32.4±0.7	32.6±1.8
RTC	CRM024-050	10	THg (mg kg^{-1})	0.70±0.02	0.71
RTC	CRM021-100	10	THg (mg kg^{-1})	4.73±0.15	4.7
IRMM*	BCR-580	20	MeHg (mg kg^{-1})	0.070±0.007	0.075±0.004

IRMM: Institute for Reference Materials and Measurements

NIST: National Institute of Standards and Technology.

RTC: Resource Technology Corporation

Table 2. Hg in ambient air, precipitation, irrigation water, and overlying water at artisanal Hg mining site, abandoned Hg mining site, and regional background of Huaxi (mean±SD)

Sample matrix	Hg species	Artisanal Hg mining site (Gouxi)	Abandonded Hg mining Site (Wukeng)	Regional background area of Huaxi[2]
Ambient air[1]	Hg^0 (ng m^{-3})	403±388	28±13	6.2±3.0
Precipitation[1]	HgT_{unf} (ng L^{-1}) [3]	2599±1874	445±296	27±17
	$MeHg_{unf}$ (ng L^{-1}) [3]	0.48±0.20	0.30±0.15	0.28±0.14
	$MeHg_{unf}/HgT_{unf}$ (%)	0.031±0.028	0.16±0.20	0.76±0.41
Irrigation[1] water	HgT_{unf} (ng L^{-1})	159±67	513±215	7.1±4.0
	HgT_f (ng L^{-1}) [3]	39±9.4	195±45	
	$MeHg_{unf}$ (ng L^{-1})	0.75±0.65	1.7±1.1	0.14±0.044
	$MeHg_f$ (ng L^{-1}) [3]	0.31±0.30	0.96±0.50	
	$MeHg_{unf}/HgT_{unf}$ (%)	0.71±0.93	0.45±0.53	2.2±0.98
Paddy water[1]	HgT_{unf} (ng L^{-1})	189±117	430±279	7.5±4.3
	HgT_f (ng L^{-1})	105±58	196±78	
	$MeHg_{unf}$ (ng L^{-1})	13±16	1.1±0.52	0.71±0.66
	$MeHg_f$ (ng L^{-1})	4.7±4.2	0.62±0.29	
	$MeHg_{unf}/HgT_{unf}$ (%)	5.9±4.4	0.48±0.63	10±7.9

[1] Hg species concentrations in ambient air and precipitation were averaged with data sets of five sampling campaigns at Days 20, 40, 60, 80 100; Hg species concentrations in irrigation water and paddy water were averaged with data sets of four sampling campaigns at Days 20, 40, 60, 80.

[2] data were obtained from Zheng, (207), Meng et al. (2010) and Meng (2011).

[3] HgT_f unfiltered total mercury; HgT_f, filtered total mercury; $MeHg_{unf}$, unfiltered methylmercury; $MeHg_f$, filtered methylmercury;

Table 3. Contribution of Hg species derived from deposition and irrigation water to the surface soil layer at an artisanal Hg mining site and abandoned Hg mining site.

Sampling sites	Hg species in surface soil layer (0-2 cm)	Irrigation water (%)	Atmospheric deposition (%)	Native soil pool (%)
Gouxi	THg	0.06	3.7	96.24
	MeHg	0.26	0.65	99.1
Wukeng	THg	0.014	0.049	99.9
	MeHg	0.79	0.54	98.67

Table 4. General Water Quality Characteristics of irrigation water and overlying water at the artisanal Hg mining site and abandoned Hg mining site (mean±SD, range)

Sample matrix	Parameters	Artisanal Hg mining site (Gouxi)	Abandonded Hg mining Site (Wukeng)
Irrigation water (ng L^{-1})	T (^{o}C)	24±1.7 (23-26)	25±2.1 (23-27)
	pH	8.3±0.24 (8.1-8.6)	11±0.45 (11-12)
	DO (mg L^{-1})	7.4±0.43 (6.9-8.0)	7.4±0.56 (6.8-8.1)
Paddy water	T (^{o}C)	28±4.4 (24-33)	25±2.7 (23-29)
	pH	7.2±0.24 (6.9-7.4)	8.6±1.3 (7.3-9.8)
	DO (mg L^{-1})	3.0±0.95 (1.8-3.9)	4.4±0.73 (3.6-5.2)

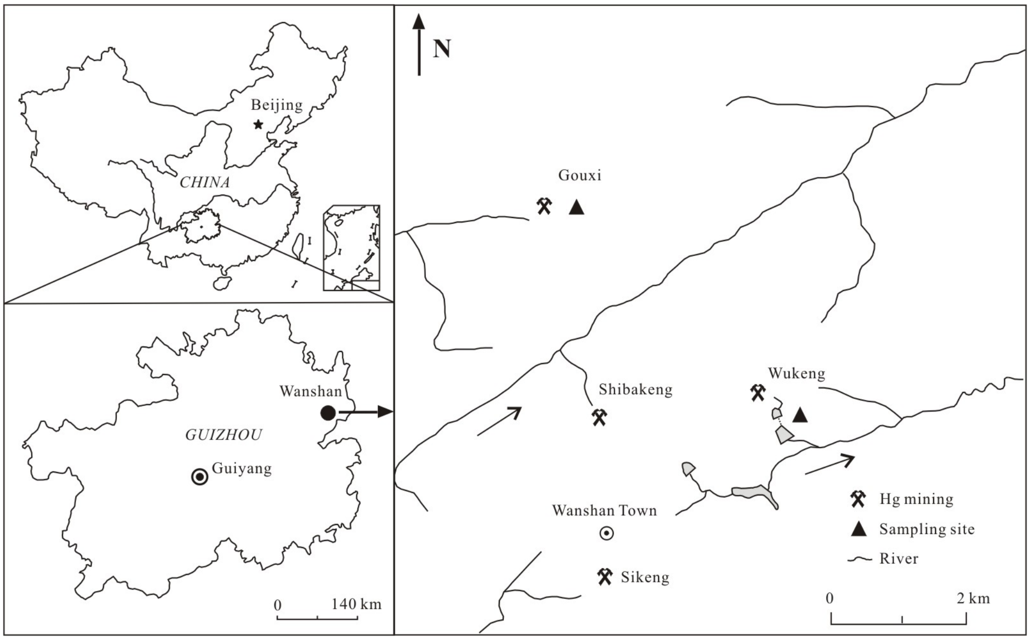

Figure 1. Map of the study area and sampling sites including abandoned Hg mining site (Wukeng) and artisanal Hg mining site (Gouxi).

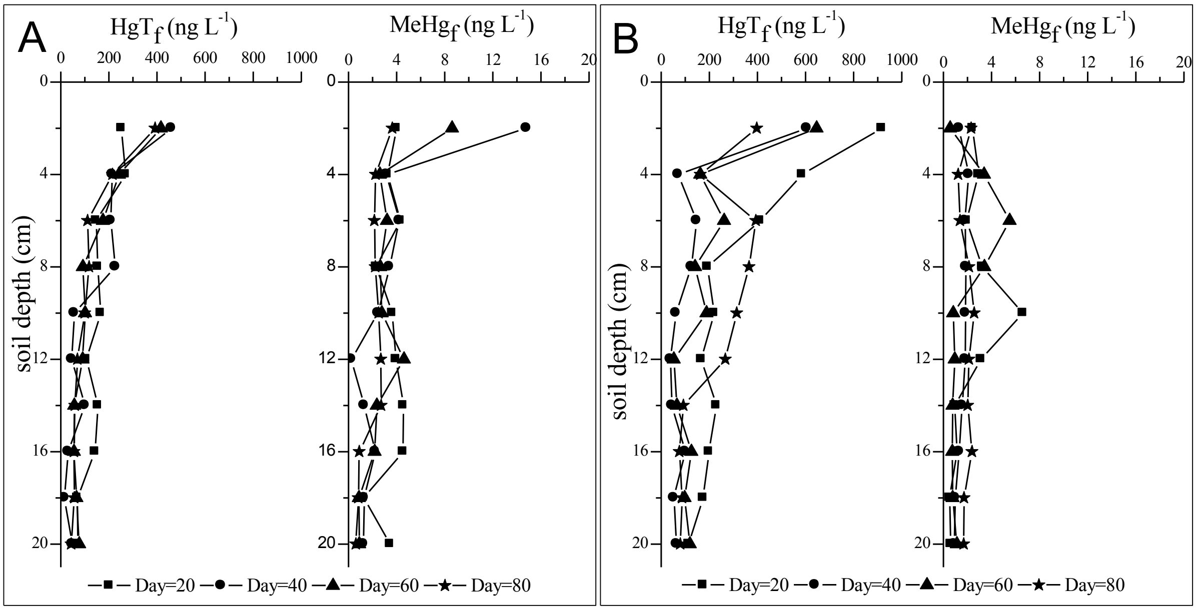

Figure 2. Concentration of HgT_f and $MeHg_f$ in pore water during the rice growing season on Days 20, 40, 60, and 80 (A: artisanal Hg mining site of Gouxi; B: abandoned Hg mining site of Wukeng).

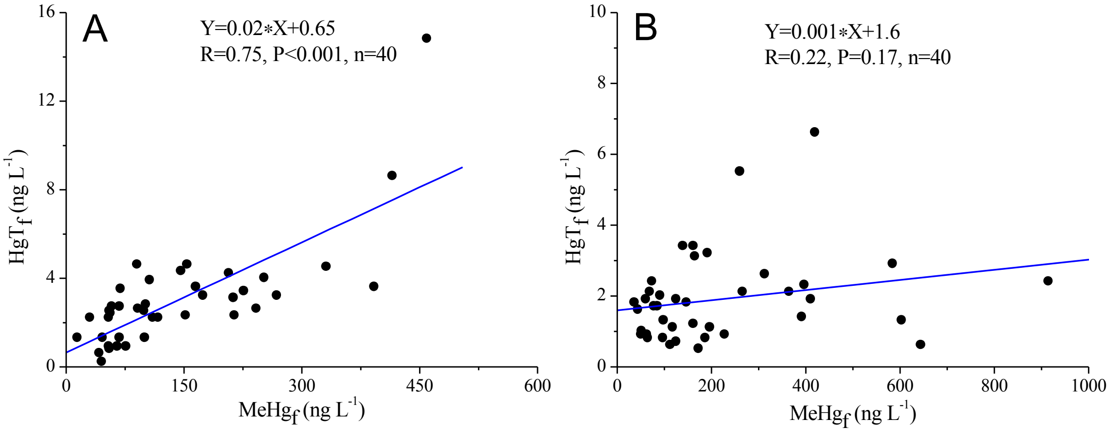

Figure 3. Correlation between HgT_f and $MeHg_f$ concentrations in soil pore water during the rice growing season on Days 20, 40, 60, and 80 (A: artisanal Hg mining site of Gouxi; B: abandoned Hg mining site of Wukeng).

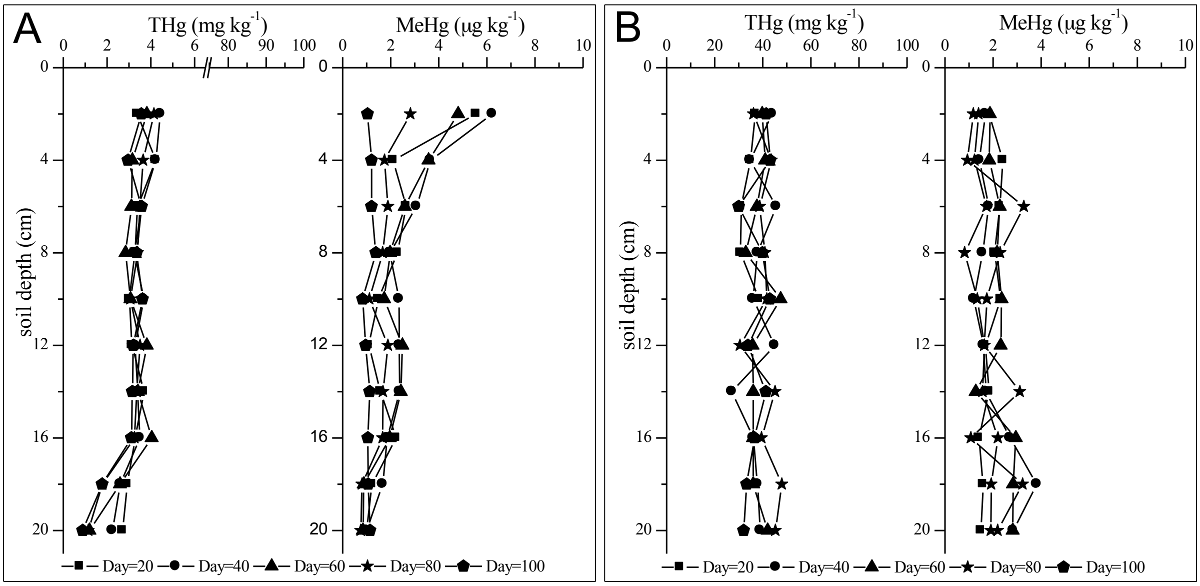

Figure 4. Concentration of THg and MeHg in soil cores during the rice growing season on Days 20, 40, 60, 80, and 100 (A: artisanal Hg mining site of Gouxi; B: abandoned Hg mining site of Wukeng).