The local impact of a coal-fired power plant on inorganic mercury and methyl-mercury distribution in rice (*Oryza sativa* L.)

Xiaohang Xu [a, b], Bo Meng [a], Chao Zhang [a, b], Xinbin Feng [a], Chunhao Gu [c], Jianyang Guo [a], Kevin Bishop [d, e], Zhidong Xu [a, b], Sensen Zhang [f], Guangle Qiu [a, *]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
[c] Department of Ecosystems Science and Management, University of Wyming, 82071, United States
[d] Department of Earth Sciences, University of Uppsala, Uppsala, Sweden
[e] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden
[f] School of Geosciences and Info-Physics, Central South University, CAS, Changsha, 410000, China

ABSTRACT

Emission from coal-fired power plants is one of the major anthropogenic sources of mercury (Hg) in the environment, because emitted Hg can be quickly deposited nearby the source, attention is paid to the effects of coal-burning facilities on levels of toxic methyl-mercury (MeHg) in biota near such sources. Since rice is an agricultural crop that can bio-accumulate MeHg, the potential effects of a large Hg-emitting coal-fired power plant in Hunan Province, China on both inorganic Hg (Hg(II)) and MeHg distributions in rice was investigated. Relatively high MeHg (up to 3.8 μg kg^{-1}) and Hg(II) (up to 22 μg kg^{-1}) concentrations were observed in rice samples collected adjacent to the plant, suggesting a potential impact of Hg emission from the coal fired power plant on the accumulation of Hg in rice in the area. Concentrations of MeHg in rice were positively correlated with soil MeHg, soil S, and gaseous elemental Hg (GEM) in ambient air. Soil MeHg was the most important factor controlling MeHg concentrations in rice. The methylation of Hg in soils may be controlled by factors such as the chemical speciation of inorganic Hg, soil S, and ambient GEM.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Mercury (Hg) is a highly toxic and non-essential element (Clarkson, 1998). Both inorganic and organic forms exist in the environment. The inorganic Hg (Hg(II)) can be transformed into methyl-mercury (MeHg), the most toxic Hg form, under certain conditions. The health risks posed by MeHg due to its bio-magnification in the aquatic food chain are well-known. Trace amounts of MeHg in water can result in much higher and harmful concentrations of MeHg in fish and their predators. The consumption of fish has been considered as the major pathway for human MeHg exposure (WHO, 1990).

Studies have recently reported that the consumption of rice rather than fish is the major pathway for human exposure to both MeHg and Hg(II) in Hg mining regions of China (Qiu et al., 2008; Zhang et al., 2010a; Li et al., 2015). Rice is a diet staple for many people around the world, with daily intake up to 0.5 kg (dry weight) for the majority of the Chinese population as well as in a number of other Asian countries (Zhang et al., 2010b; Rothenberg et al., 2014). The positive correlation, which was observed between rice MeHg intake and hair MeHg levels in residents from Hg mining areas, confirmed that the primary pathway of MeHg exposure was via rice consumption (Zhang et al., 2010a). A significant positive correlation between paired results for urine Hg concentrations and serum creatinine was observed, suggesting that renal injury may occur in local populations due to Hg(II) exposure (Li et al., 2015).

Coal-fired power plants are considered as the major anthropogenic source of atmospheric Hg around the world and currently contribute to approximately 47% of the industrial Hg emissions in China (UNEP, 2010; Yin et al., 2014; Xu et al., 2016). Although gaseous elemental Hg (GEM) emitted from power plants can be

---

transported over long distances, significant amounts of oxidized and particulate forms are deposited nearby. Thus the most highly impacted areas are in the vicinity (around 3 km) of the power plants (Carpi, 1997; Flues et al., 2002; Keeler et al., 2006). Due to China's rapidly growing economy, coal burning power plant associated Hg discharged into the atmosphere have also increased at a high speed, resulting in local Hg deposition loads in China that are 1–2 orders of magnitude higher than those found in North America and Europe (Fu et al., 2012).

Studies have revealed that atmospheric Hg deposition had a direct correlation with MeHg accumulation in aquatic food webs (Fitzgerald and Hammerschmidt, 2005; 2006; Orihel et al., 2007). Similarly, high rates of atmospheric Hg deposition leads to high MeHg in rice grains at Hg contaminated sites even when the rice grows in uncontaminated soils transported in from background areas rather than in local contaminated soil (Meng et al., 2011). Researchers also found that variations in atmospheric Hg deposition can have immediate impacts on fish Hg concentrations (Hrabik and Watras, 2002). These studies postulated that the amount of new Hg deposition to the ecosystem is an important source of bioavailable Hg(II) ready for introduction into the food web. This suggests that once the atmospheric Hg deposition near an emission source is enhanced, then a corresponding increase of MeHg in the biota could be expected.

Rice shows a strong capacity to bio-accumulate MeHg in its grains (Zhang et al., 2010b). Rice is generally cultivated in water-flooded conditions, which generate reducing conditions in soil that are conducive to net Hg(II)-methylation. MeHg in the soil and water can then be taken up by rice roots and then stored in the grains (Meng et al., 2012). In mercury mining areas, it has been shown that newly deposited mercury is easier to be converted into MeHg and then accumulated in rice (Meng et al., 2011). Nevertheless, it is not well known whether local deposition of Hg emitted from coal-fired power plants will affect absorption of Hg(II) and MeHg in rice plants. Currently in China, large numbers of paddy fields are located near coal-burning power plants (Qin et al., 2008; Xuan et al., 2004), therefore, it is of great importance to evaluate the impact of Hg emission from coal-fired power plants on both Hg(II) and MeHg accumulation in rice cultivated in the vicinity of the power plants.

China is the greatest contributor of SO_2 in the world, and coal burning power plant facilities are the biggest emission source, contributing for half of the overall SO_2 emission in 2005 (Stern, 2005; Xu, 2010). Anthropogenic S deposition rates several times higher than natural S deposition rates increase the S level in soil (Eriksson et al., 1992). As the significance of sulfate reducing bacteria (SRB) for mercury methylation procedure, increased SO_4^{2-} will do contribution to enhanced Hg(II)-methylation in lake and terrestrial ecosystems (Compeau and Bartha, 1985; Orem et al., 2011; Marvin-DiPasquale et al., 2014). Human activities can not only influence climate but also S and Hg loading to the environment (Åkerblom et al., 2013). Some researches show the availability of SO_4^{2-} for SRB and the bioavailability of inorganic Hg-sulfur compounds play a crucial role in regulating the MeHg level in mire (Skyllberg, 2008). Sulfate amendment experiments to mires indicate a positive relationship with net MeHg production (Jeremiason et al., 2006; Åkerblom et al., 2013).

The current study displayed characteristics of Hg(II) and MeHg in rice effected by S and GEM from proximity to a coal-fired power plant. We hypothesized that close proximity to a coal-fired power plant would enhanced Hg and S deposition, which will result in more S and Hg in paddy soil and subsequently enriched Hg(II) and MeHg concentrations in rice in the environment nearby a coal-fired power plant compared with the reference locations further away. However, we do not know the exact mechanism and distribution characteristics of Hg(II) and MeHg in rice in the vicinity of a coal-fired plant. This study is an initial step in testing our hypothesis and the first time the impact from power plants on nearby rice has been evaluated.

2. Experimental and materials

The Yueyang Coal-fired Power Plant (YCPP) was selected for the investigation. This is the largest coal fired power plant in Yueyang City (population 5.3 million), Hunan Province, China. With a total capacity of 2×600 MW, the YCPP is also the biggest power facility of its kind in Hunan province, China. The flue gas desulphurization (FGD) technique was employed in 2006, which typically reduces Hg emissions by 78% (Nolan et al., 2004; Zhang et al., 2008). The YCPP is adjacent to the Xiangjiang River, along which rice is cultivated. There were two other potential mercury emission sources, both located about 5 km downwind from the YCPP. The region has a humid climate of the northern subtropical monsoon, and prevailing wind direction is from the southwest. The annual average temperature is 17 °C and annual rainfall is 1300 mm.

2.1. Sample collection and preparation

In September 2011, rice grain samples were collected from 13 sites, which were divided into six separate groups according to the distances from YCPP (A:#1 and #2; B: #6 and #8; C: #3, #4, #5, and #9; D: #7 and #10; E: #11, #12; F: #13 and #14) along a northeast transect (paralleling the river) that spanned a distance of 2–15 km downwind from the YCPP (Fig. 1). Sampling density was highest closer to the plant. Each rice sample was collected in quintuplicate within an area of about 5–10 m^2 in one site. In situ, rice plants were cleaned with drinking water. After being transported to the laboratory, ultrapure water rinses, then frozen-dried steps were conducted in steps. The husk were removed from rice seeds with a pestle and mortar, and then the polished rice were crushed with a grinder (IKA-A11 basic, IKA, Germany) and sieved through a #80 mesh (size: 177 μm).

Surface soil samples from the rice paddy were co-collected with rice samples (At two sites around 3 km where rice was harvested before a sampling, only soils were collected.). Soil samples were collected quintuplicate in rhizosphere (top 0–20 cm of soil) after removing impurities (e.g. leaf, stones). At each sampling point, a final sample consisted of 3–5 subsamples collected within about 5–10 m^2 following a diagonal sampling pattern to ensure that the soil is representative of the site. Soil samples for analysis of total mercury (THg), MeHg, and selective sequential extraction were kept in polyethylene bags and frozen immediately after sample collection. The aim of the selective sequential extraction procedure is to get different phases of Hg in order to estimate the transformation and potential bioavailability of Hg in the soil (Kocman et al., 2004). In the laboratory, frozen soil samples were freeze-dried, grounded with a mortar and pestle and sieved through a #200 mesh (size: 74 μm). Briefly, bioavailable fractions of Hg were as follows: water soluble (F1: deionized water), "human stomach acid" soluble (F2: 0.01 M HCl+0.1 M CH_3COOH), and organo-chelated F3 (1 M KOH) according to Bloom et al. (2003).

At rice sampling sites, a Lumex RA-915$^+$ Portable Hg Vapor Analyzer (Lumex Ltd., Russia) was employed to obtain gaseous elemental Hg (GEM) data in ambient air. The detectable limit of Lumex RA-915$^+$ is 0.5 ng m^{-3} at a flow speed of 10 l min^{-1} (Yang et al., 2009).

2.2. Analysis

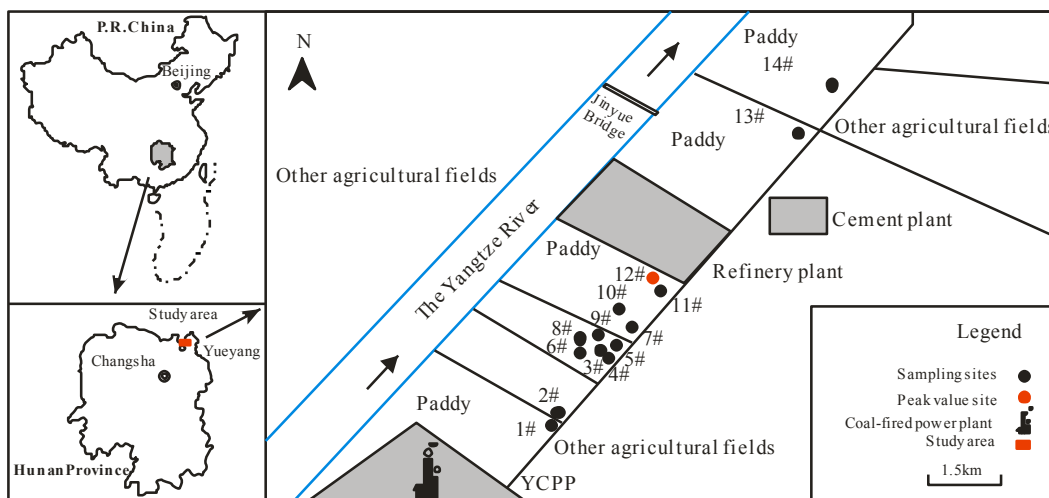For rice THg analysis, approximately 0.5–1.0 g of rice sample

Fig. 1. Map of the study area. Note the petroleum refinery and the cement plant 5 km downwind from the Yueyang Coal Power Plant (YCPP).

was digested at 95−140 °C with a mixture of HNO_3 and H_2SO_4 (4:1, v/v). Rice samples were measured using cold vapor atomic fluorescence spectroscopy (CVAFS) in accordance with Method 1631E (USEPA, 2002). For rice MeHg determination, approximately 0.2−0.5 g rice sample was weighed for digestion using 25% KOH-methanol at 75−80 °C for 3 h. Then MeHg in rice samples was leached with dichloromethane (CH_2Cl_2) and back-extracted into water phase for determination based on Method 1630 (USEPA, 2001; Liang et al., 1996). The inorganic Hg (Hg(II)) of rice discussed below was defined by the subtraction of MeHg from THg (Lin et al., 2008; Shi et al., 2005a,b).

For soil THg measurement, about 0.1−0.3 g of sample was heated at 95 °C for 30 min using water bath in a mixed solution of HCl and HNO_3 (3:1, v/v). Then an appropriate amount of digestive soil solution was determined using cold-vapor atomic absorption spectrometry (CVAAS), with a detection limit of 0.01 μg kg^{-1} (Feng et al., 2007; Qiu et al., 2008). The bio-geochemically relevant fractionations of THg were determined similar to total Hg analysis. For soil MeHg determination, about 0.2−0.5 g soil sample was extracted with CH_2Cl_2 after HNO_3 leaching (Liang et al., 1996). Then a proper amount of digestive solution was used for determination by GC-CVAFS according to Method 1630 (USEPA, 2001).

Soil total sulfur (S) was measured by an Elementar vario macro cube (Zhou et al., 2013). Duplicated measurements for S were performed and the accepted variation of 3 replicated measurements was below 5%. Standard samples were measured in every 10 samples with recoveries in the range of 95%−105% using AR-4018 as the soil S standard.

In all sample analyses, QA/QC of THg and MeHg were executed using duplicates, method blanks, matrix spikes and standard reference materials (GBW07405; BCR 580; TORT-2). In rice duplicate samples, the relative percentage difference for THg and MeHg were <9.8% and <16.5%, respectively. In rice samples, recoveries from matrix spikes ranged from 104 to 116% for THg and 72−99% for MeHg. TORT-2 certified material was measured for MeHg and the average MeHg value (151 ± 7.1 μg kg^{-1}, n = 5) obtained was consistent with the certified concentration (152 ± 13 μg kg^{-1}). In rice, the method detection limits for THg and MeHg were 0.013 μg kg^{-1} and 0.003 μg kg^{-1}, respectively.

In soil sample duplicates, the relative percentage difference for THg and MeHg were <8.7% and <18.6%, separately. For THg in soil, certified material (GBW07405) measured, and the average THg concentration (0.30 ± 0.01 mg kg^{-1}, n = 5) observed was

compatible with the certified value (0.29 ± 0.04 mg kg^{-1}). In the soil samples, matrix spike recoveries varied from 92% to 107% for THg and 87%−109% for MeHg. BCR 580 reference material was determined for soil MeHg, and the achieved MeHg value (76 ± 6 μg kg^{-1}, n = 5) was compatible with the certified value (75 ± 4 μg kg^{-1}). The detection limits for THg and MeHg were 0.01 μg kg^{-1} and 0.002 μg kg^{-1} in soil, respectively.

2.3. Calculations & statistics

All error terms reported reflect standard deviations. Pearson correlation statistics were run and the Pearson correlation statistic (r) is reported. P values associated with correlations <0.05 are deemed to be significant. Rice Hg(II) ratio was calculated by the ratio of Hg(II)/THg in rice, meanwhile, rice MeHg ratio was obtained by the ration of MeHg/THg in rice. Soil BF represents biogeochemical Hg fractions (F1+F2+F3) in soil.

3. Results

3.1. MeHg and Hg(II) in rice

In rice samples, MeHg concentrations varied from 1.7 to 3.8 μg kg^{-1} with a mean of 2.4 ± 0.72 μg kg^{-1} (n = 13). The maximum MeHg concentrations in rice were observed at the sites 1.5 km and 5 km from the YCPP (Fig. 2). The correlation between rice MeHg concentrations and distance from the YCPP was not significant (r = 0.56, p < 0.5), even if there is a positive tendency.
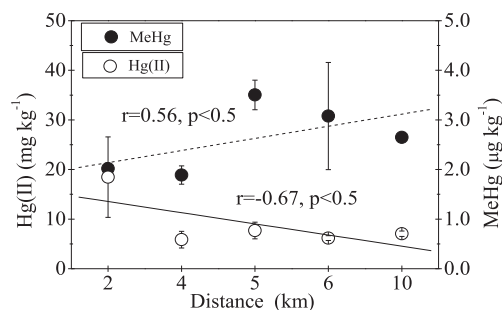

Fig. 2. Distribution of Hg(II) and MeHg concentrations in rice with distance from the Yueyang Coal Power Plant (YCPP).

In rice samples, Hg(II) concentrations varied from 2.0 to 22 µg kg^{-1} with an mean value of 5.7 µg kg^{-1} (n = 13). Hg(II) contents in rice samples from current study were higher than the mean of 3.3 µg kg^{-1} with a range of 2.0–5.8 µg kg^{-1} in a control site reported by Meng and coauthors (2010). The maximum value of Hg(II) concentration was observed in the sample collected at a distance of 1.5 km from the YCPP. The THg concentration of this sample (24 µg kg^{-1}) exceeded the Chinese national standard limitation of 20 µg kg^{-1} for THg in cereal foods (GB2762-2012).

3.2. Total Hg and MeHg in soil

In soil samples, the THg varied from 68 to 220 µg kg^{-1}, with a mean value of 130 ± 40 µg kg^{-1} (n = 14) (Fig. 3). Peak concentrations of THg in soil were observed at sites approximately 5 km and 6 km downwind, indicating that impacts may be from both the YCPP, as well as the petroleum refinery and/or the cement plant. Except for the highest concentration observed at approximately 5 km from the YCPP, THg concentrations of all the soil samples were below in agricultural soil standard (THg: 200 µg kg^{-1}) issued by the Chinese Government.

The MeHg in soil samples ranged from 0.30 to 3.5 µg kg^{-1} with an average of 1.6 ± 1.0 µg kg^{-1} (n = 14). In soils, peak concentrations of MeHg exhibited a pattern similar to that for THg concentrations. The higher values of soil MeHg were observed at the two sites which are 5 km and 10 km away from the YCPP.

3.3. Potential factors controlling MeHg distribution in rice

3.3.1. Soil Hg

MeHg concentrations in rice have strong positive correlations with both soil MeHg (r = 0.68, p < 0.01) and soil THg (r = 0.66, p < 0.05). Rice MeHg was positively correlated with biogeochemical fractions (BF) = water soluble (F1) + "human stomach acid" soluble (F2) + organo-chelated soluble (F3) (r = 0.74, p < 0.005) in soil. Rice MeHg has no obvious correlation with water soluble (F1) and "human stomach acid" soluble (F2), however, a positive correlation with organo-chelated soluble (F3) (r = 0.70, p < 0.05). Meanwhile, rice MeHg has a weak positive correlation with soil MeHg ratio (Fig. 4).

3.3.2. Soil S

Sulfur concentrations in soil varied from 0.11% to 0.56% with an average of 0.30%, were positively correlated with rice MeHg (r = 0.56, p < 0.05) as well as MeHg ratio (r = 0.68, p < 0.01) (Fig. 5). Surprisingly, the S content of soil was inversely correlated with concentrations of rice Hg(II) (r = −0.54, p < 0.05) and rice Hg(II) ratio (r = −0.68, p < 0.01).
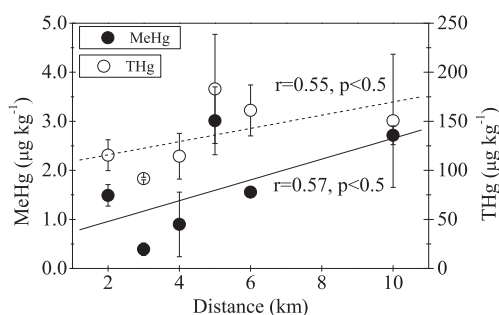
3.3.3. Gaseous elemental mercury

GEM concentrations observed ranged from 21 to 39 ng m^{-3} with an average of 28 ± 4.4 ng m^{-3}. Generally, the GEM demonstrated a decrease trend with the increase of distance, however, there existed a peak value around 5 km. GEM in ambient air was positively correlated to rice MeHg (r = 0.73, p < 0.005). Significant positive correlations between GEM and soil BF (r = 0.68, p < 0.05) as well as soil S (r = 0.52, p = 0.054) were observed (Fig. 6).

4. Discussions

4.1. MeHg and Hg(II) in rice

The highest concentrations of rice MeHg were obtained 5 km away from the YCPP. Both the petroleum refinery and cement plant are located in this vicinity and may be contributing to MeHg accumulation in rice. The highest Hg(II) concentration in rice was obtained near 2 km from the YCPP (Fig. 2), and the concentrations of Hg(II) decline sharply then remained steady with distance from YCPP. There was however, slightly more Hg(II) in the site near the refinery and cement factories than further away. There existed a positive related relation between soil Hg(II) and rice MeHg (Fig. 7), which indicates that Hg(II) in soil can affect rice MeHg substantially. This suggests that the YCPP contributes most of the Hg(II) deposition, while the refinery and cement factory might also contribute some Hg deposition in the area, and the near-source deposition substantially affects MeHg accumulation in local rice plants. Furthermore, the high GEM concentrations in ambient air observed in the region should be related to Hg emission from the coal fired power plants, which will cause high deposition rates of atmospheric Hg that could be an explanation for the increase of MeHg in rice nearby the coal fired power plant. With the Hg emission from YCPP, inorganic sulfur from refinery plant and cement plant simulate the MeHg production process in anaerobic microbes, like sulfate reducing bacteria (SRB) in soil can transform Hg(II) to MeHg in soil (Trust and Fry, 1992; Barton and Hamilton, 2007; Schuhmacher et al., 2004). This MeHg is then taken up into rice through the roots (Meng et al., 2011) (cf. Section 3.3).

Previous studies indicated that Hg(II) concentrations in plants largely depend on GEM in the atmosphere and the above-ground parts of plants accumulating Hg from the atmosphere (Ericksen et al., 2003; Fay and Gustin, 2007; Stamenkovic and Gustin, 2009; Meng et al., 2011). In rice, the highest concentration of Hg(II) might be mostly attributed to high air Hg emitted from the YCPP facility. Hence, the enhanced rice Hg(II) found nearby the YCPP was consistent with the hypothesis that the activity of the coal burning could result in nearby rice Hg(II) contamination.

The highest value of Hg(II), found in rice samples adjacent to the YCPP, was not consistent with the observed MeHg in rice. We also found that levels of Hg(II) in rice grains were negatively correlated to distances from the YCPP (r = −0.67, p < 0.5). These relationships suggested that near-source deposition of Hg emission from the YCPP had significantly higher localized impacts on rice Hg(II) compared to that on MeHg. A potential explanation for the difference between rice Hg(II) and MeHg might be that the pathway of Hg(II) entry into rice plants differs from that by which MeHg enters into rice plants. Meng et al. (2010, 2012) reported that rice Hg(II) generally assimilated via atmospheric Hg while MeHg in rice is absorbed from the soil. Another alternative explanation is that other environmental parameters, such as sulfur-dioxide emitted from power plant, that is then converted to sulfate, can affect the processing of Hg(II)-methylation in paddy soils, thus influencing rice MeHg absorption and accumulation (Gilmour et al., 1992; Branfireun et al., 1999; Jeremiason et al., 2006; Åkerblom et al., 2013).
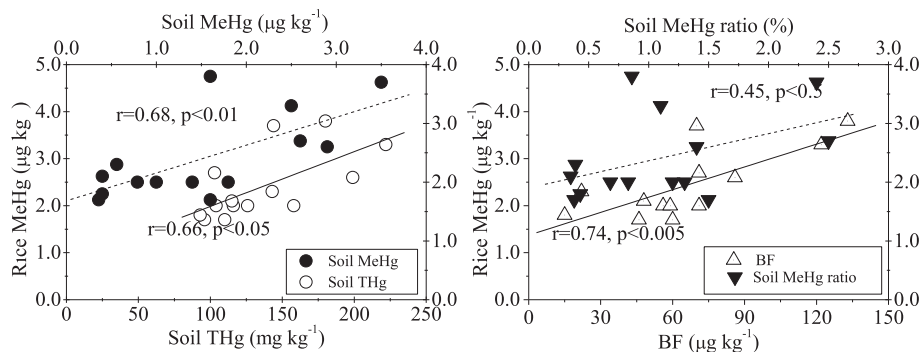

Fig. 3. Distribution of MeHg and THg concentrations in soil with distance from the YCPP.

Fig. 4. The concentrations of rice MeHg versus soil THg, soil MeHg, biogeochemical fractions (BF) = water soluble (F1) + "human stomach acid" soluble (F2) + organo-chelated soluble (F3), as well as the soil MeHg ratio.
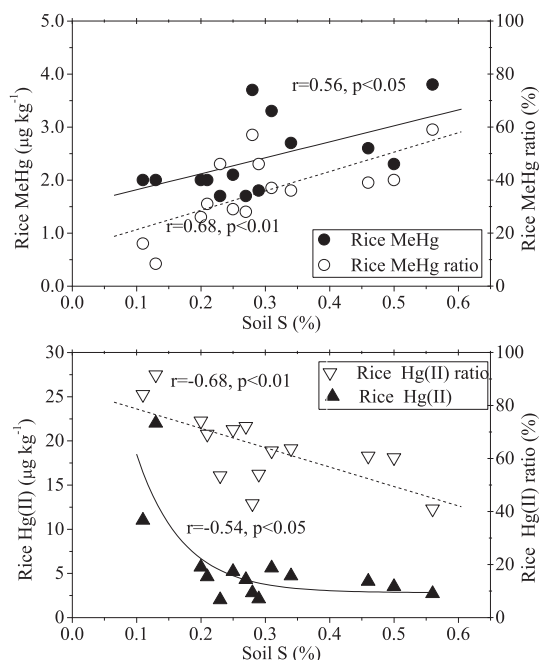

Fig. 5. The concentrations of soil S versus rice MeHg, rice MeHg ratio, rice Hg(II), and rice Hg(II) ratio.
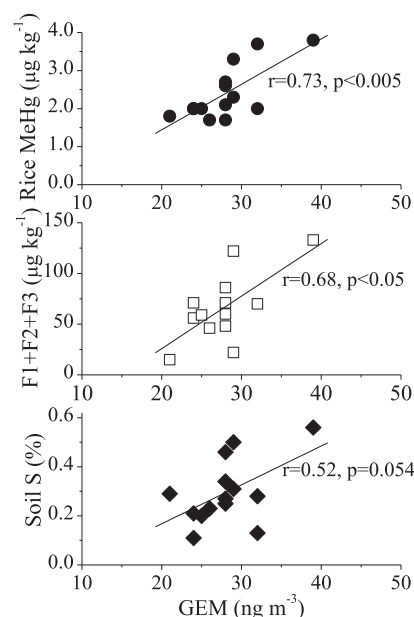

Fig. 6. The concentrations of GEM in ambient air versus soil S, biogeochemical fractions, and rice MeHg.

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) established the provisional tolerable weekly intake (PTWI) for Hg(II) of 4 µg kg^{-1} body weight (bw) instead of 5 µg kg^{-1} for total Hg (THg), and 1.6 µg kg^{-1} bw for MeHg, according to an evaluation results from a variety of epidemiological studies focused on and developmental neurotoxicity fish-eating populations (JECFA, 2010). A daily adult intake of MeHg through rice can cause up to 1.8 µg kg^{-1} bw MeHg (Qiu et al., 2008). Since rice does not contain the docosahexaenoic acid (DHA, an omega-3 long chain poly-unsaturated fatty acid), arachidonic acid (an omega-6), and iodine as does fish, which can promote neural development (Budtz-Jørgensen et al., 2007; Jacobson et al., 2008), there is all the more reason to scrutinize anthropogenic impacts on MeHg in rice as a staple food.

In the current study, MeHg concentrations in rice samples in current study had no statistically significant difference with the average background concentration of 2.9 ± 1.0 µg kg^{-1} for MeHg obtained from a control site (Meng et al., 2010). This confirms that the coal-fired power plant did not lead to serious MeHg accumulation in rice in the area. However, as the IHg in rice suggest YCPP is
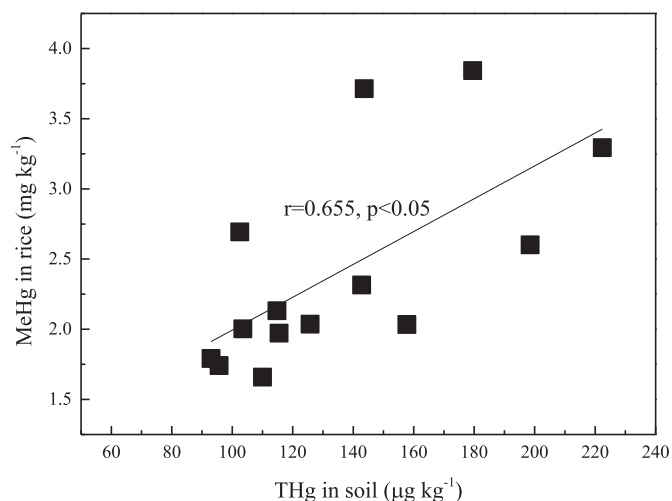

Fig. 7. The correlations between rice MeHg and soil THg.

the main GEM source, though lower than results obtained around 5 km, 6 km, and 10 km, a peak value of MeHg concentration in the rice cultivated nearest to the YCPP, and a decrease trend at first two groups. The refinery plant and cement can release inorganic sulfur, which can improve the MeHg production in low IHg condition (Trust and Fry, 1992; Schuhmacher et al., 2004; Åkerblom et al., 2013). This phenomenon demonstrated that Hg emission from the coal-fired power plant does have an impact on MeHg accumulation in rice.

4.2. Total Hg and MeHg in soil

In this research, THg in all the soil samples did not exceed the PEC, compared with the probable effect concentration (PEC) of 1.06 mg kg^{-1} (MacDonald et al., 2000), implying no harmful effects to organisms dwelling in the paddy soil.

Different Hg fractions showed different ratios to THg. The average ratio of different Hg fractions to THg in the soils presented a sequences of F3(42%) > F2(2.85%) >F1(1.77%). For F1, the ratios ranged from 0.59% to 4%. For F2, the ratios varied from 0.93% to 8.7%. For F3, the ratios ranged from 7% to 61%, and the highest F3 obtained in the nearest site to YCPP. The highest MeHg value of 3.5 μg kg^{-1} (which comprised 2.4% of THg in that soil) came from the sample site approximately 5 km from YCPP. This could reflect influences from the petroleum refinery and the cement plant as well as the YCPP. Water soluble (F1) mercury has high environmental risk, which can be absorbed by plants directly (Shi et al., 2005a,b; Issaro et al., 2009). "Stomach acid" soluble (F2) can represent the bioavailability of Hg inside of organisms (Bloom et al., 2003). MeHg appears largely in the F3 fraction (Bloom et al., 2003), and MeHg had a remarkable positive correlation with F3 fraction (r = 0.59, p < 0.05). Although the MeHg contents in soil are lower than Hg(II) data, however, what is noteworthy that it is easily accumulated and of high bioavailability in rice (Meng et al., 2010).

4.3. Potential factors controlling MeHg distribution in rice

Generally, the coal-fired power plants are the largest sulfur dioxide (SO$_2$) emitter to the atmosphere, hence resulting in enhanced levels of sulfate (SO$_4^{2-}$) deposition, which may stimulate SRB activity and influence net MeHg production in aquatic systems (Branfireun et al., 1999; Jeremiason et al., 2006; Rothenberg and Feng, 2012). Previous studies also verify that Hg binds strongly to S containing thiols (Xia et al., 1999; Skyllberg et al., 2000; Hesterberg et al., 2001; Khwaja et al., 2006; Skyllberg, 2008). In present research, the content of S and THg as well as MeHg exhibited positive correlations in soils. Hence SO$_4^{2-}$ deposition could be considered as a possible factor controlling net MeHg production in the present study. Xiang (2011) found 13–21 kg S ha^{-1} yr^{-1} deposited into the nearby areas in Hunan Province, which might be responsible for elevated MeHg in rice.

When the content of total S were higher than 0.2%, fairly low concentrations of Hg(II) accumulation were consistently observed in the rice samples. Studies indicated that above-ground parts of rice uptake Hg(II) mainly from atmospheric Hg (Ericksen et al., 2003; Fay and Gustin, 2007), however, they obtain MeHg from soil MeHg (Meng et al., 2010, 2011). Soil S concentrations were negatively correlated with Hg(II) concentration in grain samples. This may be due to the conversion of atmospherically derived sulfate to more reduces S forms (e.g. sulfide and organic associated thiols), which strongly bind Hg(II) (Skyllberg, 2008) and may thereby limit Hg(II) uptake from soil into rice. Although, the S concentrations show positive correlations with rice MeHg contents, these results indicate that S may also act a crucial role in restricting the bio-accessibility, uptake, and transportation of the Hg(II) in rice.

This phenomenon may be attributed to the production of Hg-S insoluble compounds in the paddy soil.

The measured values of GEM at sampling sites were more elevated than those monitored in urban regions, such as Guiyang, Chongqing, Changchun, and Guangzhou, which were 10.54 ± 10.26 ng m^{-3}, 6.74 ± 0.37 ng m^{-3}, 18.4 ng m^{-3}, and 4.86 ± 1.36 ng m^{-3}, respectively (Fang et al., 2004; Feng et al., 2004; Yang et al., 2009; Liu et al., 2011, 2012). Compared to GEM in rural areas in the range of 1.6–4.0 ng m^{-3} (Wan et al., 2009; Fu et al., 2012), the average GEM concentration was 10–20 times higher.

We also found weakly positively correlations between GEM and soil THg and MeHg. Most previous studies have revealed that Hg(II) in aboveground biomass is from air (Ericksen et al., 2003; Meng et al., 2010), however, no strong correlations were found in previous studies of the relationship between GEM and rice Hg(II) (Meng et al., 2012; Zhang et al., 2010a). In the aboveground parts of plants, Hg uptake generally occurs at concentrations above a critical atmospheric concentration or compensation point, which was reported to range from about 10 to 25 ng m^{-3} for tree seedlings (Hanson et al., 1995). In this study, the high concentrations of GEM with an average value just around the range of compensation point would be the most plausible explanation for the absence of impacts on rice Hg(II).

Owing to the considerable amounts of oxidated and particulate Hg emitted from coal-fired power plants (Tang et al., 2007; Wang et al., 2010; Wu et al., 2012) and their rapid local deposition rates (Keeler et al., 2006), sampling sites close to coal-fired power plants are easier to undergo higher atmospheric Hg deposition than ecosystems farther away. These elevated Hg deposition rates could lead to elevated MeHg uptake from soil in rice, since newly deposited Hg is more easily converted to MeHg (Meng et al., 2010, 2012). This means that levels of GEM in ambient air plays an important role for Hg deposition, which in turn promotes rice MeHg accumulation. This could be the best explanation for high levels of GEM correlating to high rice MeHg (Fig. 5). Although the rice was slightly polluted in the study area, the GEM concentrations were extraordinarily high; indicating that the amount of Hg discharged from ambient industrial effluents was also likely very high. This also indicates that there exists Hg contamination risk for rice in areas with high GEM levels due to the industrialization in China.

5. Conclusions

This study demonstrates that the Hg emissions from coal-fired power plants can increase both the Hg(II) and MeHg of rice. Positive correlations of rice MeHg with soil Hg species, soil S, and GEM were observed. Furthermore, we also found indications that other facilities significantly contributed to the MeHg production in the soil. The ambient air GEM and soil S both enhanced MeHg levels in rice. Nevertheless, soil S was also negatively correlated to rice uptake of Hg(II) from soil. Since the amount of rice samples in this study was limited by the limited rice planting in the study area, more comprehensive sampling in space and time around other major coal plants would be of value.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.11.042

References

Åkerblom, S., Bishop, K., Björn, E., Lambertsson, L., Eriksson, T., Nilsson, M.B., 2013. Significant interaction effects from sulfate deposition and climate on sulfur concentrations constitute major controls on methylmercury production in peatlands. Geochimica Cosmochimica Acta 102, 1–11.

Barton, L.L., Hamilton, W.A. (Eds.), 2007. Sulphate-reducing Bacteria: Environmental and Engineered Systems. Cambridge University Press.

Bloom, N.S., Preus, E., Katon, J., Hiltner, M., 2003. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. Anal. Chim. Acta 479 (2), 233–248.

Branfireun, B.A., Roulet, N.T., Kelly, C., Rudd, J.W., 1999. In situ sulphate stimulation of mercury methylation in a boreal peatland: toward a link between acid rain and methylmercury contamination in remote environments. Glob. Biogeochem. Cycles 13 (3), 743–750.

Budtz-Jørgensen, E., Grandjean, P., Weihe, P., 2007. Separation of risks and benefits of seafood intake. Environ. Health Perspect. 323–327.

Carpi, A., 1997. Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. Water, Air, Soil Pollut. 98 (3–4), 241–254.

Clarkson, T.W., 1998. Human toxicology of mercury. J. Trace Elem. Exp. Med. 11 (2–3), 303–317.

Compeau, G.C., Bartha, R., 1985. Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Appl. Environ. Microbiol. 50 (2), 498–502.

Ericksen, J.A., Gustin, M.S., Schorran, D.E., Johnson, D.W., Lindberg, S.E., Coleman, J.S., 2003. Accumulation of atmospheric mercury in forest foliage. Atmos. Environ. 37 (12), 1613–1622.

Eriksson, E., Karltun, E., Lundmark, J.E., 1992. Acidification of forest soils in Sweden. Ambio 21, 150–154.

Fang, F., Wang, Q., Li, J., 2004. Urban environmental mercury in Changchun, a metropolitan city in Northeastern China: source, cycle, and fate. Sci. Total Environ. 330 (1), 159–170.

Fay, L., Gustin, M., 2007. Assessing the influence of different atmospheric and soil mercury concentrations on foliar mercury concentrations in a controlled environment. Water, Air, Soil Pollut. 181 (1–4), 373–384.

Feng, X., Shang, L., Wang, S., Tang, S., Zheng, W., 2004. Temporal variation of total gaseous mercury in the air of Guiyang, China. J. Geophys. Res. Atmos. 109 (D3).

Feng, X., Li, P., Qiu, G., Wang, S., Li, G., Shang, L., Meng, B., Jiang, H., Bai, W., Li, Z., Fu, X., 2007. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou Province, China. Environ. Sci. Technol. 42 (1), 326–332.

Fitzgerald, W.F., Hammerschmidt, C.R., 2005. Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. Environ. Sci. Technol. (9), 3034–3039.

Flues, M., Moraes, V., Mazzilli, B.P., 2002. The influence of a coal-fired power plant operation on radionuclide concentrations in soil. J. Environ. Radioact. 63 (3), 285–294.

Fu, X., Feng, X., Sommar, J., Wang, S., 2012. A review of studies on atmospheric mercury in China. Sci. Total Environ. 421, 73–81.

GB2762-2012, 2012. National Safety Standards for Foods and Maximum Levels of Contaminant in Foods. Ministry of Health of the People's Republic of China.

Gilmour, C.C., Henry, E.A., Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environ. Sci. Technol. 26 (11), 2281–2287.

Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury in freshwater fish linked to atmospheric mercury deposition. Environ. Sci. Technol. 40 (24), 7764–7770.

Hanson, P.J., Lindberg, S.E., Tabberer, T.A., Owens, J.A., Kim, K.H., 1995. Foliar exchange of mercury vapor: evidence for a compensation point. Water, Air, Soil Pollut. 80 (1–4), 373–382.

Hesterberg, D., Chou, J.W., Hutchison, K.J., Sayers, D.E., 2001. Bonding of Hg (II) to reduced organic sulfur in humic acid as affected by S/Hg ratio. Environ. Sci. Technol. 35 (13), 2741–2745.

Hrabik, T.R., Watras, C.J., 2002. Recent declines in mercury concentration in a freshwater fishery: isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. Sci. Total Environ. 297 (1), 229–237.

Issaro, N., Abi-Ghanem, C., Bermond, A., 2009. Fractionation studies of mercury in soils and sediments: a review of the chemical reagents used for mercury extraction. Anal. Chim. Acta 631 (1), 1–12.

Jacobson, J.L., Jacobson, S.W., Muckle, G., Kaplan-Estrin, M., Ayotte, P., Dewailly, E., 2008. Beneficial effects of a polyunsaturated fatty acid on infant development: evidence from the Inuit of Arctic Quebec. J. Pediatr. 152 (3), 356–364.

JECFA. (2010). Joint FAO/WHO Food Standards Programme, Committee of the Codex Alimentarius Commission, Thirty-third Session. Availiable: http://www.fsis.usda.gov/PDF/2010-CAC/cac33_15e.pdf [accessed 20 July 2010].

Jeremiason, J.D., Engstrom, D.R., Swain, E.B., Nater, E.A., Johnson, B.M., Almendinger, J.E., Monson, B.A., Kolka, R.K., 2006. Sulfate addition increases methylmercury production in an experimental wetland. Environ. Sci. Technol.

40 (12), 3800–3806.

Keeler, G.J., Landis, M.S., Norris, G.A., Christianson, E.M., Dvonch, J.T., 2006. Sources of mercury wet deposition in eastern Ohio, USA. Environ. Sci. Technol. 40 (19), 5874–5881.

Khwaja, A.R., Bloom, P.R., Brezonik, P.L., 2006. Binding constants of divalent mercury (Hg^{2+}) in soil humic acids and soil organic matter. Environ. Sci. Technol. 40 (3), 844–849.

Kocman, D., Horvat, M., Kotnik, J., 2004. Mercury fractionation in contaminated soils from the Idrija mercury mine region. J. Environ. Monit. 6 (8), 696–703.

Li, P., Du, B., Chan, H., Feng, X., 2015. Human inorganic mercury exposure, renal effects and possible pathways in Wanshan mercury mining area, China. Environ. Res. 140, 198–204.

Liang, L., Horvat, M., Cernichiari, E., Gelein, B., Balogh, S., 1996. 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 (11), 1883–1888.

Lin, L., Chang, L., Jiang, S., 2008. Speciation analysis of mercury in cereals by liquid chromatography chemical vapour generation inductively coupled plasma-mass spectrometry. J. Agric. Food Chem. 56 (16), 6868–6872.

Liu, N., Qiu, G., Landis, M.S., Feng, X., Fu, X., Shang, L., 2011. Atmospheric mercury species measured in Guiyang, Guizhou province, southwest China. Atmos. Res. 100 (1), 93–102.

Liu, M., Chen, L., Tao, J., Xu, Z., Zhu, L., Qian, D., Fan, R., 2012. Seasonal and diurnal variation of total gaseous mercury in Guangzhou City. China Environ. Sci. 32 (9), 1554–1558 ([In Chinese with English abstract]).

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives Environ. Contam. Toxicol. 39 (1), 20–31.

Marvin-DiPasquale, M., Windham-Myers, L., Agee, J.L., Kakouros, E., Kieu, L.H., Fleck, J.A., Alpers, C.A., Stricker, C.A., 2014. Methylmercury production in sediment from agricultural and non-agricultural wetlands in the Yolo Bypass, California, U. S. A. Sci. Total Environ. 484, 288–299.

Meng, B., Feng, X., Qiu, G., Cai, Y., Wang, D., Li, P., Shang, L., Sommar, J., 2010. Distribution patterns of inorganic mercury and methylmercury in tissues of rice (Oryza sativa L.) plants and possible bioaccumulation pathways. J. Agric. Food Chem. 58 (8), 4951–4958.

Meng, B., Feng, X., Qiu, G., Liang, P., Li, P., Chen, C., Shang, L., 2011. The process of methylmercury accumulation in rice (Oryza sativa L.). Environ. Sci. Technol. 45 (7), 2711–2717.

Meng, B., Feng, X., Qiu, G., Wang, D., Liang, P., Li, P., Shang, L., 2012. Inorganic mercury accumulation in rice (Oryza sativa L.). Environ. Toxicol. Chem. 31 (9), 2093–2098.

Nolan, P., Redinger, K., Amrhein, G., Kudlac, G., 2004. Demonstration of additive use for enhanced mercury emissions control in wet FGD systems. Fuel Process. Technol. 85 (6), 587–600.

Orem, W., Gilmour, C., Axelrad, D., Krabbenhoft, D., Scheidt, D., Kalla, P., McCormick, P., Gabriel, M., Aiken, G., 2011. Sulfur in the South Florida ecosystem: distribution, sources, biogeochemistry, impacts, and management for restoration. Crit. Rev. Environ. Sci. Technol. 41 (S1), 249–288.

Orihel, D., Paterson, M., Blanchfield, P., Bodaly, R., Hintelmann, H., 2007. Experimental evidence of a linear relationship between inorganic mercury loading and methylmercury accumulation by aquatic biota. Environ. Sci. Technol. 41 (14), 4952–4958.

Qin, P., Xiao, G., Luo, C., Zhang, F., Wang, B., 2008. Study on the application amount of desulfurized gypsum from coal-fired power plant in improving alkalized soil to plant sweet sorghum. Mod. Agric. Sci. 12, 013.

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

Rothenberg, S.E., Feng, X., 2012. Mercury cycling in a flooded rice paddy. J. Geophys. Res. Biogeosci. 117 (G3).

Rothenberg, S.E., Windham-Myers, L., Creswell, J.E., 2014. Rice methylmercury exposure and mitigation: a comprehensive review. Environ. Res. 133, 407–423.

Schuhmacher, M., Domingo, J.L., Garreta, J., 2004. Pollutants emitted by a cement plant: health risks for the population living in the neighborhood. Environ. Res. 95 (2), 198–206.

Shi, J., Liang, L., Jiang, G., 2005a. Simultaneous determination of methylmercury and ethylmercury in rice by capillary gas chromatography coupled on-line with atomic fluorescence spectrometry. J. AOAC Int. 88 (2), 665–669.

Shi, J., Liang, L., Jiang, G., Jin, X., 2005b. The speciation and bioavailability of mercury in sediments of Haihe River, China. Environ. Int. 31 (3), 357–365.

Skyllberg, U., 2008. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: illumination of controversies and implications for MeHg net production. J. Geophys. Res. Biogeosci. 113 (G2).

Skyllberg, U., Xia, K., Bloom, P.R., Nater, E.A., Bleam, W.F., 2000. Binding of mercury (II) to reduced sulfur in soil organic matter along upland-peat soil transects. J. Environ. Qual. 29 (3), 855–865.

Stamenkovic, J., Gustin, M., 2009. Nonstomatal versus stomatal uptake of atmospheric mercury. Environ. Sci. Technol. 43 (5), 1367–1372.

Stern, D.I., 2005. Global sulfur emissions from 1850 to 2000. Chemosphere 58 (2), 163–175.

Tang, S., Feng, X., Qiu, J., Yin, G., Yang, Z., 2007. Mercury speciation and emissions from coal combustion in Guiyang, southwest China. Environ. Res. 105 (2),

175—182.

Trust, B.A., Fry, B., 1992. Stable sulphur isotopes in plants: a review. Plant, Cell & Environ. 15 (9), 1105—1110.

UNEP, 2010. Study on Mercury Sources and Emissions, and Analysis of Cost and Effectiveness of Control Measures "UNEP Paragraph 29 Study". United Nations Environmental Programme, Chemicals Branch, DTIE, Geneva, Switzerland. November 2010.

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

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

Wan, Q., Feng, X., Lu, J., Zheng, W., Song, X., Han, S., Xu, H., 2009. Atmospheric mercury in Changbai Mountain area, northeastern China I. The seasonal distribution pattern of total gaseous mercury and its potential sources. Environ. Res. 109 (3), 201—206.

Wang, S., Zhang, L., Li, G., Wu, Y., Hao, J., Pirrone, N., Sprovieri, E., Ancora, M., 2010. Mercury emission and speciation of coal-fired power plants in China. Atmos. Chem. Phys. 10 (3), 1183—1192.

WHO. Methylmercury, 1990. Environmental Health Criteria 101. World Health Organization, Geneva, pp. 1—144.

Wu, Y., Rahmaningrum, D., Lai, Y., Tu, L., Lee, S., Wang, L., Chang-Chien, G., 2012. Mercury emissions from a coal-fired power plant and their impact on the nearby environment. Aerosol Air Qual. Res. 12, 643—650.

Xia, K., Skyllberg, U., Bleam, W., Bloom, P., Nater, E., Helmke, P., 1999. X-ray absorption spectroscopic evidence for the complexation of Hg (II) by reduced sulfur in soil humic substances. Environ. Sci. Technol. 33 (2), 257—261.

Xiang, R., 2011. Characteristics of Acid Deposition and Environmental Effects of Typical Acid Rain Areas in Southern China. PhD Thesis, pp. 1—106.

Xu, Y., 2010. Improvements in the operation of SO2 scrubbers in China's coal power plants. Environ. Sci. Technol. 45 (2), 380—385.

Xu, X., Liu, N., Landis, M.S., Feng, X., Qiu, G., 2016. Characteristics and distributions of atmospheric mercury emitted from anthropogenic sources in Guiyang, southwestern China. Acta Geochim. 35 (3), 240—250.

Xuan, Y., Li, J., Li, Y., Hao, J., Wei, W., Bu, W., Yang, H., Teng, H., Sha, L., 2004. Discussions on results of environmental background radiation level investigation for Tianwan nuclear power plant. J. Nucl. Sci. Technol. 41 (Suppl. 4), 251—254.

Yang, Y., Chen, H., Wang, D., 2009. Spatial and temporal distribution of gaseous elemental mercury in Chongqing, China. Environ. Monit. Assess. 156 (1—4), 479—489.

Yin, R., Feng, X., Chen, J., 2014. Mercury stable isotopic compositions in coals from major coal producing fields in China and their geochemical and environmental implications. Environ. Sci. Technol. 48 (10), 5565—5574.

Zhang, L., Zhuo, Y., Chen, L., Xu, X., Chen, C., 2008. Mercury emissions from six coal-fired power plants in China. Fuel Process. Technol. 89 (11), 1033—1040.

Zhang, H., Feng, X., Larssen, T., Qiu, G., Vogt, R.D., 2010a. In inland China, rice, rather than fish, is the major pathway for methylmercury exposure. Environ. Health Perspect. 118 (9), 1183.

Zhang, H., Feng, X., Larssen, T., Shang, L., Li, P., 2010b. Bioaccumulation of methylmercury versus inorganic mercury in rice (Oryza sativa L.) grain. Environ. Sci. Technol. 44 (12), 4499—4504.

Zhou, J., Feng, X., Liu, H., Zhang, H., Fu, X., Bao, Z., Wang, X., Zhang, Y., 2013. Examination of total mercury inputs by precipitation and litterfall in a remote upland forest of Southwestern China. Atmos. Environ. 81, 364—372.