Environmental Science & Technology

Article

pubs.acs.org/est

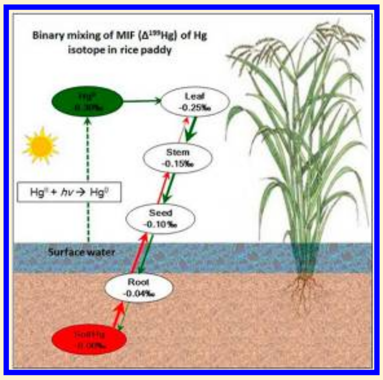
Stable Mercury Isotope Variation in Rice Plants (*Oryza sativa* L.) from the Wanshan Mercury Mining District, SW China

Runsheng Yin,[†,‡] Xinbin Feng,*[,†] and Bo Meng[†]

[†]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guizhou 550002, China

[‡]State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, China

Supporting Information



ABSTRACT: To study the sources and transformations of Hg in the rice plant (*Oryza sativa* L.), stable Hg isotope variations in different tissues (foliage, root, stem, and seed) of rice which were collected from the Wanshan mercury mine (WSMM, Guizhou province, SW China) were investigated by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). In comparison, Hg isotope compositions of paddy soil, lichen, and direct ambient air samples in WSMM were also analyzed. We observed that mass dependent fractionation (MDF) of Hg differed by up to ~3.0‰ in δ^{202}Hg values and that mass independent fractionation (MIF) of Hg isotopes affected the odd Hg isotopes to produce a ~0.40‰ range in Δ^{199}Hg (and Δ^{201}Hg) values in tissues of rice plant. The 1:1 Δ^{199}Hg/Δ^{201}Hg ratio in tissues of rice supported the hypothesis that a fraction of Hg in tissues of rice plants has undergone a photoreduction process prior to being accumulated by rice plants. We suggest that the variation of MIF represents a mixing between soil Hg and atmospheric Hg in rice plants. The estimated fraction of atmospheric Hg (f) in tissues of rice followed the trend of $f_{leaf} > f_{stem} > f_{seed} > f_{root}$. Finally, we demonstrated a significant MDF of >1.0‰ in δ^{202}Hg during the processes of absorption of atmospheric Hg by leaf tissues and of absorption of soil Hg by roots. Our study demonstrated that Hg isotopes may represent an important contribution both to the study of Hg transportation in plants and to the understanding of sources of Hg contamination to critical food crops.

INTRODUCTION

Mercury (Hg) is a globally distributed and extremely toxic pollutant. Among different species of Hg, methylated Hg (MeHg) is of utmost concern to public health due to its ability to be bioaccumulated and biomagnified in biota.[1] China is the largest producer of rice in the world, responsible for 29% of the global paddy rice production.[2] MeHg yields are elevated in rice paddies, where flooded conditions enhance microbial activity and promote the conversion of less toxic inorganic Hg to MeHg, which can be easily taken up in the rice plant.[3] In the inland area of China where people seldom eat fish, rice consumption has been demonstrated to be the dominant MeHg exposure pathway.[4,5] However, the sources and fates of Hg in rice plants are poorly understood and should be studied so that remediation can be appropriately targeted. To date, Hg interactions in rice have been studied with indirect measurements in solution cultures or other artificial laboratory systems, underpinned by mathematical modeling.[6−8] The lack of direct techniques for measuring interactions in intact rice plants under natural conditions, without artificial manipulations of the system, has hampered our understanding of Hg biogeochemical processes in rice plant systems.

With the improvement of analytical methods, there is an increasing interest in using Hg stable isotope ratios to identify sources and fate of Hg in the environment.[9,10] Hg possesses seven stable isotopes with the following average abundances: ^{196}Hg (0.155%), ^{198}Hg (10.04%), ^{199}Hg (16.94%), ^{200}Hg (23.14%), ^{201}Hg (13.17%), ^{202}Hg (29.73%), and ^{204}Hg (6.83%). Recent studies demonstrated that Hg isotope compositions vary significantly between different source materials[11−15] and that Hg isotopes can be systematically fractionated during specific transformation reactions.[16−25] In addition to mass-dependent fractionation (MDF), the anomalous behavior of the several Hg isotopes (e.g., ^{199}Hg, ^{200}Hg, and ^{201}Hg), resulting in mass-independent fractionation (MIF),[16,18,19,23,24] opens up the possibility to use Hg isotope ratios as a "two-dimensional" tracer by using both MDF and MIF signature indicators.[26]

In this study, total Hg (THg) concentrations and Hg isotope variations in different tissues of rice (*Oryza sativa* L.) grown in the Wanshan mercury mine (WSMM) were investigated. The objectives of this study are (1) to estimate the potential source of Hg in different tissues of rice and (2) to investigate the potential fractionation of Hg isotopes during the metabolic process in rice plant.

Received: October 22, 2012
Revised: January 23, 2013
Accepted: January 29, 2013
Published: January 30, 2013

EXPERIMENTAL SECTION

Study Area and Sampling. WSMM, located in eastern Guizhou province, SW China, and known as the "Mercury Capital" in China, is the largest Hg deposit in China. Hg mining activities have been documented for 3000 years in this area. Hg ores have been intensively extracted during the past 50 years. Exploration of Hg in WSMM has led to serious Hg contamination in several environmental compartments such as air,[27,28] soil/sediment,[29] water,[30] and foodstuffs.[3−8]

As shown in Figure S1 (Supporting Information, SI), two watersheds in WSMM were selected as our study areas. The Dashuixi (DSX) watershed was studied because it contains a large quantity of discarded calcine tailings from large-scale Hg mining activities at its headwater. Hg mining activities in DSX were ceased in 2001. The calcine tailings were recently covered by concrete to reduce the release of Hg. The Gouxi (GX) watershed was studied because several illegal artisanal Hg retorts are presently operating along the stream. A large amount of Hg is emitted to the air from the retorts due to poor distillation practices.[27,28] Rice paddy fields at DSX and GX were irrigated using polluted river water during the entire rice growing season and were heavily contaminated with Hg.[3−8]

At each site of DSX and GX, rice plants ($n = 3$) and paddy soil samples ($n = 4$) with 10−20 cm in depth were collected in September 2009 shortly before the rice was harvested. Meanwhile, epiphytic lichen samples ($n = 2$ at each site) from nearby trees (with 0.1−0.5 m above the ground) of the sampling sites were also collected. During the sampling campaign, all collected samples were stored in sealed polyethylene bags to avoid cross contamination and then shipped to the laboratory as soon after collection as possible. In the laboratory, different tissues of rice were separated into leaf, root, stem, and seed (brown rice). The hull from the rice seed was removed by a scalpel. Then, lichens and fresh tissues of rice (e.g., root, leave, and stem) were washed using Milli-Q water. Finally, lichen samples, tissues of rice, and soil samples were air-dried (25 °C, until showing constant weight), crushed, and ground prior to digestion.

Our sampling of ambient gaseous Hg (Hg^0) in both DSX and GX in WSMM was performed at >0.5 m above the paddy field surfaces. During sampling, ambient air was pumped through the trapping solution for 10 h. As illustrated in SI Figure S2, the sampling system was equipped with a vacuum pump with flow rate of 2.5 L min^{-1}. The reactor vessel (glass bubbler, 100 mL) was loaded with 40 mL of trapping solution. Trapping solutions were prepared freshly daily by dissolving 0.1% $KMnO_4$ (Aldrich) in 10% H_2SO_4 (ultrapure grade). The procedural blank of the trapping solution is usually <20 pg mL^{-1}. A 47 mm diameter quartz fiber filter was utilized at the entrance of the glass bubbler to remove particulate matters. A gold trap was attached to the outlet of the trap vessel to collect any Hg^0 that was not recovered by the trapping solution. The gold trap was heated at 550 °C for ~10 min to clean the residual Hg prior to use. After the sampling was finished, we measured the Hg content in the gold traps by Tekran 2500. The tested Hg in the gold traps usually contained <200 pg Hg, which is substantially less than 0.02% of the amount of Hg trapped by $KMnO_4$ solution. The leak of Hg across the trapping solution could result in MDF of Hg isotopes but would not cause MIF.[15] Even if we assumed a substantial difference of 8.0‰ (which corresponds to the largest deviation in $\delta^{202}Hg$ observed so far in natural samples) in $\delta^{202}Hg$ values between the ambient Hg^0 and Hg in gold traps, an insignificant difference of <0.05‰ in $\delta^{202}Hg$ values is expected to be observed between the ambient Hg^0 and Hg in $KMnO_4$ solutions.

Total Mercury Analysis. Approximately 0.2 g soil samples were digested in a water bath (95 °C) using 5 mL of fresh mixture of HCl and HNO_3 (3:1, v/v), whereas ~0.5 g rice samples were digested with a 5 mL mixture of HNO_3 and H_2SO_4 (4:1, v/v). After being digested fully, the sample solutions were diluted to 25 mL by adding Milli-Q water. THg concentrations in soil samples were measured by cold vapor atomic absorption spectrometry (CVAAS) using a F732−S spectrophotometer (Huaguang, China) according to the method developed by Li et al. (2005).[31] THg concentrations in tissues of rice plants, lichens, and trapping solutions were quantified using dual amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS, Tekran 2500, Tekran Inc., Canada) following approved methodologies.[32] Quality control for the Hg determinations was addressed with method blanks, blank spikes, matrix spikes, and certified reference materials (BCR 580 estuarine sediment). The average THg concentration of BCR 580 was 127.0 ± 7.6 $\mu g\ g^{-1}$ (2SD, $n = 5$), which is comparable with the certified value of 132 ± 3 $\mu g\ g^{-1}$. Recoveries of THg based on measurements of replicate BCR 580 digests ($n = 5$) were in the range of 89−107%. The relative standard deviation of HgT for BCR 580 duplicates was <10%.

Mercury Isotope Analysis. Prior to MC-ICP-MS analysis, an aliquot solution with the mass of 125 ng of Hg was taken up from each sample solution and were then diluted to 25 mL by adding Milli-Q water. For sample solutions with the Hg mass lower than 125 ng, only 50 ng of Hg was taken up and then diluted to the same volume as that of previous samples. NIST SRM 3133 (in the acid medium of 2% HCl) with concentration matching with that of the samples was used as the bracketing standard. Hg isotopic ratios were determined by MC-ICP-MS using a Nu-Plasma mass spectrometer equipped with 12 Faraday cups (Nu Instruments, Great Britain) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. A more detailed description of the overall instrumental setup, as well as the parameters and analytical conditions used throughout this study, can be found in literature.[33]

Hg isotopic variations are reported here in δ notation in units of permil (‰) and referenced to the NIST SRM 3133 Hg standard (analyzed before and after each sample) and using the following equation:

$$\delta^{xxx}\mathrm{Hg}(‰) = \{(^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{sample}}) / (^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{NISTSRM3133}}) - 1\} \times 1000 \quad (1)$$

where xxx is mass of each Hg isotope between 199 and 202 amu. Here only $\delta^{202}Hg$ values will be reported to indicate MDF, as they show the most significant differences among samples. MIF is reported in "capital delta" notation ($\Delta^{xxx}Hg$, deviation from mass dependency in units of permil, ‰) and is the difference between the measured $\delta^{xxx}Hg$ and the theoretically predicted $\delta^{xxx}Hg$ value using the following formulas:[9]

$$\Delta^{201}\mathrm{Hg} \approx \delta^{201}\mathrm{Hg} - (\delta^{202}\mathrm{Hg} \times 0.7520) \quad (2)$$

$$\Delta^{200}\mathrm{Hg} \approx \delta^{199}\mathrm{Hg} - (\delta^{202}\mathrm{Hg} \times 0.5024) \quad (3)$$

Table 1. Total Hg Concentration and Hg Isotope Compositions in Reference Materials, Lichens, Paddy Soils, Ambient Air, and Tissues of Rice

sample type	n	average measured δ^{202}Hg ‰	min ‰	max ‰	average measured Δ^{201}Hg ‰	min ‰	max ‰	average measured Δ^{199}Hg ‰	min ‰	max ‰	average measured HgT μg g^{-1}	min μg g^{-1}	max μg g^{-1}
Dashuixi Abandoned Hg Mining Site													
lichens	2	−2.07	−2.3	−1.83	−0.25	−0.28	−0.21	−0.27	−0.31	−0.22	3.6	3.2	4
paddy soil	4	−0.34	−0.39	−0.28	0.01	−0.01	0.02	0	−0.02	0.03	105.5	82	127
rice leaf	3	−3.08	−3.38	−2.88	−0.26	−0.35	−0.21	−0.29	−0.37	−0.23	2.05	1.86	2.37
rice root	3	−0.96	−1.08	−0.89	−0.03	−0.04	−0.01	−0.03	−0.03	−0.02	5.44	4.63	6.17
rice seed	3	−2.24	−2.33	−2.15	−0.06	−0.08	−0.04	−0.06	−0.07	−0.05	0.16	0.13	0.19
rice stem	3	−2.72	−2.82	−2.65	−0.13	−0.15	−0.11	−0.14	−0.16	−0.12	0.29	0.21	0.41
TGM	2	−2.06	−2.26	−1.85	−0.25	−0.26	−0.24	−0.25	−0.26	−0.24	57.0[a]	46.6[a]	69.2[a]
Gouxi Artisanal Hg Mining Site													
lichens	2	−2.2	−2.32	−2.16	−0.36	−0.34	−0.37	−0.34	−0.35	−0.32	19.7	17.6	21.8
paddy soil	4	−0.53	−0.65	−0.45	0.01	0.03	−0.02	0.06	0.04	0.07	65.8	54	79
rice leaf	3	−3.28	−3.36	−3.23	−0.21	−0.27	−0.17	−0.18	−0.23	−0.14	6.23	5.89	7.16
rice root	3	−1.86	−1.98	−1.75	−0.03	−0.04	−0.03	0.01	0	0.02	1.52	1.39	1.69
rice seed	3	−2.51	−2.56	−2.45	−0.05	−0.06	−0.05	−0.02	−0.02	−0.02	0.35	0.31	0.41
rice stem	3	−2.96	−3.03	−2.88	−0.11	−0.13	−0.1	−0.08	−0.08	−0.07	0.89	0.77	0.98
TGM	2	−2.24	−2.32	−2.14	−0.3	−0.32	−0.28	−0.32	−0.34	−0.3	211.0[a]	192.2[a]	230.4[a]
BCR 580	5	−0.46	−0.53	−0.42	−0.02	−0.04	0.03	−0.03	−0.06	−0.01	127.0	118.2	140.6
UM-Almadén	12[b]	−0.53	−0.67	−0.41	−0.01	−0.07	0.06	0.01	−0.06	0.06			

[a] In ng m^{-3}. [b] "n" represents the number of measured UM-Almadén standard solutions.

$$\Delta^{199}\text{Hg} \approx \delta^{199}\text{Hg} - (\delta^{202}\text{Hg} \times 0.2520) \tag{4}$$

Reproducibility of the isotopic data was assessed by measuring replicate sample digests (typically $n = 2$). We also analyzed the UM-Almadén as a secondary standard (once in every 10 samples) in addition to the bracketing standard NIST 3133. The overall average and uncertainty of δ^{202}Hg was −0.56 ± 0.08 ‰ (2SD, $n = 9$), of Δ^{201}Hg was −0.02 ± 0.05‰ (2SD, $n = 9$), and of Δ^{199}Hg was −0.01 ± 0.05‰ (2SD, $n = 9$) for all UM-Almadén measurements, which agreed well with previous established data.[9] In addition, digest replicates of BCR 580 ($n = 5$) were analyzed and the isotopic composition of Hg for BCR 580 (δ^{202}Hg = −0.46 ± 0.04 ‰, 2SD, $n = 5$; Δ^{199}Hg = −0.02 ± 0.03 ‰, 2SD, $n = 5$; Δ^{201}Hg = −0.03 ± 0.02 ‰, 2SD, $n = 5$) was similar to published values.[26] Uncertainties reported in the figures and tables of this paper correspond to the larger value of either (1) the measurement uncertainty of replicate digests or (2) the uncertainty of repeated measurements of the same digest at different analysis sessions. When the calculated 2SD was smaller than the replicate analyses of the reference material of UM-Almadén, the uncertainty associated to UM-Almadén was used instead.

RESULTS AND DISCUSSION

Total Mercury Concentration in Rice Plant and the Growth Mediums. The distribution of THg concentrations (based on dry weight) in paddy soil, lichen, and tissues of rice plants (e.g., root, leaf, stem, and seed) collected from the GX artisanal Hg mining site and the DSX abandoned Hg mining site are shown in Table 1 and SI Figure S3. The mean THg concentrations in soil samples from DSX and GX are 105.5 ± 20.3 μg g^{-1} (2SD, $n = 4$) and 65.8 ± 10.5 μg g^{-1} (2SD, $n = 4$), respectively, which are much higher than the maximum limit for Hg content (1.5 μg g^{-1}) in agriculture soil in China.[34] Hence, the soil compartments can be regarded as heavily polluted.

Lichen is a splendid representative material to reflect Hg contamination in the atmosphere.[35,36] The mean THg concentrations in lichen samples collected from DSX and GX are 3.6 ± 0.6 μg g^{-1} (2SD, $n = 2$) and 19.7 ± 3.0 μg g^{-1} (2SD, $n = 2$), respectively. On the basis of the measurement of Hg by trapping solution in WSMM (detailed in the Experimental Section), the total gaseous mercury (TGM) concentrations in ambient air at DSX and GX were estimated to be 57.9 ± 11.3 ng m^{-3}(2SD, $n = 2$) and 211.3 ± 19.1 ng m^{-3} (2SD, $n = 2$), respectively. The elevated atmospheric Hg concentration in GX resulted from Hg emission from the active artisanal Hg retorting activities. Wang et al. (2006) also demonstrated elevated total gaseous mercury (TGM) in GX (183.0 ± 65.8 ng m^{-3}) compared to that of DSX (48.6 ± 35.5 ng m^{-3}).[27]

As shown in Table 1 and SI Figure S3, the mean THg concentrations in tissues of rice plants exhibited the following distribution patterns: root (5.44 ± 0.77 μg g^{-1}, 2SD, $n = 3$) > leaf (2.05 ± 0.28 μg g^{-1}, 2SD, $n = 3$) > stem (0.29 ± 0.11 μg g^{-1}, 2SD, $n = 3$) > seed 0.16 ± 0.03 μg g^{-1}) at the DSX site and leaf (6.23 ± 0.82 μg g^{-1}, 2SD, $n = 3$) > root (1.52 ± 0.16 μg g^{-1}, 2SD, $n = 3$) > stem (0.89 ± 0.11 μg g^{-1}, 2SD, $n = 3$) > seed (0.35 ± 0.05 μg g^{-1}, 2SD, $n = 3$) at the GX site, respectively. Although rice seed samples exhibit the lowest THg content in rice plant at both DSX and GX sites, the safety of rice in WSMM is of great concern compared to the maximum permissible limit of 0.02 μg g^{-1} issued by Chinese National Standard Agency.[37]

Mercury Isotopic Composition in the Ambient Air. The isotope compositions of Hg in tissues of rice, lichen, atmosphere, and paddy soil samples are listed in Table 1. A few studies have been done to measure the isotopic composition of atmospheric Hg species in different locations directly using gold trapping.[15,38−40] For instance, Zambardi et al. (2009) collected Hg^0 (δ^{202}Hg = −1.74 ± 0.36‰, 2SD, $n = 1$) and particle Hg (Hg_p) (δ^{202}Hg = −0.74 ± 0.18‰, 2SD, $n = 4$) in a fumarole plume from an active volcano in Italy. No MIF (Δ^{199}Hg ∼ 0) was observed in any of these volcanic samples.[15] Gratz et al. (2010) collected precipitation and ambient Hg^0 samples in the Great Lakes of the United States. Precipitation samples were characterized by negative δ^{202}Hg (−0.79 to 0.18‰) and positive Δ^{199}Hg (0.04−0.52‰) values, while most Hg^0 samples displayed positive δ^{202}Hg (−0.59 to 0.43‰) and slightly negative Δ^{199}Hg (−0.21 to 0.06‰) values.[38] Sherman et al. (2010) measured ambient Hg^0 near Barrow, Alaska, by using gold traps. The Hg^0 samples show positive δ^{202}Hg (−0.12 to 0.15‰) and slightly negative Δ^{199}Hg (−0.11 to −0.22‰) values.[39] Rolison et al. (2012) investigated the isotopic composition of species-specific atmospheric Hg in the Grand Bay, US. Despite they demonstrated significant positive MIF in Hg_p (Δ^{199}Hg = 0.36−1.36‰) and intermediate MIF in gaseous oxidized Hg (Hg^{II}) (Δ^{199}Hg = −0.28 to 0.18‰), the Hg^0 (which contributes for >90% of TGM) displayed a significant negative MIF (Δ^{199}Hg = −0.41 to −0.03‰).[40] In our study, the ambient air Hg^0 has δ^{202}Hg values (DSX site, −2.26 to −1.85‰; GX site, −2.32 to −2.14‰) and Δ^{199}Hg (DSX site, −0.26 to −0.24‰; GX site, −0.34 to −0.30‰) more negative than previous values.[15,38−40] Such a discrepancy could be explained by multiple sources of the air samples, such as evaporation of elemental gaseous Hg^0 from the soil and vegetation, local anthropogenic emissions, and long-range transport of Hg from other areas. Our samples were mainly collected from the air ∼0.5 m above the paddy water surface. The photoreduction of dissolved Hg species and subsequent volatilization of Hg^0 may cause enrichment of light isotopes and negative MIF in product Hg^0.[16,17] Therefore, the low δ^{202}Hg values and negative MIF reported here suggest that the evasion flux of Hg from surface water may have contributed significantly to atmospheric Hg^0 in rice paddies in WSMM. Although recent studies demonstrated detectable MIF of ^{200}Hg in atmospheric Hg samples,[38,40,41] no significant MIF of ^{200}Hg was observed in both lichen (Δ^{200}Hg: −0.06 to 0.02‰) and direct air samples (Δ^{200}Hg: −0.07 to 0.03‰) in WSMM.

Natural filters of atmospheric contaminants (e.g., lichens and moss) were previously used as a proxy for the average isotopic composition of atmospheric Hg depositions.[35,36] MIF of Hg isotopes has been observed in lichen samples which displays depletion in odd isotopes.[35,36] Compared to direct atmospheric Hg samples,[15,38−40] significant negative Δ^{199}Hg values were observed in lichen samples.[35,36] This raised the question of the integrity of Hg isotopes measured in lichens relative to atmospheric Hg, with the possibility of MIF during bioaccumulation. In contract, in this study, the lichen samples at DSX site (δ^{202}Hg, −2.30 to −1.83‰; Δ^{199}Hg, −0.31 to −0.22‰) and GX site (δ^{202}Hg, −2.32 to −2.16‰; Δ^{199}Hg, −0.35 to −0.32‰) showed very similar pattern with that of direct air samples as shown in Figure 3. It is still debated whether Hg MIF in lichens can represent that of air samples. More future studies are needed.

Mercury Isotopic Composition in the Paddy Soils. As shown in Figure 1, soil Hg in WSMM has distinct Hg isotope signatures from the atmospheric Hg. The absence of Hg MIF is established here as an important feature of paddy soil. Available data from mineral deposits,[11,12,42,43] hydrothermal emissions,[14] and volcanoes [15] are characterized by no significant MIF. According to our previous study, no significant MIF was observed in both Hg ores and mine-waste calcines in WSMM.[43] The annually wet deposition flux of atmospheric Hg in DSX site is estimated to be 68.1 μg m^{-2} $year^{-1}$.[28] Considering the very high THg concentrations in WSMM paddy soil, atmospheric Hg deposition would only constitute a very minor fraction of Hg in soil, and therefore we would not expect a detectable MIF due to the addition of atmospheric Hg in the soil compartment. Meanwhile, Hg isotope analysis of two bioavailable Hg species (water-soluble Hg and $(NH_4)_2S_2O_3$-extractable Hg) in eight soil samples in WSMM also revealed insignificant MIF.[44]

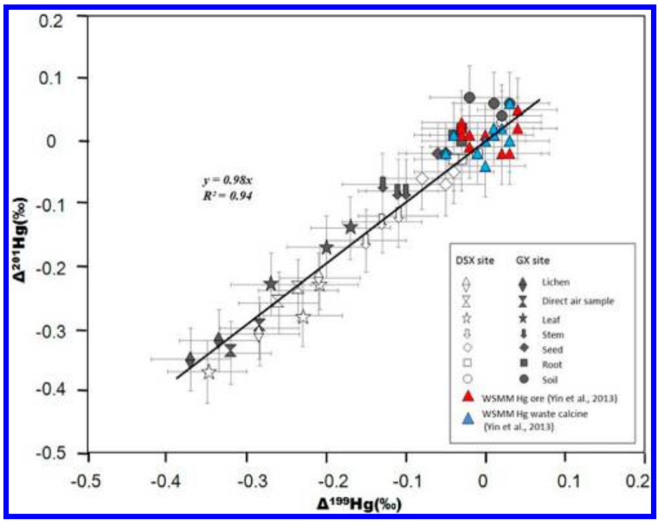


Figure 1. Δ^{201}Hg versus Δ^{199}Hg in permil of lichen, ambient air, tissues of rice plant, and paddy soil samples.

Quantifying Mercury Sources in Rice Plants Using MIF. As shown in Figure 1, the MIF of Hg isotopes in tissues of rice differed by as much as ∼0.40‰ for both the Δ^{199} and Δ^{201} values. The Δ^{199} values in tissues of rice at both DSX and GX exhibited the following distribution patterns: leaf (DSX site: −0.29 ± 0.07‰, 2SD, n = 3; GX site: −0.18 ± 0.05‰, 2SD, n = 3) < stem (DSX site: −0.14 ± 0.05‰, 2SD, n = 3; GX site: −0.08 ± 0.05‰, 2SD, n = 3) < seed (DSX site: −0.06 ± 0.05‰, 2SD, n = 3; GX site: −0.02 ± 0.05‰, 2SD, n = 3) < root (DSX site: −0.03 ± 0.05‰, 2SD, n = 3; GX site: 0.01 ± 0.05‰, 2SD, n = 3). MIF of Hg isotopes is generally understood to be caused by the nuclear volume effect (NVE) [45] and/or the magnetic isotope effects (MIE).[16,46] The NVE has been observed during abiotic dark Hg reduction,[19] elemental Hg volatilization, [24] and equilibrium Hg^{II}-thiol complexation.[25] Theoretical and experimental evidence for NVE suggest a slope >1.5 when Δ^{199}Hg is plotted against Δ^{201}Hg.[24,37] The MIE has been documented during photochemical reactions of aqueous Hg species (e.g., MeHg and Hg^{2+}), during which the odd-mass-number isotopes were preferentially reduced and lost as Hg^0.[16] When Δ^{199}Hg vs Δ^{201}Hg is plotted for each of these photochemical reduction processes, a slope of 1.36 is observed for MeHg and 1.00 for Hg^{2+} photoreduction.[16] Experiment on photoreduction of Hg^{2+} bound to low-molecular-weight organic compounds produced positive MIF in the product Hg^0.[18] Recently, Sonke (2011) developed a mass balance model of MIF of Hg isotopes on the earth. This model demonstrated that MIF of Hg isotopes is a common phenomenon at the global scale and photoreduction may play an important role in in controlling the isotopic composition of atmospheric Hg.[46] On the basis of a York regression,[47] all samples collected from WSMM paddies were characterized by a Δ^{199}Hg/Δ^{201}Hg ratio of 1.06 ± 0.08 (2 SD) as shown in Figure 1. The Δ^{199}Hg/Δ^{201}Hg ratio of ∼1, as evidenced in Figure 1, demonstrates that a fraction of Hg has undergone photoreduction process prior to being retained by tissues of rice plant. It is demonstrated that rice plants accumulate Hg through the stoma from the atmosphere and/or through the root uptake from soil via the transpiration stream.[48] In rice paddy fields, flooding regimes are manipulated. From the water layer with high DOC contents in rice paddies arises the possibility of the photoreduction of aqueous Hg species. On the basis of previous experimental studies, the gaseous Hg^0 generated by photoreduction[16] and volatilization processes[17] are thought to be enriched in light Hg isotopes. The evaporation of Hg^0 from paddy water might be afterward trapped by lichens and tissues of rice, which may be responsible for the negative MIF of Hg isotopes in different tissues of rice.

Although there is no current theoretical evidence, empirical studies show that the metabolic effects are unlikely to cause MIF.[20,21,23,49−51] Hence, the variation of MIF in rice plant in WSMM may represent a mixing between soil Hg and atmospheric Hg. This leads to calculation of fraction of atmospheric Hg in tissues of rice using the following formulas:

$$\Delta^{201}\mathrm{Hg}_{\mathrm{tissue}} = f_{\mathrm{A}}\Delta^{199}\mathrm{Hg}_{\mathrm{atm}} + (1 - f_{\mathrm{A}})\Delta^{199}\mathrm{Hg}_{\mathrm{soil}} \quad (5)$$

$$f_{\mathrm{A}}(\%) = (\Delta^{199}\mathrm{Hg}_{\mathrm{tissue}} - \Delta^{201}\mathrm{Hg}_{\mathrm{soil}}) \times 100/(\Delta^{199}\mathrm{Hg}_{\mathrm{atm}} - \Delta^{199}\mathrm{Hg}_{\mathrm{soil}}) \quad (6)$$

where $\Delta^{199}Hg_{tissue}$ is the $\Delta^{199}Hg$ values of tissues in rice plants. $\Delta^{199}Hg_{atm}$ and $\Delta^{199}Hg_{soil}$ are the $\Delta^{199}Hg$ values of atmospheric Hg (lichens and air) and soil Hg, respectively. $f_A(\%)$ is the fraction of atmospheric Hg source.

Rice, a unique flooding-tolerant crop, can grow in flooded conditions that would drown other plants. Rice plants supply atmospheric oxygen to the roots for respiration via a special vascular system. Rice root cells carry out an unusual type of cellular respiration. It was demonstrated that atmospheric constituents (e.g., Hg) may be incorporated into plant leaves, with gases entering via stomata and in some cases traversing the cuticle, possibly reaching the root.[52] According to our estimated atmospheric fractions [$f_A(\%)$] in rice tissues in DSX and GX (Figure 2), the $f_A(\%)$s in roots at DSX and GX are 10.3 ± 1.1% (2SD, $n = 3$) and 12.4 ± 2.9% (2SD, $n = 3$), respectively. This suggests the fact that the majority of Hg in rice root is of soil Hg origin. In general, the availability of soil Hg to plants is low, and there is a tendency for soil Hg to accumulate in roots.[3,7] Previous studies demonstrated that the root Hg level was directly associated with soil Hg concentrations.[48] Positive correlations between inorganic THg levels in root and THg concentrations in soil in WSMM have also been demonstrated, which suggests that Hg in paddy soil is the major source of inorganic THg in root.[3,7]

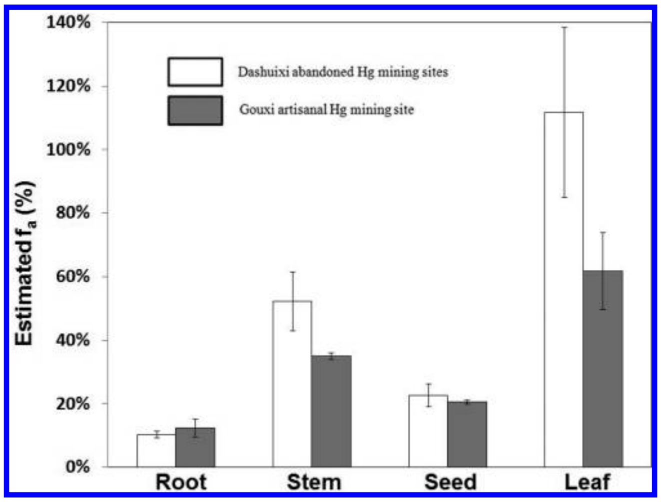


Figure 2. Estimated fraction of atmospheric Hg in different tissues of rice plant collected from Dashuixi abandoned Hg mining site and Gouxi artisanal Hg mining site.

Rice leaves predominantly incorporate gaseous Hg from the atmosphere, whereas the uptake of Hg from the root to the leaves is believed to be of less importance.[48] As shown in Figure 2, the $f_A(\%)$s in leaves at DSX and GX are 111.7 ± 26.7% (2SD, $n = 3$) and 61.7 ± 12.1% (2SD, $n = 3$), respectively. Atmospheric elemental Hg is mildly lipophilic in nature and can diffuse through the cuticle.[53] Numerous studies demonstrated that the source of foliar Hg appears to be almost exclusively from the atmosphere.[48,54] For instance, Bishop et al. (1998) estimated that 11% of total Hg and 3% of the methyl mercury in conifer needles would be derived from the soil by analyzing xylem sap.[48] Our study demonstrated that Hg stored in stems and seeds of rice plant are largely controlled by dual sources. The $f_A(\%)$s in stems in at DSX and GX sites are 52.3 ± 9.3% (2SD, $n = 3$) and 34.9 ± 1.1% (2SD, $n = 3$), respectively, and the $f_A(\%)$s in seeds in DSX and GX sites are 22.6 ± 3.6% (2SD, $n = 3$) and 20.5 ± 0.7% (2SD, $n = 3$), respectively.

Mass Dependent Fractionation of Hg in Rice Plants. We observed a ~3.00‰ range in $\delta^{202}Hg$ values in tissues of rice. A decrease pattern of $\delta^{202}Hg$ was observed for roots, seeds, stems, and leaves at both DSX and GX sites as shown in Table 1.

The "two-dimensional" tracer by utilizing both MDF and MIF indicators may provide an opportunity to quantify the MDF of Hg isotope during uptake and translocation of Hg in rice plants. From the established $f_A(\%)$ in Figure 2, the majority of Hg in leaves of rice plants is originated from air. The mean $\delta^{202}Hg$ of rice leaves (DSX: −3.08 ± 0.27‰, 2SD, $n = 3$; GX: −3.28 ± 0.07‰, 2SD, $n = 3$) are much lower than that of ambient air at both DSX and GX sites, suggesting MDF of Hg isotopes may occur during incorporation of atmospheric Hg by leaf tissues. The mean $\delta^{202}Hg$ values of rice root (DSX: −0.96 ± 0.10‰, 2SD, $n = 3$; GX: −1.86 ± 0.12‰, 2SD, $n = 3$) generally differ from those in the paddy soils in both DSX and GX sites.

As shown in Figure 3, an exponential relation was observed between $\Delta^{201}Hg$ and $\delta^{202}Hg$ values. Compared to the soil Hg, the atmospheric Hg endmember has much lower $\delta^{202}Hg$ values. If we suppose there is no MDF during Hg translocation in rice plant, then an ideally linear relation between MDF and MIF will be observed in all tissues of rice between two endmembers (the soil Hg and the atmospheric Hg) as given in Figure 3. However, the exponential line between $\delta^{202}Hg$ and $\Delta^{201}Hg$ values in tissues of rice differed significantly from the ideal line of mixing without MDF (Figure 3). The lower $\delta^{202}Hg$ values in tissues of rice compared to that plot in the ideal mixing line without MDF in Figure 3 suggested that a MDF of >1‰ in $\delta^{202}Hg$ values occurs during the process of Hg translocation in rice plants in WSMM. The negative $\delta^{202}Hg$ values observed in the leaves could be due to photochemical reduction and loss of Hg from the surface of the leaves. Previous studies demonstrated MDF during biogeochemical processes, e.g., microreduction,[20,21] methylation,[23] photoreduction,[16,18,22] volatilization,[17] and adsorption−desorption,[25,44] which result in a relative lower $\delta^{202}Hg$ in the products. Fractionation of other metal isotope systems (e.g., Fe, Cu, and Zn) has been demonstrated to occur during uptake through the root system and/or preferential translocation of light isotopes to the

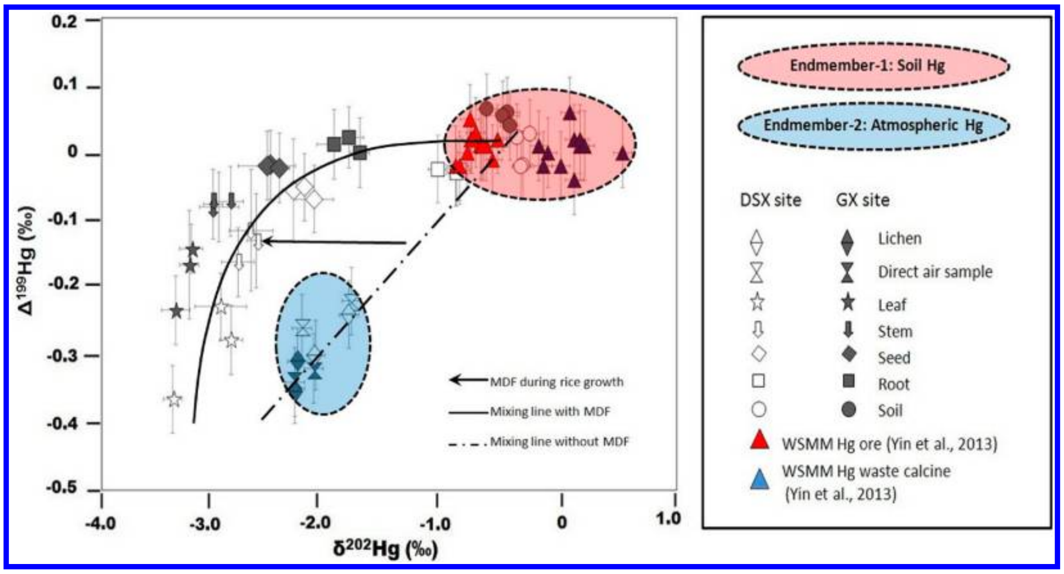


Figure 3. Mass dependent fractionation of mercury isotope in tissues of rice plants.

leaves.[55−57] It is known that plant uptake of Hg in the soil solution might be via the same uptake processes that move essential micronutrients. Roots possess a significant cation-exchange capacity due largely to the presence of carboxyl groups, which may be involved in moving ions through the outer part of the root to the plasmalemma, where fractionation of Hg isotopes may take place.[58] Hg^0 diffusion was performed in laboratory through a polymeric material and resulted in a relative smaller δ^{202}Hg in the product.[59] There are still debates about Hg uptake by plants and translocation and transformation of it inside the plants. As Hg uptake from soil is mainly controlled by the plant species, it can be assumed that Hg translocation from atmosphere to plant will be different for different species. Further research is therefore necessary to explain this.

Implications. This is the first study investigating the variation of Hg isotopic ratio in a plant organism. Our results clearly demonstrate that plants, such as rice, are able to uptake Hg from both soil and ambient air and that MIF of natural mercury isotope can provide an effective tool to differentiate from which compartment Hg has been uptaken. In addition, Hg translocation within the plant or diffusive absorption from the air exhibit significant MDF, as demonstrated for other metals. Our study has very important implications for remediation efforts in farming areas that are contaminated with Hg. However, due to constrained precision of MIF (±0.05‰ for both Δ^{201}Hg and Δ^{199}Hg) compared to the overall ~0.40‰ variations in MIF in rice plant, the ~ ± 20% uncertainties in quantifying Hg sources in the rice plant should be noted. In the future, better precision of isotope-ratio determinations should be improved to allow a better study of Hg cycling in plants. The global distribution and transformation process of Hg in biosphere is important but poorly understood. Perhaps, Hg isotope techniques may be used as an effective tool to identify and quantify sources and biogeochemical processes of Hg in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The locations of the study area and sampling sites. Illustration of the experimental set-up used for collecting atmospheric mercury. Total Hg concentration in soil, lichen, and different tissues of rice plant collected from Dashuixi abandoned Hg mining site and Gouxi artisanal Hg mining site. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86 851 5891356; fax: +86 851 5891609; e-mail: fengxinbin@vip.skleg.cn.

Notes

The authors declare no competing financial interest

■ ACKNOWLEDGMENTS

This research was funded by National Key Basic Research Program of China (2013CB430003) and Natural Science Foundation of China (40825011, 41120134005, and 41030752). We also acknowledge the Prof. Jiang G. B. and the reviewers for their relevant comments that have largely upgraded the quality of our manuscript.

■ REFERENCES

(1) Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32*, 1−7.

(2) *World Rice Statistics*; International Rice Research Institute: Metro Manila,Philippines, 2010; http://beta.irri.org/solutions/index.php?option=com_content&task=view&id=250.

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

(4) Feng, X. B.; Li, P.; Qiu, G. L.; Wang, S. F.; Li, G. H.; Shang, L. H.; Meng, B.; Jiang, H. M.; Bai, W. Y.; Li, Z. G.; Fu, X. W. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou province, China. *Environ. Sci. Technol.* **2008**, *42*, 326−332.

(5) Zhang, H.; Feng, X.; Larssen, T.; Qiu, G.; Vogt, R. D. In inland China, rice, rather than fish is the major pathway for methylmercury exposure. Environ. *Health Perspect.* **2010**, *118*, 1183−1188.

(6) Rothenberg, S. E.; Feng, X. B.; Dong, B.; Shang, L. H.; Yin, R. S.; Yuan, X. B.. Characterization of mercury species in brown and white rice (*Oryza sativa* L.) grown in water-saving paddies. *Environ. Pollut.* **2011**, DOI: 10.1016/j.envpol.2011.01.027.

(7) Meng, B.; Feng, X.; Qiu, G.; Cai, Y.; Wang, D.; Li, P.; Shang, L.; 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.* **2010**, *58*, 4951−4958.

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

(9) Blum, J. D.; Bergquist, B. A. Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* **2007**, *388*, 353−359.

(10) Yin, R.; Feng, X.; Shi, W. Application of the stable-isotope system to the study of sources and fate of Hg in the environment: a review. *Appl. Geochem.* **2011**, *25*, 1467−1477.

(11) Hintelmann, H.; Lu, S. Y. High precision isotope ratio measurements of mercury isotopes in cinnabar ores using multi-collector inductively coupled plasma mass spectrometry. *Analyst* **2003**, *128*, 635−639.

(12) Smith, C. N.; Kesler, S. E.; Klaue, B.; Blum, J. D. Mercury isotope fractionation in fossil hydrothermal systems. *Geology* **2005**, *33*, 825−828.

(13) Biswas, A.; Blum, J. D.; Bergquist, B. A.; Keeler, G. J.; Xie, Z. Q. Natural mercury isotope variation in coal deposits and organic soils. *Environ. Sci. Technol.* **2008**, *42*, 8303−8309.

(14) Sherman, L. S.; Blum, J. D.; Nordstrom, D. K.; McCleskey, R. B.; Barkay, T.; Vetriani, C. Mercury isotopic composition of hydrothermal systems in the Yellowstone Plateau volcanic field and Guaymas Basin sea-floor rift. *Earth Planet. Sci. Lett.* **2009**, *29*, 86−96.

(15) Zambardi, T.; Sonke, J. E.; Toutain, J. P.; Sortino, F.; Shinohara, H. Mercury emissions and stable isotopic compositions at Vulcano Island (Italy). *Earth Planet. Sci. Lett.* **2009**, *277*, 236−243.

(16) Bergquist, B. A.; Blum, J. D. Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* **2007**, *318*, 19.

(17) Zheng, W.; Foucher, D.; Hintelmann, H. Mercury isotope fractionation during volatilization of Hg(0) from solution into the gas phase. *J. Anal. At. Spectrom.* **2007**, *22*, 1097−1104.

(18) Zheng, W.; Hintelmann, H. Mercury isotope fractionation during photoreduction in natural water is controlled by its Hg/DOC ratio. *Geochim. Cosmochim. Acta.* **2009**, *73*, 6704−6715.

(19) Zheng, W.; Hintelmann, H. 2010 nuclear field shift effect in isotope fractionation of mercury during abiotic reduction in the absence of light. *J. Phys. Chem. A* **2010**, *114*, 4238−4245.

(20) Kritee, K.; Barkay, T.; Blum, J. D. Mass dependent stable isotope fractionation of mercury during mer mediated microbial degradation of monomethylmercury. *Geochim. Cosmochim. Acta* **2009**, *73*, 1285−1296.

(21) Kritee, K.; Blum, J. D.; Barkay, T. Mercury stable isotope fractionation during reduction of Hg(II) by different microbial pathways. *Environ. Sci. Technol.* **2008**, *42*, 9171−9177.

(22) Yang, L.; Sturgeon, R. E. Isotopic fractionation of mercury induced by reduction and ethylation. *Anal. Bioanal. Chem.* **2009**, *393*, 377−385.

(23) Rodriguez-Gonzalez, P.; Epov, V. N.; Bridou, R.; Tessier, E.; Guyoneaud, R.; Monperrus, M.; Amouroux, D. Species-specific stable isotope fractionation of mercury during Hg(II) methylation by an anaerobic bacteria (*Desulfobulbus propionicus*) under dark conditions. *Environ. Sci. Technol.* **2009**, *43* (24), 9183−9188.

(24) Estrade, N.; Carignan, J.; Sonke, J. E.; Donard, O. F. X. Mercury isotope fractionation during liquid−vapor evaporation experiments. *Geochim. Cosmochim. Acta* **2009**, *73*, 2693−2711.

(25) Wiederhold, J. G.; Daniel, K.; Infante, I.; Bourdon, B.; Kretzschmar, R. Equilibrium mercury isotope fractionation between dissolved Hg(II) species and thiol-bound Hg. *Environ. Sci. Technol.* **2010**, *44*, 4191−4197.

(26) Liu, J.; Feng, X.; Yin, R.; Zhu, W.; Li, Z. Mercury distributions and mercury isotope signatures in sediments of Dongjiang River, the Pearl River Delta, China. *Chem. Geol.* **2011**, DOI: 10.1016/j.chemgeo.2011.06.001.

(27) Wang, S.; Feng, X.; Qiu, G.; Fu, X.; Wei, Z. Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou. *China Atmos. Environ.* **2007**, *41*, 5584−5594.

(28) Dai, Z. H.; Feng, X. B.; Sommar, J.; Li, P.; Fu, X. W. Spatial distribution of mercury deposition fluxes in Wanshan Hg mining area, Guizhou province, China. *Atmos. Chem. Phys.* **2012**, *12*, 6207−6218.

(29) Qiu, G. L.; Feng, X. B.; Wang, S. F.; 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.* **2005**, *20* (3), 627−638.

(30) Zhang, H.; Feng, X.; Thorjørn, L.; Shang, L.; Vogt, R. D.; Rothenberg, S. E.; Li, P.; Zhang, H.; Lin, Y. Fractionation, distribution and transport of mercury in rivers and tributaries around Wanshan Hg mining district, Guizhou Province, Southwestern China: Part 1. Total mercury. *Appl. Geochem.* **2010**, *25*, 633−641.

(31) Li, Z. G.; Feng, X. B.; He, T. R. Determination of total mercury in soil and sediment by aquaregia digestion in the water bath coupled with cold vapor atom fluorescence spectrometry. . *Bull. China Soc. Mineral Petrol. Geochem.* **2005**, *24* (2), 140−143 (in Chinese).

(32) *Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*; United States Environmental Protection Agency: Washington, DC, 2002 pp 1−33.

(33) Yin, R. S.; Feng, X. B.; Foucher, D.; Shi, W. F.; Zhao, Z. Q.; Wang, J. High Precision Determination of Mercury Isotope Ratios Using Online Mercury Vapor Generation System Coupled with Multicollector Inductively Coupled Plasma−Mass Spectrometer. *Chin. J. Anal. Chem.* **2011**, *38* (7), 929−934.

(34) *Environmental Quality Standard for Soils, GB15618−1995*; Chinese National Environment Protect Agency (CNEPA), 1995; pp 1−6, (in Chines).

(35) Carignan, J.; Estrade, N.; Sonke, J. E.; Donard, O. F. X. Odd isotope deficits in atmospheric Hg measured in lichens. *Environ. Sci. Technol.* **2009**, *243*, 5660−5664.

(36) Estrade, N.; Carignan, J.; Donard, O. F. Isotope tracing of atmospheric mercury sources in an urban area of northeastern France. *Environ. Sci. Technol.* **2010**, *44* (16), 6062−6067.

(37) *Tolerance Limit of Mercury in Foods*; Chinese National Standard Agency (CNSA), 1994; pp 171−173 (in Chinese).

(38) Gratz, L. E.; Keeler, G. J.; Blum, J. D.; Sherman, L. S. Isotopic composition and fractionation of mercury in great lakes precipitation and ambient air. *Environ. Sci. Technol.* **2010**, *44*, 7764−7770.

(39) Sherman, L. S.; Blum, J. D.; Johnson, K. P.; Keeler, G. J.; Barres, J. A.; Douglas, T. A. Mass-independent fractionation of mercury isotopes in Arctic snow driven by sunlight. *Nature Geosci.* **2010**, *3*, 173−177.

(40) Rolison, J. M.; Landing, W. M.; Luke, W.; Cohen, M.; Salters, V. J. M. Isotopic composition of species-specific atmospheric Hg in a coastal environment. *Chem. Geol.* **2012**, DOI: 10.1016/j.chemgeo.2012.10.007.

(41) Chen, J.; Hintelmann, H.; Feng, X.; Dimock, B. Unusual fractionation of both odd and even mercury isotopes in precipitation from Peterborough, ON, Canada. *Geochim. Cosmochim. Acta* **2012**, *90*, 33−46.

(42) Sonke, J. E.; Schaefer, J.; Chmeleff, J.; Audry, S.; Blanc, G.; Dupré, B. Sedimentary mercury stable isotope records of atmospheric and riverine pollution from two major European heavy metal refineries. *Chem. Geol.* **2010**, *297*, 90−100.

(43) Yin, R.; Feng, X.; Wang, J.; Li, P.; Liu, J.; Zhang, Y.; Chen, J.; Zheng, L.; Hu, T. Mercury speciation, mercury isotope fractionation during ore roasting process and their implication to source identification of downstream sediment in Wanshan mercury mining area, SW China. . *Chem. Geol.* **2012**, DOI: 10.1016/j.chemgeo.2012.04.030.

(44) Yin, R.; Feng, X.; Wang, J.; Bao, Z.; Yu, B.; Chen, J. Mercury isotope variations between bioavailable mercury fractions and total mercury in mercury contaminated soil in Wanshan Mercury Mine, SW China. *Chem. Geol.* **2012**, DOI: 10.1016/j.chemgeo.2012.04.017.

(45) Schauble, E. A. Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochim. Cosmochim. Acta* **2007**, *71*, 2170−2189.

(46) Sonke, J. E. A global model of mass independent mercury stable isotope fractionation. *Geochim. Cosmochim. Acta* **2011**, *75*, 4577−4590.

(47) York, D. Least-squares fitting of a straight line. *Can. J. Phys.* **1966**, *44*, 1079−1086.

(48) Bishop, K. H.; Lee, Y. H.; Munthe, J.; Dambrine, E. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry* **1998**, *40*, 101−113.

(49) Laffont Laffont, L.; Sonke, J. E.; Maurice, L.; Hintelmann, H.; Sanchez-Baccarez, Y.; Perez, T.; Behra, P.; et al.et al. 2009 anomalous mercury isotopic compositions of fish and human hair in the Bolivian Amazon. *Environ. Sci. Technol.* **2009**, *43*, 8985−8990.

(50) Gehrke, G. E.; Blum, J. D.; Slotton, D. G.; Greenfield, B. K. 2011 mercury isotopes link mercury in San Francisco Bay forage fish to surface sediments. *Environ. Sci. Technol.* **2011**, *45* (4), 1264−1270.

(51) Jackson, T. A.; Muir, D. C. Mass-dependent and mass-independent variations in the isotope composition of mercury in a sediment core from a lake polluted by emissions from the combustion of coal. *Sci. Total Environ.* **2012**, *417*−*418*, 189−203.

(52) Stamenkovic, J.; Gustin, M. S. Nonstomatal versus stomatal uptake of atmospheric mercury. *Environ. Sci. Technol.* **2009**, *43* (5), 1367−1372.

(53) Okouchi, S.; Sasaki, S. The 1-octanol/water partition coefficient of mercury. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3401−3402.

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

(55) Kiczka, M.; Wiederhold, J. G.; Kraemer, S. M.; Bourdon, B.; Kretzschmar, R. Iron isotope fractionation during Fe uptake and translocation in alpine plants. *Environ. Sci. Technol.* **2010**, *44* (16), 6144−6150.

(56) Jouvin, D.; Weiss, D. J.; Mason, T. F.; Bravin, M. N.; Louvat, P.; Zhao, F.; Ferec, F.; Hinsinger, P.; Benedetti, M. F. Stable isotopes of Cu and Zn in higher plants: evidence for Cu reduction at the root surface and two conceptual models for isotopic fractionation processes. *Environ. Sci. Technol.* **2012**, *46* (5), 2652−2660.

(57) Aucour, A. M.; Pichat, S.; Macnair, M. R.; Oger, P. Fractionation of stable zinc isotopes in the zinc hyperaccumulator *Arabidopsis halleri* and nonaccumulator *Arabidopsis petraea*. *Environ. Sci. Technol.* **2011**, *45* (21), 9212−9217.

(58) Du, X.; Zhu, Y. G.; Liu, W. J.; Zhao, X. S. Uptake of mercury (Hg) by seedlings of rice (*Oryza sativa* L.) grown in solution culture and interactions with arsenate uptake. *Environ. Exp. Bot.* **2005**, *54*, 1−7.

(59) Koster, P. G.; Esser, B. K.; Williams, R.; Hunt, J. R. Mercury isotope fractionation due to permeation of a PVC polymer. *Goldschmidt Conf. Abstr.* **2009**, A687.