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Mercury Isotope Signatures of Methylmercury in Rice Samples from the Wanshan Mercury Mining Area, China: Environmental Implications

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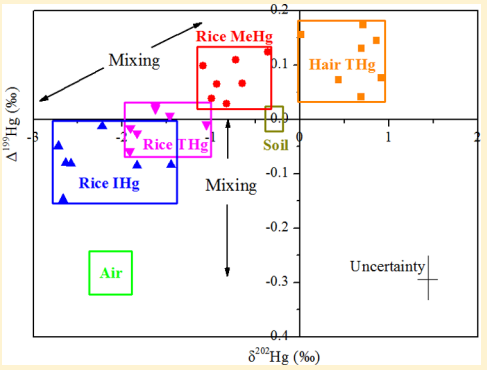
ABSTRACT: Rice consumption is the primary pathway of methylmercury (MeHg) exposure for residents in mercury-mining areas of Guizhou Province, China. In this study, compound-specific stable isotope analysis (CSIA) of MeHg was performed on rice samples collected in the Wanshan mercury mining area. An enrichment of 2.25‰ in total Hg (THg) δ^{202}Hg was observed between rice and human hair, and THg Δ^{199}Hg in hair was 0.12‰ higher than the value in rice. Rice and human hair samples in this study show distinct Hg isotope signatures compared to those of fish and human hair of fish consumers collected in China and other areas. Distinct Hg isotope signatures were observed between IHg and MeHg in rice samples (in mean ± standard deviation: $\delta^{202}Hg_{IHg}$ at −2.30‰ ± 0.49‰, $\Delta^{199}Hg_{IHg}$ at −0.08‰ ± 0.04‰, n = 7; $\delta^{202}Hg_{MeHg}$ at −0.80‰ ± 0.25‰, $\Delta^{199}Hg_{MeHg}$ at 0.08‰ ± 0.04‰, n = 7). Using a binary mixing model, it is estimated that the atmospheric Hg contributed 31% ± 16% of IHg and 17% ± 11% of THg in the rice samples and the IHg in soil caused by past mining activities contributed to the remaining Hg. This study demonstrated that Hg stable isotopes are good tracers of human MeHg exposure to fish and rice consumption, and the isotope data can be used for identifying the sources of IHg and MeHg in rice.



INTRODUCTION

Mercury (Hg) and its compounds are highly toxic pollutants that can adversely affect human health. The toxicity of Hg depends on its chemical form. Humans are exposed to organic mercury through diet and to inorganic Hg in air containing elevated Hg vapor caused by industrial emissions such as coal combustion and artisanal gold mining or by Hg released by amalgam dental fillings. Exposure to dietary methylmercury (MeHg) has caused greater health concern because MeHg is much more toxic than inorganic Hg (IHg) and bioaccumulates more strongly than IHg in aquatic organisms.[1,2] IHg can be readily methylated in aquatic ecosystems and then accumulated as MeHg in the food chains, leading to elevated MeHg concentrations in fish and human exposure to MeHg through fish consumption.[1]

Rice grown in contaminated soils, such as those near the closed Hg mining industries in Guizhou Province, China, can also contain high MeHg concentrations.[3,4] It has been found that rice paddies are hotspots of Hg methylation.[5,6] MeHg in paddy soils are absorbed by the roots of rice plants and translocated to the leaves, stalks, and seeds.[3] In contrast, IHg in rice plants originates from Hg uptake from soil or the atmosphere (mainly Hg^0 uptake via foliage).[7,8] Rice (rather than fish) has been identified as the main source of human exposure to MeHg in Guizhou Province[4,9] and the inland area of South China.[10] Health risks through co-exposure to IHg and MeHg are particularly of concern in Hg mining areas[4] and other Hg-contaminated areas of China. Understanding the source of Hg contamination and the pathways of human exposure to MeHg and IHg in these areas is critical to assessing the health risks and implementing effective pollution-control measures.

Mercury stable isotope techniques are research tools to understand the sources and environmental processes of Hg.[11,12] Mass-dependent fractionation (MDF, quantified as δ^{202}Hg) occurs in most physical, chemical, and biological processes, such as microbiological reduction,[13,14] methylation,[15] demethy-

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lation,[16] and photoreduction.[17,18] The processes exhibit distinct δ^{202}Hg signatures in IHg species (Hg^{2+} and Hg^0) and MeHg. Mass-independent fractionation (MIF, quantified as Δ^{199}Hg, Δ^{200}Hg, and Δ^{201}Hg) of both even and odd Hg stable isotopes can also affect Hg isotopic signatures of IHg and MeHg. MIF data provide useful information on the sources of Hg in the environment and human exposure pathways as well as environmental processes (such as photochemistry) contributing to the biogeochemical cycle of Hg.[17,19,20]

Signatures of stable Hg isotopes in environmental and biological samples have led to specific insights on the trophic transfer of Hg through aquatic food chains to fish consumers, such as humans, birds, and whales.[21−28] Significant MDF does not occur during the trophic transfer of Hg to fish,[26] but a δ^{202}Hg increase of ∼+2‰ has been found between fish and human hair, mammals, and birds, indicating that MDF may occur through metabolic processes.[27,29−32] Positive MIF signatures have been observed in human hair and fish, which was explained by the photodegradation of MeHg in aquatic ecosystems before biomagnification.[29−32] The absence of MIF during trophic transfer enables the use of MIF data for tracing Hg sources in food webs.[26] The correlations between δ^{202}Hg (or Δ^{199}Hg) and the MeHg fraction in total Hg (THg) found in aquatic food webs suggest that MeHg and IHg species may have distinct isotopic signatures.[33,34] This was also supported by the isotopic signature of MeHg found in marine biological samples using a compound-specific stable isotope analysis (CSIA) method.[35]

The selective extraction method (SEM) for CSIA has been applied for fish tissues because fish has relatively high MeHg concentration and Hg in fish is present primarily as MeHg.[35] However, rice samples contain relatively low MeHg concentrations and low fractions of MeHg.[3,4] In this study, a modified CSIA method was developed for determining the isotopic signatures of MeHg in rice samples collected from the Wanshan mercury mining area (WMMA), which had the largest Hg mining operation in China. Hg isotopes in hair samples of the residents in WMMA were also determined to understand the Hg exposure pathways.

MATERIALS AND METHODS

Sample Collection. Rice and human hair samples were collected in the WMMA in December 2012. The study area and sampling procedure have been described previously.[36] The Dashuixi village with a population of 100 people and 25 households was selected as the study site. A total of seven rice samples of relatively high MeHg concentrations and seven hair samples of large range of Hg concentrations were analyzed. A total of three male and four female subjects (with an average of 42.7 years old) were selected in this study. A total of one rice sample and one hair sample were collected from each participating household, and therefore, each rice and hair sample was paired. Hair samples (50−100 mg) were cut with stainless-steel scissors from the occipital region of the scalp. Each sample was bundled together in polyethylene bags and then transferred to the laboratory for analysis. The portion of hair within 0−3 cm from the scalp was selected for Hg analysis to reveal the past 3 months' exposure. Uncooked rice samples (100 g) were collected from each participating household. The food consumption information for each participant (g/day) was estimated through face-to-face interview. The rice consumed by local residents was cultivated from their own land.

Mercury Concentrations and Speciation. Each rice sample was air-dried, crushed, and passed through a 150 mesh sieve. Each hair sample was washed with nonionic detergent, distilled water, and acetone and then dried in an oven at 60 °C overnight.[37]

THg concentrations in hair and rice samples were determined using a DMA-80 analyzer (Milestone, Italy) at the Geosciences Environment Toulouse laboratory (France).[30] MeHg concentrations were determined by extracting the organic phase with tetramethylammonium hydroxide, followed by species-specific isotope-dilution analysis and gas chromatography inductively coupled plasma mass spectrometry.[38]

Mercury Isotope Analysis. Between 0.1 and 0.8 g of a rice sample or between 0.01 and 0.02 g of a hair sample (depending on the THg concentration) was digested in 5 mL of HNO_3 at 120 °C for 6 h. The digest was then diluted with Milli-Q water to 15−25 vol % acid and adjusted to yield a reverse aqua regia solution (3:1 v/v HNO_3 and HCl) with a THg concentration of 1 ng/g for Hg isotope analysis. The Hg stable-isotope composition was determined using continuous cold vapor−multiple-collector inductively coupled plasma mass spectrometer (CV−MC-ICPMS, Neptune, Thermo Fisher Scientific) at the Geosciences Environment Toulouse laboratory following a previously published method.[30] Hg MDF and MIF signatures were expressed relative to NIST SRM 3133 following the recommended nomenclature.[17]

The procedure of SEM was adapted from the method described by Masbou et al.[35] An appropriate amount of a rice sample (0.25−0.5 g) was extracted with 5 mL of acidic sodium bromide (30% w/w NaBr in 4 mol/L H_2SO_4), 10 mL of aqueous cupric sulfate (2.5% w/w $CuSO_4$), and 10 mL of toluene in a 50 mL centrifuge tube. The tube was shaken at 420 rpm for 1 h to transfer MeHgBr from the matrix to the toluene phase. The toluene phase was then removed and back-extracted with aqueous sodium thiosulfate solution (0.005 mol/L) to convert the MeHgBr into a stable MeHg−thiosulfate complex. An aliquot of the aqueous phase (containing the MeHg−thiosulfate complex) was transferred to a 5 mL tube and kept at 4 °C until analysis. For rice samples with low MeHg concentrations, the sample was extracted several times, and the extracts were combined to obtain enough Hg in solution (1 ng/g) for Hg isotope analysis. Fish CRM TORT-2 (National Research Council Canada) was used to investigate the accuracy and precision of the SEM method.

The THg concentration in each purified solution was determined by cold vapor atomic fluorescence spectroscopy (Brooks Rand Model III) at the Geosciences Environment Toulouse laboratory. The MeHg recoveries were calculated from the ratio of THg in purified solution to the initial MeHg concentrations in the rice samples. The MeHg concentration in each prepared extract was determined after aqueous ethylation, purging, trapping, and gas chromatography cold vapor atomic fluorescence spectroscopy (using a MERX instrument; Brooks Rand Instruments) analysis in the State Key Laboratory of Environmental Geochemistry. The purity of MeHg in the extract was calculated from the percentage of MeHg to the THg concentration in each solution and was used to determine the relative amounts of IHg impurities and to determine the efficiency of the extraction process.

Each purified MeHg−thiosulfate solution was diluted with a 3:1 v/v mixture of HNO_3 and HCl to give a final Hg concentration of 1 ng/g, MeHg CSIA was performed on the solution using continuous CV-MC-ICPMS. The stable isotopic

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compositions of IHg compounds were calculated from the isotopic mass balance differences using the THg and MeHg fractions isotopic compositions using eqs 1 and 2:

$$\delta^{202}Hg_{THg} = \delta^{202}Hg_{MeHg} \times R + \delta^{202}Hg_{IHg} \times (1 - R) \quad (1)$$

$$\Delta^{199}Hg_{THg} = \Delta^{199}Hg_{MeHg} \times R + \Delta^{199}Hg_{IHg} \times (1 - R) \quad (2)$$

where R is the percentage of MeHg to the THg concentration in a rice sample.

Quality Control. The quality-control procedures applied to the Hg speciation analyses involved analyzing method blanks, spiked blanks, spiked matrix samples, certified reference materials (CRM), and blind duplicates. The limits of determination (LOD) for THg and MeHg were 0.02 and 0.003 ng/g, respectively. The mean THg concentration of lichen CRM (BCR482) was 475 ± 15 ng/g (n = 5), consistent with the certified concentration of 480 ± 20 ng/g; the mean THg concentration of human hair CRM (NIES-13) was 4.3 ± 0.09 μg/g (n = 4), also consistent with the certified concentration of 4.4 ± 0.2 μg/g. A mean MeHg concentration of 154 ± 3.3 ng/g (n = 5) was obtained for fish CRM TORT-2 having a certified value of 152 ± 13 ng/g; a mean MeHg concentration of 3.74 ± 0.24 μg/g (n = 5) was obtained for NIES-13, having a certified value of 3.8 ± 0.4 μg/g. The relative percentage differences for duplicate analysis of both rice and hair samples were <10% for THg and MeHg.

The THg recoveries of acid digestion in the BCR482 for THg isotope analysis ranged from 94% to 105%, and the relative standard deviation (SD) was <10% (n = 5). The reproducibility of the isotopic data was assessed by analyzing replicate sample digests. The NIST 3133 standard was used as a bracketing standard, and the UM-Almaden standard was analyzed and used as a secondary standard. The overall mean (±2SD) δ^{202}Hg was −0.55‰ ± 0.08‰ (n = 5), and the overall mean (±2SD) Δ^{199}Hg was −0.01‰ ± 0.04‰ (n = 5) for all the UM-Almaden measurements, agreeable with previously published data.[17] The isotopic composition of Hg in the BCR482 sample (δ^{202}Hg = −1.61‰ ± 0.08‰, n = 3; Δ^{199}Hg = −0.69‰ ± 0.06‰, n = 3) was similar to previously published data.[39] The uncertainties in this study are either (1) the measurement uncertainties for replicate digests or (2) the uncertainties for repeated measurements of the same digest in different analytical sessions, amounting to 0.1‰ and 0.04‰ for δ^{202}Hg and Δ^{199}Hg, respectively.

Data Analysis. All data were analyzed using the statistics software SPSS 19.0 for Windows. In addition to descriptive statistics, Hg concentrations and Hg isotope data in rice and hair samples were compared using ANOVA at a 5% significance level.

RESULTS AND DISCUSSION

THg and MeHg Concentrations in Rice and Human Hair. Table 1 shows the Hg concentrations in all samples. The mean THg concentration in the rice samples was 83.0 ± 14.0 ng/g (n = 7) with all measured concentrations exceeding the Chinese national limit (20 ng/g). The mean MeHg concentration in the rice samples was 38.1 ± 9.3 ng/g (n = 7), ranging from 25.3 to 50.1 ng/g. MeHg in these rice samples constituted of 45.7% ± 6.5% THg on average. The THg concentrations in the hair samples ranged from 0.73 to 5.67 μg/g, with a mean of 3.37 ± 1.76 μg/g. The MeHg concentrations in the hair samples varied from 0.50 to 3.79 μg/g and averaged at 2.47 ± 1.05 μg/g. In human hair samples, MeHg is the primary form of Hg, consisting of 76.1% ± 13.4% THg on average. Most hair samples (85.7% and 71.4%) had MeHg levels exceeding the 1.0 and 2.3 μg/g recommended by United States Environmental Protection Agency (USEPA) and Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Table 1. Total Hg (THg) and Methylmercury (MeHg) Concentrations (in ng·g^{-1}) in the Selected Rice and Hair Samples (in μg·g^{-1}) of the Wanshan Hg Mining Area, China

	rice			hair		
ID	THg	MeHg	MeHg/THg (%)	THg	MeHg	MeHg/THg (%)
A3	79.2	33.9	42.8	5.67	3.79	66.8
A9	95.5	44.3	46.4	3.13	2.64	84.3
A10	95.5	50.1	52.5	2.32	1.87	80.6
A15	88.3	41.3	46.8	2.53	2.50	98.8
A21	77.7	25.3	32.6	0.73	0.50	68.5
A22	55.5	27.5	49.6	5.47	3.17	58.0
A30	89.3	44.2	49.4	3.71	2.81	75.7
average	83.0	38.1	45.7	3.37	2.47	76.1

MeHg Recoveries and Purities. The MeHg recoveries and purities in the final SEM extracts of rice samples are shown in Table 2. IHg compounds consisted of 54.3% ± 6.5% THg in the rice samples on average. The SEM method gave a mean MeHg recovery of 95.0% ± 8.7%, indicating that MeHg was quantitatively transferred from the rice to the MeHg−thiosulfate solution. The mean MeHg purity in the MeHg-thiosulfate solutions was 101.7%, indicating that little IHg impurity was present in the final extracts. No significant peaks for Hg compounds other than MeHg were observed in the chromatograms acquired by gas chromatography−cold-vapor atomic fluorescence spectroscopy. The absence of IHg impurities in the MeHg−thiosulfate extracts indicated that the SEM method was successful. In conclusion, the CSIA did not cause Hg isotope fractionation during the pretreatment.

Table 2. Methylmercury Recoveries and Purities in the Final Extracts

ID	recovery (%)	purity (%)
TORT-2	92.0	90.1
rice A3	98.2	91.6
rice A9	88.8	101.3
rice A10	85.3	95.1
rice A15	91.0	121.5
rice A21	112.9	111.5
rice A22	100.6	102.1
rice A30	91.3	100.4
average	95.0	101.7

Isotope Compositions of THg in Rice and Human Hair. THg in the rice samples had δ^{202}Hg mean of −1.63‰ ± 0.31‰ (mean ± SD, n = 7, range from −1.92‰ to ∼−1.05‰, Table 3), within the range found for rice samples in WMMA reported by Feng et al.[40] (−2.16‰ to −0.62‰) and similar to the results found by Yin et al.[41] (mean −2.24‰, from −2.33‰ to −2.15‰) and Rothenberg et al.[42] (−1.69‰ ± 0.54‰). Significant MIF was not found for THg in rice (Δ^{199}Hg from

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Table 3. Isotopic Signatures of Total Mercury, Methylmercury, and Inorganic Hg Fractions in the Rice Samples from the WMMA (in Units of Permil (‰))

ID	$\delta^{202}Hg_{THg}$	$\Delta^{199}Hg_{THg}$	$\delta^{202}Hg_{MeHg}$	$\Delta^{199}Hg_{MeHg}$	$\delta^{202}Hg_{IHg}$	$\Delta^{199}Hg_{IHg}$
A3	−1.91	−0.02	−0.83	0.03	−2.72	−0.05
A9	−1.63	0.02	−0.94	0.07	−2.23	−0.01
A10	−1.63	0.02	−0.72	0.11	−2.63	−0.08
A15	−1.84	−0.03	−0.99	0.04	−2.58	−0.08
A21	−1.92	−0.06	−0.36	0.12	−2.67	−0.15
A22	−1.05	−0.01	−0.65	0.07	−1.45	−0.08
A30	−1.47	0.01	−1.09	0.10	−1.83	−0.08
mean ± SD	−1.63 ± 0.31	−0.01 ± 0.03	−0.80 ± 0.25	0.08 ± 0.04	−2.30 ± 0.49	−0.08 ± 0.04

−0.06‰ to ∼0.02‰), consistent with earlier results (−0.06‰ ± 0.05‰, Yin et al.;[41] −0.01‰ ± 0.05‰, Feng et al.;[40] −0.04‰ ± 0.11‰, Rothenberg et al.).[42]

Rice shows distinct Hg isotope signatures compared to those of fish. The δ^{202}Hg values of rice samples in this study were significantly lower than these obtained in fish samples collected from Guangdong Province (−0.22−0.38‰, Yin et al.)[43] and Tibet (0.51 ± 0.57‰, Xu et al.).[44] Significant MIF (Δ^{199}Hg) was found in fish samples collected from Guangdong Province (0.05−0.59‰, Yin et al.)[43] and Tibet (3.84 ± 2.10‰, Xu et al.)[44] but not in the rice samples.

The δ^{202}Hg and Δ^{199}Hg means (±SD) of THg in hair samples were 0.62‰ ± 0.31‰ (n = 7) and 0.11‰ ± 0.05‰, respectively. A positive enrichment of 2.25‰ in δ^{202}Hg was observed for the THg in hair compared to rice samples (Figure 1). Similar differences have been found between δ^{202}Hg values

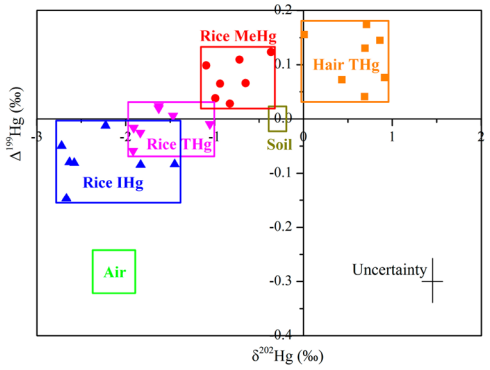

Figure 1. Total Hg (THg), inorganic Hg (IHg), and methylmercury (MeHg) isotopic signatures in rice and human hair samples. Data for Wanshan soil and air from Yin et al.[38] are shown.

in fish and human hair of fish-eating people, such as native inhabitants of Bolivia (2.0‰ ± 0.2‰),[29] dentists in the United States (∼2‰),[31] residents in France (2.2‰ ± 0.8‰),[30] whalers in the Faroe Islands (1.75‰),[32] and anglers in the Gulf of Mexico who consumed coastal and oceanic fish (1.40‰-2.35‰).[32] This MDF enrichment was explained by the demethylation process of MeHg in the intestines and by the excretion of IHg with lower δ^{202}Hg values in urine.[31]

In contrast to the δ^{202}Hg shift, a small but significant enrichment of Δ^{199}Hg (for THg) was observed between hair (0.12‰ ± 0.06‰) and rice (−0.01‰ ± 0.03‰) samples. The MIF shift are typically caused by two mechanisms, the nuclear volume effect and the magnetic isotope effect and can be distinguished using the regression slope of a Δ^{199}Hg−Δ^{201}Hg scatterplot. The nuclear volume effect gives a Δ^{199}Hg-to-Δ^{201}Hg ratio of ∼1.6, found in the volatilization of elemental Hg^0,[45] the equilibrium process of Hg−thiol complexation,[46] and the reduction of aqueous Hg(II) in the dark.[47] The magnetic isotope effect gives a Δ^{199}Hg-to-Δ^{201}Hg ratio of 1.00−1.30, found primarily during photochemical processes (e.g., photodegradation of MeHg and photoreduction of Hg^{2+}).[17,48] The THg Δ^{199}Hg-to-Δ^{201}Hg ratio for the hair samples was 1.41 ± 0.15 (Figure 2), which was similar to the

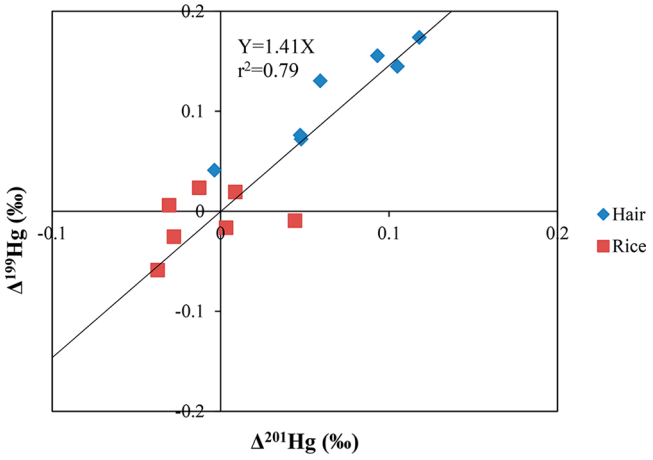

Figure 2. Δ^{199}Hg (for THg) plotted against Δ^{201}Hg (in permil (‰)) for rice and hair samples from the WMMA in China. Analytical uncertainty is Δ^{199}Hg: ± 0.04‰.

ratio found in MeHg photodegradation experiments (mean ± standard error 1.36 ± 0.02).[17] Hg isotope MIF is unlikely to occur during metabolic processes and trophic transfer, and MIF in hair is mainly inherited from the Hg input from diet.[25,26,29,30,32,49] It is likely that MeHg in flooded paddy soils undergoes partial photodemethylation before being taken up by rice plants and finally being ingested by humans and excreted in hair.

As shown in Figure 3, the THg in the hair samples had a Hg isotopic signature range that was distinct from the Hg isotopic signatures found among fish consumers and gold miners.[29−32,50,51] Specifically, the THg δ^{202}Hg and Δ^{199}Hg values were significantly lower for the hair samples of the residents of WMMA than those found among regular fish consumers. These differences possibly caused by the different food sources consumed. High δ^{202}Hg and Δ^{199}Hg values have been found in marine fish samples, and this explains the high δ^{202}Hg (adjusted for the 2‰ metabolic shift) and Δ^{199}Hg values that have been found in hair from humans consuming marine fish. THg δ^{202}Hg values in hair from the residents of WMMA were higher than those obtained in Bolivian native gold miners mainly exposed to IHg by occupational activities (amalgam making and

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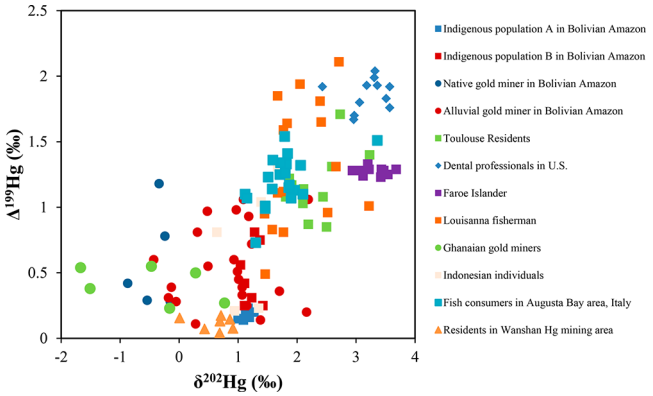

Figure 3. Hg stable isotopes fractionations measured in human hair samples from around the world. Square, fish consumer; circular, gold miner; rhombus, dental professionals; triangle, rice consumer. Indigenous people A and B in the Bolivian Amazon;[29] native (mainly occupational exposure) and alluvial (both occupational and diet exposures) gold miners in Bolivia, Toulouse residents;[30] dental professionals in United States;[31] Faroe Islander and Louisiana fisherman;[32] Ghanaian gold miners and Indonesian individuals;[50] fish consumers in Augusta Bay area, Italy;[51] and residents in the Wanshan Hg mining area, China, in this study.

burning). The same Bolivian gold miners did not consume freshwater fish but occasionally consume canned marine fish. They showed higher THg Δ^{199}Hg values in their hair than the WMMA residents, possibly due to the diet difference.[29]

The residents of WMMA eat fish rarely and the average daily fish intake was 1.2 g/day for Guizhou rural residents.[52] The average rice ingestion was 428 ± 157 g/day,[36] representing the main dietary source of MeHg in the study area.[4] The relatively lower δ^{202}Hg and Δ^{199}Hg in the hair samples most likely caused by rice consumption, as evidenced by the lower THg δ^{202}Hg in rice from WMMA compared to those found in fresh water and marine fish; and the lower THg Δ^{199}Hg in rice relative to those in human hair.[40,41] Higher Δ^{199}Hg has been found in MeHg compared to IHg in biological samples.[35] It is therefore important to explore if Δ^{199}Hg of MeHg in rice can explain the offset between rice THg Δ^{199}Hg and hair Δ^{199}Hg, as discussed in the next section.

Isotopic Compositions of MeHg and IHg Fractions in Rice. The Hg CSIA results for the rice samples are shown in Table 3. The mean (±SD) $\delta^{202}Hg_{IHg}$ and $\Delta^{199}Hg_{IHg}$ values in the rice samples were −2.30‰ ± 0.49‰ (n = 7) and −0.08‰ ± 0.04‰ (n = 7), respectively, significantly lower than the δ^{202}Hg for the MeHg species ($\delta^{202}Hg_{MeHg}$ − 0.80‰ ± 0.25‰ and $\Delta^{199}Hg_{MeHg}$ 0.08‰ ± 0.04‰, n = 7). The $\delta^{202}Hg_{MeHg}$ values were 1.50‰ higher than the $\delta^{202}Hg_{IHg}$ values, and the $\Delta^{199}Hg_{MeHg}$ values were 0.16‰ higher than the $\Delta^{199}Hg_{IHg}$ values. The positive correlation between MeHg fraction and δ^{202}Hg (or Δ^{199}Hg) in biological samples suggests that MeHg and IHg have distinct isotopic signatures,[27,33,44] and this finding has been verified for fish CRMs by Masbou et al.[35] and in this study that shows MeHg are isotopically distinguished from IHg in rice samples for the first time.

The isotopic differences between the IHg and MeHg fractions may be explained by fact that rice receives IHg from both soil and the atmosphere (TGM) but MeHg solely from microbial methylation of soil IHg. The rice IHg δ^{202}Hg and Δ^{199}Hg values are consistent with the results published by Yin et al.,[41] showing that atmospheric TGM in WMMA has δ^{202}Hg values of −3‰ and Δ^{199}Hg values of −0.3‰, much lower than the values for paddy soils (δ^{202}Hg range of −1‰ to ∼0‰ and Δ^{199}Hg ≈ 0). The IHg in the rice samples had slightly negative Δ^{199}Hg values (−0.08‰ ± 0.04‰), supporting that IHg in rice is supplied by both soil and the atmosphere.[26,49] Negative δ^{202}Hg values of −3‰ to ∼−1‰ have been found in roots, stems, and leaves, supporting that IHg is isotopically lighter because these tissues predominantly contain IHg. In contrast, MeHg is mainly produced through the methylation of bioavailable IHg in paddy soil. Water-soluble Hg in the soil of WMMA has high δ^{202}Hg values (δ^{202}Hg = 0.70 ± 0.13‰) and shows little MIF.[53] The loss of lighter Hg isotopes during the adsorption of soluble Hg to sediment particles,[46,54] microbial reduction of Hg^{2+},[13] and evasion processes[48] can all shift the bioavailable IHg to higher δ^{202}Hg. The methylation of IHg should produce MeHg with a lower δ^{202}Hg than that for the IHg.[15] However, subsequent photo- and microbial-demethylation of Hg in rice paddies can shift the MeHg to higher δ^{202}Hg values.[13,17]

We did not measure the isotopic compositions of MeHg in the paddy soils, although the MeHg in soil may be isotopically different from the MeHg in rice. Janssen et al.[55] found that the δ^{202}Hg values for MeHg of sediment were higher than the δ^{202}Hg values of THg. The enrichment of heavier Hg isotopes in MeHg was explained by the methylation of bioavailable IHg giving a higher δ^{202}Hg value or the demethylation of MeHg causing the loss of isotopically lighter Hg^0. We hypothesize that MeHg in the paddy soils has similar Hg isotopic patterns to those found by Janssen et al.[55] High δ^{202}Hg values have been observed in water-soluble Hg in the paddy soil,[53] in which demethylation of MeHg was a crucial process.[6] Investigation of Hg isotope pattern in MeHg in paddy soil and pore water are needed to appoint the pollution source and possible accumulation mechanism of MeHg in rice.

The small positive $\Delta^{199}Hg_{MeHg}$ values were likely caused by the photodemethylation of MeHg in rice paddies.[26,49] A

Table 4. Modeled and Measured THg Δ^{199}Hg Values for Hair, Determined from the Δ^{199}Hg Values for Methylmercury and Inorganic Hg in Rice Using a Mixing Model

	rice				hair		
ID	MeHg/THg	$\Delta^{199}Hg_{IHg}$ (‰)	$\Delta^{199}Hg_{MeHg}$ (‰)	$\Delta^{199}Hg_{THg}$ (‰)	MeHg/THg	measured Δ^{199}Hg (‰)	modeled Δ^{199}Hg (‰)
A3	0.428	−0.05	0.03	−0.02	0.668	0.04	0.02
A9	0.464	−0.01	0.07	0.02	0.843	0.07	0.08
A10	0.525	−0.08	0.11	0.02	0.807	0.16	0.13
A15	0.468	−0.08	0.04	−0.03	0.987	0.08	0.09
A21	0.326	−0.15	0.12	−0.06	0.683	0.14	0.13
A22	0.496	−0.08	0.07	−0.01	0.579	0.13	0.02
A30	0.494	−0.08	0.10	0.01	0.757	0.17	0.11

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positive shift of 0.12‰ in the THg Δ^{199}Hg between rice and hair was found, corresponding to the increase of the mean MeHg fraction from 45.7% in rice to 76.1% in hair. A mixing model was built to estimate the Δ^{199}Hg increase from rice to human hair with assumptions that the increases were caused by the higher MeHg fraction in hair and the Δ^{199}Hg differences between the MeHg and IHg in the rice samples. As shown in Table 4, the modeled and measured Δ^{199}Hg values in hair were consistent and confirmed our hypothesis that the positive shift between the Δ^{199}Hg values for hair and rice was caused by the higher MeHg fractions in hair than in rice.

Quantification of Hg Sources to Rice Grains in WMMA. It has been shown in earlier studies[3,4,56] that paddy soil is the only source of MeHg to rice and that IHg in rice grains comes from soil (root transfer) and the atmosphere (TGM uptake). However, the individual Hg contributions from soil and from the atmosphere to IHg in rice are still unclear. MIF data help answer this question because the uptake of Hg by plants from the air and soil is unlikely to cause MIF.[23,29] Yin et al.[41] quantified the sources (soil and the atmosphere) of THg in different tissues of rice plants grown in WMMA using a MIF-based binary mixing model based on well-estimated MIF end-members for ambient air and paddy soils, as shown in eqs 3 and 4:

$$\Delta^{199}\text{Hg-IHg}_{\text{rice}} = f_{\text{A}} \times \Delta^{199}\text{Hg-IHg}_{\text{atm}} + f_{\text{S}} \times \Delta^{199}\text{Hg-IHg}_{\text{soil}} \quad (3)$$

$$f_{\text{A}} + f_{\text{S}} = 1 \quad (4)$$

where f_{A} and f_{S} are the IHg fractions supplied by the atmosphere and soil, respectively; Δ^{199}Hg-IHg$_{\text{rice}}$ is the Δ^{199}Hg value for the IHg of the rice samples; and Δ^{199}Hg-IHg$_{\text{atm}}$ and Δ^{199}Hg-IHg$_{\text{soil}}$ are the Δ^{199}Hg values for the IHg supplied by the atmospheric and soil end-members, respectively. Because MeHg in soil only accounted for 0.001% of THg at the study site,[57] the mean Δ^{199}Hg-THg value for paddy soils reported by Yin et al.[41] was used as the soil IHg MIF end-member. The mean Δ^{199}Hg-IHg$_{\text{atm}}$ also was adopted from Yin et al.[41] because similar sampling sites were used in both studies.

The model results are shown in Figure 4. The estimated mean (±SD) atmospheric IHg fraction in the rice was 31% ± 16% (n = 7). We took MeHg into account as soil-derived Hg and estimated that the mean (±SD) atmospheric THg fraction (f_{A}) in rice was 17% ± 11% (n = 7) (Figure 4), similar to the estimate of 22.6% ± 3.6% (n = 3) in Yin et al.[38] as well as the results reported by Strickman and Mitchell.[56]

Environmental Implications. Rice consumption is one of the major pathway of MeHg exposure in the inland areas of South China. It is an emerging concern because rice is an important dietary component not only in China but also in many other parts of the world. Rice shows distinct Hg isotope signatures compared to those found in fish. For fish-eating populations, an increase of approximately 2‰ in the δ^{202}Hg values between fish tissue and human hair but no MIF shift is seen. The observations in this study support the use of Hg isotopes to trace the sources of Hg in diet and demonstrated that stable isotope signatures of MeHg exposure through rice consumption is distinguished from through fish consumption using isotopic measurements of human hair. It is also shown that IHg and MeHg fractions in rice are isotopically different and that the differences can be detected using human hair. Further studies of Hg isotopes in the biomass samples of humans will improve our understanding on the behaviors and toxicological effects of different Hg species. Using the stable Hg isotope data (MIF in particular), the contributions of IHg from soil and the atmosphere to plants can be also quantified. Such information is important to the development of Hg remediation strategies for improving food safety.

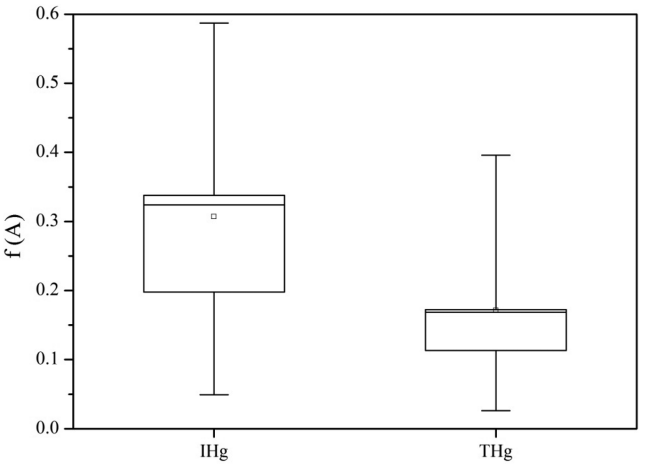

Figure 4. Estimated contributions of atmospheric Hg to inorganic Hg (IHg) and total Hg (THg) in rice grains from the WMMA, China. Each box-plot represents the interquartile range (25th and 75th percentile); the band inside the box is the 50th percentile (the median), the whisker represents the fifth and 95th percentile, and the dot is the mean.

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Notes

The authors declare no competing financial interest.

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