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Use of Mercury Isotopes to Quantify Mercury Exposure Sources in Inland Populations, China

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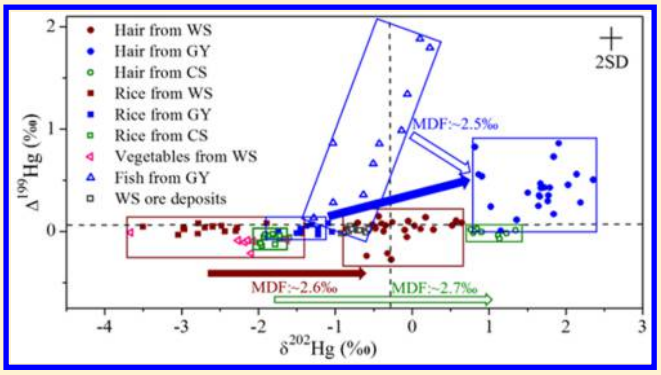
Supporting Information

ABSTRACT: Mercury (Hg) isotopic compositions in hair and dietary sources from Wanshan (WS) Hg mining area, Guiyang (GY) urban area, and Changshun (CS) rural area were determined to identify the major Hg exposure sources of local residents. Rice and vegetables displayed low δ^{202}Hg and small negative to zero Δ^{199}Hg, and are isotopically distinguishable from fish which showed relatively higher δ^{202}Hg and positive Δ^{199}Hg. Distinct isotopic signatures were also observed for human hair from the three areas. Shifts of 2 to 3‰ in δ^{202}Hg between hair and dietary sources confirmed mass dependent fractionation of Hg isotopes occurs during metabolic processes. Near zero Δ^{199}Hg of hair from WS and CS suggested rice is the major exposure source. Positive Δ^{199}Hg of hair from GY was likely caused by consumption of fish. A binary mixing model based on Δ^{199}Hg showed that rice and fish consumption accounted for 59% and 41% of dietary Hg source for GY residents, respectively, whereas rice is the major source for WS and CS residents. The model output was validated by calculation of probable daily intake of Hg. Our study suggests that Hg isotopes can be a useful tracer for quantifying exposure sources and understanding metabolic processes of Hg in humans.



INTRODUCTION

Mercury (Hg) is a globally distributed trace-element pollutant.[1] In the environment, inorganic mercury (IHg) is readily transformed to methylmercury (MeHg), a toxin that causes neurological damages such as visual, auditory, and sensory disturbances, numbness, and difficulty in walking.[2] MeHg has a strong bioaccumulation capability. Methylation of Hg readily occurs microbially in aquatic ecosystems, and bioaccumulation of MeHg can result in high levels of MeHg in fish that are long-lived and/or at the top of the food chain.[3] Fish consumption is considered as the major exposure pathway of Hg to humans.[4] Mercury exposure due to nonfish dietary sources is thought to be limited due to the short nature of food chain length. However, in Hg mining areas and many extreme Hg-contaminated sites, crops (especially rice) at the base of the food chain can also contain high levels of IHg and MeHg. Rice paddies have been shown to enhance Hg methylation, explaining high MeHg levels in rice.[5−8] In Guizhou province, China, rice as a staple food can be an important source of human Hg exposure.[9,10] Mercury exposure from nondietary sources is also important to specific population, such as Hg miners and gold miners.[11,12] Identifying Hg exposure pathways to a specific population is important for the health risk assessment, however this is often difficult because a comprehensive investigation of Hg concentration and speciation in numerous dietary sources is often needed to make the evaluation representative.[5]

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Mercury stable isotope geochemistry has been demonstrated as a useful approach to unravel sources and biogeochemical processes of Hg in the environment.[13,14] Mercury's seven stable isotopes (196−204 amu), can undergo mass-dependent isotope fractionation (MDF, reported as δ values) and mass-independent fractionation (MIF, reported as Δvalues) during various biogeochemical processes.[13] MDF occurs under both kinetic and equilibrium conditions, while Hg MIF for odd-mass numbers (Δ^{199}Hg and Δ^{201}Hg) is affected by magnetic isotope effect and nuclear volume effect,[15,16] and the even-mass-number isotopes (Δ^{200}Hg and Δ^{204}Hg) is likely a result of gas phase reactions in the atmosphere.[17] Combining "MDF-MIF" of Hg isotopes can provide multidimensional information about sources and geochemical fates of Hg in the environment. Hg isotopes have been used as tracers to understand exposure sources and bioaccumulation processes in food chains[18−21] and humans.[22−28] No significant MDF and MIF of Hg isotopes have been observed during consumption of dietary MeHg by fish.[19−21,29] However, an offset of ∼2‰ in δ^{202}Hg was observed between fish and hair of fish-consumers such as humans and whales, indicating that MDF of Hg isotopes may occur during metabolic processes in mammals.[22−27] Significant MIF signatures have also been reported in fish and fish-consumers, however the MIF was mainly explained by Hg photodegradation in ecosystems prior to trophic transfer, not by metabolic and trophic transfer processes.[18,30−34] The absence of MIF during metabolic and trophic transfer processes suggests that MIF can be a robust tracer to identify Hg sources in food webs.

In previous studies, Hg isotopes in hair were successfully used to identify exposure sources of Hg for gold miners[23,35] and fish-consumers.[22,24−27] Recently, the isotopic composition of Hg in rice from the Wanshan Mercury Mine in China was investigated, and rice showed more negative δ^{202}Hg and Δ^{199}Hg than fish.[28,36−38] We hypothesized that populations from Guizhou Province, China may have distinct hair isotopic signatures compared to previous results, since rice consumption is the most important pathway for human Hg exposure in Guizhou.[9,10] To test this hypothesis, we investigated the isotopic composition of Hg in human hair samples from local residents from three areas of the Guizhou Province, China, in a mining, an urban and a rural area. The isotopic composition of potential dietary Hg sources (e.g., rice, fish, and vegetables consumed by the study populations) were investigated as well.

EXPERIMENTAL SECTION

Site Description and Sample Collection. Three primary schools at Guiyang (GY), Changshun (CS), and Wanshan (WS) in Guizhou Province, SW China, were selected in our study (Supporting Information (SI) Figure S1. GY primary school is located in Guiyang (N 26°34′30.29″/E 106°3′21.66″, 1080 a.s.l.), the capital of Guizhou. Coal combustion is the major Hg emission source in GY.[39] The average of gaseous elemental Hg (9.72 ng m^{-3}) in ambient air in GY in 2009 was slightly higher than most of the cities in China such as Beijing, Shanghai, Chongqing and Nanjing, but much lower than Changchun and Guangzhou.[40] WS primary school (N 26°11′48.61″/E 106°32′57.91″, 1244 a.s.l.) is located in a small village in the Wanshan Hg mine area, the largest Hg mine in China. Mercury mining in WS has been documented for thousand years, and Hg mining and retorting activities intensified from the 1950s to 2001 when the mine was officially closed.[41] Long-term Hg mining and retorting activities have resulted in serious contamination of Hg to the surrounding environment (soil, sediment, food, water, and atmosphere).[42,43] CS primary school (N26°11′16.19″, E106°33′34.84″, 1282m a.s.l.) is located in a rural area, in a small residential community, 70 km far from Guiyang. CS has been used as a control site by previous study[9] due to lack of significant industrial activities, and a reliance on agriculture (rice and tobacco planting) as the main source of income for the local residents. Previously results showed that the average concentrations for gaseous elemental Hg in CS was only 7.9 ng m^{-3}, which was lower than GY (unpublished data).

Pupils and their supervision were selected for investigation. Sampling work was conducted from November 2013 to October 2014. Regarding human sampling, 26, 21, and 9 participants in WS, GY, and CS, respectively, were randomly selected for hair sample collection. Ages, gender, weight, heights, dental Hg amalgam using, and dietary information about each participant were investigated and summarized in SI Table S1. As shown in SI Table S1, people from GY consume more fish than WS and CS residents. Every participant signed a consent agreement before starting the survey. The present study obtained ethics approval from the Institute of Geochemistry, Chinese Academy of Sciences.

Hair samples (0.2−0.5 g) were cut with stainless steel scissors from the occipital region of the scalp, bundled together by stapler, placed and sealed in polythene bags, according the method by Li et al.[44] Fillet fish (15−20 g), rice (15−20 g), and vegetables (10−25 g) were collected from the kitchen of each participant. According to our investigation, rice and vegetables collected from WS and CS were grown and harvested locally, but food samples collected from GY were bought from the market. The fish samples were collected directly from the participant's house to ensure that these species were consumed regularly by the local residents. The fish species were not identified but Guizhou Province is an inland area and most of fish obtained the market are caught from freshwater aquaculture. All the hair and food samples were kept in a cooler before being delivered to the laboratory. The samples were washed with distilled water. The fillet fish and vegetables samples were freeze-dried (−55 °C, 72 h), and the rice samples were air-dried (72 days). The dried samples were then powdered and stored in polyethylene bags in room temperature until chemical analyses.

Total Mercury Concentration Analysis. The total Hg concentrations (THg) in all hair and fillet fish samples, as well as vegetable and rice samples from WS, was measured by atomic absorption spectroscopy (RA915+ with a pyrolysis unit Pyro-915+, Lumex, Russia) following a method reported previously.[45] The limit of detection is 0.5 ng g^{-1}. For rice samples from GY and CS, approximately 0.1−0.2 g of each sample was digested with 5 mL of acid mixture (HNO_3:H_2SO_4 = 4:1, v:v) at 95 °C for 3 h. Then the THg concentrations in digestive solutions were determined by cold vapor atomic fluorescence spectroscopy (CVAFS) following the Method 1631E,[46] with limit of detection of 0.3 ng g^{-1}.

The internal calibration of RA915+ was verified prior to sample measurement using a saturated Hg^0 vapor source. When the relative standard deviation (RSD) was <5%, the instrument can be used for analysis. Duplicates were measured for each sample, and the relative difference percentages were lower than 5%. Certificated Reference Materials (CRMs) of GBW07601 (human Hair), GBW10020 (citrus leaves), TORT-2 (lobster), and GBW10014 (cabbage) were used for quality control of

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samples with different matrixes. The average recoveries of these CRMs were 94 ± 5% (n = 16), 104 ± 8% (n = 12), 99 ± 7% (n = 10), and 97 ± 7% (n = 10) respectively.

MeHg Concentration Analysis. Hair and fillet fish samples were digested with 25% KOH, while rice and vegetable samples were digested using the KOH-methanol/solvent extraction technique, following previous methods.[47,48] The MeHg concentration in digest solutions were measured using the aqueous ethylation, purge and trap, and GC−CVAFS (Brooks Rand Model III) following Method 1630.[49] The limit of detection is 0.3 ng g^{-1}. Method blanks, CRMs, and sample duplicates were included for quality control. Recoveries for NIES-13 and TORT-2 were 94 ± 5% (n = 17) and 87 ± 6% (n = 15), respectively. The relative difference percentages were lower than 10% for duplicate samples.

Mercury Isotope Measurement. Mercury isotopes were measured by a Nu-Plasma II multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) following a previous method.[50] For all hair and fillet fish samples, and vegetable and rice samples from WS, approximately 0.1−0.5 g of samples was digested in a water bath (95 °C, 3 h) using 5 mL of fresh mixture of HNO_3/H_2SO_4 (v/v, 4:1). After complete digestion, the sample solutions were diluted to Hg concentrations of 1 ng mL^{-1} and acid concentrations of 10−20%, prior to isotopic ratio analysis. Standard reference materials (BCR482: lichen) and sample duplicates were prepared. For lower THg concentrations (rice samples from GY and CS), 5 g of each sample was digested in a water bath (95 °C, 3 h) using 50 mL of acid mixture (HNO_3:H_2SO_4= 4:1, v/v). Each digest was diluted to 250 mL and reduced by $SnCl_2$, and Hg was purged into 5 mL 40% reverse aqua regia using Hg-free N_2 gas (300 L min^{-1}). The trapping solutions were subsequently diluted to Hg concentration of 1 ng mL^{-1} Hg and acid concentrations of 10−20%. A 18.2-ΩM-grade water (Millipore, Bedford, USA) was used for dilution. Standard reference materials were also prepared in the same way. Instrumental mass bias was corrected using an internal Tl standard (NIST SRM 997, 20 ng mL^{-1}) and sample-standard bracketing. Mercury concentrations and acid matrices of the bracketing standard (NIST SRM 3133) were systematically matched to the neighboring samples. Mercury concentration in sample solutions were determined by MC-ICP-MS using ^{202}Hg signals, the results of which were matched within 10% by Lumex RA915+ or CVAFS.

Hg-MDF is expressed in δ^{202}Hg notation in units of permil (‰) referenced to the neighboring NIST-3133 Hg standard (eq 1):

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

where xxx refers to the mass of each isotope between 199 and 202 amu. MIF is expressed as the difference between the measured δ^{xxx}Hg values, the value predicted based on MDF, and the δ^{202} Hg value (eqs 2 and 3).

$$\Delta^{199}\mathrm{Hg} = \delta^{199}\mathrm{Hg} - 0.252 \times \delta^{202}\mathrm{Hg} \quad (2)$$

$$\Delta^{200}\mathrm{Hg} = \delta^{200}\mathrm{Hg} - 0.502 \times \delta^{202}\mathrm{Hg} \quad (3)$$

$$\Delta^{201}\mathrm{Hg} = \delta^{201}\mathrm{Hg} - 0.752 \times \delta^{202}\mathrm{Hg} \quad (4)$$

UM-Almadeń[51] and ETH-Fluka[52] secondary standard solutions (diluted to 1 ng mL^{-1} Hg in 10% acid) were analyzed as a secondary standard, using the same analytical treatment. Our results for UM-Almadeń (δ^{202}Hg = −0.56 ± 0.15‰; Δ^{199}Hg = −0.02 ± 0.06‰; Δ^{200}Hg = 0.02 ± 0.04‰; Δ^{201}Hg= −0.03 ± 0.06‰, 2SD; n = 10) and ETH-Fluka (δ^{202}Hg = −1.47 ± 0.23‰; Δ^{199}Hg = 0.09 ± 0.05‰; Δ^{200}Hg = 0.03 ± 0.04‰; Δ^{201}Hg = 0.02 ± 0.10‰, 2SD; n = 9) agreed well with previous results.[51,52] The determined isotopic composition of BCR482 (δ^{202}Hg = −1.52 ± 0.20‰; Δ^{199}Hg= −0.60 ± 0.15‰; Δ^{200}Hg = 0.05 ± 0.05‰; Δ^{201}Hg = −0.57 ± 0.13‰, 2SD; n = 6) was also comparable with previous results.[53] The external precision of replication UM-Almadeń secondary standard solution was used to represent the analytical uncertainty (2SD).

Statistical Analysis. Statistical analyses were performed with SPSS 19 for Windows. The data are tested for normal distribution by the Kolmogorov−Smirnov test. If they were not normally distributed, the data were log transformed for further statistical analysis. The characteristics of the data were described in Mean ± Standard Deviation (SD) for descriptive statistics. Mean values of the data at different sites were compared using independent-sample t tests and one-way analysis of variance (ANOVA). The correlation coefficients were determined by Pearson correlation analysis. Results of statistical tests were considered statistically significant if $p < 0.05$.

RESULTS AND DISCUSSION

THg and MeHg Concentrations in Hair and Diet. THg and MeHg concentrations of all samples are shown in SI Table S2 . For rice and hair samples, Hg concentrations were reported in dry weight, and for fillet fish and vegetable samples, concentrations were reported in wet weight. The mean hair THg concentration in WS (mining site) was 4478 ± 3422 ng g^{-1} (2SD, n = 26), which was significantly higher than in the urban site, GY (398 ± 396 ng g^{-1}, 2SD, n = 21) and in the rural site, CS (334 ± 236 ng g^{-1}, 2SD, n = 9). Mean MeHg concentrations in hair showed similar patterns with THg, which were also the highest in WS (2242 ± 1922 ng g^{-1}, 2SD, n = 25), followed by GY (236 ± 192 ng g^{-1}, 2SD, n = 21) and CS (213 ± 134 ng g^{-1}, 2SD, n = 9). MeHg fractions in hair accounted for 51 ± 26%, 65 ± 42%, and 63 ± 28% of THg concentrations at WS, GY, and CS, respectively. No significant correlations were observed between hair Hg concentrations and basic information (e.g., age, weight, and height) of the studied population (SI Figure S2 of SI).

The mean rice THg and MeHg concentration in WS (THg: 79 ± 78 ng g^{-1}; MeHg: 17 ± 16 ng g^{-1}; 2SD, n = 15) were also significantly higher than those in GY (THg: 3.6 ± 1.0 ng g^{-1}; 1.8 ± 1.2 ng g^{-1}; 2SD, n = 11) and CS (THg: 4.8 ± 1.0 ng g^{-1}; 2.7 ± 0.6 ng g^{-1}; 2SD, n = 14). Average MeHg content represented 25 ± 28%, 51 ± 30% and 57 ± 14% of THg in rice samples from WS, GY and CS, respectively. No significant differences were observed between THg concentrations in rice samples collected from GY and CS ($p > 0.05$). Significant differences in rice MeHg proportions as THg (%MeHg) were observed between WS and GY, as well as between WS and CS, which indicated different MeHg production potential at these sites. The THg and MeHg concentrations, and %MeHg in rice and hair samples collected from WS were comparable with previous results reported by Feng et al.[9] and Li et al.,[54] at the same sampling sites.

The mean THg concentration in vegetables in WS was 139 ± 280 ng g^{-1} (2SD, n = 8), which was comparable with previous results (87−436 ng g^{-1}) by Zhang et al.[10] and Feng et al.[9] at

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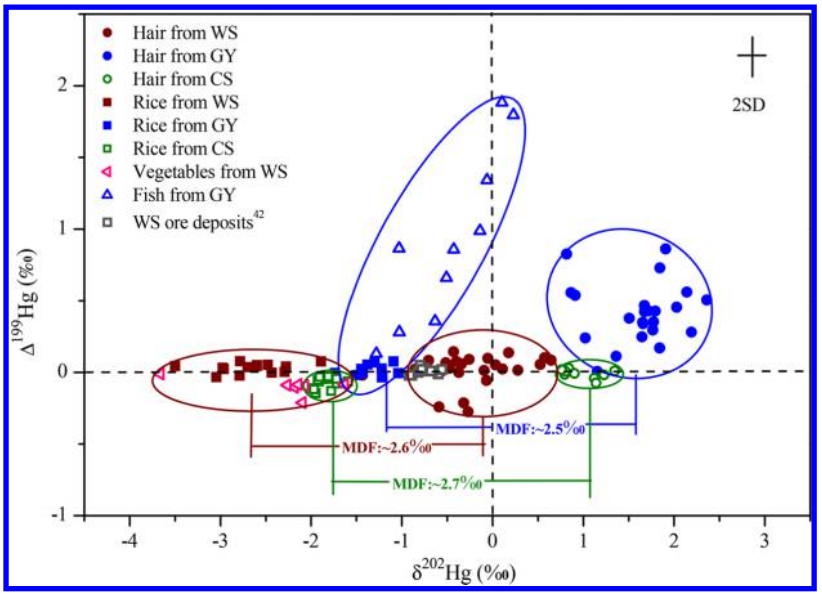

Figure 1. Hg isotopic compositions in human hair, fish, rice, and vegetables samples collected from WS, GY, and CS.

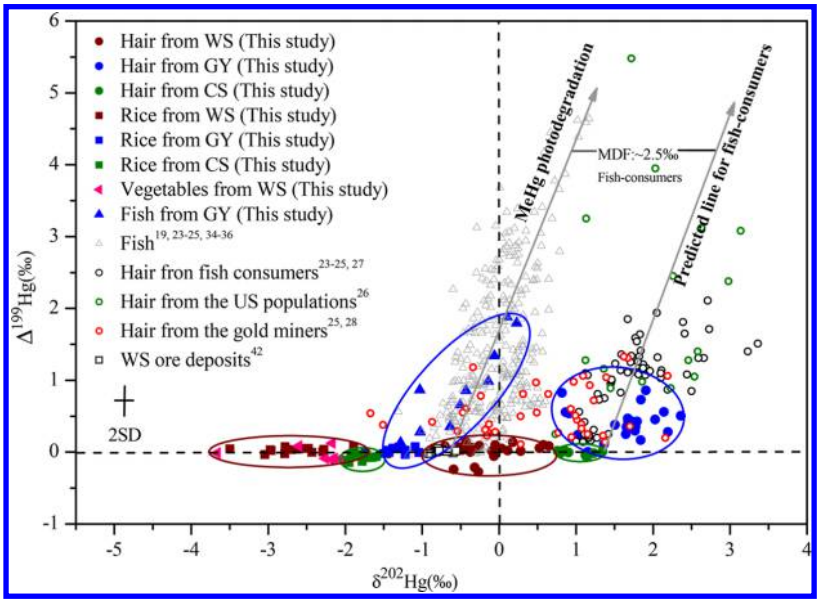

Figure 2. Hg isotopic compositions between human hair and diet samples. Hair of fish-consumers were from France,[24] Bolivian Amazon,[23] Gulf of Mexico,[26] the United States,[25] and Augusta Bay.[22] Hair of gold miners were from Boliva[24] and Ghanaian.[35]

the same site. Generally, MeHg constitutes a small fraction (0.1% to 0.2%) of THg in vegetables, and human MeHg exposure through vegetable consumption can be negligible.[9,10] The mean THg and MeHg concentration in fillet fish samples collected from GY was 43 ± 70 ng g^{-1} and 27 ± 32 ng g^{-1} (2SD, n = 10), respectively. On average, the MeHg accounted for 70% ± 38% of THg in the fillet fish samples.

Hg Isotope Compositions of Dietary Sources. Hg isotopes compositions of all samples were shown in SI Table S2, and, plotted for comparison in Figure 1. Rice samples were isotopically distinguishable among the three sites. The mean δ^{202}Hg and Δ^{199}Hg values in rice samples collected from WS were −2.59 ± 0.98‰ and 0.03 ± 0.06‰ (2SD, n = 15) respectively. The δ^{202}Hg were consistent with previous results from Yin et al. (−2.38 ± 0.32‰, 2SD, n = 6),[38] but lower than those from Feng et al. (−1.60 ± 2.80‰, 2SD, n = 14)[36] and Rothenberg et al. (−1.23 ± 1.38‰, 2SD, n = 8).[28] The Δ^{199}Hg values were within the range of previous studies.[28,36,43] Rice samples collected from GY showed relatively higher mean δ^{202}Hg values (−1.35 ± 0.38‰, 2SD, n = 11) but similar Δ^{199}Hg values with WS rice (0.02 ± 0.08‰; 2SD; n = 11). Rice samples collected from CS showed intermediate δ^{202}Hg values (−1.83 ± 0.24‰, 2SD, n = 14), but characterized with slightly negative Δ^{199}Hg (−0.07 ± 0.08‰, 2SD, n = 14). Vegetables collected from WS showed negative δ^{202}Hg (−2.34 ± 1.12‰, 2SD, n = 9) and Δ^{199}Hg (−0.05 ± 0.14‰, 2SD; n = 9). Fillet fish samples collected from GY had mean δ^{202}Hg of −0.48 ± 1.04‰, and mean Δ^{199}Hg of 0.96 ± 1.30‰ (2SD; n = 10), which are distinct from rice and vegetable samples (Figure 1).

As shown in Figure 1, rice and vegetables showed negative δ^{202}Hg values, which have been explained by the significant MDF of −3 to −1‰ during incorporation of Hg by plants.[55,56] Plants receive Hg mainly from atmosphere and soil. Previous

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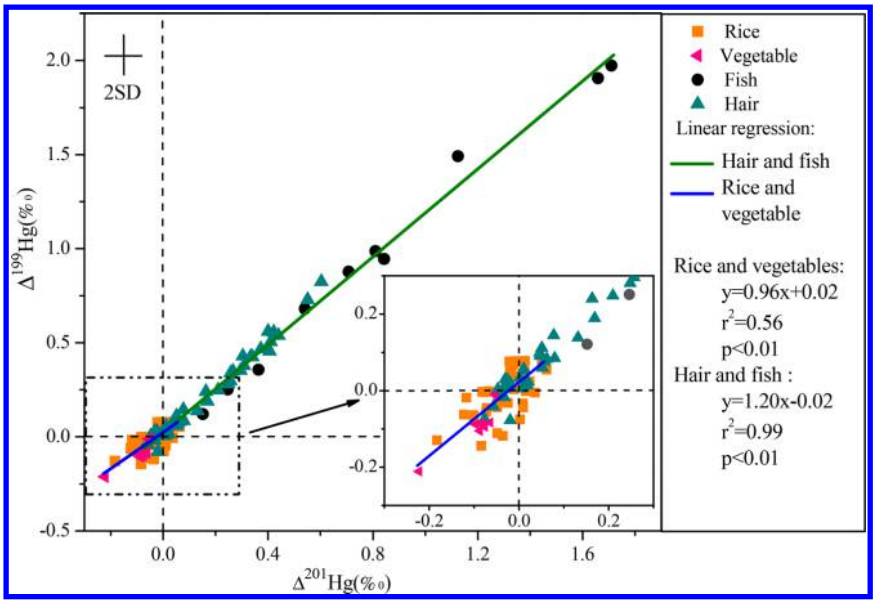

Figure 3. Δ^{201}Hg versus Δ^{199}Hg in hair and diet samples.

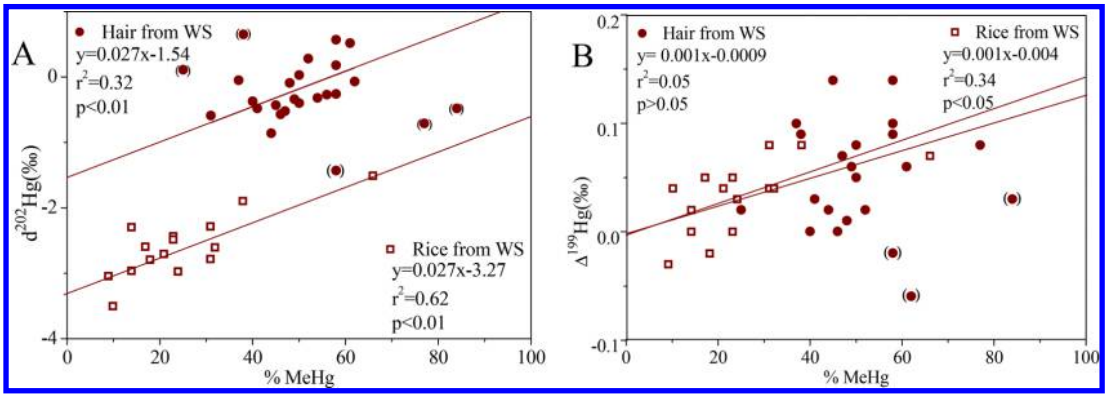

Figure 4. Correlation between Hg isotopic composition and %MeHg of hair and rice from WS.

studies showed that the metabolic effects are unlikely to cause MIF.[23,32,38] The near-zero Δ^{199}Hg values in rice samples were similar to the previous results of soils in WS and GY, which showed limited MIF signals. This was consistent with previous studies, which demonstrated that Hg in rice is mainly derived from soils.[38] Lichens[55] and plant leaves[38,57−59] showed negative Δ^{199}Hg values, which have been explained by the uptake of atmospheric Hg^0 by foliage. Vegetables from WS showed variable Δ^{199}Hg values with a range of −0.10 to 0.08‰. Few of our vegetables have negative Δ^{199}Hg values, indicating that atmospheric Hg(0) is the major source. However, most of the vegetables showed limited MIF signals, which may be explained by the contribution of soil Hg in these samples.

The higher δ^{202}Hg and Δ^{199}Hg in GY fillet fish are in general agreement with previous results for freshwater and marine fish (Figure 2).[21,34] Previous studies have shown the absence of both MDF and MIF during Hg metabolism and trophic transfer in aquatic food chains,[19,20] and the higher δ^{202}Hg and Δ^{199}Hg values in fish have been explained by photodegradation of MeHg in the water column.[60] Δ^{199}Hg/Δ^{201}Hg ratios of 1.20−1.36 were previously reported for aquatic organisms and human hair samples, which have been attributed to the MeHg photodegradation processes in the aquatic environment before MeHg was transferred and bioaccumulated in food chains.[34,60−62] In addition, a ratio of about 1.0 for Δ^{199}Hg/Δ^{201}Hg was observed for samples with lower MeHg fractions (e.g., soils, plants, and atmosphere), and this MIF was mainly a result of aqueous Hg^{2+} photoreduction.[18,63] In our study, rice and vegetables showed a Δ^{199}Hg/Δ^{201}Hg ratio of 0.96 ± 0.24 (2SD, r^2 = 0.55, p < 0.01), suggesting Hg has undergone Hg^{2+} photoreduction before being incorporated into the plants. Fillet fish from GY showed Δ^{199}Hg/Δ^{201}Hg of 1.20 ± 0.05 (2SD), suggesting MIF was mainly caused by MeHg photodegradation (Figure 3). Interestingly, slightly positive Δ^{200}Hg values (0.14 ± 0.12‰, 2SD, n = 10) were observed in fillet fish from GY (SI Table S2), and similar extent of positive Δ^{200}Hg were previously reported for fish from Lake Michigan (0.12 ± 0.04‰, 2SD).[18] The Δ^{200}Hg values in fillet fish seems to be a result of methylation of precipitation-derived Hg^{2+} in surface water after being deposited, whereas slightly positive Δ^{200}Hg values (0.09 ± 0.12‰, 2SD) were reported in precipitation from Guiyang.[64]

Significant correlations between Hg isotope signatures (δ^{202}Hg and Δ^{199}Hg) and %MeHg were observed in rice collected from WS (Figure 4). All rice samples in WS were collected from a small region and therefore we proposed that Hg isotope signatures (δ^{202}Hg and Δ^{199}Hg) in these rice samples were mixed by IHg and MeHg. Using the regression equations, we calculated the isotope compositions of MeHg and IHg in rice samples. The mean $\delta^{202}Hg_{IHg}$ and $\Delta^{199}Hg_{IHg}$

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values in the rice samples were −3.30‰ and 0.01‰, respectively, which were significantly lower than the $\delta^{202}Hg_{MeHg}$ and $\Delta^{199}Hg_{MeHg}$ (δ^{202}Hg: − 0.49‰, Δ^{199}Hg: 0.15‰). The $\delta^{202}Hg_{MeHg}$ was 2.8‰ higher than the $\delta^{202}Hg_{IHg}$, and the $\Delta^{199}Hg_{MeHg}$ was 0.16‰ higher than the $\Delta^{199}Hg_{IHg}$. Our results were comparable with the results from Li et al. (2017),[37] which proved that IHg and MeHg in rice have distinct Hg isotopic compositions.[37] However, no significant correlations between Hg isotope signatures (δ^{202}Hg and Δ^{199}Hg) and %MeHg were observed in rice and fish samples collected from GY and CS (SI Figure S3). The rice and fish samples collected in GY were bought from the market, which showed complex Hg isotope signatures. Because of narrow range of %MeHg in rice samples collected from CS and no significant correlations were obtained between Hg isotope signatures and %MeHg (SI Figure S3).

Mercury Isotope Compositions of Human Hair. Hg isotopic signatures in hair samples can also be distinguished among the three sites (Figure 1). The mean δ^{202}Hg and Δ^{199}Hg values in hair samples collected from WS were −0.24 ± 0.94‰ and 0.02 ± 0.22‰ (2SD; n = 25), respectively. Hair samples collected from CS showed higher mean δ^{202}Hg values (0.99 ± 0.44‰; 2SD; n = 9), and near zero Δ^{199}Hg−0.01 ± 0.03‰; 2SD; n = 9). Hair samples collected from GY showed the highest δ^{202}Hg values (1.62 ± 0.86‰; 2SD, n = 21) and positive Δ^{199}Hg values (0.42 ± 0.42‰; 2SD; n = 21). For each site, no significant differences in hair δ^{202}Hg and Δ^{199}Hg values were observed between males and females, nor between children and adults.

For hair samples collected from WS, significant correlation between δ^{202}Hg and %MeHg was observed when removing five anomalous values (Figure 4). The regression line of hair δ^{202}Hg vs %MeHg were parallel to that of rice δ^{202}Hg vs %MeHg. Using the regression equations, we calculated the isotope compositions of MeHg and IHg in hair samples. Shifts of about 1.7‰ were both observed between hair and rice $\delta^{202}Hg_{MeHg}$ and between hair and rice $\delta^{202}Hg_{IHg}$. It indicated that MDFs of both IHg and MeHg during metabolic process in human body (rice to hair) were 1.7‰. Nearly same regression equation of hair Δ^{199}Hg vs %MeHg was obtained with that of rice in WS, which proved that no MIF occurred during metabolic process of Hg in human body. However, no significant correlations between isotope signatures and %MeHg of hair samples from GY and CS were observed (SI Figure S3).

The positive correlation ($y = 0.040x + 0.19$, $r = 0.58$, $p < 0.01$, n = 23, Pearson analysis) between the number of fish meals and human hair Δ^{199}Hg values from GY also demonstrates that fish consumption is one of the main explanation for the positive MIF in GY hair (Figure 5). Most of the participants (15/23) in GY consumed 4−9 fish meals/month. Individuals who ingested >8 fish meals/month have hair Δ^{199}Hg of 0.58 ± 0.30‰ (2SD, n = 5), higher than those who ingested <8 fish meals/month (0.46 ± 0.28‰, 2SD, n = 7). Our results are consistent with those of Rothenberg et a,[28] who found that participants who consumed fish ≥ twice/weekly had significant higher hair Δ^{199}Hg values than those who consumed fish less often.

Distinct Hg isotopic signatures have been observed in hair samples from different populations when plotting all previous results as shown in Figure 2. For example, hair of fish-consumers in previous studies[22−24,26] were characterized by largely positive δ^{202}Hg and Δ^{199}Hg values. The δ^{202}Hg and Δ^{199}Hg for hair of fish-consumers are positively and linearly correlated, and the regression line for the hair of fish consumers

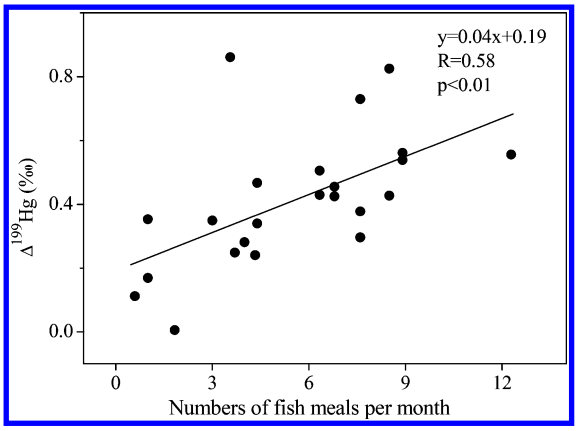

Figure 5. Hair Δ^{199}Hg versus numbers of fish meals per month for GY residents.

is in parallel to that of fish samples (Figure 2.). The δ^{202}Hg and Δ^{199}Hg values of fish are often positively correlated, which can reflect MeHg photodemethylation in the water column before its incorporation into the food chain.[60] Using the methods presented in Bergquist and Blum,[18] we estimated that about 10−20% of MeHg is photodemethylated prior to being bioaccumulated by fish. Incorporation of water MeHg in fish is not associated with MDF and MIF.[19,20] An offset of about 2‰ in δ^{202}Hg values is evident between fish and hair of fish consumers, which can be explained by MDF during MeHg demethylation within the liver in mammals, and the excretion of inorganic Hg^{2+} with lower δ^{202}Hg in urine.[27] As shown in Figure 2, hair of fish consumers and fish samples showed a similar range of Δ^{199}Hg values, which is consistent with the observation that metabolic processes and tropic transfer do not cause MIF.[19,20] Gold miners in general showed relatively less positive δ^{202}Hg and Δ^{199}Hg values in hair than fish consumers.[23,25] Liquid Hg used for gold extraction has been characterized by negative δ^{202}Hg values (−0.31 ± 0.48‰, 2SD, n = 5) and no MIF (Δ^{199}Hg: − 0.02 ± 0.08‰, 2SD, n = 5).[23] A similar offset of δ^{202}Hg (~2‰) can be observed between liquid Hg and hair of gold miners. The small positive MIF in gold miners can be explained by consumption of fish, because fish is an important dietary source of Hg for gold-miners working in the Amazon basin.[23] Rice consumers from Daxin, China showed lower δ^{202}Hg and Δ^{199}Hg values in hair than Amazonian fish consumers and gold miners, which has been explained by the lower frequency of fish consumption.[28]

Our study shows some of the lowest hair δ^{202}Hg and Δ^{199}Hg values observed to date, especially those at WS and CS (Figure 2). Rice has been demonstrated as the major dietary source of MeHg for populations in Guizhou, China.[9,10] Rice in this study and in previous studies in general has more negative δ^{202}Hg values than fish and Hg ore deposits (Figure 2). Offsets of about 2‰ to 3‰ (2.39‰, 2.42‰, and 2.83‰ in WS, GY, and CS, respectively) were also observed when comparing rice δ^{202}Hg values to hair at the same locations. Rice as a dominant source of Hg exposure is also revealed by the absence of MIF in hair at CS, as rice in CS has near zero Δ^{199}Hg values. Major Hg exposure sources for WS residents include rice and vegetables.[10] Rice and vegetables at WS showed slightly negative to zero MIF. Considering the low proportion of % MeHg, and the low bioavailability of inorganic Hg in vegetable, the contribution of vegetable Hg should be much lower than that of rice. Hair from GY have positive Δ^{199}Hg values (0.01 to

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0.86‰), which cannot be explained by rice consumption. As shown in SI Table S1, rice is the primary but not exclusive dietary source of MeHg exposure for GY residents. Fish consumption may be the main reason for the positive MIF observed in GY hair. Hair samples from GY showed $\Delta^{199}Hg/\Delta^{201}Hg$ of 1.21 ± 0.05 (2SD), consistent with that of GY fillet fish (Figure 3). Unlike fish, hair from GY showed near zero $\Delta^{200}Hg$ value (0.02 ± 0.04‰; 2SD; n = 23), which may be caused by the dilution of Hg from rice and other dietary sources, or the fish caught from surface water where there was not receiving significant precipitation-derived Hg^{2+} or MeHg.

Quantifying Hg Sources in the Human Diet and Other Exposure Pathways by Isotope Mass Balance. Due to the absence of MIF during metabolic process and trophic transfer, the MIF in human hair may be used as an indicator to differentiate Hg sources and pathways. A binary mixing model was used here to evaluate the exposure of Hg by consumption of fish and nonfish sources (eqs 5 and 6):

$$\Delta^{199}Hg_{hair} = F_{non-fish} * \Delta^{199}Hg_{non-fish} + F_{fish}\Delta^{199}Hg_{fish} \quad (5)$$

$$F_{fish} = 1 - F_{non-fish} \quad (6)$$

where $\Delta^{199}Hg_{hair}$, $\Delta^{199}Hg_{fish}$, and $\Delta^{199}Hg_{nonfish}$ are the $\Delta^{199}Hg$ values of hair, fish, and rice at each site respectively, and, F_{fish} and $F_{nonfish}$ represent the fraction of Hg from fish and nonfish sources, respectively. The mean $\Delta^{199}Hg$ for GY fish was used as the end-member for the fish source, and the mean $\Delta^{199}Hg$ of local rice was used as the end-member for the nonfish dietary source at each of the three sites. According to our model output, the nonfish source of Hg constitutes 59% ± 42% (2SD, n = 17) of THg in GY hair, whereas $F_{nonfish}$ values in WS and CS were 95% ± 12% (2SD, n = 25) and 96% ± 6% (2SD, n = 16) (Figure 6). This is consistent with the previous result that residents from GY consumed more fish (9.1 g per day) than in rural areas of Guizhou (1.2 g per day).[65]

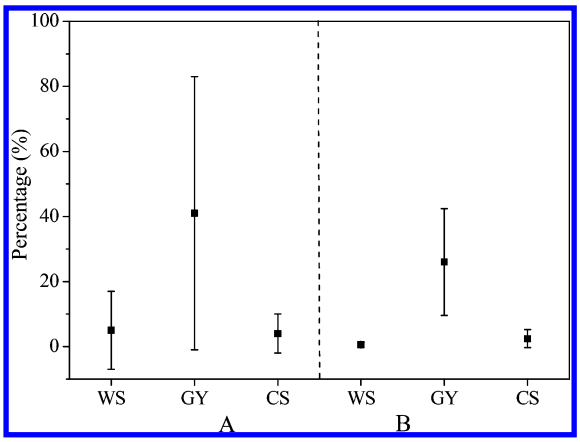

Figure 6. Relative contribution of fish consumption to hair mercury by MIF mixed model (A) and diet calculation (B).

The concentrations of potential exposure sources including rice, fish, vegetables, meat and inhalation have been previously reported.[9,10,66−68] To independently evaluate the Hg exposure of the three populations in this study, a dietary model that includes major dietary Hg sources was explored, using the following eqs 7 and 8):

$$DAA = \sum (C^{i}_{MeHg} \times IR^{i} \times AE^{i}_{MeHg} + C^{i}_{IHg} \times IR^{i} \times AE^{i}_{IHg}) \quad (7)$$

$$f^{i} = (C^{i}_{MeHg} \times IR^{i} \times AE^{i}_{MeHg} + C^{i}_{IHg} \times IR^{i} \times AE^{i}_{IHg})/DAA \quad (8)$$

where DAA refers to the daily absorption amount, is in micrograms per day; C is the concentration of Hg in the exposed medium; IR is intake rate (or ingestion rate or inhalation rate); AE is absorption efficiency; i refers to intake of rice, fish, vegetables, meat, and air; and f (%) refers to the fraction of Hg exposure. IR values were obtained from the Guizhou Bureau of Statistics (GBS),[65] and AE values were based on the World Health Organization (WHO).[69,70] Details about the parameters (e.g., DAA, C, IR, AE, i and f) are listed in SI Table S3. eq 8 was modified from Zhang et al.,[10,70] which calculated the daily intake of the THg based on the intake of rice, fish, vegetables, meat, and air and corresponding THg and MeHg concentrations. However, they did not consider the differences in absorption efficiencies of IHg and MeHg in human body. In this study, the absorption efficiencies of IHg and MeHg were considered as shown in eqs 7 and 8.

These dietary calculations show that the relative contribution of Hg from rice, fish, vegetable, meat, and air account for 58% ± 38%, 0.58% ± 0.7%, 25% ± 27%, 7.0% ± 3.0%, and 10% ± 21%, respectively, for human exposure in WS; 81% ± 9.8%, 2.3% ± 2.8%, 5.4% ± 2.8%, 2.5% ± 0.02%, and 9.1% ± 1.8%, respectively, for human exposure in CS; and 44% ± 15%, 26% ± 16%, 7.9% ± 3.9%, 5.2% ± 0.1%, and 17 ± 17%, respectively, for human exposure in GY (SI Figure S4).These results are in general agreement with those estimated by the MIF binary mixing model, confirming that rice consumption was the dominant source for human Hg exposure in WS and CS, whereas GY residents also absorb Hg from other dietary sources (e.g., fish, vegetables, and meat) (Figure 6).

Environmental Implications. Our study has potential implication in identification of human Hg exposure source and risk controls. Mercury poses a substantial human-health risk via fish consumption. More recently, and specifically in China, rice is regarded as an important dietary source of Hg because rice is capable of bioaccumulating Hg from paddy soils, especially at polluted sites.[6,9] Identifying and quantifying human Hg exposure sources remain challenges due to the complexity of the dietary sources. In this study, Hg isotopes were an effective tracer for "fingerprinting" exposure sources and metabolic processes in humans. The MIF signature of Hg is particularly useful in identifying exposure sources. We showed that rural residents in Guizhou, China have significantly lower Hg-MIF compared to urban fish-consumers. The low MIF suggests nonfish intake (mostly from rice) is the major exposure source of Hg to Guizhou residents. This study shows certain advantages of using Hg isotopes for human risk assessment, compared with the traditional method of dietary calculation. Using a binary mixing model based on the MIF signals, the Hg exposure from different sources can be quantified, which can be used to advise risk controls of human Hg exposure.

The results obtained in this study can better understand metabolic processes of Hg in human body. The offsets of $\delta^{202}Hg$ values between rice and rice consumers' hair at the three sites ranged from 2‰ to 3‰. About 1.7‰ of MDF occurred both for MeHg and IHg during the metabolic process in human body, and the elevation of %MeHg from rice to hair resulted in these higher offsets (2.5−2.7‰). It was well-known that ~2‰ of offsets were observed between fish and fish consumers' hair.[23,27] MeHg is the dominated form (>90%) of Hg in fish and hair samples in Europe and North America, and there were

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nearly no changes of %MeHg from fish to hair of fish consumer. More researches on isotope fractionation of different Hg species during metabolic processes in human body are needed to verify this hypothesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b05638.

Tables (Table S1−S3) and Figures (Figures S1−S4). Gender, age, height, weight, and dietary information on participants (Table S1). THg and MeHg concentrations, %MeHg and Hg isotopic composition in human hair and dietary samples (Table S2). Parameters used in calculation of daily absorption amount (Table S3). Locations of studied sites (Figure S1). Correlations between hair THg and MeHg concentrations and ages, heights, and weights (Figure S2). Correlation between Hg isotopic composition and %MeHg of hair, rice, and fish (Figure S3) from GY and CS. Relative contribution of different THg exposure sources for populations from WS, GY, and CS (Figure S4) (PDF)

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■ REFERENCES

(1) Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; Pirrone, N. Mercury as a global pollutant: sources, pathways, and effects. *Environ. Sci. Technol.* **2013**, *47* (10), 4967−4983.

(2) Clarkson, T. W. The three modern faces of mercury. *Environ. Health. Perspect.* **2002**, *110*, 11−23.

(3) Fitzgerald, W. F.; Lamborg, C. H.; Hammerschmidt, C. R. Marine biogeochemical cycling of mercury. *Chem. Rev.* **2007**, *107*, 641−662.

(4) Mergler, D.; Anderson, A. H.; Chan, H. M.; Mahaffey, R. K.; Murray, M.; Sakamoto, M.; Stern, H. A. Methylmercury exposure and health effects in humans: a worldwide concern. *Ambio* **2007**, *36*, 3−11.

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

(6) 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* (12), 4499−540.

(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* (8), 4951−4958.

(8) Rothenberg, S. E.; Feng, X.; Dong, B.; Shang, L.; Yin, R.; Yuan, X. Characterization of mercury species in brown and white rice (Oryza Sativa L.) grown in water-saving paddies. *Environ. Pollut.* **2011**, *159* (5), 1283−1289.

(9) 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.

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

(11) Li, P.; Feng, X.; Qiu, G.; Li, Z.; Fu, X.; Sakamoto, M.; Liu, X.; Wang, D. Mercury exposures and symptoms in smelting workers of artisanal mercury mines in Wuchuan, Guizhou, China. *Environ. Res.* **2008**, *107* (1), 108−114.

(12) Yard, E. E.; Horton, J.; Schier, J. G.; Caldwell, K.; Sanchez, C.; Lewis, L.; Gastañaga, C. Mercury exposure among artisanal gold miners in Madre de Dios, Peru: a cross-sectional study. *J. Med. Toxicol.* **2012**, *8* (4), 441−8.

(13) Blum, J. D.; Sherman, L. S.; Johnson, M. W. Mercury isotopes in earth and environmental sciences. *Annu. Rev. Earth Planet. Sci.* **2014**, *42* (1), 249−269.

(14) Yin, R.; Feng, X.; Li, X.; Yu, B.; Du, B. Trends and advances in mercury stable isotopes as a geochemical tracer. *Trends Environ. Anal. Chem.* **2014**, *2*, 1−10.

(15) 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* (9), 2170−2189.

(16) Buchachenko, A. L. Magnetic Isotope Effect: Nuclear Spin Control of Chemical Reactions. *J. Phys. Chem. A* **2001**, *105* (44), 9995−10011.

(17) Sun, G.; Sommar, J.; Feng, X.; Lin, C. J.; Ge, M.; Wang, W.; Yin, R.; Fu, X.; Shang, L. Mass -dependent and -independent fractionation of mercury isotope during gas-phase oxidation of elemental mercury vapor by atomic Cl and Br. *Environ. Sci. Technol.* **2016**, *50* (17), 9232.

(18) Bergquist, B. A.; Blum, J. D. Mass-dependent and mass-independent fractionation of Hg isotopes by photo-reduction in aquatic systems. *Science* **2007**, *318* (5849), 417−420.

(19) Kwon, S. Y.; Blum, J. D.; Chirby, M. A.; Chesney, E. J. Application of mercury isotopes for tracing trophic transfer and internal distribution of mercury in marine fish feeding experiments. *Environ. Toxicol. Chem.* **2013**, *23*, 2322−2330.

(20) Kwon, S. Y.; Blum, J. D.; Carvan, M. J.; Basu, N.; Head, J. A.; Madenjian, C. P.; David, S. R. Absence of fractionation of mercury isotopes during trophic transfer of methylmercury to freshwater fish in captivity. *Environ. Sci. Technol.* **2012**, *46* (14), 7527−7534.

(21) Tsui, M. T.; Blum, J. D.; Kwon, S. Y.; Finlay, J. C.; Balogh, S. J.; Nollet, Y. H. Sources and transfers of methylmercury in adjacent river and forest food webs. *Environ. Sci. Technol.* **2012**, *46* (20), 10957−64.

(22) Bonsignore, M.; Tamburrino, S.; Oliveri, E.; Marchetti, A.; Durante, C.; Berni, A. Tracing mercury pathways in Augusta bay (southern Italy) by total concentration and isotope determination. *Environ. Pollut.* **2015**, *205*, 178−185.

(23) Laffont, L.; Sonke, J. E.; Maurice, L.; Hintelmann, H.; Pouilly, M.; Sánchez, B. Y.; Perez, T.; Behra, P. Anomalous mercury isotopic

compositions of fish and human hair in the bolivian amazon. *Environ. Sci. Technol.* **2009**, *43* (23), 8985−8990.
(24) Laffont, L.; Sonke, J. E.; Maurice, L.; Monrroy, S. L.; Chincheros, J.; Amouroux, D.; Behra, P. Hg speciation and stable isotope signatures in human hair as a tracer for dietary and occupational exposure to mercury. *Environ. Sci. Technol.* **2011**, *45* (23), 9910−9916.
(25) Li, M.; Schartup, A. T.; Valberg, A. P.; Ewald, J. D.; Krabbenhoft, D. P.; Yin, R.; Balcom, P. H.; Sunderland, E. M. Environmental origins of methylmercury accumulated in subarctic estuarine fish indicated by mercury stable isotopes. *Environ. Sci. Technol.* **2016**, *50* (21), 11559−11568.
(26) Li, M.; Sherman, L. S.; Blum, J. D.; Grandjean, P.; Mikkelsen, B.; Weihe, P.; Sunderland, E. M.; Shine, J. P. Assessing sources of human methylmercury exposure using stable mercury isotopes. *Environ. Sci. Technol.* **2014**, *48* (15), 8800−8806.
(27) Sherman, L. S.; Blum, J. D.; Franzblau, A.; Basu, N. New insight into biomarkers of human mercury exposure using naturally occurring mercury stable isotopes. *Environ. Sci. Technol.* **2013**, *47* (7), 3403−3409.
(28) Rothenberg, S.; Yin, R.; Hurley, J. P.; Krabbenhoft, D. P.; Ismawati, Y.; Hong, C.; Donohue, A. Stable mercury isotopes in polished rice (Oryza Sativa L.) and hair from rice consumers. *Environ. Sci. Technol.* **2017**, *51* (11), 6480−6488.
(29) Zheng, W.; Obrist, D.; Weis, D.; Bergquist, B. A., Mercury isotope compositions across North American forests. *Global. Biogeochem. Cycles* **2016**, *30*(10).147510.1002/2015GB005323
(30) 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.
(31) 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.
(32) Kritee, K.; Blum, J. D.; Johnson, M. W.; Bergquist, B. A.; Barkay, T. Mercury stable isotope fractionation during reduction of Hg (II) to Hg (0) by mercury resistant microorganisms. *Environ. Sci. Technol.* **2007**, *41*, 1889−1895.
(33) Gehrke, G. E.; Blum, J. D.; Slotton, D. G.; Greenfield, B. K. Mercury Isotopes Link Mercury in San Francisco Bay Forage Fish to Surface Sediments. *Environ. Sci. Technol.* **2011**, *45* (4), 1264.
(34) Perrot, V.; Pastukhov, M. V.; Epov, V. N.; Husted, S.; Donard, O. F. X.; Amouroux, D. Higher Mass-Independent Isotope Fractionation of Methylmercury in the Pelagic Food Web of Lake Baikal (Russia). *Environ. Sci. Technol.* **2012**, *46* (11), 5902.
(35) Sherman, L. S.; Blum, J. D.; Basu, N.; Rajaee, M.; Evers, D. C.; Buck, D. G.; Petrlik, J.; Gangi, J. P. Assessment of mercury exposure among small-scale gold miners using mercury stable isotopes. *Environ. Res.* **2015**, *137*, 226−234.
(36) Feng, C.; Pedrero, Z.; Li, P.; Du, B.; Feng, X.; Monperrus, M.; Tessier1, E.; Berail1, S.; Amouroux, D. Investigation of Hg uptake and transport between paddy soil and rice seeds combining Hg isotopic composition and speciation. *Elementa: Sci. of the Anthro.* **2015**, *4*, 000087.
(37) Li, P.; Du, B.; Maurice, L.; Laffont, L.; Lagane, C.; Point, D. Mercury isotope signatures of methylmercury in rice samples from the wanshan mercury mining area, china: environmental implications. *Environ. Sci. Technol.* **2017**, *51* (21), 12321.
(38) Yin, R.; Feng, X.; Meng, B. Stable mercury isotope variation in rice plants (Oryza Sativa L.) from the Wanshan mercury mining district, SW China. *Environ. Sci. Technol.* **2013**, *47* (5), 2238−2245.
(39) Feng, X. B.; Li, G. L.; Qiu, G. L. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China—part 1: mercury emission from zinc smelting and its influences on the surface waters. *Atmos. Environ.* **2004**, *38* (36), 6223−6230.
(40) Wang, S. X.; Zhang, L.; Wang, Q. R. A review of atmospheric mercury emissions, pollution and control in china. *Front. Environ. Sci. Eng.* **2013**, *8* (5), 631−649.
(41) Jiang, G. B.; Shi, J. B.; Feng, X. B. Mercury pollution in China. An overview of the past and current sources of the toxic metal. *Environ. Sci. Technol.* **2006**, *40* (12), 3673−3678.
(42) Feng, X.; Qiu, G. Mercury pollution in Guizhou, Southwestern China — an overview. *Sci. Total Environ.* **2008**, *400* (1), 227−237.
(43) Yin, R.; Feng, X.; Wang, J.; Li, P.; Liu, J.; Zhang, Y.; Chen, J.; Zheng, L.; Hu, T. Mercury speciation and mercury isotope fractionation during ore roasting process and their implication to source identification of downstream sediment in the Wanshan mercury mining area, SW China. *Chem. Geol.* **2013**, *336* (SI), 72−79.
(44) Li, P.; Feng, X.; Qiu, G.; Wan, Q. Hair can be a good biomarker of occupational exposure to mercury vapor: simulated experiments and field data analysis. *Sci. Total Environ.* **2011**, *409* (20), 4484−4488.
(45) Sholupov, S.; Pogarev, S.; Ryzhov, V.; Mashyanov, N.; Stroganov, A. Zeeman atomic absorption spectrometer RA-915+ for direct determination of mercury in air and complex matrix samples. *Fuel Process. Technol.* **2004**, *85* (6), 473−485.
(46) USEPA. *Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, And Cold Vapor Atomic Fluorescence Spectrometry*; USEPA: WA, 2002.
(47) USEPA. *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Absorption Fluorescence Spectrometry*; USEPA: WA, 2002.
(48) Liang, L.; Horvat, M.; Bloom, N. S. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. *Talanta* **1994**, *41*, 371−379.
(49) Liang, L.; Horvat, M.; Cernichiari, E.; Gelein, B.; Balogh, S. Simple solvent extraction technique for elimination of matrix interferences in the determination of methylmercury in environmental and biological samples by ethylation gas chromatography cold vapor atomic fluorescence spectrometry. *Talanta* **1996**, *43*, 1883−1888.
(50) USEPA. *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS*; USEPA: WA, 2001.
(51) Yin, R.; Feng, X.; Foucher, D.; Shi, W.; Zhao, Z.; Wang, J. High precision determination of mercury isotope ratios using online mercury vapor generation system coupled with multicollector inductively coupled plasma-mass spectrometer. Chinese. *J. Anal. Chem.* **2010**, *38* (7), 929−934.
(52) Blum, J. D.; Bergquist, B. A. Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* **2007**, *388* (2), 353−359.
(53) Wiederhold, J. G.; Cramer, C. J.; 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* (11), 4191−7.
(54) Estrade, N.; Carignan, J.; Sonke, J. E.; Donard, O. F. Measuring Hg Isotopes in Bio-Geo-Environmental Reference Materials. *Geostand. Geoanal. Res.* **2010**, *34* (1), 79−93.
(55) Li, P.; Feng, X.; Chan, H. M.; Zhang, X.; Du, B. (2015). Human body burden and dietary methylmercury intake: the relationship in a rice-consuming population. *Environ. Sci. Technol.* **2015**, *49* (16), 9682−9689.
(56) Enrico, M.; Roux, G. L.; Marusczak, N.; Heimbürger, L. E.; Claustres, A.; Fu, X.; Sun, R.; Sonke, J. E. Atmospheric Mercury Transfer to Peat Bogs Dominated by Gaseous Elemental Mercury Dry Deposition. *Environ. Sci. Technol.* **2016**, *50* (5), 2405−2412.
(57) Demers, J. D.; Blum, J. D.; Zak, D. R. Mercury isotopes in a forested ecosystem: Implications for air-surface exchange dynamics and the global mercury cycle. *Global Biogeochem. Cy.* **2013**, *27* (1), 222−238.
(58) Jiskra, M.; Wiederhold, J. G.; Skyllberg, U.; Kronberg, R. M.; Hajdas, I.; Kretzschmar, R. Mercury Deposition and Re-emission Pathways in Boreal Forest Soils Investigated with Hg Isotope Signatures. *Environ. Sci. Technol.* **2015**, *49* (12), 7188−7196.
(59) Yu, B.; Fu, X.; Yin, R.; et al. Isotopic composition of atmospheric mercury in china: new evidence for source and transformation processes in air and in vegetation. *Environ. Sci. Technol.* **2016**, *50* (17), 9262−9269.

DOI: 10.1021/acs.est.7b05638
Environ. Sci. Technol. 2018, 52, 5407−5416

(60) Blum, J. D.; Popp, B. N.; Drazen, J. C. Methylmercury production below the mixed layer in the North Pacific Ocean. *Nat. Geosci.* **2013**, *6* (10), 879−884.
(61) Senn, D. B.; Chesney, E. J.; Blum, J. D.; Bank, M. S.; Maage, A.; Shine, J. P. Stable isotope (N, C, Hg) study of methylmercury sources and trophic transfer in the Northern Gulf of Mexico. *Environ. Sci. Technol.* **2010**, *44* (5), 1630−1637.
(62) Tsui, M. T.; Blum, J. D.; Finlay, J. C.; Balogh, S. J.; Nollet, Y. H.; Plen, W. J.; Power, M. E. Variation in terrestrial and aquatic sources of methylmercury in stream predators as revealed by stable mercury isotopes. *Environ. Sci. Technol.* **2014**, *48* (17), 10128−10135.
(63) Sonke, J. E.; Schäfer, 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**, *279* (3), 90−100.
(64) Wang, Z.; Chen, J.; Feng, X.; Holger, H.; Sheng, L.; Liu, Y.; Cai, H.; Wang, S. Mass-dependent and mass-independent fractionation of mercury isotopes in precipitation from Guiyang, SW China. *C. R. Geosci.* **2015**, *347* (7−8), 358−367.
(65) GBS. *Guizhou Statistical Yearbook 2012*, Guizhou Bureau of Statistics; China Statistics Press: Beijing, 2012.
(66) Fu, X.; Feng, X.; Qiu, G.; Shang, L.; Zhang, H. Speciated atmospheric mercury and its potential source in Guiyang, China. *Atmos. Environ.* **2011**, *45* (25), 4205−4212.
(67) Qiu, G. L.; Feng, X. B.; Wang, S. F.; Fu, X. W.; Shang, L. H. Mercury distribution and speciation in water and fish from abandoned Hg mines in Wanshan, Guizhou province. *Sci. Total Environ.* **2009**, *407*, 5162−5168.
(68) Wu, Y.; Zhang, H.; Liu, G.; Zhang, J.; Wang, J.; Yu, Y.; Lu, S. Concentrations and health risk assessment of trace elements in animal-derived food in southern china. *Chemosphere* **2016**, *144*, 564−570.
(69) WHO. *Inorganic Mercury Environmental Health Criteria.* Vol. *118*, World Health Organization, Geneva, 1991.
(70) WHO. *Environmental health criteria 101: Methylmercury*. World Health Organization, Geneva, 1990.

DOI: 10.1021/acs.est.7b05638
Environ. Sci. Technol. 2018, 52, 5407−5416