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Tracing Mercury Contamination Sources in Sediments Using Mercury Isotope Compositions

XINBIN FENG,*,† DELPHINE FOUCHER,‡
HOLGER HINTELMANN,‡ HAIYU YAN,†
TIANRONG HE,† AND GUANGLE QIU†

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China, and Department of Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario, K9J 7B8, Canada

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Mercury (Hg) isotope ratios were determined in two sediment cores collected from two adjacent reservoirs in Guizhou, China, including Hongfeng Reservoir and Baihua Reservoir. Hg isotope compositions were also analyzed in a soil sample collected from the catchment of Hongfeng Reservoir and three cinnabar samples collected from the Wanshan Hg mine. Baihua Reservoir was contaminated with runoff from Guizhou Organic Chemical Plant (GOCP) when metallic Hg was used as a catalyst to produce acetic acid. Hongfeng Reservoir, located upstream of Baihua, receives Hg from runoff and atmospheric deposition. We demonstrated that δ^{202}Hg values relative to NIST 3133 of sediment in Baihua Reservoir ranging from −0.60 to −1.10‰ were distinctively different from those in Hongfeng Reservoir varying from −1.67 to −2.02‰. While sediments from both Baihua and Hongfeng Reservoirs were characterized by mass dependent variation (MDF), only Hongfeng Reservoir sediments were characterized by mass independent variation (MIF). Moreover, by using a binary mixing model, we demonstrated the major source of Hg in sediment of Hongfeng Reservoir was from runoff due to soil erosion, which was consistent with the conclusion obtained from a previous Hg balance study. This study demonstrates Hg isotope data are valuable tracers for determining Hg contamination sources in sediments.

Introduction

Hg is a highly toxic metal that can travel long distances in the atmosphere, and therefore it is regarded as a global pollutant. Both human activities and natural processes release Hg to the environment (*1*). Verifying sources of Hg in the environment is critical for policy development and mitigation of pollution (*2*). However, the methodologies for source apportionment of Hg in the environment are still under development (*2*).

Hg isotope ratios could be an effective tool for tracing the sources of Hg in the environment (*3, 4*). With the development and application of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), accurate measurements of isotope ratios of heavy elements are possible. Natural fractionation of Hg isotopes has been the subject of many studies, including those concerning meteorites and moon rocks (*5, 6*), hydrothermal ores (*7*−*11*), coal samples (*4, 12*), soils (*4, 13*), volcanic emission (*14, 15*), sediments (*3, 16*−*20*), biological samples (*13, 21, 23*), and mine-waste calcine (*24*). A few studies were also conducted to investigate Hg fractionation resulting from natural processes such as volatilization (*25, 26*), reduction induced by chemical, photo and bacterial processes (*22, 27*−*29*), methlyation and demethylation (*30, 31*), and ethylation (*27*). These studies reported a wide range of Hg isotope ratios (typically expressed as δ^{202}Hg) and demonstrated the existence of Hg isotopic fractionation in nature. Additionally, these studies also suggested that Hg isotope signatures might be used to trace the sources and chemical processes of Hg in the environment. However, it is still debated whether researchers can use Hg isotopic compositions of known Hg sources to identify sources and trace Hg pollution.

Foucher et al. (*3*) investigated Hg isotope ratios of sediments collected from the Idrijca River, the Soča/Isonzo River, and the Gulf of Trieste. The Hg isotopic composition of river sediment was similar to that of cinnabar ore from the mine upstream, and the authors concluded the sediments throughout the watershed of Soča/Isonzo River to Gulf of Trieste were dominated by Hg exported from the headwaters near the Idrija Hg mine. Stetson et al. (*24*) pointed out that Hg isotope fractionation occurred during Hg retorting process and δ^{202}Hg values of calcines were as much as 3.24‰ enriched with heavy isotopes compared to cinnabar prior to retorting. It was suggested to use the Hg isotope composition of calcines to trace Hg sources from Hg mining areas (*24*). To date, however, the proof of Hg isotopic compositions to source attribution in the environment is still limited.

Here, we examined the Hg isotope composition of sediment cores from two adjacent reservoirs in Guizhou, China with different Hg contamination sources to evaluate the feasibility of employing Hg isotope composition to track sources of Hg. This study demonstrated that Hg isotopic composition was an effective tool to distinguish sources of Hg contamination in sediments.

Materials and Methods

Study Area. Locations for Baihua and Hongfeng Reservoirs are shown in Figure 1. Baihua Reservoir with a surface area of 14.5 km^2 is situated 16 km northwest of Guiyang, the capital of Guizhou Province. Hongfeng Reservoir, located upstream of Baihua, was established in 1960 with a surface area of 57.2 km^2. Both reservoirs are long and narrow with a main inlet and only one outlet. The reservoirs were constructed for the purpose of hydroelectric power generation, flood control, tourism, drinking-water supply, and fishery production.

Between 1971 and 1997, Baihua Reservoir was seriously contaminated by the Guizhou Organic Chemical Plant (GOCP), which used metallic Hg as a catalyst to produce acetic acid. GOCP is located at the upper reach of Baihua Reservoir and downstream of Hongfeng Reservoir as shown in Figure 1. From 1971 to 1985, 573 tons of Hg were consumed by the plant, producing some atmospheric Hg emissions and Hg-laden wastewater. The latter was discharged directly to the Zhujia River without any treatment (*32*), which flowed into Baihua Reservoir via Dongmen River, resulting in serious Hg contamination. Beginning in 1985, an Hg removal device was used to prevent Hg discharges into the Zhujia River, and since 1997, GOCP stopped using Hg technology to produce acetic acid. At present, total Hg concentrations in this river still range from 250 to 1000 ng L^{-1} (*32*). Additional Hg

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

† Chinese Academy of Sciences.

‡ Trent University.

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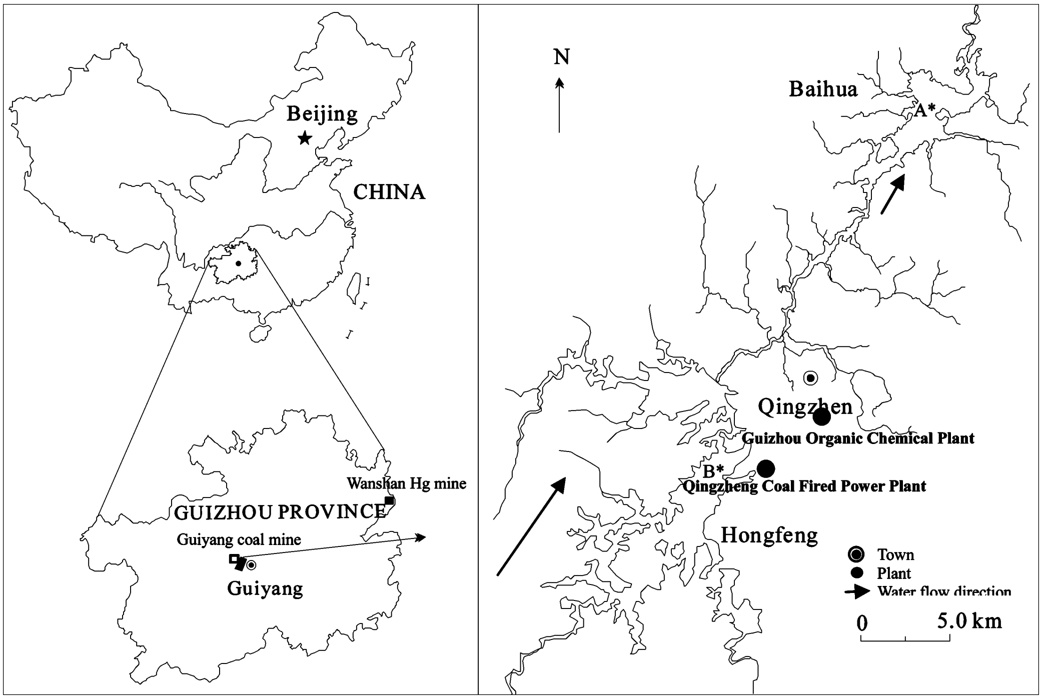

FIGURE 1. Locations of Baihua and Hongfeng Reservoirs in Guizhou, China. A* represents the sampling site of sediment core collected at Matou site in Baihua Reservoir; B* represents the sampling site of sediment core collected at Houwu site in Hongfeng Reservoir.

contamination sources to Baihua Reservoir include seven small coal mines, one iron mine, and the Guizhou Aluminum Plant, which are situated near the upper reaches of Baihua Reservoir. However, compared to total amount of Hg discharge from GOCP, these sources are considered trivial.

Hg sources to the Hongfeng Reservoir include a large coal fired power plant (300 MW), which is situated on the southeast bank of Hongfeng Reservoir. Winds carry Hg emitted from the power plant downwind to the reservoir, making the power plant an important contamination source of atmospheric Hg. In addition, soil erosion deposited through runoff is also an important Hg source to the sediment of Hongfeng Reservoir. Soil erosion and atmospheric deposition of Hg emitted from the coal fired power plants also contributed to Hg contamination to Baihua Reservoir, but their contributions are minimal compared to Hg discharge from GOCP.

Sampling Methods. Sediment cores used in this study were collected in 2003 and 2004 from Baihua and Hongfeng Reservoirs, respectively (*32, 33*). Sediment cores from the Matou site (location A* in Figure 1) in Baihua Reservoir and the Houwu site (location B* in Figure 1) in Hongfeng Reservoir were chosen for Hg isotope composition analysis. Both sites are located in the center of the reservoirs. Sediment cores were taken by means of a gravity corer and sliced on site into 1 cm layers in a glovebag filled with nitrogen. In the laboratory, sediment samples were centrifuged at 3500 rpm for 25 min at 4 °C to remove porewater, and the remaining sediment samples were freeze-dried. The bedrock of the watershed of both reservoirs is dominated by limestone and dolomite, and the soil type is mainly calcareous soil. One soil sample was collected in the catchment about 10 km upstream of Hongfeng Reservoir to represent the Hg isotope signature from soil erosion. The soil sample was a mixture of five subsamples of top soil collected from an area of 1 m^2. The soil sample was air-dried, homogenized, ground, and sieved through a 0.074 mm pore size screen. Three cinnabar samples were also collected from Wanshan Hg mines for characterization of Hg isotope composition, since Hg produced from this mine was used at GOCP in form of metallic Hg. Cinnabar samples were ground and sieved through a 0.074 mm pore size screen.

Sample Processing. Detailed information on sample processing is given by Foucher et al. (*3, 17*). The dried sediments were digested by conventional heating on a hot plate at 120−140 °C for a period of approximately 6 h with a mixture of either HNO_3/HCl (10 mL, 7:3 v/v) or HNO_3/H_2SO_4 (10 mL, 7:3 v/v). On completion of the digestion, Milli-Q water was added to reach a final volume of 40 mL. This dilution is necessary to keep the acid concentration below 25% (v/v), above which matrix interferences affect Hg isotopic measurements. The mass of digested sediment was adjusted (from 0.2 to 0.8 g) to yield a final Hg concentration of at least 1 $\mu g\ L^{-1}$.

Reagents and Solutions. The Hg (1−5 $\mu g\ L^{-1}$) and Tl (20 $\mu g\ L^{-1}$) working standard solutions were prepared daily by sequentially diluting commercial stock solutions in 0.12 M HCl. The Hg solutions were obtained from an ampule of NIST 3133. The Tl solution was made up from a Tl atomic absorption standard solution (1.000 g L^{-1} Tl in 0.16 MHNO_3, Aldrich). A 0.16 M (3% w/v) solution of stannous chloride ($SnCl_2$, purity >98%, Aldrich) was prepared in 1.20 M HCl. Prior to use, the reductant solution was vigorously purged with Hg-free nitrogen for few hours to liberate any Hg. All acids were of analytical grade (HNO_3 and HCl, certified ACS Plus, Fisher Scientific) and all samples, standard solutions, and reagents were diluted with high quality water that was provided by a Milli-Q purification system (Millipore, Bedford, MA) capable of producing 18.2 ΩM-grade water.

Total Hg Analysis. The concentrations of total Hg (THg) in sediment samples were determined at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS) using CVAFS (*32, 33*) by reduction with $SnCl_2$ solution subsequently to oxidation by acid digestion (*34*). More detailed information is available in the Supporting Information (SI). For comparison, THg concentrations were also estimated by MC-

ICP-MS using ^{202}Hg signals, when the samples were analyzed for Hg isotope ratios at Trent University.

Hg Isotope Composition Analysis. Hg isotopic ratios were determined by MC-ICP-MS using a Neptune mass spectrometer equipped with nine Faraday cups (Thermo Fisher Scientific, Germany). The sample introduction system consisted of a continuous-flow cold-vapor generation system (*35*) coupled to an Apex desolvation unit (Elemental Scientific Inc., Omaha, NE) for Hg and Tl introduction, respectively. $SnCl_2$ was used as reducing agent and mixed online with Hg standards or sample digests to generate volatile elemental Hg. Hg vapors from the CV generation system were mixed with a dry Tl aerosol produced via the desolvation device. Instrumental mass bias correction was achieved using Tl as internal standard and external standard-sample bracketing with a NIST SRM 3133 Hg solution. An exponential fractionation law was applied for internal mass bias correction assuming a reference value of 2.3871 for the ratio ^{205}Tl/^{203}Tl. Data were acquired by monitoring ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{203}Tl, and ^{205}Tl isotopes for a period of 10 min (1 block, 150 cycles with 4 s integrations). A typical sequence consisted of measuring the NIST SRM 3133 Hg solution after every batch of three samples. To ensure optimum results of instrumental mass bias correction, the concentration of the bracketing solution was systematically adjusted to within 10% of the Hg concentration in the sample digest (typically between 1 and 5 μg Hg L^{-1}). 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 Foucher and Hintelmann (*17*).

All isotope ratio variations were expressed relative to the bracketing Hg standard using the customary δ-notation expressed in per mil (‰), that is:

$$\delta^{XXX}\mathrm{Hg} = 1000\{[(^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{sample}}/(^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{NIST3133}}] - 1\} \quad (1)$$

with XXX = 199, 200, 201, or 202, $^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{sample}}$ being the measured isotope ratios of the sample, and $^{XXX}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{standard}}$ the isotope ratio of the reference standard solution (NIST SRM 3133). Mass independent fractionation was reported as Δ-values and represents the difference between the measured and theoretically predicted value of δ^{XXX}Hg (*36*):

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

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

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

Uncertainties reported in the figures and tables of the manuscript correspond to the larger value of either (i) the measurement uncertainty of replicate sediment digests, or (ii) the uncertainty of repeated measurements of the same digest at different analysis sessions. When the calculated 2SD was smaller than of the replicate analyses of the reference material UM-Almaden (*36*), the uncertainty associated to UM-Almaden was used instead.

Results and Discussion

Total Hg in Sediment Cores. The THg distribution in sediment cores from Baihua and Hongfeng Reservoirs is depicted in SI Figure S1. THg estimated from MC-ICP-MS detection at Trent University was compared with data obtained by using the CVAFS method at IGCAS. The differences between the two data sets were on average 8.8 ± 4.8%, and 10.9 ± 4.6% for Hongfeng and Baihua Reservoirs, respectively. THg concentrations in the sediment core of Baihua Reservoir varied from 1.6 to 38.1 μg g^{-1}, but those of Hongfeng Reservoir only ranged from 0.20 to 0.49 μg g^{-1}. It is obvious that the sediment of Baihua Reservoir was seriously contaminated with Hg compared to Hongfeng Reservoir although these two reservoirs were adjacent. Previous studies showed that Hg contamination from Baihua was mainly from wastewater discharge of GOCP (*32*), whereas Hg inputs to Hongfeng Reservoir were from runoff and atmospheric deposition (*33*).

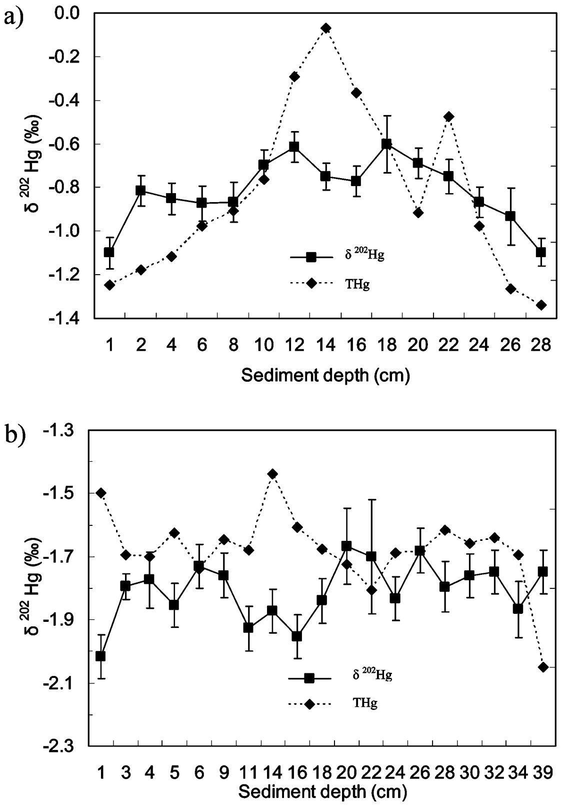

FIGURE 2. The distribution of THg concentrations and δ^{202}Hg values of sediment cores in Baihua and Hongfeng Reservoirs. (a) the sediment core collected from Baihua Reservoir; (b) the sediment core collected from Hongfeng Reservoir.

Isotopic Composition of Hg in Sediment Cores. The variation in δ^{202}Hg together with THg distribution is presented in Figure 2 and the detailed Hg isotope data (δ^{199}Hg, δ^{200}Hg, δ^{201}Hg, δ^{202}Hg, Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg values) of the sediment cores for Baihua and Hongfeng Reservoirs are listed in SI Tables S1 and S2. Given the proximity of these two reservoirs, THg concentrations in Baihua Reservoir sediments would be expected to be comparable to Hongfeng Reservoir sediments, and likewise one might expect to find similar Hg isotopic signatures in sediments from both reservoirs. However, higher THg concentrations in Baihua Reservoir and different Hg isotopic signatures in sediments from the two reservoirs strongly suggests an additional and important source of Hg to the Baihua Reservoir. The lowest THg concentrations occurring in the top and bottom of the sediment core of Baihua Reservoir (3.6 and 1.6 μg g^{-1}, respectively) were 9.7 and 4.3 times the average THg concentration measured in the sediment core of Hongfeng Reservoir, respectively. Sediment cores from these two reservoirs have distinct Hg isotopic compositions. The δ^{202}Hg values of sediment from Baihua Reservoir ranged from −0.60 to −1.10 ‰, and those from Hongfeng Reservoir varied from −1.67 to −2.02 ‰. This significant difference suggests that Hg discharged from GOCP has a distinct Hg isotope signature that may be used to trace the pollution source to the factory.

Sediment from Hongfeng Reservoir was enriched with lighter Hg isotopes relative to Baihua Reservoir. The surface

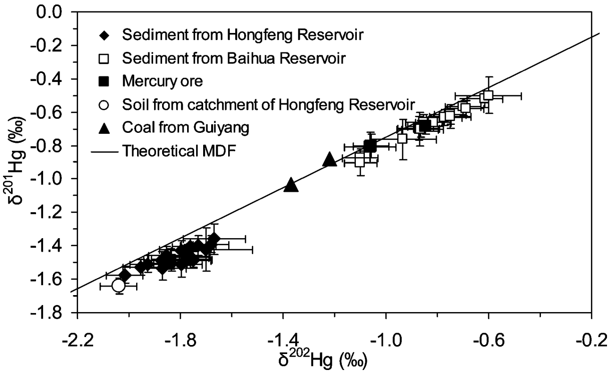

FIGURE 3. Three-isotope plot δ^{201}Hg vs δ^{202}Hg of all samples. Isotopic compositions are reported in per mil (‰) relative to the Hg standard NIST 3133. The solid line represents the theoretical mass-dependent fractionation line based on the exponential law (*36*) and using IUPAC atomic weight values: $\delta^{201}\mathrm{Hg} = 0.7520 \times \delta^{202}\mathrm{Hg}$. Hg isotopic composition data of coal samples in Guiyang were from Biswas and coauthors (*4*).

and the bottom sediment of Baihua Reservoir had the lowest THg concentrations and therefore was less contaminated by wastewater discharged from GOCP compared to the sediments in the middle of the sediment core. δ^{202}Hg values in the top and bottom sediments of Baihua Reservoir suggest dilution by other Hg sources, which have similar Hg isotope compositions as those in Hongfeng Reservoir.

Figure 3 shows a three-isotope plot of δ^{201}Hg vs δ^{202}Hg for all sediment, soil, and coal samples from Guiyang and cinnabar samples collected from the Wanshan Hg mine. All samples plotted well against the theoretical mass-dependent fractionation line. This graph reveals a clear separation between the two reservoirs, illustrating the presence of two Hg sources with distinct isotope ratios. Moreover, the plot suggests that Hg used in GOCP was mainly from the Wanshan Hg mine, which was the largest Hg mine in China and was located in the same province. We collected three cinnabar ores representing the major type of Hg ore from the Wanshan Hg mine. Mass dependent fractionation may occur during Hg retorting processes (*24*); however, the fractionation should be small because the majority mass (~90%) of Hg in ore is transferred to liquid Hg. Figure 3 shows the Hg isotopic ratios of Hg ores fall well within the range of sediment from Baihua Reservoir; this suggests that GOCP was the source of Hg pollution to the sediments of Baihua Reservoir.

Previous studies (*33*) showed the major sources of Hg to Hongfeng Reservoir were from runoff due to soil erosion and from atmospheric deposition. It was further estimated that the annual total Hg input from runoff was 18.9 kg and annual total Hg deposition from the atmosphere was 3.88 kg in Hongfeng Reservoir (*33*). Therefore, runoff was the major contributor of Hg to Hongfeng Reservoir since this source constituted 83% of the total input. This conclusion was in a good agreement with the result of a Hg mass balance study of two other reservoirs (Wujiangdu and Dongfeng Reservoirs) in the same region (*37*).

Since Qingzheng coal fired power plant is located adjacent to Hongfeng Reservoir, the main source of Hg in precipitation is presumed to originate from coal combustion from the power plant (*38*). The Hg isotopic compositions of two coal samples collected from Guiyang coal basin analyzed by Biswas and coauthors (*4*) are considered to be representative of the Hg isotope signatures of atmospheric deposition. The Hg isotopic ratio of one soil sample collected from the upstream catchment of Hongfeng Reservoir was also analyzed to represent the Hg isotopic signature in soil erosion from runoff. Despite these various assumptions, it is striking that the Hg isotope compositions in sediment of Hongfeng Reservoir all fall between the two end points that relate to the cacthment soil and coal as shown in Figure 3. Using the following simple binary mixing-model proposed by Foucher and coauthors (*3*), the relative contribution of all Hg sources to reservoir sediments was calculated as follows:

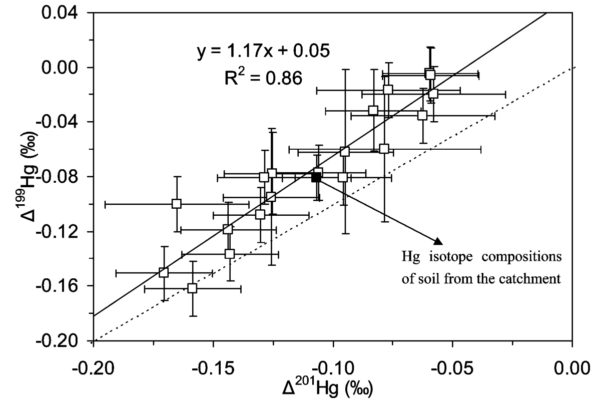

FIGURE 4. Δ^{199}Hg vs Δ^{201}Hg of sediment samples from Hongfeng Reservoir and a soil sample collected in the catchment of Hongfeng Reservoir. The dashed line represents that Δ^{201}Hg: Δ^{199}Hg is equal to 1.

$$\delta^{202}\mathrm{Hg}_{\mathrm{sed}} = X_{\mathrm{soil}} \times \delta^{202}\mathrm{Hg}_{\mathrm{soil}} + X_{\mathrm{coal}} \times \delta^{202}\mathrm{Hg}_{\mathrm{coal}} \qquad (5)$$

$$X_{\mathrm{soil}} + X_{\mathrm{coal}} = 1 \qquad (6)$$

where $\delta^{202}\mathrm{Hg}_{\mathrm{sed}}$, $\delta^{202}\mathrm{Hg}_{\mathrm{soil}}$, and $\delta^{202}\mathrm{Hg}_{\mathrm{coal}}$ are the isotopic compositions of sediment, soil and coal, respectively; X_{soil} and X_{coal} are the respective soil erosion and atmospheric deposition fractions in sediment samples. The calculations show that the average fraction of Hg from soil erosion is 69% with a range from 50 to 97%. This result based on Hg isotope ratios supports the previous estimation (83% of THg input was from soil erosion) by the Hg mass balance study (*33*).

Mass independent isotope fractionation (MIF) was observed for all sediment samples from Hongfeng Reservoir, whereas Baihua Reservoir showed only mass dependent fractionation. Coal from Guiyang basin did not show MIF, but the soil sample collected from the Hongfeng Reservoir catchment showed the same small extent of MIF found in the sediment. This further suggests that soil erosion could be the major source of Hg in the sediment.

MIF is generally understood to be caused by the nuclear field shift and/or the magnetic isotope effect (*39*). Previous studies demonstrated that MIF is caused by photochemical reduction of Hg^{2+} and methyl-Hg to Hg^0 (*22*). 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 methyl-Hg and 1.00 for Hg^{2+} photoreduction (*22*), though Zheng and co-workers (*29*) indicated that photoreduction of Hg-NOM species can produce slopes ranging from 1.19 to 1.31. The Δ^{199}Hg vs Δ^{201}Hg plot of sediment samples from Hongfeng Reservoir has a slope of 1.17 as shown in Figure 4 indicating that the cause of MIF could be photochemical reduction of Hg^{2+}. Interestingly, the soil sample fell exactly on the regression line of the sediment samples as shown in Figure 4. This suggested that Hg in soil in this region may undergo photoreduction process before being deposited to soil.

In this study, we evaluated the feasibility of using Hg isotope composition as a tool to trace Hg contamination sources in sediment. Baihua Reservoir was contaminated with Hg by GOCP that used metallic Hg as a catalyst to produce acetic acid, and the sediment in Baihua Reservoir contained the same Hg isotopic signature as the cinnabar used to produce this metallic Hg. Sediment in Baihua

Reservoir and Hg ores not only showed the same range of δ^{202}Hg values, but were both also void of any mass independent variation (i.e., MIF) of Hg isotopes. The sediment of Hongfeng Reservoir on the other hand showed more negative δ^{202}Hg values than Baihua Reservoir. MIF of Hg isotopes was also observed in sediment of Hongfeng Reservoir. Hg isotope ratios of sediment of Hongfeng Reservoir fell into a range between two end points that represented the Hg isotopic signatures of soil erosion and atmospheric deposition, respectively. By using a binary mixing model, we demonstrated that the major source of Hg in sediment of Hongfeng Reservoir is from soil erosion by runoff. This conclusion was further supported by the fact that Hg in coal in this region did not show MIF, whereas the soil in the catchment of Hongfeng Reservoir showed the same extent of MIF as the sediment. The relative contribution of each source to the overall sediment Hg budget was also consistent with the conclusion obtained from a previous Hg balance study of Hongfeng Reservoir (*33*). This study suggests that processes in lakes/reservoirs related to internal Hg cycling (likely associated with organic matter cycling and degradation) do not appear to destroy or confound the Hg isotopic composition, and thus future studies may use this approach to trace sources of Hg contamination to the environment.

Acknowledgments

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Supporting Information Available

Additional text, figures, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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