Environmental Science & Technology
Article
pubs.acs.org/est

Environmental Impacts of the Tennessee Valley Authority Kingston Coal Ash Spill. 1. Source Apportionment Using Mercury Stable Isotopes

Gideon Bartov,[‡,*] Amrika Deonarine,[§,†] Thomas M. Johnson,[‡] Laura Ruhl,[∥] Avner Vengosh,[∥] and Heileen Hsu-Kim[§]

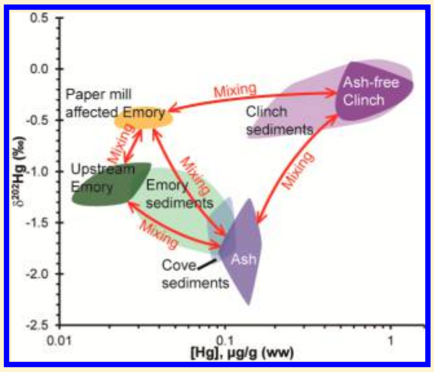
[‡]Department of Geology, 208 Natural History Building, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States

[§]Department of Civil and Environmental Engineering, 121 Hudson Hall, Box 90287, Duke University, Durham, North Carolina 27708, United States

[∥]Division of Earth and Ocean Sciences, Nicholas School of the Environment, 205 Old Chemistry Building, Box 90227, Duke University, Durham, North Carolina 27708, United States

Supporting Information

ABSTRACT: Mercury stable isotope abundances were used to trace transport of Hg-impacted river sediment near a coal ash spill at Harriman, Tennessee, USA. δ^{202}Hg values for Kingston coal ash released into the Emory River in 2008 are significantly negative (−1.78 ± 0.35‰), whereas sediments of the Clinch River, into which the Emory River flows, are contaminated by an additional Hg source (potentially from the Y-12 complex near Oak Ridge, Tennessee) with near-zero values (−0.23 ± 0.16‰). Nominally uncontaminated Emory River sediments (12 miles upstream from the Emory-Clinch confluence) have intermediate values (−1.17 ± 0.13‰) and contain lower Hg concentrations. Emory River mile 10 sediments, possibly impacted by an old paper mill has δ^{202}Hg values of −0.47 ± 0.04‰. A mixing model, using δ^{202}Hg values and Hg concentrations, yielded estimates of the relative contributions of coal ash, Clinch River, and Emory River sediments for a suite of 71 sediment samples taken over a 30 month time period from 13 locations. Emory River samples, with two exceptions, are unaffected by Clinch River sediment, despite occasional upstream flow from the Clinch River. As expected, Clinch River sediment below its confluence with the Emory River are affected by Kingston coal ash; however, the relative contribution of the coal ash varies among sampling sites.



INTRODUCTION

Mercury Contamination. Mercury (Hg) is a widespread contaminant.[1,2] Industrialization has increased total Hg input into the environment by as much as a factor of 2.[3] The main anthropogenic inputs of Hg into the environment are coal burning and losses from gold mining operations,[1] though many other sources and pathways have been reported. For example, point sources of Hg contamination have been reported from the Idrija region in Slovenia to the Brazilian Amazon.[4−12] Studies have also shown that Hg cycles through the atmosphere and can get deposited far from point sources[13−16] and accumulate in biota.[17−19]

The chemistry of Hg plays a major role in evaluation of Hg mobility, bioavailability, and biological impacts. The dominant inorganic valences of Hg in nature are Hg(0) and Hg(II); Hg(0) is sparingly soluble and generally a less reactive volatile species, whereas Hg(II) is soluble but highly reactive, forming many aqueous complexes with various ligands and surface complexes on solids, and forming solids like HgS and HgSe.[20] The ability of Hg(II) to adsorb onto sediments allows it to remain sequestered in solid materials for long periods of time. Hg also has various organic forms, the most important of which is methylmercury, a deadly neurotoxin that bioaccumulates in biota and causes most of Hg's biological impact.

Coal-fired power plants release Hg into the environment both through smokestack emissions and releases of coal ash, which contains elevated levels of Hg and other contaminants.[21] According to the EPA, there are at least 240 coal ash storage facilities containing various coal combustion residuals (fly ash, bottom ash, coal slag, and flue gas desulfurization residue) across the United States. As of August 2009, 30 facilities and 49 surface impoundments are considered to have a high hazard potential, which is defined as a high probability for significant economic and human life loss if an impoundment failure were to occur.[21]

On December 22, 2008, a coal ash dredge cell failed at the Tennessee Valley Authority (TVA) Kingston coal-fired power

Received: July 31, 2012
Revised: October 19, 2012
Accepted: November 16, 2012
Published: November 16, 2012

plant at Harriman, TN, releasing approximately 4.1 million cubic meters of coal ash into the Emory and Clinch Rivers in Tennessee. Measurements of Hg in the sediment, ash, and fish samples taken after the spill have shown that Hg is above its toxicological screening threshold for benthic organisms (0.18 mg/kg dry weight) and over the human health screening values in the fish (0.0406 mg/kg).[22,23] These high concentrations of Hg are of concern because Hg bioaccumulates and poses a risk to humans and wildlife.

Hg stable isotope measurements have grown as a tool for examining sources and chemical transformations of Hg in the environment.[6−12,24−27] Hg has 7 stable isotopes with nominal masses 196, 198, 199, 200, 201, 202, and 204 amu. Variations in their relative abundance are measured as variations in the $^{199}\mathrm{Hg}/^{198}\mathrm{Hg}$, $^{200}\mathrm{Hg}/^{198}\mathrm{Hg}$, $^{201}\mathrm{Hg}/^{198}\mathrm{Hg}$, and $^{202}\mathrm{Hg}/^{198}\mathrm{Hg}$ isotopes ratios (the other two ratios are usually not used because of analytical issues).[28] These variations are reported in permil (‰) deviations from NIST Standard Reference Material 3133. For example, $^{202}\mathrm{Hg}/^{198}\mathrm{Hg}$ ratio variations are expressed using

$$\delta^{202}Hg = \left(\frac{\frac{202}{198}Hg_{\text{sample}}}{\frac{202}{198}Hg_{\text{standard}}} - 1 \right) * 1000‰ \tag{1}$$

Hg isotope ratio variations can be induced by mass-dependent isotopic fractionation (MDF). During reduction of Hg(II) to Hg(0) (microbial[29,30] and abiotic[31]), lighter isotopes react at a slightly greater rate causing enrichment of lighter isotopes in reaction products and enrichment of heavier isotopes in the reactant pool. Other MDF reactions include methylation,[32] evaporation,[33] and equilibration between aqueous and adsorbed species.[34,35] Blum and Bergquist[28] give a good summary of how to report isotope ratios. Mass-dependent isotopic variations are determined by measuring $\delta^{202}\mathrm{Hg}$, with $\delta^{200}\mathrm{Hg}$ serving to confirm results. Recent studies have found $\delta^{200}\mathrm{Hg}$ can vary from the predicted mass dependent calculations;[36,37] however, no studies exist showing $\delta^{200}\mathrm{Hg}$ varying from the predicted mass dependent calculations in sediments or ash.

The odd isotopes of Hg ($^{199}\mathrm{Hg}$ and $^{201}\mathrm{Hg}$) have been shown to vary by other processes in addition to those causing mass-dependent fractionation. These phenomena are known as mass independent fractionation (MIF). The dominant cause of MIF appears to be photochemical transformations,[31] though other, smaller MIF effects have been reported.[33,38] MIF is reported as the per mil deviation of the measured $\delta^{199/198}\mathrm{Hg}$ and $\delta^{201/198}\mathrm{Hg}$ values from the expected mass-dependent fractionation derived from the measured $\delta^{202}\mathrm{Hg}$ of the same sample. These are calculated as $\Delta^{199}\mathrm{Hg}$ and $\Delta^{201}\mathrm{Hg}$, respectively.[28]

The Hg isotope ratios of various sources of Hg in the environment differ due to MDF and/or MIF.[10,24−26] These variations provide the potential to determine the source(s) of Hg in systems where multiple sources of contamination exist, or to distinguish contaminant Hg sources from the natural background. Multiple studies have used Hg isotopes in order to trace Hg contamination and sources through natural systems, for example, studies in the Idrija region in Slovenia,[6] Lake Baikal,[8] northern France,[9] San Francisco Bay, California,[10] and China.[7,11,39] However, the Hg isotope ratios of the sources are not necessarily immutable signatures; tracing of sources can be disrupted by isotopic shifts resulting from chemical reactions.

In this study, we present an extensive Hg isotope data set for river sediments near the Kingston, TN, coal ash spill. The river system also contains historical Hg from the Y-12 plant complex at the Oak Ridge Reservation.[22,23] The objectives of this study are (1) determine whether the Hg isotopic values of the four different sources (coal ash, Y-12 Hg, paper mill impacted sediments, and natural background) are distinct from each other; and (2) to estimate the relative contributions of these three sources and the regional Hg background to the sediments' Hg contents at various locations. To achieve this, we determined the isotopic compositions of the various Hg sources into the system and developed evidence that these compositions are not greatly changing over time. The resulting Hg sourcing information is used in a companion article[40] to determine if the availability of Hg for methylation is greater for the recent coal ash-derived Hg, relative to older Hg in the system, or whether the other elements found in the coal ash act as nutrients that increase methylation rates for existing Hg in the sediments.

■ METHODS AND MATERIALS

Field Setting and Sampling Procedures. The Kingston coal fired power plant is located at the confluence of the Emory and Clinch Rivers in Tennessee, USA (Figure 1). Water flow is to the south and west on the Emory and Clinch Rivers, respectively. Under normal conditions, the Emory River discharge is exceeded by that of the Clinch.[41] During normal plant operations, cooling water is drawn from the Emory River, which can sometimes cause the Clinch River water to flow upstream in the Emory for ∼2 miles to the plant intake.[42]

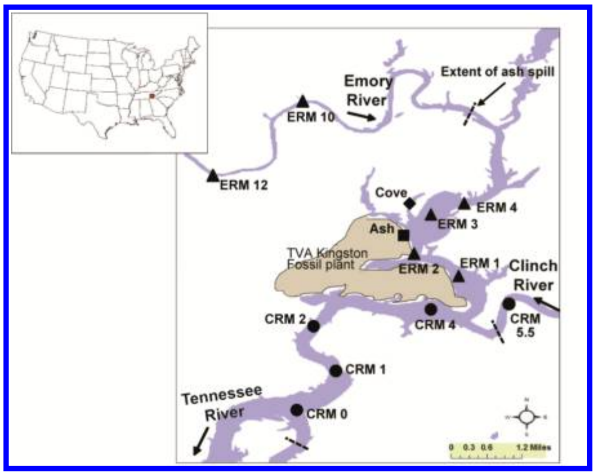


Figure 1. Map of the Kingston power plant site showing river sampling locations (rivers are in dark blue). Emory River sampling sites are marked using triangles (△), Clinch River samples are marked using circles (○), and the cove samples are marked with a diamond (◊). Arrows below river names represent flow directions. Dashed lines indicate extent of ash found immediately after the spill.

Ash from the 2008 spill was found mainly between Emory River Mile 1 (ERM 1; one mile upstream from its confluence with the Clinch River) to ERM 5.5, with a one mile stretch containing an ash layer up to 30 feet thick. Ash traveled upstream to ERM 6, up the Clinch River to Clinch River Mile (CRM) 5, and was found as far downstream as Tennessee River Mile 563.[23,43] Dredging in the Emory River from 2009 to 2010 removed 65% of the 4.1 million cubic meters of spilled ash.[44] Ash samples were collected from the dredge cell from early to late 2009. A cove across from the dredge cell (but on the same

Table 1. Mean Analyses ± SD for the Four End-Member Materials

material	concentration (mg kg^{-1})	δ^{202}Hg	Δ^{199}Hg	Δ^{201}Hg	n
Kingston Fly Ash	0.133 ± 0.023	−1.78 ± 0.35‰	−0.21 ± 0.03‰	−0.14 ± 0.04‰	4
CRM 5.5 Sediment	0.813 ± 0.291	−0.23 ± 0.16‰	−0.07 ± 0.02‰	−0.07 ± 0.02‰	6
ERM 12 Sediment	0.021 ± 0.008	−1.17 ± 0.13‰	−0.21 ± 0.06‰	−0.15 ± 0.03‰	6
ERM 10 Sediment	0.035 ± 0.009	−0.47 ± 0.04‰	−0.13 ± 0.01‰	−0.15 ± 0.02‰	4

side of the river) was completely filled with ash during the spill. Sediments from this cove were sampled in late 2009.

Three river locations were chosen to provide sediments uncontaminated by the ash spill. Emory River Mile 12 (Figure 1) samples have relatively low Hg concentrations and were unaffected by the ash spill because they are located several miles upstream. There are no known point sources of Hg upstream of ERM 12, and we thus assume the observed Hg is some combination of atmospheric deposition, mostly derived from coal-fired power plants, and natural Hg derived from rock weathering. Thus, analyses of the six ERM 12 results serve as a proxy for the regional Hg background. Emory River Mile 10 is located one mile downstream of a former paper mill with known presence of Hg in its surrounding sediments.[45] ERM 10 is, therefore, assumed to represent a mixture of background sediments and sediments affected by the paper mill Hg. Clinch River sediments are known to be contaminated by Hg released from activities at the U.S. Dept. of Energy Y-12 plant complex near Oak-Ridge, TN decades ago.[22,23,46] Our analyses of sediment from Clinch River Mile 5.5, which was not affected by the 2008 ash spill, were used to represent the composition of Clinch River sediments prior to any mixing with the ash.

Sediments from the river bottom were collected using a Wildco box corer (up to 25 cm depth).[47] Samples were generally obtained close to the river channel midpoints. Samples were homogenized by hand and kept at 4 °C (for about 1−3 days) until transport to the lab, where they were frozen upon arrival (−20 °C). Samples were kept frozen until use.

Analytical Methods. Samples for Hg isotope measurements were thawed and up to 0.1g (wet weight) of sediments were weighed into 30 mL glass tubes. The sediment samples were then digested overnight in 4 mL aqua regia (3:1 $HCl:HNO_3$) at 95 °C. Sediments containing Hg concentrations ≤2 mg kg^{-1} were preconcentrated after digestion using an anion exchange step adapted from Malinovsky et al.[48] The anion exchange resin (0.4 mL bed volume) was washed with 5% (m/v) thiourea, conditioned with 2 M HCl, and samples were eluted using 4 mL 5% thiourea solution. Fresh thiourea solutions were made immediately prior to each ion exchange session. Final Hg concentrations of sample solutions used for mass spectrometry were 1−3 ng g^{-1}.

Mass spectrometry followed the methods of Mead and Johnson.[49] Samples were spiked with a calibrated double isotope tracer solution containing ^{196}Hg and ^{204}Hg and allowed to chemically equilibrate overnight. Spiking was done after digestion and prior to any further chemical processing. Isotopic compositions were measured on a Nu Plasma HR multi-collector inductively coupled plasma mass spectrometer at the University of Illinois at Urbana−Champaign. Hg was introduced into the instrument via a cold-vapor generation device using a $SnCl_2$ reductant. For samples prepared using ion exchange, the reductant solution was made strongly basic; this weakens thiourea−Hg complexes and enables the $SnCl_2$ to reduce the Hg(II). Sample uptake rate was 0.5 mL min^{-1}. The instrument's mass-bias was corrected using the measured ^{204}Hg/^{196}Hg ratio and a previously described double-spike data reduction routine.[37] Isobaric interferences were monitored by measuring ^{194}Pt^{+}, ^{203}Tl^{+}, ^{206}Pb^{+}, and ^{196}HgH^{+}; and corrected for the HgH^{+} interferences.

The long-term precision of the isotopic method was evaluated by preparing and analyzing 12 samples multiple times, on different days, for a total of 27 replicate samples. The root-mean-square of the δ^{202}Hg difference is 0.06‰; we thus estimate our 95% confidence precision to be ±0.12‰. The 95% confidence precision for Δ^{199}Hg and Δ^{201}Hg are ±0.07‰ and ±0.06‰, respectively. Blanks were also prepared with each digestion batch and averaged 95 pg Hg, whereas the minimum Hg mass per sample was 4 ng. Concentrations of Hg in the sediments were calculated using isotope dilution; the double-spike concentration is calibrated against a concentration standard (TCLP Hg standard, Ricca Chemical Co.).

Mixing Calculations. Standard equations were used to calculate the isotope ratios and concentrations of sediment mixtures derived from variable proportions of upstream Clinch River sediment, background and paper mill impacted Emory River sediments, and fly ash. Compositions of these four components, or end-members, were represented by average compositions of multiple analyses of CRM 5.5, ERM 12, ERM 10, and fly ash, respectively. The series of equations required is

$$\delta^{202}\mathrm{Hg}_{\mathrm{Mixture}} = (f_{\mathrm{Ash}}\delta_{\mathrm{Ash}}C_{\mathrm{Ash}} + f_{\mathrm{ERM10}}\delta_{\mathrm{ERM10}}C_{\mathrm{ERM10}} + f_{\mathrm{ERM12/CRM5.5}}\delta_{\mathrm{ERM12/CRM5.5}}C_{\mathrm{ERM12/CRM5.5}}) / (f_{\mathrm{Ash}}C_{\mathrm{Ash}} + f_{\mathrm{ERM10}}C_{\mathrm{ERM10}} + f_{\mathrm{ERM12/CRM5.5}}C_{\mathrm{ERM12/CRM5.5}}) \tag{2}$$

$$C_{\mathrm{Mixture}} = f_{\mathrm{Ash}}C_{\mathrm{Ash}} + f_{\mathrm{ERM10}}C_{\mathrm{ERM10}} + f_{\mathrm{ERM12/CRM5.5}}C_{\mathrm{ERM12/CRM5.5}} \tag{3}$$

$$1 = f_{\mathrm{Ash}} + f_{\mathrm{ERM10}} + f_{\mathrm{ERM12/CRM5.5}} \tag{4}$$

Where ERM 12 is used to calculate the mixture for the Emory River samples (with the exception of 2 samples), and CRM 5.5 is used in the Clinch River samples' mixing model. Variable f represents the mass fraction of each end-member present in the mixture, and δ and C give the measured δ^{202}Hg value and concentration of the mixture and each end-member. In order to determine the fraction of each end-member in each measured mixture, the equations were rearranged and solved iteratively for f as a function of the samples' δ and C values.

■ RESULTS

Coal-Ash and Upstream Sediments from the Emory and Clinch Rivers. Sediments collected from the upstream Emory River (site ERM 12) yielded the lowest Hg concentrations (0.014−0.033 mg kg^{-1}), about 38 times lower than the Clinch River Mile 5.5 sediments (0.49−1.2 mg kg^{-1}), and the largest variability (∼38% RSD). Emory River Mile 10 sediments contained higher concentrations of Hg (0.024−0.043

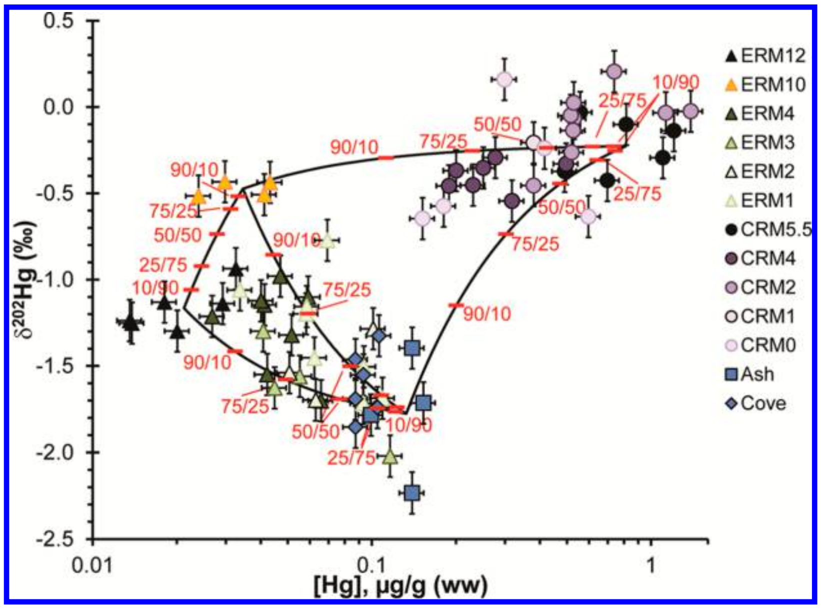


Figure 2. δ^{202}Hg values relative to log Hg concentration. Ash samples are blue squares (□), cove samples are blue diamonds (◊), Clinch River sediments are purple circles (○), and Emory River sediments are green and orange triangles (△). Lighter colors indicate sites farther downstream. The black lines indicate mixing curves between pairs of the end-members, and the red tick marks give mixing proportions at various points along those lines. All Emory River sediments, except two, plot between the Emory River and ash end-members. The Clinch River sediments are more complex and vary with time. Vertical error bars represent 2SD uncertainty, horizontal error bars represent 10% uncertainty.

mg kg^{-1}) and very consistent δ^{202}Hg values (−0.47 ± 0.04‰). In contrast, the four coal-ash samples exhibited higher Hg concentrations (0.099−0.15 mg kg^{-1}) and substantial variability of δ^{202}Hg values, ranging from −1.40‰ to −2.23‰ (Table 1, Figure 2). The ERM 12 and CRM 5.5 locations were remarkably consistent in δ^{202}Hg (−1.17 ± 0.13‰ and −0.23 ± 0.16‰, respectively) considering they were sampled over 5 (ERM 12) and 11 (CRM 5.5) month periods (Figure 2). The Δ^{199}Hg and Δ^{201}Hg also remained consistent over time. The MIF signatures also clustered such that Clinch River samples were distinct from the Emory and Ash samples − which were indistinguishable from each other (Figure 3, Table 2).

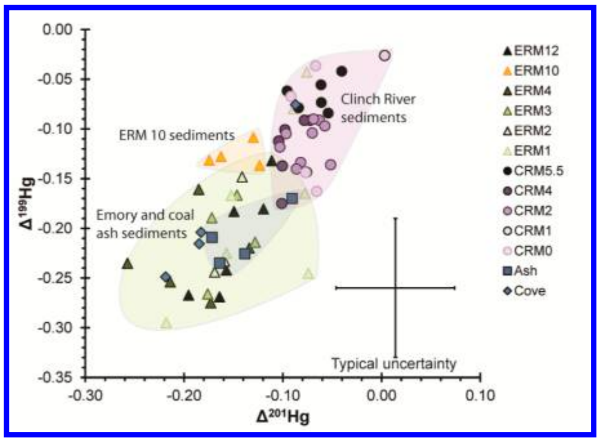


Figure 3. Mass independent anomalies Δ^{199}Hg plotted against Δ^{201}Hg. Ash samples are blue squares (□), cove samples are blue diamonds (◊), Clinch River sediments are purple circles (○), and Emory River sediments are green and orange triangles (△). Lighter colors indicate sites farther downstream. Clinch River sediments plot in a distinct group from the Kingston ash and Emory River sediments, which are indistinguishable from each other. Error bars represent 2SD uncertainty.

River Sediments. Table 2 gives mean values of the various river locations aside from those used as end-members for the various Hg sources. Complete analytical results are reported in Tables S1−S3 of the Supporting Information. Figure 2 presents results from individual samples, along with curves delineating calculated mixing models (δ^{202}Hg vs inverse concentration in the Supporting Information). Six samples from the cove area plot with the ash samples. This is expected since the cove was completely filled with ash from the spill.

Nearly all Emory River samples are consistent with being mixtures of ash and Emory River sediments, without any Clinch River influence. Two exceptions are one ERM 1 sample and one ERM 2 sample, which plot in the Clinch River mixing field. We also note that some ERM 1 and ERM 2 samples, and one ERM 3 sample, fall within the field defined by the cove and ash samples, indicating the former locations are at times dominated by ash-derived Hg. In contrast, none of the samples from the ERM 4 location, the farthest upstream of the spill-contaminated locations sampled, plot within that field (Figure 2).

Data from the Clinch River sediments below the confluence are more complex. Some locations on the Clinch appear to be dominated by Emory River sediments at certain times, but sediments at these locations also vary with time and are sometimes dominated by coal ash. However, all CRM 2 samples, with the exception of one, plot within the field defined by the upstream CRM 5.5 location indicating limited Emory influence (Figure 2).

Mass independent fractionation of ^{199}Hg and ^{201}Hg provides a second, independent isotopic difference between the Clinch River sediments and those from the upstream Emory River and the Kingston Coal Ash (Figure 3). The Clinch River Mile 5.5 sediments have significantly greater Δ^{199}Hg and Δ^{201}Hg than the Emory River upstream samples and the ash. The mean Δ^{199}Hg and Δ^{201}Hg of the Clinch River sediments are −0.06 ± 0.03‰ (2 SD) and −0.07 ± 0.04‰ (2 SD) respectively, whereas the means for the ERM 12 and coal ash are −0.21 ±

Table 2. Average Concentration, δ^{202}Hg, δ^{200}Hg, Δ^{199}Hg, and Δ^{201}Hg ±SD of River Locations

river location	concentration (mg kg^{-1})	δ^{202}Hg	δ^{200}Hg	Δ^{199}Hg	Δ^{201}Hg	n
Cove	0.094 ± 0.01	−1.60 ± 0.19‰	−0.83 ± 0.08‰	−0.19 ± 0.08‰	−0.17 ± 0.06‰	6
ERM 4	0.047 ± 0.01	−1.27 ± 0.24‰	−0.670 ± 0.17‰	−0.22 ± 0.04‰	−0.15 ± 0.08‰	7
ERM 3	0.064 ± 0.04	−1.63 ± 0.30‰	−0.85 ± 0.13‰	−0.21 ± 0.04‰	−0.16 ± 0.02‰	4
ERM 2	0.072 ± 0.03	−1.51 ± 0.21‰	−0.85 ± 0.22‰	−0.21 ± 0.04‰	−0.16 ± 0.01‰	3
ERM 1	0.072 ± 0.02	−1.32 ± 0.33‰	−0.72 ± 0.18‰	−0.18 ± 0.09‰	−0.12 ± 0.06‰	7
CRM 4	0.28 ± 0.11	−0.40 ± 0.09‰	−0.22 ± 0.06‰	−0.12 ± 0.03‰	−0.09 ± 0.01‰	7
CRM 2	0.66 ± 0.33	−0.10 ± 0.18‰	−0.05 ± 0.09‰	−0.10 ± 0.03‰	−0.07 ± 0.03‰	9
CRM 1[a]	0.38 ± 0.04	−0.21 ± 0.12‰	−0.04 ± 0.13‰	−0.03 ± 0.07‰	0.00 ± 0.06‰	1
CRM 0	0.33 ± 0.18	−0.39 ± 0.35‰	−0.24 ± 0.21‰	−0.10 ± 0.06‰	−0.08 ± 0.01‰	4

[a] Uncertainty listed is 10% for concentration and 2SD external reproducibility for isotopic values.

0.09‰ (2 SD) and −0.15 ± 0.09‰ (2 SD), respectively, and ERM 10 are −0.15 ± 0.06 (2 SD) and −0.13 ± 0.02 (2 SD), respectively (Tables S1−S3 of the Supporting Information).

DISCUSSION

Evidence for Stability of Hg Isotope Ratios in Sediments over Time. Previous studies have demonstrated that Hg isotope ratios may differ among Hg sources in sediments of natural systems and suggested that the relative contributions of each source can be estimated at various locations by using the Hg isotopic systematics.[6−11,39] However, these studies implicitly assume that the isotopic ratios of sediment from each source do not change over time. If this assumption is incorrect, spatial variations in the ratios may be attributable to modifications of the isotopic ratios of the sediments rather than source differences, thus it would be impossible to calculate the percent contribution of each Hg source with confidence.

A recent study employing sequential extraction out of the Kingston coal ash has shown that most (roughly 93%) of the Hg is strongly complexed in the ash.[50] Recent studies looking into the interaction of Hg and organic matter have shown that Hg complexes very strongly with dissolved organic matter (DOM).[51−53] Isotopically, Hg bound by thiol groups is up to 0.63‰ lighter than its dissolved species;[34] however, Jiskra et al.[35] found that the sorption process does not impart any isotopic fractionation on Hg when sorbing onto goethite. Given the strong interaction of Hg with DOM and the lack of fractionation associated with sorption processes off of goethite, it is very unlikely that the Hg isotopic composition is changing over time.

Loss of labile Hg from the sediments has the potential to cause a shift in its Hg isotopic ratios.[34,53−55] For example, reduction of Hg(II) to Hg(0) and subsequent loss of isotopically light Hg(0) vapor could result in an increase of the remaining δ^{202}Hg. It is important to note that a significant fraction of the Hg must release from the sediments to cause a detectable isotopic shift. Chemical alteration of Hg having no contact with the environment − trapped inside a sediment grain, for example − will not affect the isotopic values. Similarly, loss of Hg with an isotopic composition matching that of the average sediment Hg will not cause a shift in the isotopes. However, it is very likely there are multiple forms of Hg within the sediments and that these forms are isotopically distinct. A preferential loss of one of those forms will shift the measured values in the sediments.

The data from the present study provide evidence that sediments in this system have stable Hg isotope ratios that do not change significantly with time. We observe that CRM 5.5 and ERM 12 isotopic values scatter over narrow ranges (0.40‰ and 0.36‰, respectively). The Clinch River is known to have been affected by Hg released from the U.S. Dept. of Energy Y-12 complex near Oak Ridge, TN, since the 1950s.[22] If the Hg isotope ratios of the Clinch River sediment have been evolving over time, we would expect the chemical reactions or other processes would cause a variable isotopic shift in space. Our data require that either the sediments have no major shift in their original isotopic values or they have all shifted precisely the same amount. The latter scenario is highly unlikely. Similarly, the nominally uncontaminated background Emory River sediments show little variation, and it is thus unlikely that major Hg isotope shifts occur as sediments age in the river. Given this evidence, we suggest the Hg does not change isotopically over time in this system and therefore can treat the measured Hg isotope ratios as semipermanent signatures.

Estimates of Sediment Contributions from the Three Sources. The relative contributions of the two Hg contaminant sources (Y-12 Hg and TVA ash) to the sediments at various points in the system is of great importance as the region recovers from the spill. Using the data from this study, we are able to estimate the amounts of sediment sourced from the Clinch River, the Emory River, and the coal ash spill, even though the sediments might not have an obvious visual indicator of contamination (i.e., distinctive sediment type). Our ability to distinguish the different contributors of Hg into the system should be useful in tracking the Hg and efficacy of the remediation efforts.[23]

The Hg concentration and isotopic composition of all samples can be successfully modeled as mixtures of the TVA coal ash, upstream Clinch River sediment as represented by CRM 5.5, and Emory River sediments as represented by ERM 12 and ERM 10. We used the mean Hg isotopic and concentration values at these locations (Table 1) as end-members, which then mix to produce the compositions observed in the samples (Table 2). The ERM 12, ERM 10, and CRM 5.5 end-members represent sediment unaffected by the coal ash spill and the limited ranges of isotopic values are taken to represent limited inherent variability in those three sources. The wider isotopic range (0.84‰) of the coal ash end-member in the model is expected because TVA imports coal from multiple locations in the United States.[56] Previous studies have shown that coal isotopic values may vary between, and within, regions in the United States.[24,26]

In Figure 2, the Hg concentration and δ^{202}Hg values of all possible mixtures of the four chosen end-member sediments define two distorted triangles. The curves forming the sides of each field represent binary mixtures containing two of the four sources. The Emory River sediments plot within the three end-member mixing field delineated by ERM 12 (background), ERM 10 (paper mill), and the coal ash end-members, and do not trend toward the Clinch sediments end-member. Clinch River sediments are more complicated. Clinch River Mile 1 and all but one of the CRM 2 samples plot close to the area of zero contribution of the coal ash end-member, whereas sediments from CRM 4 and CRM 0 appear to have a coal ash component in them. This result is consistent with microscopic analysis of sediment particle characteristics along the Clinch River showing primarily native sediments at CRM 2 and a significant coal ash component at CRM 0.[43] This result can be explained by the difference in channel width between CRM 4 and CRM 0, narrowing at CRM 2 and CRM 1 and widening at CRM 4 and 0.[57] The microscopic analysis did not, however, distinguish between the Emory and Clinch sediments, which we were able to do using the resultant Hg isotope data.

The Hg concentration and isotopic composition of each sample, combined with the mixing model (Figure 2), can be used to calculate estimates of the relative contributions of the four sediment sources. These estimates carry significant uncertainties because the four end-members have variable compositions that depart from the compositions used to define the model. In order to estimate the uncertainty of the calculations, we used the most extreme values for the calculations and found that the uncertainties for the Emory and Clinch Rivers are about ±14% and ±40%, respectively (discussion in the Supporting Information).

According to the model calculations, Clinch River sediments comprise less than 5% (and only 9% in the most extreme case as discussed above) of sampled sediment at all Emory River locations, while the Kingston coal ash was found far up the Emory River, with substantial contributions up to ERM 4 (Table 3). This is consistent with previous observations.[23,43]

Table 3. Percent Sediment Contribution of Each End-Member to Specific River Locations[a]

river location	% Clinch	% ash	% ERM 12	% ERM 10	*n*
ERM 4	0	4−40	0−88	0−82	7
ERM 3	0	14−85	15−79	0−26	4
ERM 2	0−3	26−48	0−67	0−50	3
ERM 1	0−4	6−76	0−56	3−91	7
CRM 4	18−36	6−57	0	16−69	7
CRM 2	39−100	0−41	0	0−31	9
CRM 1	36	0	0	64	1
CRM 0	11−57	0−28	0	0−44	4

[a] Uncertainties are estimated to be 14% and 40% for ERM and CRM samples, respectively. Clinch end-member contribution to ERM samples does not exceed 9% (discussion in the Supporting Information).

At a few locations in the Clinch River, about 57% of the sediments are sourced from the TVA power plant spill (Figure 2). However, most Clinch River samples (19 of 22) have less than 40% coal ash according our calculations. Overall, there is no clear pattern that describes the Clinch River results; this is not surprising given the known sediment dynamics (below).

The Δ^{199}Hg and Δ^{201}Hg data cannot be used to calculate sediment mixing proportions, because of the lack of a significant difference between the Kingston ash and ERM 12, and the small magnitude of the Clinch versus Emory/Ash difference relative to the measurement uncertainty. However, the separate grouping of the Clinch and Emory/Ash samples supports our conclusion that Clinch River sediments comprise less than 5% of the sediments found at the Emory River locations.

The observed patterns of sediment mixing, and the variability observed, are consistent with known patterns of water flow and observed sediment dynamics. The presence of Clinch River sediment within the Emory River is caused by periodic artificial reversals of flow direction. During normal plant operation water is pumped from the Clinch/Emory confluence and flow up the Emory River approximately 2 miles into the plant intake (Figure 1).

Immediately following the spill, most of the ash remained in the Emory River,[23] and was observed to transport downstream only in distinct pulses related to flooding events.[23,58] The most significant ash transport event occurred in May 2009.[58] Accordingly, we expect spatial and temporal variability of the sediments at each sampling location downstream of the spill site; this is a potential complicating factor in attempting to define patterns of contamination using our data and similar isotopic data in other studies.[59] For example, one sample might be derived from old, prespill sediments exposed in recent scour, and the next sample at the same nominal location might be dominated by spill material, and another sample might be primarily recently deposited uncontaminated sediments. This could occur either because the exact sampling location varied by a few meters or because the river's bedforms migrated or changed seasonally. It is important to note that the sediments themselves do not have different δ^{202}Hg values, but the resultant mixture can produce a different isotopic value at each sampling location.

Broader Implications. The results of this study demonstrate the ability to use Hg isotopes as tracers of contaminated river sediments affected by a recent spill event. This approach enables us to distinguish between different sources without the need to have visually distinct sediment compositions (i.e., coal ash versus river sediments). Compared to other studies which apportion Hg in systems that only have chronic contamination,[6−12] this study shows that Hg may be stable in some sediments to allow for immediate apportionment of sources during a single contamination event superimposed on an old, chronic contamination problem. Our ability to distinguish between sources, and estimate their contribution to the system, is a powerful tool in tracking Hg as active remediation occurs.

Determining the relative contributions of various Hg sources is useful in understanding both the transport of contaminated sediments and the potential for differing biogeochemical properties of Hg coming from those sources. In a companion article,[40] we use the results of the present study to determine whether Hg sourced from the coal ash is more bioavailable for methylation than the Hg already present in the system or alternatively whether nutrients derived from the ash are responsible for increased Hg methylation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Three tables containing individual sample concentration, isotopic composition, and calculated mixture percents; UM Almadén values; inverse concentration mixing diagram; MIF and mixing model calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gbartov2@illinois.edu.

Present Address

[†]U.S. Geological Survey, Reston, VA.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Restoration Services Inc. and Environmental Standards Inc. for their assistance with field sampling and quality oversight, respectively. This work was supported in part by a grant from the Oak Ridge Associated Universities and the Tennessee Valley Authority.

REFERENCES

(1) *Mercury Study Report to Congress 2*; EPA-452/R-97−003; *Office of Air Quality and Planning and Standards*, Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC, 1997.

(2) *EPA's Roadmap for Mercury*; EPA-HQ-OPPT-2005−0013; U.S. Environmental Protection Agency: Washington, DC, 2006.

(3) Yin, R.; Feng, X.; Shi, W. Application of the stable-isotope system to the study of sources and fate of Hg in the environment: A review. *Appl. Geochem.* **2010**, *25*.

(4) Fréry, N.; Maury-Brachet, R.; Maillot, E.; Deheeger, M.; de Mérona, B.; Boudou, A. Gold-mining activities and mercury contamination of native amerindian communities in French Guiana: key role of fish in dietary uptake. *Environ. Health Perspect.* **2001**, *109*, 449−505.

(5) Harada, M.; Nakanishi, J.; Yasoda, E.; Pinheiro, M.; Oikawa, T.; de Assis Guimarâes, G.; da Silva Cardoso, B.; Kizaki, T.; Ohno, H. Mercury pollution in the Tapajos River basin, Amazon: mercury level of head hair and health effects. *Environ. Int.* **2001**, *27*, 285−375.

(6) Foucher, D.; Ogrinc; Hintelmann, H. Tracing mercury contamination from the Idrija mining region (Slovenia) to the gulf of trieste using Hg isotope ratio measurements. *Environ. Sci. Technol.* **2009**, 43.

(7) Feng, X.; Foucher, D.; Hintelmann, H.; Yan, H.; He, T.; Qiu, G. Tracing mercury contamination sources in sediments using mercury isotope compositions. *Environ. Sci. Technol.* **2010**, *44*, 3363−3371.

(8) Perrot, V.; Epov, V.; Pastukhov, M.; Grebenshchikova, V.; Zouiten, C.; Sonke, J.; Husted, S.; Donard, O.; Amouroux, D. Tracing sources and bioaccumulation of mercury in fish of Lake Baikal − Angara River using Hg isotopic composition. *Environ. Sci. Technol.* **2010**, *44*, 8030−8037.

(9) Estrade, N.; Carignan, J.; Donard, O. Tracing and quantifying anthropogenic mercury sources in soils of northern France using isotopic signatures. *Environ. Sci. Technol.* **2011**, *45*, 1235−1242.

(10) Gehrke, G. E.; Blum, J. D.; Marvin-DiPasquale, M. Sources of mercury to San Francisco Bay surface sediment as revealed by mercury stable isotopes. *Geochim. Cosmochim. Acta* **2011**, *75*.

(11) Liu, J.; Feng, X.; Yin, R.; Zhu, W.; Li, Z. Mercury distributions and mercury isotope signatures in sediments of Dongjiang, the Pearl River Delta, China. *Chem. Geol.* **2011**, 287.

(12) Sherman, L.; Blum, J.; Keeler, G.; Demers, J.; Dvonch, J. Investigation of local mercury deposition from a coal-fired power plant using mercury isotopes. *Environ. Sci. Technol.* **2012**, *46*, 382−472.

(13) Wang, Q.; Kim, D.; Dionysiou, D.; Sorial, G.; Timberlake, D. Sources and remediation for mercury contamination in aquatic systems–a literature review. *Environmental Pollution (Barking, Essex: 1987)* **2004**, *131*, 323−359.

(14) Fitzgerald, W.; Engstrom, D.; Lamborg, C.; Tseng, C.-M.; Balcom, P.; Hammerschmidt, C. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. *Environ. Sci. Technol.* **2005**, *39*, 557−625.

(15) Yang, H.; Battarbee, R.; Turner, S.; Rose, N.; Derwent, R.; Wu, G.; Yang, R. Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. *Environ. Sci. Technol.* **2010**, *44*, 2918−2942.

(16) Yang, H.; Engstrom, D.; Rose, N. Recent changes in atmospheric mercury deposition recorded in the sediments of remote equatorial lakes in the Rwenzori Mountains, Uganda. *Environ. Sci. Technol.* **2010**, *44*, 6570−6575.

(17) St Louis, V.; Derocher, A.; Stirling, I.; Graydon, J.; Lee, C.; Jocksch, E.; Richardson, E.; Ghorpade, S.; Kwan, A.; Kirk, J.; Lehnherr, I.; Swanson, H. Differences in mercury bioaccumulation between polar bears (*Ursus maritimus*) from the Canadian high- and sub-Arctic. *Environ. Sci. Technol.* **2011**, *45*, 5922−5930.

(18) Guigueno, M.; Elliott, K.; Levac, J.; Wayland, M.; Elliott, J. Differential exposure of alpine ospreys to mercury: melting glaciers, hydrology or deposition patterns? *Environ. Int.* **2012**, *40*, 24−56.

(19) Nicolardi, V.; Cai, G.; Parrotta, L.; Puglia, M.; Bianchi, L.; Bini, L.; Gaggi, C. The adaptive response of lichens to mercury exposure involves changes in the photosynthetic machinery. *Environmental pollution (Barking, Essex: 1987)* **2012**, *160*, 1−11.

(20) Yudovich, Y. E.; Ketris, M. P. Mercury in coal: A review Part 2. Coal use and environmental problems. *Int. J. Coal Geology* **2005**, *62*.

(21) Coal Combustion Residues (CCR): *Surface Impoundments with High Hazard Potential Rating Fact Sheet* EPA530-F-09−006; U.S. Environmental Protection Agency: 2009; p 4.

(22) *Kingston Ash Incident Evaluation of Potential Legacy Contamination in Local Sediments*; Tennessee Valley Authority: Knoxville, TN, 2009.

(23) *TVA Kingston fossil fuel plant release sito on-scene coordinator report for the time-critical removal action May 11, 2009 through December 2010, Harriman, Roane County, Tennessee*; EPA-AO-030; Tennessee Valley Authority: Knoxville, TN, 2011.

(24) Biswas, A.; Blum, J.; Bergquist, B.; Keeler, G.; Xie, Z. Natural mercury isotope variation in coal deposits and organic soils. *Environ. Sci. Technol.* **2008**, *42*, 8303−8312.

(25) Stetson, S.; Gray, J.; Wanty, R.; Macalady, D. Isotopic variability of mercury in ore, mine-waste calcine, and leachates of mine-waste calcine from areas mined for mercury. *Environ. Sci. Technol.* **2009**, *43*, 7331−7337.

(26) Lefticariu, L.; Blum, J.; Gleason, J. Mercury isotopic evidence for multiple mercury sources in coal from the Illinois basin. *Environ. Sci. Technol.* **2011**, *45*, 1724−1729.

(27) Day, R.; Roseneau, D.; Berail, S.; Hobson, K.; Donard, O.; Vander Pol, S.; Pugh, R.; Moors, A.; Long, S.; Becker, P. Mercury stable isotopes in seabird eggs reflect a gradient from terrestrial geogenic to oceanic mercury reservoirs. *Environ. Sci. Technol.* **2012**, *46*, 5327−5362.

(28) Blum, J.; Bergquist, B. Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* **2007**, *388*, 353−362.

(29) Kritee, K.; Blum, J.; Johnson, M.; Bergquist, B.; Barkay, T. Mercury stable isotope fractionation during reduction of Hg(II) to Hg(0) by mercury resistant microorganisms. *Environ. Sci. Technol.* **2007**, *41*, 1889−1984.

(30) Kritee, K.; Blum, J.; Barkay, T. Mercury stable isotope fractionation during reduction of Hg(II) by different microbial pathways. *Environ. Sci. Technol.* **2008**, *42*, 9171−9178.

(31) Bergquist, B.; Blum, J. Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science (New York, N.Y.)* **2007**, *318*, 417−437.

(32) Rodríguez-González, P.; Epov, V.; Bridou, R.; Tessier, E.; Guyoneaud, R.; Monperrus, M.; Amouroux, D. Species-specific stable isotope fractionation of mercury during Hg(II) methylation by an anaerobic bacteria (*Desulfobulbus propionicus*) under dark conditions. *Environ. Sci. Technol.* **2009**, *43*, 9183−9191.

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

(34) 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*, 4191−4197.

(35) Jiskra, M.; Wiederhold, J.; Bourdon, B.; Kretzschmar, R. Solution speciation controls mercury isotope fractionation of Hg(II) sorption to goethite. *Environ. Sci. Technol.* **2012**, *46*, 6654−6716.

(36) Gratz, L.; Keeler, G.; Blum, J.; Sherman, L. Isotopic composition and fractionation of mercury in Great Lakes precipitation and ambient air. *Environ. Sci. Technol.* **2010**, *44*, 7764−7770.

(37) JiuBin, C.; Holger, H.; XinBin, F.; Brian, D. Unusual fractionation of both odd and even mercury isotopes in precipitation from Peterborough, ON, Canada. *Geochim. Cosmochim. Acta* **2012**, *90*.

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

(39) Runsheng, Y.; Xinbin, F.; Jianxu, W.; Ping, L.; Jinling, L.; Ying, Z.; Jiubin, C.; Lirong, Z.; Tiandou, H. 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.* **2012**, DOI: 10.1016/j.chemgeo.2012.04.030.

(40) Deonarine, A.; Bartov, G.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Environmental impact of the Tennessee Valley Authority Kingston coal ash spill. 2. Methylmercury in historically contaminated river sediments. *Environ. Sci. Technol.* Submitted for publication.

(41) *Kingston Ash Recovery Project Weekly Report October 25−31, 2010*; Tennessee Valley Authority: Knoxville, TN, 2010.

(42) *TVA Community Involvement Plan for the Kingston Ash Recovery Project*; Tennessee Valley Authority: Knoxville, TN, 2010.

(43) *Continuing Investigation of the Nature and Extent of Ash in the Emory, Clinch and Tennessee River Bottoms*; Tennessee Valley Authority: Knoxville, TN, 2009.

(44) Zeller, C. In *TVA Kingston recovery project Roane County, TN*, TVA-Kingston Fly Ash Release Environmental Research Symposium, Harriman, TN, August 2−3, 2011; Harriman, TN, 2011.

(45) *Expanded Site Investigation Report Potential Hazardous Waste Site Clinch River Corporation*; Tennessee Department of Environment and Conservation Division of Remediation − Knoxville Field Office: Knoxville, TN, 2011.

(46) Brooks, S.; Southworth, G. History of mercury use and environmental contamination at the Oak Ridge Y-12 Plant. *Environmental pollution (Barking, Essex: 1987)* **2011**, *159*, 219−247.

(47) Ruhl, L.; Vengosh, A.; Dwyer, G.; Hsu-Kim, H.; Deonarine, A. Environmental impacts of the coal ash spill in Kingston, Tennessee: an 18-month survey. *Environ. Sci. Technol.* **2010**, *44*, 9272−9280.

(48) Malinovsky, D.; Sturgeon, R.; Yang, L. Anion-exchange chromatographic separation of Hg for isotope ratio measurements by multicollector ICPMS. *Anal. Chem.* **2008**, *80*, 2548−2603.

(49) Mead, C.; Johnson, T. Hg stable isotope analysis by the double-spike method. *Anal. Bioanal. Chem.* **2010**, *397*, 1529−1567.

(50) Matsumoto, A.; Schwartz, G. E.; Deonarine, A.; Hsu-Kim, H. Assessment of mercury speciation in coal ash by sequential extractions. In *Geological Society of America Abstracts with Programs*, Proceedings of 2011 GSA Annual Meeting, Minneapolis, Minnesota, 9−11 October; **2011**; 418.

(51) Haitzer, M.; Aiken, G.; Ryan, J. Binding of mercury(II) to aquatic humic substances: influence of pH and source of humic substances. *Environ. Sci. Technol.* **2003**, *37*, 2436−2441.

(52) Dong, W.; Bian, Y.; Liang, L.; Gu, B. Binding constants of mercury and dissolved organic matter determined by a modified ion exchange technique. *Environ. Sci. Technol.* **2011**, *45*, 3576−3583.

(53) Gu, B.; Bian, Y.; Miller, C.; Dong, W.; Jiang, X.; Liang, L. Mercury reduction and complexation by natural organic matter in anoxic environments. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 1479−1562.

(54) Delphine, F.; Holger, H.; Tom, A. A.; Kerry, T. M. Mercury isotope fractionation in waters and sediments of the Murray Brook mine watershed (New Brunswick, Canada): Tracing mercury contamination and transformation. *Chem. Geol.* **2012**, DOI: 10.1016/j.chemgeo.2012.04.014.

(55) Runsheng, Y.; Xinbin, F.; Jianxu, W.; Zhengduo, B.; Ben, Y.; Jiubin, C. Mercury isotope variations between bioavailable mercury fractions and total mercury in mercury contaminated soil in Wanshan Mercury Mine, SW China. *Chem. Geol.* **2012**, DOI: 10.1016/j.chemgeo.2012.04.017.

(56) Tennessee Valley Authority, The TVA power system. In *Environmental Impact Statement of TVA's Integrated Resource Plan TVA's Environmental & Energy Future*, Knoxville, Tennessee, **2011**; Vol. 8, pp 39−55.

(57) Scott, S. H. *Long Term Simulation of Residual Fly Ash Transport and Fate in the Watts Bar Reservoir System*; Coastal and Hydraulics Laboratory U.S. Army Engineering Research and Development Center at Waterways Experimentation Station: 2012.

(58) Tennessee Valley Authority Kingston ash release Emory River high-flow event of May 4, 2009. http://www.tva.gov/kingston/emory.htm (December 4),

(59) Baker, T.; Smith, J. In *The Complexity of Reservoir Benthic Habitats: Deciphering the Effects of the Kingston Fly Ash Release on the Benthic Macroinvertebrate Community*, TVA-Kingston Fly Ash Release Environmental Research Symposium, Harriman, TN, August 2−3, 2011; Harriman, Tennessee, 2011.