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Environmental Impacts of the Tennessee Valley Authority Kingston Coal Ash Spill. 2. Effect of Coal Ash on Methylmercury in Historically Contaminated River Sediments

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Abstract

The Tennessee Valley Authority Kingston coal ash spill in December 2008 deposited approximately 4.1 million m³ of fly ash and bottom ash into the Emory and Clinch River system (Harriman, Tennessee, USA). The objective of this study was to investigate the impact of the ash on surface water and sediment quality over an eighteen month period after the spill, with a specific focus on mercury and methylmercury in sediments. Our results indicated that surface water quality was not impaired with respect to total mercury concentrations. However, in the sediments of the Emory River near the coal ash spill, total mercury concentrations were 3- to 4-times greater than sediments several miles upstream of the ash spill. Similarly, methylmercury content in the Emory and Clinch River sediments near the ash spill were slightly elevated (up to a factor of 3) at certain locations compared to upstream sediments. Up to 2% of the total mercury in sediments containing coal ash was present as methylmercury. Mercury isotope composition and sediment geochemical data suggested that elevated methylmercury concentrations occurred in regions where native sediments were mixed with coal ash (e.g., less than 28% as coal ash in the Emory River). This coal ash may have provided substrates (such as sulfate) that stimulated biomethylation of mercury. The production of methylmercury in these areas is a concern because this neurotoxic organomercury compound can be highly bioaccumulative. Future risk assessments of coal ash spills should consider not only the leaching potential of mercury from the wastes, but also the potential for methylmercury production in receiving waters.

21 Introduction

22 Coal-fired power plants currently contribute approximately 50% of the total mercury 23 emissions in the USA [1]. Mercury emissions are of concern because deposition of atmospheric 24 mercury is a widely recognized source of mercury to aquatic systems, where transformation to 25 the bioaccumulative and neurotoxic methylmercury species can occur [2].

With the implementation of the Mercury and Air Toxics Standard (2011), air pollution control devices for mercury releases at coal-fired power plants are expected to transfer this element from flue gas to solid wastes. As a result, there is a growing need to consider the fate of mercury after the disposal of coal combustion byproducts (CCBs) such as fly ash, bottom ash, and flue gas desulfurization products [3, 4]. In the USA, 56% of the 130 Mt of coal ash produced annually is disposed in landfills or surface impoundments [5]. These structures are not always closely regulated, and leaching and impoundment failures can result in the mobilization of CCBs and their associated contaminants into aquatic systems. The production of CCBs is predicted to increase along with the use of coal over the next few decades [6]. As such, the fate and transformation of these materials and their contaminant-bearing leachates in aquatic systems are issues of concern.

Mercury concentrations ranging from 10^{-3} to $10 \ \mu g/g$ have been measured in CCBs [7, 8]. Mercury in these materials is typically bonded to sulfur, chlorine, and carbon as Hg(I) and Hg(II) species [7, 8]. Sequential extraction and leaching experiments have determined that total mercury does not leach significantly from fly or bottom ash into deionized water or acidic solutions (pH < 4.93); measured concentrations in extractants ranged from 14.4 ng/L to quantities below analytical detection limits (< 500 ng/L) [9-11]. However, the results of these studies are not representative of the fate of mercury in real ecosystems, as they do not account for environmental variables such as anaerobic conditions, the presence of natural organic matter, and
biological activity that can influence transformations and bioavailability of mercury in benthic
sediments of rivers and lakes.

In addition to mercury, CCBs may also be enriched in labile organic carbon and sulfate [12, 13]. All three constituents can contribute to microbial production of methylmercury [14] in aquatic ecosystems. The production of methylmercury primarily occurs in the anaerobic zones of aquatic sediments, where anaerobic bacteria (mainly sulfate reducers) are able to transform inorganic mercury compounds to methylmercury [15, 16]. The production of methylmercury is a critical step towards bioaccumulation of methylmercury in the aquatic food web. However, the methylation potential of mercury and leachates associated with CCBs on methylmercury production are poorly understood.

On December 22, 2008, the failure of a holding pond at the Tennessee Valley Authority (TVA) Kingston plant in Tennessee, USA resulted in the release of 4.1 million m³ of combined fly and bottom ash into the adjacent Emory River and Clinch River system (Figure 1). This event was one of the largest coal ash spills in U.S. history [17, 18]. Mercury concentrations in the ash were approximately 0.14 μ g/g and exceeded the background concentration of 0.04 to 0.05 μ g/g in Tennessee soil [19]. The objective of this study was to utilize the opportunity provided by the spill event and conduct a field-based study to assess the impact of coal ash on methylmercury production in a river ecosystem. We hypothesized that ash provided a source of mercury and other constituents that could stimulate microbial mercury methylation in river sediments.

65 Materials and Methods.

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3 4	66	Study site. The TVA plant is located near the point of convergence of the Emory and Clinch			
5 6 7	67	Rivers in Tennessee, USA (Figure 1). The plant uses the Emory River as a source of cooling			
8 9	68	water, with the intake located at Emory River Mile 2 (ERM2) and the discharge located along			
10 11	69	the Clinch River, just upstream of Clinch River Mile 2 (CRM2).			
12 13	70	The ash was released into the river between ERM2.5 and ERM3. The resulting ash wave			
14 15 16	71	distributed the ash as far upstream as ERM6. High-flow events that followed in the months after			
17 18	72	the spill distributed ash further downstream in the Clinch River from CRM5 to CRM0, and in the			
19 20 21	73	Tennessee River [19, 20]. Remediation efforts involved dredging operations that commenced in			
21 22 23	74	the Emory River in May 2009 and continued to May 2010 [20], removing approximately 92% of			
24 25	75	the material that spilled into the main river channel and leaving 0.18 million m ³ of ash in the			
26 27 28	76	Emory [20].			
29 30	77	Before the spill, the Emory-Clinch system was already impaired with respect to mercury.			
31 32	78	This mercury is mainly attributed to historical releases from U.S. Department of Energy facilities			
33 34 35	79	in Oak Ridge, TN (about 20-30 km upstream along the Clinch River) [21]. A portion of this			
36 37	80	mercury has migrated downstream along the Clinch River, including locations near the spill.			
38 39	81	Furthermore, the TVA plant diverts large volumes of river water through the cooling water			
40 41 42	82	intake situated along Emory River (near its confluence with the Clinch) [22-24], resulting in			
43 44	83	periodic backflows and possible mobilization of Clinch River sediments upstream into the			
45 46 47	84	Emory. Thus, the Clinch River provides a source of legacy mercury to this site. Other sources of			
47 48 49	85	mercury to the rivers could include non-point sources such as atmospheric deposition and runoff			
50 51	86	from a mercury-contaminated mill at ERM11.3 (non-operational from 2002), and point sources			
52 53 54	87	such as the Harriman municipal wastewater treatment plant (WWTP). Effluent from the WWTP			
55 56 57	88	was released at ERM 10.5 from December 2008 to October 2010 at an average daily flow rate of			

1.25 MGD (NPDES permit #TN0025437). We did not consider the WWTP effluent to be a significant source of mercury to sediments since the temporary discharge contained undetectable quantities of mercury (< 200 ng/L) and the effluent flow rate was small relative to flow of the Emory River during the study period (median flow: 470 MGD) [25]. Both the Emory and Clinch Rivers are currently under fish consumption advisories that pre-date the ash spill [26]. Field sampling and chemical analyses. Ten site locations along the Emory and Clinch Rivers were sampled approximately every month from August 2009 to August 2010 (Figure 1) for surface water and sediments. Sites ERM1, ERM2, ERM3, ERM4, and ERM12 were located along the Emory while sites CRM0, CRM1, CRM2, CRM4, and CRM5.5 were located along the Clinch. ERM12 and CRM5.5 were situated along sections of the Emory and Clinch Rivers upstream of the spill. An additional upstream site along the Emory River (ERM10) was sampled in June 2011. Details on sample collection and chemical analyses are provided in the SI Section. In summary, field samples at each site included surface water samples (top 0.2 m), surface sediments (uppermost 5 to 25 cm), and sediment porewater obtained by filtering sediment with 0.45-µm vacuum filters immediately after collection. Analyses of samples included total mercury and methylmercury in water and sediments using standard procedures [27-31]. Sediments were also analyzed for acid volatile sulfide (AVS) [32, 33] and total organic carbon (TOC). Porewater samples were analyzed for trace elements and anions (including sulfate).

Mercury isotope measurements. The presence of multiple sources of mercury to this ecosystem 112 posed a challenge for assessing the environmental consequences of the ash spill. In a companion 113 paper [34], we quantified mercury isotope composition in sediments (δ^{202} Hg) to identify the 114 contribution of the various sources of mercury and their spatial distribution in the Emory-Clinch 115 River system. As summarized in the SI section, the δ^{202} Hg value for a sample represents the 116 202 Hg/¹⁹⁸Hg isotope ratio relative to a reference material. The δ^{202} Hg data was utilized to assess 117 the impact of the ash on methylmercury production in the river sediments.

Results and Discussion.

Surface water quality. Surface water quality was not negatively impacted by the ash with respect to mercury and methylmercury. Total mercury concentrations at all locations were below the US EPA surface water quality guideline for aquatic life (12 ng/L) [35]. The exception to this occurred with samples from two locations along the Clinch River in November 2009 and June 2010, in which total mercury concentrations were 20.3 and 20.5 ng/L, respectively (Tables S1 through S9). The higher concentrations may have been due to sampling during a storm event (e.g., June 2010) and/or concurrent dredging operations which resuspended surface sediments. Methylmercury concentrations were similar at all sampling locations, even under high flow conditions (Tables S1 through S9) and ranged from <0.08 to 0.9 ng/L in the Emory and Clinch Rivers. These values were similar to the range typically observed in rivers and streams across the United States ($\leq 0.8 \text{ ng/L}$) [36].

Total mercury in sediment. In the Emory River, total mercury concentrations in sediment at sites ERM4, ERM3, ERM2, and ERM1 were $0.10 \pm 0.003 \,\mu$ g/g, slightly less than the mercury

3 4	134	concentration measured in the ash, $0.14 \pm 0.004 \ \mu g/g$ (Figure 2a). Both concentration average						
5 6 7	135	5 were greater than mercury in sediment at ERM12 ($0.03 \pm 0.004 \ \mu g/g$) and ERM10 ($0.05 \pm 0.004 \ \mu g/g$)						
8 9	136	$6 \mu g/g$), sites located several miles upstream of the spill. An analysis of variance coupled w						
10 11	137 posthoc pairwise comparisons was performed to determine if the mean mercury co							
12 13 14	$\frac{2}{3}$ 138 were statistically different at the various sites. Total mercury concentrations at site							
15 16	139	ERM3, ERM2, and ERM1 were significantly different from both ERM12 and ERM10 ($p <$						
17 18 19	140	0.05), indicating that the ash increased the average mercury concentration in Emory River						
20 21	141	sediments by a factor of 2 to 3 relative to upstream sediments.						
22 23	²² 142 In the Clinch River, average total mercury concentration in sediments varied b							
²⁴ ₂₅ 143 Total mercury concentrations at the upstream site CRM5.5 ($1.04 \pm 0.05 \ \mu g/g$), CRM								
27 28	144 0.05 μ g/g) and CRM1 (1.02 ± 0.05 μ g/g) were higher than mercury concentrations a							
29 30 21	145	$(0.58 \pm 0.05 \ \mu\text{g/g})$ and CRM0 $(0.62 \pm 0.06 \ \mu\text{g/g})$ ($p < 0.05$). The lower concentration could be a						
32 33	result of dilution due to the mixing of ash and Emory River sediments with Clinch Riversediments that are enriched with mercury.							
34 35								
 Mercury concentrations also varied with respect to time, with no apparent s Mercury concentrations also varied with respect to time, with no apparent s monthly trend. While dredging of the Emory River occurred during the course of o 								
					41 42	 the concentrations of total mercury and methylmercury concentrations in river sed 42 		
43 44 45	 151 appear to change appreciably during and after completion of dredging (Figure S1). 152 Overall, sediment mercury concentrations in the Clinch were higher than in the 17 							
46 47								
48 49	⁸ 153 River (Figure 2a), consistent with historical contamination of the Clinch River (e.g. r							
50 51 52	154	mercury from Oak Ridge) [26, 37].						
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Methylmercury in sediment. Both the methylmercury concentration (Figure 2b) and the percentage of total mercury present as methylmercury (% as MeHg) in sediments (Figure 3) varied temporally and spatially. A seasonal effect was observed: the highest methylmercury concentrations and % as MeHg values occurred during the spring, summer, and fall months (April to November) compared to the winter months (December to March) (p < 0.05) (Figure S2). Similar seasonal patterns have been reported in previous studies [38, 39]. Factors such as lower temperature, differences in nutrient loading, and senescent vegetation during the winter months are thought to reduce bacterial activity and methylmercury production compared to other times of the year [38, 39].

Our data also suggested a spatial pattern in sediment methylmercury concentration. Methylmercury concentrations in the Emory River were up to two times greater at sites ERM4 $(1.12 \pm 0.18 \text{ ng/g})$ and ERM1 $(1.63 \pm 0.17 \text{ ng/g})$ compared to the upstream ERM12 site $(0.59 \pm 0.17 \text{ ng/g})$ 0.26 ng/g). The average methylmercury concentration at ERM1 was statistically different from ERM12 (p < 0.05); ERM10 was excluded from this analysis due to too few samples (n = 3). The comparison of methylmercury concentrations at ERM4 and ERM12 was not significant (p >0.05). However, the *p*-value obtained (0.07) was close to the significance level of 0.05, and we note that the number of samples for ERM12 (n = 11) was fewer than for other ERM sites (n = 18) to 27). Sediment methylmercury concentrations at ERM4 and ERM1 were also higher than concentrations at ERM2 (0.29 \pm 0.20 ng/g) and ERM3 (0.60 \pm 0.18 ng/g) (p < 0.05). In addition, average methylmercury concentrations at sites ERM3 and ERM2 were not different from ERM12 (p > 0.05).

177 In the Clinch River, methylmercury concentrations at CRM4 ($2.89 \pm 0.18 \text{ ng/g}$) and 178 CRM0 ($3.19 \pm 0.23 \text{ ng/g}$) were as much as 3-times greater than in upstream sediments at

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179	CRM5.5 ($1.27 \pm 0.18 \text{ ng/g}$) and at sites CRM2 ($1.51 \pm 0.18 \text{ ng/g}$) and CRM1 ($1.02 \pm 0.05 \text{ ng/g}$).
180	Methylmercury concentrations at CRM4 and CRM0 were statistically different from upstream
181	site CRM5.5 ($p < 0.05$) while concentrations at site CRM2 were similar to CRM5.5 ($p > 0.05$).
182	CRM1 was omitted from statistical analyses due to the small sample size $(n = 3)$.
183	At all locations along the Emory and Clinch Rivers, methylmercury was a small fraction
184	(up to 2%) of the total mercury present in sediments (Figure 3). These % as MeHg values were
185	within the range observed in previous studies for unpolluted freshwater sediments and in
186	sediments that were impacted by elevated sulfate (< 12% as MeHg) [38]. We used the % as
187	MeHg values to compare the potential for mercury methylation in Emory and Clinch River
188	sediments.
189	Despite larger methylmercury sediment concentrations at ERM4 compared to upstream
190	site ERM12, % as MeHg values at ERM4 (1.55 \pm 0.16%) were not statistically different from
191	ERM12 (1.80 \pm 0.23%) ($p > 0.05$). Downstream of ERM4, % as MeHg values followed a spatial
192	pattern similar to methylmercury sediment concentrations; % as MeHg values at ERM3 (0.90 \pm
193	0.25%) and ERM2 (0.34 \pm 0.09%) were lower compared to ERM4 and then increased at ERM1

194 $(1.4 \pm 0.21\%)$. Sites ERM3 and ERM2 were found to be statistically different from ERM4 and 195 ERM1 (p < 0.05).

In the Clinch River, % as MeHg values also followed a spatial distribution that was similar to sediment methylmercury concentrations. At sites CRM4 ($0.54 \pm 0.07\%$) and CRM0 ($0.65 \pm 0.12\%$), % as MeHg values were higher than at sites CRM2 ($0.13 \pm 0.01\%$), CRM1 ($0.12 \pm 0.01\%$) and CRM5.5 ($0.13 \pm 0.02\%$). Percent (%) as MeHg values at CRM4 and CRM0 were statistically different from both the upstream site CRM5.5 and site CRM2 (p < 0.05).

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201 Our data indicated that a larger proportion of mercury occurred as methylmercury in the 202 Emory River, suggesting that biogeochemical conditions may be more conducive for the 203 production and persistence of methylmercury in sediments of the Emory than in the Clinch. 204 Furthermore, the spatial variation in methylmercury along each river may be due to differences 205 in the local sediment conditions (e.g. redox potential, microbial productivity) which could 206 contribute to differences in methylmercury concentration.

Mercury isotopic composition in river sediments. Mercury in the Emory and Clinch Rivers could be derived from numerous sources (e.g. coal ash, Oak Ridge, atmospheric deposition). To determine the distribution of mercury sources in river sediments, we applied δ^{202} Hg values to a ternary mixing model in which the proportion of the sediment sample mass f_x was a combination of four end-members x: Clinch River sediment collected at the upstream CRM5.5 site; Emory River sediment collected at upstream sites ERM12 and ERM10; and ash from the TVA plant and holding pond. The calculations for f_x were obtained from Bartov et al. [34] and are summarized in the SI. Sediment samples used for these isotopic measurements were collected during spring, summer, and fall months when mercury methylation was highest. ERM10 sediments were collected downstream of the closed paper mill (ERM11.3), and are considered representative of upstream Emory River sediments that may have been impacted by mercury contamination from the mill.

Our mixing calculations indicated that the majority of Emory River sediments collected contained no sediment from the Clinch River, with the exception of two samples which contained 3% and 4% as ash, respectively (Figure 4). The remaining proportion in the samples (96 to 100 %) was a mixture of upstream Emory sediments (either ERM12 or ERM10) and the

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224 ash. This suggested that the reversal of flow in the Emory River during water intake events at the 225 plant resulted in deposition of a small proportion of Clinch River sediments ($f_{Clinch} < 4\%$) onto 226 the surface sediments of the Emory at the time of our survey [34]. 227 In the Clinch River, sources of material to the sediments at each site varied according to 228 location. Sediments from CRM4 and CRM0 were largely mixtures of upstream CRM5.5, 229 ERM10, and ash while sediments collected from CRM2 and CRM1 consisted of the upstream 230 CRM5.5 and ERM10 end-members only (Figure 4). An exception was that one of the five 231 CRM2 sediment samples contained 64% ash (Figure 4). The lack of coal ash at CRM2 and 232 CRM1 may be explained by the proximity of these sites to the plant's cooling water discharge, 233 which prevents sedimentation of fine particles such as ash. At the other Clinch River sites, the 234 presence of ash in river sediments may have influenced methylmercury production in the rivers; 235 average methlymercury concentrations and % as MeHg values at CRM4 and CRM0 were greater 236 than the other Clinch River sites with no coal ash (CRM 5.5, CRM 2, and CRM 1) (Figures 2b 237 and 3).

238 To further investigate the relationship between coal ash and methylmercury concentration, we plotted sediment methylmercury concentration versus f_{Ash} , the mass fraction as 239 240 coal ash in each sediment sample. In sediment samples with methylmercury concentrations 241 exceeding upstream levels (at either ERM 12 or CRM5.5), 89% of these samples contained ash. 242 This observation suggested that the mixing of ash with native sediment, or an input of 243 constituents derived from the ash, resulted in an increase of net mercury methylation. In the 244 Clinch, 90% of sediments that contained more methylmercury than the reference site (CRM5.5) 245 contained 39 to 64% ash (Figure 5a). In the Emory River, methylmercury concentrations were 246 elevated relative to upstream sediments only in samples collected from ERM1 and ERM4; these

samples contained $\leq 28\%$ ash, except for one sample containing 76% ash (Figure 5b). Several Emory River sediments, however, did not appear to follow this pattern between methylmercury concentration and ash content, suggesting that parameters other than f_{Ash} were influential in mercury methylation. Examples could include total mercury content and geochemical factors important for the productivity of anaerobic bacteria and mercury bioavailability (e.g., sulfide, sulfate and organic carbon).

253 For each sediment sample, we also calculated the proportion of total mercury that was254 derived from each end-member using the formula:

$$\% as Hg_x = \frac{f_x \cdot C_x \cdot 100}{C_{mixture}}$$
(1)

where x represents either the ash, upstream Emory or upstream Clinch end-member, f_x is the mass fraction of sediment derived from end-member x, C_x is the concentration of total mercury in end-member x, and $C_{mixture}$ is the concentration of total mercury in each sample. Our calculations indicated that total mercury in Emory River sediments near the spill was largely derived from ERM12 (up to 50%), ERM10 (up to 83%), and coal ash (up to 96%). In the majority of these sediments, our calculations did not demonstrate a contribution of mercury from Clinch River end-member CRM5.5. In sediments collected along the Clinch River, total mercury was mostly derived from upstream Clinch (58 to 100%) and ash (0 to 32%) (Figure S3).

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265 Correlation of methylmercury with other sediment parameters

We performed linear correlations of sediment methylmercury with other sediment parameters (Table 1, Figures S4 to S11). This list of parameters included those known to be related to mercury methylation by anaerobic microbes, such as whole sediment total Hg, TOC and AVS concentrations, and sediment porewater concentrations of sulfate [14]. Porewater arsenic, strontium, and boron concentrations were also included in the analysis, as these
parameters have been identified as leachable contaminants from the TVA ash [19, 40]. The
productivity of methylating microbes tends to be decreased during the winter months. Therefore,
we focused only on the spring, summer and fall months (April to November) for the correlations
with methylmercury.

At Emory River locations directly impacted by the spill (ERM4 to ERM1), sediment methylmercury was positively correlated with sediment AVS ($r^2 = 0.57$) and TOC ($r^2 = 0.61$), and negatively correlated with porewater sulfate ($r^2 = 0.68$) and boron ($r^2 = 0.36$) concentrations (Table 1). Methylmercury was poorly correlated with total Hg, porewater arsenic, and porewater strontium. Porewater sulfate and boron concentrations were positively correlated throughout the sampling period ($r^2 = 0.31$). In the subset of Emory River sediments with $f_{Ash} \le 28\%$, methylmercury concentrations were negatively correlated with porewater sulfate ($r^2 = 0.61$) and positively correlated with sediment AVS ($r^2 = 0.34$), TOC ($r^2 = 0.72$), total Hg ($r^2 = 0.53$), and porewater arsenic ($r^2 = 0.51$) and strontium ($r^2 = 0.42$) (Table 1, Figures S4 to S8). Methylmercury in this subset of Emory sediments was poorly correlated with boron. The relationships observed amongst methylmercury, TOC, AVS, and porewater sulfate concentrations indicated that increasing methylmercury concentration was associated with anaerobic redox conditions and the extent of sulfate-reducing microbial processes in the Emory River. These relationships could provide an explanation for the spatial distribution of methylmercury concentrations in the Emory River, i.e. lower methylmercury concentrations and % as MeHg values observed at ERM2 and ERM3 compared to ERM1 and ERM4. In the methylmercury research literature, the conventional paradigm is that methylmercury production is negatively correlated with AVS [41, 42]. However, this

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relationship generally applies to systems with relatively high sulfate levels (>100 μ M [42-44]) and probably does not apply to the Emory River that has lower sulfate (<100 μ M) and AVS concentrations (< 0.1 μ M). In Emory River sediments, the activity of sulfate-reducing bacteria may be sulfate-limited [38].

The correlation of porewater boron with porewater sulfate suggested that the ash may be a source of both leachable sulfate and boron in river sediments at the spill site, as indicated by our previous results [19, 40]. Furthermore, during the winter months, the correlation of porewater sulfate with boron was stronger ($r^2 = 0.52$, p = 0.045) compared to the spring, summer and fall months ($r^2 = 0.29$, p = 0.13) (Table 1, Figure S6). This observation is consistent with the fact that the biogeochemical pathways of sulfate and boron are different. In the winter months, when MeHg concentrations were lower than in other parts of the year, we presumed that sulfate-reducing microbial activity was lower and thus less sulfate was consumed by sulfate-reducing bacteria (including those that methylate mercury) in anaerobic sediments. Thus, boron and sulfate were highly correlated during the winter months and less strongly correlated during the spring, summer and fall months. We do not believe that municipal wastewater effluent discharge upstream of the spill at ERM 10.5 was a source of sulfate because of the small effluent discharge relative to the Emory River flow [25].

The ash was also enriched in arsenic and strontium [19]. Although sediment methylmercury was poorly correlated with arsenic and strontium concentrations in porewater for all Emory River sediment samples, methylmercury was positively correlated with porewater arsenic and positively but not significantly correlated with porewater strontium in Emory sediments with $f_{Ash} \le 28\%$. It is possible that in these sediment samples, anaerobic conditions that led to methylmercury production may have coincided with reductive dissolution or desorption ofarsenic from arsenic-bearing minerals in sediments or ash [40].

In Emory River sediments with $f_{Ash} \leq 28\%$, methylmercury was also positively correlated with total Hg. To further explore this relationship, linear regressions of methylmercury content with % as Hg_{Ash} and % as Hg_{ERM10} were performed. However, the correlations were fairly poor $(r^2 = 0.18, p = 0.15; and r^2 = 0.16, p = 0.68, respectively)$ (Table 1, Figure S9). Correlations with % as Hg_{ERM12} and % as Hg_{Clinch} values were excluded from this analysis as the data were not normally distributed and did not satisfy the requirements for parametric statistical analysis. In the Clinch River, fewer geochemical data were collected than in the Emory (Table 1), and we could not evaluate the influence of porewater concentrations of sulfate, arsenic, strontium, and boron on mercury methylation. Nevertheless, our data indicated that sediment methylmercury was poorly correlated with AVS ($r^2 = 0.15$; p = 0.15) and TOC ($r^2 = 0.06$; p =0.43), and negatively correlated with total Hg ($r^2 = 0.30$; p = 0.04) (Table 1, Figure S10). The relationship between total Hg and methylmercury may reflect mixing of coal ash with upstream sediments, resulting in the dilution of total Hg concentrations in Clinch River sediments rather than a relationship between total Hg and microbial mercury methylation. This hypothesis was further supported by the positive correlation of sediment total Hg with f_{Clinch} ($r^2 = 0.84$; p =0.0001) (Table 1, Figure S10). As discussed previously, our % as MeHg values indicated that biogeochemical conditions (e.g., organic carbon source, bioavailability of nutrients and mercury, sediment microbial community composition, anthropogenic pollutants) were different in the Emory compared to the Clinch and may account for the inconsistencies observed in the correlations between methylmercury, AVS, and TOC in the two rivers.

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338 Environmental Significance

Total mercury and methylmercury concentrations in sections of the Emory River impacted by the ash spill were elevated compared to upstream sediments that remained unaffected by ash. The mechanism through which ash stimulated mercury methylation was not completely clear. However, our results indicated that TOC and AVS (a by-product of sulfate reduction) correlated with methylmercury production, and porewater data collected in the Emory River suggested that sulfate associated with the ash may have stimulated microbial methylation.

345 The Emory-Clinch River system is susceptible to methylmercury biomagnification in the 346 aquatic food web, as documented before the spill [26]. While the ash appeared to influence net 347 methylmercury production in river sediments, its subsequent influence on the food web remains 348 unclear. The methylation of mercury by sediment microbes is only an initial step towards, and 349 not a guarantee of, food web accumulation. The ash could also have changed conditions that 350 influenced trophic transfer of methylmercury. For example, coal ash is also enriched with 351 leachable selenium, an element that correlates negatively with mercury in high trophic level 352 species and possibly inhibits biomagnification of mercury [45]. The effects of ash contamination 353 on food web accumulation of methylmercury need to be studied further.

The influence of ash on net methylmercury production in sediments cannot be predicted by standard leaching protocols [9, 46, 47] such as the Toxicity Characteristic Leaching Procedure (TCLP), a procedure conducted with an acetic acid solution (pH 2.88 or 4.93) and a single solid-to-liquid ratio [48]. Our work highlights the inadequacies of this strategy to use acidleachable mercury concentration as proxies for risk, particularly when the key experimental variables for existing protocols are simply pH and solid-to-liquid ratio [9, 46, 47, 49]. Such leaching protocols do not consider environmental complexities such as organic matter, redox 361 processes, and microbial activity that are relevant for mercury solubility and bioavailability. We 362 suggest that methylation potential (rather than leaching of total mercury at pH < 5) should be the 363 metric for assessing the hazards of mercury associated with coal ash. A focus of future studies 364 could be the development of lab-based protocols, such as anaerobic incubation studies, to assess 365 methylation potential.

Much of the environmental assessments performed by the TVA and EPA near the spill site have focused on the river water column composition, leachable contaminants from sediments (at pH 5), and lethal toxicity of sediments to benthic organisms [24]. This study highlights the need to consider longer term transformations and bioavailability of contaminants in sediments. Monitoring of methylmercury production in sediments and accumulation in aquatic organisms along the Emory and Clinch Rivers should continue in the future, particularly as the ash that remained in the river after dredging will likely have a long retention time in the river sediments. The potential for enhanced methylmercury production and bioaccumulation in regions impacted by coal ash highlights the need to minimize the risk of ash spills to aquatic ecosystems and the need to adequately monitor structures used for their storage and disposal.

40 376

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382 Supporting Information Available

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3 4	383	The SI section contains additional descriptions of experimental methods, mercury isotope
5 6 7	384	ternary mixing calculations, geochemical data of samples, and analyses of data by linear
7 8 9 10 11	385	correlations. This information is available free of charge via the Internet at <u>http://pubs.acs.org/.</u>
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References

1. US EPA. Mercury and Air Toxics Standards - Cleaner Power Plants. <<u>http://www.epa.gov/airquality/powerplanttoxics/powerplants.html</u>> Accessed June 11, 2012.

2. Mergler, D.; Anderson, H. A.; Chan, L. H. M.; Mahaffey, K. R.; Murray, M.; Sakamoto, M.; Stern, A. H., Methylmercury exposure and health effects in humans: A worldwide concern. *Ambio* **2007**, *36*, (1), 3-11.

3. Carlson, C. L.; Adriano, D. C., Environmental impacts of coal combustion residues. *J. Environ. Qual.* **1993**, *22*, 227-247.

4. Hower, J. C.; Robl, T. L.; Anderson, C.; Thomas, G. A.; Sakulpitakphon, T.; Mardon, S. M.; Clark, W. L., Characteristics of coal combustion products (CCP's) from Kentucky power plants, with emphasis on mercury content. *Fuel* **2005**, *84*, 1338-1350.

5. American Coal Ash Association, Coal Combustion Product (CCP) Production & Use Survey Report.

http://acaa.affiniscape.com/associations/8003/files/2008_ACAA_CCP_Survey_Report_FINAL_100509.pdf

6. U.S. Energy Information Administration, Annual Energy Outlook 2011 with Projections to 2035; DOE/EIA-0383(2011); 2011.

7. Pavlish, J. H.; Sondreal, E. A.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A., Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **2003**, *82*, 89-165.

8. Al-Abed, S. R.; Jegadeesan, G.; Scheckel, K. G.; Tolaymat, T., Speciation, characterization, and mobility of As, Se, and Hg in flue gas desulphurization residues. *Environ. Sci. Technol.* **2008**, *42*, 1693-1698.

9. Hassett, D. J.; Pflughoeft-Hassett, D. F.; Laudal, D. L.; Pavlish, J. H., Mercury release from coal combustion by-products to the environment. In *Mercury in the environment, Proceedings of the Air and Waste Management Association, Minneapolis, MN, Sept. 15-17.*, Air and Waste Management Association: Pittsburg, PA, 1999; pp 485-493.

10. Noel, J. D.; Biswas, P.; Giammar, D. E., Evaluation of a sequential extraction process used for determining mercury binding mechanisms to coal combustion by-products. *J. Air Waste Manage. Assoc.* **2007,** *57*, 856-857.

11. Gustin, M. S.; Ladwig, K., An assessment of the significance of mercury release from coal fly ash. *J. Air Waste Manage. Assoc.* **2004**, *54*, 320-330.

12. Maroto-Valer, M. M.; Taulbee, D. N.; Hower, J. C., Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation. *Fuel* **2001**, *80*, 795-800.

13. Izquierdo, M.; Querol, X., Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* **2011**, *94*, (1), 54-66.

14. Benoit, J. M.; Gilmour, C. C.; Heyes, A.; Mason, R. P., and Miller, C.L., Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In *Biogeochemistry of Environmentally Important Trace Elements: ACS Syposium Series #835.*, Chai, Y., and Braids, O.C., Ed. American Chemical Society: Washington, D.C., 2003; pp 262-297.

15. Compeau, G.; Bartha, R., Sulfate reducing bacteria: principal methylators of Hg in anoxic estuarine sediments. *Appl. Environ. Microbiol.* **1985**, *50*, 498-502.

16. Gilmour, C. C.; Henry, E. A.; Mitchell, R., Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* **1992**, *26*, 2281-2287.

17. US EPA, EPA to oversee cleanup of TVA Kingston Fossil Fuel Plant release. http://yosemite.epa.gov/opa/admpress.nsf/a883dc3da7094f97852572a00065d7d8/7e39c49bea40 7817852575b30064e666!OpenDocument (November 2, 2011),

18. Chatterjee, R., Coal ash spills highlight ongoing risk to ecosystems. *Environ. Sci. Technol.* **2009**, *43*, (9), 3003-3004.

19. Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A.; Bergin, M.; J., K., Survey of the potential environmental and health impacts in the immediate aftermath of the coal ash spill in Kingston, Tennessee *Environ. Sci. Technol.* **2009**, *43:6326-6333*.

20. Tennessee Valley Authority. Kingston Ash Release Expanded Information. <u>http://www.tva.gov/kingston/moreinfo.htm</u> (February 4, 2011.),

21. Brooks, S.; Southworth, G. R., History of mercury use and environmental contamination at the Oak Ridge Y-12 plant. *Environ. Pollut.* **2011**, *159*, 219-228.

22. Tennessee Valley Authority, Corrective action plan for the TVA Kingston Fossil Plant ash release. <u>http://www.tva.gov/kingston/admin_record/pdf/G/G4.pdf</u> (November 2, 2011),

23. Tennessee Valley Authority, Reservoir Operations Study. http://www.tva.gov/environment/reports/ros_eis/ (November 2, 2011),

24. Tennessee Valley Authority Corrective action plan for the TVA Kingston fossil plant ash release. <u>http://www.tva.gov/kingston/admin_record/pdf/G/G4.pdf</u> (November 9, 2011),

25. USGS National Water Information System: Daily streamflow data for 03540500 Emory River at Oakdale, TN. <<u>http://waterdata.usgs.gov/tn/nwis/uv?site_no=03540500</u>> Accessed May 25, 2012.

26. Denton, G. M. Mercury levels in Tennessee fish. http://tn.gov/environment/wpc/publications/pdf/fishmercurylevels.pdf 27. Fitzgerald, W. F.; Gill, G. A., Subnanogram determination of mercury by two-stage gold amalgamation and gas-phase detection applied to atmospheric analysis. *Anal. Chem.* **1979**, *51*, (11), 1714-1720.

28. Bloom, N. S.; Crecelius, E. A., Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* **1983**, *14*, 49-59.

29. US EPA, EPA Method 7473: Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, 1998.

30. Bloom, N. S., Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* **1989**, *46*, 1131-1140.

31. Horvat, M.; Liang, L.; Bloom, N. S., Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples: Part II. Water. *Anal. Chim. Acta* **1993**, *282*, 153-168.

32. Allen, H. E.; G.;, F.; Deng, B., Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* **1993**, *12*, (8), 1441-1453.

33. Cline, J. D., Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* **1969**, *14*, (3), 454-458.

34. Bartov, G.; Deonarine, A.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H., Environmental impacts of the Tennessee Valley Authority Kingston coal ash spill. 1. Source apportionment using mercury stable isotopes. *Environ. Sci. Technol., in review* **2012**.

35. EPA, Code of Federal Regulations, Title 40: Protection of Environment, Part 131 - Water Quality Standards, Subpart D - Federally Promulgated Water Quality Standards, 131.36 Toxics for Criteria for those states not complying with Clean Water Act Section 303 (c)(2)(B). **1992**.

36. Scudder, B. C.; Chasar, L. C.; Wentz, D. A.; Bauch, N. J.; Brigham, M. E.; Moran, P. W.; Krabbenhoft, D. P., Mercury in fish, bed sediment, and water from streams across the United States, 1998-2005: US Geological Survey Scientific Investigations Report 2009-5109. **2009**.

37. DOE Remedial investigation/feasibility study for the Clinch River/Poplar Creek Operable Unit Volume 1.; Department of Energy: 1996.

38. Gilmour, C. C.; Henry, E. A., Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* **1991**, *71*, 131-169.

39. Korthals, E. T.; Winfrey, M. R., Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Appl. Environ. Microbiol.* **1987**, *53*, (10), 2397-2404.

40. Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A., The environmental impacts of the coal ash spill in Kingston, Tennessee: an eighteen-month survey. *Environ. Sci. Technol.* **2010**, *44*, (24), 9272-9278.

41. Benoit, J. M.; Gilmour, C. C.; Mason, R. P., Estimation of of mercury-sulfide speciation in sediment porewaters using octanol-water partitioning and implications for availability to methylating bacteria. *Environ. Toxicol. Chem.* **1999**, *18*, 2138-2141.

42. Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Heyes, A., Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **1999**, *33*, (6), 951-957.

43. Gilmour, C. C.; Riedel, G. S.; Ederington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. A.; Stordal, M. C., Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* **1998**, *40*, 327-345.

44. Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Riedel, G. S.; Riedel, G. F., Behavior of mercury in the Patuxent River estuary. *Biogeochemistry* **1998**, *40*, 249-265.

45. Bjerregaard, P.; Fjordside, S.; Hansen, M. G.; Petrova, M. B., Dietary selenium reduces retention of methyl mercury in freshwater fish. *Environ. Sci. Technol.* **2011**, *45*, 9793-9798.

46. Ziemkiewicz, P. F.; Knox, A. S., Prediction of coal ash leaching behavior in acid mine water: comparison of laboratory and field studies. In *Coal combustion byproducts and environmental issues*, Sajwan, K. S. T., I.; Punshon, T.; ALva, A.K., Ed. Springer: New York, NY, 2006; pp 50-58.

47. Hjelmar, O., Leachate from land disposal of coal fly ash. *Waste Manage. Res.* **1990**, *8*, 429-449.

48. US EPA, EPA Method 1311: Toxicity Characteristic Leaching Procedure, 1992. .

49. Thorneloe, S. A.; Kosson, D. S.; Sanchez, F.; Garrabrants, A. C.; Helms, G., Evaluating the fate of metals in air pollution control residues from coal-fired power plants. *Environ. Sci. Technol.* **2010**, *44*, (19), 7351-7356.



Figure 1. Map of the TVA Kingston Fossil Plant, the Emory-Clinch River system and sampling sites. ERM and CRM denote Emory River Mile and Clinch River Mile markers, respectively. Dashed lines indicate approximate extent of coal ash spill [20]. Numbers in parentheses indicate distance from location of ash release in miles (point of ash release indicated by blue star).



Figure 2. (a) Total mercury (Hg) and (b) methylmercury concentrations in sediment samples along the Emory and Clinch Rivers. Data points represent the mean concentration for each site during the sampling from August 2009 to August 2010 (n = 11 to 27, except for CRM1 with n = 3) and June 2011 (ERM10, n = 8). Error bars represent the mean standard error. All data are presented in Tables S1 through S9.



Figure 3. The proportion of total mercury present as methylmercury in sediments (% as MeHg). Data points represent the mean concentration for each site during the sampling period (n = 11 to 27, except for CRM1 with n = 3). All data are presented in Tables S1 through S9.



Figure 4. Ternary diagrams showing the mass fraction (in % units) of sediment derived from TVA coal ash (f_{Ash}), ERM12 (f_{ERM12}), ERM10 (f_{ERM10}) and upstream Clinch (f_{Clinch}) end-members [34]. Each data point represents a single sample (n = 1). Uncertainties for the mixing model calculations were estimated to be 14% for f_{ERM10} , f_{ERM12} and f_{Ash} , and 40% for f_{Clinch} [34]. Sample locations are shown in Figure 1.



Figure 5. Methylmercury concentration as a function of f_{Ash} (the mass fraction of TVA coal ash in each sediment sample in % units) in (a) Clinch River and (b) Emory River sediments. Methylmercury concentration was highest in Emory River sediments from ERM4 and ERM1 where $f_{Ash} \le 28\%$ and $f_{Ash} = 76\%$, and in Clinch River sediments from CRM4 and CRM0 where $39\% \le f_{Ash} \le 64\%$. Data points represent single sediment samples (n = 1).

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Table 1. Linear correlation parameters derived from log-log plots of MeHg with other parameters including sediment acid volatile sulfide (AVS), sediment total organic carbon (TOC), and total Hg (whole) sediment, and sediment porewater concentrations of sulfate, boron, strontium, and arsenic using SAS JMPTM. Except where noted, the sample data corresponding to April through November dates were utilized for the correlations.

Group	Dependent variable	Independent variable	R^2	р	n
Emory River	sediment MeHg	sediment AVS	0.57	0.001^{*}	20
sediment	sediment MeHg	porewater sulfate	0.68	0.003^{*}	10
	sediment MeHg	sediment TOC	0.61	0.001^{*}	20
	sediment MeHg	porewater B	0.36	0.02^{*}	14
	sediment MeHg	porewater Sr	0.08	0.44	10
	sediment MeHg	porewater As	0.05	0.46	14
	sediment MeHg	sediment total Hg	0.04	0.37	20
	porewater sulfate	porewater B	0.29	0.13	9
	porewater sulfate	porewater B	0.31 [†]	0.02^{*}	17
	porewater sulfate	porewater B	$0.52^{\text{\xef{4}}}$	0.045^{*}	8
Clinch River	sediment MeHg	sediment TOC	0.06	0.43	12
sediment	sediment MeHg	sediment AVS	0.15	0.15	15
	sediment MeHg	sediment total Hg	0.30	0.04^{*}	15
	sediment total Hg	f_{Clinch}	0.84	0.0001^{*}	20
Subset of Emory	sediment MeHg	porewater sulfate	0.61	0.02^{*}	8
River sediments	sediment MeHg	sediment AVS	0.34	0.02^{*}	16
containing $f_{Ash} \leq 28$	sediment MeHg	sediment TOC	0.72	0.0002^{*}	13
% coal ash	sediment MeHg	porewater Sr	0.42	0.17	6
	sediment MeHg	porewater As	0.51	0.07	7
	sediment MeHg	porewater B	0.06	0.57	8
	sediment MeHg	sediment total Hg	0.53	0.001^{*}	16
	sediment MeHg	% as Hg_{Ash}	0.18	0.15	13
	sediment MeHg	% as Hg _{ERM10}	0.16	0.68	12

* indicates that relationship was statistically significant (p < 0.05).

† indicates that data from all months in the sampling period were included.

¥ indicates that data from the winter months (December to March) of the sampling period were included.

