Survey of the Potential Environmental and Health Impacts in the Immediate Aftermath of the Coal Ash Spill in Kingston, Tennessee

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An investigation of the potential environmental and health impacts in the immediate aftermath of one of the largest coal ash spills in U.S. history at the Tennessee Valley Authority (TVA) Kingston coal-burning power plant has revealed three major findings. First, the surface release of coal ash with high levels of toxic elements (As = 75 mg/kg; Hg = 150 μg/kg) and radioactivity (^{226}Ra + ^{228}Ra = 8 pCi/g) to the environment has the potential to generate resuspended ambient fine particles (<10 μm) containing these toxics into the atmosphere that may pose a health risk to local communities. Second, leaching of contaminants from the coal ash caused contamination of surface waters in areas of restricted water exchange, but only trace levels were found in the downstream Emory and Clinch Rivers due to river dilution. Third, the accumulation of Hg- and As-rich coal ash in river sediments has the potential to have an impact on the ecological system in the downstream rivers by fish poisoning and methylmercury formation in anaerobic river sediments.

Introduction

On Monday, December 22, 2008, the containment structure surrounding the storage of coal ash at the Kingston coal-burning power plant of the Tennessee Valley Authority (TVA) collapsed, which resulted in massive release of coal combustion products (CCP) ash to the environment near Harriman, Tennessee. The CCP material, consisting of fly ash and bottom ash, spilled into tributaries of the Emory River and directly

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into the Emory River (Figure 1), which joins the Clinch River that flows to the Tennessee River, a major drinking water source for downstream users. The Kingston coal ash spill released over 4.1 million cubic meters of ash, which is one of the largest spills in U.S. history. Some previous coal ash spills in the United States include the 2000 Martin County spill in Kentucky, which released over 1.1 million cubic meters of coal slurry into abandoned mines and nearby creeks (*1*), and the 1972 Buffalo Creek incident in West Virginia, which released almost a half million cubic meters of coal mining residue slurry into a nearby town (*2*). Numerous studies have shown that coal ash contains high levels of toxic metals that can harm the environment (*3−14*) and some of these elements are soluble in water and easily leached in aquatic systems (*13−16*).

This paper aims to provide an initial assessment of the potential environmental impacts and health risks associated with the Kingston TVA coal ash spill. In particular, the paper examines the reactivity of trace metals known to be enriched in CCP ash (*9, 13*) in surface water and the potential ecological effects associated with the accumulation of CCP ash in river sediments. Furthermore, the paper emphasizes the relatively high content of radionuclides in CCP ash and the potential health impact of their resuspension in the atmosphere. While most studies have investigated the potential for radon emanation from cement and fly ash used as building materials (*17−20*), here we examine possible health risks associated with elevated radium activity in CCP ash. The study includes measurements of trace metals in solid ash, sediments from the river, and water samples that were collected in the vicinity of the coal ash spill. Given the limited data collection since the accident, this paper provides only an initial evaluation, and does not provide a comprehensive assessment of the overall environmental impacts of the TVA coal ash spill.

Analytical Methods and Materials

Coal ash, sediments from the rivers, and water samples from tributaries, the Emory and Clinch Rivers, and springs near the spill area in Kingston and Harriman, TN (Table S1; Figure 1) were collected in three fieldtrips on January 9−10, February 6−7, and March 27−28, 2009. The surface water samples were collected near the river shoreline from sites located upstream and downstream (at different distances) of the spill. Each location was determined by availability of public access and/or allowance by property owners. Water sampling strictly followed USGS protocol (*21*); trace metal and cation samples were filtered in the field (0.45 μm syringe filters) into new and acid-washed polyethylene bottles containing high-purity HNO_3. Trace metals in water were measured by inductively coupled plasma mass spectrometry (ICP-MS); mercury in sediments and coal ash was measured by thermal decomposition, amalgamation, atomic absorption spectroscopy (Milestone DMA-80) (*22*); and radium isotopes were measured by γ-spectrometry (see supporting text S1).

Results and Discussion

Coal Ash and Sediments. A comparison of the chemical composition of the TVA coal ash and local soil in Kingston, Tennessee (Table 1) shows marginal enrichments of major elements of calcium (by a factor of 2), magnesium (1.3), and aluminum (1.5), and large enrichments of trace elements such as strontium (30), arsenic (21), barium (5), nickel (5), lithium (5), vanadium (4), copper (3), and chromium (2). The high arsenic concentration in the TVA coal ash (mean = 75 mg/kg) is consistent with previously reported As in ash
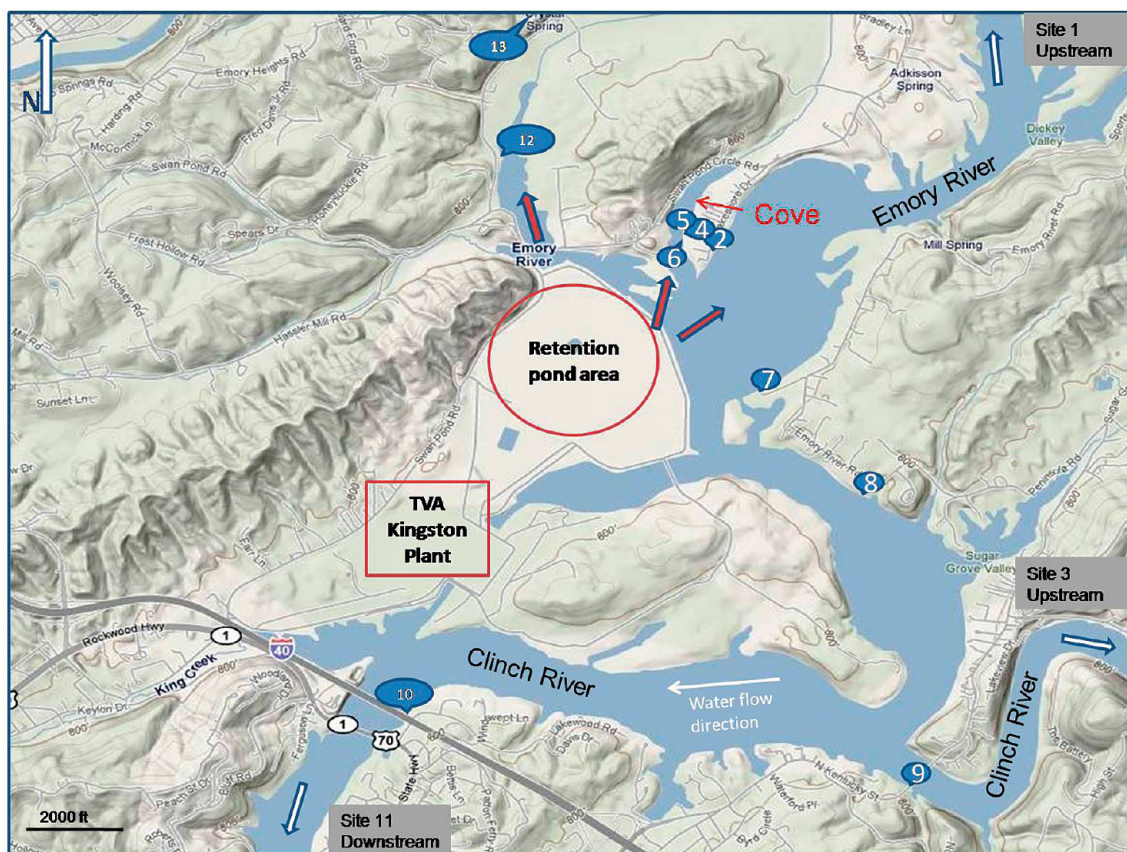
FIGURE 1. Map of the sampling sites of the TVA coal ash spill in Kingston, Tennessee. Site descriptions are reported in Supporting Information (Google maps provided the base map).

TABLE 1. Average Metals Concentrations (mg/kg) in TVA Coal Ash and Background Soil in Kingston, TN[a]

material	n	Al	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Li	Mg	Mn	Mo	Ni	Se	Sr	V	Zn
coal ash																					
average (mg/kg)	12	14109	74.6	354.2	3.1	0.03	3325	24.8	13.5	46.2	13333	19.0	24.6	1616	102	2.1	23.0	0.2	201.0	76.7	40.4
STD		7264	20.4	248.8	1.8	0.08	1142	7.6	6.0	16.6	2807	6.6	6.8	1531	54	2.0	8.0	0.6	39.3	30.6	12.5
background soil																					
average (mg/kg)	12	9367	3.5	73.8	0.3	0.01	1418	11.9	7.3	15.9	15200	16.5	5.3	1211	1056	0.2	4.4	0.9	6.8	20.9	29.7
STD		3485	2.3	51.9	0.3	0.21	933	5.3	7.8	35.2	6729	8.4	1.9	5580	1007	0.4	4.7	1.8	4.3	4.4	11.7
ash/soil ratio		1.5	21.4	4.8	9.4	3.0	2.3	2.1	1.9	2.9	0.9	1.1	4.6	1.3	0.1	13.4	5.2	0.2	29.8	3.7	1.4

[a] Samples were collected and analyzed by the Tennessee Department of Environment and Conservation and the Tennessee Department of Health.

residue of both hard coal (anthracites, bituminous, and subbituminous A and B; As = 50 mg/kg) and brown coal (lignites and subbituminous C; As = 49 mg/kg) (7). In addition, the mercury level of the TVA coal ash (an average of $151.3 \pm 15.9 \mu$g/kg; Table 2) is higher than background soil in Tennessee (45 μg/kg) (23). These concentrations are consistent with the range of values reported in fly ash (100−1500 μg/kg) (24). Likewise, the ^{226}Ra (a mean of 4.4 ± 1.0 pCi/g) and ^{228}Ra (3.1 ± 0.4 pCi/g) activities of the coal ash are higher than those in local soil in Kingston (1.1 ± 0.2 and 1.4 ± 0.4 pCi/g, respectively; Table 3). The Ra activity of the TVA coal ash is similar to the levels reported previously for fly and bottom ash from a Kentucky utility (Table 3) with a consistent activity ^{228}Ra/^{226}Ra ratio of ∼0.7 (25). The potential impact of Ra on the environment and human health is an important consideration in remediation of the spill and is discussed below.

The Hg concentration increases from 16−54 μg/kg in upstream sediments, collected at the shoreline of the Emory and Clinch Rivers, to a level of 53 μg/kg directly across from the spill site (Site 8; Figure 1), and up to 92−130 μg/kg in sediments from the downstream Clinch River at Sites 9 and 10 (Tables 2 and S1). The Hg concentrations of the upstream sediments are consistent with previously reported Hg data for the overall Tennessee River (Table 2) (23). A historical massive release of Hg from the Oak Ridge Y-12 plant into East Fork Poplar Creek has resulted in accumulation of Hg in the sediments from the downstream Clinch River (26, 27), which could have provided a Hg legacy source for the Clinch River sediments. Our direct sampling of two sites in the upstream Clinch River (relative to the coal ash spill; Table 2) and downstream of the Y-12 source in Oak Ridge resulted, however, in low Hg contents of the river sediments (16 ± 5 upstream and $54 \pm 11 \mu$g/kg downstream of Poplar Creek), which are similar to background values we report for the Emory River (Table 2). In contrast, sediments from the downstream Clinch River (sites 9 and 10) have higher Hg content (>100 μg/kg), which suggests a significant contribution of Hg from the coal ash to the river sediments. We therefore conclude

TABLE 2. Hg Results (μg/kg) in Coal Ash and River Sediments Associated with the Spill Area in Kingston, TN[a]

sample ID	site no. in Figure 1	description	total Hg, μg/kg average $\pm$ SD ($n = 3$)	
			Feb 7	March 28
		upstream		
LR2	site 2	upstream Emory River	43 $\pm$ 0.5	10 ($n = 1$)
LR11	upstream of site 3	upstream Clinch River (just downstream of Oak Ridge)	NA	16 $\pm$ 5
LR10	site 3	upstream Clinch River	NA	54 $\pm$ 11
LR1	site 7	close to the spill on Emory River	29.7 $\pm$ 3	22 $\pm$ 0.2
		coal ash		
RC8S1	site 6	spilled ash pile	139 $\pm$ 5	NA
RC8S2	site 6	spilled ash pile	145 $\pm$ 12	NA
		downstream		
RC3	site 8	across from spill on Emory River	53 $\pm$ 3	NA
LR9	site 9	convergence of Clinch and Emory Rivers	130 $\pm$ 5	104 $\pm$ 12
LR8	site 10	downstream Clinch River (I-40)	115 $\pm$ 9	92 $\pm$ 32
LR6	site 11	downstream Clinch River	NA	81 $\pm$ 38
LR7	downstream of site 11	downstream Clinch River (before convergence with TN river)	NA	51 $\pm$ 10
		Background soil, Tennessee		
		Lower Clinch River ($n = 9$)	45 $\pm$ 12	
		Upper Tennessee hydrological unit ($n = 73$)	47 $\pm$ 27	
		Roane County	56 $\pm$ 23	

[a] Background data of Hg in Tennessee soil from ref 23.

TABLE 3. Radioactivity Data (pCi/g Unit) and Activity Ratios of Coal Ash and Background Data from the Spill Area in Kingston, TN[a]

sample/site	material	^{226}Ra	^{228}Ra	210-Pb	total Ra	^{228}Ra/^{226}Ra
the cove						
RC8S1	coal ash	4.9	3.2	3.57	8.1	0.65
RC5S	coal ash	2.6	2.1	3.54	4.6	0.79
RC8S2	coal ash	4.9	3.1	5.01	7.9	0.63
TDEC data						
average for coal ash ($n = 12$)	coal ash	4.4 $\pm$ 1.0	3.1 $\pm$ 0.4		7.5 $\pm$ 1.4	0.70 $\pm$ 0.07
average background soil ($n = 15$)	soil	1.1 $\pm$ 0.2	1.4 $\pm$ 0.5		2.6 $\pm$ 0.7	1.21 $\pm$ 0.28
Kentucky coal ash						
fly ash (average, $n = 17$)	fly ash	4.4 $\pm$ 0.6	3.4 $\pm$ 0.6	6.5 $\pm$ 1.9	7.8 $\pm$ 0.9	0.77 $\pm$ 0.15
bottom ash (average, $n = 6$)	bottom ash	4.0 $\pm$ 1.2	2.9 $\pm$ 0.9	2.2 $\pm$ 2.9	7.3 $\pm$ 1.3	0.71 $\pm$ 0.21

[a] TDEC data are from the Tennessee Department of Environment and Conservation and the Tennessee Department of Health. Kentucky coal ash data are from ref 25.

that ash transport and deposition in the Clinch River has increased the Hg content in the river sediments.

Water Contamination. Results show that the tributary that was dammed by the coal ash spill and turned into a standing pond ("the Cove" in the area of Swan Pond Circle Road; Figure 1) has relatively high levels of leachable coal ash contaminants (LCAC), including arsenic, calcium, magnesium, aluminum, strontium, manganese, lithium, and boron (Table 4; Figure 2). Some of these elements are highly enriched in coal ash (6, 8) (Table 1), and are known to be highly soluble in aquatic systems (8). Among the LCACs, arsenic stands out with concentrations of up to 86 μg/L in the Cove area. Groundwater data from the other tributary (Figure 1) show negligible LCAC levels, thus indicating that the shallow groundwater is not contaminated. In this hydrological setting, noncontaminated groundwater discharges into the dammed tributary and causes leaching of LCAC from the coal ash. Under restricted water exchange, the formation of standing water in the Cove resulted in contaminated surface water. In contrast, surface waters from the Emory River and Emory–Clinch River downstream from the breached dam show only slight LCAC levels, and all river inorganic dissolved constituents concentrations are below the EPA Maximum Contaminant Levels (MCL) and EPA

Criterion Continuous Concentration (CCC) for aquatic life (Table 4) (28, 29).

The upstream Clinch River has a distinct chemical composition (higher Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, and SO_4^{2-}) relative to the upstream Emory (Table 4), and thus the major inorganic constituents show mixing relationships between these two water sources (Line M1 in Figure 2) downstream from the confluence of the Emory and Clinch rivers (Figure 1). The concentrations of arsenic, strontium, and boron in the downstream river samples deviate toward higher values, however, relative to these river mixing relationships (Figure 2). These geochemical shifts reflect a small but traceable indication of leaching of contaminants from coal ash that was spilled into the river and further mixing with the uncontaminated river water (Line M2 in Figure 2). The data show that the river flow is effective in reducing the LCAC's contents by an order of magnitude relative to directly contaminated water measured in the Cove.

The water samples were collected near the shoreline of the river, which may be an underestimate of the concentration of dissolved elements throughout the river vertical profile. The spatial distribution of contaminants (dissolved and suspended particulate fractions) in a river water column depends on a number of factors including particulate size,

TABLE 4. Chemical Composition of Major (mg/L) and Trace (μg/L) Elements of Water Samples in the Area of the TVA Coal Ash Spill in Kingston, TN[a]

sample ID	location	site	Ca	Mg	Na	Cl	SO$_4$	Li	B	Al	Mn	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Cr	U
								upstream river													
TN3	upstream Emory River	1	5.8	1.3	1.6	2.7	9.9	0.5	5.9	50	23	0.1	1.1	0.1	5.7	0.1	0.4	1.4	26.4	0.2	–
TN3U	upstream Emory River	1	5.5	1.2					7.2	131	15	0.1	–	0.4	8.0	–	0.3	1.4	23.8	–	–
RC9	upstream Emory River	1	7.4	1.6	2.6	3.6	12.7	0.4	5.8	19	72	0.4	1.1	0.2	4.8	0.1	0.1	1.0	31.3	0.2	0.1
RC10	upstream Clinch River	3	36.6	11.2	9.5	6.8	30.5	3.0	13.4	5	5	0.2	1.0	0.5	9.2	0.4	0.4	1.0	134.5	0.4	0.4
								The Cove													
TN1	The Cove	4	38.9	7.0	2.8	16.8	98.1	13.2	431.9	–	847	2.1	4.0	1.5	16.5	69.6	2.4	15.6	578.4	1.9	0.1
TN1U	The Cove	4	42.5	8.0					425.9	344	974	3.1	–	5.0	42.4	95.2	0.4	17.1	632.6	–	–
RC5	The Cove	4	93.2	12.7	3.2	12.6	260.3	19.6	470.8	22	3014	7.0	9.0	1.6	47.2	85.6	3.8	23.8	1244.5	1.9	1.1
TN9	The Cove	5	13.0	3.1	1.7	5.0	20.4	3.1	84.9	43	296	0.3	4.3	0.8	12.2	9.3	0.5	5.0	108.3	6.6	0.0
TN9U	The Cove	5	14.9	4.5					112.9	197	332	1.2	–	3.5	24.9	12.6	0.0	6.2	120.1	–	0.0
RC8	The Cove	6	35.2	6.1	3.0	5.5	76.7	7.4	229.6	40	556	1.9	1.7	2.8	36.6	20.7	1.8	6.3	455.9	0.5	0.5
								downstream river													
TN2	riverside of Lakeshore Dr.	2	6.4	1.4	1.8	3.1	9.8	0.5	8.7	58	34	0.1	1.3	1.1	11.3	0.6	0.2	2.0	31.0	0.2	–
TN2U	riverside of Lakeshore Dr.	2	6.5	4.8					23.4	154	28	0.4	–	2.1	14.4	0.9	0.1	2.0	28.8	–	–
RC6	riverside of Lakeshore Dr.	2	9.1	2.1	2.4	3.7	13.1	0.7	38.1	40	60	0.3	0.9	0.5	5.1	3.1	0.6	1.3	59.3	0.3	0.2
TN5	Emory River	7	7.3	2.0	1.6	2.7	9.4	0.4	7.9	51	15	2.6	1.0	0.4	1.5	0.3	0.4	1.2	27.6	0.4	–
TN5U	Emory River	7	7.3	2.1					9.7	466	16	0.4	–	0.5	4.3	0.3	0.1	1.9	26.5	–	–
RC2	Emory River	7	7.3	1.9	2.5	3.5	11.0	0.4	6.6	23	42	0.3	1.1	34.0	8.0	0.1	0.1	1.0	28.1	0.3	0.1
RC3	Emory River	8	16.5	4.8	4.8			1.2	10.1	34	22	1.2	1.0	0.8	5.1	0.3	0.2	1.1	61.6	0.4	0.2
TN6	convergence of Emory and Clinch	9	37.3	11.9	8.6	5.9	31.9	2.5	19.3	56	5	0.0	1.1	0.6	1.8	0.6	0.6	1.1	137.5	0.4	0.4
TN6U	convergence of Emory and Clinch	9	37.9	12.1					14.2	56	17	0.2	–	0.9	3.2	0.4	0.3	1.2	144.2	–	0.1
RC1	convergence of Emory and Clinch	9	37.3	11.5	8.6	6.9	29.7	3.0	14.1	19	5	0.2	1.2	1.1	6.5	0.4	0.2	1.0	130.4	0.4	0.4
TN7	Clinch River at I 40 Bridge	10	23.4	7.3	5.4	4.6	21.7	1.6	14.8	34	13	0.0	1.2	0.6	2.1	0.7	0.5	1.1	89.0	0.3	0.2
TN7U	Clinch River at I 40 Bridge	10	24.7	7.5					13.7	149	20	0.1	–	0.9	2.1	1.2	0.2	1.5	94.1	–	–
RC4	Clinch River at I 40 Bridge	10	35.1	10.3	8.7	7.5	27.0	2.8	15.4	20	18	0.2	1.2	0.9	5.5	0.7	0.4	1.0	121.3	0.5	0.4
TN12	city of Kingston Gravel pit park	11	24.9	7.8	5.5	4.7	22.6	1.8	20.2	32	17	0.0	1.0	1.1	3.2	0.8	0.5	1.2	92.4	0.4	0.3
TN12U	city of Kingston Gravel pit park	11	25.6	7.9					15.3	176	20	0.2	–	1.0	6.2	1.3	0.5	1.5	97.8	–	0.1
RC11	city of Kingston Gravel pit park	11	29.8	8.9	7.7	6.2	25.7	2.9	14.7	12	17	0.2	1.0	0.9	6.5	0.5	0.5	1.0	110.6	0.4	0.4
								groundwater													
TN4	spring water flow to the Cove	12	34.1	8.2	2.6	5.8	18.1	0.1	12.3	15	109	2.1	0.9	0.1	3.9	0.2	0.6	0.8	61.3	0.4	0.2
TN4U	spring water flow to the Cove	12	34.5	8.5					14.6	38	108	0.7	–	0.1	4.7	0.1	0.9	0.8	59.0	–	–
TN8	spring water flow to the Cove	12	14.7	7.6	0.6	1.7	3.1	0.3	7.1	5	0.1	0.1	0.3	0.2	5.3	0.1	0.2	0.7	15.5	0.3	–
TN8U	spring water flow to the Cove	13	15.4	8.0					7.4	18	0.3	0.0	–	0.1	5.3	–	0.4	0.7	15.6	–	–
RC7	spring water flow to the Cove	13	19.9	10.5	0.6	1.3	1.4	0.2	2.6	4	0.4	0.1	0.3	0.1	4.8	0.1	0.0	0.7	15.9	0.4	0.2
								EPA regulations													
EPA MCL	Maximum Contaminant Level for drinking water													1300		10	50			100	30
EPA CCC	Criterion Continuous Concentration for aquatic life									87			52	9	120	150	5			(III):74,(VI):11	

[a] "U" refers to unfiltered samples. EPA MCL is the Maximum Contaminant Level for drinking water and EPA CCC is the Criterion Continuous Concentration, which is an estimate of the highest concentration of a material in surface fresh water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (28, 29). For Site location see Figure 1 and Supporting Information.
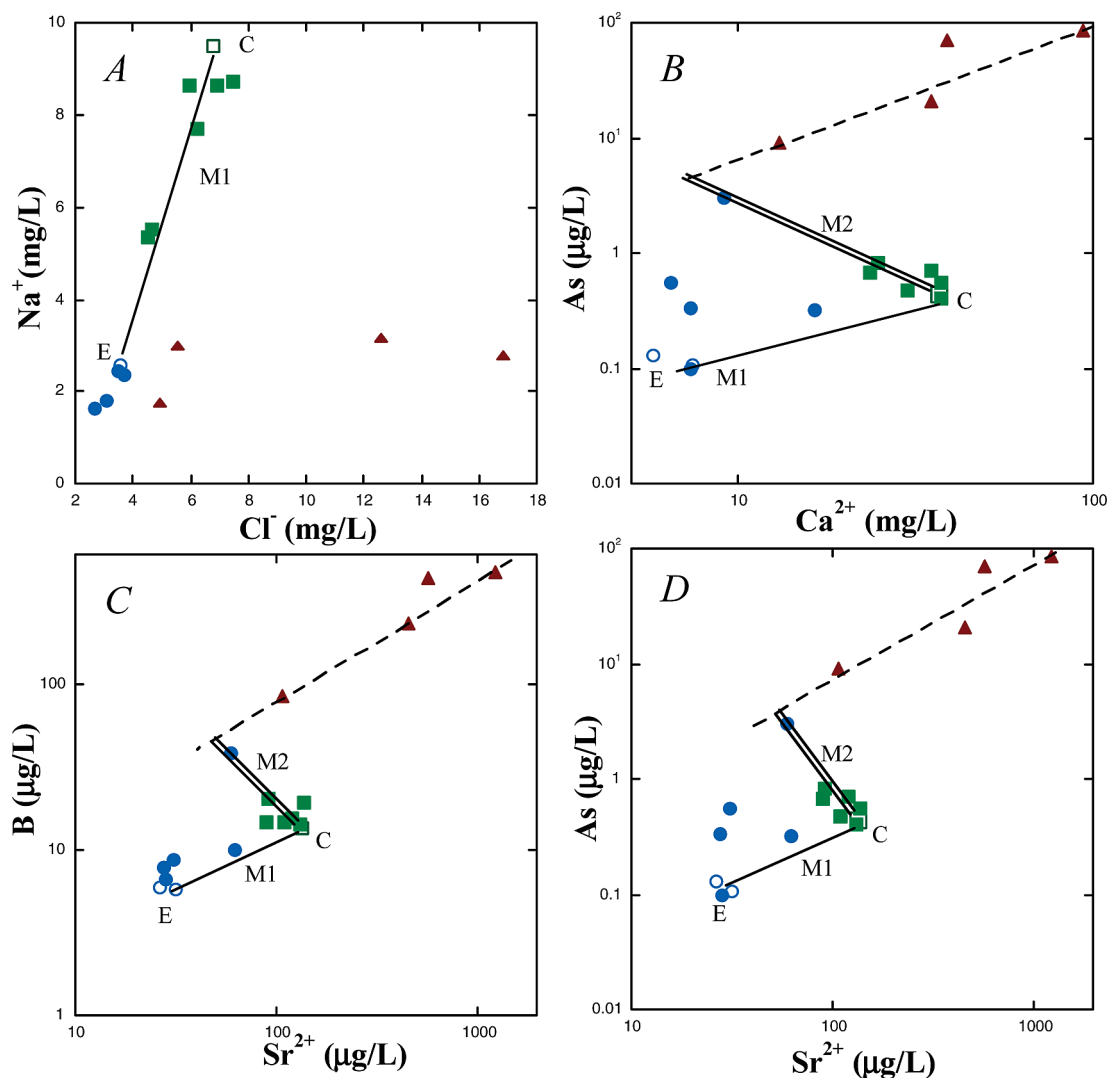
FIGURE 2. Variations of Na$^+$ and Cl$^-$ (A), Ca^{2+} and As (B), Sr^{2+} and B (D), and Sr^{2+} and As (D) in water samples from the Cove (triangles), Emory River upstream (open circles) and downstream (closed circles), and Emory−Clinch upstream (open squares) and downstream (closed squares). Mixing of Emory and Clinch Rivers (Line M1) is identified by the major ion composition (A). Elements that are enriched in coal ash, as reflected by the high concentrations in the Cove area (dashed line), show higher concentrations in the downstream Emory−Clinch river samples relative to the expected Emory−Clinch river mixing composition (Line M1). Line M2 reflects possible mixing of contaminants derived from coal ash leaching near the spill area (dashed line) and the uncontaminated Clinch River composition (Line M1).

turbulent flow conditions, seasonal flow changes, and channel morphology (*30*). The dissolved phase, which was measured in this study, is typically homogeneously distributed in a river, but can vary with the proximity to a point source of pollution (*30*). Assuming that metal mobilization in the river derives from both suspended ash and bottom sediments, the distribution of dissolved constituents in the water column would depend on numerous factors such as differential river velocity, rate of mobilization, and water depth (*31*). Further investigation is therefore required to determine the vertical distribution of metals in the river water, and whether sampling of the upper river section represents the most diluted segment of the river flow.

Potential Environmental Impacts. While the downstream river water shows only trace levels of LCACs (at the surface), the downstream river sediments show high Hg concentrations similar to the coal ash levels (115−130 μg/kg; Table 2). The ecological effects of Hg in the coal ash and sediments depend on the chemical lability of Hg in the solids and the potential for mercury methylation in the impacted area. While previous studies have demonstrated that Hg in CCP ash is not readily soluble through acid-leaching protocols (*32*), Hg has a high

affinity for natural organic matter (*33, 34*), which can promote desorption if the Hg is associated with weaker binding sites on metal-oxide minerals in the ash material (*35*). Furthermore, the transformation of Hg to methylmercury by anaerobic bacteria in river sediments is a concern because of bioaccumulation of methylmercury in food webs. Previous studies have shown that sulfate addition can promote methylation in freshwater ecosystems by stimulating sulfate-reducing bacteria (*36*), the primary organisms responsible for producing methylmercury in the environment (*37*). In coal-ash-containing waters, a 10- to 20-fold increase in SO$_4^{2-}$ concentrations was observed in the Cove area relative to unaffected upstream sites (Table 4). Therefore, the methylation potential of mercury from this material could be high because the coal ash also provides an essential nutrient (SO$_4^{2-}$) that encourages microbial methylation. In addition, accumulation of arsenic-rich fly ash in bottom sediment in an aquatic system could cause fish poisoning via both food chains and decrease of benthic fauna that is a vital food source (*7, 38*).

Potential Health Impacts. Of particular concern to human health is the wind-blown resuspension of fly ash into the

atmosphere. It is well-known that wind-blown dust can travel long distances, as exemplified by Asian dust storms that result in transport to locations as far away as the U.S (39). It is possible that coal ash exposed to the atmosphere can be resuspended and transported to populated areas where human exposure may occur. Fly ash-airborne particles with diameters less than 10 μm (PM10) are regarded as respirable and may affect the human lung and bronchus (40–42). The process of particulate resuspension will depend on a variety of factors, including the fly ash particulate size and related chemical and physical properties, wind speed and atmospheric turbulence, and likely the relative humidity and surface moisture (43, 44). The particles that are of most importance for human health are in the fine particulate (PM$_{2.5}$) mode, which readily deposit deep in the lung (45). Past work has shown that CCP ash has particulate sizes ranging from less than 1 μm to 100s of micrometers in size (46, 47). In addition, there is a compositional relationship as a function of fly ash particle size (46). Several studies have also measured ambient fine particulate matter associated with elevated concentrations of toxic metals in the vicinity of coal-fired power plants (42, 48–50). In some cases, fly ash-airborne particles were also found in remote areas (up to 30 km from power stations) (42, 51). Overall, past work indicates that coal ash contains inhalable particulate matter, and that fly ash emitted from the burning of coal is readily transported in the atmosphere.

The high concentrations of trace metals (Tables 1 and 2) and radioactivity (Table 3) reported in this study for the bulk TVA coal ash are expected to magnify, as fine fractions of fly ash (which may be resuspended and deposited in the human respiratory system) are typically 4–10 times enriched in metals relative to the bulk ash and the coarse size fraction (7, 46). The toxic metal content in coal ash, the sizes of fly ash particulates, and the ionizing radiation (IR) exposure (both incorporated and external) may act synergistically or, less frequent, antagonistically, affecting human health directly (predominantly through inhalation of contaminated air) and indirectly through the food chains (consuming contaminated agricultural products) (14). Coal ash was recognized as a Group I human carcinogen (based on occupational exposure studies) associated with increased risks of skin, lung, and bladder cancers (52). Arsenic and radium exposures in humans are associated with increased risks of skin, lung, liver, leukemia, breast, bladder, and bone cancers (53) for exposure predominantly due to chronic ingestion or chronic inhalation, with the dose–response curve dependent on location, sources, and population susceptibility and/or tolerance.

Health impacts of CCP ash have been predominantly studied on animal models and human cell lines, with few short-term epidemiological follow-ups. CCP ash particulates affect lung epithelial and red blood cells in animal studies and human in vitro models, causing inflammation, changing the sensitivity of epithelia, altering immunological mechanisms and lymphocyte blastogenesis, and increasing the risk of cardiopulmonary disease (e.g., pulmonary vasculitis/hypertention) (54–57). Individuals with pre-existing chronic obstructive pulmonary disease, lung infection, or asthma are more susceptible to the coal ash affliction (58). Several epidemiological studies have proved the significant health hazards (such as enhanced risk for adverse cardiovascular events) of fine-particulate air pollution for individuals with type II diabetes mellitus and people with genetic and/or disease-related susceptibility to vascular dysfunction, who are a large part of the population (59).

Radium-226 and ^{228}Ra, which are the main sources of low-dose IR exposure in coal ash, can remain in the human lung for several months after their inhalation, gradually entering the blood circulation and depositing in bones and teeth with this portion remaining for the lifetime of the individual. When inhaled, the radionuclides can affect the respiratory system even without the presence of the other coal ash components. Thus, the airborne particles containing radioactive elements inhaled by cleanup workers of the nuclear accident at the Chernobyl nuclear power plant caused bronchial mucosa lesions, in some cases preneoplastic, with an increased susceptibility to the invasion of microorganisms in bronchial mucosa (60, 61). Consequently, the combined radioactivity of coal ash at the TVA spill, together with other enriched trace metals such as Ni, Pb, and As, may increase the overall health impact in exposed populations, depending on duration of exposure, and particularly for susceptible groups of the population. It is important to underscore the fact that at this time it is not possible to estimate the health impacts of CCP ash resuspended particulates due to a lack of information on the rate at which they are entrained into the atmosphere, as well as their chemical, physical, and synergistic properties linked to morbidity and mortality. Clearly future studies are needed linking ambient element and radionuclide concentrations with ground level CCP ash characteristics, ambient meteorological characteristics, and human population exposure.

This study has provided an initial assessment of the environmental impacts and potential health effects associated with the TVA coal ash spill in Kingston, Tennessee. The study shows that the high metals contents of coal ash and their high solubility resulted in contamination (e.g., As) of surface water associated with the coal ash spill in areas of restricted water exchange. In the downstream Emory and Clinch Rivers the leaching of trace metals is significantly diluted by the river flows. While the levels of contaminants in the downstream Emory and Clinch Rivers are below the MCL levels, high concentrations of Hg found in the river sediments pose a serious long-term threat for the ecological system of these rivers. This study also highlights the high probability of atmospheric resuspension of fine fly ash particulates, which are enriched in toxic metals and radioactivity, and could have a severe health impact on local communities and workers. Based on these initial results, this study provides a framework for future and long-term monitoring of the TVA coal ash spill and remediation efforts. Future studies should focus on evaluating the ecological ramifications, such as methylmercury formation in the sediments in the downstream Emory and Clinch Rivers, and the composition of particulate matter in the air in the vicinity of the spill area. Finally, future prognoses of the health impacts of residents exposed to coal ash requires long-term follow-ups of various population groups, including children and adolescents, pregnant women, persons exposed *in utero*, and individuals with pre-existing broncho-pulmonary diseases and diabetes mellitus. All these factors must be included in remediation efforts for the TVA Kingston coal ash spill.

Acknowledgments

Supporting Information Available

Supplementary description of the analytical techniques and sample location. This material is available free of charge via the Internet at http://pubs.acs.org.

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