Water quality monitoring of the Emory and Clinch Rivers: the impact of the TVA coal ash spill, Kingston, TN

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Introduction:

On Monday, December 22, 2008, the containment structure surrounding the storage of coal ash at the Kingston coal-burning power plant of Tennessee Valley Authority (TVA) collapsed, which resulted in massive release of coal combustion products (CCP) 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 into the Emory River, which joins the Clinch River and 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. Numerous studies have shown that coal ash contains high levels of toxic metals that can harm the environment and some of these elements are soluble in water and easily leached in aquatic systems.

This paper aims to provide an assessment of the potential environmental impacts and remediation activities associated with the Kingston TVA coal ash spill by monitoring the water quality of the Emory and Clinch rivers and testing the boron and strontium isotopes as potential proxies for identification of coal ash contamination. The study includes measurements of trace metals and mercury in solid ash, sediments from the river, and water samples that were collected in the vicinity of the coal ash spill, in addition to leaching experiments of the TVA spilled ash.

Figure1. Location of Kingston, TN USA

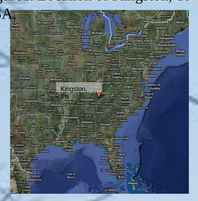


Figure 2. Map of TVA Kingston plant and River Mile Markers (base map from Google maps).

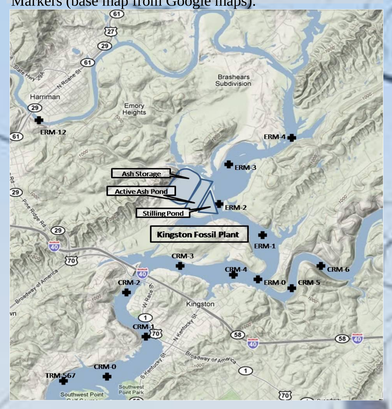
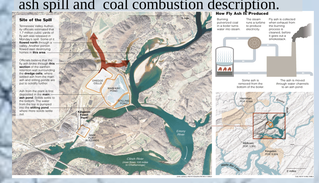
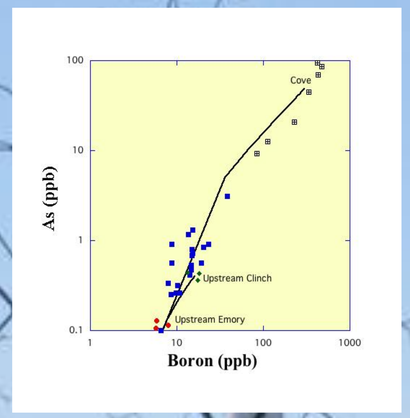
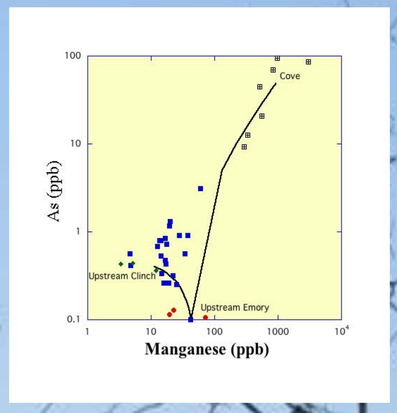


Figure 3. Map of TVA Kingston plant coal ash spill and coal combustion description.







Figures 6 (left) and 7 (right). The mixing relationships of As and B and As and Mn in the Emory (red circles) and Clinch (green diamonds) rivers and the cove (black cross-square). The blue squares show the mixing of the leachable elements from the spilled ash into the downstream river.

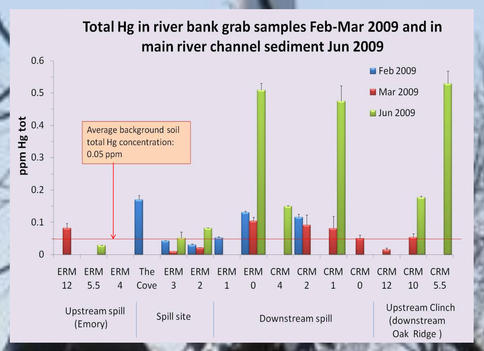


Figure 8. Total Hg concentrations in sediments at spill site are high relative to background levels (0.05 ppm, [Ruhl et al. 2009]). Total Hg concentrations range from 0.001 ppm to 0.53 ppm. Error bars represent one standard deviation from mean (n=2-3). Higher concentrations (0.5 ppm) along the Clinch River may be due to contamination from upstream legacy sources.

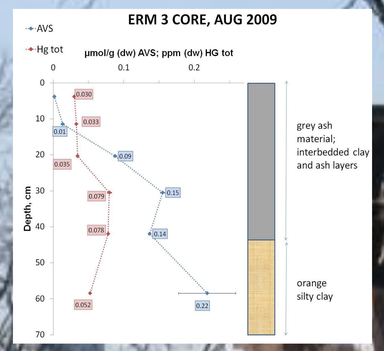


Figure 9. Sediment core total Hg concentrations range from 0.03 to 0.08 ppm; acid volatile sulfide (AVS) concentrations range from approximately 0 to 0.22 µmol/g (dw). Error bars represent one standard deviation from the mean (n=2-3). Error bars not seen are smaller than data markers.

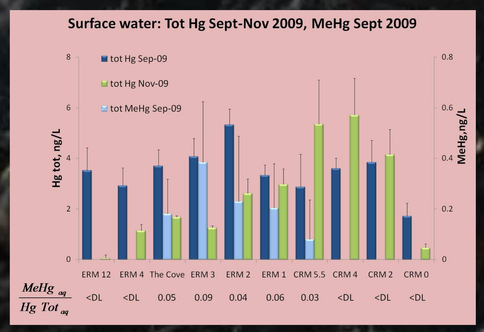


Figure 10. Total Hg concentrations range from 0.1 to 5.7 ng/L while MeHg concentrations range from <0.08 to 0.38 ng/L. Total Hg and MeHg concentrations are relatively low (Tennessee surface water limit 0.77 µg/L total Hg). MeHg/Tot Hg concentration ratios range from <DL (MeHg non-quantifiable, detection limit 0.08 ng/L) to 0.09. Error bars represent one standard deviation from mean (n=3)

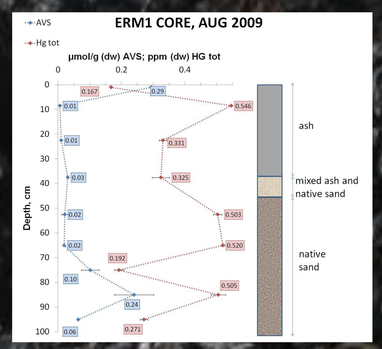
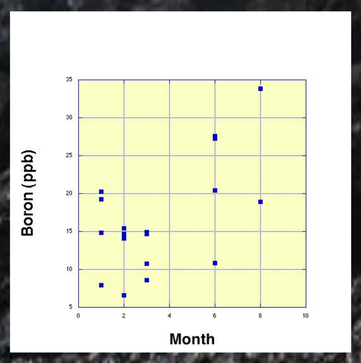


Figure 11. Sediment core total Hg concentrations range from 0.19 to 0.52 ppm; acid volatile sulfide (AVS) concentrations range from approximately 0 to 0.24 µmol/g (dw). Error bars represent one standard deviation from the mean (n=2-3). Error bars not seen are smaller than data markers.



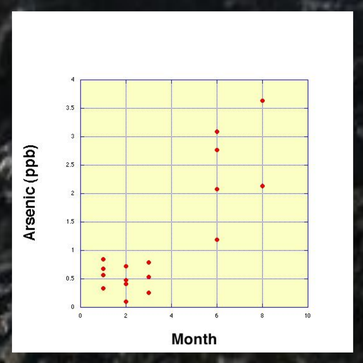


Figure 4 and 5. The monthly measurements of boron and arsenic (LCACs) concentrations in the same four downstream locations measured almost monthly. The concentrations of the LCACs demonstrate a peak in the summer months of June and August 2009. These elevated concentrations could indicate changes in river flow.

Analytical Methods:

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 (Figure2) were collected in six field trips in 2009. The surface water samples were collected near the river shoreline and in different locations and depths in the river at sites located upstream and downstream (at different distances) from the ash spill.

- Trace metals in water were measured by inductively coupled plasma mass spectrometry (ICP-MS);
- Cations were measured by direct current plasma spectrometer (DCP).
- Anions were measured by an ion chromatograph(IC);
- Boron and strontium isotopes were measured in a thermal ionization mass spectrometer (TIMS).
- Total Hg in water was sampled and measured using EPA Method 1631.
- Total MeHg in water was sampled and measured using EPA Method 1630.
- Total Hg in sediment was sampled and measured using EPA Method 7473.
- AVS in sediment was sampled and measured using Allen et al. (1976).
- MeHg in sediment was sampled and measured using Horvat et al. (2003)

Results and Discussion:

- The chemical composition of the **TVA coal ash** in Kingston, Tennessee shows marginal **enrichments** of **calcium, magnesium, and aluminum** and large enrichments such as **strontium, arsenic, barium, nickel, lithium, vanadium, copper, and chromium** relative to local soil in TN.

- 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) has relatively **high levels of leachable coal ash contaminants** (LCAC), including **arsenic, calcium, magnesium, aluminum, strontium, manganese, lithium, and boron**.

- Surface waters from the Emory River and Clinch River downstream from the breached dam show relatively low 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.

Results and Discussion Continued:

- Surface water Hg and MeHg concentrations are low at all sample sites, whereas **sediment Hg** is high compared to background TN soil concentrations.

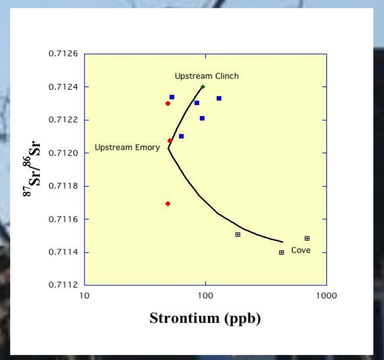
- Core acid volatile sulfide (AVS) measurements demonstrate that regions of the river sediments are sulfidic. The presence of sulfide indicates that these regions are reducing, and this in turn suggests that bacteria capable of methylating Hg (such as sulfate-reducing bacteria) may be active.

- The concurrence of reducing conditions, sulfate-reducing bacteria and Hg may provide ideal conditions for biotic Hg methylation. As such, river sediments should be closely monitored for MeHg production.

Results and Discussion Continued:

- Isotope measurements reveal that the **$^{87}Sr/^{86}Sr$** ratio of LCAC derived from the TVA ash is **0.7113**. The upstream Emory River has a $^{87}Sr/^{86}Sr$ ratio of 0.7117- 0.7121, while the upstream clinch river has a $^{87}Sr/^{86}Sr$ ratio of 0.7124. Downstream of the spill the $^{87}Sr/^{86}Sr$ ratio is 0.7121-0.7123 (Figure 6). The Sr isotope composition of LCAC is therefore similar to that of the upstream surface water.

- The **$\delta^{11}B$ values** of surface water associated with the coal ash spill in Kingston (the cove area; Fig.15) is **- 12‰** (relative to NIST951). This isotope ratio is consistent with the isotopic data of boron in TVA ash leachates over a wide range of pH values ($\delta^{11}B$=-16 to -21‰; Fig.14). The upstream Emory river has $\delta^{11}B$ values of +10‰ to +14‰, while the upstream Clinch River has a $\delta^{11}B$ range of +5.2‰ to +10.2‰. Downstream of the ash spill and after the convergence of the clinch and Emory Rivers the $\delta^{11}B$ values are -0.7‰ to +5.5‰ (Figure 7). While the absolute concentrations of boron in the downstream and upstream river samples are indistinguishable, their boron isotope ratios are different, which reflects the sensitivity of the method for elucidating the contribution of boron from the ash in the downstream river. The **boron isotope signature of the LCAC is therefore significantly different from that of common boron** in uncontaminated aquatic systems.



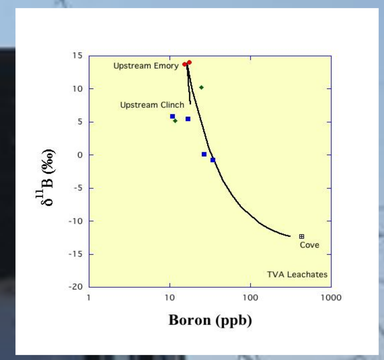


Figure 12 (left) and 13 (right). The $^{87}Sr/^{86}Sr$ values are plotted against the Sr concentrations found in the Emory (red circles) and Clinch (green diamonds) Rivers and the cove (black cross-squares). The sampling points downstream of the spill (blue squares) indicate that the LCAC Sr composition is similar to the value found upstream. Figure 7 models the mixing between the rivers and ash with the $\delta^{11}B$ values and the B concentration. The $\delta^{11}B$ value for the ash is significantly more depleted (-12‰) than the Emory and Clinch Rivers (+5 to +14 ‰).

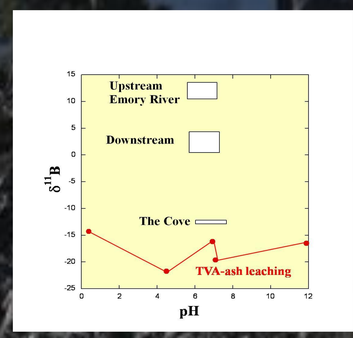


Figure 14. The $\delta^{11}B$ values are shown for the TVA leaching experiments as a function of pH. The Cove samples from the spill site reveal a $\delta^{11}B$ signal similar to that of the leachates, while the upstream samples have a positive $\delta^{11}B$.

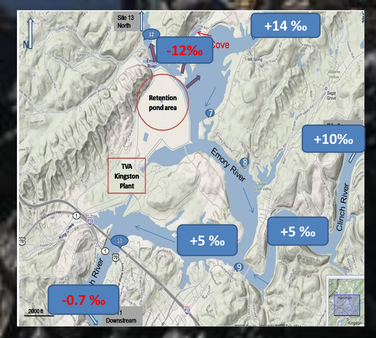


Figure 15. Map of boron isotope results in $\delta^{11}B$ notation. Both rivers have higher positive $\delta^{11}B$ values while the ash has a very negative value. Water sampled downstream after mixing with the ash has a much lower $\delta^{11}B$ value.

Conclusions:

- Leaching of contaminants from the spilled coal ash in Kingston, TN has caused contamination of surface waters in areas of restricted water exchange, but only trace levels were measured in the downstream Emory and Clinch Rivers due to river dilution.
- The distinguished boron isotope composition of the LCAC provides a novel geochemical tool for delineating and quantifying the CCP impact on the environment.
- The data show that under the current hydrological conditions (2009) ash dredging in the Emory and Clinch Rivers has not caused a major change in the surface water quality. However, river **sediments** should be closely monitored for the formation of methylmercury.

References:

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- Liang, L., Horvat, M., Feng, X., Shan, L., Li1, H., and Pang, P. (2004) Re-evaluation of distillation and comparison with HNO3 leaching/solvent extraction for isolation of methylmercury compounds from sediment/soil samples. *Appl. Organometal. Chem.; 18: 264 – 270.*
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Acknowledgements:

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