Differential leaching of trace metals and their isotopes from coal combustion products

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Introduction:

On December 22, 2008, the retaining wall broke on a waste retention pond at the Tennessee Valley Authority's (TVA) Kingston Fossil Plant, Tennessee, and an estimated 4.1 million m^3 of coal ash slurry was spilled onto the land surface and into the adjacent Emory and Clinch Rivers. This, the largest coal ash spill in US history, brought coal combustion waste storage to the nation's attention. Because over 70 million tons of coal combustion products (CCP) is stored in 194 landfills and 161 ponds in 47 states, one of the major potential hazards of coal ash storage in ponds is the continuous leaching of contaminants and their transport to the hydrological system.

The aims of this investigation are to provide an in-depth evaluation how different coal sources and their major chemical composition control the levels and abundances of CCPs' contaminants, the environmental conditions in which the CCPs contaminants are mobilized, and the possible fate of these contaminants in aquatic systems. Investigation of the environmental impacts of the TVA coal ash spill has indicated that trace elements from CCPs can be mobilized into the environment (Ruhl et al., 2009). This project seeks to develop geochemical and isotopic tools for delineating and modeling the impact of coal ash on the environment based on systematic leaching experiments of different CCPs.

Methods:

We have conducted laboratory leaching experiments on bulk, fly, and bottom coal ashes from the TVA Kingston plant and lime-treated ash samples from the coal plant in Duke University. Leaching experiments were simulated reactions of CCPs with strong acid (HCl in 0.5N), weak acid (HCl in 0.02N), strong-basic (NaOH in 0.2N), weak-basic (NaOH in 0.00063N), deionized water under two S/L ratios, and Toxicity Characteristic Leaching Procedure (TCLP; EPA method 1311). Each simulation was run for ~24 hours, then the liquid was decanted off, filtered, and then analyzed in the method designated below. Leaching conditions varied over a wide range of acidity (pH of 0.4 to 12). Coal ash from the spill area in Kingston and Harriman, TN, as well as fly and bottom ash from the Kingston plant were collected in 2009.

- •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).

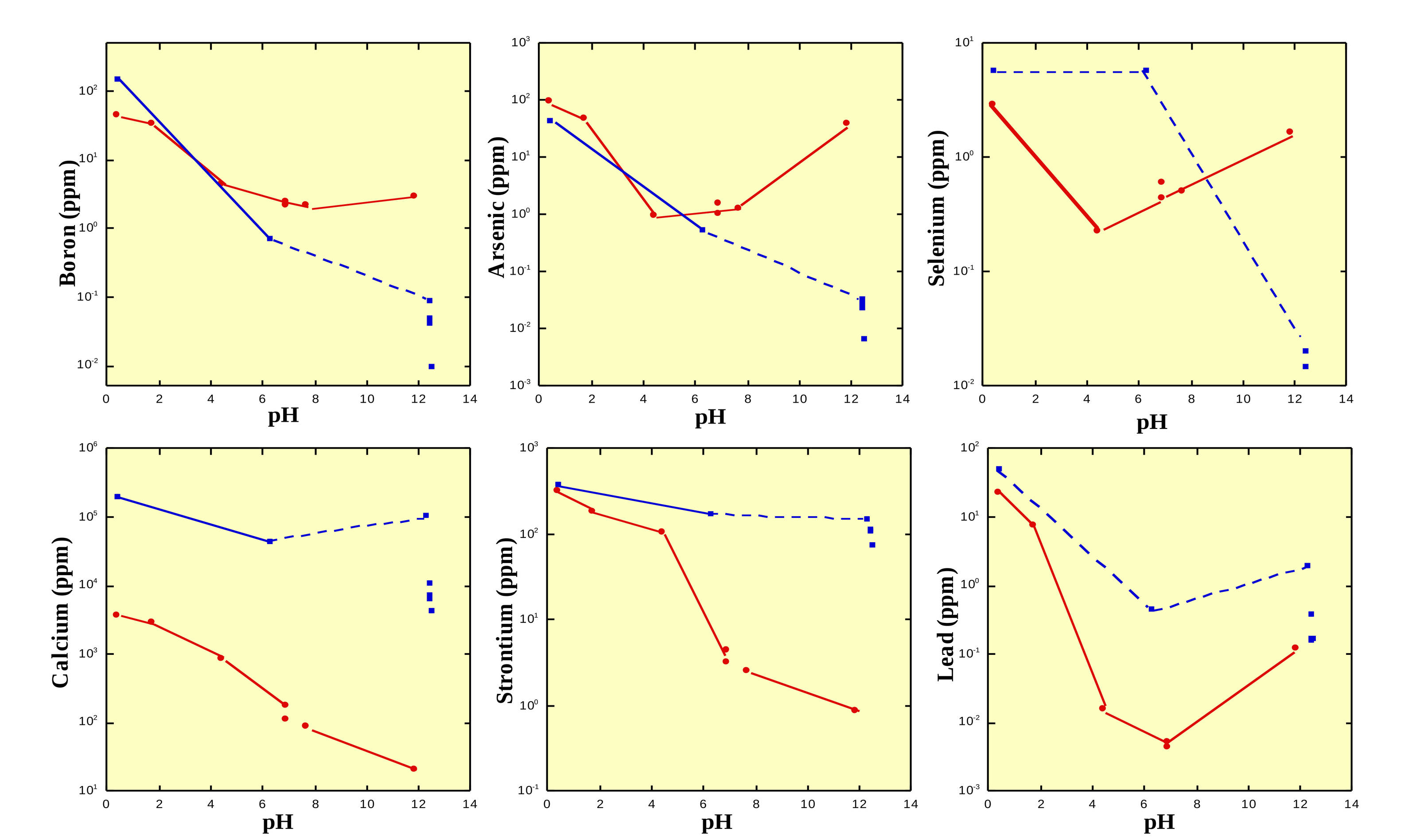
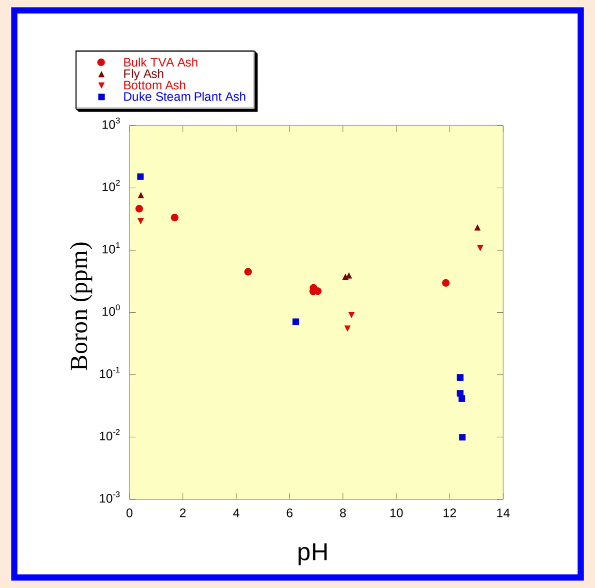
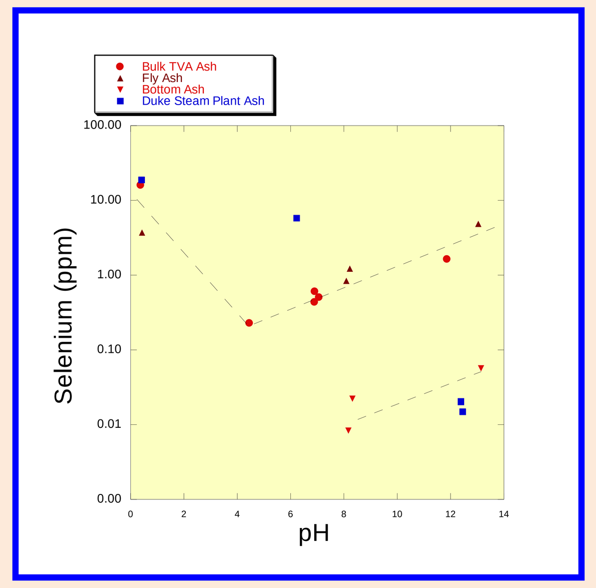
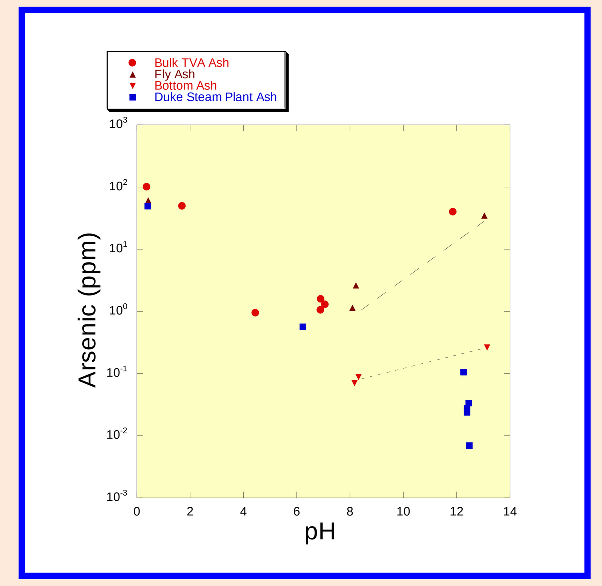


Figure 1: Boron, As, Se, Sr, Ca, and Pb concentration (ppm, normalized to ash weight) versus pH measured in leaching experiments performed on the Kingston TVA ash (red circles) and Duke University ash (blue squares). Results for Ca, As, B, Sr, Pb, and Se show large variations in the magnitude and composition of metals and metalloids in the leachates.







Figures 2, 3, and 4: Chemical variations as a function of pH in TVA bulk, fly, and bottom ash as compared to the Duke University steam plant ash. The results show differentiation in the variations of different metals as a function of pH for different ash materials: boron, arsenic, selenium and lead show maximum leaching for extreme acidic (pH=0.4 to 1.7) and basic (pH=12) conditions for the bulk TVA ash, while in Duke ash the maximum leaching for these metals occur only under acidic conditions. The data indicate the properties of the CCP itself (i.e., the Ca content and acidity), in addition to the environmental conditions, would determine the level and composition of toxic metals in the leachates. Leachate composition reflects the enrichment of volatile elements in fly ash relative to bottom ash (As, Se, B are higher in fly ash). Also Se/As ratios vary with pH showing that at pH=6-8, Se/As ratio increases, which indicates higher Se mobilization under these conditions.

Results:

Preliminary results from the leaching experiments have revealed several distinctive patterns:

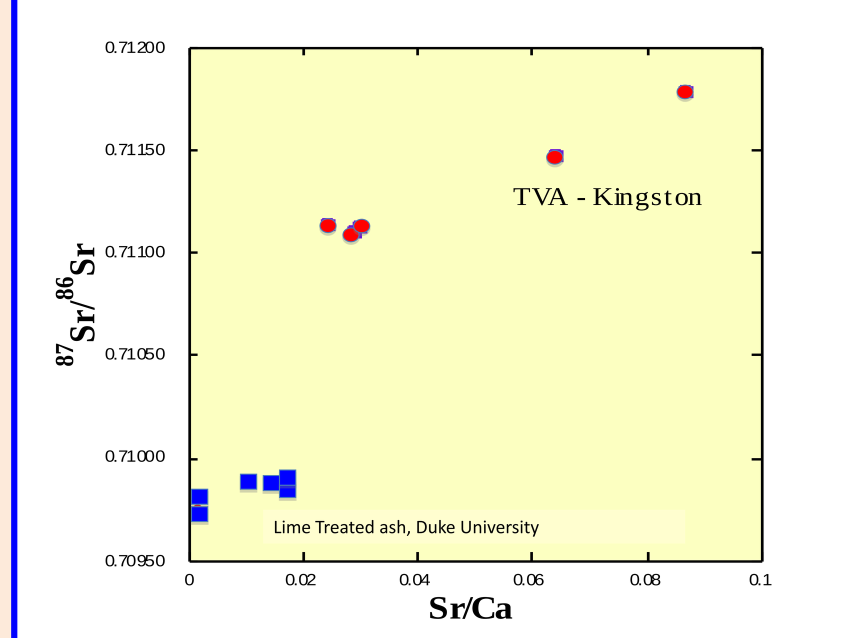
(1) The CCPs composition and acidity control the pH of the leachates and consequently the magnitude of contaminants leaching;

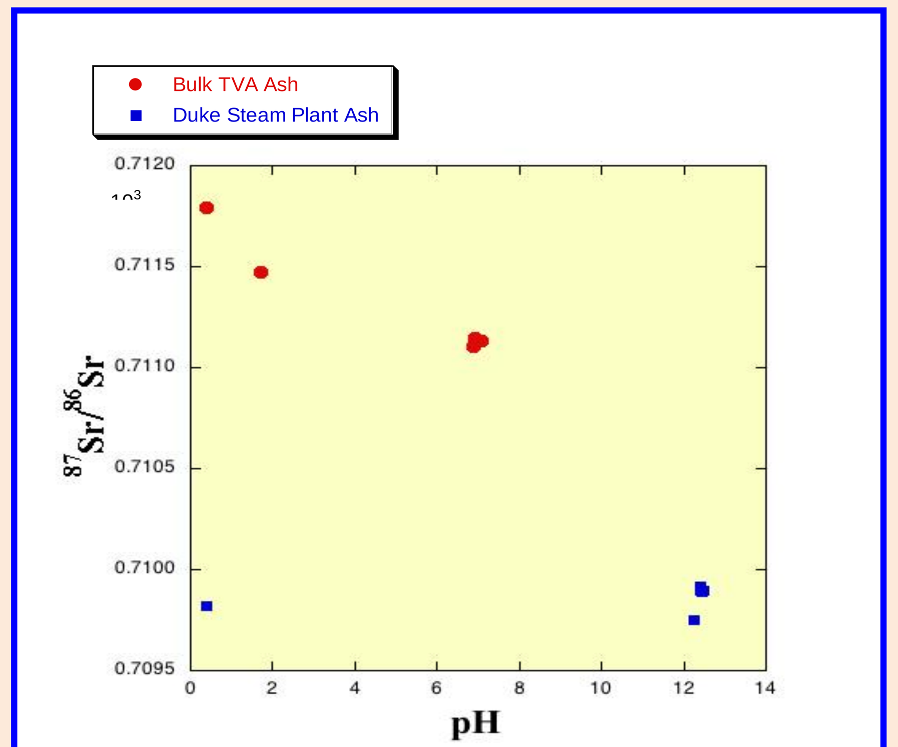
(2) Differentiation between oxyanion (B, As, Se) and cationic (Ca, Sr) species, in which the former show maximum mobilization under low and high pH conditions while the latter show progressive increase in mobilization with increasing acidity;

(3) Differentiation of trace elements abundances in fly ash relative to bottom ash (e.g., relative enrichment of As, Se, Pb, B);

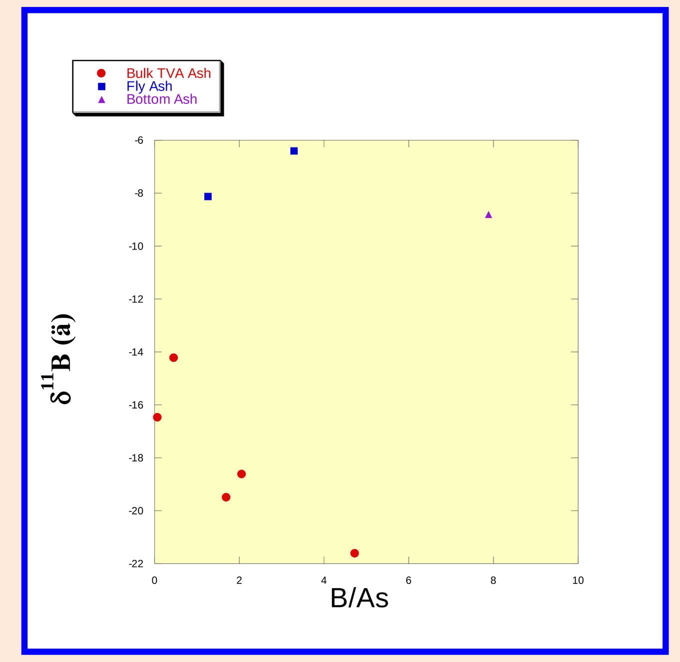
(4) Systematic distinctive boron isotope ratios ($^{11}B/^{10}B$) in leachates originated from a wide pH conditions that are significantly different from the isotope ratios of natural occurring boron in the hydrosphere;

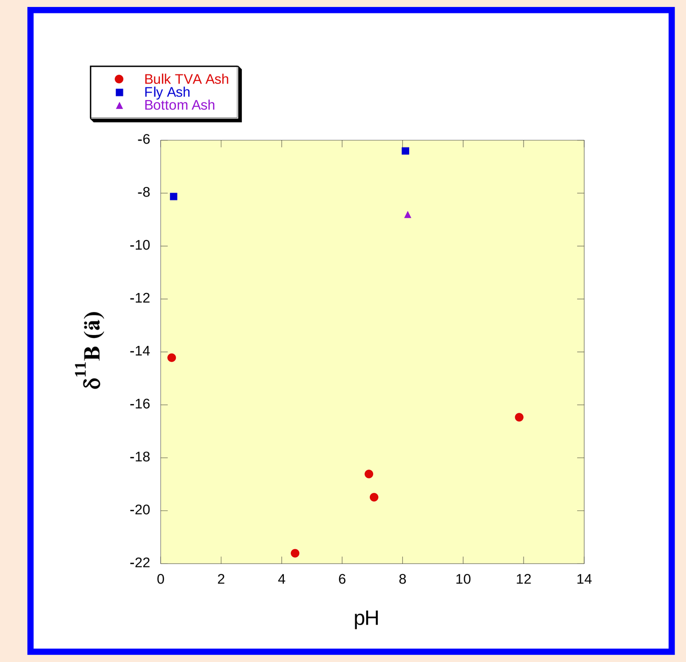
(5) Preliminary strontium isotope ($^{87}Sr/^{86}Sr$) results show that the TVA leachates are different from that Duke ash, which could be related to the original coal source and/or lime treatment of the Duke ash.

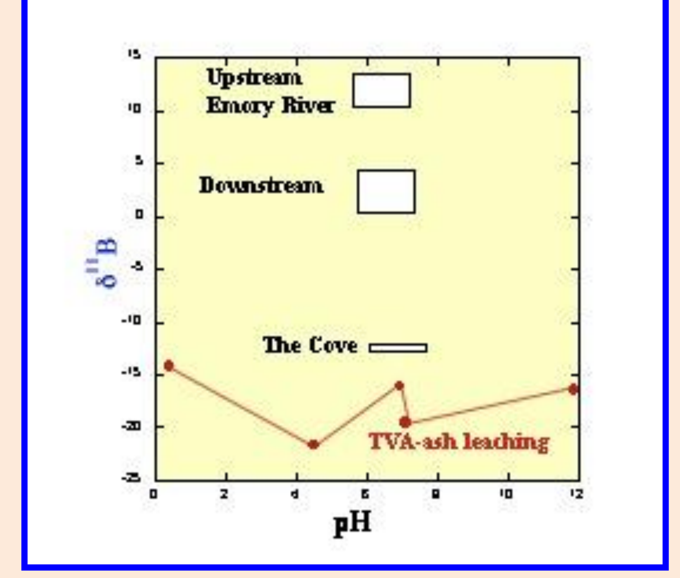




Figures 5 (left) and 6 (right): Figure 5 shows the relationship between Sr/Ca ratios and the Sr isotope ratios. The lime treated Duke ash has a noticeably different isotopic ratio, which could reflect it's treatment with lime and/or different coal source. Figure 6 shows the Sr isotopic variation as a function of pH. The TVA ash has a higher $^{87}Sr/^{86}Sr$ ratio relative to the Duke steam plant ash.







Figures 7 (top left), 8 (top right), and 9 (bottom): Figure 7 and 8 show the variations of $\delta^{11}B$ and B/As ratios with pH. Relatively higher mobilization of B over As is associated also with lower $\delta^{11}B$ values in bulk TVA ash. Figure 9 compares the leaching experiments with the environmental samples collected at the TVA spill site. Results from both the impacted area in Kingston TN and the experimental leaching results reveals a distinctive lower $\delta^{11}B$ signal, showing that the CCP impact can be traced in the environment by using boron isotope systematic.

Conclusions:

The leaching experiments' data indicate that the combination of CCPs properties and environmental conditions such as pH and speciation of oxyanion species would control mobilization of contaminants from CCPs. Boron isotopes can be used to predict species distribution of oxyanion species while strontium isotopes can be applied as a surrogate for the origin of cationic species. Consequently, modeling of the mobilization of metals and metalloids from coal ash requires an in-depth understanding of the metal behavior under different geochemical constraints such as acidity, salinity, water composition (e.g., ion-pair formation for boron species), and the characteristics (e.g., acidity) of the ash itself. These promising preliminary results are based on both field work at Kingston, TN and laboratory leaching experiments that demonstrate the ability of boron and strontium isotopes to trace the origin of CCPs contaminants in the environment. Knowledge of the CCPs composition, possible links to the coal sources, and the quality of effluents that are produced in holding ponds would provide better management tools and adequate preparations for expected future EPA legislations, in which discharged effluents from CCPs ponds will be regulated.

References:

•Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Deonarine, A, Bergin, M, and Kravchenko, J. (2009) Survey of the Potential Environmental and Health Impacts in the Immediate Aftermath of the Coal Ash Spill in Kingston, Tennessee. *Env. Sci& Technol., 43, 6326–6333.*

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