Assessment of mercury and methylmercury in the Emory, Clinch and Tennessee River system after the December 2008 coal ash spill at the Kingston Fossil Plant, TN

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Motivation

The coal ash released from the TVA Kingston Fossil Plant was found to be enriched in mercury (Hg) (~0.15 mg/kg[1]) relative to background levels in the sediment of the Emory River (~0.06 mg/kg). As the coal ash accumulates and re-mobilizes within the river sediments, leaching of Hg could negatively impact the aquatic ecosystem if converted to methylmercury (MeHg), the bioaccumulative form of this toxic metal. Here, we investigated the potential for methylmercury production by anaerobic bacteria in sediments near the spill site.

Objectives

- To evaluate surface water and sediment quality with respect to Hg and MeHg after the coal ash spill.
- To locate areas in the river sediments where MeHg production is relatively high.

Sampling plan

Surface water, surface sediment samples and sediment cores were collected at monthly intervals from February to December 2009 at the sampling locations near the spill site.

In surface water samples, total Hg and total MeHg was determined using cold vapor atomic fluorescence methods (EPA Methods 1631 and 1630).
In sediments, total Hg was quantified by atomic absorption spectroscopy (EPA Method 7473), total MeHg was quantified by acid-dichloromethane extraction, and acid volatile sulfide (AVS) was quantified by a purge-and-trap method followed by colorimetric analysis.

Results

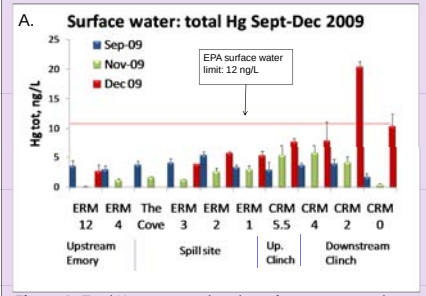


Figure A. Total Hg concentrations in surface water were lower than the EPA surface water quality limit and ranged from 0.1 to 10.3 ng/L. One sample with levels (20.3 ng/L) exceeding this guideline was observed in Dec.2009 and probably reflected high suspended solids in the water caused by storm flow conditions.

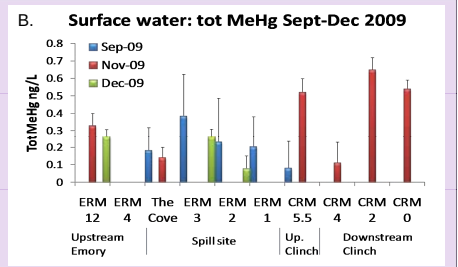
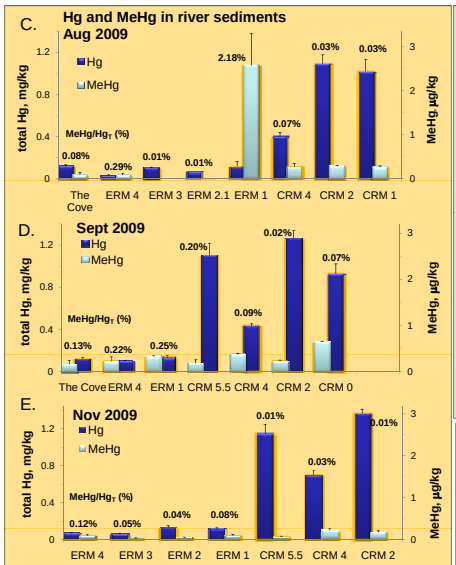


Figure B. MeHg surface water concentrations were less than 1 ng/L at all sites and varied both spatially and temporally. In Sept. 2009, the highest concentrations were observed near the spill site along the Emory River, but in Nov., the highest concentrations were observed further downstream in the Clinch. Data not shown were below the limit of quantification (0.08 ng/L).



Figures C, D, and E. MeHg production in sediments depends on two factors: 1) productivity of anaerobic bacteria who methylate mercury, and 2) bioavailability of inorganic Hg to these bacteria. **We used the ratio of MeHg/total Hg in river sediments as an indicator of MeHg production potential.**

In the Clinch River which is historically contaminated by acitvities from Oak Ridge, MeHg/Hg values were less than 0.09% from Aug. to Nov. Near the ash spill site (ERM 1-3 and the Cove) this ratio varied both spatially and temporally with the highest values (0.25%, 2.18%) at ERM 1 in Aug. and Sept. These results suggested that Hg methylation was occurring in the Emory and that the coal ash introduced conditions (either bioavailable Hg or nutrients to stimulate anaerobic bacteria) that encouraged methylation. In Nov., a decrease in relative MeHg levels may have resulted from less microbial activity (from the onset of winter season) or from dredging operations that removed the ash from the river bottom .

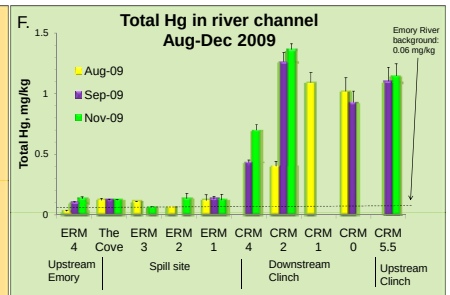


Figure F. In sediments near the spill site, total Hg ranged from 0.07 to 0.2 mg/kg, greater than background Hg levels in Emory River sediments upstream of the spill. Hg content in the Clinch River (up to 1.4 mg/kg) was probably caused by historical releases of mercury from the Y-12 facility at Oak Ridge, TN (upstream of the Clinch River).

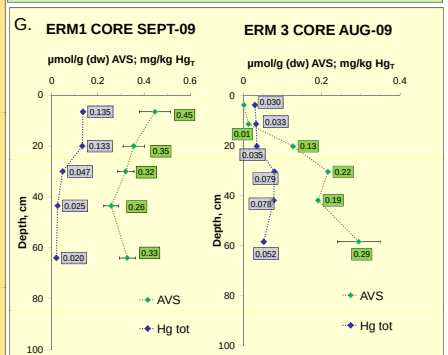


Figure G. Examples of sediment cores obtained during Sept. and Aug. 2009. The presence of acid volatile sulfide (AVS) indicated that anoxic regions existed in the river sediment. Such conditions are necessary for Hg-methylating bacteria such as sulfate-reducing bacteria to thrive.

Hg methylation

Methylmercury (MeHg) is the most dangerous form of Hg in the environment because it is extremely toxic to humans and other organisms and accumulates in the food chain.

MeHg occurs primarily in the anoxic (i.e., no oxygen) regions of aquatic sediments. In these sediments, microorganisms such as sulfate-reducing bacteria are able to methylate Hg.

Factors which influence Hg methylation include the fraction of Hg that is available to microorganisms (i.e., Hg speciation) and compounds associated with coal ash that can stimulate microbial growth (e.g., orgnaic carbon and sulfate).

Preliminary assessment

Overall, surface water quality was not impacted by the ash, as Hg and MeHg surface water concentrations were generally low. However, during storm flow conditions, sediment-bound Hg and MeHg may be re-suspended in the water column, resulting in total Hg concentrations that are above the EPA water quality limit (12 ng/L).

Sediment Hg data indicates that there are at least two sources of Hg in this region: Hg in coal ash and legacy Hg contamination from the Oak Ridge Y-12 plant.

MeHg production appears to be taking place in the river sediment at sites near the spill along the Emory River. At these sites, both surface water and sediment MeHg data vary spatially and temporally, possibly in response to coal ash distribution along the river bottom.

Our data indicate that the coal ash has impacted river sediment quality with respect to MeHg and is influencing Hg methylation in the river sediment.

Future and ongoing work

Total organic carbon (TOC) and dissolved sulfate in the sediments will provide additional indication of mercury methylation potential.

Hg isotope fractionation will enable differentiation between coal ash and legacy Hg sources.

Overall sediment and water data (relative MeHg content, TOC, sulfide, sulfate) will be used to determine the factors that are controlling MeHg production in this river system.