Transformations of mercury, arsenic, and selenium in river sediments contaminated with coal ash: Sediment microcosm studies

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Coal combustion products represent the largest industrial waste stream in the United States and contain elevated levels of toxic elements such as mercury (Hg), arsenic (As), and selenium (Se).¹ Much of this waste is stored in unlined holding ponds that are not always monitored for their discharge to adjacent waters.² Moreover, these holding ponds are susceptible to failures such as the disaster at the Tennessee Valley Authority (TVA) Kingston Plant in 2008.³ In such cases, the fate of toxic elements associated with coal ash is greatly influenced by environmental conditions such as redox potential and microbial activities that induce transformations and leaching of contaminants.

In aquatic environments, anaerobic organisms can transform mercury to methyl mercury (MeHg), which is a highly bioaccumulative neurotoxin and a dietary exposure risk for humans.⁴ The production of MeHg is a function of the bioavailability of Hg in anaerobic settings and the productivity of the methylating microorganisms.⁵ Data from the TVA spill showed higher levels of MeHg in areas in the vicinity of the coal ash spill than in nearby areas previously contaminated with Hg.⁶ These data indicate that Hg associated with coal ash might have a greater methylation potential than Hg from other contamination sources—due either to the bioavailability of its speciation or due to co-dissolution of substrates (e.g. sulfate) from the coal ash that stimulated microbial MeHg production. The leachability and mobility of elements such as As and Se are intimately tied to their oxidation state and redox reactions. Field studies of coal ash impacted sites have shown high levels of As in sediment porewater, indicating that As is more mobile under reducing conditions.²,⁷ In contrast, the highest concentrations of dissolved Se were found in the surface water, indicating that Se is more mobile under oxic conditions.

Here, we investigated the mobilization of coal ash contaminants in sediments using sediment slurry microcosms to mimic an ash spill event. Sediment microcosms were prepared using surface water and sediment from a site on the Emory River several miles upstream of the TVA spill site. We cultured the slurries anaerobically and amended a selection of the microcosms with coal ash to explore how the addition of coal ash under low redox conditions could influence trace element speciation and MeHg production.
Results showed that coal ash increased the amount of dissolved As and Se in the slurries at the initial time point. Over 7 days of incubation, dissolved As continued to increase while dissolved Se decreased, suggesting that arsenic was converting from As(V) to more soluble As(III) species while selenium was converting from oxidized forms (e.g. selenate or selenite) to less soluble, reduced forms (e.g. elemental Se, selenide).

The effect of coal ash on MeHg production was tracked over 5 days of incubation. The experiment was done three times: (1) with low microbial growth conditions and low sulfate ash, (2) with high microbial growth conditions and low sulfate ash, and (3) with high microbial growth conditions and high sulfate ash. MeHg was observed in all the slurries, but the effect of coal ash on Hg speciation was mixed. Coal ash did not stimulate MeHg production in the slurries amended with low sulfate ash—even though these slurries, in both experiments, showed a clear decrease in sulfate over time. Coal ash did provide a stimulating effect on MeHg production in slurries optimized for microbial growth that were amended with high sulfate ash. Yet, there was no clear trend of sulfate reduction over time for these samples.

Overall, our research highlights the need to consider environmental conditions, including redox potential and microbial activities, when assessing the hazards of coal ash contaminants. By excluding these parameters, we may be greatly underestimating the environmental risk of our current coal ash disposal practices.