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Leaching potential and redox transformations of arsenic and selenium in sediment microcosms with fly ash

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ABSTRACT

The unintended release of coal ash to the environment is a concern due to the enrichment of contaminants such as arsenic (As) and selenium (Se) in this solid waste material. Current risk assessments of coal ash disposal focus on pH as the primary driver of leaching from coal ash. However, redox speciation of As and Se is a major factor for their mobilization potential and has received much less attention for risk assessments, particularly in disposal scenarios where coal ash will likely be exposed to microbially-driven redox gradients. The aim of this study was to demonstrate the differences of aerobic and anaerobic conditions for the leaching of As and Se from coal ash. Batch sediment-ash slurry microcosms were performed to mimic an ash spill scenario and were monitored for changes in As and Se speciation and mobilization potential. The results showed that the dissolved As concentrations were up to 50 times greater in the anaerobic microcosms relative to the aerobic microcosms during the two week incubation. This trend was consistent with As redox speciation determined by X-ray absorption spectroscopy, which indicated that 55% of the As in the solid phase at the end of the experiment was present as As(III) (a more leachable form of arsenic relative to As(V)). In the aerobic microcosms, only 13% of the As was As(III) and the rest was As(V). More than half of the Se was present as Se(IV) in the original fly ash and in the aerobic microcosms, while in the anaerobic microcosms Se was gradually transformed to less soluble Se(0) species. Likewise, dissolved Se concentrations were up to 25 times greater in the aerobic microcosms relative to anaerobic conditions. While the overall observations of As and Se mobilization potential from coal ash were consistent with expectations for aqueous and solid phase speciation of these elements, the findings directly show the relevance of these processes for coal ash disposal. These results highlight the need to select appropriate environmental parameters to include in risk assessments as well as provide potential geochemical monitoring tools through the use of dissolved Se/As ratios to determine the redox conditions of ash storage and spill sites.

1. Introduction

Coal ash is the solid waste by-product of coal combustion and includes bottom ash, fly ash, and sludge from flue gas desulfurization units. Every year, over 60 Mt of coal ash are disposed in 300 landfills and 600 holding ponds across the United States (American Coal Ash Association; US EPA, 2013d). Ash wastes are enriched in many potentially toxic elements, and the presence of arsenic (As) and selenium (Se) are a particular concern because of their relatively high mobilization potential at neutral to alkaline pH values that are typical of ash disposal impoundments (Izquierdo and Querol, 2012; Meij, 1994). Moreover, these elements have the tendency to bioaccumulate in the aquatic food web and impart ecotoxicological effects (Izquierdo and Querol, 2012; Lemly, 2004; Rowe, 2014; Sharma and Sohn, 2009; Thorneloe et al., 2010).

Coal ash impoundments are not always closely monitored, particularly for effluent discharge to surface waters, seepage to

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groundwater, and structural integrity. Consequently, impoundment effluent discharge is a major source of As and Se contamination to certain aquatic environments, with approximately 36,000 kg of As and 102,000 kg of Se discharged annually to surface waters in the United States (US EPA, 2013a). Ash impoundments have been cited in 132 documented cases of groundwater and surface water contamination (US EPA, 2007, 2013a). Moreover, impoundment failures and direct release of ash have been reported by at least 41 different power plants in the last 15 years (US EPA, 2012a). These impoundment failures include the 2008 ash spill at the Tennessee Valley Authority (TVA) Kingston Fossil Plant. Arsenic and selenium originating from the spilled ash were two contaminants of concern at the site (Ruhl et al., 2009, 2010).

The mobility of As and Se in the environment is intimately linked to redox speciation of these elements and the propensity of individual species to associate with soil and sediment particles through adsorption/desorption reactions and precipitation/dissolution reactions (Fernández-Martínez and Charlet, 2009; Masscheleyn et al., 1991). The As(V) oxyanion arsenate tends to sorb more strongly to mineral phases such as iron oxides when compared to the reduced As(III) arsenite form (Goldberg and Johnston, 2001; Masscheleyn et al., 1991; Raven et al., 1998). If sulfide is present in sufficient quantities, insoluble arsenic-sulfide species ($As_2S_{3(s)}$) and soluble thioarsenicals may form (O'Day et al., 2004; Wilkin et al., 2003). In contrast to As, the Se(VI) oxyanion selenate has little tendency to adsorb to solids or to precipitate out of solution compared to selenite Se(IV), which has greater sorption affinity to metal oxyhydroxides, clays, and organic matter (Fernández-Martínez and Charlet, 2009). In anaerobic conditions, selenium can persist as elemental selenium Se(0) or metal selenide mineral phases that are sparingly soluble in water. Organo-Se compounds such as selenocysteine and selenomethionine are a reduced forms of Se that are biologically active (Lemly, 1993).

Arsenic associated with coal ash exists mainly as As(V) species while Se is typically found as Se(IV) and elemental Se(0) species (Chappell et al., 2014; Deonarine et al., 2015; Huggins et al., 2007; Liu et al., 2013). The mobilization of As and Se from coal ash is typically assessed using deionized water under aerobic conditions and perhaps under a wide range of pH values (Bednar et al., 2010; Izquierdo and Querol, 2012; Liu et al., 2013; Thorneloe et al., 2010). Much less attention has been given to redox transformations that can occur during ash disposal, even though these processes are critical for As and Se mobilization, as stated above. Two studies have attempted to address redox conditions by taking ash-deionized water mixtures and purging a subset with nitrogen gas (Bednar et al., 2010; Liu et al., 2013). The results of the work showed no or minimal differences between the oxic and N_2-purged mixtures with respect to As and Se redox speciation and leaching potential from the ash. These results were inconsistent with our previous field studies at the TVA Kingston ash spill site and at several North Carolina ash holding ponds, where the mobilization of As and Se from coal ash appeared to change as a function of local redox conditions (Ruhl et al., 2012, 2010, 2009). Comprehensive measurements of As and Se speciation were not available from these field sites to verify the mechanisms of leaching from the ash.

This study aimed to delineate the effects of redox gradients for As and Se mobilization from coal ash using laboratory sediment microcosms that more closely mimic the complexity of biogeochemical redox processes in the environment. Another objective was to improve our understanding of processes that were previously observed at coal ash spill sites and perhaps identify geochemical tools for monitoring coal ash contaminants in redox gradients. Batch sediment slurry microcosms were constructed with aerobic and anaerobic conditions and were amended with fly ash to simulate a coal ash spill into a benthic sediment-water system. The microcosms were monitored for total dissolved concentrations of As and Se, speciation of these elements in the aqueous and solid phases of the microcosms, and other water chemistry variables relevant for As and Se leaching.

2. Materials and methods

2.1. Materials

All chemicals for reagents were purchased from Sigma Aldrich (St. Louis, MO), unless otherwise stated. Trace metal grade acids (Fisher Scientific, Pittsburgh, PA) were used for acid digestions and pH adjustments of samples. All reagents and calibration standards were prepared with >18 MΩ-cm Milli-Q-grade filtered water (EMD Millipore).

The microcosms comprised of mixtures of sediment and water from the Emory River (Tennessee, USA). Surface water and bottom sediment samples for the microcosms were collected in April 2014 from mile marker 10 of the Emory River near Kingston (35.9475941°, −84.53178889°), which is located several miles upstream of the TVA Kingston ash spill (Bartov et al., 2012; Deonarine et al., 2013; Ruhl et al., 2009, 2010). The sediment was a mixture of brown, organic fines and sand. Water samples were taken at 0.15 m depth and were stored in acid-cleaned plastic jugs. Bulk sediment was collected from the top layer of sediment (approximately 15 cm) using a Ponar dredge (Wildco) and placed in screw top buckets. The sediment and water samples were stored on ice for shipment to Duke University and stored at 4 °C in the laboratory. These sediment and water samples were used within one month after collection for the microcosm experiments. Prior to the construction of the microcosms, the water was analyzed for trace element concentration, pH, and conductivity.

The coal ash used for the microcosm experiments was collected at the TVA John Sevier fossil plant in April 2011. The sample was a composite of fly ash collected from electrostatic precipitator hoppers at each of the plant's four units. The composite fly ash sample was characterized for major mineral oxide content (by X-ray fluorescence) and for total As and Se concentrations (methods described in Section 2.3).

2.2. Microcosm preparation and sampling

Sediment slurry microcosm experiments were conducted on two separate occasions: the first under aerobic conditions, followed by the second under anaerobic conditions. Each treatment type (with and without ash; aerobic and anaerobic) was performed in duplicate microcosms.

The microcosms were designed to mimic a stagnant, ash-impacted environment. The sediment to surface water ratio in the microcosms was chosen to provide an environment where sufficient overlying water would be available for sampling and analyses but microbial activity would not be limited. Each microcosm was prepared in a 1-L acid-washed, glass jar and consisted of 240 g of sediment (wet weight basis) and 600 mL of surface water. The sediment was thoroughly homogenized by stirring before microcosm construction. The river water was amended with a carbon substrate for microbial activity, 0.5-mM pyruvate and 0.5-mM acetate, immediately prior to microcosm construction.

The aerobic microcosms were continuously stirred and purged with hydrated air using Teflon tubing and aquarium air stones during the experiments. After an incubation period of three days, 56 g of coal ash was added to the microcosms designated for ash amendment. This amount of coal ash corresponded to 40% (w/w) of dry sediment, an amount that was observed at the TVA Kingston ash spill site after dredging was completed (Deonarine et al., 2013).