Arsenic Partitioning to Iron Oxides and Sulfides: Local Environment and Oxidation State

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Introduction

Arsenic in ground water and surface water poses a risk to ecosystem and human health. Because of this risk, environmental concern is rising over arsenic levels in water resources. Arsenic has been documented at concentrations up to about 100 mg/L in ground water systems across the U.S., or about 4 orders of magnitude greater than the revised U.S. EPA maximum concentration limit (MCL) of 0.01 mg/L (effective in 2006). Arsenic contamination is associated with weathering processes, mineral deposits, mining activities, industrial, and agricultural uses. More detailed information is needed on the factors that govern arsenic transport and fate in the environment, especially natural processes that remove arsenic from the mobile phase such as reactions that occur at mineral surfaces. A clearer understanding of these processes is needed in order to optimize contaminant remediation systems and to better predict the long-term behavior of arsenic at hazardous waste sites.

The sorption of arsenate to ferrihydrite in oxic environments has received significant attention in the literature [1-5]. In general, poorly crystalline iron (hydr)oxides such as ferrihydrite have the largest arsenate sorption capacity, in part, due to high surface area [6-7]. However, much of the research examining arsenate sorption to ferrihydrite has been conducted over relatively short reaction periods. Studies examining metal sorption to ferrihydrite over longer aging periods suggest that the reversibility of ion sorption may decrease due to transformation of ferrihydrite to more crystalline phases such as goethite or hematite [7]. The extent that aging may limit arsenate mobility must be understood to accurately assess arsenate transport in subsurface systems.

The mobility of arsenic under anoxic, sulfate-reducing conditions is expected to be governed by interactions with amorphous or crystalline iron sulfides and dissolved hydrogen sulfide or bisulfide. Iron sulfide minerals are especially common components of soil/sedimentary environments, and reactions at the surfaces of iron sulfides play pivotal roles in metal retention, mobility, and bioavailability [7-8]. Although essential for predicting the fate of arsenic, details of reaction mechanisms, geochemical pathways, and the limiting factors that govern metal uptake by iron sulfides (iron monosulfides and iron disulfides) are incompletely understood. The kinetic nature of these interactions are currently being investigated at EPA's Ground Water and Ecosystems Restoration Division (Ada, OK) where experimental studies evaluate the effects of pyrite nucleation rate and growth rate on the uptake of arsenic. X-ray absorption spectroscopy experiments are needed in order to better understand the bonding environment of arsenic contained in iron sulfides.

Although our overall objective for this research program is to develop a more comprehensive understanding of the biogeochemical controls on arsenic mobility in the environment, the focus of this report is the result of studies being conducted to assess the mineralogical associations of arsenic in the oxic portions of a contaminated site.

Methods and Materials

Iron-bearing sediments were collected from the oxidized zone of a shallow lake contaminated with arsenic. Sediments were incubated in their native water at room temperature for a period of 2.5 years. Following aging, the <2 ?m size fraction was collected from the sediments samples for mineralogical characterization and arsenic speciation. Aged sediments were extracted with 1 N HCl to determine the fraction of labile arsenic. The distribution of arsenic species in the extract was determined using ion chromatography-hydride generation-atomic fluorescence spectroscopy (IC-HG-AFS). The oxidation state of arsenic in sediments (before and after extraction) was assessed using X-ray absorption spectroscopy at beamline Sector 20-BM (Pacific Northwest Consortium - Collaborative Access Team (PNC-CAT)) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. Sediment samples were loaded into 1-mm-thick plastic sample holders and sealed with strips of Kapton tape. Absorption spectra were collected at room temperature at the As K-edge (11867 eV) in fluorescence mode using a 13-element solid-state Ge-detector. The synchrotron was operated at 7 GeV with a nominal 100 mA fill current (top-up fill status). Energy calibration was accomplished by assigning the first inflection point of Au (LIII) foil to 11919 eV. The monochromator step size was 0.25 eV per step in the XANES region (11845-11900 eV). Multiple scans were collected and summed for each sample (3 to 9). The XANES fluorescence data were normalized to the edge-jump height and the K-edge inflection point was determined as the energy at the maximum in the first derivative of the normalized spectra. Mineral reference compounds were synthesized in the laboratory, including arsenate adsorbed to or coprecipitated with hematite.

Results

Ferrihydrite was identified as the primary mineral component in the <2 ?m size fraction for unaged sediments with a fraction of the mineral hematite present in sediment WI01-NEP. Following aging, the fraction of hematite increased in sediment WI01-NEP, but ferrihydrite remained as the predominant mineral component. Characterization of sediment WI04 revealed nearly complete conversion of ferrihydrite to the mineral goethite. The oxidation state of arsenic in aged sediments was assessed by XANES spectroscopy (Fig. 1). The predominant arsenic oxidation state in aged sediment WI01-NEP was As(V), which was the measured arsenic speciation in the HCl extract (94% As(V), 6% As(III)). In contrast, the aged sediment WI04 had a mixture of As(III) and As(V) based on XANES analysis. This was also consistent with the distribution of extracted arsenic species (78% As(V), 22%

As(III)). There was an observable reduction in the relative intensity of the As(III) edge feature in the spectrum for sample WI04-2 following extraction.

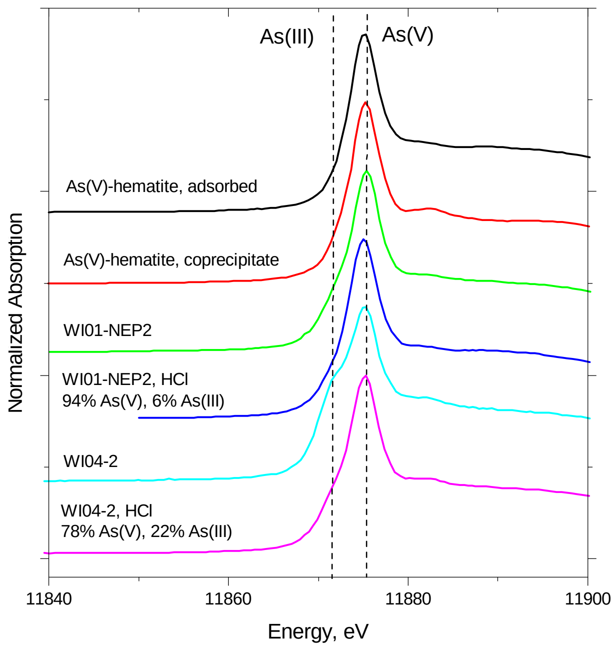

Fig. 1. Arsenic XANES data for aged sediments before and after extraction with 1 N HCl. Percentages of As(V) and As(III) indicated were measured in the extract by IC-HG-AFS.

Discussion

The distribution of arsenic oxidation states observed for in aged sediment samples provide evidence that sediment WI04 was subject to more reducing conditions during formation and/or transformation as a result of incubation. This is corraborated by the observed mineralogical distribution prior to and following aging. The apparent rate and mineralogical endpoint of aged sediment WI04 is consistent with the rapid transformation of ferrihydrite to goethite observed in synthetic laboratory systems [10-11]. The rate of ferrihydrite conversion to goethite is accellerated at circumneutral pH in thre presence of reducing ligands and/or microbial iron respiration, which drives the reductive dissolution of ferrihydrite and nucleation of more crystalline phases [12]. The results of this study has implications for arsenic mobility in iron-rich soil or sediment systems, since synthetic laboratory experiments have shown stabilization of sorbed arsenic during transformation of ferrihydrite to goethite/hematite [7].

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