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Arsenic solid-phase partitioning in reducing sediments of a contaminated wetland

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Abstract

The geochemical partitioning of arsenic in organic-rich sediments from a contaminated wetland is examined using X-ray absorption spectroscopy and selective chemical extraction procedures, and evaluated in context to the anoxic diagenesis of iron and sulfur. The interaction between ground water and surface water has a significant influence on iron sulfide formation in the wetland sediments. Ground-water seeps supply concentrations of sulfate, dissolved hydrocarbons, ferrous iron, and arsenic, and sediments located near seeps are anomalously enriched in arsenic, reactive iron, and acid-volatile sulfides. Degree-of-sulfidation (DOS) values are high in sediments adjacent to sites of ground-water discharge, ranging from 0.57 to 1.0. Pyrite (FeS_2) formation is apparently not limited by the abundance of any one primary reactant, e.g., organic carbon, sulfate, or reactive iron; instead, persistence of precursor iron monosulfides is attributed to slow pyrite formation kinetics due to low concentrations of reactive intermediate sulfur species or possibly due to high concentrations of arsenite, dissolved organic-carbon, or other solutes that adsorb to iron monosulfides surfaces and impede transformation reactions to pyrite. Greigite (Fe_3S_4) accounts for >80% of total reduced sulfur in sediments rich in acid-volatile sulfide and X-ray absorption spectroscopy data for magnetic separates provide direct evidence that As(III) is, at least in part, associated with reduced sulfur in the form of greigite. However, pyrite can only account for a small percentage, <20%, of the total arsenic budget in the reduced sediments. Although pyrite is the predicted stable endpoint for reactive iron and sulfur, it appears that within a 30 y time period pyrite is a relatively unimportant host for arsenic in the system investigated here. The abundance of reactive iron in the sediments prevents accumulation of dissolved sulfide and thus prevents formation of soluble thioarsenic species. X-ray absorption near-edge structure (XANES) spectroscopy indicates only the presence of As(III) in the reduced sediments. Results of linear combination fitting of reference spectra to sediment spectra are consistent with sulfur- and/or oxygen-coordinated As(III) in association with iron monosulfides and ferrous-bearing carbonates or hydroxides.
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Keywords: Arsenic; Iron; Pyrite; Greigite; Anoxic sediments; Contaminated sediments; Ground-water/surface-water interactions; XANES spectroscopy; Stable sulfur isotopes

1. Introduction

Complex chemical and physical processes control arsenic concentration profiles in contaminated sediments and adjacent water bodies. Yet predictions about whether arsenic will remain sequestered in the solid

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phase of sediment matrices or leach into surrounding pore water and overlying water bodies often do not account for this complexity. Model predictions are frequently based solely on examinations of trends in geochemical parameters, such as pH and the oxidation-reduction potential. More complete appraisals of arsenic transport and fate include consideration of microbially mediated redox reactions in sediments involving organic carbon, sulfur, iron, and manganese (e.g., Pierce and Moore, 1982; Aggett and O'Brien, 1985; Edenborn et al., 1986; Brannon and Patrick, 1987; Riedel et al., 1987; Moore et al., 1988; Belzile and Tessier, 1990; Widerlund and Ingri, 1995; Sullivan and Aller, 1996; Kneebone and Hering, 2000; La Force et al., 2000; Mucci et al., 2000; Bose and Sharma, 2002; Chaillou et al., 2003; Nicholas et al., 2003). For instance, oxidized forms of arsenic are often associated with iron oxyhydroxides but can be mobilized via reductive processes, relocalized in the sediment column, and/or diffuse to the overlying water column. Reliable assessments of the biological hazards associated with arsenic from natural and anthropogenic sources depend upon a detailed knowledge of the biogeochemical cycling of this element, in addition to characterization approaches that provide accurate insight into sequestration, transformation, and mobilization processes.

Geochemical relationships among sulfur, iron, and organic carbon in anoxic sediments are primarily governed by the metabolic activity of sulfur bacteria, particularly sulfate-reducing bacteria. These bacteria use dissolved sulfate as the terminal electron acceptor in heterotrophic respiration of organic matter (e.g., Jørgensen, 1982). As bacterial sulfate reduction proceeds, organic carbon is oxidatively consumed and coupled to the reduction of sulfate to sulfide. Biogenic sulfide thus produced can follow a number of pathways (see, e.g., Berner, 1984). A most important pathway with respect to trace metal behavior in sediments is reaction of dissolved sulfide with ferrous iron to precipitate iron sulfides that may be responsible for metal uptake via sorption and/or co-precipitation (e.g., Huerta-Diaz and Morse, 1992; Morse, 1994). The iron disulfide, pyrite, specifically has been viewed as an important carrier of arsenic and other elements (e.g., Raiswell and Plant, 1980; Belzile and Lebel, 1986; Harrison et al., 1991; Kornicker and Morse, 1991; Saunders et al., 1997; Dellwig et al., 2002; Bostick and Fendorf, 2003). Dissolved sulfide can also react directly with arsenic oxyanions (or other trace metals) to form stable complexes, or insoluble precipitates if conditions are favorable, for example, orpiment (As_2S_3) or realgar (As_4S_4). However, a transition from reducing to oxidizing conditions, due either to a shift of predominant redox boundaries or to physical sediment disruption (i.e., dredging, bioturbation), can lead to dissolution of sulfides and potentially arsenic release (Morse, 1994; Saulnier and Mucci, 2000).

Although metal sulfides provide a possible sink for arsenic in anoxic sediments (Moore et al., 1988; Huerta-Diaz et al., 1998; Kneebone and Hering, 2000; Mucci et al., 2000; Dellwig et al., 2002; Chaillou et al., 2003; Bostick et al., 2004), a comparative study suggested that arsenic was less effectively retained in anoxic sediments in Saanich Inlet (British Columbia) relative to equivalent nearby oxic sediments (Peterson and Carpenter, 1983). This observation is noteworthy and likely reflects the overall greater tendency for As(V) oxyanions to bond to mineral surfaces compared to As(III) oxyanions and thioarsenite ions (e.g., Pierce and Moore, 1982). The major mineralogical endpoints of bacterial sulfate reduction are acid-volatile iron monosulfides (mackinawite and greigite) and pyrite. Arsenic adsorption on the surfaces of these phases and/or co-precipitation is thought to be the most important uptake process for metals and metalloids in reducing environments (e.g., Farquhar et al., 2002; Wolthers et al., 2005a). Yet there is scant evidence showing an association between arsenic and iron monosulfide phases. In contrast, more conclusive data show the occurrence of arsenic in pyrite (arsenian pyrite). The concentration of arsenic in various textural forms of pyrite, including euhedral grains and framboids, ranges from ~0 to approximately 10 wt.% (e.g., Ostwald and England, 1979; Jacobs et al., 1985; Vavelidis, 1995; Graham and Robertson, 1995; Kolker et al., 1998). Recent molecular studies indicate that arsenic substitutes for sulfur in pyrite (FeS_2) as a solid solution (Savage et al., 2000). This finding has environmental significance because pyrite is highly insoluble over a range of geochemical conditions; consequently, pyrite is potentially a stable host in reducing environments for contaminants such as arsenic. Limited field and laboratory evidence suggests that rates of pyritization in natural systems may be quite variable and dependent on several key factors that include, for example, pH, redox conditions, and concentrations of reactive species and reaction inhibitors (e.g., Rickard et al., 1995; Gagnon et al., 1995; Hurtgen et al., 1999; Morse, 1999).

The objective of this study is to characterize, using an array of analytical methods, the distribution and associations of arsenic in contaminated, anoxic wetland sediments that were deposited in an urban watershed. Of particular interest is the development of an improved understanding about the relationships between arsenic cycling and the diagenetic behaviors of iron and sulfur

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