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Biogeochemical processes controlling the speciation and transport of arsenic within iron coated sands

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Abstract

Iron (hydr)oxides exert a domineering control on the dissolved concentration and transport of arsenic within surface and subsurface environments. Here we examine desorption and transport of As(V) (arsenate) and As(III) (arsenite) within ferrihydrite-coated sand under hydrodynamic conditions during biotic and abiotic induced transformations. For sands containing active cultures of the Fe(III) and As(V) respiring bacterium *Sulfospirillium barnesii* (an iron and arsenic respiring organism), an initial pulse (within 2 days) of arsenic desorption was followed by an exponential decrease (tailing) in eluted arsenic concentration for both As(V) and As(III)-in both columns, As(III) was the only species eluted after 2 days of reaction. The pulse in arsenic release was coincident with changes in iron mineralogy brought about by Fe(II) production. For As(V) loaded columns containing a culture of As(V) respiring *Bacillus benzoevorans* (an organism capable of As(V) respiration but incapable of dissimilatory Fe(III) reduction), the major pulse of arsenic release was delayed but remained elevated, with As(III) being the predominant species eluted after 1 day of reaction. Arsenic desorption in sterile columns, however, was even greater than the biologically active systems for As(V) and particularly As(III). Furthermore, despite As(III) having an adsorption maximum on ferrihydrite nearly twice that of As(V) at pH 7, As(III) desorption was more rapid and extensive than for As(V). Batch desorption experiments illustrate that Fe(II) and cellular organic materials aided the retention of arsenic (i.e., they depressed the extent of desorption), particularly for As(V). Our findings therefore suggest that arsenic desorption from ferrihydrite (or other labile iron oxides) and transport is greatest at the onset of an oxidizing to reducing transition and are promoted by mildly reducing conditions where arsenic reduction occurs but limited aqueous Fe(II) concentrations result.

Keywords: Arsenic; Iron (hydr)oxide sands; Adsorption; Desorption; Bacterial reduction

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1. Introduction

Arsenic is a naturally occurring trace element that poses a human health risk when incorporated into food or drinking water supplies (Mandal and Suzuki, 2002). In surface and ground water environments, arsenic often occurs in sediments as adsorbed or precipitated species, which pose little risk if left undisturbed. Geochemical factors that may enhance arsenic mobility are highly variable and complex, with ion displacement, oxidative dissolution of sulfides, reduction of arsenic, and reductive dissolution of iron (hydr)oxides all being possible release mechanisms (Cullen and Reimer, 1989; Smith et al., 1998; Smedley and Kinniburgh, 2002).

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Over the last few decades, many bacteria and archaea capable of oxidizing or reducing arsenic and iron (hydr) oxides have been recognized (Lovley, 1991; Oremland and Stolz, 2003). Such microbial activity, in combination with geochemical factors, will control arsenic speciation and uptake and release mechanisms in natural environments.

Arsenic mobility in soils and sediments is governed in part by the tendencies of different arsenic redox species to associate with particulate matter. Two oxidation states of arsenic, As(V) and As(III), predominate in surface and near-surface environments. In solution, arsenic exists primarily as weak acids as arsenate [As(V) as H_3AsO_4] and arsenite [As(III) as H_3AsO_3] (Smith et al., 1998; Goldberg and Johnston, 2001). Other soluble forms of arsenate and arsenite may be present [e.g., methylated-arsenic (Smith et al., 1998; Smedley and Kinniburgh, 2002), thio-arsenic (Helz et al., 1995; Rochette et al., 2000; Wilkin et al., 2003) and carbonato-arsenic (Kim et al., 2000; Lee and Nriagu, 2003)], but probably occur as only minor constituents within aquatic (independent of marine systems) or soil environments.

Both arsenate and arsenite can adsorb onto sediments and minerals, with arsenate generally binding more strongly to clays and aluminum hydroxides than arsenite (Xu et al., 1988; Manning and Goldberg, 1997a,b; Smith et al., 1998). Ferric (hydr)oxides and magnetite, in contrast, exhibit a greater retention of arsenite than arsenate at all but acidic conditions (Raven et al., 1998; Goldberg, 2002; Dixit and Hering, 2003). Soluble forms of As may also bind to organic matter in sediments (Thanabalsingam and Pickering, 1986; Grafe et al., 2001, 2002; Redman et al., 2002; Ko et al., 2004). However, organic matter content tends to be poorly correlated to arsenic in comparison to Fe, Al, or P (Chen et al., 2002), suggesting that its contribution to arsenic retention in soils and sediments is typically limited.

Displacement of As from the solid phase, and inhibition of As adsorption, can occur when incoming waters or indigenous sediments contain high levels of dissolved inorganic and organic ions (Manning and Goldberg, 1996; Reynolds et al., 1999; Dixit and Hering, 2003). Soluble Fe(II) and CO_3^{2-} may alter As (V) and As(III) adsorption behavior on iron minerals such as ferrihydrite and goethite (Van Geen et al., 1994; Villalobos and Leckie, 2001; Appelo et al., 2002). Natural organic matter may also complex with As and inhibit arsenic adsorption onto iron (hydr) oxides due to competitive adsorption reactions (Xu et al., 1991; Redman et al., 2002). Other anions, such as Cl^-, SO_4^{2-}, and NO_3^-, appear to have minimal impacts on As desorption, yet these ions can contribute to ionic strength and salinization effects on As desorption in sediments (Gupta and Chen, 1978; Smith et al., 1998).

In most soils and sediments, total As levels correlate with iron content rather than aluminum or clay content (Smedley and Kinniburgh, 2002), and microbial reduction of Fe(III) in the iron (hydr)oxide minerals may release Fe(II) and adsorbed As(V) or As(III) into solution (Cummings et al., 1999; Langner and Inskeep, 2000; Herbel and Fendorf, 2005). The most readily bioreducible Fe(III) (hydr)oxides are the high surface area, least thermodynamically stable phases such as ferrihydrite and lepidocrocite (Schwertmann and Taylor, 1989; Lovley, 1991; Roden and Zachara, 1996). Ferrous iron produced during Fe(III) reduction induces a transformation of ferrihydrite (or lepidocrocite) to more stable Fe (III) minerals, such as goethite (α-FeOOH), and mixed Fe(II)–Fe(III) minerals, such as magnetite (Fe_3O_4) (Zachara et al., 2002; Hansel et al., 2003). Despite having a nearly equal affinity for arsenic, transformation of ferrihydrite to more crystalline phases (goethite, hematite, or magnetite) almost universally decreases their available surface area and thus diminishes their capacity to retain arsenic (Dixit and Hering, 2003; Herbel and Fendorf, 2005).

Microbial reduction of arsenate to arsenite may also impact arsenic retention. Arsenate-respiring bacteria and archaea have recently been isolated from a diversity of natural environments, including freshwater streams and sediments, alkaline and saline lakes, and hot springs (Stolz and Oremland, 1999; Huber et al., 2000; Oremland et al., 2002; Oremland and Stolz, 2003). Arsenic-respiring bacteria are not only capable of reducing soluble arsenate, but also adsorbed arsenate (Herbel and Fendorf, 2005) and arsenate within solids such as scorodite (Newman et al., 1997), with recent evidence suggesting reduction first proceeds through a dissolution step (Saltikov and Newman, 2003). Dissimilatory arsenate reduction may enhance the solubility of As, particularly in environments with low iron (hydr)oxide content given the specificity arsenite shows for ferric phases. Zobrist et al. (2000), for example, showed that reduction of As (V) adsorbed or coprecipitated on amorphous aluminum hydroxides by *Sulfospirillium barnesii* greatly increased dissolved As(III) concentrations.

Arsenic desorption appears to be enhanced most appreciably by a transition from aerobic to anaerobic conditions (Hounslow, 1980; Meng et al., 2001; Inskeep et al., 2002; Smedley and Kinniburgh, 2002; Takahashi