The role of alluvial aquifer sediments in attenuating a dissolved arsenic plume

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ABSTRACT

In a crude-oil-contaminated sandy aquifer at the Bemidji site in northern Minnesota, biodegradation of petroleum hydrocarbons has resulted in release of naturally occurring As to groundwater under Fe-reducing conditions. This study used chemical extractions of aquifer sediments collected in 1993 and 2011–2014 to evaluate the relationship between Fe and As in different redox zones (oxic, methanogenic, Fe-reducing, anoxic-suboxic transition) of the contaminated aquifer over a twenty-year period. Results show that 1) the aquifer has the capacity to naturally attenuate the plume of dissolved As, primarily through sorption; 2) Fe and As are linearly correlated in sediment across all redox zones, and a regression analysis between Fe and As reasonably predicted As concentrations in sediment from 1993 using only Fe concentrations; 3) an As-rich "iron curtain," associated with the anoxic-suboxic transition zone, migrated 30 m downgradient between 1993 and 2013 as a result of the hydrocarbon plume evolution; and 4) silt lenses in the aquifer preferentially sequester dissolved As, though As is remobilized into groundwater from sediment after reducing conditions are established. Using results of this study coupled with historical data, we develop a conceptual model which summarizes the natural attenuation of As and Fe over time and space that can be applied to other sites that experience As mobilization due to an influx of bioavailable organic matter.

1. Introduction

The mobilization of naturally occurring arsenic (As) to groundwater from aquifer minerals poses a threat to human health. An estimated 130 million people worldwide are at risk for diseases related to As concentrations in drinking water exceeding the World Health Organization (WHO) and U.S. Environmental Protection Agency (USEPA) standard of 10 μg/L (Ravenscroft et al., 2009); long-term exposure to As concentrations > 10 μg/L has been linked to skin, lung, and bladder cancers (Knobeloch et al., 2006; Nordstrom, 2002; Smith et al., 2002).

A notable example of elevated As concentrations in groundwater associated with alluvial aquifers is Southeast Asia (Nordstrom, 2002), where release of naturally occurring As from alluvial and deltaic sediments to groundwater has resulted in widespread As poisoning for the past 30–40 years (Harvey et al., 2002; McArthur et al., 2004; Mukherjee et al., 2006; Ravenscroft et al., 2009). Elevated concentrations of As have also been documented in other alluvial aquifers, including regions of northern China (Luo et al., 1997; Ma et al., 1999), Hungary and Romania (Lindberg et al., 2006; Varsányi and Kovács, 2006), and Argentina (Bhattacharya et al., 2006), and in glacially derived aquifers in

the Midwestern United States (Erickson and Barnes, 2005; Kelly et al., 2005; Korte, 1991; Root et al., 2010; Warner, 2001).

In alluvial aquifers, As often associates with Fe, Mn, and Al hydroxides (McArthur et al., 2001; Smedley and Kinniburgh, 2002). Arsenic association with ferric (Fe(III)) hydroxides is particularly important due to the strong sorption affinity between As and Fe(III) and the abundance of Fe(III) hydroxides in alluvial aquifer sediments (De Vitre et al., 1991; Manning and Goldberg, 1996; Pierce and Moore, 1982; Stollenwerk, 2003). When As is sorbed to Fe(III) hydroxides, and groundwater has circumneutral pH, the Fe(III) hydroxide is thermodynamically stable, and As remains associated with sediment. However, the presence of bioavailable organic carbon (BOC) can spur microbial activity that rapidly consumes oxygen in groundwater. Following oxygen depletion, reducing geochemical conditions promote microbially mediated reduction of Fe(III) hydroxides coupled with the oxidation of organic carbon, releasing aqueous Fe(II) and previously adsorbed As to groundwater (McArthur et al., 2001; McArthur et al., 2004; Nickson et al., 1998; Nickson et al., 2000; Smedley et al., 2002).

The mobilization of As due to biodegradation of natural BOC is well-documented (see Smedley and Kinniburgh (2002) for review).

Heterogeneously distributed accumulations of solid-phase natural BOC in aquifers can trigger reducing conditions that promote As mobilization (Whaley-Martin et al., 2016). However, recent work has documented that anthropogenic sources of organic matter, including petroleum hydrocarbon and biofuels plumes (Cozzarelli et al., 2016; Hering et al., 2009; Ziegler et al., 2015), sewage plumes (Amirbahman et al., 2006; Kent and Fox, 2004), and landfills (deLemos et al., 2006; Keimowitz et al., 2005) can also generate the conditions necessary to mobilize naturally occurring As from aquifer sediments.

In addition to influencing the release of As to groundwater in alluvial aquifers, redox (bio)geochemistry can also play an important role in mitigating As transport in groundwater in these systems. Geochemical conditions that promote oxidization of dissolved Fe(II) to solid Fe(III) hydroxides generates new sorption sites for As (Amirbahman et al., 2006; Giménez et al., 2007; He et al., 2010; Hering et al., 2009; Stollenwerk et al., 2007; West et al., 2012). Mechanisms that have been documented for As sequestration due to oxidation include: 1) precipitation of Fe(III) minerals, followed by re-sorption of dissolved As (Giménez et al., 2007; Hering et al., 2009; Stollenwerk, 2003); 2) co-precipitation of As in the Fe-hydroxide crystal structure (Fuller et al., 1993; Gorra et al., 2012); and 3) oxidation of arsenite (As(III)) to the less mobile arsenate (As(V)) at circumneutral-to-acidic pH, spurring re-sorption of As(V) to sediment (Amirbahman et al., 2006; Stollenwerk et al., 2007; Zhao et al., 2011). Although oxidation is an important process for the retention of dissolved As, As can also be sequestered by other Fe-bearing aquifer minerals (e.g., siderite, ferroan calcite, magnetite) in the absence of oxygen (Guo et al., 2011; Guo et al., 2007a; Jönsson and Sherman, 2008).

Despite the abundant literature on the mobilization and transport of As in groundwater in alluvial aquifers, there is much to be learned about the mechanisms of As cycling. Evaluating how naturally occurring As is both released from, and potentially sequestered within, sediment is critical for optimizing the long-term management of As-contaminated aquifers and design of remediation systems. Two interrelated challenges arise in studying As cycling between groundwater and sediments during biodegradation of natural BOC. First, natural BOC is often heterogeneously dispersed in aquifers, and the areas where As can be mobilized are also heterogeneous, resulting in a "patchy" distribution of dissolved As (Erickson and Barnes, 2005; Pal et al., 2002; Quicksall et al., 2008; Root et al., 2010; Rowland et al., 2007). Second, the dispersed nature of natural BOC often creates intermittent periods of reducing conditions during water-table fluctuations or recharge events that promote As mobilization into groundwater and oxic-suboxic conditions that favor As retention by aquifer sediments (McArthur et al., 2004). Combined, these two factors make it difficult to monitor time series changes in As concentrations in aquifer sediments, and thus, to evaluate larger patterns of As cycling, including ability of the aquifer to attenuate As.

This study investigates the role of aquifer sediments in attenuating As in groundwater under long-term reducing conditions. This study is focused on a crude-oil spill site near Bemidji, MN, where biodegradation of petroleum hydrocarbons coupled with Fe-reduction has resulted in the mobilization of naturally occurring As from aquifer sediments into groundwater, creating a plume of dissolved As (Cozzarelli et al., 2016). Hydrocarbons have been in place at the site for more than three decades (the spill occurred in 1979), and estimates suggest that the hydrocarbons will be present in the aquifer for another ~75 years (Revesz et al., 1995), though Bekins et al. (2005) cautioned that biodegradation rates quantified early in life of the plume might not accurately reflect future biodegradation rates due to depletion of electron acceptors, and thus, the life span of the plume might be longer than original estimates. Given the well-documented history of this site, we have a unique opportunity to examine the complex interactions of As with Fe in the aquifer sediment under more controlled conditions due to the breadth of literature characterizing the Bemidji aquifer and geochemical reactions occurring in the plume than is typical for most As-contaminated aquifers. The presence of BOC has also created redox zones (methanogenic, Fe reducing, oxic) in the aquifer that have changed over time, which also allows the opportunity to evaluate how As mobilization from sediments to groundwater changes as redox conditions evolve. In this study, we analyzed chemical and physical characteristics of sediment cores collected from the oil-spill site and used modern and historical groundwater chemistry data to 1) examine interactions of As and Fe in aquifer sediments in different redox zones of the modern plume, and 2) compare As-Fe patterns in sediment from the modern plume to those in 1993. We use the results to develop a conceptual model that describes the distribution of Fe and As over space and time in an aquifer with an ample source of organic carbon.

2. Methods

2.1. Study site

In 1979, a crude oil pipeline ruptured near Bemidji, MN and sprayed 10,700 barrels of crude oil onto glacial outwash deposits (Pfannkuch, 1979). After clean-up efforts, 2600 barrels of oil remained in the subsurface floating on the water table, causing hydrocarbons to dissolve into groundwater, creating a dissolved hydrocarbon plume (Fig. 1). The Bemidji spill site is a U.S. Geological Survey (USGS)-sponsored National Crude Oil Spill Research Site. At the site, the hydrocarbon plume is naturally attenuated by biodegradation coupled mainly with Fe reduction, with a heterogeneous methanogenic zone near the oil body (Bekins et al., 2005; Bekins et al., 2001; Cozzarelli et al., 2001).

The aquifer is comprised mainly of gravel, sand, and silt originating from crystalline and carbonate source rocks deposited by glacial activity (Bennett et al., 1993). Uncontaminated sediments have roughly 1% Fe content with complex Fe mineralogy, including silicates (epidote, clinochlore, and muscovite), oxides and hydroxides (goethite, hematite, magnetite, and a ferrihydrite-like phase), and to a lesser degree, carbonates (ferroan calcite) (Zachara et al., 2004). Groundwater in the plume has a typical pH range of ~6.5 to 7.5, with pH near the oil body being on the lower end of the range. Concentrations of other common potential electron acceptors (e.g., nitrate and sulfate) are low or non-detectable in groundwater. Bicarbonate is elevated in contaminated groundwater due to biodegradation reactions.

Cozzarelli et al. (2016) recently reported findings of elevated concentrations of As (> 230 μg/L) in groundwater in the anoxic plume at Bemidji. Using groundwater chemistry from wells inside and outside of the plume, along with chemical digestions of uncontaminated sediments, Cozzarelli et al. (2016) showed that As was mobilized into groundwater due to the biodegradation of dissolved hydrocarbons coupled with Fe-reduction. The plume of As co-occurs with the anoxic plume where there are also elevated concentrations of benzene and dissolved Fe. The highest As concentrations (100–230 μg/L) were detected in groundwater near the oil body, largely defined as a methanogenic zone based on geochemical and microbiological data (Bekins et al., 2001; Cozzarelli et al., 2001). Elevated As (10–100 μg/L) is also detected in Fe-reducing groundwater, defined by dissolved Fe > 1 mg/L (Cozzarelli et al., 2016). Concentrations of Fe and As in groundwater gradually decrease with distance from the oil body in the plume, and eventually are below detection in the "transition" zone at the leading edge of the plume where anoxic groundwater from the plume mixes with regionally oxic groundwater. Upgradient and downgradient from the plume where groundwater is oxic, As concentrations in groundwater are below detection (< 1 μg/L). Together, these data support the hypothesis that microbially mediated Fe-reduction within the plume is responsible for As release, and that As re-associates with aquifer sediments when groundwater chemistry becomes more oxic downgradient from the plume.