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# A mass balance approach to investigate arsenic cycling in a petroleum plume<sup>☆</sup>

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## ABSTRACT

Natural attenuation of organic contaminants in groundwater can give rise to a series of complex biogeochemical reactions that release secondary contaminants to groundwater. In a crude oil contaminated aquifer, biodegradation of petroleum hydrocarbons is coupled with the reduction of ferric iron (Fe(III)) hydroxides in aquifer sediments. As a result, naturally occurring arsenic (As) adsorbed to Fe(III) hydroxides in the aquifer sediment is mobilized from sediment into groundwater. However, Fe(III) in sediment of other zones of the aquifer has the capacity to attenuate dissolved As via resorption. In order to better evaluate how long-term biodegradation coupled with Fe-reduction and As mobilization can redistribute As mass in contaminated aquifer, we quantified mass partitioning of Fe and As in the aquifer based on field observation data. Results show that Fe and As are spatially correlated in both groundwater and aquifer sediments. Mass partitioning calculations demonstrate that 99.9% of Fe and 99.5% of As are associated with aquifer sediment. The sediments act as both sources and sinks for As, depending on the redox conditions in the aquifer. Calculations reveal that at least 78% of the original As in sediment near the oil has been mobilized into groundwater over the 35-year lifespan of the plume. However, the calculations also show that only a small percentage of As (~0.5%) remains in groundwater, due to resorption onto sediment. At the leading edge of the plume, where groundwater is suboxic, sediments sequester Fe and As, causing As to accumulate to concentrations 5.6 times greater than background concentrations. Current As sinks can serve as future sources of As as the plume evolves over time. The mass balance approach used in this study can be applied to As cycling in other aquifers where groundwater As results from biodegradation of an organic carbon point source coupled with Fe reduction.

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## 1. Introduction

Monitored natural attenuation is commonly employed as a remediation strategy in aquifers impacted by organic contaminants (National Research Council, 2000). Several natural processes, including adsorption (Brusseau et al., 1989; Eganhouse et al., 1993; Chaplin et al., 2002; Cozzarelli et al., 2010; Eganhouse et al., 2001), and biodegradation (Borden and Bedient, 1986; Cerniglia, 1993; Cozzarelli et al., 1990) limit the large-scale transport of organic contaminants. Although these processes can attenuate the organic

contaminants, the reactions can create secondary water quality impacts that can also diminish groundwater quality. Examples include depletion of dissolved oxygen (DO) (Baedecker et al., 1993; Rees, 1980), microbial reduction and mobilization of iron (Fe) and manganese (Mn) (Baedecker et al., 1993; Jones et al., 1984; Lovley et al., 1989), increased concentrations of methane (Baedecker et al., 1993; Dojka et al., 1998), and changes in pH (Bennett et al., 1993). One of the most important secondary effects in terms of potential human health impacts is the mobilization of arsenic (As), a toxic trace element that naturally exists in aquifer sediments.

Arsenic is a human toxin and carcinogen that poses a threat to human health via ingestion. The World Health Organization has set a drinking water standard of 10 µg/L for As in drinking water. Above this threshold, chronic exposure to As in drinking water has been linked to skin, lung, and bladder cancers (Knobeloch et al., 2006; Nordstrom, 2002; Smith et al., 2000). Most As in groundwater is

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derived from geogenic sources, though anthropogenic activity can cause changing conditions that allows As to be mobile in groundwater (Smedley and Kinniburgh, 2002). Worldwide, an estimated 150 million people have been exposed to unsafe levels of As in drinking water (Ravenscroft et al., 2009).

In oxic, unconsolidated aquifers, naturally occurring As is commonly associated with Fe(III) oxyhydroxide minerals due to a strong sorption affinity (McArthur et al., 2001; Smedley and Kinniburgh, 2002). However, the presence of bioavailable organic carbon can trigger microbial depletion of DO and subsequent reduction of alternate electron acceptors, including solid phase Fe(III) minerals. Reductive dissolution of Fe(III) oxyhydroxides can result in the mobilization of previously sorbed As to groundwater (Cozzarelli et al., 2016; McArthur et al., 2001; Nordstrom, 2002; Ravenscroft et al., 2009; Smedley, 2003). Additionally, oxidation of organic carbon can be coupled with reduction of naturally occurring As(V) to As(III), which can also promote As mobilization (Tufano et al., 2008). The presence of sulfur can further complicate As cycling by the formation of aqueous thioarsenic complexes (Stucker et al., 2014) and As-bearing sulfide minerals (Harper and Kingham, 1992; Kirk et al., 2004).

Arsenic release under Fe(III)-reducing conditions can be caused by both natural and anthropogenic sources of organic carbon. For example, biodegradation of natural organic carbon in fluviodeltaic aquifers in Southeast Asia is associated with widespread As levels exceeding 10 µg/L, exposing more than 110 million people in the region to unsafe drinking water (Ravenscroft et al., 2009). Although natural organic matter can trigger Fe reduction and As release, human activity can exacerbate the reactions by adding new sources of natural organic matter to the aquifer or changing the hydrogeologic systems. For example, in Bangladesh, natural organic matter in the aquifer can cause Fe-reduction and As release (Polizzotto et al., 2008), but additional organic matter originating from constructed ponds used for groundwater irrigation of rice fields can cause further Fe reduction and As release (Neumann et al., 2010). Neumann et al. (2014) showed that sedimentary organic matter was stable and not bioavailable to microbes until recharge was introduced, dissolving the sediment-associated organic matter. On smaller scales, As can also be mobilized in aquifers contaminated by anthropogenic organic carbon such as from petroleum and biofuel spills (Cozzarelli et al., 2016; Hering et al., 2009; Ziegler et al., 2015), sewage (Amirbahman et al., 2006; Kent and Fox, 2004; Whaley-Martin et al., 2017), and landfills (deLemos et al., 2005; Keimowitz et al., 2005).

Because As in groundwater is toxic at low concentrations, understanding how As is released from geogenic sources, i.e. how the mass is partitioned between solid and aqueous phases in aquifers, is critical for predicting potential As contamination. However, quantifying As mass distribution in aquifers is challenging because of the complexity of biogeochemical processes that influence its cycling, including: pH-dependent protonation reactions; pH-dependent adsorption reactions (Dixit and Hering, 2003; Pierce and Moore, 1982; Raven et al., 1998); microbially mediated redox reactions involving both Fe and As (Kocar et al., 2006; McArthur et al., 2001; Nordstrom, 2002; Ravenscroft et al., 2009; Tufano et al., 2008); and dissolution and precipitation reactions of As-bearing minerals (Schreiber et al., 2000; Walker et al., 2006). In addition, sediment type can influence reactive transport of As. For example, fine-grained sediment can sorb As in more appreciable amounts than coarse sediment. Thus fine-grained sediments can potentially release As to groundwater for a longer time at a constant rate compared to coarser sediment because the initial sediment As concentration is higher (Ziegler et al., 2017a).

Additional complications for making quantitative assessments of As mass exchanges between sediment and groundwater include

the often extreme spatial heterogeneity, bioavailability and biodegradation kinetics of the carbon source that drives As mobilization. For example, in the fluviodeltaic aquifers in Southeast Asia, spatially heterogeneous organic matter can cause dissolved As concentrations in some wells to increase, remain constant for a period, or decrease over time (McArthur et al., 2004). In the Midwestern U.S., heterogeneous and stratigraphically discontinuous glacial sediments with varying amounts of organic matter also has led to challenging predictions of As in aquifers (Erickson and Barnes, 2005; Root et al., 2010). This challenge can be simplified at an oil spill site, where there is better understanding of the organic matter and its quantity, spatial distribution, and bioavailability. Compared to natural organic carbon, a defined anthropogenic organic carbon source, such as a hydrocarbon plume, provides the opportunity to study how a plentiful and highly bioavailable carbon source influences Fe reduction and As mobilization, resulting in changes in the mass distribution of naturally occurring As in aquifers over time.

This study quantitatively describes the partitioning of As and Fe between groundwater and aquifer sediment within a hydrocarbon plume at an oil spill site near Bemidji, Minnesota. Biodegradation of petroleum hydrocarbons has created a plume of dissolved As that is naturally attenuated by an Fe(III)-rich “curtain” at the sub-oxic leading edge of the plume (Ziegler et al., 2017a). However, historical data suggest that As attenuated by the Fe curtain is not permanently sequestered, but later can be remobilized if reducing conditions are established due to plume expansion over time (Ziegler et al., 2017a). The goal of this study is to quantify how long-term continuous Fe-reducing conditions resulting from hydrocarbon biodegradation trigger As cycling and redistribute As mass in the aquifer. Improved methods for quantifying As mass redistribution are vital to assessing long-term aquifer vulnerability to As contamination. Using this approach can help in developing necessary mitigation strategies as evolving geochemical conditions may promote future mobilization or sequestration of As, which is not commonly monitored at organic-contaminated sites.

### 1.1. Study site

In 1979, a crude oil pipeline ruptured near Bemidji, MN, releasing 10,700 barrels of crude oil to a shallow unconfined aquifer (Pfannkuch, 1979). Clean-up efforts were able to remediate much of the oil, but about 25% of the spilled oil infiltrated into the subsurface where it settled on the water table, creating a plume of dissolved hydrocarbons in groundwater. In 1983, the spill site became a U.S. Geological Survey (USGS) sponsored research site through the Toxics Substances Hydrology Program. The site has been intensively studied and monitored for more than 35 years to describe natural attenuation of petroleum hydrocarbons (Bekins et al., 2001, 2005; Cozzarelli et al., 2001; Essaid et al., 2011). The vast historic database containing information on biodegradation and other natural attenuation processes makes it an ideal site to investigate less understood, secondary processes that occur at oil-contaminated sites.

The shallow alluvial aquifer is highly heterogeneous, comprised mostly of silt, sand, and gravel derived from crystalline and carbonate sources and deposited by glacial outwash (Bennett et al., 1993). Groundwater velocity estimates range from 0.05 m/d in the silty layers to 0.5 m/d in the coarse sediments (Bennett et al., 1993). A tracer test estimate yielded an average linear velocity of 0.06 m/d (Essaid et al., 2003). Several studies have provided detailed descriptions of the hydrogeology and geochemical evolution of the hydrocarbon plume at the Bemidji site (Baedecker et al., 1993; Bekins et al., 2001; Bennett et al., 1993; Cozzarelli et al., 2001). A detailed study of aquifer mineralogy at the site showed

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