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Arsenic release from Floridan Aquifer rock during incubations simulating aquifer storage and recovery operations

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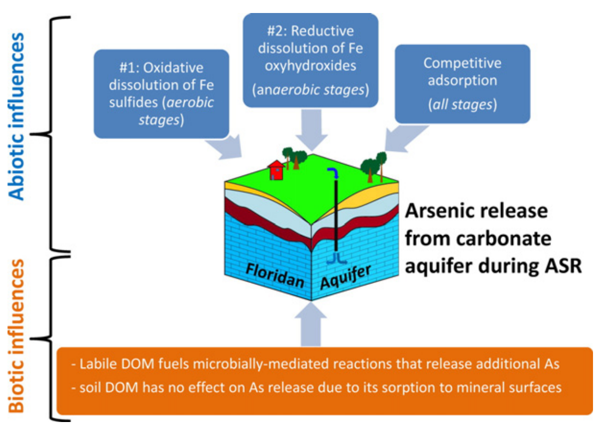
HIGHLIGHTS

- Floridan Aquifer rock was incubated under conditions mimicking ASR operations.
- As released via reductive dissolution at the start of anaerobic periods
- As released via oxidation of Fe sulfides during aerobic periods
- Labile DOM additions enhanced As releases, but refractory DOM did not.
- Redox oscillation, which occurs during ASR, causes As release.

GRAPHICAL ABSTRACT



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ABSTRACT

While aquifer storage and recovery (ASR) is becoming widely accepted as a way to address water supply shortages, there are concerns that it may lead to release of harmful trace elements such as arsenic (As). Thus, mechanisms of As release from limestone during ASR operations were investigated using 110-day laboratory incubations of core material collected from the Floridan Aquifer, with treatment additions of labile or refractory dissolved organic matter (DOM) or microbes. During the first experimental phase, core materials were equilibrated with native groundwater lacking in DO to simulate initial non-perturbed anaerobic aquifer conditions. Then, ASR was simulated by replacing the native groundwater in the incubations vessels with DO-rich ASR source water, with DOM or microbes added to some treatments. Finally, the vessels were opened to the atmosphere to mimic oxidizing conditions during later stages of ASR.

Arsenic was released from aquifer materials, mainly during transitional periods at the beginning of each incubation stage. Most As released was during the initial anaerobic experimental phase via reductive dissolution of Fe oxides in the core materials, some or all of which may have formed during the core storage or sample preparation period. Oxidation of *As*-bearing Fe sulfides released smaller amounts of As during the start of later aerobic experimental phases. Additions of labile DOM fueled microbially-mediated reactions that mobilized As, while the addition of refractory DOM did not, probably due to mineral sorption of DOM that made it unavailable for microbial

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utilization or metal chelation. The results suggest that oscillations of groundwater redox conditions, such as might be expected to occur during an ASR operation, are the underlying cause of enhanced As release in these systems. Further, ASR operations using DOM-rich surface waters may not necessarily lead to additional As releases.

1. Introduction

Arsenic (As) in drinking water is considered a major environmental concern worldwide as it is a cause of cancer and other serious ailments (Nordstrom, 2002; Ravenscroft et al., 2009; Smith et al., 1992). Thus, the release of As from rocks, sediments and soils into groundwater poses a serious threat to world's water resources as well as to human health (Harvey et al., 2002; Nordstrom, 2002; Smedley and Kinniburgh, 2002). Arsenic contamination in groundwater is of greatest concern in areas like Florida, where the entire population relies primarily on groundwater for drinking water and irrigation.

Aquifer storage and recovery (ASR) is a hydrogeologic operation that involves injection of surface water into a confined aquifer, where it is stored for later use (Lazareva et al., 2015; Pyne, 2005). It is an effective water management strategy and has been implemented to meet increasing water demand in many regions in the world (Antoniou et al., 2012; Izbicki et al., 2010; Vanderzalm et al., 2011), including Florida (Arthur et al., 2005; Williams et al., 2002). However, release of As from aquifer materials into groundwater has occurred at many ASR sites (Antoniou et al., 2014; Jones and Pichler, 2007; Mirecki et al., 2012; Vanderzalm et al., 2011). In Florida, As concentrations of up to 130 μg/L in ASR-produced groundwater have been recorded (Arthur et al., 2005; Arthur et al., 2002; Williams et al., 2002), far exceeding drinking water standards of 10 μg/L (USEPA, 2009; WHO, 2004).

Three mechanisms of As mobilization from geologic materials are commonly proposed: 1) reductive dissolution of *As*-bearing minerals such as iron (Fe) oxides/oxyhydroxides (Anawar et al., 2003; Harvey et al., 2002; Swartz et al., 2004), 2) oxidative dissolution of As-bearing minerals such as pyrite (Arthur et al., 2005; Arthur et al., 2002; Jones and Pichler, 2007; Lazareva et al., 2015), and 3) desorptive release due to exchange of surface-associated As with other chemical species such as bicarbonate (Dang Duc et al., 2013; Saalfield and Bostick, 2010; Swartz et al., 2004). Leaching experiments conducted under different redox conditions are needed to identify how and when ASR is likely to lead to As mobilization. Thus far, there has only been one such study (Lazareva et al., 2015) and this one was conducted in a flow-through column type system and over a relatively short time scale (6 h).

Dissolved organic matter (DOM) is also known to play an important role in governing the cycling of metals in the subsurface (Dang et al., 2014; Lee et al., 2005a). The direct and indirect association between DOM and As mobility in groundwater has drawn the attention of researchers studying a range of systems globally (e.g., Al Lawati et al., 2012; Anawar et al., 2013; McArthur et al., 2004). For example, a strong correlation between DOM and aqueous As concentrations was reported for aquifers in southern China (Wang et al., 2012) and Bangladesh (Anawar et al., 2011; Reza et al., 2010). More specifically, in the Bangladesh aquifer, not only did DOM drive the mobilization of As via reductive dissolution of Fe oxyhydroxides, but it was, itself, a source of As (Anawar et al., 2013). A recent study in the Datong Basin in China found both a role of labile DOM in promoting As release by driving the system toward anoxia and of quinone-like humic substances in acting as electron shuttles, enhancing As mobilization via facilitation of reductive dissolution (Pi et al., 2015).

Although the influence of DOM on As mobilization is attracting more research attention, most studies have examined systems such as the sandy Bangladesh/West Bengal aquifer where As is bound to Fe oxyhydroxides (e.g., Anawar et al., 2013). Few of these types of studies have examined As mobilization in carbonate systems such as the Floridan Aquifer where As is thought to be associated primarily with pyrite (Jones and Pichler, 2007; Lazareva et al., 2015; Price and Pichler, 2006). Presently, by state regulation, water injected into ASR wells in Florida must meet Florida's drinking water quality standards (Mirecki, 2004; Reese and Alvarez-Zarikian, 2007), since there are concerns that injecting untreated surface waters (likely rich in organic matter, or OM) may lead to groundwater contamination, possibly via As release (Arthur et al., 2005; Williams et al., 2002). However, Floridan Aquifer materials contain and release OM (Jin and Zimmerman, 2010) and use of surface waters to recharge aquifers is being considered. No study, to our knowledge, has examined how DOM may influence As mobilization in during ASR. Thus, this study aims to 1) identify the mechanism(s) leading to mobilization of As from Floridan Aquifer carbonate rocks during ASR operations, and 2) examine the potential influences of biotic/DOM reactions on As release. The relative importance of reductive dissolution, oxidative dissolution, and As desorption, were tested by manipulating redox conditions and solution chemistry in laboratory incubations. Treatment amendments of microbial extracts, refractory DOM (soil extracts) and labile DOM (Na-acetate) were added to test whether As mobilization was stimulated by microbially-mediated or abiotic DOM reactions.

2. Materials and methods

Laboratory incubations of preserved Floridan Aquifer carbonate core material in sealed reaction vessels were carried out in three experimental phases, designed to simulate the likely stages of an ASR operation. In the first phase of the experiment, core material that had been stored anaerobically was equilibrated with native groundwater (NGW) to attain pre-injection background conditions in the aquifer. In the second phase, the ASR injection process was simulated by replacing the NGW in the vessels with typical ASR source water (SW) containing a fixed amount of oxygen. Some vessels were also treated with additions of microbes and/or labile or refractory DOM at this point. In the last phase, the vessels were opened to the atmosphere to provide an unlimited oxygen supply to the system. These three experimental phases are designated as 'NGW', 'SW/N_2 headspace', and 'SW/Air headspace', respectively, in the following figures and discussion.

2.1. Aquifer core materials

Detailed core collection and preservation procedures are described elsewhere (Norton, 2011). In brief, the entire thickness of the Suwannee Limestone Formation, from 290 to 480 ft below ground surface (bgs), was cored at the Southwest Florida Water Management District (SWFWMD) ROMP TR 9-1 well site in Hillsborough County, FL (27° 44′ 16″N, 82° 27′ 38″W, Appendix Fig. A.1). Cores were collected using the SWFWMD's wire-line coring rig (CME-85 drill rig) and a 2-inch core barrel. Surface casings were installed, prior to coring, to maintain bore-hole competence within the upper unconsolidated sediments and to prevent cross-connection of waters between productive intervals of the Hawthorn Group, including the Arcadia Formation and its Tampa Member, and the underlying Suwannee Limestone.

To minimize atmospheric exposure during drilling, the new borehole was allowed to flow under artesian pressure overnight before core retrieval. Upon retrieval, the cores were placed onto 5-ft sections of longitudinally split 2-inch Sch. 40 PVC. The two halves were then taped together and the cores were placed in cylindrical core containers constructed of 3-inch Sch. 80 PVC pipe, fitted with gas-tight seals and valves. The core containers were then immediately N_2-flushed and evacuated three times and, finally, sealed under positive N_2 pressure