



# Arsenic mobilization from sediments in microcosms under sulfate reduction



Jing Sun <sup>a, b</sup>, Andrew N. Quicksall <sup>c</sup>, Steven N. Chillrud <sup>b</sup>, Brian J. Mailloux <sup>d</sup>, Benjamin C. Bostick <sup>b, \*</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, Columbia University, Mail Code 5505, New York, NY 10027, USA

<sup>b</sup> Lamont-Doherty Earth Observatory of Columbia University, PO Box 1000, 61 Route 9W, Palisades, NY 10964, USA

<sup>c</sup> Department of Civil and Environmental Engineering, Southern Methodist University, 3101 Dyer Street, Dallas, TX 75205, USA

<sup>d</sup> Department of Environmental Sciences, Barnard College, 3009 Broadway, New York, NY 10027, USA

## HIGHLIGHTS

- Microcosms with sediments from two distinct contaminated sites are conducted.
- Sulfate reduction is stimulated to examine the effect on immobilizing arsenic.
- Arsenic in the microcosms as conducted releases from sediments to solution.
- Reactive iron(III) affects the efficiency of arsenic retention by metal sulfides.

## ARTICLE INFO

### Article history:

Received 20 June 2015

Received in revised form

19 February 2016

Accepted 28 February 2016

Available online 31 March 2016

Handling Editor: X. Cao

### Keywords:

Arsenic

Sulfate reduction

Iron(III) minerals

Contaminated sediments

Microcosm experiment

## ABSTRACT

Arsenic is often assumed to be immobile in sulfidic environments. Here, laboratory-scale microcosms were conducted to investigate whether microbial sulfate reduction could control dissolved arsenic concentrations sufficiently for use in groundwater remediation. Sediments from the Vineland Superfund site and the Coeur d'Alene mining district were amended with different combination of lactate and sulfate and incubated for 30–40 days. In general, sulfate reduction in Vineland sediments resulted in transient and incomplete arsenic removal, or arsenic release from sediments. Sulfate reduction in the Coeur d'Alene sediments was more effective at removing arsenic from solution than the Vineland sediments, probably by arsenic substitution and adsorption within iron sulfides. X-ray absorption spectroscopy indicated that the Vineland sediments initially contained abundant reactive ferrihydrite, and underwent extensive sulfur cycling during incubation. As a result, arsenic in the Vineland sediments could not be effectively converted to immobile arsenic-bearing sulfides, but instead a part of the arsenic was probably converted to soluble thioarsenates. These results suggest that coupling between the iron and sulfur redox cycles must be fully understood for *in situ* arsenic immobilization by sulfate reduction to be successful.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Arsenic is a well-known human carcinogen, and consumption of water containing unsafe levels of dissolved arsenic also causes cardiovascular disease and inhibits intellectual development of children (Chen et al., 2009; Wasserman et al., 2004). Unfortunately, groundwater arsenic contamination is currently a global problem

and also a concern at numerous former mining operations and industrial sites in the United States (Mandal and Suzuki, 2002). So far, groundwater arsenic contamination has been difficult to remediate in a timely and cost effective manner (EPA, 2002; EPA, 2013). One attractive option for remediating groundwater arsenic is *in situ* immobilization, which removes dissolved arsenic from groundwater by precipitating and/or adsorbing arsenic to the sediment and soil matrix.

Arsenic can form insoluble sulfide minerals, including orpiment (As<sub>2</sub>S<sub>3</sub>), realgar (AsS) and arsenopyrite (FeAsS), can substitute within a variety of metal sulfides, including mackinawite (FeS),

\* Corresponding author.

E-mail address: [bostick@ldeo.columbia.edu](mailto:bostick@ldeo.columbia.edu) (B.C. Bostick).

greigite (Fe<sub>3</sub>S<sub>4</sub>) and pyrite (FeS<sub>2</sub>), and can exist as a sorption complex on these sulfides (Bostick and Fendorf, 2003; Burton et al., 2014; Kirk et al., 2010; O'Day et al., 2004). The formation of sulfide minerals is typically achieved through stimulating the activity of indigenous sulfate-reducing bacteria (SRBs) by supplying an electron donor and, in some cases, extra inorganic sulfate to the sediments and soils. Through such processes, dissolved arsenic can be converted to immobile arsenic-bearing sulfides under some conditions (Burton et al., 2014; Omoregie et al., 2013; Onstott et al., 2011). However, the formation of reduced sulfides also can be recycled and can enhance the solubility of arsenic as thiolated arsenic compounds (Burton et al., 2011; Keimowitz et al., 2007; ocar et al., 2010; Poulton et al., 2004; Saalfield and Bostick, 2009). These potential complications have made it difficult to determine under which conditions the sulfide-based strategy can or cannot be reliably applied in groundwater arsenic immobilization technologies.

The objectives of this study were to stimulate sulfate reduction and sulfide production within microcosms containing sediments from arsenic-contaminated sites, and to evaluate the effect of sulfide production on immobilizing arsenic. The sediments were from two distinct sites in the United States: a Superfund site, the Vineland Chemical Company site, and a former heavy metal sulfide mining site, the Coeur d'Alene mining district. The geochemical evolution of solution composition and sediment mineralogy/speciation were traced concurrently in these microcosms. The data suggest that coupling between iron and sulfur cycling can preclude sulfate reduction from producing insoluble arsenic-bearing sulfides, and that the long-term stability of the sulfide-based immobilization strategy also merits careful evaluation.

## 2. Materials and methods

### 2.1. Site and sample information

The Vineland Chemical Company Superfund site is located in southern New Jersey. Arsenic contamination at the Vineland site resulted from improper storage of arsenic-containing herbicides and salts between 1949 and 1994. A large pump-and-treat (P&T) system, as well as several other strategies, are involved in the current site mitigation activities. Descriptions of the Vineland site have been previously reported (Sun et al., 2016; Wovkulich et al., 2014). The sediments used in this study were derived from a pit that was freshly dug down below the water table. Immediately after retrieval, the sediment were homogenized and sealed in new epoxy-lined metal paint cans. The Vineland sediments are composed of mostly quartz (no other minerals can be detected by powder X-ray diffraction). Bulk sediment arsenic, iron and manganese concentrations are 123, 1190 and 12 mg kg<sup>-1</sup>, respectively, based on acid digestion. The groundwater used was collected from a P&T well (RW-02) adjacent to the sediment collection location. The sediments and groundwater were kept in the dark at 4 °C once collected and brought back to the laboratory for microcosm experiments. The groundwater composition was largely unchanged during transport, with the exception of the small quantity of iron that quickly precipitated out (about 0.1 mg L<sup>-1</sup>).

The Coeur d'Alene mining district is located in northern Idaho. The Coeur d'Alene mining district had large metal sulfide deposits including silver, gold, cadmium, copper, lead and zinc (Hobbs et al., 1965). Since the start of the 20th century, over 72 million tons of mine tailings were dumped into the Coeur d'Alene River (Javorka, 1991). Fluvially reworked tailings and more recent mine dredged sediments have formed thick deposits of contaminated sediments on the modern floodplain and adjacent to the river. Detailed descriptions of the Coeur d'Alene site also have been previously

reported (La Force et al., 2000). The sediments used in this study were collected from a seasonally flooded wetland near the mouth of the Coeur d'Alene River. The sediments were collected during early spring flooding below standing water. Immediately after retrieval, the sediments were homogenized and sealed in plastic bottles. The Coeur d'Alene sediments are composed of primarily quartz with small quantities of feldspar, mica and clay minerals. Bulk sediment arsenic, iron and manganese concentrations are 4, 10,800 and 307 mg kg<sup>-1</sup>, respectively, based on acid digestion. The sediments were kept in the dark at 4 °C once collected and brought back to the laboratory for microcosm experiments.

### 2.2. Microcosm experiments

Homogenized wet sediments from the Vineland site and local groundwater were used for the Vineland microcosms. These Vineland microcosms were performed at room temperature (22 °C) with a suspension density of 50 g L<sup>-1</sup>, in high-density polyethylene bottles. The sediment-groundwater suspensions were pre-equilibrated for 24 h in sealed bottles prior to treatments. The microcosm experiments were performed in duplicate as follows: (i) treatment free, (ii) 10 mM sodium sulfate + 10 mM sodium lactate. The addition of reactive organic carbon, lactate, with extra inorganic sulfate, is a common strategy to stimulate sulfate reduction (Burton et al., 2011, 2014; Omoregie et al., 2013; Onstott et al., 2011; Saalfield and Bostick, 2009). No additional nutrients were added to the microcosms. Although incubations were not made under strictly anaerobic conditions, they were sealed and quickly became anaerobic and maintained those conditions for the duration of the experiment. Traces of oxygen at the onset of the experiment also made the initial experimental conditions similar to the slightly oxidizing conditions typical of Vineland sediments (Sun et al., 2016). The duration of this experiment was 38 days, during which the microcosms were periodically monitored for redox potential (Eh, with respect to the standard hydrogen electrode) and pH, and solution-sediment aliquots were subsampled and filtered to 0.2 μm. The filtered solutions were acidified with hydrochloric acid for elemental composition and dissolved organic carbon (DOC) analyses. The sediments contained on filter membranes were preserved in glycerol immediately (to prevent exposure to oxygen and preserve oxidation state) and frozen (−20 °C) for X-ray absorption spectroscopy (XAS) analysis.

The Coeur d'Alene microcosms were conducted in similar fashion to the Vineland microcosms. Homogenized wet sediments from the Coeur d'Alene site and distilled water with selected treatment, either (i) 10 mM sodium lactate or (ii) 3 mM sodium sulfate + 10 mM sodium lactate, were used in the Coeur d'Alene microcosms. Less sulfate was used to account for the higher background organic matter and sulfate content of these sediments. These microcosms were performed at 30 °C (water bath) with a suspension density of 140 g L<sup>-1</sup>, in high-density polyethylene bottles. The duration of this experiment was 32 days, during which solution-sediment aliquots were periodically subsampled from the microcosms and filtered. The filtered solutions were acidified for elemental composition analysis. The sediments contained on filter membranes were preserved in glycerol and frozen for XAS analysis.

### 2.3. Analytical procedure

#### 2.3.1. Solution analysis

Dissolved elemental concentrations in the solutions from the Vineland microcosms were determined by inductively coupled plasma mass spectrometry (ICP-MS) with a high-resolution Axiom Single Collector instrument (Thermo Elemental, Germany). Germanium was added as an internal response standard and used

Download English Version:

<https://daneshyari.com/en/article/4407639>

Download Persian Version:

<https://daneshyari.com/article/4407639>

[Daneshyari.com](https://daneshyari.com)