ARSENIC MOBILIZATION FROM SEDIMENTS IN MICROCOSMS UNDER SULFATE REDUCTION

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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 to 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.

KEYWORDS

Arsenic, Sulfate reduction, Iron(III) minerals, Contaminated sediments, Microcosm experiment

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_2S_3), realgar (AsS) and arsenopyrite (FeAsS), can substitute within a variety of metal sulfides, including mackinawite (FeS), greigite (Fe_3S_4) and pyrite (FeS_2), 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; Keimowitz et al., 2007; 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; Kocar 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 metal 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⁻¹, 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⁻¹).

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, 10800 and 307 mg kg⁻¹, 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⁻¹, in high-density polyethylene bottles. The sediment-groundwater suspensions were pre-equilibrated for 24 hours 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; Burton et al., 2014; Omoregie et al., 2013; Onstott et al., 2011; Saalfeld 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⁻¹, 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 for monitoring instrument drift. For analyzing arsenic, the instrument was set at resolving power $\sim 10,000$, to resolve the ^{75}As peak from argon-chloride interference. Quantification for each element was based on comparison to a six-point standard curve from a multi-element standard. Accuracy was within $100 \pm 5\%$ based on certified NIST standards. DOC concentrations in the solutions were determined by high-temperature catalytic oxidation method on a Shimadzu total organic carbon (TOC) VCSN analyzer. Quantification was based on comparison to a six-point calibration curve from standards prepared from potassium hydrogen phthalate (Nacalai Tesque, Inc.) and certified low TOC water (Shimadzu). The samples and standards were analyzed using the non-purgable organic carbon mode.

Dissolved elemental concentrations in the solutions from the Coeur d'Alene microcosms were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES) using a Thermo Intrepid II XSP with radial optics. An internal standard of scandium, yttrium, and indium was run in-line to track and correct for plasma condition changes. Spectral interferences were calculated by analyses of high purity standards, and accounted for in data reduction when necessary. Quantification for each element was based on comparison to a four-point calibration curve from a multi-element standard. Accuracy was within $100 \pm 5\%$ based on certified NIST standards.

2.3.2. Sediment Analysis.

Arsenic X-ray absorption near edge structure (XANES) spectra were collected on representative Vineland and Coeur d'Alene sediment samples, at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 4-1. Iron extended X-ray absorption fine-structure (EXAFS) spectra were also collected on the same beamline, on representative Vineland sediment samples. The beamline was configured with a silicon(220) monochromator with a ϕ angle of 90 degrees. Sample fluorescence spectra were measured with a 13-element germanium detector, in combination with a $6\text{ }\mu\text{x}$ germanium filter or a $6\text{ }\mu\text{x}$ manganese filter for arsenic XANES and iron EXAFS, respectively. The spectra were processed in SIXpack (Webb, 2005) using standard procedures (Saalfeld and Bostick, 2009; Sun et al., 2016). Normalized arsenic XANES spectra of the Vineland and Coeur d'Alene samples were compared with reference spectra of arsenate, arsenite and arsenic sulfides. The k^3 -weighted iron EXAFS spectra of the Vineland samples were compared with reference spectra of ferrihydrite, goethite, hematite, magnetite, mackinawite, siderite and iron-rich

illite, consistent with earlier studies on the Vineland aquifer (Sun et al., 2016; Wovkulich et al., 2014). Least-squares linear combination fitting (LCF) was used to quantify the percentage of each reference. Errors in LCF reported by SIXpack account for error propagation from fitting, spectral noise in sample and reference spectra, and similarities between reference spectra (Webb, 2005).

Sulfur XANES spectra were collected on representative Vineland sediment samples at SSRL beamline 4-3, configured with a silicon(111) monochromator. The spectra were processed in WinXAS (Ressler, 1998) using standard procedures (Saalfeld and Bostick, 2009; Schroth et al., 2007). Sample sulfur speciation was determined by XANES-LCF with reference spectra of inorganic sulfate, zero valent sulfur (S^0) and sulfide. Organic sulfur species were not significant if included in fitting, and are likely only a small portion of the total sulfur based on mass balance calculates, and thus are omitted. They contain less carbon (100-400 mg kg^{-1}) than sulfur (300 mg kg^{-1} or more following sulfate amendments), and organic sulfur is typically only a small fraction of organic carbon. Errors for sulfur speciation are estimated from a sensitivity analysis and comparisons to known mixtures, which are within 2% for oxidized sulfur species and 5% for reduced sulfur species (Schroth et al., 2007).

2.4. Thermodynamic Modeling.

Arsenic Eh-pH diagram was constructed using Geochemist's Workbench (Rockware Inc., Golden, CO) with the Lawrence Livermore National Laboratories combined database (Delany and Lundeen, 1990), which was updated for arsenic speciation (Couture and Van Cappellen, 2011; Helz and Tossell, 2008).

3. RESULTS

3.1. Coeur d'Alene Microcosms.

In the lactate-only-treated Coeur d'Alene microcosm without extra sulfate, dissolved sulfur concentrations, which are representative of dissolved sulfate, were still measurable and increased over time during incubation (Fig. 1). Dissolved arsenic concentrations continued to increase, ultimately reaching 0.06 mg L^{-1} . Dissolved phosphorus concentrations, which are representative of dissolved phosphate, also increased over time and ultimately reached 0.12 mg L^{-1} . Dissolved iron and manganese concentrations increased initially, and followed by partial removal. In the Coeur d'Alene microcosm treated with both lactate and extra sulfate, dissolved sulfur concentrations started at 101 mg L^{-1} , decreased consistently over time and depleted completely at the end of the incubation. The pH rose from

neutral to about pH 7.5 during the experiment, and the redox potential decreased from +0.3 V to a final value of -0.255 V during the experiment. Dissolved phosphorus, iron and manganese behaved generally similarly to those in the lactate-only-treated microcosms, but dissolved phosphorus concentrations were higher, and the partial removal of dissolved iron and manganese occurred at faster rates. Dissolved arsenic concentrations started at 0.03 mg L⁻¹, which were higher than those in the lactate-only-treated microcosms, but fell under the detection limit of the ICP-OES instrument (0.007 mg L⁻¹) 15 days after the treatment addition (Fig. 1). Therefore, the supply of extra sulfate is necessary for remediation to be successful. However, this arsenic removal was transient, as dissolved arsenic concentrations increased again to a final value of 0.02 mg L⁻¹. Arsenic XANES indicated that initial Coeur d'Alene wetland sediment arsenic was present as a mixture of arsenate and arsenite, and the fraction of arsenite increased following the sulfate-lactate addition and no arsenic sulfides were produced (Fig. 2).

3.2. Vineland Microcosms.

In the sulfate-lactate-treated Vineland microcosms, dissolved sulfur concentrations started high because of the sulfate addition, increased slightly in the first 10 days of incubation, and then decreased consistently over time by about 100 mg L⁻¹ (Fig. 1). The change in DOC concentrations was used as a proxy for tracking the microbial oxidation of lactate. DOC concentrations started at about 30 mM because of the lactate addition (10 mM lactate = 30 mM DOC) and then consistently decreased over time to 6 mM (Fig. 3). Similar to the Coeur d'Alene case, dissolved iron and manganese concentrations in these sulfate-lactate-treated Vineland microcosms also increased initially, and followed by partial removal. The Vineland microcosms contained lower dissolved iron and manganese than the Coeur d'Alene microcosms, due to lower sediment iron and manganese contents. The sulfate-lactate-treated Vineland microcosms became more reducing over the course of the incubation with Eh decreasing from +0.21 V to -0.21 V, and pH increased from pH 5.6 to 6.7 because of the sulfate-lactate addition and then stabilized (Fig. 4). Although the evolution of solution composition and the Eh/pHs suggest active sulfate reduction, arsenic was not effectively sequestered within reduced sulfide minerals and instead released from the Vineland sediments (Fig. 1). There was a transient arsenic removal from solution starting at Day 12, coinciding with a decline in dissolved sulfur, iron and manganese concentrations. However, dissolved arsenic concentrations quickly rebounded and ultimately reached 1.9 mg L⁻¹. Dissolved phosphorus concentrations decreased from approximately 0.3 mg L⁻¹ to 0.1 mg L⁻¹ within the first 5 days of incubation and then stabilized. Overall, although some small differences in solution composition were observed, duplicated Vineland microcosms behaved similarly. Initial Vineland sediment iron was dominated by iron(III), especially poorly-

crystalline ferrihydrite, and following the sulfate-lactate addition, most of this ferrihydrite converted to more crystalline goethite and lesser quantity of iron sulfides (Fig. 5A). Initial Vineland sediment arsenic was present as > 95% arsenate, and remained as arsenate despite the reducing environment (Fig. 2). Rather than insoluble sulfides, the majority of the reduced sulfur within the sulfate-lactate-treated sediments was zero valent sulfur (Fig. 5B). In the treatment-free Vineland microcosms, pH and most solution species measured, including dissolved arsenic concentrations, remained stable relative to those in the sulfate-lactate-treated microcosms; Eh decreased from +0.23 V to +0.14 V over the course of the incubation; and dissolved phosphorus concentrations decreased gradually from approximately 0.3 mg L⁻¹ to 0.15 mg L⁻¹ (Fig. 1, Fig. 3 and Fig. 4).

4. DISCUSSION

4.1. Interplay between Sulfate Reduction, Iron(III) Reduction, and Arsenic Concentration.

The addition of sulfate and lactate to the Coeur d'Alene microcosms resulted in lower dissolved arsenic concentrations than the addition of lactate alone (Fig. 1), which implies that sulfate reduction indeed can be important to regulating dissolved arsenic levels. Such addition to the Vineland microcosms, however, caused dissolved arsenic concentrations to exceed WHO drinking water standard (0.010 mg L⁻¹) by 2 orders of magnitude. The concurrent changes in dissolved iron and sulfur concentrations, in both the Coeur d'Alene and Vineland microcosms, suggest that parallel redox processes were active. (Given that sediment manganese concentrations are 2 orders of magnitude lower than sediment iron concentrations, manganese(IV) reduction is not the focus of the discussion.) The implicit relationship between iron(III) and sulfate reduction within these microcosms, and within many natural subsurface environments, and the conditions under which their interaction either sequesters or liberates arsenic, are not simple in that it involves a complex network of microbial and chemical (abiotic) redox pathways, sediment-solution interchanges, and thermodynamic and kinetic constraints. Based on the observations in this study and published studies on sulfate reduction (Burton et al., 2011; Couture and Van Cappellen, 2011; Kirk et al., 2010; Kocar et al., 2010; Poulton et al., 2004), we propose a generalized conceptual model that describes how iron and sulfur are cycled and addresses whether the phases immobilize arsenic (Fig. 6).

Iron(III) and sulfate reduction pathways differ between different microcosms. In the lactate-only-treated microcosms, iron(III) reduction was probably the dominant process affecting the systems, and iron-reducing bacteria (FeRBs) were responsible for the reductive dissolution/transformation of iron(III)

minerals. In contrast, in the sulfate-lactate-treated microcosms, although a microbial lag phase of the sulfate-reducing bacteria (SRBs) seems to exist at the onset of the experiments (Fig. 1), sulfate reduction probably proceeded at comparable speed with iron(III) reduction or even took over during certain stages owing to kinetic reasons (Bethke et al., 2011; Wang and Van Cappellen, 1996) and sulfate was reduced by SRBs to hydrogen sulfide (a mixture of HS⁻ and H₂S, pK_{a,H2S} = 7.02):

Free sulfides are able to produce insoluble iron and/or arsenic sulfide minerals when these minerals reach saturation (i.e., saturation index > 0) (Fig. 6). If reactive iron(III) minerals such as ferrihydrite are present, free sulfides also reductively react with them and produce iron(II) and zero valent sulfur (possibly along with lesser quantity of thiosulfate):

This reaction, which is surface-controlled and involves electron transfer, is a rapid chemical process and directly coupled to microbial sulfate reduction (Kocar et al., 2010; Poulton et al., 2004). The presence of zero valent sulfur is a diagnostic indicator of sulfate reduction, since it only forms through sulfide oxidization. The zero valent sulfur, then, undergoes disproportionation which might be microbially mediated, and regenerates sulfide and sulfate (Burton et al., 2011; Cypionka et al., 1998; Saalfield and Bostick, 2009):

Such processes (Reaction 1, 2 and 3) create an efficient biogeochemical sulfur cycle that catalyzes iron(III) reduction and buffer dissolved sulfide concentrations at relatively low levels, until reactive iron(III) is exhausted (Fig. 6).

The sulfur cycling (indicated by accumulation of zero valent sulfur, Fig. 5B) explains why the sulfate-lactate treatment was unable to immobilize arsenic in the Vineland case, even though sulfate reduction was apparent. Arsenate reduction is a necessary step in arsenic co-precipitation with sulfides (Saalfield and Bostick, 2009). Free sulfides, if appreciable, not only can reduce reactive iron(III) minerals (Reaction 2), but can reduce arsenate (Helz and Tossell, 2008; Rochette et al., 2000). Although this may happen under sustained reduction (Burton et al., 2014; Onstott et al., 2011), due to the reaction of sulfide with reactive ferrihydrite which is abundant in the Vineland sediments and subsequent sulfur cycling (Fig. 6), arsenate reduction and the transformation to arsenic sulfide minerals are inhibited (Fig. 2). This buffering of sulfide activities at low levels also slows the transformation from ferrihydrite to iron sulfide minerals (Fig. 5A). Instead, ferrihydrite reduction produces ferrous iron, causing its conversion to goethite and/or magnetite

(Kocar et al., 2010), which decreased surface area and led to arsenic desorption from the Vineland sediments.

Similar to arsenic, phosphate is also often present as adsorbed species in sediments and soils. In the Coeur d'Alene microcosms, following the sulfate-lactate addition, phosphate was released while arsenic was removed from solution (Fig. 1). In the Vineland microcosms, however, arsenic was released while phosphate was sequestered within the sediments, even after extensive ferrihydrite reduction. The contrast between the fates of dissolved arsenic and phosphate in these microcosms can be explained by their significant differences in reactivity with dissolved sulfide. Different from arsenic, phosphate does not readily react with dissolved sulfide to form insoluble minerals or solution complexes. In the sulfate-lactate-treated Coeur d'Alene microcosm, phosphate is released due to reduction and depletion of sorption sites, while co-precipitation and/or adsorption to sulfide minerals removes arsenic from solution. In the sulfate-lactate-treated Vineland microcosms, the retention of phosphate suggests that sorption sites are available, but that arsenic solubility is enhanced by the formation of dissolved thiolated arsenic compounds such as $\text{HAsS}_3\text{O}^{2-}$ and AsS_4^{3-} (Burton et al., 2011; Keimowitz et al., 2007; Kocar et al., 2010; Suess et al., 2009):

Such thioarsenates can also be produced through the oxidation of arsenite oxyanions by zero valent sulfur (Burton et al., 2013). Arsenic Eh-pH diagram provides insight into the overall thermodynamic controls on arsenic speciation under the dynamic redox environment (Fig. 4). The diagram suggests that such thioarsenates indeed became stable in the sulfate-lactate-treated Vineland microcosms.

Sediment iron mineralogy regulates the rates of iron(III) and sulfate reduction, and thus sulfur cycling (Postma et al., 2010; Poulton et al., 2004). La Force et al. (2000) suggests that the Coeur d'Alene wetland sediments used in this study, which were collected during early spring flooding, may contain limited quantities of reactive iron(III) minerals due to the flooding-induced anoxia. Without reactive iron(III) to poise sulfide activities at low levels, sulfate reduction could more efficiently produce insoluble sulfide minerals. The persistence of phosphate in solution while arsenic was retained in the sulfate-lactate-treated Coeur d'Alene microcosm (Fig. 1) is indirect evidence for arsenic retention within sulfide minerals. Such arsenic retention was probably associated with iron sulfides such as mackinawite since they are more

likely to form than orpiment or realgar under our iron-rich experimental conditions (Burton et al., 2014; Kirk et al., 2010) and arsenic sulfides were indeed not detected (Fig. 2).

4.2. Implication for Remediating Groundwater Arsenic Contamination.

Although many limitations exist when simplistically extrapolating laboratory data to the field, this study indicates that remediation intended to produce immobile arsenic-bearing sulfides may not always be effective, and that any arsenic remediation approach that involves redox transformations must be implemented with caution to avoid the unintended release of sediment arsenic into groundwater.

Microbial sulfate reduction does not impact dissolved arsenic concentrations in a straight-forward manner because the solubility of arsenic-bearing sulfides is minimized only when sulfide activities are about 0.5 μM (Eary, 1992; Helz et al., 1995), a condition which is difficult to control and maintain. In natural environments, the activity of sulfide is often affected by its reaction with iron(III) and other oxidants; thus the efficacy of sulfate reduction must consider sediment/soil iron mineralogy when evaluating its potential as a groundwater remediation strategy. Since the catalytic sulfur cycling, which keeps sulfide activities low, breaks down if there is no facile oxidant like reactive iron(III) minerals, the formation of insoluble sulfides and arsenic immobilization may be more effective within relatively reduced systems, for example, within landfill sites. Under those conditions, however, porewater iron(II) concentrations might be low and the production of iron sulfide minerals might be slow. As a result, sulfate reduction potentially enhances arsenic solubility through the formation of thiolated arsenic compounds (Fig. 6). In fact, both enhanced removal and release may occur at the same site as site condition evolves, as evidenced by the transient arsenic removal observed in the microcosms (Fig. 1). Even if immobile arsenic-bearing sulfides are formed, reduced sulfide minerals are susceptible to oxidation under oxidized condition and to dissolution with higher sulfide activity (Burton et al., 2011; Couture and Van Cappellen, 2011; Kirk et al., 2010). Therefore, the long-term stability of the arsenic hosts also requires additional investigations, to better understand the viability of the sulfide-based immobilization strategies.

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356 **SUPPLEMENTARY MATERIAL**

357 Tables S1 and S2, and figures S1 and S2. These tables and figures contain sediment iron EXAFS spectra and
358 fits, and sediment sulfur XANES spectra and fits.

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FIGURE LEGEND

Fig. 1. Dissolved sulfur, arsenic, phosphorus, iron and manganese concentrations from the microcosms over time. The time of treatment addition was defined as time zero. Sediment arsenic, iron and manganese suspension densities were calculated using elemental concentrations in sediments and suspension densities used in the microcosms. Left column: Coeur d'Alene. Right column: Vineland. The starting points (Day -0.1) are from the Vineland microcosms after 24 hour pre-equilibration and right before the treatment addition. Duplicated Vineland microcosms were shown separately in the figure.

Fig. 2. Normalized arsenic XANES spectra of the initial sediments and the sulfate-lactate-treated sediments from the microcosms at the end of the incubations (Day 32 for Coeur D'Alene and Day 38 for Vineland). The spectra are vertically offset for clarity. Different arsenic reference spectra are included for comparison.

Fig. 3. Dissolved organic carbon (DOC) concentrations from the Vineland microcosms over time.

Fig. 4. Arsenic Eh–pH diagram for the As–O–H–S system calculated with condition: system with 10 μM arsenic, 10 μM iron and 100 μM sulfur. Equilibrium with $\text{S}(\alpha)_8(\text{s})$ is imposed for the diagram. The yellow areas indicate the predominance of solid arsenic species, whereas the blue areas indicate the predominance of solution arsenic species. The black dotted line indicates where the boundary between $\text{H}_3\text{AsO}_3(\text{aq})$ and $\text{As}(\text{s})$ would be if the system contained only 1 μM sulfur. Redox data from the Vineland microcosms are plotted. Initial conditions represent the Vineland microcosms after 24 hour pre-equilibration and right before the treatment addition. Each point is the average of the duplicate microcosms, and the errors are the standard deviations, some of which are smaller than the size of symbols used. The dashed lines with arrows indicate the directions of the Eh/pH changes over time.

Fig. 5. Iron mineral composition (A) and sulfur speciation (B) in initial Vineland sediments and in the sulfate-lactate-treated Vineland sediments at the end of the incubation (Day 38), as determined by iron EXAFS and sulfur XANES linear combination fitting. Iron EXAFS spectra and fits are in [Supplementary Material Table S1](#) and [Fig. S1](#), and sulfur XANES spectra and fits are in [Table S2](#) and [Fig. S2](#).

Fig. 6. Conceptual iron transformation and sulfur redox cycle, and arsenic partitioning among different phase. In this figure, SI = saturation index, ads = adsorption, sub = substitution.

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