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Article

# Mobilization of As, Fe, and Mn from Contaminated Sediment in Aerobic and Anaerobic Conditions: Chemical or Microbiological Triggers?

Cherie L. DeVore,* Lucia Rodriguez-Freire, Noelani Villa, Maedeh Soleimanifar, Jorge Gonzalez-Estrella, Abdul Mehdi S. Ali, Juan Lezama-Pacheco, Carlyle Ducheneaux, and José M. Cerrato

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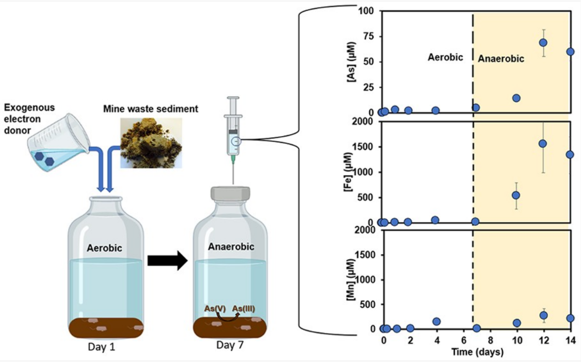

**ABSTRACT:** We integrated aqueous chemistry, spectroscopy, and microbiology techniques to identify chemical and microbial processes affecting the release of arsenic (As), iron (Fe), and manganese (Mn) from contaminated sediments exposed to aerobic and anaerobic conditions. The sediments were collected from Cheyenne River Sioux Tribal lands in South Dakota, which has dealt with mining legacy for several decades. The range of concentrations of total As measured from contaminated sediments was 96 to 259 mg $kg^{-1}$, which co-occurs with Fe (21 000−22 005 mg $kg^{-1}$) and Mn (682−703 mg $kg^{-1}$). The transition from aerobic to anaerobic redox conditions yielded the highest microbial diversity, and the release of the highest concentrations of As, Fe, and Mn in batch experiments reacted with an exogenous electron donor (glucose). The reduction of As was confirmed by XANES analyses when transitioning from aerobic to anaerobic conditions. In contrast, the releases of As, Fe and Mn after a reaction with phosphate was at least 1 order of magnitude lower compared with experiments amended with glucose. Our results indicate that mine waste sediments amended with an exogenous electron donor trigger microbial reductive dissolution caused by anaerobic respiration. These dissolution processes can affect metal mobilization in systems transitioning from aerobic to anaerobic conditions in redox gradients. Our results are relevant for natural systems, for surface and groundwater exchange, or other systems in which metal cycling is influenced by chemical and biological processes.

**KEYWORDS:** *arsenic, mine waste, redox, reductive dissolution, microorganisms*

## ■ INTRODUCTION

Arsenic (As) is a potentially toxic and redox-active metalloid that can affect humans by ingestion and inhalation pathways.[1−3] A previous investigation of the Cheyenne River Watershed in South Dakota reported arsenic (As) concentrations in mining-impacted sediments ranging from 96 to 285 mg $kg^{-1}$, which are above the regionally accepted crustal average of 9−10 mg $kg^{-1}$ of As.[4] Although chemical mechanisms for As release in the Cheyenne River Watershed were previously investigated,[4−7] the contribution of microbiological processes on the release of As from these solids remains unknown. Differentiating between the chemical and microbial mechanisms responsible for the release of As and other co-occurring metals, such as Fe and Mn, is difficult due to the complex nature of environmental samples. Thus, investigating the biogeochemical factors impacting the mobilization of As and other co-occurring metals from contaminated sediment is necessary for informing geochemical research, (bio)remediation technologies, and risk assessments among other disciplines.

Biogeochemical processes affect the transport of As in the environment, which in turn influences speciation in a range of oxidizing and reducing conditions. For example, As(V) ($H_2AsO_4^-$ and $HAsO_4^{2-}$) is the predominant species in oxidizing environments, while As(III) ($H_3AsO_3$ and $H_2AsO_3^-$) is predominant in reducing environments. The redox transformations of As are important to consider because of the higher toxicity and enhanced mobility of As(III). Arsenic solubilization from contaminated solids can result from four main processes: (i) competitive ion displacement with ions such as phosphate and silicate,[4,8] (ii) limited adsorption onto media or desorption,[7,9] (iii) arsenate reduction to arsenite,[10−12] and (iv) reductive mineral dissolution from many

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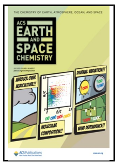

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forms of oxyhydroxides.[13−15] Arsenic co-occurs with other metals: Fe and Mn oxides.[11,16] Microbiological mechanisms for As, Fe, and Mn reduction can occur by respiration or detoxification.[17−19] Numerous microorganisms can withstand a wide range of oxidation−reduction potentials and use As, Fe, Mn, and other metals as electron acceptors.[15,20,21] Additionally, the transition to anaerobic conditions is a key driver in promoting As desorption through the reduction of As(V) or reductive dissolution of Fe oxides.[22] Mn and Fe oxides have been reported to affect As mobilization in numerous studies by adsorption or oxidation of arsenite.[23] For instance, As(V) reduction and reductive dissolution of iron (hydr)oxides is hypothesized to be a principal control in porewater As concentrations.[11] The organic carbon source (electron donor) used in anaerobic respiration plays an important role in the reduction of As(V), Fe(III), and Mn(VI).[24]

Arsenic mobilization and exposure have gained attention from groundwater investigations related to naturally occurring As under anaerobic conditions in Vietnam, China, and Bangladesh.[25−28] Completely aerobic or anaerobic conditions are described in experimental and field conditions. However, the literature related to the investigation of metal release resulting from the transition between aerobic to anaerobic redox conditions with contaminated soil is limited. Environments that have surface and groundwater exchange, waterlogging, burial, and resuspension provide an important context for these redox conditions. Labile organic matter in these zones can enhance the reduction and subsequent dissolution of Fe oxides, which can release adsorbed As.[29] While the reduction of As, Fe, and Mn have been investigated separately,[30−34] their simultaneous reduction in contaminated soils undergoing a redox transition with native microorganisms can be further explored. Geogenic As mobilization from groundwaters with Fe/Mn oxyhydroxides is a widely discussed and accepted driver of metal release in many places in the world. Our study builds upon known geochemical mechanisms for mobilization in highly contaminated soil that undergo transitions between oxidizing and reducing conditions. A diversity of metal-utilizing bacteria has also been isolated from a variety of soil systems, including mine waste environments. The inoculation of soil using As-utilizing bacteria in previous studies also illustrates their important role on the transformation and partitioning of As under controlled laboratory conditions. Our work seeks to advance knowledge on the role of native soil microorganisms for As−Fe−Mn mobilization from the study area. Understanding these processes is necessary to improve our knowledge of metal transport in contaminated environments.

The objective of this study is to evaluate chemical and microbiological processes affecting the release of soluble As, Fe, and Mn from contaminated sediments under laboratory-controlled aerobic and anaerobic conditions. We integrate microbiology techniques, aqueous chemistry, and spectroscopy to better understand microbially catalyzed As release from reacted sediments incubated under aerobic-to-anaerobic conditions in the presence of an electron donor. The novelty of this study is the identification of the simultaneous As−Fe−Mn release triggered by the transition of aerobic to anaerobic conditions in contaminated sediments with the *in situ* microbial community, which is relevant to environments that undergo redox gradients. While many redox investigations employ single microbial strains, the use of the native microbial community from contaminated sediment provides environmental relevance. Improving our understanding of As mobility using controlled laboratory amendments with an electron donor can aid in developing strategies to reduce risk and exposure to populations located near redox transition zones.

## ■ MATERIALS AND METHODS

**Sample Collection.** Contaminated sediment samples were collected from Cherry Creek riverbank coinciding with sample collection from a previous investigation in the Cheyenne River Watershed.[2] A hand trowel was rinsed with 10% nitric acid solution and used to collect half a gallon of sediment from the riverbank and bed. Samples were placed in one-gallon plastic bags and cooled to 4 °C for shipment with water samples to the University of New Mexico (UNM). The authors were escorted by the Cheyenne River Sioux Tribe (CRST) Department of Environment and Natural Resources staff while conducting sampling.

**Solid Chemistry.** Sediment samples were dried for 12 h at 60 °C in a controlled temperature oven. The dried sediment samples were crushed and homogenized using a shatter box. One gram of the dried sediment was weighed and added to a 50 mL digestion tube. All the samples were acid-digested (2.0 mL of $HNO_3$ and 3 mL of HCl) in triplicate to determine the extractable elemental concentrations. The mixture was digested for 60 min at 65 °C and then for an additional 60 min at 90 °C. The digested samples were diluted with deionized water to 25 mL. The digested and diluted samples were then filtered through a 0.45 $\mu$m filter to remove any particulate matter for aqueous elemental analyses. The dried solid samples from the field and laboratory analyses were analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), and X-ray Adsorption Spectroscopy (XAS).

*X-ray Diffraction.* We also used the Rigaku Smart Lab X-ray diffractometer (XRD), using Cu Ka radiation with a scintillation detector and a graphite monochromator, to obtain information on the crystallinity, mineral structure, and normalized approximate percentage amounts of mineral phases present in the sediment samples. The XRD data were analyzed using Jade software.

*X-ray Fluorescence.* X-ray fluorescence (XRF) measurements were conducted to determine the bulk elemental composition using an EDAX Orbis with a Rh tube source and a titanium adsorption edge filter. Samples were measured in a vacuum with a filament voltage of 20 kV and a current of 15 $\mu$A.

*X-ray Absorption Spectroscopy.* The oxidation and structural states of solid-phase arsenic were determined using XANES. The As K-edge XANES spectra were analyzed by linear combination fitting using As(III) and As(V) standards. The X-ray measurements for As were performed at Beamline 7-3 at the Stanford Synchrotron Radiation Laboratory. Samples were measured at the As K-edge in fluorescence mode using a 32 element Ge detector and a double crystal Si(220) monochromator, calibrated at the first inflection point of, and Au metal foil absorption at, 11919.0 eV. Measurements were performed at room temperature. Powdered samples were placed on Al holders between two layers of Kapton tape. No beam damage was observed between measurements as spectra was consistent throughout different scans.

**Aqueous Chemistry.** Aqueous elemental analyses for this study were performed using inductively coupled optical emission spectrometry (ICPOES) (PerkinElmer Optima 5300DV) and inductively coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer NexION 300D-Dynamic Reaction

Cell) in aqueous solutions for trace element content (As, Fe, and Mn). Samples for ICP-MS were filtered using a 0.45 $\mu$m Basix filter and preserved with 2% $HNO_3$. A Thermo Fisher Scientific Ion Chromatogram (ICS-1100) was used to analyze 0.45 $\mu$m filtered nonacidified water samples for major anion concentrations. Aqueous Fe(II) was measured by the ferrozine assay, and Fe(II) standards were prepared from ferrous ammonium sulfate (GFS Chemicals). All reagents used in the experiments and analyses were analytical grade. No unexpected or unusually high safety hazards were encountered.

**Redox cycling experiments.** A series of batch experiments were performed to better understand the chemical and microbial driven release of As, Fe, and Mn in the sediments. Batch reactors were conducted in 160 mL serum bottles sealed with butyl rubber stoppers and aluminum crimps. The incubations were supplied with 135 mL of basal medium (Table S1) and 10 g of riverbank sediment under aerobic and anaerobic conditions. The bottles were supplied with an exogenous electron donor at a concentration of 0.125 g COD $L^{-1}$ as glucose. Control treatments were supplied only with deionized water and basal medium. Additional assays were supplied with 10 mM $Na_2HPO_4$, consistent with the experimental conditions and soil from the same study area, to compare the chemically driven release as described in a previous study.[4] The maximum percentage released was calculated by using the mass of the unreacted sediment, the volume of solution in the serum bottles, and the concentration of metals in the unreacted sediment. All treatments were executed in triplicate. The bottles for aerobic conditions were covered with a sterile cotton ball and gauze. The bottles for anaerobic conditions were flushed with a gas mix of $N_2/CO_2$ (80:20). All the bottles were incubated for 336 h at 25 °C with mechanical shaking at 130 rpm. Sampling was conducted using sterile needles and syringes. A summary of the experimental setup is provided in the SI (Table S2).

**Microbial Community Characterization and Alpha Diversity Study.** Sediment samples from bottles supplied with 0.125 g $L^{-1}$ of COD glucose were taken at 168 h and at the end of the experiment at 336 h. One gram was also taken from the original field sample. All details of DNA extraction have been previously described.[35] The DNA samples were sent to MR DNA Laboratory (Molecular Research, Texas) for MiSeq Illumina DNA sequencing (2 × 300bp PE illumina 20 000 sequence diversity assays), the DNA sequences were analyzed using MR DNA analysis pipeline (MR DNA, Shallowater, TX, USA), and based on 97% similarity, operational taxonomical units (OTU) were generated. BLASTn against a RDPII and NCBI curated database (www.ncbi.nlm.nih.gov, http://rdp.cme.msu.edu) was used for OTU data classifications. Mothur v.1.39.5 software[36,37] was used for statistical analysis of the OTU data. Richness was calculated with no subsampling. Shannon's Diversity Index (H)[38,39] was performed by subsampling (the smallest sample size) of the OTU data.

$$H = -\sum_{i=1}^{S} p_i \ln(p_i) \qquad (1)$$

Here, $S$ is the number of different species (species richness), and $p_i$ is the percentage of the individual species in the sample. Nonmetric multidimensional scaling (NMDS) beta diversity analysis to illustrate similarity of samples was run by Bray–Curtis similarity with subsampling.

## RESULTS AND DISCUSSION

**Initial Analyses of Contaminated Solids.** The arsenic concentrations in contaminated sediment using acid digestions were measured in the range of 96–259 mg $kg^{-1}$ (Table S3). These values exceed the regionally established background concentration of 10 mg $kg^{-1}$ and are consistent with the concentrations measured in a previous study near the site.[4] The concentrations of acid-extractable Fe and Mn measured in these contaminated samples were in the range of 21 000–22 005 mg $kg^{-1}$ for Fe and 682–703 mg $kg^{-1}$ for Mn. XRF measurements show an abundance of Si, Ca, Al, and Fe. Low organic content (1–3%) was measured in the sediment using loss-on-ignition. The mineralogy of the solids for this study has similar characteristics from a study in our group,[4] in which the primary XRD patterns (Figure S1) were consistent with quartz ($SiO_2$), albite ($AlSi_3NaO_8$), and calcite ($CaCO_3$). The predominance of As(V) was detected in the bulk for these solids using XANES. Mixtures of 52:48 As(V)/As(III) and 80:20 Fe(III)/Fe(II) oxidation states were detected in the near surface (5–10 nm) by XPS. The differences in percentages of As(V) versus As(III) are due to the fact that XANES detects bulk while XPS detects the near surface, and these measurements can be often different, as shown in other studies.[4,35,40] Microbiological characterization of the sediment was conducted to better understand the potential mechanisms for metal release.

**Illumina DNA Sequencing of Microbial Community in Contaminated Solids.** The microbial community in sediments from Cherry Creek shows a high diversity in common soil microorganisms (*Clorophexi* 3%, *Actinobacteria* 3%, and *Bacillus* 1%), including nitrogen fixating (*Bradyrhizobium*, 1%) and ammonia oxidizers (*Nitrososphaera*, 3%) among the most predominant species. *Bacillis*, *Acidobacteria*, and *Actinobacteria* are major phyla in meta-analyses of contaminated soils across the world.[41−43] A number of dissimilatory arsenic-reducing bacteria (DARB) and arsenic-oxidizing bacteria (AOB) have also been identified in mixed cultures collected from sediments from Cheyenne River Watershed (SI Table 4), accounting for 4.7% of the total microbial communities, with DARB and AOB representing 1.9% and 2.8%, respectively. The DARB were dominated by *Geobacter* (54% of total DARB OTU and 1% of total OTU), *Thermus* (20% of total DARB OTU), and *Desulfosporosinus* (18% of total DARB OTU) species. Species of the *Geobacter* genus are known for their ability to oxidize and reduce metals, including Fe, Mn, and As.[44] Arsenic reduction by *Geobacter* species is controlled by detoxification mechanisms, but dissimilatory As(V) reduction genes have been identified in *Geobacter* genes, and As(V) respiration has been confirmed by various *Geobacter* species.[45,46] *Thermus* species are capable of heterotrophic oxidization of As(III) and of As(V) respiration as a terminal electron acceptor.[47] *Desulfosporosinus* was shown to be able to respire As(V) heterotrophically and chemoautotrophically, using $H_2$ + $CO_2$ as an electron donor and carbon source.[48,49] The AOB were clearly dominated by *Rhizobium* (62% of total AOB OTU, 1.7% of total OTU), followed by *Herminiimonas* (21% of total AOB OTU) and *Azoarcus* (8% of total AOB OTU). *Rhizobium* species usually live in rhizosphere environments, but some have been found to be chemolithotrophic As(III) oxidizers that are able to use a diverse source of electron donors and carbon sources.[21] *Herminiimonas arsenicoxydans* (formerly named *Caenibacter arsenoxydans*) and *Azoarcus* have been charac-

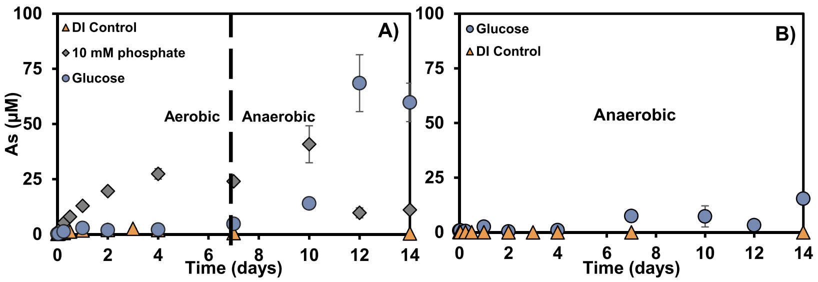


**Figure 1.** As release under (A) aerobic-to-anaerobic cycling conditions and (B) completely anaerobic conditions.

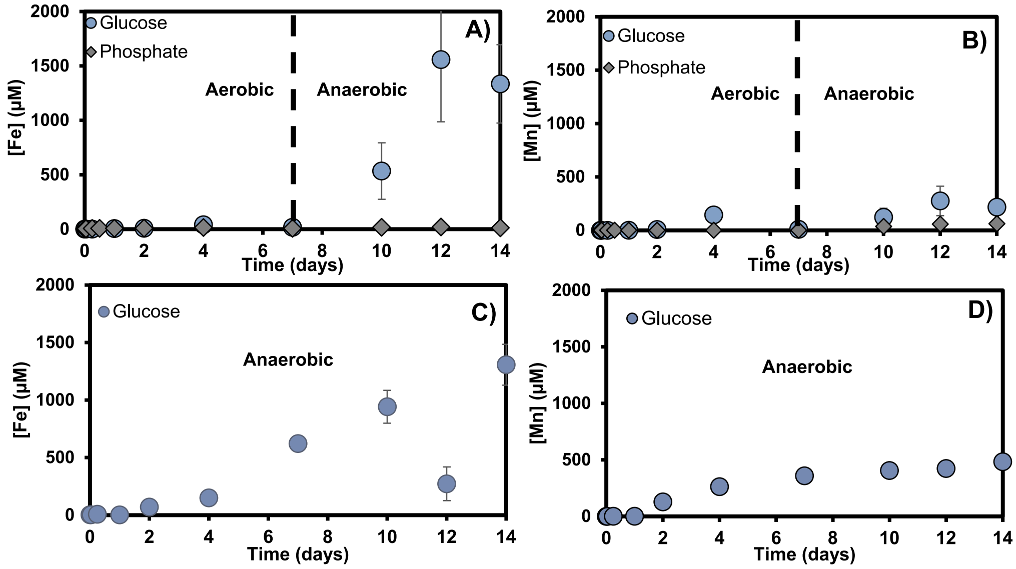


**Figure 2.** Fe release under (A) aerobic-to-anaerobic cycling conditions and (B) completely anaerobic conditions; Mn release under (C) aerobic-to-anaerobic cycling conditions and (D) completely anaerobic.

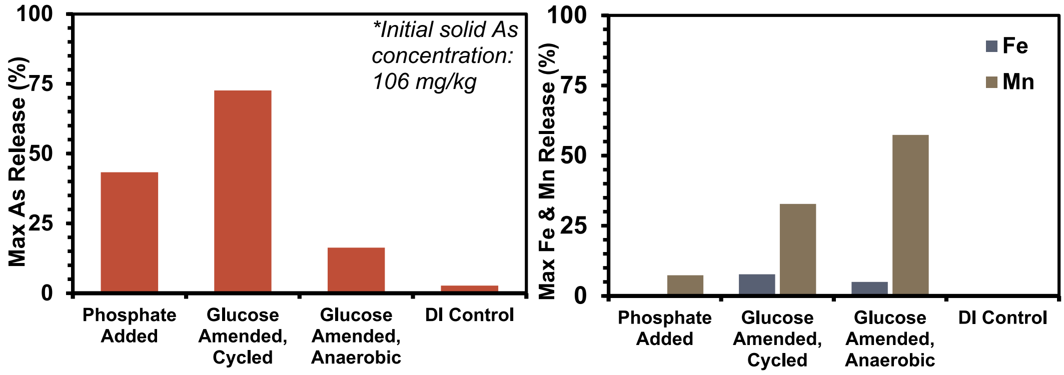
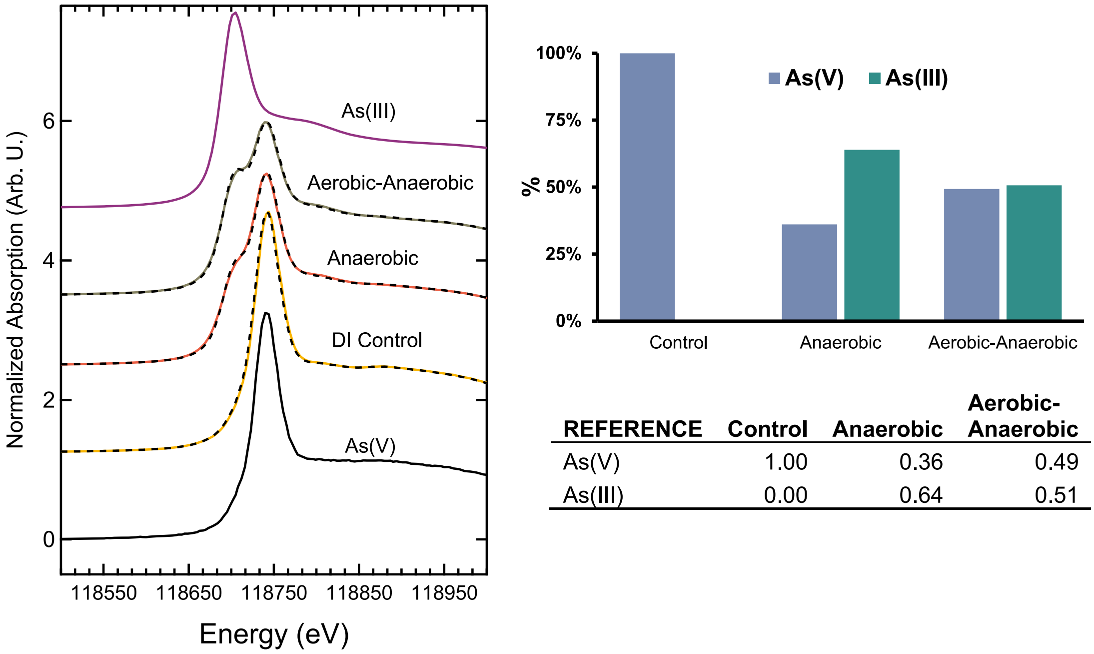


**Figure 3.** (A) Max release (%) of As and (B) max release of Fe and Mn under a range of 531 biogeochemical conditions: aerobic transitioned to anaerobic with 10 mM phosphate; aerobic transitioned to anaerobic amended with glucose; completely anaerobic amended with glucose.

terized as As(III) oxidizers and they are widespread in the environment because they are able to use various electron donors to support their metabolism.[50−52] Hence, the Cherry Creek sediments have a rich diversity of microorganisms related to As cycling in the environment.

*Redox Cycling Experiments. Chemical Metal Release: Reaction with Deionized Water and Phosphate.* The arsenic concentrations in solution measured from aerobic batch experiments reacting contaminated sediments with phosphate were at least five times higher than those reacted with deionized water (Figure 1A). For instance, a maximum concentration of 17 μM As (43% of the total As) was released from batch reactors supplied with 10 mM phosphate under aerobic conditions compared with 2.5 μM As released (2.7% of the total) from batch experiments reacting contaminated sediments with deionized water under aerobic conditions (Figure 3A,B). Once the maximum release of As was obtained under aerobic conditions, the concentrations remained stable when the batch reactors were transitioned to anaerobic conditions (Figure 1A). Thus, the use of phosphate in the batch reactors over the experimental time frame was not controlled by redox conditions.

The maximum concentrations of released Fe and Mn were 6.8 μM Fe and 1.8 μM Mn when reacting with deionized water



| REFERENCE | Control | Anaerobic | Aerobic-Anaerobic |
|---|---|---|---|
| As(V) | 1.00 | 0.36 | 0.49 |
| As(III) | 0.00 | 0.64 | 0.51 |

**Figure 4.** As K-edge XANES analysis for control, anaerobic, and aerobic–anaerobic samples.

and 8.9 $\mu$M Fe and 0.8 $\mu$M Mn when reacting with 10 mM phosphate. The release of Fe and Mn increased after transitioning to anaerobic conditions, which ranged from 20 to 61 $\mu$M (Figure 2). A total of 0.04% Fe and 0.2% Mn was released from the sediments after reaction with deionized water, while a maximum release of 0.1% of the total Fe and 7.2% of the total Mn was released after reaction with 10 mM phosphate after transitioning to anaerobic conditions (Figure 3).

Phosphate induced the release of As from the contaminated sediments under aerobic conditions because of competitive ion displacement, which is in agreement with our previous findings. The mobilization of As can be caused by $PO_4$ ions since they are competing oxyanions for surface sites with similar chemical structures and p$K_a$s.[4,8,53] Lower magnitudes of soluble Fe and Mn release from phosphate incubations, and deionized water confirms that ion displacement is the driving mechanism for As release under these conditions (0–168 h).

*Microbial Metal Release: Glucose Amendments.* Assays amended with glucose as an electron donor released the highest concentration of As in experiments transitioning from aerobic to anerobic conditions. Metal concentrations in solution increased when transitioning from aerobic to anaerobic conditions because of microbial respiration and were at least 10 times higher than those obtained from the chemical experiments with phosphate explained in the previous subsection. For example, maximum concentrations of 69 $\mu$M As, 1559 $\mu$M Fe, and 276 $\mu$M Mn were obtained in experiments amended with glucose transitioning from aerobic to anaerobic conditions. Soluble Fe(II) ranged from 5.5 to 968 $\mu$M in assays provided with glucose after cycling from aerobic to anaerobic conditions. In addition, the maximum percentage of metals released were at least twice as high as those chemically released by the addition of phosphate (Figure 3). These results indicate that the addition of an exogenous electron donor, in this case glucose, and transitioning from aerobic to anaerobic favors the metal mobilization.

Limited metal release was detected in batch experiments amended with glucose under aerobic conditions (0–168 h). The metal release observed in experiments amended with glucose was comparable with that obtained after reaction with deionized water under aerobic conditions. Both glucose and deionized water are weak chemical reactants under aerobic conditions, as suggested by the maximum percentage released in Figure 3. Total metal release (As, Fe, Mn) ranged from 0.46 to 61 $\mu$M for phosphate experiments compared with 4.7–1558 $\mu$M for glucose experiments. Overall, glucose amendments released more metals from the contaminated solid compared with the chemically driven phosphate releases measured in the above batch experiments.

The transition from aerobic to anaerobic conditions enabled the microbial community in the contaminated sediments to use As, Mn, and Fe as electron acceptors with glucose as an electron donor. Several field experiments[54−56] and laboratory microbial batch incubations under anaerobic conditions[28,34,57−59] have shown that the addition of labile organic matter, such as glucose, to aquifer sediments leads to greater rates of arsenic release to groundwater. The highest concentration of As coincided with high releases of total Fe from glucose amendments after cycling to anaerobic conditions. Our results indicate that glucose, an exogenous electron donor, can support the reductive dissolution of mineralized forms of As and Fe from contaminated sediments.

Pseudo-first-order rate constants were obtained for As, Fe, and Mn released in experiments that transitioned from aerobic to anaerobic conditions and were amended with glucose. The pseudo-first-order rate constants ($k_1$) were only obtained for experiments transitioning from aerobic to anaerobic conditions and amended with glucose, which yielded the highest metal release for all experiments conducted in this study. The $k_1$ values obtained for As, Fe, and Mn range from 0.552 to 0.859 $d^{-1}$ (Figure S2). The $R^2$ values obtained for the regressions for the pseudo-first-order rate analysis of ln[Metals] derived from the integration of Equation S-1 were all greater than 0.95. The $k_1$ values obtained for this study were within the same order of

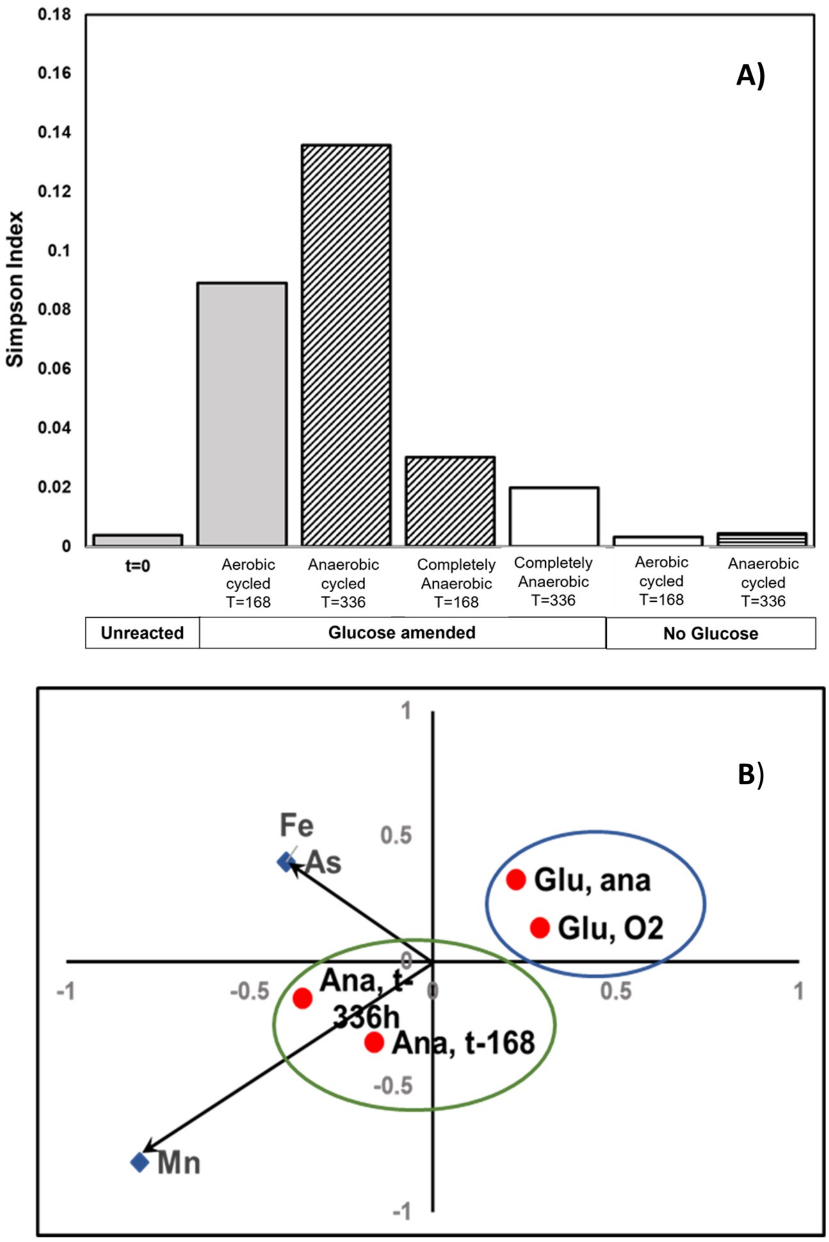


**Figure 5.** (A) Alpha diversity of the microbial community changes with aerobic-to-anaerobic cycling with and without glucose amendment. (B) NMDS analysis of the correlation between the microbial community changes and As, Fe, and Mn dissolution rates due to the aerobic−anaerobic cycling ("Glu, O2" and "Glu, ana") or under fully anaerobic condition (Ana).

magnitude as those measured in previous microbial reduction studies for Fe and Mn.[60,25,23] For instance, the kinetics of microbial Fe(III) reduction during the anaerobic incubation of wetland sediments followed first order rates (0.075−0.138 $d^{-1}$) in the presence of organic matter.[61] Recently, similar microbial reduction rates of As(V) were obtained using a kinetic model for systems with microorganisms and Fe oxides.[62] Time-dependent microbial reduction rate coefficients in experiments with As, Fe oxides, and microorganisms highlight the importance of differentiating between chemical, microbial, and physical mechanisms for kinetic investigations.[63]

Experiments amended with glucose and cycling conditions released higher concentrations compared with unamended or nontransitioned incubations. Iron concentrations remained stable until being transitioned to anaerobic conditions, after which a maximum concentration of 1335 $\mu$M was reached. The mobilization of As and co-occurring metals from anaerobic environments have been previously investigated using natural field samples and controlled laboratory incubations.[64−66] Additional analyses were conducted to assess the speciation of As in reacted contaminated sediments.

*Speciation of As in Reacted Contaminated Solids Amended with Glucose.* The results from linear combination fitting of As K-edge XANES spectra indicate that As reduction occurred in the solids after exposure to anaerobic conditions (Figure 4). The unreacted sample is dominantly As(V), as suggested by the linear combination fits using scorodite ($FeAsO_4$) and adsorbed As(V) as end members, which corroborates that the anaerobic culture reduced As(V) to As(III). Additionally, linear combination fits were performed to the control, anaerobic, and aerobic−anaerobic samples using the unreacted sample and adsorbed As(III) as end members to better understand the transformation from the unreacted As(V) to As(III). After exposure to anaerobic conditions, 64% As(III) was detected and was comparable with the 51% detected in the aerobic−anaerobic scenario, especially given that the error in the linear combination fitting of XANES spectra is within 10%. The reduction of As observed in the solid analyses is consistent with the As and Fe released in the aqueous chemistry analyses, which supports that anaerobic respiration can cause the reductive dissolution of As and Fe minerals in contaminated sediments.

*Microbial Community Changes in Response to Aerobic−Anaerobic Cycling with Endogenous Electron Donor.* DNA Illumina sequencing allowed us to evaluate microbial community changes under different experimental conditions. Figure 5A shows the changes in microbial diversity (Simpson Index) and richness and how they relate with glucose amendment and redox conditions. The addition of an exogenous electron donor increased the microbial diversity of the samples and drove the major changes in the microbial communities. The microbial richness of the sediments did not change during the treatments and was maintained between 1583 and 1816. The Simpson Index was 0.004 in the untreated sediments, and it did not change in the endogenous treatments during the aerobic−anaerobic cycling. However, the Simpson Index increased 10× to 0.03 in the fully anaerobic experiment after the addition of glucose. This increase was even greater during the cycling of aerobic to anaerobic conditions. The Simpson Index was 0.09 at the end of the aerobic incubation and 0.16 at the end of the anaerobic period when glucose was amended to the sediments.

The changes in the microbial communities and their correlation with As, Fe, and Mn dissolution rates were evaluated using NMDS, and they are shown in Figure 5B. In this analysis, similar microbial communities (i.e., data sets) group closer together through a Bray−Curtis similarity analysis, and the vectors represent the rate of As, Fe, or Mn dissolution that drives changes in the microbial communities. This statistical analysis demonstrated that redox cycling modified the makeup of the microbial communities. Further, As and Fe dissolution rates drove the same change in the microbial community, since their vectors cluster together, while the Mn dissolution rate influenced the community structure in an opposite direction. The changes in the microbial community speciation was further investigated.

Changes in the proportion of As and Fe utilizers in the treatments were evaluated (Figure S3), and Table S5 provides details on the As and Fe utilizer composition. The addition of an exogenous electron donor stimulated metal-reducing heterotrophs under reducing conditions. The addition of glucose under fully anaerobic conditions fueled a significant increase on As- and Fe-utilizing microorganisms, while the proportion of As- and Fe-utilizers did not significantly change in the other treatments. The As and Fe concentrations in solution increase in anaerobic conditions with the addition of an exogenous electron donor. Additionally, an increase in *Geobacter* was detected from 121 to 5179 OTU, which accounts for 0.4 and 16.8% of the total OTU in the sediments, respectively. The results suggest that these conditions (e.g., anaerobic conditions and the addition of an exogenous electron donor) could stimulate microbially catalyzed metal mobilization. In addition, the genus of As-reducing bacteria *Desulfosporosinus* also increased from 71 to 1748 OTU (0.2% to 5.6% total OTU), and the Fe-reducing bacteria *Clostridium* increased from 336 to 5515 OTU (1.1% to 17.64% total OTU).

Altogether, the link between the As and Fe biogeochemical cycles controls As mobility and dissolution in sediments. As and Fe dissolution rates drive the same changes in the structure of the microbial communities, which is expected since microbial metabolism pathways are found frequently on the same microorganisms. Interestingly, the greater concentration of As- and Fe-reducing microorganisms in the sediments did not translate to an increase in As and Fe mobilization rates, which was enhanced under aerobic-to-anaerobic cycling conditions. However, the increase in As(III) detected in sediments did correspond with a decrease in As and Fe mobilization compared with the phosphate-amended and transitioned experiment. Hence, glucose-amended anaerobic conditions contributed to a decrease on the labile fraction of As and Fe in the sediments.

*Biogeochemical Considerations.* Previous studies have reported that the microbial reduction of metal-bearing solids can influence the release of As, Fe, and Mn under various redox conditions.[67] The potential processes driving metal release from the contaminated sediments used in this study are (1) the transition from aerobic to anaerobic conditions, which induces the microbial reduction of As, Fe, and Mn from contaminated sediment in experiments amended with glucose, an exogenous electron donor, and (2) the influence of competitive ion displacement, which can drive the release of surface-bound As under aerobic conditions. The release of 74% As that was originally present in the contaminated sediments reacted with glucose was catalyzed by microbial reduction, as observed in experiments transitioning from aerobic to anaerobic conditions. However, only 43% of the As that was originally present in the contaminated sediments was released by competitive ion displacement, as observed in experiments reacted with phosphate. The release of As, Fe, and Mn reacted with water and glucose are comparable under aerobic conditions because glucose is expected to be neutrally charged at the pH range investigated in this study. Therefore, the concentrations released aerobically after reaction with glucose and water represent a labile fraction.

The transition from aerobic to anaerobic conditions triggers microorganisms to catalyze the reduction of As, Fe, and Mn as electron acceptors in contaminated sediments in the presence of an electron donor (e.g., glucose). The release of As versus Fe follows a linear trend ($R^2 = 0.967$) in the anaerobic portion of the experiments after transitioning from aerobic to anaerobic conditions and amendment with glucose, which suggests a reductive dissolution of As- and Fe-bearing minerals (Figure S4A). Reduction from As(V) to As(III) of the contaminated sediments was confirmed in the bulk using XANES. The microbial reductive dissolution of As, Fe, and Mn can depend on the oxidation−reduction potential, electron donor source, microbial community composition, and solution chemistry.[57,68−72] The glucose incubations from our experiments released a higher proportion of Fe compared with As under completely anaerobic conditions. Similarly, another study that used glucose as an electron donor reported a higher release of Fe compared with As from sediments obtained from the Mekong delta to reductive mineral dissolution.[73] The extent of As release in completely anaerobic conditions can be doubled by the addition of glucose via the reduction of As(V) and Fe(III) oxides, compared with incubations without an electron donor.[74] These reductive processes are key drivers of As release to solution from the solid phase.[11,75]

In agreement with our findings, the reductive dissolution and enhanced release of metals have been reported in redox-sensitive studies amended with electron donors such as acetate, glucose, and lactate.[20,59,62,72,76] For example, As, Fe, and Mn release rates obtained from a contaminated sediment under anaerobic-to-aerobic conditions amended with lactate had a similar release trend under anaerobic conditions.[56,59] However, the order of redox changes of anaerobic to aerobic was the opposite of that evaluated in our study (aerobic to anaerobic, as shown in Figures 1 and 2). Similar to the microbial reduction illustrated in our study, dissimilatory As reduction catalyzed by well-known microorganisms (e.g., *Shewanella*, *Geobacter*) can contribute to As enrichment in groundwater or other reduced zones.[12,22,24,62,72] In reduced zones, coupled Fe and sulfur (S) redox cycles can control dissolved arsenic concentrations. Previous studies show that the rate of microbially mediated sulfate reduction limits the concentration of dissolved arsenic, which depends on the solubility of sulfide phases.[77,78] The sulfate concentrations in solution from our study increased under aerobic conditions and decreased under anaerobic conditions (Figure S5). Similarly, under the completely anaerobic scenario, sulfate decreased over the experimental period. These data confirm that sulfate utilization likely occurred under anaerobic conditions, but more analyses are needed to evaluate sulfur's relative contribution to the mobilization of metals.

In contrast to microbially driven mobilization, the release of As and Fe did not follow a linear trend in experiments reacting contaminated sediments with 10 mM phosphate ($R^2$=0.357) (Figure S6). In a previous study from our group from the same site, As was preferentially released compared with Fe, which indicates that competitive ion displacement was a predominant process for release under aerobic conditions.[4] The limited release of As and Fe was also not linear in experiments reacting contaminated sediments with glucose under aerobic conditions ($R^2$=0.1994), which confirms that the release of As and Fe corresponds to a labile fraction. This result is consistent with other studies that reacted deionized water and weak extractants with sediments from the watershed.[4,6,79] Altogether, less Fe and Mn was released in experiments reacting contaminated sediments with deionized water, glucose, and phosphate under aerobic conditions. Many oxyanions, like phosphate, can interact with the surface of Fe oxides and affect the adsorption/desorption of As.[80,81] The ion displacement of As(V) with phosphate is a proposed mechanism of As release from Fe oxide phases under aerobic conditions.[82−84] The presence of similar high-affinity anions for surface sites on Fe oxides, such as phosphate, silicic acid, and bicarbonate, can contribute to the mobility of As under oxidizing conditions.[8,80,85,86] However, a higher magnitude and similar distribution of As, Fe, and Mn release resulting from reductive dissolution is observed in various studies, compared with only aerobic As release because of ion displacement.[56,62,85]

## ■ CONCLUSION

The results in this study show the important role of microbial reduction in controlling metal release after transitioning from aerobic to anaerobic conditions. Although the As concentrations released in solution were lower compared with Fe and Mn, 74% of the As was released after the biogeochemical conditions evaluated in this study. These results indicate that As was the most amenable to be released under the chemical and microbiological conditions tested in this study when compared with Fe and Mn. The higher release of Fe is consistent with the initial concentration of Fe in the sediment, which was more enriched compared with Mn and As. The release of Fe represents only 7% of the total Fe in the contaminated sediments, which indicates that it was mostly present in mineral solid phases such as albite and grunerite, as indicated by XRD.

The elevated concentrations of As in riverbank sediments of the Cheyenne River watershed on tribal land is a concern for nearby communities given that the river receives contaminated sediment loads from the Homestake Mine upstream. In addition to previously reported chemical mechanisms affecting the release of As, the reductive dissolution of As, Fe, and Mn catalyzed by native microorganisms and redox cycling in contaminated sediments is also important to consider. We observed the highest microbial diversity and the release of the highest concentrations of As, Fe, and Mn in batch experiments that transition from aerobic to anaerobic redox conditions. The potential for long-term reductive dissolution of As and other metals could be a driving mechanism for metal release in reduced environments. The environmental samples used in batch incubations for this study were collected from regions of the watershed that house medicinal plants and food resources. Future studies are necessary to investigate the role of plants and organic matter in soils to better understand the pathways of exposure to As.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00370.

> Details on the pseudo-first order kinetic analysis and loss-on-ignition measurements; basal medium composition for redox batch experiments and summary of experimental setup; summary of metal concentrations in parent material from the study area used in batch experiments; summary of arsenic-utilizing microorganisms in original sediment samples and their changes after incubation conditions; XRD patterns of unreacted sediment; As, Fe, and Mn release and pseudo-first-order rate constants in batch experiments transitioning from aerobic to anaerobic conditions; changes in microbial communities after changing redox conditions with glucose amendments; As versus Fe release in batch reactors under aerobic conditions and after cycling from aerobic to anaerobic conditions amended with glucose and phosphate; sulfate release under completely anaerobic conditions and under aerobic conditions transitioned to anaerobic conditions (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Cherie L. DeVore** − *Department of Civil, Construction & Environmental Engineering, MSC01 1070, University of New Mexico, Albuquerque, New Mexico 87131, United States; Department of Earth Systems Science, Stanford University, Stanford, California 94305, United States;* orcid.org/0000-0001-9094-7529; Phone: (001) (505) 277-0870;

Email: cldevore@stanford.edu; Fax: (001) (505) 277-1918

### Authors

**Lucia Rodriguez-Freire** − *Department of Civil & Environmental Engineering, New Jersey Institute of Technology, Newark, New Jersey 07102, United States;* orcid.org/0000-0003-1296-0001

**Noelani Villa** − *Department of Civil, Construction & Environmental Engineering, MSC01 1070, University of New Mexico, Albuquerque, New Mexico 87131, United States*

**Maedeh Soleimanifar** − *Department of Civil & Environmental Engineering, New Jersey Institute of Technology, Newark, New Jersey 07102, United States*

**Jorge Gonzalez-Estrella** − *Department of Civil, Construction & Environmental Engineering, MSC01 1070, University of New Mexico, Albuquerque, New Mexico 87131, United States; School of Civil and Environmental Engineering, Oklahoma State University, Stillwater, Oklahoma 74078, United States;* orcid.org/0000-0002-4873-0454

**Abdul Mehdi S. Ali** − *Department of Earth and Planetary Sciences, MSC03 2040, University of New Mexico, Albuquerque, New Mexico 87131, United States*

**Juan Lezama-Pacheco** − *Department of Earth Systems Science, Stanford University, Stanford, California 94305, United States*

**Carlyle Ducheneaux** − *Department of Environment and Natural Resources, Cheyenne River Sioux Tribe, Eagle Butte, South Dakota 57625, United States*

**José M. Cerrato** − *Department of Civil, Construction & Environmental Engineering, MSC01 1070, University of New Mexico, Albuquerque, New Mexico 87131, United States;* orcid.org/0000-0002-2473-6376

Complete contact information is available at: https://pubs.acs.org/10.1021/acsearthspacechem.1c00370

### Notes

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## ■ REFERENCES

(1) Gonzales, M.; Erdei, E.; Hoover, J.; Nash, J. A Review of Environmental Epidemiology Studies in Southwestern and Mountain West Rural Minority Populations. *Curr. Epidemiol. Rep.* **2018**, *5* (2), 101−113.

(2) Welch, A. H.; Westjohn, D. B.; Helsel, D. R.; Wanty, R. B. Arsenic in Ground Water of the United States: Occurrence and Geochemistry. *Ground Water* **2000**, *38*, 589−604.

(3) Islam, R.; Salminen, R.; Lahermo, P. Arsenic and other toxic elemental contamination of groundwater, surface: Water and soil in Bangladesh and its possible effects on human health. *Environ. Geochem. Health* **2000**, *22* (1), 33−53.

(4) DeVore, C. L.; Rodriguez-Freire, L.; Mehdi-Ali, A.; Ducheneaux, C.; Artyushkova, K.; Zhou, Z.; Latta, D. E.; Lueth, V. W.; Gonzales, M.; Lewis, J.; et al. Effect of bicarbonate and phosphate on arsenic release from mining-impacted sediments in the Cheyenne River watershed, South Dakota, USA. *Environ. Sci.: Processes Impacts* **2019**, *21*, 456−468.

(5) Cherry, J. A.; Morel, F. M.; Rouse, J. V.; Schnoor, J. L.; Wolman, M. G. Hydrochemistry of sulfide and arsenic-rich tailings and alluvium along Whitewood Creek, South Dakota. *Miner. Energy Resour.* **1986**, *29* (4).

(6) Pfeifle, B.; Stamm, J.; Stone, J. Arsenic Geochemistry of Alluvial Sediments and Pore Waters Affected by Mine Tailings along the Belle Fourche and Cheyenne River Floodplains. *Water, Air, Soil Pollut.* **2018**, *229* (6), 183.

(7) Fuller, C. C.; Davis, J. A. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. *Nature* **1989**, *340* (6228), 52−54.

(8) Dixit, S.; Hering, J. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37* (18), 4182−4189.

(9) Bostick, B.; Fendorf, S. Arsenite sorption on troilite (FeS) and pyrite (FeS2). *Geochim. Cosmochim. Acta* **2003**, *67* (5), 909−921.

(10) Waychunas, G.; Rea, B.; Fuller, C.; Davis, J. Surface chemistry of ferrihydrite. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* **1993**, *57* (10), 2251−2269.

(11) Tufano, K.; Reyes, C.; Saltikov, C.; Fendorf, S. Reductive Processes Controlling Arsenic Retention: Revealing the Relative Importance of Iron and Arsenic Reduction. *Environ. Sci. Technol.* **2008**, *42* (22), 8283−8289.

(12) Cummings, D.; Caccavo, F.; Fendorf, S.; Rosenzweig, R. Arsenic mobilization by the dissimilatory Fe (III)-reducing bacterium Shewanella alga BrY. *Environ. Sci. Technol.* **1999**, *33* (5), 723−729.

(13) Zobrist, J.; Dowdle, P.; Davis, J.; Oremland, R. Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate. *Environ. Sci. Technol.* **2000**, *34* (22), 4747−4753.

(14) Fendorf, S.; Kocar, B. D.; Masue, Y.; Tufano, K. J.; Nico, P. S. Arsenic chemistry in soils and sediments. *Develop. Soil Sci.* **2010**, *34*, 357−378.

(15) Borch, T.; Kretzschmar, R.; Kappler, A.; Van Cappellen, P.; Ginder-Vogel, M.; Voegelin, A.; Campbell, K. Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. *Environ. Sci. Technol.* **2010**, *44* (1), 15−23.

(16) Ehlert, K.; Mikutta, C.; Kretzschmar, R. Effects of Manganese Oxide on Arsenic Reduction and Leaching from Contaminated Floodplain Soil. *Environ. Sci. Technol.* **2016**, *50* (17), 9251−9261.

(17) Turpeinen, R.; Pantsar-Kallio, M.; Häggblom, M.; Kairesalo, T. Influence of microbes on the mobilization, toxicity and biomethylation of arsenic in soil. *Sci. Total Environ.* **1999**, *236* (1−3), 173−180.

(18) Macur, R. E.; Wheeler, J. T.; McDermott, T. R.; Inskeep, W. P. Microbial populations associated with the reduction and enhanced mobilization of arsenic in mine tailings. *Environ. Sci. Technol.* **2001**, *35* (18), 3676−3682.

(19) Paez-Espino, D.; Tamames, J.; de Lorenzo, V.; Canovas, D. Microbial responses to environmental arsenic. *BioMetals* **2009**, *22* (1), 117−130.

(20) Focardi, S.; Pepi, M.; Ruta, M.; Marvasi, M.; Bernardini, E.; Gasperini, S.; Focardi, S. E. Arsenic precipitation by an anaerobic arsenic-respiring bacterial strain isolated from the polluted sediments of Orbetello Lagoon, Italy. *Lett. Appl. Microbiol.* **2010**, *51* (5), 578−585.

(21) Santini, J. M.; Sly, L. I.; Schnagl, R. D.; Macy, J. M. A new chemolithoautotrophic arsenite-oxidizing bacterium isolated from a gold mine: phylogenetic, physiological, and preliminary biochemical studies. *Appl. Environ. Microbiol.* **2000**, *66* (1), 92−97.

(22) Kocar, B. D.; Fendorf, S. Thermodynamic constraints on reductive reactions influencing the biogeochemistry of arsenic in soils and sediments. *Environ. Sci. Technol.* **2009**, *43* (13), 4871−4877.

(23) Ehlert, K.; Mikutta, C.; Kretzschmar, R. Impact of birnessite on arsenic and iron speciation during microbial reduction of arsenic-bearing ferrihydrite. *Environ. Sci. Technol.* **2014**, *48* (19), 11320−11329.

(24) Stuckey, J. W.; Schaefer, M. V.; Kocar, B. D.; Benner, S. G.; Fendorf, S. Arsenic release metabolically limited to permanently water-saturated soil in Mekong Delta. *Nature Geoscience* **2016**, *9* (9), 70−76.

(25) Chen, X.; Zeng, X. C.; Wang, J.; Deng, Y.; Ma, T.; Guoji, E.; Mu, Y.; Yang, Y.; Li, H.; Wang, Y. Microbial communities involved in arsenic mobilization and release from the deep sediments into groundwater in Jianghan plain, Central China. *Sci. Total Environ.* **2017**, *579*, 989−999.

(26) Postma, D.; Jessen, S.; Hue, N. T. M.; Duc, M. T.; Koch, C. B.; Viet, P. H.; Nhan, P. Q.; Larsen, F. Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. *Geochim. Cosmochim. Acta* **2010**, *74* (12), 3367−3381.

(27) Schaefer, M. V.; Ying, S. C.; Benner, S. G.; Duan, Y.; Wang, Y.; Fendorf, S. Aquifer Arsenic Cycling Induced by Seasonal Hydrologic Changes within the Yangtze River Basin. *Environ. Sci. Technol.* **2016**, *50* (7), 3521−3529.

(28) Anawar, H. M.; Akai, J.; Yoshioka, T.; Konohira, E.; Lee, J. Y.; Fukuhara, H.; Tari Kul Alam, M.; Garcia-Sanchez, A. Mobilization of arsenic in groundwater of Bangladesh: evidence from an incubation study. *Environ. Geochem. Health* **2006**, *28* (6), 553−565.

(29) Mladenov, N.; Zheng, Y.; Miller, M. P.; Nemergut, D. R.; Legg, T.; Simone, B.; Hageman, C.; Rahman, M. M.; Ahmed, K. M.; McKnight, D. M. Dissolved Organic Matter Sources and Consequences for Iron and Arsenic Mobilization in Bangladesh Aquifers. *Environ. Sci. Technol.* **2010**, *44* (1), 123−128.

(30) Jiang, Y.; Xi, B.; Li, R.; Li, M.; Xu, Z.; Yang, Y.; Gao, S. Advances in Fe (III) bioreduction and its application prospect for groundwater remediation: A review. *Front. Environ. Sci. Eng.* **2019**, *13*, 89.

(31) Lovley, D. R.; Phillips, E. J. Organic matter mineralization with reduction of ferric iron in anaerobic sediments. *Appl. Environ. Microbiol.* **1986**, *51* (4), 683−689.

(32) Myers, C. R.; Nealson, K. H. Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor. *Science* **1988**, *240* (4857), 1319−1321.

(33) Burdige, D. J.; Dhakar, S. P.; Nealson, K. H. Effects of manganese oxide mineralogy on microbial and chemical manganese reduction. *Geomicrobiol. Journal* **1992**, *10* (1), 27−48.

(34) Islam, F. S.; Gault, A. G.; Boothman, C.; Polya, D. A.; Charnock, J. M.; Chatterjee, D.; Lloyd, J. R. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* **2004**, *430* (6995), 68−71.

(35) Blake, J. M.; Avasarala, S.; Artyushkova, K.; Ali, A. M.; Brearley, A. J.; Shuey, C.; Robinson, W. P.; Nez, C.; Bill, S.; Lewis, J.; et al. Elevated Concentrations of U and Co-occurring Metals in Abandoned Mine Wastes in a Northeastern Arizona Native American Community. *Environ. Sci. Technol.* **2015**, *49* (14), 8506−8514.

(36) Schloss, P. D.; Westcott, S. L.; Ryabin, T.; Hall, J. R.; Hartmann, M.; Hollister, E. B.; Lesniewski, R. A.; Oakley, B. B.; Parks, D. H.; Robinson, C. J.; et al. Introducing Mothur: Open-Source, Platform-Independent, Community-Supported Software for Describing and Comparing Microbial Communities. *Appl. Environ. Microbiol.* **2009**, *75* (23), 7537−7541.

(37) Kozich, J. J.; Westcott, S. L.; Baxter, N. T.; Highlander, S. K.; Schloss, P. D. Development of a Dual-Index Sequencing Strategy and Curation Pipeline for Analyzing Amplicon Sequence Data on the MiSeq Illumina Sequencing Platform. *Appl. Environ. Microbiol.* **2013**, *79* (17), 5112−5120.

(38) Shannon, C. E.; Weaver, W. *The Mathematical Theory of Communication*; The University of Illinois Press, 1998.

(39) Simpson, E. H. Measurement of Diversity. *Nature* **1949**, *163* (4148), 688−688.

(40) Saup, C.; Williams, K.; Rodriguez-Freire, L.; Cerrato, J.; Johnston, M.; Wilkins, M. Anoxia stimulates microbially catalyzed metal release from Animas River sediments. *Environ. Sci.: Processes Impacts* **2017**, *19* (4), 578−585.

(41) Valverde, A.; Gonzalez-Tirante, M.; Medina-Sierra, M.; Santa-Regina, I.; Garcia-Sanchez, A.; Igual, J. M. Diversity and community structure of culturable arsenic-resistant bacteria across a soil arsenic gradient at an abandoned tungsten-tin mining area. *Chemosphere* **2011**, *85* (1), 129−134.

(42) Fierer, N.; Jackson, R. B. The Diversity and Biogeography of Soil Bacterial Communities. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103* (3), 626.

(43) Fierer, N.; Breitbart, M.; Nulton, J.; Salamon, P.; Lozupone, C.; Jones, R.; Robeson, M.; Edwards, R. A.; Felts, B.; Rayhawk, S.; et al. Metagenomic and Small-Subunit rRNA Analyses Reveal the Genetic Diversity of Bacteria, Archaea, Fungi, and Viruses in Soil. *Appl. Environ. Microbiol.* **2007**, *73* (21), 7059−7066.

(44) Reguera, G.; Kashefi, K. The electrifying physiology of Geobacter bacteria, 30 years on. *Adv. Microbiol. Physiol.* **2019**, *74*, 1−96.

(45) Giloteaux, L.; Holmes, D. E.; Williams, K. H.; Wrighton, K. C.; Wilkins, M. J.; Montgomery, A. P.; Smith, J. A.; Orellana, R.; Thompson, C. A.; Roper, T. J.; et al. Characterization and transcription of arsenic respiration and resistance genes during in situ uranium bioremediation. *ISME J.* **2013**, *7* (2), 370−383.

(46) Ohtsuka, T.; Yamaguchi, N.; Makino, T.; Sakurai, K.; Kimura, K.; Kudo, K.; Homma, E.; Dong, D. T.; Amachi, S. Arsenic dissolution from Japanese paddy soil by a dissimilatory arsenate-reducing bacterium Geobacter sp. OR-1. *Environ. Sci. Technol.* **2013**, *47* (12), 6263−6271.

(47) Gihring, T. M.; Banfield, J. F. Arsenite oxidation and arsenate respiration by a new Thermus isolate. *FEMS Microbiol. Lett.* **2001**, *204* (2), 335−340.

(48) Liu, A.; Garcia-Dominguez, E.; Rhine, E. D.; Young, L. Y. A novel arsenate respiring isolate that can utilize aromatic substrates. *FEMS Microbiol. Ecol.* **2004**, *48* (3), 323−332.

(49) Pérez-Jiménez, J. R.; DeFraia, C.; Young, L. Y. Arsenate respiratory reductase gene (arrA) for Desulfosporosinus sp. strain Y5. *Biochem. Biophys. Res. Commun.* **2005**, *338* (2), 825−829.

(50) Muller, D.; Médigue, C.; Koechler, S.; Barbe, V.; Barakat, M.; Talla, E.; Bonnefoy, V.; Krin, E.; Arsène-Ploetze, F.; Carapito, C.; et al. A tale of two oxidation states: bacterial colonization of arsenic-rich environments. *PLoS Genet.* **2007**, *3* (4), e53.

(51) Simeonova, D. D.; Micheva, K.; Muller, D. A.; Lagarde, F.; Lett, M. C.; Groudeva, V. I.; Lièvremont, D. Arsenite oxidation in batch reactors with alginate-immobilized ULPAs1 strain. *Biotechnol. Bioeng.* **2005**, *91* (4), 441−446.

(52) Rodríguez-Freire, L. a.; Sun, W.; Sierra-Alvarez, R.; Field, J. A. Flexible bacterial strains that oxidize arsenite in anoxic or aerobic conditions and utilize hydrogen or acetate as alternative electron donors. *Biodegradation* **2012**, *23* (1), 133−143.

(53) Peryea, F.; Kammereck, R.; et al. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Water, Air, Soil Pollut.* **1997**, *93* (1−4), 243−254.

(54) Harvey, C. F.; Swartz, C. H.; Badruzzaman, A. B. M.; Keon-Blute, N.; Yu, W.; Ali, M. A.; Jay, J.; Beckie, R.; Niedan, V.; Brabander, D.; et al. Arsenic Mobility and Groundwater Extraction in Bangladesh. *Science* **2002**, *298* (5598), 1602−1606.

(55) Stucker, V. K.; Williams, K. H.; Robbins, M. J.; Ranville, J. F. Arsenic geochemistry in a biostimulated aquifer: An aqueous speciation study. *Environ. Toxicol. Chem.* **2013**, *32* (6), 1216−1223.

(56) Neidhardt, H.; Berner, Z. A.; Freikowski, D.; Biswas, A.; Majumder, S.; Winter, J.; Gallert, C.; Chatterjee, D.; Norra, S. Organic carbon induced mobilization of iron and manganese in a West Bengal aquifer and the muted response of groundwater arsenic concentrations. *Chem. Geol.* **2014**, *367*, 51−62.

(57) van Geen, A.; Rose, J.; Thoral, S.; Garnier, J. M.; Zheng, Y.; Bottero, J. Y. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. *Geochim. Cosmochim. Acta* **2004**, *68* (17), 3475−3486.

(58) Akai, J.; Izumi, K.; Fukuhara, H.; Masuda, H.; Nakano, S.; Yoshimura, T.; Ohfuji, H.; Md Anawar, H.; Akai, K. Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. *Appl. Geochem.* **2004**, *19* (2), 215−230.

(59) Freikowski, D.; Neidhardt, H.; Winter, J.; Berner, Z.; Gallert, C. Effect of carbon sources and of sulfate on microbial arsenic mobilization in sediments of West Bengal, India. *Ecotoxicol. Environ. Saf.* **2013**, *91*, 139−146.

(60) Nealson, K. H.; Saffarini, D. Iron and Manganese in Anaerobic Respiration: Environmental Significance, Physiology, and Regulation. *Annu. Rev. Microbiol.* **1994**, *48* (1), 311−343.

(61) Roden, E.; Wetzel, R. Kinetics of microbial Fe (III) oxide reduction in freshwater wetland sediments. *Limnol. Oceanogr.* **2002**, *47* (1), 198−211.

(62) Shi, Z.; Hu, S.; Lin, J.; Liu, T.; Li, X.; Li, F. Quantifying Microbially Mediated Kinetics of Ferrihydrite Transformation and Arsenic Reduction: Role of Arsenate-reducing Gene Expression Pattern. *Environ. Sci. Technol.* **2020**, *54* (11), 6621−6631.

(63) Lin, J.; Hu, S.; Liu, T.; Li, F.; Peng, L.; Lin, Z.; Dang, Z.; Liu, C.; Shi, Z. Coupled Kinetics Model for Microbially Mediated Arsenic Reduction and Adsorption/Desorption on Iron Oxides: Role of Arsenic Desorption Induced by Microbes. *Environ. Sci. Technol.* **2019**, *53*, 8892−8902.

(64) Ying, S.; Kocar, B.; Griffis, S.; Fendorf, S. Competitive Microbially and Mn Oxide Mediated Redox Processes Controlling Arsenic Speciation and Partitioning. *Environ. Sci. Technol.* **2011**, *45* (13), 5572−5579.

(65) Masscheleyn, P.; Delaune, R.; Patrick, W. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* **1991**, *25* (8), 1414−1419.

(66) Rajpert, L.; Kolvenbach, B. A.; Ammann, E. M.; Hockmann, K.; Nachtegaal, M.; Eiche, E.; Schäffer, A.; Corvini, P. F. X.; Skłodowska, A.; Lenz, M. Arsenic Mobilization from Historically Contaminated Mining Soils in a Continuously Operated Bioreactor: Implications for Risk Assessment. *Environ. Sci. Technol.* **2016**, *50* (17), 9124−9132.

(67) Cai, X.; ThomasArrigo, L. K.; Fang, X.; Bouchet, S.; Cui, Y.; Kretzschmar, R. Impact of Organic Matter on Microbially-Mediated Reduction and Mobilization of Arsenic and Iron in Arsenic (V)-Bearing Ferrihydrite. *Environ. Sci. Technol.* **2021**, *55* (2), 1319−1328.

(68) Lovley, D. R.; Phillips, E. J. P. Novel Mode of Microbial Energy Metabolism: Organic Carbon Oxidation Coupled to Dissimilatory Reduction of Iron or Manganese. *Appl. Environ. Microbiol.* **1988**, *54* (6), 1472−1480.

(69) Stolz, J. F.; Oremland, R. S. Bacterial respiration of arsenic and selenium. *FEMS Microbiol. Rev.* **1999**, *23* (5), 615−627.

(70) Yamamura, S.; Amachi, S. Microbiology of inorganic arsenic: From metabolism to bioremediation. *J. Biosci. Bioeng.* **2014**, *118* (1), 1−9.

(71) Xiu, W.; Ke, T.; Lloyd, J. R.; Shen, J.; Bassil, N. M.; Song, H.; Polya, D. A.; Zhao, Y.; Guo, H. Understanding Microbial Arsenic-Mobilization in Multiple Aquifers: Insight from DNA and RNA Analyses. *Environ. Sci. Technol.* **2021**, *55* (22), 15181−15195.

(72) Das, S.; Liu, C.-C.; Jean, J.-S.; Lee, C.-C.; Yang, H.-J. Effects of microbially induced transformations and shift in bacterial community on arsenic mobility in arsenic-rich deep aquifer sediments. *J. Hazard. Mater.* **2016**, *310*, 11−19.

(73) Stuckey, J. W.; Schaefer, M. V.; Benner, S. G.; Fendorf, S. Reactivity and speciation of mineral-associated arsenic in seasonal and permanent wetlands of the Mekong Delta. *Geochim. Cosmochim. Acta* **2015**, *171*, 143−155.

(74) Schaefer, M. V.; Guo, X.; Gan, Y.; Benner, S. G.; Griffin, A. M.; Gorski, C. A.; Wang, Y.; Fendorf, S. Redox controls on arsenic enrichment and release from aquifer sediments in central Yangtze River Basin. *Geochim. Cosmochim. Acta* **2017**, *204*, 104−119.

(75) Fendorf, S.; Herbel, M. J.; Tufano, K. J.; Kocar, B. D. *Biogeochemical Processes Controlling the Cycling of Arsenic in Soils and Sediments. in Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments* **2007**, 313−338.

(76) Duan, Y.; Schaefer, M. V.; Wang, Y.; Gan, Y.; Yu, K.; Deng, Y.; Fendorf, S. Experimental constraints on redox-induced arsenic release and retention from aquifer sediments in the central Yangtze River Basin. *Sci. Total Environ.* **2019**, *649*, 629−639.

(77) Sun, J.; Quicksall, A. N.; Chillrud, S. N.; Mailloux, B. J.; Bostick, B. C. Arsenic mobilization from sediments in microcosms under sulfate reduction. *Chemosphere* **2016**, *153*, 254−261.

(78) O'Day, P.; Vlassopoulos, D.; Root, R.; Rivera, N. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc.Natl.Acad. Sci. U. S. A.* **2004**, *101* (38), 13703−13708.

(79) U.S. Geological Survey Toxic Substances Hydrology Program. *Toxic substances in surface waters and sediments: a study to assess the effects of arsenic-contaminated alluvial sediment in Whitewood Creek, South Dakota*; Kuwabara, J. S., Fuller, C. C., Eds.; U.S. Geological Survey Professional Paper, Vol. *1681*; U.S. Geological Survey: Denver, CO, 2003.

(80) Hongshao, Z.; Stanforth, R. Competitive adsorption of phosphate and arsenate on goethite. *Environ. Sci. Technol.* **2001**, *35* (24), 4753−4757.

(81) Goldberg, S.; Suarez, D. Arsenate Adsorption by Unsaturated Alluvial Sediments. *Soil Sci. Soc. Am. J.* **2013**, *77* (3), 782−791.

(82) Choi, S.; O'Day, P. A.; Hering, J. G. Natural Attenuation of Arsenic by Sediment Sorption and Oxidation. *Environ. Sci. Technol.* **2009**, *43* (12), 4253−4259.

(83) Borch, T.; Masue, Y.; Kukkadapu, R. K.; Fendorf, S. Phosphate Imposed Limitations on Biological Reduction And Alteration of Ferrihydrite. *Environ. Sci. Technol.* **2007**, *41* (1), 166−72.

(84) Zeng, H.; Fisher, B.; Giammar, D. Individual and competitive adsorption of arsenate and phosphate to a high-surface-area iron oxide-based sorbent. *Environ. Sci. Technol.* **2008**, *42* (1), 147−152.

(85) Su, C.; Puls, R. W. Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. *Environ. Sci. Technol.* **2001**, *35* (22), 4562−4568.

(86) Jain, A.; Loeppert, R. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. *J. Environ. Qual.* **2000**, *29* (5), 1422−1430.