Elevated oxidizing compounds influencing the biogeochemistry of arsenic in subsurface environments

W.J. Sun

Department of Civil and Environmental Engineering, Southern Methodist University, Dallas, Texas, USA

ABSTRACT: Arsenic contamination of groundwater and surface water is a worldwide problem, which poses health risks to millions of people in the world. The arsenic in the groundwater is of natural origin, and is released from the weathering of arsenic bearing minerals into the groundwater, owing to the anaerobic conditions of the subsurface. In this study, the oxidation of arsenite (As(III)) to arsenate (As(V)) linked to oxidizing compounds under anoxic conditions was shown to be a widespread microbial activity in anaerobic sludge and sediment samples that were not previously exposed to arsenic contamination. The results indicate that microbial oxidation of As(III) and Fe(II) linked to denitrification resulted in the enhanced immobilization of aqueous arsenic in anaerobic environments by forming Fe(III) (hydr)oxide coated sands with adsorbed As(V). Thus, the elevated oxidizing compounds could play critical roles in influencing the biogeochemistry of arsenic in subsurface environments.

1 INTRODUCTION

Arsenic contamination of groundwater and surface water is a worldwide problem, which poses the health risks to millions of people in the world (Smedley & Kinniburgh, 2002). The arsenic in the groundwater is largely of natural origin, and is released from the weathering of arsenic bearing minerals into the groundwater, owing to the anoxic conditions of the subsurface. As presented in Figure 1, microbiological processes play significant roles in controlling the fate and transport of arsenic in the natural environments. Under reducing conditions, microbial reduction of arsenate (As(V)) to arsenite (As(III)) and ferric (hydr)oxides to soluble Fe(II) are considered as the dominant mechanisms of arsenic mobilization in subsurface environments. On the other hand, if oxidizing conditions can be restored, arsenic can be immobilized by the formation of As(V) and ferric (hydr)oxides. As(V) is more strongly adsorbed than As(III) at circum-neutral conditions by common non-iron metal oxides in sediments such as those of aluminium. Ferric (hydr)oxides have strong affinity

for both As(III) and As(V) in circum-neutral environments. Nitrate or (per)chlorate can be considered as alternative oxidants with advantages over elemental oxygen due to their high aqueous solubility and lower chemical reactivity which together enable them to be better dispersed in the saturated subsurface. The main objective of this study was to illustrate the importance of anoxic oxidation of As(III) and Fe(II) linked to oxidizing compounds (nitrate or (per)chlorate) under anoxic conditions in the biogeochemical cycle of arsenic.

2 METHODS/EXPERIMENTAL

2.1 Microorganisms

Sludge and sediment samples obtained from different sources, including aerobic activated sludge and anaerobically digested sewage sludge, methanogenic granular sludges, and pond sediments, were used as inocula.

2.2 Batch bioassay

Batch bioassays were performed under anoxic conditions in serum flasks that were supplied with 120 mL of a basal mineral medium (pH 7.0–7.2) containing bicarbonate as the only carbon source. The medium was also supplemented with As(III) as the electron donor and nitrate (typically 10 mM, unless otherwise specified) as the electron acceptor. Various controls (e.g., abiotic controls, killed sludge controls, controls without electron acceptor) were applied based on the requirements of each experiment. All assays were conducted in triplicate.

Figure 1. Biogeochemical redox cycles of arsenic and iron.

Table 1. Summary of microbial As(III) oxidation under denitrifying conditions.

Inoculum		As(V) formation		Time
Name	Sources	With NO_3^-	Without NO_3^-	Days
NGS	Industrial UASB reactor	0.423 ± 0.004	ND	6
EGS	Industrial UASB reactor	ND	ND	ND
ADS	Anaerobic digested sludge	0.425 ± 0.003	ND	13
RAS	Aerobic activated sludge	ND	ND	ND
TDE	Thiosulfate-oxidizing denitrifier	0.416 ± 0.002	ND	10
DPS	Lake sediment	0.415 ± 0.003	ND	6
WCS	Winogradsky column	0.413 ± 0.001	ND	5
PCS	Pinal creek sediment	0.295 ± 0.020	0.298 ± 0.014	>14

ND: Not Detected

2.3 Column study

Anoxic As(III) and Fe(II) oxidation under denitrifying conditions was investigated in two glass sand packed bed columns that were fed continuously with synthetic basal medium and inoculated with As(III)-oxidizing denitrifying culture. The treatment column (SF1) was the biologically active column inoculated with chemolithotrophic As(III)-oxidizing denitrifying bacteria and fed with basal medium, As(III) (0.5 mg L^{-1}) and Fe(II) (20 mg L^{-1} Fe) as electron donating substrates, nitrate ($155 \text{ mg L}^{-1} \text{ NO}_3^-$) as the electron acceptor. The control column (SF2) was the same as SF1 but lacked nitrate in the medium.

2.4 Analytical method

As(III) and As(V) were analyzed by ion chromatography–inductively coupled plasma–mass spectroscopy (HPLC–ICP–MS). Nitrate and nitrite were analyzed by suppressed conductivity ion chromatography using a Dionex 3000 system. Other analytical determinations (e.g., pH, TSS, VSS) were conducted according to standard methods (APHA, 1999).

3 RESULTS AND DISCUSSION

3.1 Batch results

Sediments and sludge samples from environments not known to be contaminated with arsenic were incubated with As(III) either in the presence and absence of NO_3^- and were incubated in the absence of elemental oxygen. As presented in Table 1, six out of the eight inocula tested displayed microbial activity towards the anoxic oxidation of As(III) by nitrate. Five out of the six positive samples showed a dependency on the presence of NO_3^- for the anoxic oxidation of As(III). One of

Figure 2. (A) Removal of soluble total As in two sand packed columns fed with $6.67 \mu\text{M}$ As(III) and $360 \mu\text{M}$ Fe(II). Column SF1 (fed with 2.5 mM nitrate): ($\blacktriangle$) influent, ($\triangle$) effluent. Column SF2 (without nitrate): ($\bullet$) influent, ($\circ$) effluent. The dashed line indicates the day when the steady state operation was achieved. (B) Arsenic speciation in the influent and effluent of sand packed columns SF1 or SF2: As(III) (solid bars) and As(V) (empty bars).

the positive samples, PCS, had this activity both in the presence and absence of added NO_3^- , which may have been due to high levels of oxidized manganese species known to occur in that sediment (Lind & Hem, 1993). The average molar yield of nitrate linked As(III) oxidation was $0.94 \pm 0.04 \text{ mol As(V) formed mol}^{-1} \text{ As(III) consumed}$ and the value for the PCS sediment was similar. The results demonstrated that the anoxic oxidation of As(III) to As(V) linked to denitrification is a widespread microbial activity in anaerobic sludge and sediment samples that were not previously exposed to arsenic contamination.

3.2 Column results

The oxidation of As(III) linked to the use of common-occurring nitrate as an electron acceptor may be an important missing link in the biogeochemical cycling of arsenic. Thus, a bioremediation strategy was explored that is based on utilizing nitrate to support the microbial oxidation of Fe(II) and As(III) in the subsurface as a means to immobilize arsenic. Continuous flow columns packed with sand were used to simulate a natural anaerobic groundwater and sediment system with co-occurring As(III) and Fe(II) in

the presence (column SF1) or absence (column SF2) of nitrate, respectively.

The time-course of the influent and effluent total soluble arsenic concentrations from the two columns is illustrated in Figure 2A. The result shows that the release of soluble As was greater in SF2 compared to SF1, which is in accordance with the expected adsorption of As on the Fe(III) (hydr)oxides formed from anoxic Fe(II) oxidation. Figure 2B illustrates the average soluble arsenic species in the influent and effluent of columns SF1 and SF2 during the steady state period of operation from day 30 onward. The results show that 99.7% As(III) was eliminated from column SF1 and that it was not recovered as soluble As(V) in the effluent. In contrast, As(III) removal was marginal (9.7%) in the control column lacking nitrate (SF2). The results suggest that no adsorption had occurred, consistent with the low retention of Fe in the column.

4 CONCLUSIONS

Microbial oxidation of As(III) and Fe(II) by denitrifying microorganisms led to the formation of ferric (hydroxides) which adsorbed As(V) formed from As(III)-oxidation. The studies demonstrated that anoxic microbial oxidation of As(III) and Fe(II) linked

to denitrification significantly enhance the immobilization of arsenic in the anaerobic subsurface environments and may reduce the risk of arsenic contaminated water to public health and environmental ecological systems.

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