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Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation

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Abstract

Arsenic is a prevalent contaminant at US Superfund sites where remediation by pump and treat systems is often complicated by slow desorption of As from Fe and Al (hydr)oxides in aquifer solids. Chemical amendments that either compete with As for sorption sites or dissolve Fe and Al (hydr)oxides can increase As mobility and improve pump and treat remediation efficiency. The goal of this work was to determine optimal amendments for improving pump and treat at As contaminated sites such as the Vineland Chemical Co. Superfund site in southern New Jersey. Extraction and column experiments were performed using As contaminated aquifer solids (81 ± 1 mg/kg), site groundwater, and either phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) or oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). In extraction experiments, phosphate mobilized between 11% and 94% of As from the aquifer solids depending on phosphate concentration and extraction time (1 mM–1 M; 1–24 h) and oxalic acid mobilized between 38 and 102% depending on oxalic acid concentration and extraction time (1–400 mM; 1–24 h). In column experiments, phosphate additions induced more As mobilization in the first few pore volumes but oxalic acid was more effective at mobilizing As overall and at lower amendment concentrations. At the end of the laboratory column experiments, 48% of As had been mobilized from the aquifer sediments with 100 mM phosphate and 88% had been mobilized with 10 mM oxalic acid compared with 5% with ambient groundwater alone. Furthermore, simple extrapolations based on pore volumes suggest that chemical treatments could lower the time necessary for clean up at the Vineland site from 600 a with ambient groundwater alone to potentially as little as 4 a with 10 mM oxalic acid.

1. Introduction

1.1 Background

Arsenic is present at more than 500 US Superfund sites and is the second most common contaminant of concern after Pb (EPA, 2002, 2007). Elevated groundwater As can be the result of mobilization of As naturally occurring in minerals, sediments and soils or the result of anthropogenic inputs from As-based biocides, swine and poultry farming, mine tailings, coal

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combustion, wood treated with chromated copper arsenate, etc. (Leist, et al., 2000; Mandal and Suzuki, 2002; Oremland and Stolz, 2003; Smedley and Kinniburgh, 2002). Sites with contaminated groundwater commonly use pump and treat remediation technologies (Mackay and Cherry, 1989; Palmer and Fish, 1992). However, aquifer conditions (pH, oxidation-reduction potential, etc.) impact As mobility and the slow desorption of As from Fe and Al (hydr)oxides in solids can decrease the effectiveness of pump and treat systems (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Chemical amendments have the potential to accelerate As mobilization from soils and sediments and thus improve the efficiency of pump and treat remediation Palmer and Fish, 1992. By increasing As mobilization, more As contaminant would be removed from the aquifer system with each volume of groundwater extracted by the pump and treat system. This study examines the potential impact of phosphate and oxalic acid to accelerate As release from contaminated aquifer solids using laboratory extraction and column experiments.

Pump and treat is a widely used remediation option; the US EPA estimates there are more than 700 such systems in operation in the USA (EPA, 2003). However, pump and treat remediation can sometimes require decades to reach target clean up levels and systems tend to have high operation and maintenance costs; in a recent survey, the mean annual cost per site was \$570,000 for 79 sites reporting costs (EPA, 2001, 2003; Palmer and Fish, 1992). During remediation, the rate of decline in contaminant concentration can progressively decrease, a phenomenon sometimes referred to as tailing, making it difficult to reach target cleanup levels even with long treatment times (Kuhlmeier, 1997; Mackay and Cherry, 1989; Palmer and Fish, 1992). At sites where contaminant removal from the aquifer is controlled largely by chemical processes (adsorption, precipitation), it may be possible to enhance pump and treat remediation by altering aquifer chemistry (Palmer and Fish, 1992). Arsenic mobility can depend on adsorption-desorption reactions between As and Al, Fe, and Mn oxides in soils and sediments; these sorption processes can be impacted by a variety of factors including As speciation, pH, groundwater oxidation-reduction potential, microbial activity, and the presence of chemical species such as anions or ligands (EPA, 2002; Kuhlmeier, 1996; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Here the focus is on adding chemical species in order to increase As mobilization with the ultimate goal of improving the pump and treat operation efficiencies at As contaminated Superfund sites. The presence of various chemical anions or ligands can promote As release by competing with As for soil and sediment sorption sites or can lead to complexation reactions that mobilize As (Darland and Inskeep, 1997; Hongshao and Stanforth, 2001; Klarup, 1997; Panias, et al., 1996; Tao, et al., 2006; Zeng, et al., 2008). Though it is recognized that chemical additions could positively impact pump and treat remediation (i.e., the principles behind the methods are understood), the authors know of few other studies that have investigated potential applications of chemical additions at sites contaminated with As (Keimowitz, et al., 2005b; Palmer and Fish, 1992).

Two promising chemical amendments for As release are phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), both of which are often included in As sequential soil extraction schemes (Keon, et al., 2001; Swartz, et al., 2004; Wenzel, et al., 2001). Phosphate and arsenate are chemically analogous and numerous studies have shown that the presence of phosphate inhibits the adsorption of arsenate (As V) and arsenite (As III) by competing for suitable surface binding sites in soils and sediments and on Al and Fe (hydr)oxides (Darland and Inskeep, 1997; Dixit and Hering, 2003; Jain and Loeppert, 2000; Jeong, et al., 2007). Additionally, phosphate fertilizers have been shown to increase As release from orchard soils that were previously treated with lead arsenate pesticides (Peryea, 1991). Oxalic acid is a low molecular weight organic acid found naturally in soil solutions, typically at concentrations of 0–50 μM but has been observed at concentrations as high as 1 mM (Fox and Comerford, 1990; Strobel, 2001; van Hees, et al., 2000). Oxalic acid is effective at dissolving Al and Fe (hydr)oxides and is involved in the vertical transport of Al and Fe in soils (van Hees, et al., 2000). Arsenic is often

associated with or adsorbed to Al and Fe (hydr)oxides (De Vitre, et al., 1991; Jain and Loeppert, 2000; Sullivan and Aller, 1996); therefore, oxalic acid treatments should mobilize As co-precipitated or associated with amorphous Al and Fe (hydr)oxides (Keon, et al., 2001). A study by Zhang et al. (2005) showed that As mobilization by low molecular weight organic acids (including oxalic) was significantly correlated with Fe, Al and Mn mobilization in extraction experiments; they suggested a possible mechanism of As release from Fe, Al and Mn (hydr) oxides. Other studies suggest low molecular weight organic acids may lead to As release through competitive sorption mechanisms or suggest that both mechanisms may play a role (Shi, et al., 2009).

Through extraction and column experiments the ability of phosphate and oxalic acid for mobilizing As from contaminated aquifer solids was explored. Extractions were performed first and used to guide the design of column experiments. All experiments were performed with aquifer solids from the Vineland Superfund site. Though the chemical mechanisms are different, both phosphate and oxalic acid have the potential to increase As mobilization, making these chemical amendments promising candidates for accelerating pump and treat remediation at As contaminated sites.

1.2 Site Overview

The Vineland Chemical Company site is located in southern New Jersey, overlying the unconsolidated sands of the Cohansey Formation, which are interbedded with thin silt and clay layers. The Vineland Chemical Company produced As-based biocides from 1950–1994, during which time hundreds of tons of waste As were released into the environment due to improper chemical storage and disposal practices (EPA, 2006; Keimowitz, et al., 2005c). This resulted in extensive contamination of subsurface solids and groundwater with both organic and inorganic As species. Prior to the start of treatment, groundwater concentrations exceeded the current US EPA drinking water standard for As (10 µg/L) by up to 3 orders of magnitude. Discharge to an adjacent stream, Blackwater Branch, caused significant contamination of the stream's floodplain as well as bottom sediments of the nearby Maurice River and Union Lake (EPA, 2006). Site remediation includes a large groundwater pump and treat facility, designed to treat up to 7.5×10^6 L per day (2 million gallons), as well as excavating, cleaning, and replacing unsaturated zone sands and flood plain area soils. The pump and treat system has an estimated annual operation and maintenance cost of \$4 million (EPA, 2001). Soil washing at the Vineland Superfund site has significantly decreased the amount of As in the unsaturated zone; contaminated unsaturated zone sediments (~0–4.6 m below ground surface) in the former “hot” zone had a maximum >500 mg As/kg while cleaned sediments have As concentrations of <20 mg/kg. In comparison, offsite samples suggest that a representative background As concentration of these sandy sediments is less than 5 mg/kg. Only unsaturated zone sediments and the top 0.3–1 m of materials found below the water table were treated at the soil washing plant (maximum excavation to depths of ~4.9–5.6 m below ground surface). Since aquifer materials below this depth can still have elevated As, with typical As concentrations of 20–250 mg/kg, this reservoir of As can continue to contaminate the groundwaters; recent measurements at the recovery wells show As concentrations can still be several hundred µg/L.

2. Methods

2.1 Field Methods

Aquifer solids were obtained from a pit freshly dug down below the water table with a backhoe in the most contaminated region of the site (with As concentrations in the aquifer sediments typically 20–250 mg/kg). This section of the site is composed of medium to coarse-grained sands. The subsurface materials are largely oligotrophic and composed of quartz sand with a

thin layer of topsoil or fill in places. At the time of sampling, the majority of the unsaturated zone sediments had been removed from the most contaminated region of the site to be processed to remove As at a soil washing facility; the backhoe removed the remaining ~1 m depth of the unsaturated zone before sampling the aquifer sediments. The sandy aquifer solids were sealed in new metal paint cans (0.004 m³ each) and kept refrigerated until use. Groundwater for the column experiments was collected from a pump and treat well (RW 11) approximately 500 m from the sediment collection location; previous sampling suggested this well had low As and low Fe concentrations (7 µg/L and 230 µg/L, respectively). Groundwater parameters (pH, oxidation-reduction potential, electrical conductivity, and dissolved O₂) were monitored and allowed to stabilize to ensure the well was sufficiently flushed before collecting water in plastic cubitainers (Fisher Scientific). The water was allowed to equilibrate with the atmosphere for several days before moving it to cold storage to minimize subsequent microbial activity.

2.2 Extraction Experiments

Approximately 2 g of wet contaminated aquifer sediment (~80 mg/kg in As), equivalent to an average of ~1.9 g dry sediment, was combined with 10 mL of the desired extraction solution. The following solutions were used in separate extraction trials: 1 mM, 100 mM, and 1 M sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O) and 1 mM, 10 mM, 100 mM, and 400 mM oxalic acid dihydrate (C₂H₂O₄·2H₂O). The pH of each solution was measured (Fig. 1) but not adjusted. Samples were extracted for 1, 2, 4 or 24 h and were agitated on an adjustable rocker table (Cole-Parmer). Suspensions were centrifuged at 3000 rpm (Damon/IEC Division) for 10 min and the supernatants were decanted into acid washed bottles. Additional batch experiments were carried out to test the efficacy of increasing pH or inducing reducing conditions on the mobilization of As from Vineland aquifer sediments (see Supplementary Information).

2.3 Column Experiments

Contaminated aquifer sediments were used for the 5 column experiments. The sandy aquifer material was wet packed into a section of Geoprobe Macro-Core[®] liner approximately 25 cm × 4.2 cm ID. Glass wool (0.25–1.5 cm) was packed into each end to help distribute solution over the full cross sectional area of the column; the columns were sealed with PVC end caps. The columns were run in upflow mode at 2–3 m/d using a peristaltic pump (Rainin Instrument Co.) to control the flow rate. The flow velocity was in the range of estimated average groundwater flow under the study site during active pumping for treatment (estimate based on site dimensions and pump and treat plant design parameters). For initial experiments, solutions of ambient groundwater (column 1), ~1 mM phosphate in groundwater (column 2), and 1 mM oxalic acid in groundwater (column 3) were pumped through separately prepared columns for ~3 days (between 22 and 34 pore volumes depending on the column). Once results from those experiments were obtained, two other column experiments were designed, one involving introduction of a 100 mM phosphate solution in groundwater in 3 pulses of ~2 pore volumes each and groundwater washes between each pulse (column 4) and the other involving an influent solution of 10 mM oxalic acid in groundwater for ~21 pore volumes, followed by several more pore volumes of groundwater alone (column 5). A Br⁻ tracer test was used to constrain the porosity of each column. Bromide was measured with a portable Br⁻ electrode (Thermo Scientific); effective porosity was calculated using Br⁻ breakthrough curves and was estimated to be 0.27–0.33 depending on the column (typical porosity values at the field site are 0.2–0.4). The average influent As concentration was <10 µg/L for all experiments. For all oxalic acid and phosphate trials, unamended groundwater was flowed through the column initially until the effluent was visually clear of fine solids, at least ~1.4 pore volumes. Effluent samples were collected and monitored for pH and electrical conductivity, trace metals, and anions. A fraction collector (LKB Bromma) was used to collect effluent samples for the oxalic acid and phosphate trials (columns 2–5). Trace metal samples were acidified to 1% acid using

either HCl (groundwater alone, 1 mM oxalic acid, and 1 mM phosphate columns) or HNO₃ (10 mM oxalic acid and 100 mM phosphate columns) and filtered through a 0.45 µm PES syringe filter (Whatman) prior to analysis; the acid used (HCl vs. HNO₃) should not impact the results as the goal for preserving the samples was to lower the pH below 2 (EPA, 1996; van Geen, et al., 2003). Anion samples were filtered through a 0.45 µm PES syringe filter into non-acid washed bottles.

2.4 Sediment Digests

Samples of contaminated aquifer solids (N=5) were digested using HNO₃, H₃ClO₄, and HF and analyzed for total As, Fe, Al and Mn concentration (Fleisher and Anderson, 1991). After completion of the 100 mM phosphate column (column 4) and 10 mM oxalic acid (column 5) experiments, the columns were divided into 2–3 cm sections (10–11 sections per column) and one sample per section (~2 g dry) was digested and analyzed to evaluate the distribution of As along the columns following the experiments.

2.5 Analytical Techniques

2.5.1 Inductively Coupled Plasma Mass Spectrometry—Samples were analyzed for As, Fe, Mn Al, S and P content using inductively coupled plasma mass spectrometry (ICP MS) with a high-resolution Axiom Single Collector instrument (Thermo Elemental, Germany). In-115 was added to each sample as an internal response standard and was used to correct for instrument drift prior to quantification. ²⁷Al, ³¹P, ³⁴S, ⁵⁵Mn, ⁵⁷Fe, ⁷⁵As and ¹¹⁵In were determined with the instrument set at >8500 resolving power, which is sufficient to resolve the ⁷⁵As peak from Ar-Cl⁺ interference. Each sample and standard was run 3 times and averaged. Three to 4 point calibration curves were run at least once every 30 samples; calibration curves used for analysis of the data presented here had R² >0.98.

2.5.2 Ion Chromatography—Samples were analyzed for oxalic acid concentrations using a Dionex ICS-2000 (Sunnyvale, CA) ion chromatography system with an IonPac AS-11 HC column. Samples were run in gradient mode with eluent concentrations increasing from 5 to 60 mM KOH over the course of the sample run. Four point calibration curves were used for quantification; calibration curves used for analysis had R² >0.99.

2.5.3 X-Ray Diffraction (XRD)—XRD was performed at The Mineral Lab, Inc (Lakewood, CO). The detection limit for an average mineral is ~1–3%.

2.5.4 X-Ray Absorption Near Edge Spectroscopy (XANES)—Arsenic XANES was performed at the Stanford Synchrotron Radiation Lightsource (Palo Alto, CA) on beam line 11-2.

3. Results

3.1 Aquifer Sediment Characterization

Complete digestion of the aquifer sediments collected for these experiments averaged (±1 standard deviation): total As = 81 ± 1 mg/kg (N=5), total Fe = 1050 ± 180 mg/kg (N=5), total Al = 1070 ± 110 mg/kg (N=3), and total Mn = 12 ± 2 mg/kg (N=5). All subsequent calculations of percent of an element mobilized from the aquifer solids are based on these average concentrations. Based on X-ray diffraction (XRD) measurements, both the bulk and clay-sized fraction of the aquifer sediment samples are >95% quartz with the remaining <5% unidentified. X-ray absorption near edge spectroscopy (XANES) indicates that As in these aquifer solid samples may be >95% arsenate.

3.2 Extraction Experiments

In the phosphate batch experiments, 1 mM phosphate extractions mobilized 11–20% of As, 100 mM mobilized 32–50%, and 1 M mobilized 89–94% of As from the aquifer solids depending on extraction time (Fig. 1). Increasing extraction time led to increased As release for 1 mM and 100 mM trials; 1, 2, and 4 h extractions all yielded 89–90% As release for the 1 M extractions. Less than 5% of the Fe was released during these extractions, less than 2% of the Mn was released, and Al was not measured (Fe and Mn data not shown).

In the oxalic acid batch experiments, 1 mM oxalic acid extractions mobilized 38–56% of As from the aquifer sediment, 10 mM mobilized 83–93%, 100 mM mobilized 86–99%, and 400 mM mobilized 90–102% of the As (Fig. 1). Arsenic release increased with extraction time. Although oxalic acid is known to be effective at dissolving Fe and Al (hydr)oxides (van Hees, et al., 2000), the % Fe and Al mobilized tended to be low. Less than 7% of the Fe was mobilized in the 1 and 2 h extractions. The amount of Fe mobilized was 12% or less except for the 24 h extractions with 100 mM and 400 mM oxalic acid where the Fe mobilized from the aquifer solids was 27% and 41%, respectively. Additionally, the amount of Al mobilized was less than 19% except for the 24 h extractions with 100 mM and 400 mM oxalic acid where the Al mobilized was 27% and 29%, respectively. The amount of Mn mobilized was always 6% or less (Fe, Al, and Mn data not shown).

3.3 Column Experiments

3.3.1 Groundwater—Column experiment 1 using ambient groundwater from the site was performed to establish a baseline of As mobilization with no amendments. The effluent As concentration started high, approximately 6000 µg/L, but dropped below 1000 µg/L after 9 pore volumes and continued to fall through the rest of the experiment (Fig. 2a). The As release rate had stabilized after 9 pore volumes and As concentration began to stabilize at 270 µg/L by the end of 29 pore volumes. The effluent pH decreased from ~8 to ~5.5 over the course of the experiment; influent pH increased from 4.8–5.5, presumably as the influent water equilibrated with atmospheric CO₂.

3.3.2 Phosphate—During the ~1 mM phosphate trial (column 2), unamended groundwater was flowed through the column for 1.6 pore volumes, followed by phosphate for the remainder of the experiment. The effluent P concentrations leveled off to match the influent concentration at 5.4 pore volumes (data not shown). The actual influent phosphate concentration was 0.85 mM based on P data from the ICP MS. Approximately 90% of the influent P was captured in the effluent. The effluent As concentrations increased to ~21,000 µg/L, with a peak at 3.5 pore volumes, soon after initially introducing the phosphate solution to the column (Fig. 2b). Effluent As then decreased and remained below 2000 µg/L from 8.5 pore volumes until the end of the experiment. The effluent pH decreased from ~7.1 to 5.6 over the course of the experiment; influent pH was between 4.8–4.9.

Because of the decrease in effectiveness for removing As after ~5 pore volumes with the ~1 mM phosphate treatment, two changes were introduced for the subsequent phosphate column (column 4). The influent phosphate concentration was increased to 100 mM and the phosphate solution was introduced to the column as 3 pulses with groundwater washes between each pulse. The shaded areas in the background of Figure 2b show the timing of the phosphate pulses. The effluent P showed 3 peaks, one for each pulse of phosphate introduced (data not shown). Comparison of influent and effluent P data indicates that there was no significant adsorption of P to the solids in this experiment. A peak in effluent [As] occurred following each introduction of phosphate. The first pulse of phosphate started at 1.5 pore volumes and the peak in As occurred at 2.7 pore volumes with an effluent [As] of ~120,000 µg/L. The second pulse of phosphate started at 11.0 pore volumes and the peak in As occurred at 12.5 pore

volumes with an effluent [As] of ~29,000 µg/L. The third pulse of phosphate started at 20.2 pore volumes and the peak in As occurred at 21.7 pore volumes with an effluent [As] of ~16,000 µg/L. The effluent pH started at 7.2 but varied between 6.1 and 4.6 for the rest of the experiment; the pH of the phosphate influent was ~4.2 and the pH of the groundwater influent was ~5.7.

3.3.3 Oxalic Acid—During the 1 mM oxalic acid column (column 3), unamended groundwater was flowed through the column for 1.6 pore volumes followed by 1 mM oxalic acid for the remainder of the experiment. Approximately 85% of the oxalic acid introduced to the column was collected in the effluent. Effluent As concentrations showed a small peak in [As] at ~4.1 pore volumes with a concentration of ~2700 µg/L and then fell to ~2000 µg/L (Fig. 2c). The [As] began to increase substantially from ~7–13 pore volumes; for the remainder of the experiment, [As] was ~8000–10,000 µg/L. Iron and Al data are also shown with the oxalic acid columns (column 3 and 5) because oxalic acid was expected to mobilize these elements. The effluent Al increased rapidly after 3.7 pore volumes and remained above 13,000 µg/L from 6.0 pore volumes through the rest of the experiment (Fig. 3). The Fe concentration started relatively low, less than 200 µg/L, until about 15 pore volumes at which time the concentration began to increase and finally leveled off ~8000 µg/L at ~30 pore volumes (Fig. 3). Amounts of Fe and Al mobilized from the aquifer sediments by the end of the experiments were 1% and 8%, respectively. There was also little Mn release (<1%) from the solids. The effluent pH decreased from 7.2 to 3.6 over the course of the experiment; influent pH was between 2.9–3.0 for the duration of the experiment.

Based on the extraction data, increasing oxalic acid concentrations above 10 mM made little additional improvement in terms of fraction of As mobilized; therefore, the 10 mM concentration was chosen for the next oxalic acid column (column 5). For this experiment (Fig. 2c), unamended groundwater was flowed through the column until 1.5 pore volumes, followed by 10 mM oxalic acid until 21.1 pore volumes, and then unamended groundwater again. Approximately 99% of the influent oxalic acid was recovered in the effluent. The effluent As concentration peaked at 5.8 pore volumes with a maximum of nearly 100,000 µg/L. The effluent [As] decreased below 2000 µg/L after 14 pore volumes. At the end of the experiment (30 pore volumes), the effluent As concentration stabilized around 40 µg/L; 88% of the As had been mobilized. Effluent Fe and Al (data not shown) also exhibited peaks in concentration following the introduction of 10 mM oxalic acid; effluent Fe reached a maximum of ~100,000 µg/L at 5.8 pore volumes and effluent Al reached a maximum of ~150,000 µg/L at 4.4 pore volumes. Due to instrumental limitations, the Al data for this column has greater uncertainty; several samples exceeded the replicate %RSD threshold for acceptance of 10%. Therefore, the Al numbers for this one column should only be used as a first-order guide. Effluent Fe and Al concentrations remained above 10,000 µg/L until the influent was switched to ambient groundwater. Though effluent As and Fe reached their maximum values at the same time, the initiation of As release preceded that of Fe release. Based on effluent concentrations, total percentages of Fe and Al mobilized were 9% and 16%, respectively. Since 98% of the influent Mn was recovered in the effluent, there was no indication of Mn release from the sediment. The effluent pH fell from 6.5 to 2.2 after the introduction of the 10 mM oxalic acid and increased to pH 4, within the range found at the Vineland site, after 8 pore volumes of groundwater had been washed through the column. The 10 mM oxalic acid influent solution had pH 2.2 and the pH of the groundwater influent was 5.8.

3.3.4 Cumulative Percentage As Mobilized—At the end of the experiments, 5% of the As was mobilized from the aquifer solids after 29 pore volumes with ambient groundwater (column 1), 12% after 22 pore volumes with ~1 mM phosphate (column 2), 44% after 34 pore volumes with 1 mM oxalic acid (column 3), 48% after 28 pore volumes with pulsed 100 mM phosphate (column 4), and 88% after 30 pore volumes with 10 mM oxalic acid (21 pore volumes) and groundwater (9 pore volumes) (column 5). The ~1 mM phosphate column had

a higher cumulative percentage As mobilized than the 1 mM oxalic acid column until 14 pore volumes, beyond which 1 mM oxalic acid values were higher (Fig. 4). The 100 mM phosphate had higher cumulative percentage As mobilized than the 10 mM oxalic acid until 5 pore volumes, after which the 10 mM oxalic acid values were always higher (Fig. 4). Samples prior to ~1.4 pore volumes, before the effluent solution was clear of fine particles, were not included in the percentage mobilization calculations.

After the 100 mM phosphate (column 4) and 10 mM oxalic acid (column 5) experiments were complete, sediment was separated into approximately 2–3 cm sections and one sample (~2 g dry) from each section was digested and analyzed for total As content. The average As concentration after the 100 mM phosphate experiment was 45.2 mg/kg with a standard deviation of 5.7 mg/kg, indicating 44% of the As had been removed from the aquifer sediment. The average As concentration after the 10 mM oxalic acid experiment was 8.5 mg/kg As $\pm$ 1.5 mg/kg; 89% of the As had been removed from the aquifer solids. The results for percentage mobilization obtained from the solids data agree well with percentages estimated from the effluent solution data for As. However, variability in solid Fe, Al and Mn concentrations in the starting aquifer material together with the relatively small amount of mobilization of these elements during the 10 mM oxalic acid column experiment, indicates it may be better to assess the mobilization with effluent solution chemistry; solution chemistry suggested 9% Fe mobilization, 16% Al mobilization and 0% Mn.

4. Discussion

4.1 Supporting Information

In addition to the extraction and column experiments discussed here, mobilization of As was also investigated by stimulating microbial respiration to induce reducing conditions (28 day and 49 day incubations) and by incrementally increasing pH in a batch reaction vessel from 4.1–9.4 to maximize the electrostatic repulsions between arsenate and surface binding sites. These methods and results are reported in the Supporting Information. A much higher degree of As mobilization was generally achieved using chemical amendments than for microbial respiration or pH adjustment experiments.

4.2 Batch Extraction Experiments

At the same molar concentrations, oxalic acid extractions consistently mobilized a higher percent of As from the aquifer sediment than phosphate extractions. The 1 mM oxalic acid extractions mobilized more As (38–56%) than the 100 mM phosphate extractions (32–50%). Greater than 80% As mobilization was achieved with 10 mM oxalic acid or 1 M phosphate suggesting that addition of oxalic acid or phosphate could lead to significant increases in As release from contaminated sediments. The greater effectiveness of oxalic acid at lower concentration may be attributed to differences in the mechanism or kinetics of mobilization. While phosphate acts through anion exchange for arsenate and arsenite species, oxalic acid is thought to complex and dissolve Fe and Al, thereby also dissolving any As that is co-precipitated with or adsorbed to Fe and Al (hydr)oxides (though competitive sorption mechanisms may also play a role in As release by oxalic acid).

In batch and column experiments, Darland and Inskeep (1997) show that adsorption of phosphate or arsenate can be slow to reach equilibrium even though the actual chemical adsorption step is quick (milliseconds) and suggest that the kinetics of phosphate exchange for arsenate may be limited by arsenate desorption. In the phosphate extractions presented here, As release increased with extraction time suggesting that an equilibrium state may not yet have been attained and perhaps further As mobilization would occur with longer extraction times. Additionally, phosphate may not entirely out-compete arsenate for binding sites even when

phosphate concentrations exceed the calculated binding site capacity (Darland and Inskeep, 1997). This idea is mirrored by Jain and Loeppert (2000) who performed batch adsorption experiments on ferrihydrite and suggest that while some adsorption sites are common to both phosphate and arsenate, some are more suited to one or the other. Other batch sorption studies have shown that arsenate can bind more strongly than phosphate on goethite (Hongshao and Stanforth, 2001). It is possible therefore that some binding sites in the Vineland aquifer materials favor As species over phosphate, and until there is an extremely large excess of phosphate (1 M phosphate or more) there is not complete exchange.

Previous studies have shown a positive correlation between As mobilized by low molecular weight organic acids (0–10 mM, including oxalic) and mobilized Fe, Al, and Mn; Zhang et. al. (2005) suggested that the As was released from Fe, Al and Mn (hydr)oxides. In the oxalic acid extractions presented here (1–400 mM), there was also a positive correlation between mobilized As and mobilized Fe, Al and Mn at each extraction time. The R^2 values for the 1 and 2 h extractions fit with linear regressions were all >0.8 (except the relationship between Mn and As in the 1 h extraction where $R^2=0.48$ which may be related to the low overall percentage of Mn mobilized). The 24-h extractions also showed a positive correlation but were better fit by exponential curves and had $R^2 \geq 0.75$. The batch extraction data are consistent, therefore, with As mobilization occurring as a result of Fe, Al, and Mn (hydr)oxide dissolution despite the low percentages of Fe, Al and Mn mobilized. However, the oxalic acid column data discussed later calls this simple mechanism into question.

Even though oxalic acid was shown to be more effective at mobilizing As than phosphate at lower concentrations in the extraction experiments, the applicability of these experiments to *in situ* conditions is hindered by the low solid to water ratio (1:~5). This concern was addressed using column experiments.

4.3. Phosphate Columns

4.3.1 As Release—In the ~1 mM phosphate column (column 2), the effluent As concentration increased rapidly shortly after the introduction of phosphate; the peak was at 3.5 pore volumes with a concentration of ~21,000 $\mu\text{g/L}$. The effluent As concentration decreased quickly but still remained higher than the effluent As concentrations of the unamended groundwater column (column 1), indicating greater As removal from the system compared with groundwater alone. Similar results have been seen in other studies involving a sand column treated with arsenate first and then phosphate; there was a peak in effluent As after phosphate was introduced but the effluent As concentration began to show tailing after ~5 pore volumes (Darland and Inskeep, 1997). While the two experiments were somewhat different in design, both show a decrease in effluent As concentration even with continuous phosphate input. This decrease in As mobilization may indicate that the remaining As was adsorbed more strongly and/or that some of the available binding sites were more suited to As species than phosphate. The incomplete exchange of phosphate for arsenate may also suggest a kinetic limitation for As desorption (Darland and Inskeep, 1997). Despite the incomplete exchange of phosphate for arsenate, both phosphate columns discussed in this paper, ~1mM phosphate (column 2) and 100 mM pulsed phosphate (column 4), showed increased As release compared to groundwater alone (column 1).

4.3.2 Phosphate Adsorption—Previous studies have shown that Fe and Al (hydr)oxides can be significant sinks for phosphate (Darke and Walbridge, 2000). The results show that in this system and with the concentrations of phosphate used here, there was minimal phosphate adsorption. Effluent P concentrations quickly approached their influent levels after introduction of phosphate solutions (data not shown) suggesting fast exchange of phosphate for arsenate on surface sites. The lack of phosphate adsorption limits concerns over nutrient

pollution and subsequent eutrophication of downstream surface water bodies in hydrological systems controlled by pump and treat; the phosphate would be collected and processed by the pump and treat operation, leaving little residual phosphate in the aquifer system. It is reiterated, however, that the authors are only considering use of these types of chemical amendments *in situ* at sites that currently use pump and treat technologies to ensure capture of amendments and mobilized As.

4.4 Oxalic Acid Columns

4.4.1. As Mobilization and Fe, Al, and Mn Release—Arsenic, Fe and Al were all mobilized by the oxalic acid treatments. Both oxalic acid columns (column 3 and 5) showed substantial release of As compared with groundwater alone (column 1) (Figs 2 and 4). In the 1 mM oxalic acid column, the order of element release occurred as Al, then As, then Fe. The effluent Al concentration began to increase after ~3.7 pore volumes, the effluent As concentration had a small peak around 4.1 pore volumes then began to increase substantially after ~7.6 pore volumes, and finally the effluent Fe concentration began to increase after ~17.5 pore volumes (Fig. 3). The order of element release was the same for the 10 mM oxalic acid column (though there was no visible small peak in As before the large increase), however, the process was accelerated and the maximum effluent concentrations were ~10x higher due to the higher concentration of oxalic acid. The relative timing of Al and Fe release, Al early and Fe later, may be related to the differences in the mechanisms of Al and Fe mobilization by oxalic acid (Li, et al., 2006; Panias, et al., 1996). The relative timing may also indicate that the Al (hydr)oxides in these aquifer materials were more amorphous and thus more easily dissolved than the Fe (hydr)oxides. Since the oxalic acid treatment performed here mimics soil podzolization to an extreme degree, the earlier release of Al than Fe could be thought of in terms of the proto-imogolite theory of podzolization, in which Al-rich proto-imogolites dissolve more readily than Fe oxides (Lundstrom, et al., 2000). The podzolization process is characterized in a soil profile by a weathered soil horizon, depleted of Fe and Al, underlain by a horizon enriched in Fe and Al. One mechanism that explains this phenomenon involves complexation of Fe and Al species with organic acids (produced by decaying organic matter, etc.) and subsequent transport and precipitation of Fe and Al in a lower soil horizon (Lundstrom, et al., 2000). In these experiments, a significant quantity of organic acid was introduced, in this case oxalic acid, to enhance the leaching process and we maintained oxalic acid concentrations to avoid the re-precipitation process. While these techniques mimic podzolization in many ways, there would certainly be differences between introduction of oxalic acid during an *in situ* experiment vs. podzolization. If oxalic acid were introduced into the aquifer on site, predominant transport would occur horizontally (vs. vertically in podzolization) with higher flow rates, shorter time frames, and would lack the solid materials being subjected to cycles of wet and dry (as would occur in natural soil podzolization).

A small peak in effluent As in the 1 mM oxalic acid column coincided with the increase in Al concentration and may indicate that just a small portion of the As in these solids was associated with Al (hydr)oxides; when the Al (hydr)oxides began dissolving that portion of the As was also released. Because there was little to no effluent Mn beyond what was introduced in the influent, it seems unlikely that As release was related to dissolution of Mn (hydr)oxides in these columns. Presumably, therefore, the majority of the As would be associated with Fe (hydr)oxides since they can serve as major As adsorption sites in soils and sediments. However, the significant increase in [As] did not coincide with the increase in Fe. Therefore, these results suggest that while a small amount of As may be released as Al was dissolved, As release may have been largely decoupled from the release of Al and Fe. Previous studies have also shown As mobilization decoupled from Fe release, although those studies looked at As release under reducing conditions (Horneman, et al., 2004; Keimowitz, et al., 2005a; van Geen, et al., 2004). In the experiments presented here, the dissolution of Al and Fe (hydr)oxides may not

entirely account for the mobilization of As in these column experiments. Other mechanisms may be at play; perhaps there was secondary Fe mineral formation which prevents Fe from being released in the effluent with the As or perhaps oxalic acid was acting on the As itself or competing with As for sorption sites in order to induce mobilization. Another possibility is that the initial release of As was coincident with the dissolution of Al and Fe hydr(oxides), but that there were differences in retardation of the 3 elements making transport and ultimate export from the column vary due to differences in partitioning. Current work is focused on elucidating mechanisms by which oxalic acid mobilizes As.

4.4.2 Oxalic Acid Adsorption—In the oxalic acid columns, between 85% and 99% of the oxalic acid introduced in the influent was collected in the effluent. This indicates that there is little sorption or degradation of oxalic acid within the column over the limited time period of the experiments; 0.1 – 0.5 mmol oxalic acid were degraded or remained in the oxalic acid columns discussed here. The lack of oxalic acid sorption is an asset when considering application to a contaminated site because the oxalic acid will not remain in the environment; it will be removed with the contaminated groundwater delivered to the pump and treat facility. Even if a small amount of oxalic acid remains sorbed to the sediments, microbes are known to degrade this small organic compound (Sahin, 2003). Concentrations up to 1 mM oxalic acid have been found in certain natural soils (Fox and Comerford, 1990).

4.5 Columns – Cumulative Percentage As Mobilized

In comparing the cumulative percentage As mobilized, it is clear that each chemical amendment was able to mobilize more As than ambient groundwater alone (groundwater mobilized just 5%) with a maximum of 88% As mobilized from the aquifer sediments with the 10 mM oxalic acid treatment (Fig.4). Phosphate was able to initiate As mobilization faster but oxalic acid resulted in greater cumulative mobilization by the end of the experiments and did so with lower amendment concentrations. The 1 mM oxalic acid treatment mobilized a similar amount As (44% after 34 pore volumes) as the 100 mM phosphate treatment (48% after 28 pore volumes) but required much lower amendment concentration. Additionally, the 10 mM oxalic acid treatment mobilized nearly twice as much total As from the aquifer solids (88%) as the 100 mM phosphate column (48%).

4.6 Implications For Site Remediation

Based on an estimation of the aquifer volume, the groundwater beneath the Vineland site has a residence time of ~200 days if the pump and treat plant operates at full capacity, 7.5×10^6 L per day (2 million gallons); therefore, each pore volume in a simplified field scale study would require 200 days of injection and pumping. The groundwater column experiment was designed to simulate the current situation on site, i.e., groundwater flushing through the system. Based on the results from this experiment and using a pore-volume-in-column to pore-volume-in-field extrapolation, the 15-a time frame (27 pore volumes) that the site information reports for pump and treat remediation (EPA, 2006), would release ~5% of the As from the aquifer sediments and leave behind a substantial reservoir of As to continue to contaminate the groundwaters (e.g. effluent As concentrations at the end of the groundwater only column experiment were ~270 µg/L). Five % As removal in 15 a is consistent with onsite estimates based on a comparison between the mass of As removed by pump and treat and estimates of the mass of As within the contaminated aquifer. Using the current As removal rates by the Vineland pump and treat system, 4–9% of the As would be removed from the contaminated aquifer with a total of 15 a of pump and treat remediation. If the As release rate continued as extrapolated from the groundwater column experiment, almost 600 a could be required to reach the site's soil washing clean up target of 20 mg/kg. Similar extrapolations were performed for the 1 mM oxalic acid, 10 mM oxalic acid, and ~1 mM phosphate experiments. Assuming uniform exposure of all site aquifer solids with elevated As concentrations to the chemical

treatment, using 10 mM oxalic acid could decrease the cleanup timeframe to ~4 a (Table 1). If instead a clean up goal of 5 mg/kg is used (closer to the uncontaminated background As concentration), longer clean up times are calculated based on each of the column experiments; however, 10 mM oxalic acid treatment still shows dramatic decrease vs. groundwater alone (24 a for 10 mM oxalic acid vs. 750 a for groundwater alone) (Table 1). For ease of calculation, these projections were based on clean up goals of a certain As concentration on the solids. It could take longer than this to decrease groundwater concentrations below the current US drinking water standard of 10 µg/L; for instance, the concentration at the end of the 10 mM oxalic acid column (column 5) was still 40 µg/L even with 88% of the As removed (final solid concentration of As of 8.5 mg/kg). One can also use similar extrapolations to estimate the percentage clean up goal reached (using 20 mg/kg as the goal) after 5 or 15 a (Table 1). After 15 a with ambient groundwater, the site would only be 7% closer to the clean up goal and still have very elevated groundwater As concentrations. In less than 5 a the treatment goal of 20 mg/kg would be surpassed using the 10 mM oxalic acid treatment. These calculations have assumed As concentrations in the aquifer sediments to be the same as those used in the column experiments (~80 mg/kg). While the As concentrations in the aquifer sediments of the most contaminated region on site are variable (typically 20–250 mg/kg), these calculations allow for approximations of clean up times as well as comparisons between treatment methods. Additionally, the column experiments did not account for the contribution of fine particles to As mobility; fine particles were eluted in the first ~1.4 pore volumes and these data were not included in the mobilization calculations. Fine particles may play a role in As mobility *in situ*, which could impact necessary treatment times. Even with the limitations for extrapolating laboratory data to the field, the results and calculations presented here clearly suggest 1) pump and treat alone is not likely to be an effective means of remediation on a reasonable time scale for the Vineland site and 2) adding chemical amendments could substantially decrease the cumulative time necessary for remediation provided injection methods can be developed for delivering the amendment to all of the contaminated aquifer sediments.

5. Conclusions

Both phosphate and oxalic acid can accelerate release of As from contaminated solids. Based on results from extraction and column experiments, oxalic acid appears to be more effective at mobilizing As at lower amendment concentrations. Significant As mobilization by oxalic acid was decoupled from Fe and Al release, indicating that an As release mechanism independent of Fe or Al may be significant. For As contaminated sites using pump and treat as part of clean up, chemical amendments like phosphate or oxalic acid could improve remediation efficiency and thus could significantly decrease the cumulative treatment time.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Batch extraction experiments using 3 different concentrations of phosphate (1 mM, 100 mM and 1 M) and 4 different concentrations of oxalic acid (1 mM, 10 mM, 100 mM, and 400 mM) as the chemical amendment. The pH of the extraction solution is also listed. There were no 4 h extractions for the oxalic acid experiments.

Figure 2.

Results from column experiments shown as effluent As concentration on a log scale versus number of pore volumes that had passed through the column. Influent solutions were (a) unamended groundwater, (b) phosphate (1 mM and pulsed 100 mM phosphate introductions shown), and (c) oxalic acid (1 mM and 10 mM oxalic acid). A fraction collector was used to collect samples for all columns except the unamended groundwater column (a). Gaps in sampling points exist for the unamended groundwater column (a) during overnight periods when composite samples were taken. The pulses of phosphate in (b) are shown by the shaded regions. The switch from an influent solution of 10 mM oxalic acid to groundwater in (c) is shown by the vertical line on the x-axis.

Figure 3. Effluent Al, As and Fe versus number of pore volumes for the 1 mM oxalic acid column experiment. Note that the element concentrations are not on a log scale as in Figure 2.

Figure 4. Cumulative percentage As mobilized from the aquifer solids as a function of pore volume for each of the column experiments. Samples prior to ~1.4 pore volumes, before the effluent solution was visually clear of fine particles, were not included.

Table 1

Extrapolations to the study site

Amendment	Length of remediation (a) based on clean up target of X mg/kg ^{a, b}		Percent clean up goal reached after Y a ^e	
	20 mg/kg	5 mg/kg	5 a	15 a
Unamended groundwater	590	750	4%	7%
1 mM phosphate	180	230	12%	18% ^f
1 mM oxalic acid	28	34	7%	46%
100 mM pulsed phosphate	-- ^c	-- ^c	41%	64% ^f
10 mM oxalic acid	4 ^d	24	111% ^g	118% ^g

-- Estimate not made for this experiment.

^aTwo remediation endpoints were examined for these calculations. The first is based on the time it would take to clean the solids to 20 mg/kg; that is the clean up target for the solids being treated at the site's soil washing plant. The second is based on the time it would take to clean the solids to 5 mg/kg; the uncontaminated background As concentration is <5 mg/kg.

^bWe have assumed that the As release rate would continue to be similar to that at the end of each column experiment.

^cThe design for the 100 mM phosphate experiment was different; 3 pulses of phosphate were introduced instead of a continuous flow. Therefore, this calculation would not be as straightforward.

^dThe clean up goal was reached during the course of the experiment so it was not necessary to assume that the release rate would continue to be similar to that at the end of the column experiment.

^eThe clean up goal used for this calculation was an As concentration on the solids of 20 mg/kg.

^fThe 1 mM phosphate experiment hadn't proceeded to the number of pore volumes equivalent to 15 a in the field. Therefore, the percentage clean up goal reached after 15 a of treatment was calculated by assuming the As release rate to be similar to the release rate at the end of the experiment. The 100 mM phosphate experiment also had not proceeded to the number of pore volumes equivalent to 15 a in the field; it was short by <1 pore volume. The same assumptions described above were used.

^gValues greater than 100% indicate that the As concentration of the solids had been decreased below the target clean up level of 20 mg/kg.