



Effect of oxalic acid treatment on sediment arsenic concentrations and lability under reducing conditions



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HIGHLIGHTS

- Arsenic mobilization from aquifer sediments by oxalic acid treatment was examined.
- Sediments from two distinct As-contaminated U.S. Superfund sites are studied.
- Oxalic acid is a promising amendment for enhanced pump-and-treat at both sites.
- Residual sediment As after treatment is less vulnerable to microbial reduction.
- Iron mineralogy controls the reactivity of residual sediment As after treatment.

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ABSTRACT

Oxalic acid enhances arsenic (As) mobilization by dissolving As host minerals and competing for sorption sites. Oxalic acid amendments thus could potentially improve the efficiency of widely used pump-and-treat (P&T) remediation. This study investigates the effectiveness of oxalic acid on As mobilization from contaminated sediments with different As input sources and redox conditions, and examines whether residual sediment As after oxalic acid treatment can still be reductively mobilized. Batch extraction, column, and microcosm experiments were performed in the laboratory using sediments from the Dover Municipal Landfill and the Vineland Chemical Company Superfund sites. Oxalic acid mobilized As from both Dover and Vineland sediments, although the efficiency rates were different. The residual As in both Dover and Vineland sediments after oxalic acid treatment was less vulnerable to microbial reduction than before the treatment. Oxalic acid could thus improve the efficiency of P&T. X-ray absorption spectroscopy analysis indicated that the Vineland sediment samples still contained reactive Fe(III) minerals after oxalic acid treatment, and thus released more As into solution under reducing conditions than the treated Dover samples. Therefore, the efficacy of enhanced P&T must consider sediment Fe mineralogy when evaluating its overall potential for remediating groundwater As.

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1. Introduction

Groundwater arsenic (As) contamination is currently a global public health problem and also a concern at hundreds of U.S. Superfund sites [1,2]. At many of these sites, groundwater As is derived from anthropogenic As inputs, such as manufacturing and using As-based chemicals, mining, and swine and poultry farming [2].

At other contaminated sites, there are no anthropogenic As inputs but rather naturally occurring As, and groundwater As is mobilized from local host minerals in the sediments via reduction of As-bearing Fe(III) (oxyhydr)oxides, oxidation of As-bearing sulfides, and competitive desorption from phosphate and other similar ions; these mechanisms can be triggered or intensified by human activities [2–5]. Formulating remedial options at such distinct sites needs to consider these differences [6].

Pump-and-treat (P&T) is widely used for groundwater remediation of point-source pollution, because it limits groundwater migration, and decreases contaminant loading by mobilizing contaminants under controlled conditions [7]. There are currently

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more than 700 P&T systems in operation at U.S. Superfund sites, requiring operation and maintenance costs over the lifetime of the projects [8]. However, the effectiveness of traditional P&T for As remediation often progressively decreases due to incomplete desorption and other factors. Additions of amendments such as oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) that enhance As mobilization from the aquifer matrix are potentially useful to improve P&T efficiency. Oxalic acid is biodegradable and relatively inexpensive, and can be found naturally in environments at concentrations up to 4 mM [9–12]. It can complex and dissolve Fe (oxyhydr)oxides and aluminum (Al) (oxyhydr)oxides, which are often the major As host minerals in aquifers, and can also compete with As oxyanions for sorption sites [11,13–19]. Our previous studies [20–22] have shown that oxalic acid can accelerate As mobilization from sediments at laboratory to pilot field scales at the Vineland Chemical Company Superfund site, a site with As derived from industrial sources. Given its promising potential in use for enhanced P&T, the transferability of oxalic acid to other sites is worth exploring. Furthermore, any residual sediment As following P&T can still be a substantial As reservoir. Whether this residual As can potentially continue to contaminate the groundwater also requires careful investigation.

The objectives of this study were (i) to investigate the effect of oxalic acid on As mobilization at sites with different As input sources and redox conditions; (ii) to examine the impact of microbial reduction on residual sediment As after oxalic acid treatment; and (iii) to inform the prospects for remediating groundwater As contamination using oxalic acid. In this study, sediments from the Dover Municipal Landfill and Vineland Chemical Company Superfund sites were collected and characterized by different techniques including synchrotron based X-ray absorption spectroscopy (XAS), and laboratory batch extractions, column flow-through experiments and microcosm incubations were performed on these sediments.

2. Material and methods

2.1. Site and sample information

2.1.1. The Dover Municipal Landfill Superfund site

The Dover site (Dover, New Hampshire) was classified as a Superfund site in 1983, with the primary constituents of concern being volatile organic compounds (VOCs) and As [23]. There is no known anthropogenic As source at this site, and this landfill site is similar to other landfill sites where elevated groundwater As concentrations were caused by the reducing conditions beneath the landfill mobilizing As from unconsolidated local sediments [4,5]. Traditional P&T and vapor extraction were chosen as the remediation strategies for the Dover site in 2009, and following that decision, a network of extraction wells was installed in 2011 along the down-gradient toe of the landfill. Groundwater VOC concentrations have decreased owing to successful vapor extraction, natural attenuation and degradation processes associated with flushing. Groundwater As concentrations, however, have not decreased and some wells have dissolved As concentrations up to $150 \mu\text{g L}^{-1}$. The aquifer sediments used in this study were collected when extraction wells EW1 and EW8b were installed at the southwest and southeast toe, respectively. The sediments were collected immediately following sonic vibration drilling, as top (6–9 m below ground surface (BGS)), middle (9–12 m BGS) and bottom (12–15 m BGS) sediments. Once collected, the sediments were homogenized and refrigerated in steel cans with epoxy liners (0.004 m^3 each), and returned to laboratory for experiments. Aliquots of the sediments were preserved in glycerol (to prevent exposure to oxygen and preserve oxidation state) and frozen for XAS analysis. Aliquots of the sediments were also freeze-dried for X-ray diffraction (XRD) and

X-ray fluorescence (XRF) analyses, and oven-dried to determine water content.

2.1.2. The Vineland Chemical Company Superfund site

Arsenic contamination at the Vineland site (Cumberland County, New Jersey) was caused by improper storage of As-containing chemicals and waste products. The sediments used in this study were collected from the aquifer and the vadose zone during several remediation activities, representing a subsample of concentrations present prior to the remediation activities being completed. Descriptions of the site and sediment collection procedures have been published in detail elsewhere [20–22,24]. Vineland sediments were handled in a similar fashion to Dover sediments.

2.2. Artificial groundwater preparation

Synthetic solution media was prepared freshly before each experiment, which began with typical groundwater composition [25,26]—artificial groundwater (A-GW) and then processed further as needed with additional chemical amendments, pH adjustment and/or nitrogen gas (N_2 , ultra-high purity) purging. The A-GW consisted of Milli-Q water (18.2 M Ω) amended with 0.02 mM NH_4Cl , 1 mM KCl, 0.4 mM MgSO_4 , 0.4 mM CaCl_2 , and 0.33 mM Na-lactate.

2.3. Batch extractions

In each extraction, 2 g of wet sediments were combined with 10 mL of ambient extraction solution. The extraction solutions included 1 mM, 10 mM, and 100 mM oxalic acid containing A-GW. The extraction solutions were used both without pH adjustment, which had pH 3.1, 2.2, and 1.4, respectively, and with pH adjustment (with NaOH or HCl). The suspensions were shaken in polyethylene centrifuge tubes at room temperature for 24 h. At the end of the extraction, the suspension pH was measured and the suspensions were then centrifuged. The supernatants were filtered to $0.2 \mu\text{m}$ through nylon membrane syringe filters (Whatman) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for trace metal composition. Batch extractions using oxalate-free A-GW, which were adjusted to the same initial pHs (i.e., pH 3.1, 2.2, and 1.4) with HCl, were conducted for Dover sediments, for comparison with extractions with oxalate to isolate the effect of pH change alone on As mobilization.

2.4. Column set-up and flow condition

To conduct column experiments, Dover sediments were homogenized and mixed with autoclaved sand (50%/50% w/w dry mass, pure sand from Acros Organics, 40–100 mesh) to improve flow properties. The sediments were homogenized in an anaerobic glove box filled with a 95%/5% N_2/H_2 mixture, and then wet-packed into three identical sections of polycarbonate tube (McMaster-Carr) with 1 cm ID and 0.3 cm walls (Supplementary Material (SM) Fig. S1). Glass wool was packed into each end to help distribute solution over the full cross sectional area of the columns. Column lengths packed with sediments were 15 cm. One of the three columns was used for determining effective porosity using a bromide breakthrough curve, which was estimated to be 0.29, similar to the Dover site (between 0.20 and 0.33). The other two columns were treated simultaneously with pH 7.0 A-GW and 10 mM oxalic acid containing A-GW, respectively. The pH 7.0 A-GW was buffered with 10 mM PIPES, whereas 10 mM oxalic acid containing A-GW was unbuffered (other than by oxalic acid) and had an initial pH of 2.2. The influents were purged with N_2 throughout the experiment. The columns were oriented vertically with flow going up. The flow was controlled by a peristaltic pump (ISMATEC) at 1 m day^{-1} , to mimic the groundwater velocity during P&T cycles. To condition the columns

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