



Research article

Vinegar-amended anaerobic biosand filter for the removal of arsenic and nitrate from groundwater

Kathryn V. Snyder³, Tara M. Webster², Giridhar Upadhyaya¹, Kim F. Hayes, Lutgarde Raskin^{*}

Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI 48109, United States

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ABSTRACT

The performance of a vinegar-amended anaerobic biosand filter was evaluated for future application as point-of-use water treatment in rural areas for the removal of arsenic and nitrate from groundwater containing common ions. Due to the importance of sulfate and iron in arsenic removal and their variable concentrations in groundwater, influent sulfate and iron concentrations were varied. Complete removal of influent nitrate (50 mg/L) and over 50% removal of influent arsenic (200 µg/L) occurred. Of all conditions tested, the lowest median effluent arsenic concentration was 88 µg/L. Iron removal occurred completely when 4 mg/L was added, and sulfate concentrations were lowered to a median concentration <2 mg/L from influent concentrations of 22 and 50 mg/L. Despite iron and sulfate removal and the establishment of reducing conditions, arsenic concentrations remained above the World Health Organization's arsenic drinking water standard. Further research is necessary to determine if anaerobic biosand filters can be improved to meet the arsenic drinking water standard and to evaluate practical implementation challenges.

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1. Introduction

Arsenic is a naturally-occurring groundwater contaminant around the world, including in the United States, Mexico, Peru, Chile, India, Bangladesh, Nepal, and Vietnam (Ravenscroft et al., 2009; Sharma et al., 2014). Inorganic arsenic can be reduced arsenite (As(III)) or oxidized arsenate (As(V)). Arsenite is most common in groundwater in South Asia (Kinniburgh and Smedley, 2001; Ravenscroft et al., 2009). Above the World Health Organization's (WHO) arsenic drinking water standard of 10 µg/L (World Health Organization, 2008), exposure to arsenic through drinking water can cause increased risk for multiple health problems including skin lesions and cancer (Berg et al., 2001; McClintock et al., 2012). Commonly used arsenic removal technologies rely on arsenic

adsorption to ferric oxyhydroxide solids and subsequent filtration (Bissen and Frimmel, 2003; Mohan and Pittman, 2007). While these systems effectively remove arsenic, other co-contaminants, including nitrate, can be found in arsenic-contaminated groundwater (Berg et al., 2001; Cole et al., 2004; Fytianos and Christophoridis, 2004). In many arsenic-affected areas, including West Bengal, India and Bangladesh, arsenic contamination has been extensively characterized, but co-occurring contaminants are less well studied. In arsenic-contaminated groundwater in India, nitrate concentrations ~20 mg/L have been measured (Kundu et al., 2008; Rahman et al., 2011). In these areas, technologies capable of removing multiple contaminants simultaneously are needed. Furthermore, arsenic-bearing wastes disposal often involves anaerobic environments, such as landfills and ponds (Badruzzaman, 2003; Clancy et al., 2013; Ghosh et al., 2006). However, wastes produced by aerobic treatment processes can be unstable in anaerobic environments, as demonstrated by the release of arsenic adsorbed to ferric oxyhydroxides under reducing landfill conditions (Ghosh et al., 2006). Anaerobic disposal environments instead favor the stability of reduced arsenic and iron solids (Burton et al., 2011; Jong and Parry, 2005; O'Day et al., 2004). Therefore, for anaerobic disposal environments, anaerobic arsenic removal may produce wastes that are less susceptible to arsenic

* Corresponding author.

E-mail address: raskin@umich.edu (L. Raskin).¹ Present address: Giridhar Upadhyaya is now at Carollo Engineers, Orange County, CA, 92626 United States.² Present address: Tara Webster is now at Cornell University, Soil and Crop Sciences, Ithaca NY, 14853 United States.³ Present address: Kathryn Snyder is now a Peace Corps Volunteer, Comarca Ngäbe-Buglé, Panama.

release. Other benefits of anaerobic biological contaminant removal when compared to reverse osmosis and ion exchange include lower energy costs, fewer chemical inputs (no membrane cleaning or resin regeneration), and lower production of concentrated waste streams.

Upadhyaya et al. (Upadhyaya et al., 2010) previously reported the performance of an acetate-fed anaerobic continuous-flow biologically active carbon (CF-BAC) filter for arsenic and nitrate removal from groundwater. Anaerobic biological arsenic removal depends on microbial reduction of arsenate, sulfate, and ferric iron, the precipitation of arsenic sulfide solids, and the adsorption to and/or co-precipitation of arsenic with iron sulfides solids (Gallegos et al., 2007; Kirk et al., 2010; Luo et al., 2008; O'Day et al., 2004; Upadhyaya et al., 2010). These removal mechanisms are highly dependent on pH and relative arsenic, sulfide, and iron concentrations (Burton et al., 2011; Gallegos et al., 2007; Kirk et al., 2010; O'Day et al., 2004). In the CF-BAC system, arsenic was reduced from 200 µg/L to <20 µg/L, and nitrate was reduced from 50 mg/L to <0.2 mg/L (Upadhyaya et al., 2012, 2010). This system, however, would not be applicable for decentralized water treatment. Rather, a “household-scale” biosand filter may be more readily accepted and adapted for such use, given its lower cost, simple construction from local materials, and ease of operation and maintenance (Sobsey et al., 2008).

Biosand filters are point-of-use treatment systems that work by slow, intermittent water filtration through a sand bed, resulting in microbial growth (Elliott et al., 2006; Stauber et al., 2006). Once sufficient microbial biomass accumulation occurs, microbial contaminant removal takes place through mechanisms similar to traditional slow sand filters with a “schmutzdecke” (Bauer et al., 2011; Haig et al., 2011). In contrast to typical biosand filters, sand filtration for arsenic has primarily focused on the removal of arsenic via sorption to iron either present in the groundwater (Berg et al., 2006; Leupin and Hug, 2005; Leupin et al., 2005; Nitzsche et al., 2015) or iron amendments (Hussam and Munir, 2007; Neumann et al., 2013). In these arsenic-removing sand filters, microbial growth was typically avoided and filters were often drained in between uses to maintain aerobic conditions. Only one other study reported the use of a biosand filter for arsenic removal, whereby standing water was maintained to support microbial growth and rusted nails were added as an iron amendment, but found arsenic removal to be limited due to competition with phosphate and low iron concentrations in the groundwater (Chiew et al., 2009).

To leverage the benefits of anaerobic treatment for simultaneous removal of nitrate and arsenic (Upadhyaya et al., 2010), we developed and tested a vinegar-amended anaerobic biosand filter to treat groundwater containing arsenic, nitrate, sulfate, and iron. Influent sulfate and iron concentrations were varied to reflect natural differences in contaminated groundwater and were hypothesized to be the variables controlling arsenic removal. Water quality was monitored over time and spatially within the filter to investigate potential mechanisms for contaminant removal.

2. Materials and methods

2.1. Synthetic groundwater

Synthetic groundwater contained sodium, calcium, chloride, magnesium, potassium, carbonate, and bicarbonate, as previously described (Upadhyaya et al., 2010), along with 200 µg/L arsenate, 50 mg/L nitrate, 22 or 50 mg/L sulfate, 0 or 4 mg/L ferrous iron, 50 mg C/L vinegar (~5% acetic acid), and 100 µg P/L phosphoric acid. Synthetic groundwater was prepared in batches with all constituents except vinegar and iron, stored in a tank with a floating cover, and purged daily for 20 min with nitrogen gas to remove dissolved

oxygen (DO). The pH of the groundwater was 8.7 ± 0.4 (average \pm standard deviation) before vinegar addition and was measured using a Mettler Toledo pH meter (Columbus, OH). Vinegar was added as an electron donor in excess of the stoichiometric requirement for reduction of nitrate and sulfate present in the influent. When iron was added, ferrous iron was mixed with oxygen-free vinegar in an anaerobic glove box (Coy, Grass Lake, MI). This mixture (or vinegar only) was added to the nitrogen-purged groundwater just before addition to the filter.

2.2. Biosand filter construction

The biosand filter was constructed in a 23 L plastic bucket with a non-airtight lid. Four sampling ports were installed along the depth of the filter (Fig. 1). The bucket contained 5 cm (3 kg) of gravel (grain size 6–12.5 mm) topped with 12.5 cm (10 kg) of sand (grain size ≤ 4.38 mm). The potential for the sand and gravel to act as a source of sulfate through the dissolution of minerals was determined through a short-term leaching experiment under anaerobic conditions, in the presence of deionized water and filter leachate (Supporting Information (SI)). Water drained through an outlet pipe located in the gravel bed slightly below port 4, and the volume was controlled by a stand pipe. The filter was inoculated with biomass collected from the backwash of the previously described anaerobic arsenic- and nitrate-removing CF-BAC filter (Upadhyaya et al., 2010).

2.3. Filter operation and maintenance

An extended start-up period (days 0–153) was required to adjust operational parameters (e.g., frequency and volume of water drained, electron donor concentration required due to the presence of electron acceptors in the sand and gravel, as described in the SI). After this period, the filter was tested with three different groundwater compositions with varying sulfate and iron concentrations. Groundwater compositions were 22 mg/L sulfate and 0 mg/L iron (“S22,” days 154–232), 50 mg/L sulfate and 0 mg/L iron (“S50,” days 233–381), and 50 mg/L sulfate and 4 mg/L iron (“S50Fe4,” days 382–420).

The filter was operated at room temperature (23.2 ± 1.2 °C) for 420 days. Every day, 3 L of treated water were drained from the filter and replaced with 3 L of synthetic groundwater, poured through a diffuser plate to prevent disturbance of the sand and biofilm. The total volume of water in the filter was 13.3 L, resulting in an average residence time of 4.4 days. Filter cleaning occurred approximately every two weeks to remove excess biomass. Cleaning was performed after draining 3 L of treated water, using a brush to remove the biofilm along the inside wall. The top 2.5 cm of sand was agitated, and the remaining water above the sand bed was scooped out. Finally, the filter was refilled with groundwater. The solids removed during cleaning were the only waste regularly produced by this system.

2.4. Sample collection

Liquid samples were collected from ports 1 and 4 approximately every other day. All samples were collected before draining the treated water. Sample pH was measured immediately. Samples were filtered through a 0.2 µm filter (Fisher, Pittsburg, PA) and stored at 4 °C until analysis for arsenic, iron, nitrate, sulfate, and acetate as described below. Before storage, samples for arsenic and iron analyses were preserved with hydrochloric acid at a final concentration of 5 mM. The DO concentration was measured occasionally during filter start-up using a WTW Multi 340 DO meter (Weilheim, Germany) by submerging the tip of the probe in the

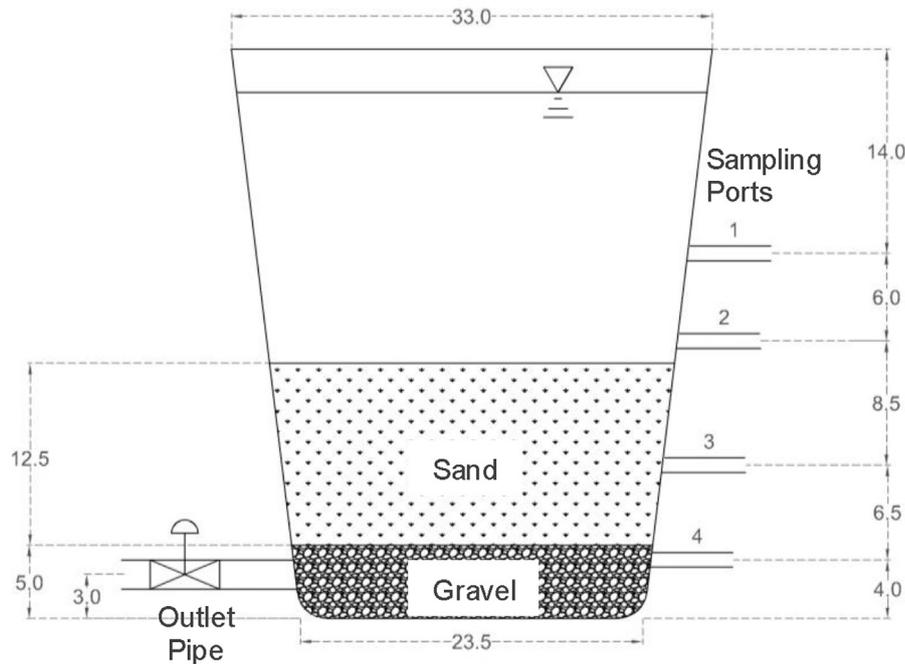


Fig. 1. Biosand filter schematic showing sand and gravel layers; sampling ports 1–4; and outlet pipe (dimensions in centimeters).

standing water above the filter bed prior to draining.

Liquid profile samples were collected periodically to evaluate the spatial variation of contaminant removal. Samples were collected from port 1 to 4 and analyzed for sulfide in addition to pH, arsenic, iron, nitrate, sulfate, and acetate. Sulfide was measured using a sulfide ion selective electrode (Fischer Scientific). Sulfide samples were collected in a syringe and immediately filtered through a 0.2 μm filter into sulfide antioxidant buffer in a second syringe (Pikaar et al., 2011). The syringe was capped and stored in an anaerobic glove box until analysis. Occasionally, samples were collected for arsenic speciation analysis. They were filtered through a 0.2 μm filter, sealed, and stored in an anaerobic glove box until analysis.

2.5. Sample analyses

Arsenic and iron concentrations were measured within two weeks of sample collection using an inductively coupled plasma mass spectrometer (ICP-MS: PerkinElmer ALEN DRC-e, Waltham, MA) with detection limits of 1.1 $\mu\text{g/L}$ arsenic and 0.18 mg/L iron. Acetate, nitrate, and sulfate concentrations were measured within one week of sample collection by ion chromatography (IC). A Dionex DX 100 conductivity detector (Dionex, Sunnyvale, CA) was used with a Dionex AS-14 column and an AG-14 guard column. The eluent was 1 mM bicarbonate and 3.5 mM carbonate at a flow rate of 1 mL/min. The detection limit was 0.2 mg/L for all ions measured by IC. Sulfide was measured using a Silver/Sulfide Ion Electrode (Cole-Parmer, Vernon Hills, IL) within 6 h of sample collection. Measurement of arsenic species as aqueous arsenate and arsenite was performed by IC-ICP-MS using a Dionex AS-18 column and AG-18 guard column. The eluent was 10 mM oxalic acid at a flow rate of 0.3 mL/min. Arsenic speciation samples were analyzed within 8 h of collection.

2.6. Statistical analyses

Statistical analyses were performed to determine if analyte

concentrations were significantly different at each port for the different groundwater compositions. Analysis of variance (ANOVA) was performed in Excel on arsenic, sulfate, and acetate concentrations at each port. Iron concentrations were not evaluated due to the large number of results below the detection limit. Two-tailed t-tests (assuming equal variance) were performed when ANOVA indicated statistically significant concentration differences at a 95% confidence level. Additionally, to assess the effect of acetate, iron, and sulfate on arsenic removal, multiple linear regression analysis was performed, as described in the SI.

2.7. Geochemical modeling

The equilibrium solubility of arsenic sulfide solids (orpiment, amorphous As_2S_3 , and realgar) in the filter was modeled using Visual MINTEQ version 3.0 (Gustafsson, 2012). Ionic strength was fixed at 3 mM, and the Davies Equation was used for ionic strength corrections. Calculations were performed at 25 $^\circ\text{C}$ and pH at 7.5 and 8.1. For realgar modeling, the pe was fixed at -3.6 , assuming that sulfate reduction was the controlling redox couple (Morel and Hering, 1993). The relevant constants for all aqueous species and solids are presented Tables S2 and S3, respectively.

3. Results

3.1. Arsenic

Arsenic removal varied both within and between different groundwater compositions, but never met the 10 $\mu\text{g/L}$ WHO standard (Fig. 2a). Groundwater S22 produced the lowest median effluent arsenic concentration which was 88 $\mu\text{g/L}$. Median effluent arsenic concentrations were 145 $\mu\text{g/L}$ and 133 $\mu\text{g/L}$ for groundwater S50 and S50Fe4, respectively. These concentrations represent total arsenic following filtration through a 0.2 μm filter. Unfiltered samples were not consistently measured, but analyses during the period with groundwater S50Fe4 indicated that the differences between filtered and unfiltered samples ranged from 9 to 34 $\mu\text{g/L}$.

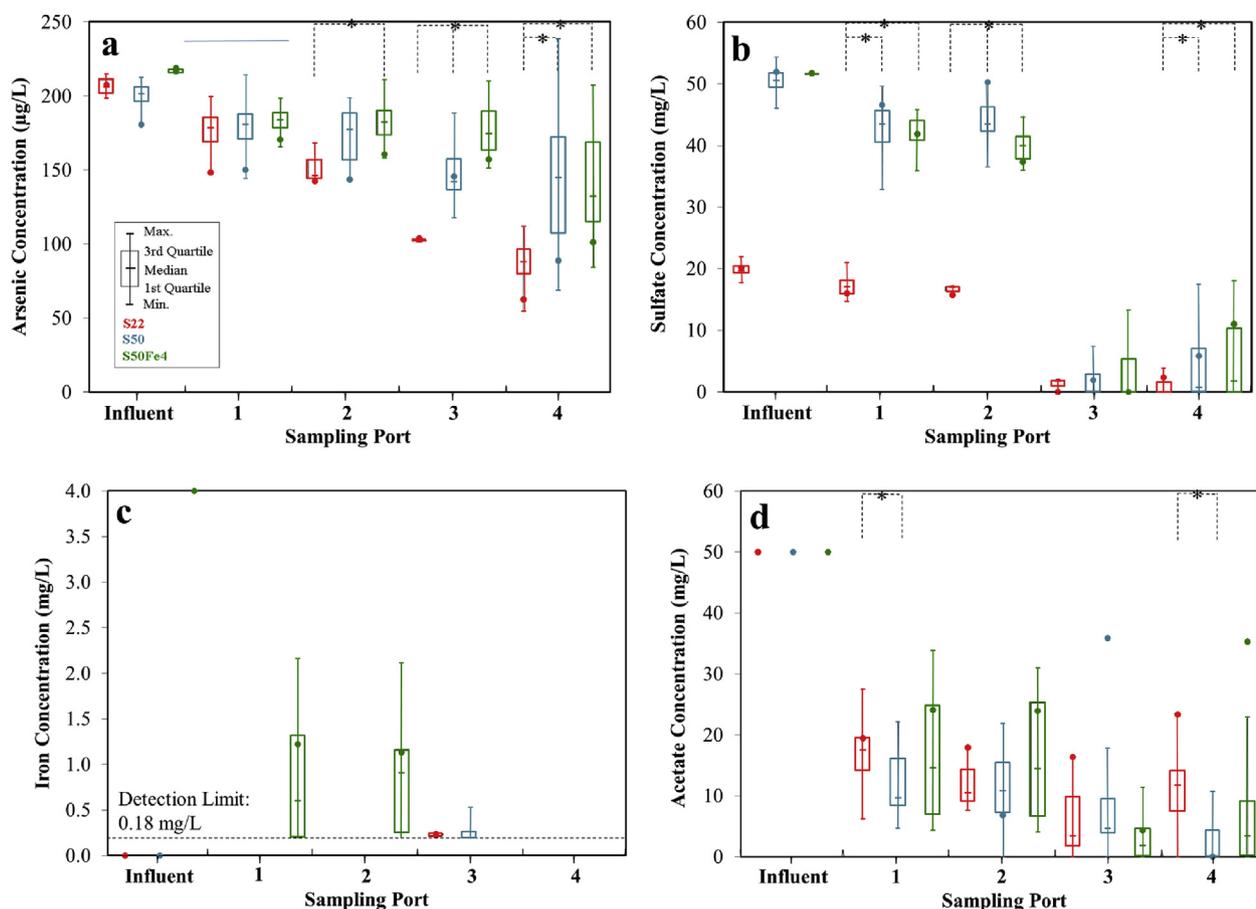


Fig. 2. Box and whisker plots showing the median and range of concentrations of arsenic (a), sulfate (b), iron (c), and acetate (d) at ports 1–4 for all samples collected during each groundwater composition (S22 (red), S50 (blue) and S50Fe4 (green)). Dots indicate the profile samples shown in Fig. 3. Asterisks mark statistically significant differences between groundwater compositions ($p < 0.05$). Acetate concentrations above the calibration range (60 mg/L) were excluded in box plots and significance tests. For S22, $n = 30$ for ports 1 and 4, and $n = 3$ for ports 2 and 3. For S50, $n = 25$ for ports 1 and 4, and $n = 10$ for ports 2 and 3. For S50Fe4, $n = 16$ for all ports. For influent samples, $n = 19$ for S22, $n = 27$ for S50, and $n = 2$ for S50Fe4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Although the concentrations from the profile samples were not always close to the median concentrations (Fig. 2), the relative concentrations indicate relationships among arsenic, sulfate, sulfide, iron, nitrate, and acetate and can be used to examine spatial trends and removal mechanisms. Arsenic removal from the aqueous phase took place throughout the filter (Fig. 3). For groundwater S22, arsenic removal occurred above the filter bed (ports 1 and 2), in the sand bed (between ports 2 and 3), and in the gravel bed (between ports 3 and 4). For groundwaters S50 and S50Fe4, arsenic removal took place both above the filter bed and in the gravel bed, but not in the sand bed. Arsenic speciation performed for groundwater S50 (day 293) showed that influent arsenate was reduced to arsenite (Fig. 4). Approximately one third of the arsenic was oxidized to arsenate in the sand bed (port 3), but dissolved arsenic was reduced in the gravel bed (port 4) and present only as arsenite. Speciation analyses on other days also indicated the presence of arsenate in the sand bed but not anywhere else (data not reported).

3.2. Sulfate

Sulfate reduction, like arsenic removal, varied within and between different groundwater compositions. For approximately half of the filter operation, complete sulfate reduction (detection limit 0.2 mg/L) occurred in the sand and gravel beds (ports 3 and 4,

respectively) (Fig. 2b). The effluent sulfate concentration was significantly lower with groundwater S22 than with groundwater S50 or S50Fe4 ($p < 0.05$), although the total amount of sulfate reduced was higher for groundwaters S50 and S50Fe4 (influent 50 mg/L; effluent 0–10 mg/L) than for groundwater S22 (influent 22 mg/L; effluent 0–2 mg/L), indicating greater potential sulfide generation for S50 and S50Fe4.

Most sulfate reduction occurred in the sand bed, between ports 2 and 3 (Fig. 3). For all groundwaters, the sulfate concentration increased in the gravel bed, between ports 3 and 4. This observed increase in sulfate may have been caused by leaching from the gravel, abiotic or biotic sulfide oxidation, or a combination of these mechanisms. Results from the short-term (<3 days) leaching experiment showed that sulfate leached from the gravel and sand used in the filter (Fig. S1). The arsenic concentrations in the sand bed (port 3) and gravel bed (port 4) were positively correlated ($p < 0.05$) with both the influent sulfate concentration and the sulfate concentration in the sand bed (Table S1). Even though most sulfate reduction occurred within the sand bed, the sulfide concentration was the lowest here. The highest sulfide concentration was observed in the gravel bed (port 4). Sulfide concentrations in the gravel bed increased as the influent sulfate concentration increased, and were 4.28 ± 0.16 mg/L for groundwater S22, 5.17 ± 0.53 mg/L for groundwater S50, and 6.14 ± 0.42 mg/L for groundwater S50Fe4.

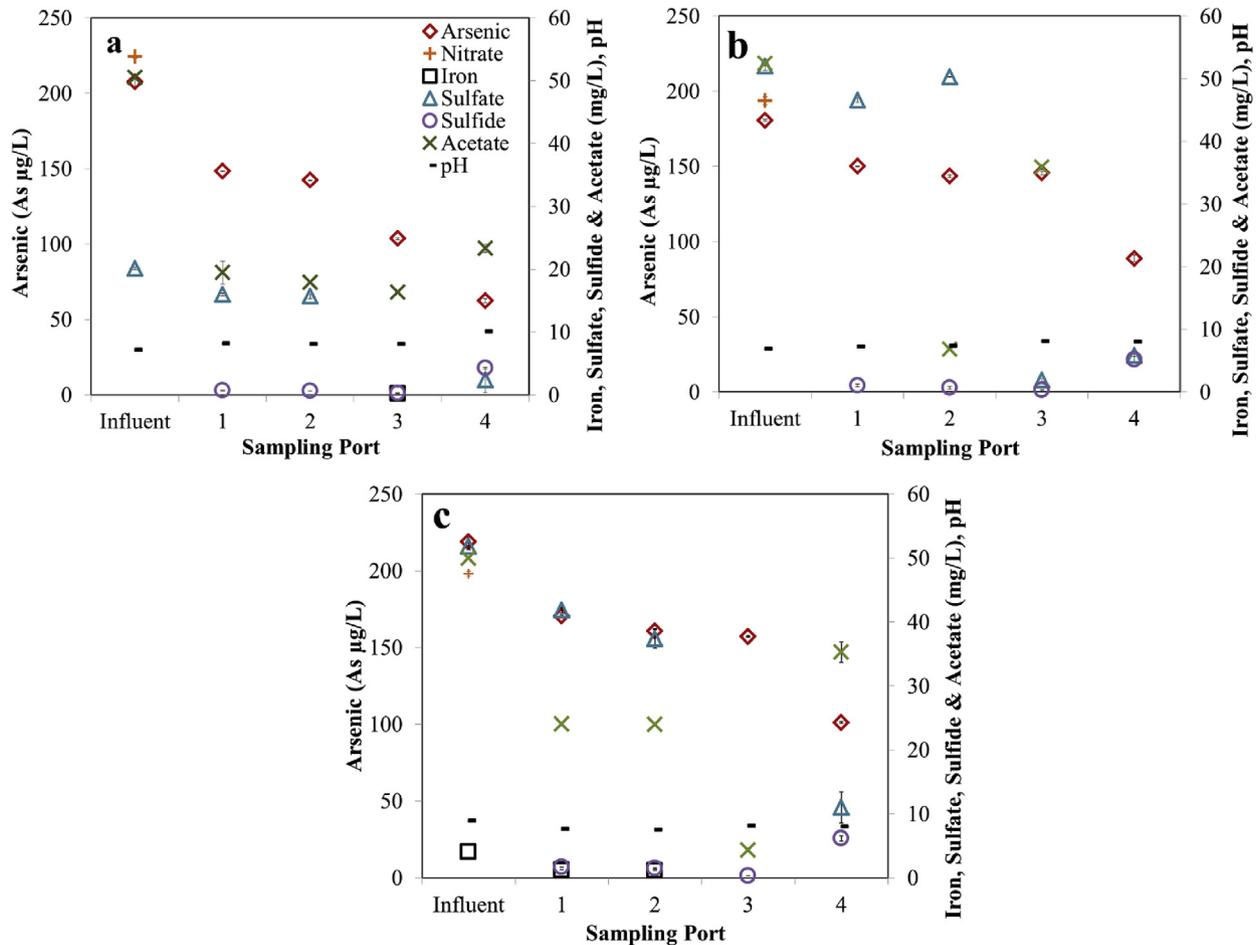


Fig. 3. Samples collected at each port for groundwater S22 on day 178 (a), groundwater S50 on day 330 (b), and groundwater S50Fe4 on day 409 (c) showing arsenic, nitrate, iron, sulfate, sulfide, and acetate concentrations and pH, in the influent and along the depth of the reactor. Arsenic, iron, and sulfide concentrations are averages of two analytical replicates, and sulfate and acetate concentrations are averages of three analytical replicates except for groundwater S50Fe4 which are averages of two replicates. Error bars show one standard deviation. For groundwater S50, the acetate concentration was above 60 mg/L at port 1 and below the detection limit (0.2 mg/L) at port 4. Nitrate, sulfate, and iron concentrations below the detection limits of 0.2 mg/L, 0.2 mg/L, 0.18 mg/L, respectively, are not shown.

3.3. Iron

Influent iron concentration was positively correlated ($p < 0.05$) with higher arsenic concentrations at port 3 (Table S1), indicating that increasing influent iron concentration did not improve arsenic removal. Although dissolved iron was always detected above the filter bed (ports 1 and 2) for groundwater S50Fe4, it was never detected in the filter bed (Fig. 2c). For groundwater S22, dissolved iron was always detected in the sand bed (port 3), but not elsewhere. For groundwater S50, dissolved iron was sometimes detected in the sand bed, but not detected anywhere else in the filter. The median iron concentration in the sand bed decreased from 0.24 mg/L for groundwater S22 to <0.18 mg/L for groundwaters S50 and S50Fe4, although there were some iron concentrations measured above 0.18 mg/L for groundwater S50.

3.4. Nitrate, dissolved oxygen, and pH

The biosand filter remained anaerobic for all groundwater compositions as demonstrated by the absence of measurable nitrate and DO. Complete denitrification (initial concentration of 50 mg/L nitrate) took place above the filter bed, and nitrate was below the detection limit (0.2 mg/L) at all ports (Fig. 3). The filter effluent met the WHO's nitrate drinking water standard of 45 mg/L.

The DO concentration above the filter bed was below the detection limit (0.01 mg/L). Median pH of aqueous samples collected from all ports ranged between 7.4 and 8.0 for all groundwater compositions (Table S4).

3.5. Acetate and microbial growth

The decrease in acetate concentration with filter bed depth indicates its use by microorganisms as an electron donor (Fig. 3). Most acetate was consumed above the filter bed where denitrification occurred. Acetate was always present above the filter bed (ports 1 and 2), but was not consistently present within the filter bed (ports 3 and 4) (Fig. 2d). The absence of acetate in the filter bed potentially created electron donor-limited conditions and was correlated with higher arsenic concentrations in the gravel bed at port 4 (Table S1). This correlation was statistically significant ($p < 0.05$).

Biofilm was always visible on the inside wall of the container and on top of the sand bed. Considerable biofilm regrowth was observed within two days of filter cleaning, indicating that the microbial community quickly reestablished itself after disturbance. Furthermore, arsenic removal was not affected by cleaning. For all groundwater compositions, the biofilm and upper layer of sand were dark in color, but the sand layer became especially dark

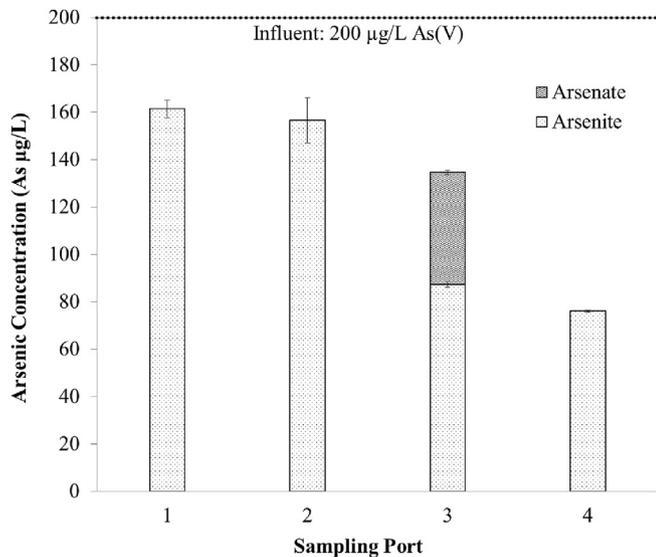


Fig. 4. Aqueous arsenic speciation results from ports 1 to 4 during groundwater S50 (day 293). The sum of arsenate and arsenite concentrations was within 12% of the total arsenic concentration at port 1 and within 5% at ports 2–4. Concentrations are the average of two or three analytical replicates, and error bars indicate one standard deviation.

during operation with groundwater S50Fe4.

4. Discussion

4.1. Arsenic removal by adsorption/co-precipitation with iron sulfide solids

The relative changes in arsenic, sulfate, sulfide, and iron concentrations along the depth of the filter (Fig. 3) are consistent with arsenic removal mechanisms described previously for anaerobic CF-BAC systems (Upadhyaya et al., 2010), including the formation of arsenic sulfide solids, the formation of iron sulfide solids, arsenic adsorption to iron sulfide solids, and co-precipitation of arsenic with iron sulfide solids. In reduced environments containing arsenic, sulfide, and iron, such as this filter, the precipitation of iron sulfide solids is more favorable than the precipitation of arsenic sulfide solids, so iron sulfide would have precipitated first (Keimowitz et al., 2007; Kirk et al., 2010; Wilkin et al., 2003). Dissolved sulfide was always present in the filter bed, while iron was not (Figs. 2 and 3), indicating that iron sulfide formation was iron-limited. The groundwater S22 profile sample was the only case where iron was present and arsenic was removed in the sand bed (Fig. 3a). For groundwater S22, the sulfate concentration decreased in the sand bed (between ports 2 and 3) without an equivalent increase in sulfide concentration, which could be explained by the precipitation of iron sulfides. For groundwater S50, iron was not present nor was arsenic removed in the sand bed (Fig. 3b). In contrast, for groundwater S50Fe4 arsenic removal with iron sulfide solids occurred above the sand bed where dissolved iron was present and dark particles were observed (Fig. 3c).

Although the data indicate some arsenic removal with iron sulfide solids, arsenic removal by this mechanism was limited. The majority of the sulfide generation occurred within the sand bed (Fig. 3). For groundwater S22 and S50 sulfide was present in excess of iron in the sand bed indicating dissolved iron was limiting (Fig. 3a and b). For groundwater S50Fe4, the majority of sulfide generation occurred within the sand bed, but dissolved iron was present only above the sand bed (Fig. 3c). This lack of co-location of

dissolved iron and sulfide could have limited the formation of iron sulfide solids which, in turn, limited arsenic removal. Previous studies of arsenic removal through adsorption to oxidized iron solids in aerobic sand filters have reported that an iron-to-arsenic ratio of 40–250 (w/w) is necessary to achieve effluent arsenic concentrations below 10–50 µg/L (Berg et al., 2007; Meng et al., 2002). The influent iron-to-arsenic ratio for groundwater S50Fe4 was only 20 (w/w), so it is not surprising that sufficient arsenic removal did not occur in this system through adsorption to and/or co-precipitation with iron sulfide solids. Another potential limitation of arsenic removal by iron solids could have been phosphate competition for adsorption sites. The effect of competing ions is especially important for implementation using real groundwater, as has been shown previously (Chiew et al., 2009; Meng et al., 2002).

Iron present in the sand likely played a role in arsenic removal, but was depleted over time, as indicated by the decreasing dissolved iron concentration in the sand bed (port 3) from groundwater S22 to S50 to S50Fe4 (Fig. 2c). Iron was not in the influent for groundwater S22 or S50, therefore the iron measured in the sand bed likely came from reductive dissolution of iron in the sand. When the groundwater composition changed from S50 to S50Fe4 (day 382), the influent iron concentration increased from 0 to 4 mg/L, but, by that time, iron was no longer detected in the sand bed. The depletion of iron in the sand over time, instead of changes in groundwater composition, might have contributed to the decreased arsenic removal for groundwater S50 and S50Fe4, as compared to groundwater S22, for which dissolved iron was always present in the sand bed. Although some iron from the sand was present as dissolved ferrous iron, another potential arsenic removal mechanism was adsorption of arsenic to ferric oxyhydroxide solids or to transitional forms of iron (Burton et al., 2011; Root et al., 2009; Tufano and Fendorf, 2008). Reduction of ferric oxyhydroxides in the filter would have led to the release of adsorbed arsenic, which could be one mechanism contributing to the increased arsenic concentration in the sand bed with time.

4.2. Arsenic removal by precipitation as arsenic sulfide solids

Arsenic sulfide precipitation is one potential mechanism that could explain some arsenic removal (Gallegos et al., 2007; O'Day et al., 2004; Upadhyaya et al., 2010). The arsenic concentration decreased in the presence of sulfide above the filter bed (ports 1 and 2) and in the gravel bed (between ports 3 and 4) for all groundwater compositions, as well as in the sand bed for groundwater S22 (Fig. 3). This arsenic removal occurred in the absence of iron above the filter bed (ports 1 and 2) for groundwater S22 and S50 as well as in the gravel bed (between ports 3 and 4) for all groundwater compositions. Arsenic removal through this mechanism would be limited by the solubility of arsenic sulfide solids.

Based on solubility calculations for arsenic in equilibrium with orpiment, the minimum dissolved arsenic concentration occurs when sulfide is between 1 and 3 mg/L (pH 7), depending on the species included in the model (Burton et al., 2011; Kirk et al., 2010; Wilkin et al., 2003). This minimum arsenic concentration occurs at the crossover point between orpiment or amorphous As_2S_3 controlling arsenic solubility (lower sulfide concentrations) and thioarsenite species controlling arsenic solubility (higher sulfide concentrations) (Bostick et al., 2005; Burton et al., 2011; Keimowitz et al., 2007; Kirk et al., 2010; Lee et al., 2005; Wilkin et al., 2003). Low arsenic to sulfide ratios and high sulfide to iron ratios, both present in this system, favor the formation of thioarsenite species, which control arsenic solubility at sulfide concentrations higher than this (Bostick et al., 2005; Keimowitz et al., 2007; Kirk et al., 2010; Lee et al., 2005; Wilkin et al., 2003). Based on the

modeling, orpiment, not realgar or amorphous As_2S_3 , controls the dissolved arsenic concentration, in agreement with other modeling results of arsenic in groundwater under reducing conditions (Kirk et al., 2010; Lee et al., 2005). The arsenic concentrations in this filter were slightly lower than expected based on dissolved arsenic in equilibrium with orpiment pH 7.5 and 8.1 (Fig. 5). This could be due to more crystalline orpiment phases or additional mechanisms such as adsorption to and/or co-precipitation with iron sulfide solids contributing to arsenic removal. Excess sulfide resulting from higher influent sulfate concentrations could also have increased desorption from iron sulfide solids as has been reported in experiments with As-bearing ferrihydrite in conditions with high sulfate reduction (Kocar et al., 2010).

4.3. Potential acetate limitation in the filter bed

When present, acetate was likely used as an electron donor for anaerobic microbial respiration. The constant presence of acetate above the filter bed ensured that reducing conditions were maintained and that any dissolved oxygen introduced during influent addition or by diffusion was consumed. When acetate was absent, microbial activity might have been electron donor-limited. The correlation between the presence of acetate in the gravel bed (port 4) and lower arsenic concentrations (Table S1) suggests that acetate-dependent metabolic processes were necessary for arsenic removal and/or prevention of arsenic release from previously deposited arsenic-containing solids. In the absence of acetate, other compounds can serve as electron donors, including arsenite and sulfide species (Oremland and Stolz, 2003; Straub and Schink, 2004). This would have led to the production of arsenate and sulfate, respectively, and could explain the arsenate observed in the sand bed (port 3), as well as the increase in sulfate in the gravel bed (between ports 3 and 4). Furthermore, arsenic associated with sulfide or iron sulfide solids would have been released if these solids served as an electron donor.

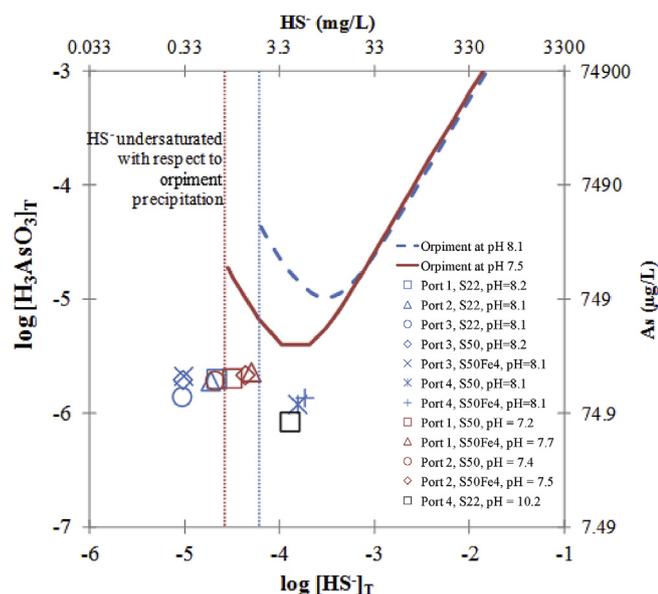


Fig. 5. Solubility of orpiment at pH 7.5 (solid red line) and at pH 8.1 (dashed blue line). For comparison, arsenic and sulfide concentrations from profile samples (Fig. 3) are shown from days 178, 330, and 409 for S22, S50, and S50Fe4, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Conclusions

These results show that anaerobic biosand filters have the ability to remove nitrate, sulfate, iron, and arsenic from a simulated groundwater. However, effluent arsenic concentrations remained above the WHO drinking water standard indicating that improvements are necessary before this filter can be operated to provide arsenic-safe water. Vinegar was used to provide acetic acid as the electron donor because vinegar is widely available at low cost. Furthermore, acetic acid has been approved by the National Sanitation Foundation for use in drinking water treatment (National Sanitation Foundation product and service listings, www.nsf.org). The construction and maintenance of the filter was simple, and biofilm cleaning did not negatively impact contaminant removal. These aspects of a vinegar-amended biosand filter offer benefits for decentralized water treatment in developing countries and could be leveraged for areas with nitrate contamination.

Future research efforts should focus on meeting the arsenic drinking water standard, field testing, developing post-treatment processes, and evaluating the stability of arsenic-laden wastes. Given that arsenic removal by iron sulfide solids was iron-limited, arsenic removal might be improved by adding iron to the gravel bed to ensure the co-location of iron and sulfide to promote arsenic removal by iron sulfide solids. Iron could be added as zero valent iron, which has been added to other arsenic-removing sand filters (Hussam and Munir, 2007; Leupin and Hug, 2005; Neumann et al., 2013). Since regression analysis indicated a correlation between the presence of acetate in the gravel bed and lower arsenic concentrations, increasing the influent acetate concentration may also improve arsenic removal. After achieving adequate arsenic removal results in the laboratory, field testing would be important to verify removal under varying conditions and with actual groundwater sources. Post-treatment would be needed for re-aeration of treated water to remove sulfides and excess carbon, polishing filtration for the removal of particles (arsenic and other solid precipitates and microbes), and disinfection. Finally, the stability of arsenic-laden wastes produced by this system must be evaluated under relevant disposal conditions. Beyond technical challenges, filter implementation, training, and maintenance remain important areas for consideration and often represent the greatest barriers to the provision of clean water (Amrose et al., 2015; Etmanski and Darton, 2014; Hossain et al., 2005). Further work is needed to determine if anaerobic biosand filters are a viable arsenic removal technology for rural areas that rely on decentralized water treatment.

Notes

The authors declare no competing financial interest.

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Appendix A. Supporting information

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2016.02.001>.

References

- Amrose, S., Burt, Z., Ray, I., 2015. Safe drinking water for low-income regions. *Ann. Rev. Environ. Resour.* 40, 203–231.
- Badruzzaman, A.B.M., 2003. Leaching of Arsenic from Wastes of Arsenic Removal Systems. In: Ahmed, M.F. (Ed.), *Fate of Arsenic in the Environment*. Bangladesh University of Engineering and Technology, The United Nations University.
- Bauer, R., Dizer, H., Graeber, I., Rosenwinkel, K.-H., López-Pila, J.M., 2011. Removal of bacterial fecal indicators, coliphages and enteric adenoviruses from waters with high fecal pollution by slow sand filtration. *Water Res.* 45, 439–452.
- Berg, M., Luzzi, S., Trang, P.T.K., Viet, P.H., Giger, W., Stüben, D., 2007. Arsenic removal from groundwater by household sand filters: comparative field study, model calculations, and health benefits. *Environ. Sci. Technol.* 41, 1051–1052.
- Berg, M., Luzzi, S., Trang, P.T.K., Viet, P.H., Giger, W., Stüben, D., 2006. Arsenic removal from groundwater by household sand filters: comparative field study, model calculations, and health benefits. *Environ. Sci. Technol.* 40, 5567–5573.
- Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environ. Sci. Technol.* 35, 2621–2626.
- Bissen, M., Frimmel, F.H., 2003. Arsenic – a review. part II: oxidation of arsenic and its removal in water treatment. *Acta Hydroch. Hydrob.* 31, 97–107.
- Bostick, B.C., Fendorf, S., Brown Jr., G.E., 2005. In situ analysis of thioarsenite complexes in neutral to alkaline arsenic sulphide solutions. *Mineral. Mag.* 69, 781–781.
- Burton, E.D., Johnston, S.G., Bush, R.T., 2011. Microbial sulfidogenesis in ferrihydrite-rich environments: effects on iron mineralogy and arsenic mobility. *Geochim. Cosmochim. Acta* 75, 3072–3087.
- Chiew, H., Sampson, M.L., Huch, S., Ken, S., Bostick, B.C., 2009. Effect of groundwater iron and phosphate on the efficacy of arsenic removal by iron-amended biosand filters. *Environ. Sci. Technol.* 43, 6295–6300.
- Clancy, T.M., Hayes, K.F., Raskin, L., 2013. Arsenic waste management: a critical review of testing and disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water. *Environ. Sci. Technol.* 47, 10799–10812.
- Cole, J.M., Ryan, M.C., Smith, S., Bethune, D., 2004. Arsenic source and fate at a village drinking water supply in Mexico and its relationship to sewage contamination. In: *Natural Arsenic in Groundwater: Proceedings of the Pre-Congress Workshop, 32nd International Geological Congress*. CRC Press, Florence, Italy, p. 67.
- Elliott, M., Stauber, C., Koksai, F., Liang, K., Huslage, D., DiGiano, F., Sobsey, M., 2006. The operation, flow conditions and microbial reductions of an intermittently operated, household scale slow sand filter. In: Gimbel, R., Graham, N.J.D., Collins, M.R. (Eds.), *Recent Progress in Slow Sand and Alternative Biofiltration Processes*. IWA Publishing, London, UK, p. 268.
- Etmanski, T.R., Darton, R.C., 2014. A methodology for the sustainability assessment of arsenic mitigation technology for drinking water. *Sci. Total Environ.* 488–489, 505–511.
- Fytianos, K., Christophoridis, C., 2004. Nitrate, arsenic, and chloride pollution of drinking water in northern Greece. *Environ. Monit. Assess.* 93, 55–67.
- Gallegos, T.J., Hyun, S.P., Hayes, K.F., 2007. Spectroscopic investigation of the uptake of arsenite from solution by synthetic mackinawite. *Environ. Sci. Technol.* 41, 7781–7786.
- Ghosh, A., Mukhi, M., Sáez, A.E., Ela, W.P., 2006. Leaching of arsenic from granular ferric hydroxide residuals under mature landfill conditions. *Environ. Sci. Technol.* 40, 6070–6075.
- Gustafsson, J.P., 2012. Visual minteq ver. 3.0. KTH, Royal Institute of Technology, Sweden.
- Haig, S., Collins, G., Davies, R., Dorea, C., Quince, C., 2011. Biological aspects of slow sand filtration: Past, present and future. *Water Sci. Technol. Water Supply* 11, 468–472.
- Hossain, M.A., Sengupta, M.K., Ahmed, S., Rahman, M.M., Mondal, D., Lodh, D., Das, B., Nayak, B., Roy, B.K., Mukherjee, A., Chakraborti, D., 2005. Ineffectiveness and poor reliability of arsenic removal plants in West Bengal, India. *Environ. Sci. Technol.* 39, 4300–4306.
- Hussam, A., Munir, A.K.M., 2007. A simple and effective arsenic filter based on composite iron matrix: development and deployment studies for groundwater of Bangladesh. *J. Environ. Sci. Health, Part A Toxic/Hazard. Subst. Environ. Eng.* 42, 1869–1878.
- Jong, T., Parry, D.L., 2005. Evaluation of the stability of arsenic immobilized by microbial sulfate reduction using TCLP extractions and long-term leaching techniques. *Chemosphere* 60, 254–265.
- Keimowitz, A.R., Mailloux, B.J., Cole, P., Stute, M., Simpson, H.J., Chillrud, S.N., 2007. Laboratory investigations of enhanced sulfate reduction as a groundwater arsenic remediation strategy. *Environ. Sci. Technol.* 41, 6718–6724.
- Kinniburgh, D.G., Smedley, P.L., 2001. Arsenic contamination of groundwater in Bangladesh. In: *British Geological Survey, Bangladesh Department of Public Health Engineering, UK Department for International Development, Bangladesh Department of Public Health Engineering, British Geological Survey*.
- Kirk, M.F., Roden, E.E., Crossey, L.J., Brealey, A.J., Spilde, M.N., 2010. Experimental analysis of arsenic precipitation during microbial sulfate and iron reduction in model aquifer sediment reactors. *Geochim. Cosmochim. Acta* 74, 2538–2555.
- Kocar, B.D., Borch, T., Fendorf, S., 2010. Arsenic repartitioning during biogenic sulfidation and transformation of ferrihydrite. *Geochim. Cosmochim. Acta* 74, 980–994.
- Kundu, M.C., Mandal, B., Sarkar, D., 2008. Assessment of the potential hazards of nitrate contamination in surface and groundwater in a heavily fertilized and intensively cultivated district of India. *Environ. Monit. Assess.* 146, 183–189.
- Lee, M.-K., Saunders, J.A., Wilkin, R.T., Mohammad, S., 2005. Geochemical modeling of arsenic speciation and mobilization: Implications for bioremediation. In: *Advances in Arsenic Research*. American Chemical Society, pp. 398–413.
- Leupin, O.X., Hug, S.J., 2005. Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* 39, 1729–1740.
- Leupin, O.X., Hug, S.J., Badruzzaman, A.B.M., 2005. Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. *Environ. Sci. Technol.* 39, 8032–8037.
- Luo, Q., Tsukamoto, T.K., Zamzow, K.L., Miller, G.C., 2008. Arsenic, selenium, and sulfate removal using an ethanol-enhanced sulfate-reducing bioreactor. *Mine Water Environ.* 27, 100–108.
- McClintock, T.R., Chen, Y., Bundschuh, J., Oliver, J.T., Navoni, J., Olmos, V., Lepori, E.V., Ahsan, H., Parvez, F., 2012. Arsenic exposure in Latin America: Biomarkers, risk assessments and related health effects. *Sci. Total Environ.* 429, 76–91.
- Meng, X., Korfiatis, G.P., Bang, S., Bang, K.W., 2002. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol. Lett.* 133, 103–111.
- Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents—a critical review. *J. Hazard. Mater.* 142, 1–53.
- Morel, F.M.M., Hering, J.G., 1993. *Principles and Applications of Aquatic Chemistry*. John Wiley & Sons, Inc., New York.
- Neumann, A., Kaegi, R., Voegelin, A., Hussam, A., Munir, A.K.M., Hug, S.J., 2013. Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environ. Sci. Technol.* 47, 4544–4554.
- Nitzsche, K.S., Lan, V.M., Trang, P.T.K., Viet, P.H., Berg, M., Voegelin, A., Planer-Friedrich, B., Zahoransky, J., Müller, S.-K., Byrne, J.M., Schröder, C., Behrens, S., Kappler, A., 2015. Arsenic removal from drinking water by a household sand filter in Vietnam — effect of filter usage practices on arsenic removal efficiency and microbiological water quality. *Sci. Total Environ.* 502, 526–536.
- O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. 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.* 101, 13703–13708.
- Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. *Science* 300, 939–944.
- Pikaar, I., Rozendal, R.A., Yuan, Z., Keller, J., Rabaey, K., 2011. Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities. *Water Res.* 45, 2281–2289.
- Rahman, M.M., Mandal, B.K., Chowdhury, T.R., Sengupta, M.K., Chowdhury, U.K., Lodh, D., Chanda, C.R., Basu, G.K., Mukherjee, S.C., Saha, K.C., Chakraborti, D., 2011. Arsenic groundwater contamination and sufferings of people in north 24-parganas, one of the nine arsenic affected districts of West Bengal, India. *J. Environ. Sci. Health, Part A Toxic/Hazard. Subst. Environ. Eng.* 38, 25–59.
- Ravenscroft, P., Brammer, H., Richards, K., 2009. *Arsenic Pollution: A Global Synthesis*. Wiley-Blackwell.
- Root, R.A., Vlassopoulos, D., Rivera, N.A., Rafferty, M.T., Andrews, C., O'Day, P.A., 2009. Speciation and natural attenuation of arsenic and iron in a tidally influenced shallow aquifer. *Geochim. Cosmochim. Acta* 73, 5528–5553.
- Sharma, A.K., Tjell, J.C., Sloth, J.J., Holm, P.E., 2014. Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Appl. Geochem* 41, 11–33.
- Sobsey, M.D., Stauber, C.E., Casanova, L.M., Brown, J.M., Elliot, M.A., 2008. Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world. *Environ. Sci. Technol.* 42, 4261–4267.
- Stauber, C., Elliott, M., Koksai, F., Ortiz, G., DiGiano, F., Sobsey, M., 2006. Characterisation of the biosand filter for *E. coli* reductions from household drinking water under controlled laboratory and field use conditions. *Water Sci. Technol.* 54, 1–7.
- Straub, K.L., Schink, B., 2004. Ferrihydrite-dependent growth of *Sulfurospirillum deleyianum* through electron transfer via sulfur cycling. *Appl. Environ. Microbiol.* 70, 5744–5749.
- Tufano, K.J., Fendorf, S., 2008. Confounding impacts of iron reduction on arsenic retention. *Environ. Sci. Technol.* 42, 4777–4783.
- Upadhyaya, G., Clancy, T.M., Snyder, K.V., Brown, J., Hayes, K.F., Raskin, L., 2012. Effect of air-assisted backwashing on the performance of an anaerobic fixed-bed bioreactor that simultaneously removes nitrate and arsenic from drinking water sources. *Water Res.* 46, 1309–1317.
- Upadhyaya, G., Jackson, J., Clancy, T.M., Hyun, S.P., Brown, J., Hayes, K.F., Raskin, L., 2010. Simultaneous removal of nitrate and arsenic from drinking water sources utilizing a fixed-bed bioreactor system. *Water Res.* 44, 4958–4969.
- Wilkin, R.T., Wallschlager, D., Ford, R.G., 2003. Speciation of arsenic in sulfidic waters. *Geochem. Trans.* 4, 1–7.
- World Health Organization, 2008. *Guidelines for Drinking-water Quality*, third ed. Geneva.