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Compost-Based Permeable Reactive Barriers for the Source Treatment of Arsenic Contaminations in Aquifers: Column Studies and Solid-Phase Investigations

RALF KÖBER,*,† BIRGIT DAUS,‡
MARKUS EBERT,† JÜRGEN MATTUSCH,‡
EDMUND WELTER,§ AND
ANDREAS DAHMKE†

Institute for Geosciences, Christian-Albrechts-University of Kiel, Ohlshausenstrasse 40, D-24098 Kiel, Germany, UFZ Centre for Environmental Research, Permoserstrasse 15, D-04318 Leipzig, Germany, and Hamburger Synchrotronstrahlungslabor am Deutschen Elektronen Synchrotron, Notkestrasse 85, D-22603 Hamburg, Germany

The bulk of arsenic (As) at contaminated sites is frequently associated with iron (hydr)oxides. Various studies ascribe increasing dissolved As concentrations to the transformation of iron (hydr)oxides into iron sulfides, which is initiated by dissolved sulfide. We investigated whether this processes can be utilized as a source treatment approach using compost-based permeable reactive barriers (PRB), which promote microbial sulfate reduction. Arsenic-bearing aquifer sediment from a contaminated industrial site showed a decrease in As content of <10% after 420 days of percolation with sulfide-free artificial groundwater. In contrast, water that had previously passed through organic matter and exhibited sulfide concentrations of 10−30 mg/L decreased As content in the sediment by 87% within 360 days. X-ray diffraction showed no arsenic sulfides, but XANES spectra (X-ray absorption near edge structure) and associated linear combinations revealed that adsorbed arsenate of the original sediment was in part reduced to arsenite and indicated the formation of minor amounts of a substance that contains As and sulfur. The speciation of dissolved As changed from initially As(V)-dominated to As(III)-dominated after sulfide flushing was started, which increases the mobility of As. Because sulfide can be supplied not only by compost-based PRBs but also by direct injection, sulfide flushing has a wide range of application for the source treatment of arsenic.

Introduction

The health of millions of people is affected by arsenic (As), which can derive from anthropogenic or geogenic sources and contaminates ground and drinking water in numerous countries around the world (*1*). Whereas geogenic As groundwater contamination generally causes regional hazards, As contamination at industrial sites is more localized. Recent developments to improve As remediation have mainly focused on advancements for plume control approaches and for innovative materials to remove As, but innovations for source treatment actions have been less intensely addressed. Source treatment by in situ soil flushing represents an alternative strategy to excavation, which is frequently expensive. Since the bulk of As is frequently associated with iron(Fe)(III) (hydr)oxides at contaminated sites (e.g., ref *2*), soil flushing should establish conditions that favor the dissociation of As from iron (hydr)oxides. This can be achieved by high pH (*3*−*5*); by high concentrations of phosphate (*6*, *7*), which competes for sorption sites; or by the dissolution of Fe (hydr)oxides, either by acid flushing (*8*) or by the establishment of reducing conditions (*4*, *9*).

The reduction of Fe(III) in iron (hydr)oxides by dissolved sulfide is a widely investigated process (e.g., refs *10* and *11*). Dissolved sulfide that is removed from solution during reductive dissolution of iron (hydr)oxides primarily precipitates as iron sulfide and elemental sulfur (e.g., ref *12*). Several studies have attributed high dissolved As concentrations to the As release from iron (hydr)oxides during Fe(III) reduction by sulfide, which originates from microbial sulfate reduction (e.g., ref *13*). To promote these process sequences, supplying dissolved sulfide could be a promising strategy to mobilize and subsequently remove As. One possibility for sulfide supply is the concept of Benner et al. (*14*), who used compost-based permeable reactive barriers (PRB) for the promotion of microbial sulfate reduction. Reactive PRB materials, which must exhibit higher permeability than the surrounding aquifer, are placed perpendicular to the groundwater flow direction and along the cross-sectional length to be treated. This approach has the advantage that sulfide can be supplied for a period of years at low costs and with low maintenance efforts. Whereas the distribution of sulfide across a certain aquifer cross section by punctiform injection through wells can occasionally be challenging due to aquifer heterogeneities, compost-based PRBs release sulfide across a wider area.

High sulfide concentrations additionally result in the formation of thioarsenites, which increases As solubility (*15*, *16*). Arsenic sulfides such as As_2S_3(amorphous), orpiment (As_2S_3), or realgar (AsS) have high solubilities at neutral pH and predominantly precipitate under acidic conditions (*15*−*19*). Supplying sulfide could nevertheless initiate the precipitation of those phases, which would affect the application of the sulfide flushing suggested.

The objectives of this study are to investigate whether compost-based PRBs that release sulfide as a result of microbial sulfate reduction and that are placed upstream of As contaminated aquifer sediments accelerate As mobilization. The question as to whether this approach can in principle be used as a source treatment action or if the precipitation of arsenic sulfides can affect the applicability was investigated on the basis of laboratory experiments with sediment from a contaminated site.

Materials and Methods

Column Experiments. Two sets of column experiments, composed of sequential columns (diameter 10 cm, length 112 cm, volume 8.8 L, HDPE) connected by Viton tubing, were performed with artificial groundwater (Figure 1). The first 10 cm of each column was filled with quartz gravel to distribute the flow across the cross-sectional area of the columns. These 10 cm are excluded in all further length specifications. A column (S1) filled with As-bearing aquifer sediment (original sediment A, OS-A) from a contaminated

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* Corresponding author phone: +49 (431)-880-2860; fax: +49 (431)-880-7606; e-mail: rkoeber@gpi.uni-kiel.de.

† Christian-Albrechts-University of Kiel.

‡ UFZ Centre for Environmental Research.

§ Hamburger Elektronen Synchrotron am Deutschen Elektronen Synchrotron.

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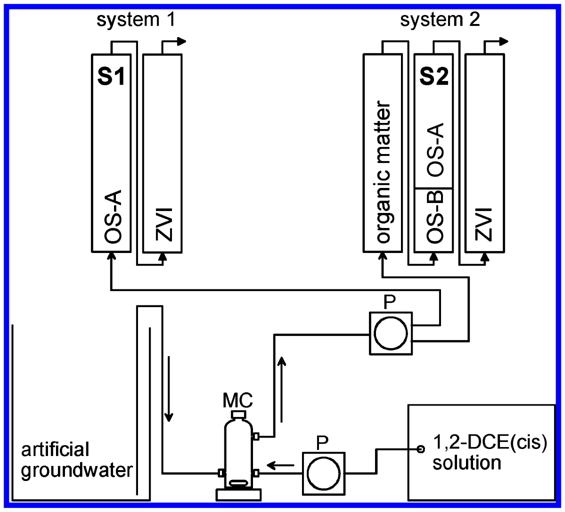


FIGURE 1. Experimental setup of column experiments (P, peristaltic pump; MC, mixing chamber with magnetic stirrer; OS-A, sediment with high As content; OS-B, sediment with low As content; ZVI, zerovalent iron).

TABLE 1: Solid-Phase Concentrations[a] from the Two Original Sediments and in Samples from S1 and S2 after Column Operation

	As	S	Fe	Mn
OS-A	17.7	1.8	116	3.5
OS-B	1.6	3.5	75	1.5
S1 (10 cm, former OS-A)	13.4	2.0	133	3.4
S1 (45 cm, former OS-A)	18.5	2.1	140	4.1
S1 (90 cm, former OS-A)	16.7	2.1	126	3.8
S2 (10 cm, former OS-B)	1.1	29.0	117	1.3
S2 (50 cm, former OS-A)	2.3	23.4	109	2.4
S2 (85 cm, former OS-A)	2.4	24.2	111	2.4

[a] Solid-phase concentrations are given in micromoles per gram.

site was set before a column filled with zerovalent iron (ZVI, iron sponge, ISPAT, Hamburg, Germany) in system 1. The first column of system 2 was filled with organic matter (40% compost, 33% chaff, 27% wood chips), the second (S2) with contaminated sediment, and the third with ZVI. The first 30 cm of S2 was filled with original sediment B (OS-B), which originated from a peripheral zone of the contamination with lower As content. The remainder of S2 was filled with OS-A. These two sediments with distinctively different As contents (for analytical results see Table 1) were used to permit differentiation between sulfide consumption due to Fe(III) reduction and sulfide decrease due to arsenic sulfide precipitation if necessary. Both sediments consist of pebbly sands that originated from a depth of 2−4 m below the surface, where fluctuating water levels established either saturated or unsaturated conditions. The column filled with organic matter was operated separately for 80 days before it was connected to column S2 for the duration of the experiments. Thus, the experimental setup selected provided double control of the effects of organic matter, first by observing a reference phase before organic matter was connected to the sediment, and second, by running a similar system in parallel without organic matter for long-term comparison.

The test solution was pumped by peristaltic pumps from the bottom to the top of the columns for 420 days at flow rates of 1.43 and 1.39 L/day for systems 1 and 2, respectively. Flow velocities were 71 and 73 cm/day in the respective systems, and 265 and 257 pore volumes were exchanged, approximating an effective porosity of 0.25. The test solution was made by adding salts and acid to tap water to achieve a pH of approximately 7.5, concentrations of 40 mg/L Na, 4 mg/L K, 150 mg/L Ca, 20 mg/L Mg, 13 mg/L Si, 70 mg/L Cl^-, 23 mg/L NO_3^-, 140 mg/L SO_4^{2-}, and an alkalinity of 5 mmol/L. In addition, 1,2-*cis*-dichloroethylene (*cis*-DCE) was added to this solution (0.2−7.4 mg/L). This compound is present at the site in addition to As, and concurrent ZVI treatment of As and *cis*-DCE was investigated in a connected study (*20*, *21*). No indications were obtained that *cis*-DCE interferes with As mobility in any respect.

Water samples were taken with syringes at the inflow and from sampling ports located along the flow path of the columns. A maximum of 100 mL of the test solution was drawn from a side port during one sampling campaign.

Analysis of Aqueous-Phase Samples. As, Fe, Mn, Ca, Mg, K, Na, and Si concentrations were determined through inductively coupled plasma with optical emission spectroscopy (ICP−OES Vista, Varian); SO_4^{2-}, NO_3^-, and Cl^- concentrations through ion chromatography with conductivity detection (DX 500, Dionex); and chlorinated ethylenes through headspace gas chromatography with electron capture and flame ionization detection (GC-ECD/FID, HP 6890). Sulfide was analyzed on the basis of photometry (PM2DL, Zeiss) by the methylene blue method, and alkalinity was measured through HCl titration. For the measurement of pH and E_H, electrodes (InLab 422, Metler Toledo; PT 8280, Schott) were used. In addition to standard analyses, several samples were analyzed for As species through the coupling of ion chromatographic separation (IC, system Gold, Beckman) and inductively coupled plasma with mass spectroscopy (ICP−MS, PQ ExCell, Thermo). IC−ICP−MS measurements were carried out at the UFZ Centre for Environmental Research Halle-Leipzig GmbH on the basis of methods described by Daus et al. (*22*) and Mattusch and Wennrich (*23*).

All samples were filtrated through 0.2 μm regenerated cellulose membrane filters (Minisart RC 25, Sartorius). Samples for ICP−OES measurements were acidified with HNO_3 (65% supra pure) to a pH < 2. Acidification for cation samples were completed immediately after sampling and filtration, whereas samples for total As measurements were acidified, at the earliest, 3 days after sampling and at least 2 days before measurement. This was done to avoid the precipitation of arsenic sulfides in solutions containing high As and sulfide concentrations. This time period before acidification was necessary for the oxidation of sulfide in contact with the atmosphere. Acidifying the samples 2 days before measurement assured the redissolution of iron hydroxides, if such phases had been formed. The verification of the method through the additional measurement of several untreated samples immediately after sampling yielded comparable concentrations. Samples for As species analysis were shipped in headspace-free glass vials and were measured no later than 2 days after sampling.

Analysis of Solid-Phase Samples. Column S2 was cut open under argon atmosphere after completion of operations, and samples were taken at several positions along the flow path. For S1 no glovebox was used because no reducing conditions prevailed during the experiment. X-ray absorption spectroscopy and X-ray diffraction (XRD) investigations were carried out on the <63 μm fraction, which was separated from bulk sediment through wet sieving to reduce the quartz background. The separation of the fine fraction for S2 samples was carried out with nitrogen-purged H_2O under argon atmosphere. The solution containing the <63 μm fraction was collected, and water was decanted after settling of the sediment. Water-free acetone was used to accelerate drying of these samples. For digestion, the complete sediment was freeze-dried. S2 samples were stored in argon-filled gastight glass vials. All samples were ground before use.

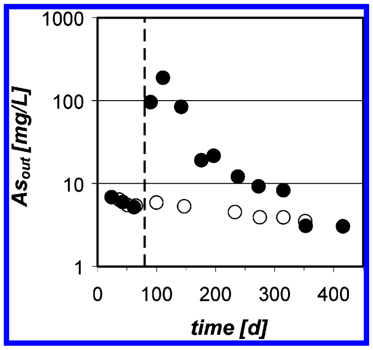


FIGURE 2. Outflow As concentrations (at 92 cm) of the sediment-filled columns S1 (○) and S2 (●). The dashed vertical line indicates the time period (80 days) during which the column filled with organic matter was connected with S2.

X-ray diffractograms were taken with a D-5000 Siemens diffractometer at a scan rate of 0.01° or 0.02° 2θ with 2−18 s of measurement/step. The instrument was operated with Cu Kα radiation at 40 kV and 30 mA. The samples (250 mg) were digested by HF/aqua regia according to the method described by Garbe-Schönberg (*24*) before ICP−OES measurement. X-ray absorption near-edge structure (XANES) spectra were taken in fluorescence mode at beamline A1 at the Hamburger Synchrotron Strahlungslabor (HASYLAB). All samples were kept under vacuum during measurement. Details of the analytical method and the preparation of samples and reference materials are described elsewhere (*21*).

Results and Discussion

An early onset of microbial sulfate reduction in the column filled with organic matter was indicated by exponentially decreasing sulfate concentrations and dissolved sulfide in the front area of this column. This was already observed during the first sampling campaign at 23 days. Sulfide concentrations decreased in the rear area of the column during the first weeks, and it took approximately 2 months until sulfide was released from that column. In all probability, sulfide was associated with the organic matter until saturation of the uptake capacity before it was released into solution. Generally, 10−30 mg/L sulfide was released within the time from the connection of organic matter column with S2 at 80 days until the end of the experiment. pH remained in the neutral (6.6−7.7) range, alkalinity increased to 7−10 mM, and E_H decreased from 200−300 mV in the influent to −50 to −100 mV in the effluent. Decreasing reactivity of the organic matter was not observed because sulfide release, alkalinity increase, and E_H decrease were relatively constant during the experiment.

The effects of organic matter and released sulfide on As mobility in the aquifer sediments is shown by outflow As concentrations measured at the last side port of the sediment-filled columns at a flow path of 92 cm (Figure 2). Outflow As concentrations of S1 run without sulfide input slowly declined with time. Arsenic dissolution in S2 resembled that of S1 during the first 2 months, when the column filled with compost was run separately. After the connection of the compost with S2 and associated sulfide input into S2, As dissolution from the sediment strongly increased, resulting in a maximum outlet As concentration of 190 mg/L. This was accompanied by a decrease in dissolved sulfide and by an increase in dissolved iron (Figure 3). Sulfide concentration decrease and iron concentration increase were initially restricted to the front area of S2 and migrated in flow direction with elapsing time. Manganese concentrations also increased after connection (data not shown) but generally remained below 2 mg/L. These results apparently suggest that sulfide which was fed from the compost to the aquifer sediment dissolved iron and manganese (hydr)oxides via reduction of solid-phase Fe(III) and Mn(VI). It is assumed that these processes are responsible for the accelerated release of arsenic from the aquifer sediment after the input of sulfide.

The percolation of OS-A in S1 for 420 days with artificial groundwater did not substantially decrease As content (Table 1). Only the sediment from the input region (10 cm), where dissolution rates were highest, showed significantly lower As concentrations (13.4 μmol/g) than OS-A (17.7 μmol/g). Assuming that each of the three samples is representative of the respective third of the column length, estimated As mass reduction for the entire column accounts for 8.5%. In contrast, sulfide treatment decreased As concentrations in OS-A sediment sampled from 50 cm in column S2 by approximately 87% within 360 days. This displays a notably more rapid decontamination compared to the percolation with sulfide-free groundwater. The fixation of sulfide increased sulfur concentrations in S2 from initially 2−3.5 μmol/g to 23−29 μmol/g. Relative concentration changes of iron and manganese were minor.

XRD analyses of samples from the fine-grained fraction of OS-A, OS-B, S1, and S2 did not detect As-bearing phases but identified quartz (SiO_2), calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], albite ($NaAlSi_3O_8$), and muscovite [$KAl_2(Si_3Al)O_{10}(OH)_2$] in all samples. Only one sample from S2, which originated at 10 cm from the influent, indicated a small amount of pyrite. Crystalline FeS and elemental sulfur were not detected. Even though iron sulfides were not detected by specific analysis, their presence in sulfide-treated sediment is presumed, in particular because the sulfide-treated sediment had a deep black color. The high Fe:S ratio in S2 (Table 1) indicates that not all of the solid-phase iron can be bound in iron sulfides after sulfide treatment, but the amount of total solid-phase iron was too low to detect those iron phases by XRD.

Arsenic K-edge XANES spectra of fine-grained fraction samples from the sediment-filled columns and the original sediment were compared with reference materials to investigate the bonding and the immediate vicinity of As (Figure 4). The white-line positions (maximum fluorescence) of sample spectra and the spectrum of arsenate adsorbed to ferrihydrite all are located at a photon energy of 11 875 eV. This clearly indicates that As in the solid phase of the original sediment and the sediments which were percolated by the sulfide-free or sulfidic solutions for more than 1 year is mainly pentavalent. While the spectra of OS-A and S1 (90 cm) show a shape comparable to that of arsenate adsorbed to ferrihydrite, the absorption edge of the S2 (50 cm) spectrum is shifted to lower energy, indicating that reduced arsenic species are included in the sample.

To estimate the percentage of the three reference species in the samples and to verify if unknown species may be incorporated, a reproduction of the sample spectra by the three reference spectra was attempted by linear combination fitting. The results show that the spectra can nearly be reproduced, indicating that bulk As is represented by the reference compounds or by substances that yield comparable spectra. Otherwise the contribution of minor amounts of additional unknown substances is pointed out by the slight but significant deviation between the fitted and the measured curves. Due to this unknown fraction, the values of the percentage weight (Figure 4), and in particular small values, should be interpreted with care. Nevertheless, the results show that arsenite is negligible in OS-A and S1 (50 cm). Sulfide treatment caused a considerable shift in the speciation of solid-phase As in S2 compared to non-sulfide-treated sediment. Approximately a third of total As is represented by arsenite, and minor amounts of orpiment or similar substances apparently had formed. Amorphous arsenic sulfide

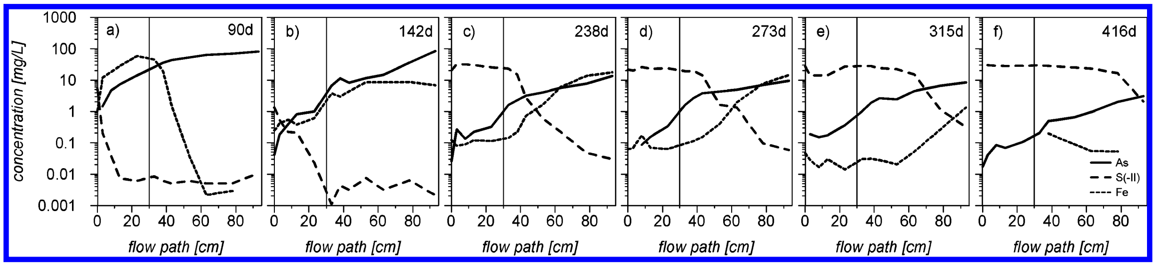
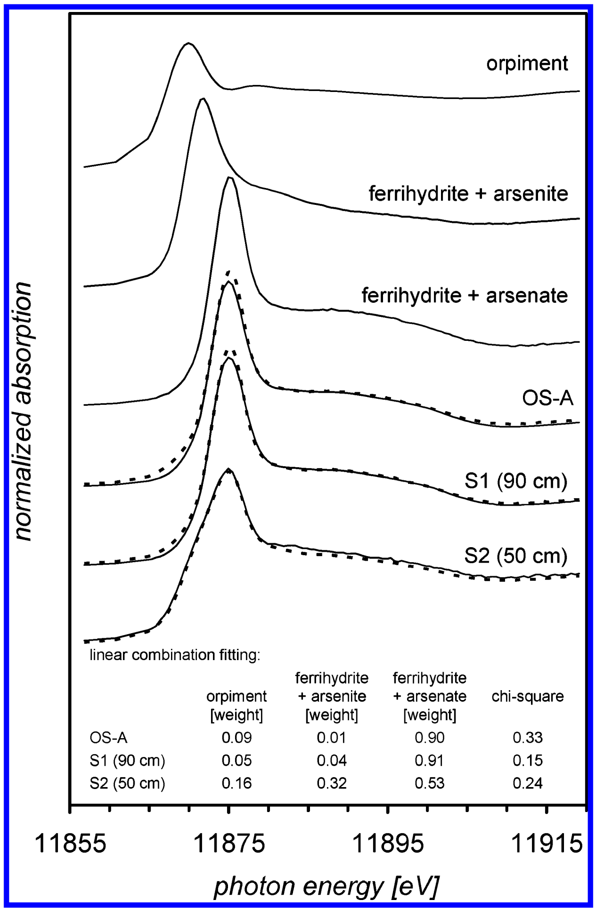


FIGURE 3. Concentrations of arsenic, sulfide, and iron for various time steps (a−f). The vertical line indicates the separation of OS-B (<30 cm) and OS-A (>30 cm).



	orpiment [weight]	ferrihydrite + arsenite [weight]	ferrihydrite + arsenate [weight]	chi-square
OS-A	0.09	0.01	0.90	0.33
S1 (90 cm)	0.05	0.04	0.91	0.15
S2 (50 cm)	0.16	0.32	0.53	0.24

FIGURE 4. XANES spectra of reference materials and samples of OS-A, S1 (flow path 90 cm), and S2 (flow path 50 cm). Dashed lines for the samples indicate fitted linear combinations of the spectra from the three reference materials. The inset values indicate the percentage weight of the three references for the linear combination and the χ^2 of the fitting error.

[$As_2S_{3(am)}$] and dissolved or adsorbed thioarsenites should yield XANES spectra similar to orpiment since the As−S bonding length of all three substances is approximately 2.8 Å (*25*). $As_2S_{3(am)}$ or thioarsenites may therefore contribute to the 16% that the linear combination fitting attributes to orpiment. These findings indicate that the bulk of the As fraction which remained in the sediment after sulfide flushing is not an As−S phase. The arsenate and arsenite retained is obviously bound to compounds that are not transformed by sulfide.

Dissolved As in S1 was predominantly arsenate (> 95%) throughout the experiment (data not shown). This correlates with the XANES results, which showed clear dominance of As(V) in the solid phase of the S1 sample (90 cm) and OS-A. The speciation of dissolved As in S2 was dominated by As(III) along the entire flow path after the input of sulfide, although elevated sulfide concentrations were restricted to the first 20 cm after 142 days (2 months of sulfide flushing) (Figure 5a). Microbial reduction may have contributed to As speciation shift (*26*, *27*). The conversion from arsenate to arsenite may have contributed to enhanced As mobility because arsenite is, in general, more mobile than arsenate at neutral pH (*1*). Samples with elevated sulfide concentrations characteristically showed an additional peak during IC−ICP−MS measurement in addition to the typical arsenite and arsenate peaks in their chromatograms (Figure 5b). The third peak was identified to be an As−S compound by simultaneous ICP−MS detection of both elements ^{75}As and S as ^{48}SO. Such As peaks in sulfidic solution are typical of thioarsenites or thioarsenates (*28*). It can be assumed that a part of the dissolved thioarsenic species detected are associated with the solid phase. This fraction presumably contributed to the percentage that was attributed to orpiment by the linear combination fitting. In conclusion, it is plausible that a small part of the dissolved As was retained as an As−S compound, but ultimately, it cannot be definitely verified from the results whether as thioarsenic species or as As_2S_3.

Figure 6 shows solubilities of As_2S_3(am) for the pH range that emerged in S2. The increasing formation of thioarsenite species at higher sulfide concentrations increases the solubility of As_2S_3(am) (*16*, *28*). Samples from the front area of S2, where sulfide concentrations are high and As concentrations increase, are undersaturated with respect to As_2S_3(am). The solution does not become oversaturated until the sulfide concentration decreases by more than 1 order of magnitude. For a pH of 7, As_2S_3(am) has its lowest solubility at a sulfide concentration of $10^{-4.2}$ M [2.1 mg/L S(-II)]. Therefore, the probability of arsenic sulfide formation would not generally increase for groundwater with sulfate concentrations higher than those outlined in our experiments and thus with higher sulfide concentrations after flow through a compost-based PRB. As long as sulfide concentrations remain high, arsenic sulfide precipitation can be excluded even for extremely high As concentrations. But independently of this initial sulfide concentration, iron sulfide formation decreases sulfide concentration, which favors As_2S_3(am) oversaturation as long as As concentrations are still high (>1.2 mg/L at pH 7).

Implications for Field Application. By the example of our experiment, we have been able to show that the widely investigated process of reductive dissolution of Fe(III) (hydr)oxides by dissolved sulfide can specifically be applied for source treatment at an As-contaminated site. Various types of iron (hydr)oxides, such as ferrihydrite, lepidocrocite, goethite, hematite, or magnetite, which may be predominant As scavengers at contaminated sites, can all be reduced by dissolved sulfide (e.g., refs *10* and *29*). The application of sulfide flushing is therefore not limited to a specific iron mineral phase to which As is bound but can be applied at a wide range of oxidic sedimentary aquifers. The formation of arsenic sulfides during sulfide treatment is of minor importance for a wide range of input sulfide concentrations, although it can cause As fixation in the treated sediment to a minor extent.

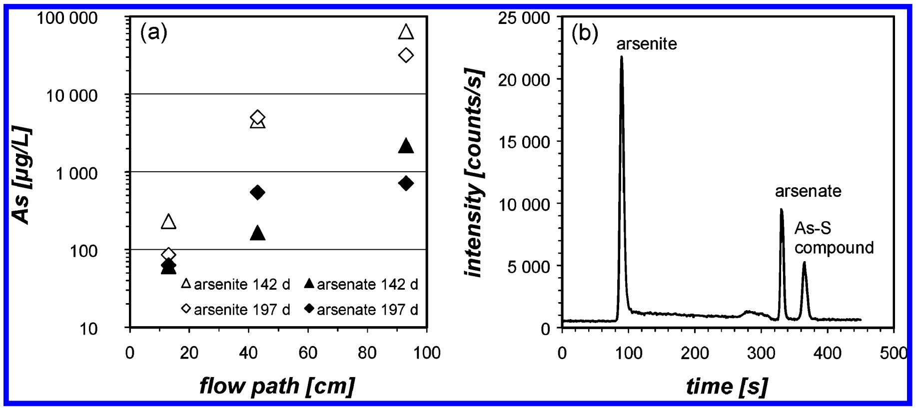


FIGURE 5. Arsenate and arsenite concentrations in S2 after connection with the column filled with organic matter at 142 and 197 days (a) and an IC−ICP−MS chromatogram of a sample from the outlet of S2 to illustrate the peak separation (b). The sample was measured by the method of Mattusch et al. (*23*).

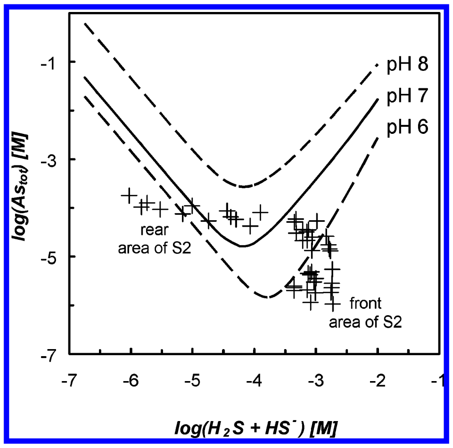


FIGURE 6. Data points of samples from S2 taken between 238 and 416 days compared to solubilities of As_2S_3(am) at different pH values (lines). pH values of samples were between 6.7 and 7.2. Equilibrium constants are taken from Wilkin et al. (*28*).

Frequently, the bonding of As and the part of As which is associated with iron (hydr)oxides or is sulfide-extractable is not known at contaminated sites. Batch tests with solid-phase samples in sulfidic solution can be a quick and simple method to test the general feasibility of sulfide flushing for a specific site. A field push−pull tracer test with dissolved sulfide as conducted by Dethlefsen (*30*) offers a space-integrated and permeability-weighted method to calculate sulfide demand, in the case of positive feasibility test results. On the basis of such investigations, it can be decided whether short-term sulfide injections are sufficient or if sulfide should rather be provided for time periods of months or years by compost-based PRBs. One appropriate method for the treatment of the resulting reducing groundwater is the use of ZVI (*21*).

Acknowledgments

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