

DEVELOPMENT OF UP- AND DOWNSTREAM PERMEABLE REACTIVE BARRIER SYSTEMS FOR
REMEDICATION OF ARSENIC AND VOC GROUNDWATER CONTAMINATIONS
(Development of PRB systems for remediation of arsenic and VOC)

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Abstract

Groundwater contamination by arsenic, one of the most harmful elements, represents a world wide problem to human health. We investigated the suitability of arsenic treatment by permeable reactive barriers systems located up- and downstream of arsenic contaminated sediments by column experiments. Organic matter used as upstream material promoted microbial sulfate reduction and generated sulfide and reduced conditions. As a result, iron- and manganese(hydr-)oxides dissolved and released arsenic which increased the concentrations by a factor of up to 20. High calcium concentrations caused by gypsum dissolution reduced the arsenic mobilization until now for between 20 to 70%. A mixture of organic matter and gypsum increased the sulfide concentrations and accelerated the arsenic dissolution compared to pure organic matter. Independently if none or one of these upstream materials was used, applying zero valent iron (Fe^0) was very promising for the sorption of arsenic and the dechlorination of 1,2-DCE(cis). Arsenic which was predominantly dissolved as As(V) without upstream material was reduced to As(III) by sulfide released from organic matter. This was advantageous for the sorption to Fe^0 since As(III) gets adsorbed more strongly to Fe^0 than As(V).

Introduction

Arsenic contaminations frequently affect large scale or even regional areas, but also smaller sized arsenic contaminations exist, generally originating from more or less localizable anthropogenic sources. Plume or source remediation are two possible strategies for such anthropogenic originating arsenic contaminations. Permeable reactive barriers (PRBs) using Fe^0 are an appropriate and field-tested approach for plume remediation that so far have been applied mainly for chlorinated ethylenes (1-3) or chromate (4). But an increasing number of investigations showed that also arsenic can be treated with Fe^0 (5-7). In contrast to most metals that could be treated with Fe^0 , the main process in arsenic remediation by Fe^0 is sorption and not reduction (8; 9). Both, As(III) and As(V) are adsorbed to iron(hydr-)oxides that are built up during contact of Fe^0 with H_2O with a stronger sorption of As(III). The stronger sorption of As(III) to granular Fe^0 is a result of the typical pH range of Fe^0 reactors (9-11) and the general observed trends of increasing arsenite adsorption with increasing pH and increasing arsenate adsorption with decreasing pH for iron(hydr-)oxides.

In industrial areas groundwater contamination is often caused by more than just one single contaminant. Fe^0 PRBs could be an encouraging remediation approach for mixed contaminations consisting of arsenic and a variety of chlorinated aliphatics comparable to the Elizabeth City site where chromate and trichloroethylene (TCE) are successfully treated by Fe^0 (4). Arsenic inhibits the corrosion of Fe^0 (8-10) but since it basically gets not reduced, adsorbed arsenate and arsenite will presumably not oxidize the iron(hydr-)oxide layer on Fe^0 which would lead to inhibited dechlorination of chlorinated aliphatics. Chlorinated aliphatics themselves are oxidants and enhance the iron corrosion which increases the formation of freshly precipitating iron(hydr-)oxides that can adsorb arsenic. So there are different ways how the sorption of arsenic by Fe^0 could interact with the concurrent dechlorination of chlorinated aliphatics.

Another field-tested PRB filling is organic matter like for example compost or wood chips which promotes bacterially mediated sulfate reduction and subsequent metal sulfide precipitation (11). Such an organic matter PRB located upstream of the arsenic source could support arsenic remediation by a downstream Fe^0 sorption barrier in two ways. On the one hand, the sulfide released from the organic matter could initiate reductive dissolution of the arsenic loaded iron- and manganese(hydr-)oxides. This would lead to increased arsenic concentrations with a shorter period of arsenic elution and a reduced remediation time. On the other hand, precipitation of arsenic sulfides could reduce the arsenic emission and extend the lifetime of a downstream sorption barrier. If one of these processes is

intended for the remediation of arsenic and the sulfate concentration of a ground water is too low, it is to assume that adding gypsum to the organic matter can increase the resulting sulfide concentrations and the aspired effect. Since it was shown that arsenic can precipitate as scarcely soluble calcium arsenates (12), elevated calcium concentrations as a result of gypsum dissolution could also cause decreased arsenic emission due to the formation of calcium arsenates.

The objectives of this study were (1) to investigate the effect of sulfide releasing organic matter implemented as an upstream PRB on the mobility of arsenic (2) to specify the potential of increasing calcium concentrations by dissolution of gypsum for the immobilization of arsenic (3) to verify if Fe^0 is an appropriate sorbate for arsenic in the long-term and under conditions produced by organic matter and (4) to study the interactions between arsenic and chlorinated aliphatics when both have to be concurrently removed from ground water by Fe^0 .

Methods

Experimental. Four sets of column experiments (\varnothing : 10 cm, L: 100 cm), respectively composed of two or three sequential columns connected by tubes are performed using artificial ground water (Figure 1). The sequence in all of the four column sets starts with a column containing the upstream PRB materials (organic matter (compost, chaff and wood chips), gypsum, mixtures of both) followed by a column filled with the arsenic contaminated sediment from a contaminated site in Wiesbaden (Germany) and ends with a Fe^0 column (sponge iron, ISPAT, Hamburg, Germany). The sediment in the columns of the systems 2-4 was low contaminated (0.15 g/kg) in the front (0 and 30 cm) and high contaminated (1.8 g/kg) in the rear area (30 and 100 cm). Only high contaminated sediment was used for system 1.

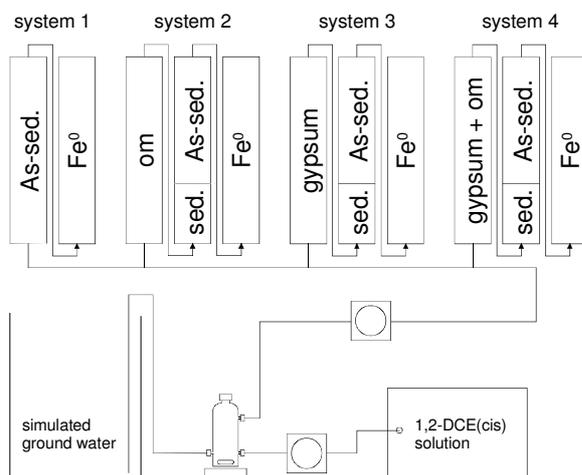


Figure 1: Setup of sequential column experiments.

Analytical. As, Fe, Mn, Ca, Mg, K, Na and Si were analyzed by ICP-OES, SO_4^{2-} , NO_3^- and Cl^- by ion chromatography with conductivity detection, and chlorinated ethylens by GC-ECD and GC-FID. Sulfide analyzes were performed by photometry and alkalinity was measured by HCl titration. For the measurement of pH and E_H electrodes were used. Additionally to the standard sampling the columns were sometimes sampled to analyze the arsenic speciation by IC-ICP-MS at the UFZ – Umweltforschungszentrum Halle-Leipzig GmbH.

Results and discussion

Reference conditions. As a first step all systems were run without the upstream materials for 2 months to establish geochemical steady state conditions in the sediment. The columns with the upstream materials were operated detached from the sediment columns and were fed with the same input solution as the sediment columns during this phase. The sediment columns of the systems 2-4 all showed comparable arsenic dissolution during this stage which resulted in output concentrations of 5-10 mg/L. The arsenic dissolution rate in the first 30 cm of these columns was lower and yielded only about 0.5 mg/L. During the reference phase, the arsenic dissolution in the low contaminated area and in the high contaminated area was stable. In the reference system (system 1) which contained only high contaminated sediment, arsenic dissolution was comparable to the high contaminated areas of systems 2-4 with an outflow concentration of 5-6 mg/L. This system was operated without upstream material during the whole experiment and showed a constant arsenic dissolution without any indications of decreasing concentrations due to leaching of arsenic. Under reference conditions

arsenic was dissolved as arsenate. The reduction of sulfate to sulfide started immediately but it took 2-3 months until the final sulfide concentrations were reached in the solution. 10 to 40 mg/L of sulfide were finally released by the pure organic matter column whereas the mixture of gypsum and organic matter produced 100 to 300 mg/L sulfide. Pure gypsum resulted in calcium concentrations of about 1000 mg/L and about 1400 mg/L of sulfate.

Effects of upstream columns. In the systems 2-4, the upstream columns were connected to the sediment columns after the reference phase to assess the effect of the upstream materials on the mobility of arsenic in sediment and its pore water. Basically the same processes were caused independently if pure organic matter or the mixture of organic matter and gypsum was switched in. Results are exemplarily shown for system 4 in Figure 2. Initially after the connection of the upstream columns with the sediment columns, sulfide was removed from the solution in the first third of the column length. This decline in sulfide concentrations gradually moved from the bottom of the column to its top. Concurrently to this process iron, manganese and arsenic concentrations increased in a comparable manner starting at the bottom and moving to the top. These processes are interpreted as dissolution of iron- and manganese(hydr-)oxides as a consequence of the low redox potential produced by the high sulfide concentrations. Associated with this dissolution, arsenic which had been adsorbed to these phases was released and caused the high arsenic concentrations of up to 200 mg/L. Arsenic concentrations in the sediment column of system 2 were similar to system 4 but arsenic was leached faster in system 4 than in system 2 which may be explained by the higher sulfide concentrations when gypsum was added to the organic matter. Precipitation of arsenic sulfides did not occur or could not compensate the dissolution of arsenic in both systems with organic matter. From these findings it can be concluded that upstream organic matter PRBs can be used for soil washing of arsenic contaminated sites where the origin of dissolved arsenic is predominately iron- and manganese(hydr-)oxidic sorption sites. While still 99% of the arsenic dissolved from the sediments in system 1 and 3 after 197 days was arsenate, sulfide flushing in system 2 and 4 caused a reduction of arsenate to arsenite. More than 90% of the total arsenic at the outflow of these sediment columns was detected as arsenite.

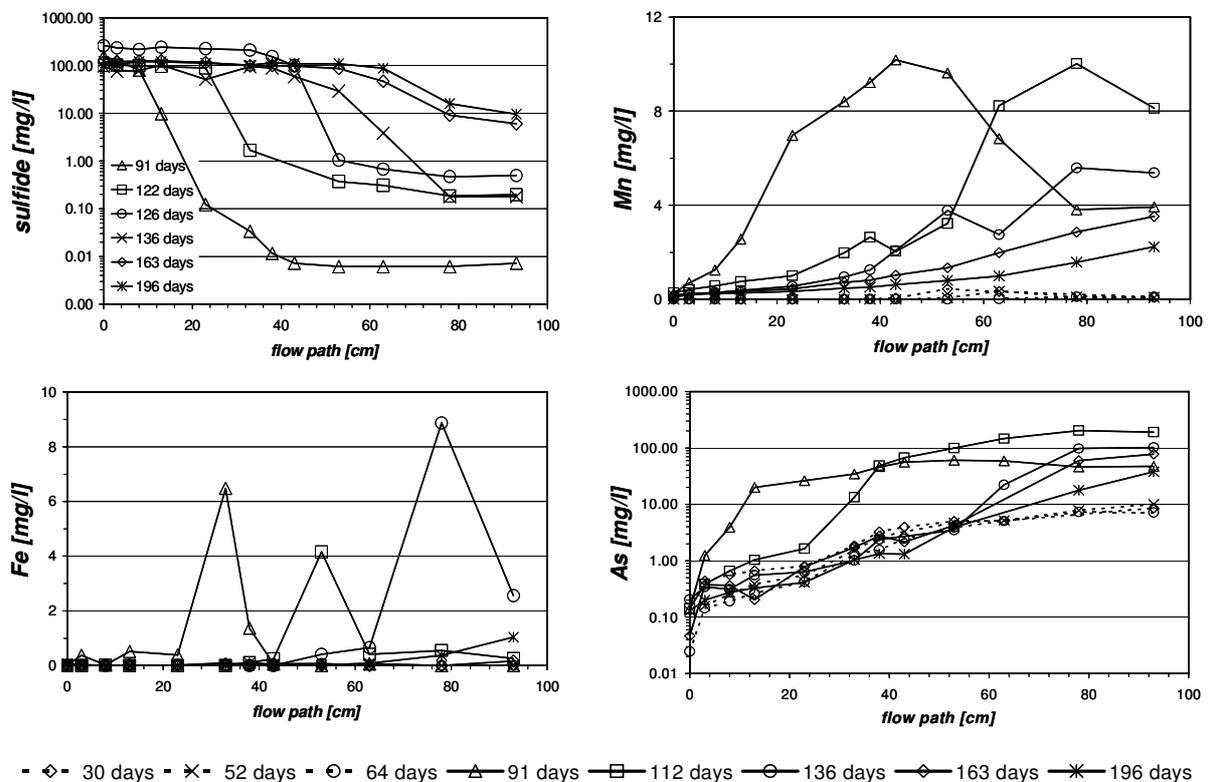


Figure 2: Sulfide, iron, manganese and arsenic concentrations in the sediment column of system 4 under reference conditions (---) and with a mixture of organic matter and gypsum as upstream material (—).

The effect of the high calcium concentration produced due to gypsum dissolution on the mobility of arsenic was low initially after the connection of the gypsum column with the sediment in system 3. At

the outflow about 20% of the arsenic release was prevented. But in the area between 30 and 70 cm where the bulk of arsenic dissolved, arsenic was immobilized stronger. In this area the arsenic immobilization increased continuously with time and resulted in a maximum arsenic immobilization of 75% at a flow path of 38 cm after 246 days. The transformation from the original arsenic association to the less mobile association after the calcium flushing seems to be a slow process. Forthcoming results of the ongoing experiment will show if the immobilization rate will be further increasing and if the immobilization will spread over the whole flow path.

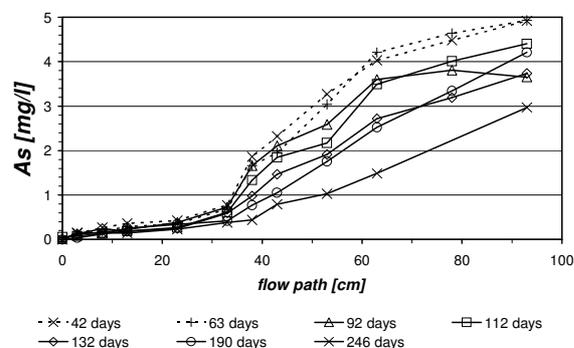


Figure 3: Arsenic concentrations in the sediment column of system 3 under reference conditions (---) and with gypsum as upstream material (—).

Fe⁰ columns. Independently of the geochemical conditions produced by the different upstream materials and sediments, sorption to Fe⁰ mostly decreased arsenic concentrations to below 0.1 mg/L in the first half of the columns and often to concentrations below 0.01 mg/L (Figure 4). Even the maximum arsenic concentrations of 100-200 mg/L were decreased for 3-4 orders of magnitude. Exhaustion of the sorption capacity is reflected in a continuous migration of the sorption front towards the columns top and in markedly decreasing sorption kinetics with elapsed time within the first 15 cm of system 1, 2 and 4. So far the exhaustion in system 3 was less pronounced than in the other systems and the sorption front even migrated towards the input after gypsum was switched in. After 190 days the sorption front was almost in the same position than at the beginning of the experiment. Since more than 90% of the arsenic dissolved from the sediments in the systems 2 and 4 with upstream organic matter was As(III), As(III) and As(V) had to be simultaneously adsorbed by Fe⁰. In agreement with an other investigation (5) As(III) was adsorbed faster than As(V) because of high pH (>10). The arsenic concentrations in general decreased to about one order of magnitude lower values for As(III) than for As(V) at the outflow despite higher As(III) input concentrations. Thus As(V) is the limiting species when mixed As(III)/As(V) contaminations should be treated with Fe⁰. This means that the effect of arsenic reduction caused by the upstream organic matter which usually would be undesired because of the higher As(III) mobility under neutral pH conditions is advantageous for the Fe⁰ treatment.

In the systems without organic matter (system 1+3) the bulk of the input 1,2-DCE(cis) is probably biodegraded in the sediment column since no effort was made to exclude oxygen from the input solution. Oxygen was consumed in the systems with organic matter and 1,2-DCE(cis) bypassed the upstream and sediment columns in these systems. 1,2-DCE(cis) was rapidly dechlorinated by Fe⁰ with half-life times of between 4 and 12 hours despite the concurrent sorption of arsenic. Dechlorination was proven by the temporary built-up of vinyl chloride which accounted for maximum concentrations of 7 µg/L. After the half of the flow path vinyl chloride was degraded to below the detection limit. In the front of the Fe⁰ columns dechlorination rates decreased with elapsing time. Whether these decreased dechlorination rates can be ascribed to the corrosion inhibiting properties of arsenic or to the fixation of other passivating substances like silica, carbonate or dissolved organic matter (DOM) (13) can not be answered. However it was shown that even huge arsenic concentrations are no exclusion criterion for the dechlorination of chlorinated ethylenes with Fe⁰.

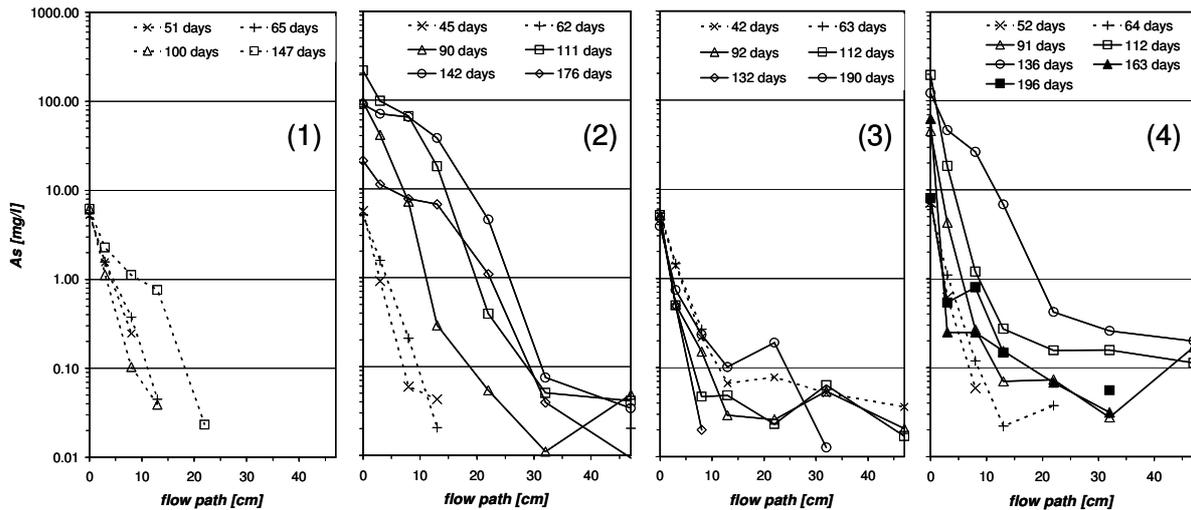


Figure 4: Sorption of arsenic by the first 47 cm of the Fe^0 columns without upstream material (1), with organic matter (2), gypsum (3) or organic matter and gypsum (4) as upstream materials. Dashed lines represent the reference phase without upstream reactor and solid lines the phase with connected upstream reactors.

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