Influence of groundwater composition on subsurface iron and arsenic removal

D. H. Moed, D. van Halem, J. Q. J. C. Verberk, G. L. Amy and J. C. van Dijk

ABSTRACT

Subsurface arsenic and iron removal (SAR/SIR) is a novel technology to remove arsenic, iron and other groundwater components by using the subsoil. This research project investigated the influence of the groundwater composition on subsurface treatment. In anoxic sand column experiments, with synthetic groundwater and virgin sand, it was found that several dissolved substances in groundwater compete for adsorption sites with arsenic and iron. The presence of 0.01 mmol L⁻¹ phosphate, 0.2 mmol L⁻¹ silicate, and 1 mmol L⁻¹ nitrate greatly reduced the efficiency of SAR, illustrating the vulnerability of this technology in diverse geochemical settings. SIR was not as sensitive to other inorganic groundwater compounds, though iron retardation was limited by 1.2 mmol L⁻¹ calcium and 0.06 mmol L⁻¹ manganese.

Key words | competitive adsorption, drinking water treatment, groundwater, subsurface arsenic removal, subsurface iron removal

INTRODUCTION

Being one of the first substances recognised as a cause of cancer, arsenic has been in the scope of the medical world for a long time. In Bangladesh, the country with the world’s most severe waterborne arsenic problem, elevated iron and arsenic concentrations have been found to often co-occur in anoxic and anaerobic groundwater (Nickson et al. 2000). The presence of both iron and arsenic are a prerequisite to the operation of subsurface iron and arsenic removal (SIR/SAR). In this process, the injection of aerated water in the subsoil promotes the oxidation of Fe²⁺, resulting in the formation of iron oxides near subsurface treatment wells (van Halem et al. 2010a). These iron oxides are capable of adsorbing other dissolved substances, among which are arsenic and iron. When abstraction is started, more water with reduced iron and arsenic concentrations can be abstracted (volume V) than was injected (volume Vᵢ). This volumetric ratio (V/Vᵢ) determines the efficiency of the system. The adsorptive capacity of iron oxides has been found to be limited by the presence of other inorganic ions, such as phosphate, silicate and bicarbonate (Stachowicz 2008). Also, Fe³⁺ adsorption and oxidation is affected by the presence of other inorganic ions, including calcium and phosphate (Sharma 2001; Ciardelli et al. 2008). The majority of these compounds are commonly found in Bangladeshi ground- and drinking water (Ciardelli et al. 2008). It is hypothesised that the groundwater composition greatly influences the site-specific effectiveness of SAR under diverse geochemical conditions.

There have been several pilot studies to investigate the potential of SAR, with various results. In Bangladesh three small-scale injection facilities (0.5 m³) were constructed with a plate aerator, allowing injection of water with 0.16 mmol L⁻¹ O₂ (Sarker & Rahman 2001). Arsenic concentrations were found to be reduced from 110 μg L⁻¹ to below 50 μg L⁻¹ (national guideline) until V/Vᵢ reached 4. At higher arsenic concentrations, namely 520 and 1,270 μg L⁻¹, the arsenic concentration did not reach values below 200 and 500 μg L⁻¹, respectively. Across the Indian border in the same Bengal Delta, Sen Gupta et al. (2009) reported that at six different community SAR plants a V/Vᵢ ratio of 4–6 could be operated providing arsenic-free water to the people. Background arsenic levels were not reported in this publication, but the surrounding wells had concentrations exceeding 500 μg L⁻¹. Arsenic removal during subsurface treatment has also been observed by Rott et al. 2002, reducing arsenic concentrations from 58 μg L⁻¹ to below 10 μg L⁻¹ after 20 cycles. van Halem et al. (2008b) found less encouraging results at sites in Bangladesh with 145 μg As(III) L⁻¹, with immediate arsenic breakthrough upon abstraction (Vᵢ=1 m³). These pilot studies have indicated that there is
potential for the technology of SAR; nevertheless at some sites the efficacy seems to be much better than at others. Unfortunately, only very little is reported on the soil and groundwater composition at these field sites, making it difficult to extract information on the influence of limiting and/or catalysing compounds. Appelo & de Vet (2005) reported the behaviour of a wide range of groundwater compounds during subsurface treatment, proposing that phosphate was responsible for sudden arsenic peaks in the abstracted water. The arsenic concentrations at the studied site were, however, many times lower (<15 μg As L⁻¹) than can be found in Bangladeshi groundwater.

The objective of this study was to investigate the effect of different inorganic groundwater ions, including phosphate, silicate, nitrate, calcium and manganese, on Fe²⁺ and As(III) removal during SIR/SAR. Such ions may limit or enhance Fe²⁺ or As(III) removal in the shifting redox conditions of an injection–abstraction cycle. In order to isolate the compounds of interest, injection-abstraction cycles of SIR/SAR were simulated in the laboratory with synthetic groundwater in sand columns.

MATERIALS AND METHODS

The experimental set-up (van Halem et al. 2012) consisted of duplicate transparent PVC columns with a length of 50 cm and an inner diameter of 56 mm (wall thickness 2 mm). During all experiments, the columns were wrapped in aluminium foil to exclude light. The columns were filled with washed (24 h with 3 mol L⁻¹ HCl) filter sand (500 g; grain size=0.5–0.8 mm). The absence of other mineral structures than quartz on the sand material was checked with X-ray Powder Diffraction (Bruker D5005; Brain PSD). The push-pull operational mode of injection–abstraction was simulated in the plug-flow environment of the columns with downflow for injection and upflow abstraction (1.1 L h⁻¹±0.05). An injection-abstraction cycle started with 14 (±0.5) pore volumes of injection water, to allow for >80% breakthrough of dissolved O₂. Subsequently the influent was switched to groundwater to allow retention of Fe²⁺ and As(III). Electrical conductivity was used as a conservative tracer from which the pore volume could be calculated to be, on average, 0.12 L (±0.002). The flow rate in the columns (2.7 m h⁻¹) was controlled with a multi-channel pump and PVC tubing with low gas permeability. Anoxic conditions were maintained in the columns by using an air-tight FESTO system (6 x 1 PUN, I.D. 4 mm) with matching connectors and valves. All injection-abstraction experiments were performed twice in the duplicate columns, with freshly filled columns before each experiment.

At the start of each experiment the columns were conditioned with synthetic groundwater (containing the compounds of interest), until complete breakthrough of iron occurred, and the $E_h$ potential stabilised. An injection mode consisted of demineralised water containing a pH buffer (5 mmol L⁻¹ NaHCO₃) and 0.28 mmol L⁻¹ O₂. The abstraction phase consisted of synthetic groundwater with pH 6.9, a temperature of 20 °C, 0.07 mmol L⁻¹ Fe²⁺, 2.7 μmol L⁻¹ As(III), pH buffer (5 mmol L⁻¹ NaHCO₃), ionic strength buffer (1.6 mmol L⁻¹ NaCl) and additionally the inorganic compound of interest (phosphate, silicate, nitrate, calcium or manganese). The chemicals (reagent grade, Sigma-Aldrich) were dosed as FeSO₄·7H₂O, FeCl₂, NaAsO₂, NaHCO₃, NaCl, Na₂HPO₄, Na₂SO₂·5H₂O, NaNO₃, Ca(NO₃)₂·4H₂O and MnSO₄·H₂O.

The synthetic groundwater was produced by distributing demineralised water through a 6 m gas stripping column containing stainless steel Pall Rings. From the bottom, pure N₂ was blown into the degassing column to sparge out all O₂. Before entering the sand columns, the water was checked for O₂ (Orbisphere; HACH Lange; M1100 Sensor; 410 Analyst) to ensure concentrations below 1.6 μmol L⁻¹. Addition of stock solutions was done with a dosing pump followed by a static mixer. pH correction was achieved by addition of HCl or NaOH and all stock solutions were sparged with N₂ in order to ensure the absence of O₂.

Iron analysis of the water samples was done with an Atomic Absorption Spectrometer (Perkin-Elmer Flame AAS 3110). Arsenic analysis was performed with a Graphite Furnace Atomic Absorption Spectrometer (Perkin-Elmer 5100PC) with an electrode discharge lamp (EDL) and a Ni(NO₃)₂·6H₂O matrix modifier. Online measurements were done for dissolved oxygen (Orbisphere and WTW Cellox 325), $E_h$ potential (WTW SenTix ORP), pH (WTW SenTix 41), and electrical conductivity (WTW TetraCon 325). Online measurements were registered on a computer with MATLAB, v5.06 software. The results of analysis were used to determine when the effluent concentration C was 50% of the influent concentration C₀, indicating 50% breakthrough of the analysed water component. The $V/V_i$ ratio at which C/C₀=50% is referred to as the retardation factor (R).

A regular injection phase during full scale SIR or SAR consists of the injection of aerated water, in most cases drinking water from the clean water reservoir. In the experiments described in this paper, demineralised water was used for injection containing a pH buffer (5 mmol L⁻¹ NaHCO₃) and a 0.28 mmol L⁻¹ O₂ concentration. After injection, the
influent was switched to synthetic groundwater for the abstraction phase, containing 0.07 mmol L\(^{-1}\) Fe\(^{2+}\), 2.7 \(\mu\)mol L\(^{-1}\) As(III), pH buffer (5 mmol L\(^{-1}\) NaHCO\(_3\)) and ionic strength buffer (1.6 mmol L\(^{-1}\) NaCl). This is the reference cycle. The retention of arsenic in the columns was investigated during injection-abstraction cycles in the presence and absence of 0.07 mmol L\(^{-1}\) Fe\(^{2+}\). Before the start of each injection-abstraction cycle the column was loaded with the synthetic groundwater until steady state conditions were reached, i.e. complete breakthrough of iron and/or arsenic. In the injection-abstraction cycle with Fe\(^{2+}\) the column material was therefore saturated with Fe\(^{2+}\) and As(III), while in the absence of Fe\(^{2+}\) the sand material was only saturated with As(III). After obtaining a reference for Fe\(^{2+}\) and As(III) removal under carefully set conditions, an individual component was added to the synthetic groundwater with each subsequent experiment. There was never more than one component of interest in the water at the same time, except for calcium and nitrate, due to the dosing of calcium as Ca(NO\(_3\))\(_2\). An injection-abstraction cycle with just nitrate as an added component to the reference solution, to check nitrate’s influence on SAR and SIR.

**RESULTS AND DISCUSSION**

**Fe\(^{2+}\) reference cycles**

The measurements in Figure 1 illustrate that once abstraction has started the tracer passed the column (electrical conductivity), with a \(C/C_0\) at 1 pore volume. The initial oxygen concentration of 0.28 mmol L\(^{-1}\) was pushed out of the column and reached <0.01 mmol L\(^{-1}\) after 5.5 pore volumes. The retardation of Fe breakthrough compared with the tracer simulates the delay of Fe front arrival at the well compared with the injection water front. The more water with low Fe concentrations can be abstracted from the well/column, the better the efficacy of SIR. In general, groundwater treatment plants operate a \(V/V_i\) ratio based on the moment Fe starts to arrive at the well, thus \(C/C_0>0\). In the experiments, Fe\(^{2+}\) is allowed to break through, in order to calculate the dimensionless retardation factor \(R\). \(R_{Fe}\) is calculated from a \(V_i\) corresponding to the pore volume when the tracer (electrical conductivity) is \(C/C_0=0.5\), and \(V\) is the number of pore volumes that can be abstracted with iron concentrations below \([Fe] \leq 0.5C_0\). The reference injection-abstraction cycles in Figure 1 show a \(R_{Fe}\) of 43, meaning that 43 times more water with \([Fe]\) \(< 0.5C_0\) can be abstracted than was injected. A drinking water supply company operating a well like that in Figure 1 would probably operate a \(V/V_i\) of approximate 25, in order to maintain the Fe concentrations below the detection limit. It is noteworthy that a \(V/V_i\) of 25 can be considered to be very effective, especially for sand material that has been unaffected by SIR in the past (van Halem et al. 2001a). More commonly reported \(V/V_i\) ratios of actual SIR wells with injections of around 0.28 mmol L\(^{-1}\) O\(_2\) are 4–12 (van Beek 1985).

**As(III) reference cycles**

Figure 2 shows that if no Fe\(^{2+}\) was present in the groundwater and column, the As(III) removal was limited to several pore volumes. In the presence of Fe\(^{2+}\), corresponding to the injection-abstraction cycle in Figure 2, the As(III) removal is much larger, with an As retardation factor of 31. Clearly, the presence of Fe\(^{2+}\) in the changing redox conditions in the column improved As(III) retention. It should be noted that, unlike for Fe, the As breakthrough starts almost immediately upon abstraction. The As breakthrough showed extensive tailing, resulting in a high \(R_{As}\). The tailing during As(III) breakthrough may indicate incomplete adsorption kinetics in the columns, which is not surprising as residence times of the synthetic groundwater in the column was no more than 10 min (empty bed contact

---

**Figure 1** | Behaviour of O\(_2\), tracer and Fe\(^{2+}\) during the reference injection-abstraction cycles.

**Figure 2** | Behaviour of As(III) during the reference injection-abstraction cycles with and without 0.07 mmol L\(^{-1}\) Fe\(^{2+}\).
time). Such residence times correlate well with actual retention times in small-scale applications of SIR/SAR (Sarkar & Rahman 2001; van Halem et al. 2000a), but reaching As(III) adsorption equilibrium on iron oxides may take longer than that (Raven et al. 1998). Irregular operation of hand pump wells may increase the residence time of groundwater in the oxidation zone, potentially increasing removal efficiencies. Additionally it should be taken into account that although As breakthrough is observed immediately, the arsenic concentration passed the WHO and Bangladeshi guideline at 4 and 8 pore volumes, respectively. An SIR/SAR efficiency of V/V<sub>i</sub>=4 without the need of any operational costs (chemicals, electricity) may well be very effective for household application.

**Effect of phosphate**

The results in Figure 1 and Figure 2 of the reference injection-abstraction cycles in the Fe<sup>2+</sup>-As(III)-O<sub>2</sub> system show promise for the household application of SIR/SAR. Nevertheless, the presence of other inorganic groundwater compounds may interfere, reducing Fe and As removal efficiencies. In Bangladesh, PO<sub>4</sub><sup>3-</sup> concentrations are measured in the shallow aquifer between <1 and 200 μmol L<sup>-1</sup> (BGS/DPHE 2001). The PO<sub>4</sub><sup>3-</sup> concentrations are relatively high compared with average groundwater composition in Bangladesh. It has been observed that the presence of >0.01 mmol L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup> at pH>7 inhibits the precipitation of Fe<sup>2+</sup> (Ciardelli et al. 2008; Guan et al. 2009). The adsorbed H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> maintains the iron oxide surfaces as negatively charged preventing the particles from hydrolyzing and subsequently precipitating. Sharma et al. (2001) observed reduced adsorptive capacity for Fe<sup>2+</sup> of virgin sand in the presence of 0.01 mmol L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>, with a 23% reduction at pH 6.8. Nevertheless, the results in Figure 3 illustrate that SIR in the sand columns is not affected by the presence of PO<sub>4</sub><sup>3-</sup>; Fe retardation remains almost the same at 45.

The effect of phosphate on the removal of As(III) during SAR is twofold, namely through: (i) inhibition of Fe<sup>2+</sup> oxidation-precipitation; and (ii) competitive adsorption. Competitive adsorption between As(III) and PO<sub>4</sub><sup>3-</sup> onto iron oxides has been studied in detail (Jain & Loeppert 2000; Ciardelli et al. 2008; Stachowicz et al. 2008), making PO<sub>4</sub><sup>3-</sup> the most important competing anion for arsenic (Su & Puls 2001; Guan et al. 2009). As(III) behaviour during oxidation and precipitation of soluble Fe<sup>2+</sup> was studied by Ciardelli et al. (2008), reporting an As(III) removal reduction from 75 to 63% in the presence of 0.07 mmol L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>-P at pH 7.2. The combination of its ability to occupy the same adsorption sites as arsenic and its elevated concentrations compared with trace amounts of arsenic makes PO<sub>4</sub> a strong competitor in natural waters. This observation correlates well with the results from the column experiments (Figure 3), showing that As retardation was reduced from 51 to 5 in the presence of 0.01 mmol L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>.

**Effect of silicate**

Silicon concentrations of groundwater in Bangladesh are commonly high, with median concentrations in the shallow aquifer of 0.33 mmol L<sup>-1</sup> (BGS/DPHE 2001). Silicon, or in groundwater, silicate, is known to interact with Fe<sup>3+</sup> to form soluble polymers and highly dispersed colloids (Iler 1979; Meng et al. 2000) and hinder the Fe<sup>3+</sup> iron oxide precipitation and aggregation (Liu et al. 2007a,b). The negative effect of silicate on the precipitation of iron oxides is larger at higher pH (7–9). This dispersed colloidal material cannot be removed by filtration (Davis et al. 2001), so it may be found to pass the injection-abstraction columns. Fe<sup>2+</sup> adsorption onto virgin sand has also been reported to be inhibited by the presence of silicate, reducing by 14 and 27% in the presence of 0.36 and 1.43 mmol L<sup>-1</sup> Si, respectively (Sharma 2001). The results (Figure 4) do not indicate a clear inhibition of iron removal after the addition of 0.2 mmol L<sup>-1</sup> SiO<sub>2</sub>, the retardation factor R<sub>Fe</sub> is even higher at 58. It is, however, noteworthy that the iron concentrations rise immediately after one pore volume to C/C<sub>0</sub>=0.06, which correlates to an approximate 5.2 μmol L<sup>-1</sup> Fe. This instant increase in iron concentration has not been observed in the absence of silicate and continues until 40 pore volumes. It is proposed that the formation of mobile colloidal material prevents the adsorption of this iron fraction onto the column sand, resulting in measurements of total iron after the columns.

Below pH 7, silicate can be found to occur as H<sub>2</sub>SiO<sub>3</sub>, whereas at higher pH it may be found as HSiO<sub>3</sub><sup>-</sup>. At higher pH the affinity of the negatively charged silicate for adsorption...
onto iron oxides increases, resulting in more competition with arsenic (Meng et al. 2000; Guan et al. 2009). Ciardelli et al. (2008) found a reduction in As(III) removal from 73 to 67% during oxidation–precipitation of Fe\(^{2+}\) after addition of 0.52 mmol \(L^{-1}\). The results show that SAR is negatively affected by the presence of 0.2 mmol \(L^{-1}\) SiO\(_2\). The retardation factor \(R_{\text{As}}\) was reduced from 31 to 6, which is very much comparable with the impact of 0.01 mmol \(L^{-1}\) PO\(_4^{3-}\).

**Effect of calcium and nitrate**

One of the major cations in groundwater is calcium, especially in the calcium–bicarbonate groundwaters of Bangladesh (Ciardelli et al. 2008). Ca\(^{2+}\) concentrations are generally much higher than Fe\(^{2+}\) concentrations, with a median and maximum in Bangladesh of 0.88 and 9.1 mmol \(L^{-1}\), respectively (BGS/DPHE 2000). Competition/exchange between these divalent cations during SIR may therefore be expected, with Ca\(^{2+}\) being in favour because of its concentration advantage. A reduction in Fe\(^{2+}\) adsorption onto virgin and iron oxide coated sand of 42 and 12%, respectively, was observed in the presence of 1.2 mmol \(L^{-1}\) Ca\(^{2+}\) at pH 6.8 (Sharma 2000). It has to be noted though, that in this column study calcium was added as Ca(NO\(_3\))\(_2\), resulting in 1.2 mmol \(L^{-1}\) Ca\(^{2+}\), but also 2.4 mmol \(L^{-1}\) NO\(_3^-\). Another experiment (Figure 4) illustrated that NO\(_3^-\) had almost no effect on Fe removal during SIR, but there was a strong effect on As removal as the retardation factor \(R_{\text{As}}\) dropped to 6. Therefore conclusions can be drawn based on the results regarding the influence of Ca\(^{2+}\) on Fe removal, but not on the removal of As. Stachowicz et al. (2008) did not observe an effect of Ca\(^{2+}\) on As(III) adsorption onto goethite. The \(R_{\text{Fe}}\) was, however, clearly lower than in earlier injection–abstraction cycles, with a variation between 16 and 25 for the duplicate experiments. The variation between the duplicate cycles cannot be explained at this stage, but the reduced \(R_{\text{Fe}}\) confirms that the presence of Ca\(^{2+}\) inhibited the removal of Fe\(^{2+}\) during SIR. Fe concentrations start to rise in the water after approximately 5–8 pore volumes, resulting in an operational \(V/V_i\) ratio of 5–8, which is much lower than the \(V/V_i=25\) of the reference cycle.

**Effect of manganese**

SIR has frequently been associated with co-removal of manganese (Hallberg & Martinell 1976; Rott 1985; van Beek 1985). Mn\(^{2+}\) oxidation is slower than abiotic Fe oxidation and it is proposed that manganese removal does not start in the subsurface until iron removal is complete. This results in a spatial separation between the formation of manganese and iron oxides, with the latter further away from the well. Mn\(^{2+}\) oxidation is known to be catalysed in the presence of Mn\(^{4+}\) oxides, and also As(III) oxidation and adsorption is suggested to be enhanced by Mn\(^{4+}\) oxides. Nevertheless, Mn\(^{2+}\) is not expected to compete with Fe\(^{2+}\) for the injected O\(_2\) in the columns, as the Mn\(^{2+}\) oxidation kinetics are much slower and the contact time in the columns is relatively short. Mn\(^{2+}\) may, however, inhibit the Fe\(^{2+}\) adsorption. Sharma (2001) observed a reduction in Fe\(^{2+}\) adsorption in the presence of 0.03 mmol \(L^{-1}\) Mn onto virgin and iron coated sand of 44 and 6%, respectively. During injection–abstraction cycles with 0.06 mmol \(L^{-1}\) Mn\(^{2+}\), the Fe removal was slightly lower compared with the reference cycles, with a \(R_{\text{Fe}}\) of 35 (Figure 4). The moment that Fe\(^{2+}\) was detected did not differ from the reference cycles, showing that the operational \(V/V_i\) ratio is not affected by the presence of 0.06 mmol \(L^{-1}\) Mn. As(III) behaviour remained the same in the presence of soluble Mn\(^{2+}\), resulting in \(R_{\text{As}}=29\).

**CONCLUSIONS**

It was found that during injection–abstraction cycles in the Fe\(^{2+}\)–As(III)–O\(_2\) column system it was possible to reach effective iron and arsenic retardation, although arsenic breakthrough started immediately upon abstraction. Arsenic removal was found to be significantly inhibited by the presence of 0.01 mmol \(L^{-1}\) phosphate, 0.2 mmol \(L^{-1}\) silicate, and 1 mmol \(L^{-1}\) nitrate, illustrating the vulnerability of this Subsurface Arsenic Removal technology in diverse geochemical settings. SIR was found not to be as sensitive to other inorganic groundwater compounds, although iron retardation was found to be limited by 1.2 mmol \(L^{-1}\) calcium and 0.06 mmol \(L^{-1}\) manganese. Total iron removal was enhanced by the presence of 0.2 mmol \(L^{-1}\) silicate, but immediate breakthrough of 5 \(\mu\)mol \(L^{-1}\) limited SIR in...
performing to its full potential. No experimental run with all components of interest together has been performed, but one would expect that the SAR and SIR efficiency would be even lower than with just phosphate, silicate or calcium added. The existence of a natural groundwater composition in which SAR will reach extremely high efficiencies (as in the reference cycle) is therefore not very plausible.

ACKNOWLEDGEMENT

The authors would like to thank InnoWATOR (Innovation Program for Water Technology of Agentschap NL), for supporting this research.

REFERENCES


Stachowicz, M., Hiemstra, T. & Van Riemsdijk, W. H. 2008 Multi-competitive interaction of As(III) and As(V) oxyanions with Ca2+, Mg2+, PO43−, and CO32− ions on goethite. Journal of Colloid and Interface Science 320, 400–414.


First received 17 November 2011; accepted in revised form 13 February 2012