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# Subsurface arsenic removal column tests: from the laboratory to the field

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## Abstract

Previous laboratory column experiments have given evidence of competitive effects between different groundwater constituents in the process of subsurface arsenic removal, a process in which arsenic is removed from groundwater by injecting water with oxygen into the subsurface. The presence of phosphate and other anions significantly limited arsenic removal. To investigate the influence of phosphate in natural groundwater, pumping stations in Loosdrecht (the Netherlands) and Subotica (Serbia) both with low phosphate concentrations ($<0.1\,\mathrm{mg\,l^{-1}}$) and considerable arsenic concentrations (30 and $110\,\mathrm{\mu g\,l^{-1}}$) were chosen, to perform experiments identical to the previous laboratory work. Despite of the absence of phosphate, the subsurface arsenic removal process performed poorly in Subotica, with 50 % arsenic breakthrough occurring after 2 to 4 column pore volumes of abstracted water. In Loosdrecht subsurface arsenic removal showed more promising results, 50 % breakthrough after 6 to 7 pore volumes, while having a lower pH than Subotica and similar silicate concentrations. The water composition of both locations gives reason to suggest that natural organic matter has a limiting effect on subsurface arsenic removal as well. The presented results have shown the complexity of factors influencing subsurface arsenic removal, making it very challenging to select appropriate sites.

## 1  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 $Fe^{2+}$, resulting in the formation of

iron oxides nearby subsurface treatment wells (Fig. 1, van Halem et al., 2010a). These iron oxides are capable of adsorbing other dissolved substances, such as arsenic and iron. When abstraction is started, more water with reduced iron and arsenic concentrations can be pumped up (volume $V$) than was injected (volume $V_i$). This volumetric ratio ($V/V_i$) 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 (Su and Puls, 2001; Stachowicz et al., 2008; Guan et al., 2009). Also, $Fe^{2+}$ adsorption and oxidation is affected by the presence of cations, including calcium and phosphate (Sharma, 2001; Ciardelli et al., 2008). The majority of these compounds are commonly found in Bangladesh groundwater and drinking water (Ciardelli et al., 2008).

There have been several pilot studies to investigate the potential of SAR. In Bangladesh three small-scale injection facilities ($0.5\,m^3$) were constructed with a plate aerator, allowing injection of water with $5.12\,mg\,l^{-1}$ oxygen (Sarkar and Rahman, 2001). Arsenic concentrations were reduced from $110\,\mu g\,l^{-1}$ to below $50\,\mu g\,l^{-1}$ (national guideline) until $V/V_i = 4$. At higher arsenic concentrations of $520\,\mu g\,l^{-1}$ and $1270\,\mu g\,l^{-1}$, the arsenic concentration did not reach values below $200\,\mu g\,l^{-1}$ and $500\,\mu g\,l^{-1}$, respectively. Across the Indian border in the same Bengal Delta, Sen Gupta et al. (2009) reported that at 6 different community SAR plants a $V/V_i$ ratio of 4 to 6 could maintained providing water with less than $10\,\mu g\,l^{-1}$ arsenic (WHO guideline). Groundwater arsenic concentrations were not reported in this publication, but the surrounding wells had concentrations exceeding $500\,\mu g\,l^{-1}$. Arsenic removal during subsurface treatment has also been observed by Rott et al. (2002), reducing arsenic concentrations from $38\,\mu g\,l^{-1}$ to below $10\,\mu g\,l^{-1}$ after repeating the process 20 times. Van Halem et al. (2010b) found less encouraging results at sites in Bangladesh with $145\,\mu g\,l^{-1}$ arsenic, with immediate arsenic breakthrough upon abstraction ($V_i = 1\,m^3$). These pilot studies have indicated that there is potential for the technology of SAR, nevertheless at some sites the efficacy seemed to be better than at others. Laboratory column experiments under controlled pH and redox conditions indicated the importance of the water composition for

subsurface arsenic and iron removal. Especially the presence of phosphate and to a lesser extent silicate, turned out to have a limiting effect on SAR (Moed et al., 2012).

The objective of this study was to investigate the efficiency of SAR, at groundwater pumping stations with a phosphate and nitrate concentration $\leq 0.1\,\mathrm{mg\,l^{-1}}$, and a silicate concentration similar to the one in the laboratory ($7\,\mathrm{mg\,l^{-1}}$ as Si), using PVC columns filled with virgin sand. This way a comparison between field results and laboratory findings can be made. Also, additional arsenite and ferrous iron were dosed, to investigate whether changing the arsenic and iron concentration would influence the results.

## 2  Materials and methods

The experimental set-up (for details see van Halem et al., 2012) consisted of duplicate transparent PVC columns with a length of 30 cm and an inner diameter of 36 mm (wall thickness 2 mm). During all experiments, the columns were wrapped in aluminium foil to exclude light, preventing it from affecting the process. The columns were filled with washed (24 h with 3 M 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 down flow for injection and up flow abstraction ($1.1\,\mathrm{l\,h^{-1}} \pm 0.05$). An injection-abstraction cycle started with 14 ($\pm 0.5$) pore volumes of injection water, to allow for >90 % breakthrough of dissolved $O_2$. Subsequently the influent was switched to groundwater to allow retention of $Fe^{2+}$ 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 ($\pm 0.002$). The flow rate in the columns ($2.7\,\mathrm{m\,h^{-1}}$) was controlled with a multi-channel pump and PVC tubing with low gas permeability. Anoxic conditions were maintained in the columns by using an airtight FESTO system ($6 \times 1$ PUN, I.D. 4 mm) with matching connectors and valves. All injection-abstraction experiments were performed twice in the duplicate columns, with virgin sand for each experiment.

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The locations that were chosen for the experiments were the Vitens groundwater pumping station (GWPS) in Loosdrecht (the Netherlands) and the Public Utility Company Subotica GWPS (Serbia). From a research perspective, the desirable characteristic of Subotica is that there is a higher arsenic concentration in the groundwater (115 µg l$^{-1}$) than in Loosdrecht, allowing the columns to run on natural arsenic concentrations. The disadvantage of this location is the low iron concentration (iron being prerequisite for SAR, Moed et al., 2012), which was overcome by spiking higher iron concentrations in several abstraction cycles. This had the intrinsic benefit of being able to compare SAR efficiency at different $Fe^{2+}$ concentrations.

At the start of each experiment the columns were conditioned with groundwater (with optional addition of a component of interest), until complete breakthrough of iron occurred, and the electrochemical potential ($E_h$) stabilised. An injection mode consisted of demineralised water containing a pH buffer (5 mM $NaHCO_3$ resulting in 300 mg l$^{-1}$ bicarbonate) and 10 mg l$^{-1}$ (±0.5) oxygen. The abstraction phase consisted of a number of pore volumes of groundwater with a composition as defined in Table 1. In some experiments extra iron or arsenic was dosed. The chemicals (reagent grade, Sigma-Aldrich) were dosed as $FeCl_2$, $NaAsO_2$ and $NaHCO_3$. The laboratory concentrations of previous experiments (Moed et al., 2012) have been listed in Table 1 for easy reference, although these components were not dosed in a single experiment, but were added one by one to investigate the effects of each individual component on SAR.

Before the water entered the sand columns, it was checked for oxygen (Orbisphere; HACH Lange; M1100 Sensor; 410 Analyser) to ensure concentrations below 0.05 mg l$^{-1}$. Addition of stock solutions was done with a dosing pump followed by a static mixer. All stock solutions were sparged with nitrogen in order to ensure the absence of oxygen.

Samples were sent to the Vitens Laboratory in the Netherlands to be analysed for calcium and silicium using ICP-MS. Iron analysis of the water samples was done with an atomic absorption spectrometer (Perkin-Elmer Flame AAS 3110), arsenic analysis with graphite furnace atomic absorption spectrometer (Perkin-Elmer 5100PC) with an

electrode discharge lamp (EDL) and a $Ni(NO_3)_2 \cdot 6H_2O$ matrix modifier. Online measurements were performed for dissolved oxygen (Orbisphere and WTW Cellox 325), $E_h$ (WTW SenTix ORP), pH (WTW SenTix 41), and electrical conductivity (WTW Tetra-Con 325). Online measurements were registered on a computer with Multilab Pilot v5.06 software. The results of analysis were used to determine when the effluent concentration $C$ was 50 % of the influent concentration $C_0$, indicating 50 % breakthrough of the analysed water component. The $V/V_i$ ratio at which $C/C_0 = 50$ % is referred to as the retardation factor ($R$).

## 3 Results and discussion

### 3.1 Loosdrecht SAR/SIR

A single, typical abstraction for two columns with Loosdrecht's natural groundwater is shown in Fig. 2, along with the results of the same experiment with a higher dosed arsenite concentration. As time progresses and more pore volumes are extracted through the columns, Fig. 2 shows how SIR and SAR progress in time.

Iron and arsenic are responsive to the recent presence of oxygen in the column. Having an iron concentration of $5.2\,\mathrm{mg\,l^{-1}}$ on average, iron is completely removed for almost 6 pore volumes. When iron starts breaking through some tailing is observed, which could indicate the presence of oxygen (van Halem et al., 2012), but the oxygen meter indicated $0.02\,\mathrm{mg\,l^{-1}}$. Experiments conducted by Sharma (2001), showed that the presence of more than $1\,\mathrm{mg\,l^{-1}}$ sulphate enhanced the iron adsorption effect. Taking into account the $15.1\,\mathrm{mg\,l^{-1}}$ of sulphate present in the Loosdrecht groundwater, this could explain the high iron removal.

After 3 PVs, less than 20 % of the $31\,\mathrm{\mu g\,l^{-1}}$ influent concentration was measured in the effluent. After 14 PV the process still had not reached a 50 % breakthrough, meaning that the retardation factor is higher than 14. The WHO guideline of $10\,\mathrm{\mu g\,l^{-1}}$ was met for at least 10 PV. Although phosphate was almost absent, the presence of silicate

(6.3 mg l$^{-1}$ as silicium) was expected to be more of a limiting factor in the process (Ciardelli et al., 2008; Stachowicz et al., 2008; Moed et al., 2012).

Performing an identical abstraction, but with an increased arsenic concentration of 160 µg l$^{-1}$, the dashed line in Fig. 2 was observed. The retardation factor in the case of an increased arsenic concentration is still 8. It has to be noted though that the Bangladeshi drinking water standard of 50 µg l$^{-1}$ is already exceeded after 4 pore volumes, not to mention the WHO 10 µg l$^{-1}$ arsenic guideline. An improvement of quality is observed nevertheless.

Groundwater components like silicate and calcium were not removed (results not shown). The slight decrease in calcium concentration measured after less than 3 pore volumes, is likely to be caused by some diffusion between the injection and abstraction water, or even cation exchange (van Halem et al., 2012). Another explanation could be fluctuations in groundwater quality.

## 3.2 Subotica SAR and SIR

Figure 3 shows the results for 3 abstractions. The 0.65 mg l$^{-1}$ iron concentration is that of the natural groundwater, while the 2.72 and 5.79 mg l$^{-1}$ Fe concentrations had been spiked in successive cycles. Experience from the Loosdrecht experiments had learned that both iron and arsenic needed more than 15 pore volumes for complete breakthrough, so the experiments in Subotica were executed for 25 pore volumes.

For the lowest iron concentration (0.65 mg l$^{-1}$), there was no breakthrough observed until after 10 pore volumes and the retardation factor was 17. With increasing iron concentration, the point of first breakthrough and 50 % breakthrough shifts to the left, as a consequence of a lower amount of iron passing through the column, which uses less oxygen and less adsorption sites The 5.79 mg l$^{-1}$ iron in Subotica results in less iron removal than the 5.2 mg l$^{-1}$ in Loosdrecht. The higher calcium and ammonium concentration in Subotica are likely to have caused this, due to competitive effects for adsorption sites (Sharma, 2001) and available oxygen, respectively.

For each sample taken after 3 to 4 pore volumes, arsenic breakthrough already exceeded 60 %. As a certain amount of iron in groundwater is prerequisite to the operation of SAR, the low efficiency observed at 0.65 mg l$^{-1}$ iron is not surprising. It was expected though, that additional ferrous iron would improve the SAR efficiency in the column experiments. No such effect can be seen, so the Fe:As ratio had no effect on removal and iron removal did not result in co-removal of arsenic.

## 3.3 Comparison with laboratory results

Laboratory research has shown that in the absence of other dissolved solids than arsenic, iron, bicarbonate and sodium, retardation factors up to 31 were observed for arsenic concentrations of 200 µg l$^{-1}$. When adding 1 mg l$^{-1}$ phosphate to that same water matrix, the $R_{As}$ dropped to 5. When adding (instead of phosphate) 7 mg l$^{-1}$ of silicate, the $R_{As}$ went down to 6. In both cases, the iron retardation factor ($R_{Fe}$) remained relatively unchanged.

Figure 4 shows the arsenic and iron retardation factors for Subotica, Loosdrecht and laboratory experiments previously performed by the authors (Moed et al., 2012).

The efficiency of SAR during the column experiments in Loosdrecht turned out to be slightly higher than in the laboratory, while the water in the laboratory contained phosphate and the Loosdrecht groundwater did not. An explanation for this could be the slightly lower arsenic concentration applied in Loosdrecht (160 µg l$^{-1}$ vs. 200 µg l$^{-1}$). Another explanation is the influence of the low bicarbonate concentration in Loosdrecht.

The removal efficiency of arsenic in Subotica is low. Although Subotica groundwater contained 64 mg l$^{-1}$ more HCO$_3$ than the laboratory's synthetic groundwater, this is unlikely to cause such a large difference, considering the relative difference in HCO$_3$ (20 % more in Subotica). Another difference in water quality is the high TOC concentration in Subotica. Natural Organic Matter (NOM) has a reducing effect on both As(III) and As(V) sorption onto ferric oxides (Redman et al., 2002). The low efficiency in Subotica can possibly be attributed to the elevated NOM concentration.

# 4 Conclusions

Taking the experimental setup from the laboratory to the field has shown that phosphate is not the only limiting component for SAR. Silicate, which is always present in groundwater, was already identified as another limiting factor. The difference in SAR efficiency measured at Loosdrecht, Subotica and laboratory experiments with silicate, cannot be attributed to the presence of silicate. There is slight evidence of bicarbonate having influence, but more likely NOM is an important limiting factor in, especially, the Subotica results. The presented results have shown the complexity of factors influencing arsenic removal during subsurface arsenic removal, making it very challenging to select appropriate sites.

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**Table 1.** Average groundwater compositions at GWPS Loosdrecht and Subotica compared to concentrations during previous laboratory experiments. Concentrations of iron and arsenic created by dosing are between brackets.

| Parameter | Loosdrecht | Subotica | Laboratory settings |
|---|---|---|---|
| pH | 7.3 | 7.57 | 6.9 |
| As (mg l$^{-1}$) | 0.032 (0.16) | 0.115 | 0.2 |
| Fe (mg l$^{-1}$) | 5.2 | 0.6 (2.72; 5.79) | 4.0 |
| Mn (mg l$^{-1}$) | 0.2 | 0.04 | 3.0 |
| Ca (mg l$^{-1}$) | 41.0 | 74.5 | 50 |
| PO$_4$ (mg l$^{-1}$) | 0.11 | 0.13 | 1.0 |
| SO$_4$ (mg l$^{-1}$) | 15.1 | 0.0 | 7.0 |
| NO$_3$ (mg l$^{-1}$) | 0.1 | 0.0 | 66 |
| HCO$_3$ (mg l$^{-1}$) | 130 | 364 | 300 |
| Si (mg l$^{-1}$) | 6.3 | 8.1 | 7.0 |
| Ammonium (mg l$^{-1}$) | 0.32 | 0.81 | 0 |
| TOC (mg l$^{-1}$) | 1.2 | 5.8 | 0 |
| Mg (mg l$^{-1}$) | 2.3 | 15.3 | 0 |
| K (mg l$^{-1}$) | 0.8 | 1.1 | 0 |

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**Fig. 1.** The principle of subsurface arsenic removal during injection **(a)** and abstraction **(b)**.
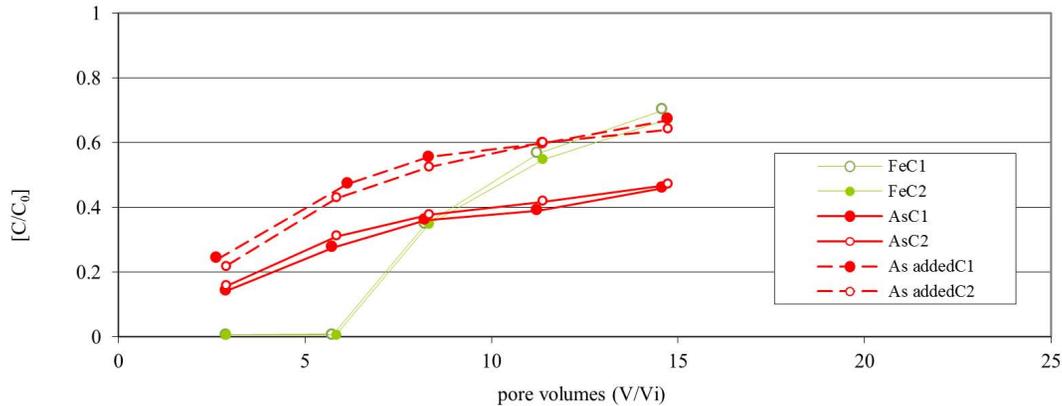
**Fig. 2.** Typical abstraction phase breakthrough curves for Loosdrecht's raw groundwater, with $C_{0,\text{Fe}} = 5.2\,\text{mg}\,\text{l}^{-1}$ $C_{0,\text{As}} = 31\,\mu\text{g}\,\text{l}^{-1}$ and $C_{0,\text{Asadded}} = 160\,\mu\text{g}\,\text{l}^{-1}$. Other concentrations are found in Table 1. Results are shown for both Column 1 (C1) and Column 2 (C2).
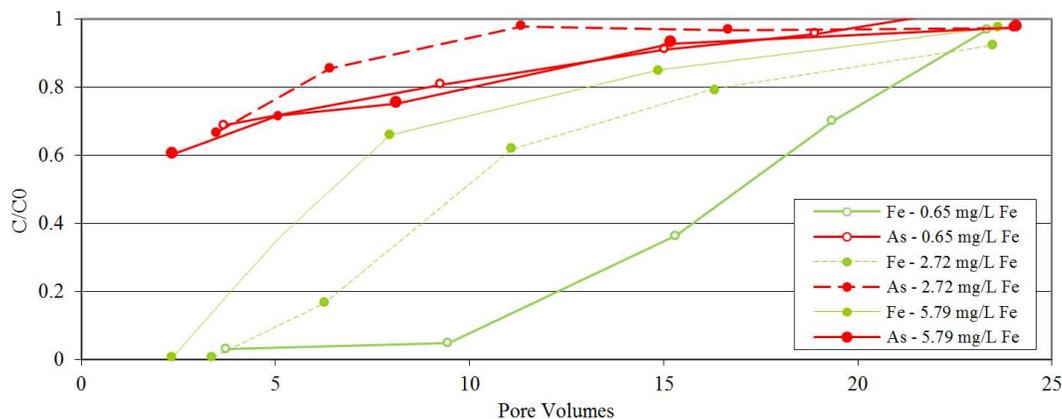
**Fig. 3.** Iron and arsenic breakthrough curves for column experiments with natural groundwater and $Fe^{2+}$ addition in Subotica (for 0.65, 2.72 and 5.79 mg l$^{-1}$ Fe, respectively). Results are the average of the two columns. The difference in result between the two was less than 5 % for each data point.
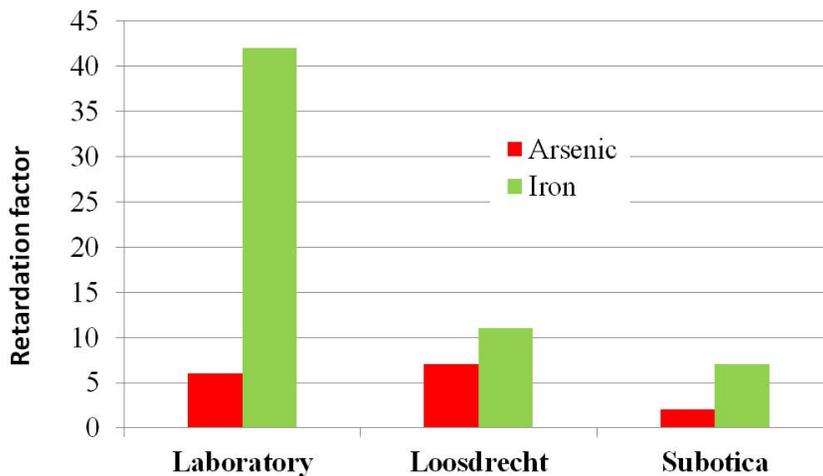
**Fig. 4.** Arsenic and iron retardation factor comparison for Loosdrecht (5.2 mg l$^{-1}$ Fe, 0.16 mg l$^{-1}$ As, 6.3 mg l$^{-1}$ Si, 130 mg l$^{-1}$ HCO$_3$), Subotica (5.79 mg l$^{-1}$ Fe, 0.115 mg l$^{-1}$ As, 8.1 mg l$^{-1}$ Si, 364 mg l$^{-1}$ HCO$_3$) and the laboratory (4 mg l$^{-1}$ Fe, 0.2 mg l$^{-1}$ As, 7 mg l$^{-1}$ Si, 300 mg l$^{-1}$ HCO$_3$, taken from Moed et al., 2012).

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