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Reactive transport modeling of subsurface arsenic removal systems in rural Bangladesh

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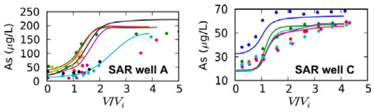
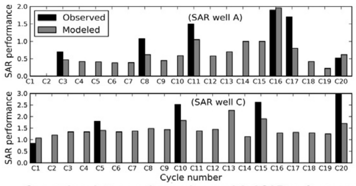
HIGHLIGHTS

- Arsenic (im)mobilization during subsurface As removal (SAR) operation were simulated with a reactive transport model (RTM).
- Si sorption on hydrous ferric oxide (HFO) is an important factor limiting As removal at the modeled sites in Bangladesh.
- Groundwater pH, As(III) oxidation, and sorption capacity of HFO dictates As levels in the extracted water.
- The developed RTM is shown to be transferable to other locations in Bangladesh.
- The RTM could be useful to identify locations for potential SAR operation in Bangladesh.

GRAPHICAL ABSTRACT



Model (lines) vs observed (dots) for 6 cycles at SAR well A.
The same model was transferred to SAR well C for 5 cycles.



Comparison between observed vs modeled SAR performance.

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ABSTRACT

Subsurface Arsenic Removal (SAR) is a technique for in-situ removal of arsenic from groundwater. Extracted groundwater is aerated and re-injected into an anoxic aquifer, where the oxygen in the injected water reacts with ferrous iron in the aquifer to form hydrous ferric oxide (HFO). Subsequent extraction of groundwater contains temporarily lower As concentrations, because As sorbs onto the HFO. Injection, storage, and extraction together is called a cycle. A reactive transport model (RTM) was developed in PHREEQC to determine the hydrogeochemical processes responsible for As (im)mobilization during experimental SAR operation performed in Bangladesh. Oxidation of Fe(II) and As(III) were modeled using kinetic-rate expressions. Cation exchange, precipitation of HFO, and surface complexation, were modeled as equilibrium processes. A best set of surface complexation reactions and corresponding equilibrium constants was adopted from previous studies to simulate all 20 cycles of a SAR experiment. The model gives a reasonable match with observed concentrations of different elements in the extracted water (e.g., the r^2 value of As was 0.59 or higher). As concentrations in the extracted water are governed by four major processes. First, As concentration decreases in response to the elevated pH of injection water and likewise increases when native neutral pH groundwater flows in. Second, the sorption capacity for As increases due to the gradual buildup of HFO. Third, As sorption is enhanced by preferential

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removal of As(V). Fourth, competitive sorption of Si limits the capacity of freshly precipitated HFO for As sorption. Transferability of the developed reactive transport model was demonstrated through successful application of the model, without further calibration, to two additional SAR sites in Bangladesh. This gives confidence that the model could be useful to assess potential SAR performance at locations in Bangladesh based on local hydrogeochemical conditions.

1. Introduction

Elevated concentrations of arsenic (As) in groundwater of the shallow Holocene alluvial aquifers of Bangladesh and West Bengal in India are a major public health concern (Acharyya et al., 1999; Ahmed et al., 2004; BGS and DPHE, 2001; Bhattacharya et al., 1997, 2002; McArthur et al., 2001; Nickson et al., 1998; Ravenscroft et al., 2005). The WHO standard for drinking water is 10 μg/L of As, while the Bangladesh standard is 50 μg/L. Alternatives for As contaminated groundwater include the use of rainwater, surface water, or deep groundwater, and a number of As removal systems with adsorption media, such as Sono and Alcan (JICA and DPHE, 2009). Potential problems with these filters include sudden arsenic breakthrough and clogging of the filter and generation of arsenic-rich sludge (Sutherland et al., 2002). The overall contribution of these removal units to arsenic mitigation of Bangladesh has been insignificant (JICA and DPHE, 2009).

Subsurface arsenic removal (SAR) is a relatively new treatment option that can be operated with negligible waste generation (Appelo and de Vet, 2003; Gupta et al., 2009; Rott et al., 2002) and has been tested in Bangladesh by Sarkar and Rahman (2001), Van Halem et al. (2009, 2010a, 2010b), and more recently by Rahman et al. (2014). SAR operation consists of the following steps: extraction of anoxic groundwater into a tank, aeration of extracted water in the tank, injection of aerated water back into the aquifer, and finally, extraction of larger volume of water with a lower level of As. All steps together are referred to as a cycle. When a SAR system works correctly, several times the volume of the injected water can be extracted before the As level rises above the drinking water standard. The basic principle of SAR is that injection of oxygenated water into the aquifer creates a subsurface iron-oxide filter for arsenic. Existing shallow tube wells can be modified to perform SAR by connecting the well with the aeration tank with pipes and valves to perform injection and extraction operations (Van Halem et al., 2010a). SAR can be a cost-effective way to provide safe drinking water in rural areas provided that the geochemical characteristics of the aquifer are suitable to SAR (Rahman et al., 2014).

Insight into the mechanisms controlling SAR is still limited (Appelo and de Vet, 2003; Van Halem et al., 2010a; Rahman et al., 2014) and therefore SAR performance is hard to estimate a priori for a given location. For example, Appelo and de Vet (2003) and Van Halem et al. (2010a) reported PO_4 whereas Rahman et al. (2014) reported H_4SiO_4 as the main competitor of As for HFO sorption sites. It is important to determine which hydrogeochemical processes are responsible for the (im)mobilization of As in the shallow subsurface during SAR operation and to develop a tool that can assess potential SAR performance based on local hydrogeochemical conditions. Reactive transport modeling represents a process based description of the geochemical reactions and mechanisms controlling the (im)mobilization of As in the shallow subsurface during SAR operation and may be used to assess potential SAR performance.

The only available reactive transport model (RTM) for subsurface As removal prior to this study was reported by Appelo and de Vet (2003) for a location in the Netherlands. They modeled subsurface As removal with an injection volume of approximately 1000 m^3 whereas the injection volumes ranges from 0.5 m^3 to 5 m^3 in this study. The maximum groundwater As concentration at their site was 14 μg/L which is approximately 15 times lower than at the study sites in this study. Kinetic oxidation of Fe(II) and As(III) was not included in their model, whereas kinetic oxidation of both Fe(II) and As(III) is simulated in this study. Appelo and de Vet (2003) reported a sudden increase in As concentration in the extracted water compared to the background As concentration when the ratio between extracted and injected volume (V/V_i) is approximately 2 due to the competitive displacement of arsenic by PO_4 and HCO_3 present in the native groundwater. After $V/V_i \approx 2$, As concentration in the extracted water drops below the background level due to better sorption of As(III).

The objectives of this study are (i) to develop a RTM that simulates the SAR experiments reported by Rahman et al. (2014), (ii) to obtain mechanistic insight into the interplay of the hydrogeochemical processes responsible for the (im) mobilization of As during SAR operation, and (iii) to determine whether the developed RTM is transferable to other locations in Bangladesh. The latter is assessed through model application to two other SAR sites in Bangladesh with different hydrogeochemical conditions.

2. SAR experiment and field site description

A reactive transport model was developed for a SAR well referred to as SAR well A, which is located in Muradnagar upazila (sub-district) in Comilla district about 100 km southeast of Dhaka, Bangladesh (23.6257834N, 90.90776674E) (Fig. 1). The reactive transport model was subsequently applied to two other SAR wells labeled SAR well B and SAR well C, without further calibration as discussed in Section 5. The conditions at SAR well A are discussed here in detail.

2.1. Hydrogeology and experimental conditions at SAR well A

The subsurface at the study site is composed predominantly of argillaceous (sand–silt–clay) facies, representing Holocene alluvial unconsolidated deposits (Aziz Hasan et al., 2009). The aquifer at the study site is composed of alternating silty clay and very fine to fine grained sands (Rahman et al., 2014).

The upper shallow sandy aquifer is covered by a heterogeneous near-surface silty section. SAR operation is conducted in a 5 m thick confined aquifer (17.67–22.55 m bsl) bounded by a thin (0.5 m) clay layer on top and a thick (~30 m) clay layer at the bottom. The sediments were colored light brown near the surface and are gray below 4.26 m bsl (Rahman et al., 2014). Hydraulic conductivity of the target aquifer is 5 m/day as determined with a slug test.

Groundwater levels in the study area fluctuate yearly between 2 and 6 m bsl. Extraction for irrigation in the dry season is the main cause for variations in the groundwater level. Groundwater flow follows the general topography of the area, i.e., from higher elevations towards lower elevations in the wet season, but the flow condition is almost reversed during the dry season due to large scale extraction for irrigation (Aziz Hasan et al., 2009). The estimated groundwater flow velocity of the study site is about 0.07 m/day.

A SAR experiment was conducted at SAR well A from December 2011 to February 2012. The volume of the tank was 5 m^3. Twenty cycles of injection, storage, and extraction were carried out. Each cycle consisted of three steps. First, water previously extracted from the aquifer was aerated and injected into the reduced aquifer. Second, the water was stored in the aquifer for 15–18 h. Third, groundwater was extracted. The first 5 m^3 of the extracted water was used to fill the