Reactive transport modeling to understand attenuation of arsenic concentrations in anoxic groundwater during Fe(II) oxidation by nitrate

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ABSTRACT: A previously published field-experimental investigation showed that injection of nitrate in anoxic groundwater that contained aqueous and sediment-bound Fe(II) diminished concentrations of As(V) and As(III) to below drinking-water limits. In the current study, reactive transport modeling confirmed that the observed attenuation was consistent with oxidation of Fe(II) by nitrate, leading to precipitation of hydrous ferric oxide, which, in turn, sorbed both As(V) and As(III). After calibration with site-specific observations, reactive transport modeling could aid in designing effective treatment to remove arsenic using injection of nitrate to oxidize Fe(II).

1 INTRODUCTION

Hazardous levels of arsenic in groundwater are often associated with high concentrations of aqueous and sediment-bound Fe(II). Field-scale observations in a contaminant plume and field-scale reactive transport experiments showed that injection of nitrate into anoxic groundwater with elevated Fe(II) concentrations resulted in oxidation of Fe(II) to hydrous ferric oxide (HFO), with concomitant attenuation of As(V) and As(III) concentrations (Smith *et al.*, 2017). The objectives of this study were to examine controls on Fe(II) oxidation by nitrate using reactive transport modeling (RTM) and the utility of RTM to aid in designing effective treatment of arsenic-contaminated groundwater using Fe(II) oxidation by nitrate.

2 METHODS

Two sets of field-scale experiments were conducted in which nitrate (NO_3^-) was injected into anoxic groundwater with elevated concentrations of dissolved and sediment-bound Fe(II) (Smith *et al.*, 2017). Each set of experiments involved withdrawing the anoxic groundwater, adding NaBr and NaNO_3 anaerobically, and reinjecting. Concentrations of nitrogen-species, major and minor cations and anions, Fe(II), As(V), As(III), and other selected solutes were monitored with time at various transport distances downgradient from the injection.

One-dimensional reactive transport simulations of experimental observations were conducted with PHREEQC (Appelo and Parkhurst, 2013). Parameters

for cation and anion sorption reactions on aquifer sediments were calibrated using experimental data from the first set of field experiments. Parameters for As(V) sorption on aquifer sediments were derived from laboratory experiments conducted with site-specific sediments. Parameters for sorption on HFO were taken from Dzombak & Morel (1990) and Gustafsson and Bhattacharya (2007). Transport parameters – pore-water velocity, dispersivity, and mass of injected tracers – were determined by fitting bromide (Br^-) time histories (e.g., Kent *et al.*, 2007).

3 RESULTS AND DISCUSSION

Time histories for NO_3^- were well-described using a rate expression that was first-order in NO_3^- concentration and biomass, causing N and O isotopic fractionation of the NO_3^- and producing transient accumulation of nitrous oxide (N_2O). Time histories for N_2O were also well described assuming a rate expression first-order in nitrite and biomass to produce N_2 (Fig. 1). The time-histories were also well-described using Monod expressions in NO_3^- and N_2O at the expense of an additional parameter that required calibration.

Aqueous Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ concentrations could be described using equilibrium cation exchange reactions. In addition to equilibrium cation exchange, Fe(II) time-histories showed clear evidence for loss of Fe(II) mass, which could be described as a rate-limited oxidation of Fe(II) by NO_3^- and N_2O according to the reactions:

Figure 1. Experimentally measured and simulated time histories of Br^- , NO_3^- , N_2O (panel A) and Na^+ , Ca^{2+} , and Fe(II) (panel B) 1.0 meter downgradient of the location where anoxic groundwater amended with approximately 1 mmol L^{-1} each of NaBr and NaNO_3 was injected in two pulses separated by several days.

Figure 2. Experimentally measured and simulated time histories of SO_4^{2-} and total dissolved P (panel A) and As(V) and As(III) at the same location described in Figure 1. Note that the WHO drinking water limit for As is $0.13 \mu\text{M}$.

Sorption of Ca^{2+} or Fe^{2+} on the freshly precipitated HFO had little impact on simulated time-histories (Fig. 1).

No attenuation of SO_4^{2-} concentrations was observed (Fig. 2). In contrast, significant attenuation of total dissolved phosphorus (P) (independently shown to equal phosphate concentrations), As(V), and As(III) concentrations was observed. Simulated time histories of all four oxyanions assuming equilibrium sorption on HFO generated by oxidation of aqueous and sorbed Fe(II) using published surface complexation parameters were in good agreement with the experimental data. Arsenic concentrations remained below the WHO drinking water limited for several weeks after the nitrate injections, after which they slowly returned to pre-treatment concentrations.

Simulations based on alternative hypotheses for reactions involving NO_3^- and Fe(II) yielded significant discrepancies compared to the experimental data. Reduction of NO_3^- and N_2O by organic carbon rather than Fe(II) yielded insufficient HFO generation to match the observed attenuation of P, As(V), and As(III)

concentrations. Reduction of NO_3^- to NH_4^+ rather than N_2 resulted in much higher NH_4^+ concentrations than observed and excessive generation of HFO, resulting in much larger decreases in SO_4^{2-} , P, As(V), and As(III) concentrations than observed.

4 CONCLUSIONS

Experimental data show that injection of NO_3^- in anoxic groundwater with aqueous and sediment-bound Fe(II) can greatly diminish both As(V) and As(III) concentrations. Reactive transport model simulations show that the observations are consistent with oxidation of Fe(II) by NO_3^- to HFO, producing transient N_2O and N_2 . Sorption of As(V) and As(III) on HFO can maintain arsenic concentrations below drinking water limits for several weeks. Once calibrated using site-specific observations, reactive transport models can provide guidance in designing treatments that minimize As(V/III) and nitrate concentrations.

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