

Arsenic mobilization in the piedmont area of the Hetao basin: an insight from a reactive transport model

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Abstract. Groundwater showed a trend from oxic-suboxic conditions in the alluvial fan to anoxic conditions in the flat plain in the Hetao basin, with increases in As, Fe²⁺, NH₄⁺, alkalinity and pH, and decreases in Eh and NO₃⁻. A 1D reactive transport model was constructed using a model flow column by PHREEQC to quantitatively interpret geochemical processes related to As mobilization in a 5000 m-long hydrogeological unit. Results indicated that groundwater As concentration was mostly controlled by Fe(III) oxide reduction and As adsorption processes. Observed Fe²⁺ was the combination of Fe(III) oxide reduction and mackinawite/siderite precipitation. Increasing alkalinity was the result of oxidation of organic carbon, rather than the dissolution of carbonates.

1 Introduction

High geogenic groundwater As has posed a huge health threat to over 100 million people in South and Southeast Asia [1] and around 20 million people in China [2]. Anoxic aquifers in river deltas and inland basins have been identified as the most critical As-affected areas [3].

Reductive dissolution of Fe(III) oxides, stimulated by organic carbon degradation, has been widely accepted as the primary mechanism for As mobilization both in river deltas and inland basins. Simultaneously, the released As from Fe(III) oxide reduction could be readsorbed on minerals in sediments, especially on Fe(III) oxides. Thus, As mobilization was largely governed by redox conditions and adsorption processes, which could be evaluated by a reactive transport modeling approach. Recent studies showed that As adsorption on sediments was quite different from synthesized Fe(III) oxides [4]. However, most of the surface complexation models (e.g. DDL, CD-MUSIC) incorporated in the reactive transport model have used synthesized Fe(III) oxides as the adsorbent [5, 6], with only few attempts using sediments [7, 8]. Therefore, building a reactive transport model coupling As adsorption onto sediments should be plausible.

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The Hetao basin, as a typical inland basin, hosted high As groundwater (As around 1000 $\mu\text{g/L}$) [9]. Previous studies showed that high groundwater As was mostly attributed to reductive dissolution of As-bearing Fe(III) oxides [10]. However, geochemical processes related to As mobilization should be different in the Hetao basin, since weakly alkaline pH and high concentrations of SO_4^{2-} was observed, compared to the river deltas with near-neutral pH and quite low SO_4^{2-} concentrations [11]. Arsenic adsorption was largely related to groundwater pH, and redox processes were greatly influenced by SO_4^{2-} , since SO_4^{2-} reduction competes electrons with Fe(III) oxide reduction. Quantitative studies of As mobilization-related geochemical processes would help us understand the mechanisms of elevated groundwater As in the Hetao basin. This study aims at evaluating geochemical processes of As mobilization by a reactive transport modeling approach.

2 The study area

The Hetao basin, located in the west of the Inner Mongolia, lies to the south of the Langshan Mountain and to the north of the Yellow River. A hydrogeological unit (around 5000 m long), which is located in the west of the Hetao basin near the Langshan Mountain, was selected to conduct this study. Previous studies showed that the unit could be divided into three zones approximately along the flow path, with 0-2000 m in the alluvial fan, 2000-3000 m in the transition area, and 3000-5000 m in the flat plain [10, 13]. Aquifer sediments were mainly composed of quartz, feldspar, muscovite, clay minerals, carbonates (mainly calcite and dolomite), and gypsum [10, 12]. A series of geochemical dissolution procedures [7] were carried out to quantify sedimentary Fe(III) oxides in four representative sediments, with Fe(III) oxide contents ranging between 46.4 and 143 mmol/kg (unpublished data). Calculations indicated that groundwater flow rates were around 20 m/yr in the alluvial fan, 10 m/yr in the transition area, and 5 m/yr in the flat plain. Along the approximate flow path, As concentrations gradually increased from 0.008 $\mu\text{mol/L}$ in the alluvial fan to around 4.98 $\mu\text{mol/L}$ in the flat plain, accompanied by the increasing trend of alkalinity (from 2.57 to 11.1 mmol/L), pH (from 7.17 to 8.24) and Fe^{2+} (0.001 to 0.063 mmol/L), and the decreasing trend of Eh (from 305 to 52.7 mV) (unpublished data).

3 Geochemical modeling

Arsenic(V) and As(III) adsorption on representative sediments were studied, including As(V) or As(III) adsorption isotherm, pH effect, and competitive adsorption by HCO_3^- and PO_4^{3-} [8, 13]. The data were then used with a non-electrostatic generalized composite surface complexation modeling (GC-SCM) [8, 14]. The established GC-SCMs provided were input into the reactive transport model to simulate As sorption.

In the reactive transport model, variable groundwater flow rates in different zones, kinetic geochemical processes (kinetic degradation of organic carbon, kinetic Fe(III) oxide reduction, and kinetic precipitation of mackinawite/siderite), As adsorption on aquifer sediment, cation exchange, and some other processes were included. Groundwater age at around 4700 m was around 1030 yr. Therefore, we presented a one dimensional reactive transport model to quantify geochemical processes of As mobilization for around 1200 yr by PHREEQC, during which two pore volumes groundwater flowed through the unit.

Organic carbon degradation was the overall engine for the matrix, which is described as a first-order reaction [7], as shown in Eq. (1).

$$-dC_{\text{organic}}/dt = C_0 \cdot 4.8 \times 10^{-5} \cdot (C/C_0)^2 \quad (\text{mol/L/yr}) \quad (1)$$

where C_0 refers to initial organic carbon concentration (mol/L), with average concentration of 1.29 mol/L, corresponding to the average contents of 0.228 wt% in the sediment (unpublished data).

Methanogenesis was thermodynamically inhibited by high concentrations of SO_4^{2-} [16], thus reductive dissolution of Fe(III) oxide reduction and SO_4^{2-} reduction were the two main processes accepting electrons. The distribution of electrons between Fe(III) oxides and SO_4^{2-} was regulated by kinetic reduction rates of Fe(III) oxides, which have both thermodynamic and kinetic contributions, as shown in Eq. (2) [7].

$$-dC_{\text{FeOOH}}/dt = m_0 \cdot 5 \times 10^{-4} \cdot (m_i/m_0)^{1.5} \cdot (1-\text{SR}_{\text{FeOOH}}) \quad (\text{mol/L/yr}) \quad (2)$$

where m_0 is the initial concentration of Fe(III) oxides in the sediment with average of 0.618 mol/L; SR_{FeOOH} is the saturation index of Fe(III) oxides; and the exponent to (m_i/m_0) reflects the heterogeneity of the Fe(III) oxides reactivity [7].

Precipitation of siderite and mackinawite occurred because of high concentrations of alkalinity, H_2S , and dissolved Fe^{2+} , both of which were kinetic controlled. The employed reaction rates were described as Eqs. (3) and (4) [7,17].

$$-dC_{\text{FeCO}_3}/dt = 1.5 \times 10^{-5} \cdot (1-\text{SR}_{\text{FeCO}_3}) \quad (\text{mol/L/yr}) \quad (3)$$

$$-dC_{\text{FeS}}/dt = 1.0 \times 10^{-5} \cdot (1-\text{SR}_{\text{FeS}}) \quad (\text{mol/L/yr}) \quad (4)$$

where $\text{SR}_{\text{FeCO}_3}$ and SR_{FeS} are saturation index of siderite (FeCO_3) and mackinawite (FeS), respectively.

4 Results and discussion

4.1 Surface complexation model

Both As(V) and As(III) adsorption showed nonlinear features. With the range of ambient groundwater pH (7-8.5), As(V) and As(III) adsorption decreased with increasing pH. Competitive effects of PO_4^{3-} on As(V) adsorption were higher than those on As(III) adsorption, while HCO_3^- competition effects on As(III) adsorption were much stronger than those on As(V) adsorption. Two GC-SCMs were obtained by optimizing geochemical constants of surface complexation reactions to fit the experimental data, which described As(III) and As(V) adsorption on the gray sediment and the brown sediment from the Hetao basin, respectively. The models well described As adsorption isotherms, competitive effects of coexisting anions (i.e. HCO_3^- and PO_4^{3-}), and pH effects, which were adapted in the reactive transport model.

4.2 Reactive transport model

The modeling results showed good agreement between the simulations and the observations. The increases in As, alkalinity, Fe^{2+} , SO_4^{2-} , pH and decrease in pe along the flow path were well simulated, suggesting the modeled geochemical processes should be in accordance with the actual situations.

No As was released in the alluvial fan, since oxic-suboxic conditions prevailed and Fe(III) oxides were not reduced. Arsenic was mostly released from Fe(III) oxide reduction in the transition area and the flat plain, and was attenuated by adsorption. Ferrous was initially released into groundwater by Fe(III) oxide reduction in the transition area and the flat plain. But concentrations of Fe^{2+} remained less than 0.063 mmol/L, because of the

precipitation of mackinawite and siderite. Siderite was the major Fe(II) precipitation phase in aquifers in the Red river floodplain [5, 7], since SO_4^{2-} concentration was normally low. Reduction of SO_4^{2-} was another important redox processes in the Hetao basin, which competes with Fe(III) oxides for electrons provided by organic carbon degradation. In spite of the reduction of SO_4^{2-} , the increasing trend of concentration of SO_4^{2-} was the result of gypsum dissolution (maximum of around 8.04 mmol/kg). In addition, calcite precipitation and dolomite dissolution were also occurred along the flow path. And the amount of calcite precipitation was much higher than that of dolomite dissolution. Although the net loss of HCO_3^- was obtained from calcite precipitation and dolomite dissolution, alkalinity still showed increasing trend along the flow path, which was attributed to the oxidation of organic carbon.

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