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Multiple isotope (O, S and C) approach elucidates the enrichment of arsenic in the groundwater from the Datong Basin, northern China

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SUMMARY

Hydrochemical data, the $\delta^{34}S$ and $\delta^{18}O$ values in dissolved sulfate $\left(SO_4^{2-}\right)$ and the $\delta^{13}C$ signature in dissolved inorganic carbon (DIC) have been analyzed and used to deduce the predominant biogeochemical/geochemical processes controlling the mobilization of arsenic within aquifers of the Datong Basin. High dissolved Fe(II), HS^- and NH_4^+ concentrations and low NO_3^-, SO_4^{2-} and ORP values were observed in the high-arsenic groundwater. The coupled occurrence of high dissolved Fe(II), HS^-, NH_4^+ and HCO_3^- concentrations in groundwater indicates that microbially mediated Fe(III) and SO_4^{2-} reduction and organic matter oxidation has occurred. Wide ranges of $\delta^{34}S$ and $\delta^{18}O$ values were measured in dissolved SO_4^{2-} (ranging from 7.0‰ to 36.8‰ and from 3.2‰ to 13.0‰ for $\delta^{34}S$ and $\delta^{18}O$, respectively) and depleted $\delta^{13}C$ values of DIC (varying from −6.9‰ to −22.0‰) were detected. The wide ranges of the $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values and the correlation between the low $\delta^{13}C_{DIC}$ values and the high $\delta^{34}S_{SO4}$ values indicate that the microbial reduction of SO_4^{2-} and organic matter biodegradation have occurred or are occurring. The correlation between $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values and Fe concentrations indicates that Fe(III) oxides/hydroxides reduction and iron sulfide formation may be the main processes controlling the enrichment of arsenic in groundwater. Furthermore, the negative correlations between the $\delta^{13}C_{DIC}$ values and the $\delta^{34}S_{SO4}$ values and Fe concentrations demonstrate that arsenic mobility are influenced by processes: (1) the reduction of arsenic-bearing crystalline Fe(III) oxide/hydroxides and SO_4^{2-} coupled to the oxidation of organic matter in aquifer sediments or unsaturated zone and (2) the reduction of amorphous Fe(III) oxyhydroxide without the significant reduction of sulfate.

1. Introduction

The natural occurrence of arsenic contaminated groundwater has been documented in many parts of the world, including the USA, China, India, Bangladesh, Argentina, Cambodia, and Vietnam (Benner et al., 2008; Bundschuh et al., 2004; Busbee et al., 2009; Eiche et al., 2008; Harvey et al., 2002; Larsen et al., 2008; Nickson et al., 2000; Nordstrom, 2002; Smedley et al., 2002, 2003; Verplanck et al., 2008; Wang et al., 2009; Xie et al., 2009). The presence of elevated concentrations of arsenic in groundwater, which is commonly extracted as drinking water in many countries, has endangered the health of more than 40 million people worldwide (Nordstrom, 2002). In the Datong Basin, China, arsenic bearing groundwater has caused severe arsenism to the local people because it has been consumed high arsenic groundwater for a long time (Li et al., 2005). The maximum value of dissolved arsenic that has been detected in the groundwater at Datong is 1820 μg/L (Xie et al., 2008). In this arid region, the groundwater is the primary source of drinking water. To mitigate the health hazards associated with exposure to high arsenic groundwater, it is imperative to understand the processes that cause the enrichment of arsenic in groundwater.

Based on worldwide-scale studies on high arsenic concentrations in groundwater, many hypotheses have been proposed to explain the mechanism of arsenic enrichment in groundwater. There is a general agreement that the geochemical behavior of arsenic is strongly associated with the geochemical and biogeochemical cycling of iron and sulfur and that the arsenic release can be associated with the reactivity of the organic matter present (Farooq et al., 2010; Postma et al., 2007; Rowland et al., 2007). In aquifer systems, Fe(III) and SO_4^{2-} are the primary electron acceptors for the oxidation of organic matter (Appelo and Postma, 1993). A number of studies have indicated that redox reactions directly or indirectly linked with microbial activity are the most important processes controlling the mobilization of arsenic within aquifers. The reduction of iron oxyhydroxide by organic matter is commonly suggested to explain elevated concentrations of arsenic in groundwater (Bauer and Blodau, 2006; Harvey et al., 2002; Islam et al.,

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2005; McArthur et al., 2004; Nickson et al., 2000; Quicksall et al., 2008). The reduction of As(V) to As(III) in the absence of Fe(III) reduction results in the desorption of arsenic from surface of Fe(III) minerals or the formation of weakly sorbing complexes under certain conditions (Bose and Sharma, 2002). Microbial SO_4^{2-} reduction can result in the formation of pyrite that can co-precipitate/sorb arsenic to reduce arsenic concentrations in groundwater (Mallik and Rajagopal, 1996; Mandal et al., 1996; Raiswell and Plant, 1980). Then, the subsequent oxidation of this pyrite can remobilize arsenic (Bhattacharaya et al., 1997; Chowdhury et al., 1999; Lowers et al., 2007; Mallik and Rajagopal, 1996; Mandal et al., 1996). Microbially mediated Fe(III), As(V) and SO_4^{2-} reduction and pyrite formation processes require some form of degradable organic matter as the electron donor (Charlet and Polya, 2006; Islam et al., 2005). Aquifer sediments are usually enriched in organic matters and can supply organic matter to support microbial activity (McArthur et al., 2004). In addition, surface-derived young organic matter can supply organic matter to drive the reduction of FeOOH (Harvey et al., 2002).

The abundance, oxidation state, and isotopic composition of sulfur in near surface environments can be modified in response to geochemical and biological processes. Sulfur isotope fractionation varies among different paths of transformations (Canfield, 2001). Large sulfur isotope fractionation is usually observed when bacteria reduce SO_4^{2-} to sulfide (Brüchert et al., 2001; Canfield, 2001; Detmers et al., 2001; Robertson and Schiff, 1994). No significantly isotope fractionation occurs when sulfides are oxidized to form SO_4^{2-}. For these reasons, studies often examine the isotopic composition of aqueous sulfur compounds to understand these processes and their reaction pathways (Canfield, 2001; Taylor et al., 1984). The oxidation of organic matter and the production of dissolved inorganic carbon (DIC) can be coupled to the reduction of Fe(III) or SO_4^{2-} within an aquifer (Holliger and Zehnder, 1996; Appelo and Postma, 1993). The formation of DIC by the microbial mineralization of organic matters can be verified using stable carbon isotopes (Aggarwal and Hinchee, 1991; Grossman, 1997). Thus, the carbon ($\delta^{13}C$) and sulfur ($\delta^{34}S$) isotopic values can provide useful information regarding Fe, S and C cycling and the mobilization of arsenic within aquifers.

In this study, we sampled and analyzed the groundwater from a known high-arsenic area in the Datong Basin to examine and demonstrate the importance of the relevant geochemical/biogeochemical processes affecting arsenic mobilization in this aquifer system. The carbon ($\delta^{13}C$) and sulfur ($\delta^{34}S$) isotope data provide insight into the reaction pathways of microbially catalyzed Fe(III) and SO_4^{2-} reduction, organic matter mineralization and arsenic release.

2. Study area

The Datong Basin is a Cenozoic basin of the Shanxi rift system (Wang and Shpeyzer, 2000).This basin is located in a semi-arid region of northern China (Fig. 1) with a mean annual rainfall of 300–400 mm and a mean evaporation rate of about 2000 mm per year. Approximately 80% of the rainfall occurs from July to August, and the rivers are ephemeral (Wang et al., 2009). The basin is bounded by the Hengshan Mountains, the Guancen Mountains and the Hongshou Mountains in the southeast, west and northwest of the basin, respectively. The ground elevation in the basin ranges from about 1000 m above sea level (ASL) along the Sanggan River to 2600 m ASL at the Huangyangjian Peak in the Guancen Mountains (Yang, 1961; Zhang, 1960). The basin is composed of Pliocene to Pleistocene unconsolidated sediments of various depths from 1500 m to 3500 m (Li et al., 2000). The grain size of the sediment generally decreases from the margin to the center of the basin. The piedmont sediments are mostly alluvial-fluvial gravel and coarse sand, while those of the central basin are lacustrine and alluvial–lacustrine sandy loam, silt, silty clay and clay with high organic contents (Guo and Wang, 2005; Li and Zhu, 2000). Based on palaeosol horizons and fossil assemblages, there are four major stratigraphic units in the Quaternary sediments (Q_1–Q_4) (Liu et al., 1986). The sediment is comprised of variable amounts of quartz, illite–smectite, feldspars, and calcite (Su, 2006). Due to intensive evaporation and a high groundwater table, saline soil is widely distributed within the Datong Basin (Han, 2008). Evaporites including halite (NaCl), mirabilite ($Na_2SO_4{\cdot}10H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) occur as ephemeral accumulations on the land surface, especially in the center of the basin.

The Quaternary groundwater systems can be divided into three groups: upper (5–60 m), middle (60–160 m) and lower aquifers (>160 m). In this area, the shallow aquifer sediments are typically made up of lacustrine and alluvial–lacustrine medium-fine sand, silty clay and clay with high organic matter contents. The organic matter content reaches as high as 1% in the aquifer sediments (Wang et al., 2009). The burial depth of the groundwater in the upper aquifer is commonly less than 2–5 m in the study area and decreases from the mountain front to the center of the basin (Fig. 1). The groundwater movement from the recharge areas near the mountain fronts to the discharge areas is slow within the Datong Basin. The velocity of the groundwater movement ranges from 0.20 m to 0.58 m per day (K = 20–58 m per day, J < 1/100) (Xie et al., 2009).

The groundwater is recharged by vertically infiltrating meteoric water, laterally flowing groundwater from the bedrocks along the mountain front and irrigation return flow. Discharge occurs mainly via evapotranspiration and artificial abstraction (Wang et al., 2009). In this area, high arsenic concentrations mainly occur in the shallow groundwater at depths less than 60 m (Xie et al., 2008) and are mainly distributed along the Huangshui River and the Sanggan River.

3. Sampling and analytical methods

3.1. Groundwater sampling

A total of thirty-five water samples was collected for isotopic and hydrochemical analyses in August 2010 in the Datong Basin. The locations of the sampling sites are shown in Fig. 1. All of the wells sampled are used for domestic supply or irrigation purposes. Groundwater was collected using a pump after purging the wells, typically for 5–10 min. Chemical and physical parameters, such as pH, EC, ORP and temperature (T), were measured on the site using Hach Instruments portable meters. One filtered (<0.45 μm) unacidified sample from each location was stored in an acid-washed and pre-cleaned 50 mL HDPE bottle for the analysis of anion concentrations, and one acidified sample (acidified to pH < 2 using ultra-pure HNO_3) was collected in a 50 mL HDPE bottle for the analysis of major cation and trace metal concentrations in the laboratory. Samples for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ isotope analyses were collected in 500 mL HDPE bottles after filtration. For stable carbon isotope analysis of the DIC, 50 ml glass bottles were filled with unfiltered groundwater and closed without head space using rubber stoppers and stored in dark until analysis.

3.2. Analytical methods

3.2.1. Hydrochemical analysis

Redox active water quality parameters, including HS^-, NH_4^+ and Fe(II) concentrations, were determined using an HACH DR2800 spectrophotometer at the time of sampling. The trace metal ion concentrations, including arsenic, were measured by inductively