Applied Geochemistry 89 (2018) 190–201

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Partitioning and reactivity of iron oxide minerals in aquifer sediments hosting high arsenic groundwater from the Hetao basin, P. R. China

Mengmeng Shen[a,b], Huaming Guo[a,b,*], Yongfeng Jia[b], Yongsheng Cao[b], Di Zhang[a,b]

[a] *State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, PR China*
[b] *MOE Key Laboratory of Groundwater Circulation and Environment Evolution, School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, PR China*

ARTICLE INFO

Handling Editor: Prof. M. Kersten

Keywords:
Inner Mongolia
Sequential extraction
Kinetic
Mineralogy
Redox

ABSTRACT

High arsenic (As) groundwater has been widely found in the Yellow River catchment, which has posed potential risks on health of local residents. However, it is still unknown how fractions and reactivity of Fe-bearing minerals control As mobility in groundwater system. As a typical basin in the catchment, the Hetao basin was selected as the study area to investigate roles of fractions and reactivity of Fe-bearing minerals in groundwater As. Seventy sediment samples and eight groundwater samples were collected in a representative borehole in the basin. Sequential extraction and kinetic experiment were carried out to characterize fractions and reactivity of Fe-bearing minerals, respectively. Results showed that groundwater in shallow zone (between 10 and 36 m depths) had lower ORP values and higher As concentrations (average = 279 μg/L) than deep zone (average = 158 μg/L). In shallow zone, the predominant reactive Fe phase was reducible oxides (Fe_{ox2}), while in deep zone it was carbonate associated Fe (Fe_{carb}). Fe_{ox2} had the highest amounts of As and As/Fe ratios, followed by Fe_{carb} and easily reducible oxides (Fe_{ox1}). Moreover, As/Fe ratios in Fe_{ox2} had the best correlation with As/Fe ratios in groundwater. The largest partition coefficients were obtained between As in Fe_{ox2} and groundwater As ($K_{d\text{-}ox2}$). Kinetic experiments showed that sediments having higher reactivity (k') and heterogeneity (γ) had higher As/Fe ratios. Reactivity of sediment samples fell into the range between synthetic lepidocrocite and poorly crystalline goethite. Arsenic partition coefficients between reactive minerals and groundwater ($K_{d\text{-}reac}$) showed a positive correlation with ORP values, indicating that reductive dissolution of Fe(III) oxides played the important role in As mobilization. Therefore, reducing conditions, high k', γ and Fe_{ox2} contents in sediments led to high As concentrations in groundwater.

1. Introduction

Arsenic (As) is a widespread carcinogenic element (Tchounwou et al., 2003). The health problems caused by arsenic poisoning (including pigmentation, keratosis, and viscera cancers), especially in groundwater, have drawn great public attention (Anawar et al., 2002; Ng et al., 2003; Kapaj et al., 2006). Many countries have strict guidelines for drinking water As, either 10 μg/L or 50 μg/L (Guo et al., 2014).

Previous studies have found that aquifer sediment As could be released into porewater or groundwater through various processes under different conditions (Guo et al., 2008a; Ni et al., 2016)., including oxidation of As bearing pyrite, reductive dissolution of Fe and/or Mn (oxyhydr)oxides, weathering of As-containing minerals, and anion competitive adsorption (McArthur et al., 2001; Mandl and Vyškovský, 1994; Horneman et al., 2004; Suzuki and Suko, 2006; Gao et al., 2011; Guo et al., 2014). Biswas et al. (2011) reported that As release in groundwater system is depth-dependent in Bengal Delta Plain. In reducing aquifers, As mobilization, in most cases, is correlated with reductive dissolution of Fe (oxyhydr)oxides, which is the predominant process contributing to As enrichment in groundwater around the world. Simultaneously, As could be readsorbed by sediments near surface (Postma et al., 2010). Adsorption capacity of Fe-bearing minerals depends on their fractionation patterns, crystallinities and paragenetic relationships with other minerals (McArthur et al., 2001; Horneman et al., 2004; Pedersen et al., 2006). Therefore, the detailed composition, properties and reactivity of Fe-bearing minerals in sediments are likely the key factors controlling As behavior in groundwater.

Many studies have focused on redox conditions and Fe mineral phases in aquifer sediments. The color of fresh drill cutting has been used as a redox indicator of sedimentary environment, showing that grey sediment aquifers generally hosted high As groundwater (Horneman et al., 2004; van Geen et al., 2013). In addition, in aquifer

---

[*] Corresponding author. School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, PR China.
E-mail address: hmguo@cugb.edu.cn (H. Guo).

https://doi.org/10.1016/j.apgeochem.2017.12.008
Received 16 September 2017; Received in revised form 6 December 2017; Accepted 12 December 2017

sediments hosting high As groundwater, pyrite and Fe (oxyhydr)oxides (such as ferrihydrite, geothite and hematite) were observed by Akai et al. (2004) using TEM. Postma et al. (2010) found the presence of goethite and hematite in sediments by Mössbauer spectra, which were not detected by powder XRD. Stuckey et al. (2015) found siderite, pyrite and Fe oxides in wetland sediments by using Fe EXAFS spectra. Although the peaks of XRD spectra were very weak, the presence of goethite, hematite, pyrite and siderite was observed in the sediment samples.

Although methods mentioned above provide important information on Fe containing minerals, their detection limits are mostly comparatively high (ca. 5% by XRD and EXAFS). Chemical extraction, such as sequential extraction (SE), is another option for quantifying Fe-bearing minerals. Since Fe aliquots are extracted from different mineral fractions with different reagents, solid-phase Fe fractionation patterns, distribution, reducibility, and associated As contents in sediments are simultaneously quantified. Although drawbacks of SE were observed, such as the poor selectivity of extractants, possible re-adsorption, reprecipitation processes during extraction (Gleyzes et al., 2002; Bacon and Davidson, 2008; Drahota et al., 2014), it has been widely used to study geochemical characteristics of aquifer sediments (Akai et al., 2004; Ni et al., 2016).

Reactivity of Fe oxide minerals and As is more important than their bulk contents. Glasauer et al. (2003) found that only poorly crystalline Fe oxides could be reduced in nutrient-limited natural environment. A reactive continuum model for time-dependent reduction rate has been used to characterize composition, reactivity and kinetic behaviors of Fe oxides and associated As (Postma, 1993; Larsen and Postma, 2001; Larsen et al., 2006; Postma et al., 2010; Zhu et al., 2014). The reactive continuum model of Fe minerals was proposed by Postma (1993), and then developed (Houben, 2003; Roden, 2004) and applied to synthetic minerals (Larsen and Postma, 2001; Pedersen et al., 2005, 2006; Davranche et al., 2013) and natural sediments (Larsen et al., 2006; Postma et al., 2010; Chen et al., 2013; Zhu et al., 2014).

Arsenic concentrations in shallow groundwaters from the Hetao Basin of Inner Mongolia ranged between 0.6 and 572 μg/L (Guo et al., 2008a), which mostly exceeds the WHO guideline value of 10 μg/L (World Health Organization, 1996). Although many studies have been carried out for groundwater chemistry, few have been done on reactivity of Fe minerals and As in aquifer sediments. Based on sequential extraction, Ni et al. (2016) found that As fractionation patterns in sediments were dependent on lithology and sampling depths. Clay and silty clay usually had higher As concentrations and higher levels of extractable As compared with sand sediments. Tong et al. (2014) reported that the As mainly occurred as strongly adsorbed on and/or coprecipitated with amorphous Fe (oxyhydr)oxides in near-surface sediments, accounting for 35% and 20%, respectively. However, little is known about the specific distribution of different Fe-oxide minerals in aquifer sediments and their reactivity. Relationship between Fe-oxide mineral distribution or reactivity and As mobilization in aquifer sediments is also not clear, which is quite important in understanding As behavior in groundwater systems.

Therefore, the objectives of this study are to investigate partitioning, distribution and reactivity of various solid-phase Fe fractionation in aquifer sediments and their effects on As concentration and mobilization in groundwater. The methods applied included elemental analysis, drill cutting color analysis, mineralogical investigations, chemical sequential extraction, and the reactive continuum model.

2. Materials and methods

2.1. Study area

The Hetao basin lies in the western of Inner Mongolia, to the north of the Yellow River, the south of the Langshan Mountains and the east of the Wuranbuh Desert (Fig. 1). The climate is arid to semiarid with low average annual rainfall (130–220 mm, mainly between July to September) and high annual evaporation (2000–2500 mm). Groundwater is mostly hosted in Quaternary alluvial, alluvial–pluvial and fluvial–lacustrine aquifers (Guo et al., 2008b).

The study area is located in the northwest of the basin. Sediments in the north are mainly composed of alluvial and pluvial sediments, and fluvial and lacustrine sediments in the south. Normally, there was a clay layer at depths around 40–45 m below land surface (BLS), above which shallow groundwater occurs and below which deep groundwater is present (Guo et al., 2016). General direction of groundwater flow in the northern part is from north to south, which is controlled by surface topography (Guo et al., 2008b). Groundwater levels have significant variations because of irrigation practice and hydrogeological settings (Guo et al., 2012). Groundwaters are near-neutral to weakly alkaline (pH 7.14–8.95), with As concentrations between 0.33 and 858 μg/L (Guo et al., 2011a). As(III) is the predominant As species in most cases (Tang et al., 1996; Guo et al., 2008b, 2011a, 2016). Relatively low Eh values (< 100 mV) in high As groundwaters showed that As mobilization was mainly due to reductive dissolution of Fe oxides (Guo et al., 2011b, 2013a).

In order to investigate kinds and reactivity of Fe minerals and As in sediments, a borehole BH02 (40°59′45.3″N, 106°58′25.1″E) was drilled near a wetland (horizontal distance around 50 m) with a depth of 90 m in September, 2012. Near the borehole, groundwater had As concentrations generally between 100 and 200 μg/L (Fig. 1).

2.2. Sediment and groundwater sampling

During drilling of BH02, sediment samples were taken at 2.0 m intervals, and additional samples were collected near lithological boundaries in case that the lithological conditions changed. Immediately after taken from borehole, sediments were wrapped tightly by tinfoil, sealed in sterile plastic bags filled with pure N_2 ($> 99.999\%$), and kept at 4 °C. After transported to laboratory, they were frozen at −80 °C before analysis.

The multilevel well was established in the BH02 following the procedure of Guo et al. (2012). Groundwater table ranged from 5 to 8 m bls. Eight groundwater samples were collected in the multilevel well-BH02. Groundwater samples were taken after pumping for usually $>$ 20 min until temperature, pH, electrical conductivity (EC) and ORP of the flowing water were stable. After being calibrated using standard solutions, a multiparameter portable meter (HANNA, HI 9828) was used to monitor groundwater temperature, pH, electrical conductivity (EC) and ORP through an in-line flow cell under minimal atmospheric contact. All groundwater samples were filtered through 0.22 μm membrane filters. Those for major cations and trace elements were collected in 120 mL HDPE bottles and acidified to pH < 2 with 6 M ultrapure HNO_3, and those for anion analysis were not acidified. Samples for As fractionation patterns were preserved with 0.25 M EDTA. DOC samples were collected in 60 mL amber glass bottles and acidified with H_3PO_4 to pH < 2. All groundwater samples were preserved in an ice box and delivered to the laboratory at 4 °C, which were analyzed within two weeks.

During groundwater sampling, S^{2-}, Fe(II) and NH_4-N were analyzed using a portable spectrophotometer (DR2800, HACH) with methylene blue, 1,10 phenanthroline, and 5 aminosalicylic acid methods, respectively. Alkalinity was measured by titration with 0.8 M H_2SO_4 using a Model 16900 digital titrator (HACH) with phenolphthalein and methyl-orange indicators.

2.3. Batch experiments

2.3.1. Full digestion and sequential extractions

Prior to full digestion and extraction experiments of iron minerals, sediments were freeze-dried and crushed to < 63 μm by mortar and pestle. Sediments samples were subjected to a mixed acid (HNO_3-