



In-situ mobilization and transformation of iron oxides-adsorbed arsenate in natural groundwater



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HIGHLIGHTS

- In situ experiments were used to delineate As mobilization from Fe(III) oxides.
- Arsenic desorption occurred from ferrihydrite, goethite and hematite.
- Arsenic was released from reductive dissolution of ferrihydrite.
- Transformation of ferrihydrite to secondary Fe minerals favored As mobilization.
- Goethite and hematite would be the major oxides controlling groundwater As content.

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ABSTRACT

Although reductive dissolution of Fe(III) oxides has been well accepted for As mobilization in alluvial aquifers, the key factors controlling this process are poorly understood. Arsenic(V)-adsorbing ferrihydrite, goethite and hematite were used to examine in-situ mobilization and transformation of adsorbed As(V) and Fe(III) oxides. In the Hetao basin, seven wells with wide ranges of groundwater As were selected to host As(V)-Fe(III) oxides sand. During 80 d experiments, As was firstly desorbed and then released via reductive dissolution of iron oxide from ferrihydrite, while only desorption was observed from goethite/hematite sand. Desorbed As was predominantly controlled by groundwater HCO_3^- and DOC, while reductive dissolution-related As release was mainly regulated by ORP values, DOC and Fe(II) concentrations. Mineral transformation from ferrihydrite to lepidocrocite and goethite/or mackinawite would also contribute to As release. Arsenic species was transformed from As(V) to As(III) on ferrihydrite, but remained unchanged on goethite and hematite. Arsenic partition between As-Fe(III) oxide sand and real groundwater ranged between 0.012 and 0.102 L/g. $K_{d\text{-sand}}$ between As-goethite sand/As-hematite sand and groundwater fell within the ranges observed between sediments and groundwater. This study suggests that As desorption, reductive dissolution and mineral transformation of ferrihydrite would be the major processes controlling As mobility.

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1. Introduction

Elevated arsenic (As) groundwaters have been widely observed throughout the world, which negatively affect 100 million villagers across Argentina, Bangladesh, China, and Romania relying on tube-wells as the main drinking water source [1,2]. Reductive dissolution of Fe(III) oxide minerals has been well accepted as a key mecha-

nism for As mobilization in shallow groundwater under reducing conditions [1–6].

Ferrihydrite, goethite and hematite have usually been found in sedimentary aquifers hosting high As groundwater, e.g. from Red River floodplain [7], Bangladesh [8,9], and Cambodia [10]. Although XRD techniques did not detect the presence of Fe oxide minerals in the Hetao basin due to their low contents or poor crystalline [6,11,12], the sequential extraction procedure showed that sediment As was mostly bound to Fe oxide minerals [2,6]. Arsenic content of naturally occurring iron oxides shows great variation ranging from an As/Fe molar ratio of 2.4×10^{-6} to 0.09 [13]. Due to their great abundance and strong affinity, ferrihydrite, goethite

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and hematite are probably the most important adsorbents for As in sandy aquifers [7,13]. Although those minerals have different stability and specific surface area, both As(V) and As(III) can be adsorbed on their surfaces via an inner and/or an outer sphere surface complex [11,14–18].

However, the releases of Fe and As during reductive dissolution of Fe(III) oxide minerals is non-stoichiometric [13,19]. The behaviors of Fe(III) oxide minerals-bound As in aquifer environments are controlled by complex interactions among hydrogeochemistry, mineralogy, and microbes. Dissolved organic carbon (DOC) and competing anions lead to As desorption [20–22], and microbial metabolism affects As affinity to Fe(III) oxide minerals, and therefore cause As mobilization [23–26]. Mineral transformation and alteration of As species cause the changes in As behaviors [25–28]. The transformation of ferrihydrite to mackinawite would release the adsorbed As [25,26,29]. Whereas the replacement of ferrihydrite by goethite/magnetite causes the bound-As to be less susceptible to mobilization in reducing conditions due to the stability of crystalline Fe(III) minerals [27]. In addition, reduction of adsorbed As(V) results in As mobility due to the lower affinity of As(III) relative to As(V) [30].

In order to clearly get insight into As mobilization during water-sediment interactions, different approaches have been employed to characterize As behaviors from aquifer sediments, including laboratory studies, field investigation, and sediment incubation [31–37]. Although all investigations have shown As release from sediments, sequence of As and Fe release is found to be different. A simultaneous release of Fe and As was observed during sediment incubation [34,35]. However, Radloff et al. and Guo et al. reported that the release of As is followed by Fe(II) release [36,37]. In contrast, Islam et al. found the release of Fe(II) prior to the release of As(III) [33]. Based on field experiments, Stuckey et al. observed that As was released only when either reactive forms of iron oxides were available or labile organic carbon were added [38]. Therefore, more investigation is needed to reveal the involved mechanisms for As mobilization.

Due to the complex physicochemical conditions of real groundwaters, it is difficult to extrapolate laboratory experimental results into natural aquifers [39–41]. In-situ investigation of As and Fe behaviors during interactions between real groundwater and specific As-loading Fe(III) oxide minerals will help in better understanding As release mechanisms in aquifer systems.

In this study, in-situ experiments was designed to elucidate effects of groundwater geochemistry and Fe(III) oxide mineralogy on As mobilization from ferrihydrite, goethite and hematite in real groundwater systems. The objectives of this article are to investigate release and transformation of adsorbed As(V) from different Fe(III) oxide minerals-coated sand and to evaluate the key factors controlling As mobilization under real groundwater environments.

2. Materials and methods

2.1. The field site and groundwater sampling and analysis

The study area, located in the western Hetao basin, Inner Mongolia, is a typical region where shallow aquifers host high As groundwater with groundwater flow rates between 10^{-6} and 10^{-5} m/s [6,42]. Recent investigation showed that groundwater As comes from geogenic sources, and the reductive dissolution of Fe(III) oxides is the major mechanism of As-mobilization [6,43]. Seven wells were drilled for groundwater chemical monitoring and in-situ experiments (Fig. S1). Screening depths of these wells are shown in Table S1.

Groundwater sampling campaign was carried out three times in 2014 during experiments. Groundwater was sampled for analysis

of major and trace elements, anions and As species after filtered through 0.45 μm membrane filters. Physicochemical parameters, including water temperature, electrical conductivity (EC), pH, ORP, and alkalinity were measured in the field. More details are provided in Supplementary materials.

2.2. Synthesis of Fe(III) oxides and Fe(III) oxides sands

Iron(III) oxides sands were synthesized according to the procedure of Schwertmann and Cornell [14]. After frozen-dried, two-line ferrihydrite, goethite, and hematite were added to 0.01 M NaNO_3 solution and mixed with quartz sand at pH 2.5 to synthesize Fe(III) oxides sands. Ferrihydrite-coated sand was used within 5 days of its synthesis to minimize mineral transformation [44]. All chemical reagents used were of analytical grade. More details are provided in Supplementary materials.

2.3. Arsenate loading-Fe(III) oxides sands

Arsenate loading-Fe(III) oxides sands were prepared by mixing Fe(III) oxides sand into 500 mg/L As(V) in a polyethylene flask (Nalgene) at 150 rpm at room temperature for 5 days at pH around 7.5. Finally, As(V) loading-Fe(III) oxides sand was washed with deionized water twice. Arsenate adsorbing ferrihydrite, goethite, and hematite-coated sand were assigned as As-ferrihydrite sand, As-goethite sand, and As-hematite sand, respectively.

2.4. In-situ experiments on As release

Arsenic-loading Fe(III) oxides sand (normally 0.5 g each) was encapsulated in a nylon container with the pore size of 0.1 mm (150 mesh). Then samples were held in a Teflon tube and deployed within the depth of well screening (Table S1). A peristaltic pump was used to purge each well for 1 h before sample deployment. Sampling of As-loading Fe(III) oxide sand was carried out at different time intervals. Immediately after taken out of the wells, the packed As-loading Fe(III) oxide sand was kept in an amber anaerobic bottle filled with ultra-pure N_2 (99.999%), and preserved at 4 °C during transportation. Back to laboratory, the samples were dried in the anaerobic chamber (Coy, USA) and stored at –20 °C for further analysis. Each experiment was deployed in duplicate for each well.

2.5. Analytical methods

Samples were examined by SEM to obtain morphology information using a Zeiss Supra 35VP SEM at an accelerating voltage of 3–10 kV, which is equipped with EDS for chemical analyses.

Arsenic and Fe K-edge XANES were recorded at the beamline BL14W, at 3.5 GeV and 300 mA, in Shanghai Synchrotron Radiation Facility (SSRF), China. A Si(111) monochromator was used. XANES spectra of As and Fe were acquired in the energy range from –50 to +150 eV relative to K-edge of As and Fe, respectively. In addition, synchrotron X-ray diffraction (μ -XRD) was used to quantify Fe mineral phases in selected As-loading Fe(III) oxides sand. Chemical composition was analyzed by total digestion with microwave digestion system (Mars 6, CEM) [45]. Details can be found in Supplementary materials.

3. Results

3.1. Characterization of Fe(III) oxides sands and As-loading Fe(III) oxides sands

Scanning electron microscopy (SEM) shows that two-line ferrihydrite are spherically coated on quartz sand as loose agglom-

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