Effect of iron oxide reductive dissolution on the transformation and immobilization of arsenic in soils: New insights from X-ray photoelectron and X-ray absorption spectroscopy

Jian-Xin Fan [a,b], Yu-Jun Wang [a,*], Cun Liu [a], Li-Hua Wang [c], Ke Yang [c], Dong-Mei Zhou [a,*], Wei Li [d], Donald L. Sparks [d]

[a] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] School of River and Ocean Engineering, Chongqing Jiaotong University, Chongqing 400074, China
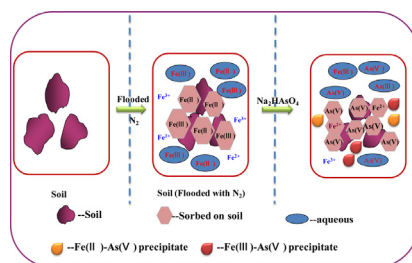[c] Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of sciences, Shanghai 201204, China
[d] Environmental Soil Chemistry Group, Delaware Environmental Institute and Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19717-1303 United States

HIGHLIGHTS

- Immobility and transformation of As on different Eh soils were investigated.
- μ-XRF, XANES, and XPS were used to gain As distribution and speciation in soil.
- Sorption capacity of As on anaerobic soil was much higher than that on oxic soil.
- Fe oxides reductive dissolution is a key factor for As sorption and transformation.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The geochemical behavior and speciation of arsenic (As) in paddy soils is strongly controlled by soil redox conditions and the sequestration by soil iron oxyhydroxides. Hence, the effects of iron oxide reductive dissolution on the adsorption, transformation and precipitation of As(III) and As(V) in soils were investigated using batch experiments and synchrotron based techniques to gain a deeper understanding at both macroscopic and microscopic scales. The results of batch sorption experiments revealed that the sorption capacity of As(V) on anoxic soil was much higher than that on control soil. Synchrotron based X-ray fluorescence (μ-XRF) mapping studies indicated that As was heterogeneously distributed and was mainly associated with iron in the soil. X-ray absorption near edge structure (XANES), micro-X-ray absorption near edge structure (μ-XANES) and X-ray photoelectron spectroscopy (XPS) analyses revealed that the primary speciation of As in the soil is As(V). These results further suggested that, when As(V) was introduced into the anoxic soil, the rapid coprecipitation of As(V) with ferric/ferrous ion prevented its reduction to As(III), and was the main mechanism controlling the immobilization of As. This research could improve the current understanding of soil As chemistry in paddy and wetland soils.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding authors at: Institute of Soil Science, Chinese Academy of Sciences, Key Laboratory of Soil Environment and Pollution Remediation, No. 71 East Beijing Road, Nanjing 210008, China. Tel.: +86 2586881180; fax: +86 2586881000.
E-mail addresses: yjwang@issas.ac.cn (Y.-J. Wang), dmzhou@issas.ac.cn (D.-M. Zhou).

1. Introduction

Arsenic (As) is a serious environmental concern, since it is one of the most toxic metalloids impacting many countries and regions around the world. Both oxidation states of As, As(III) and As(V), are toxic to human health, and As(III) bearing species are considered to be much more toxic and mobile [1]. The biogeochemistry of As has been discussed by Ferguson and Gavis [2]. Arsenate [As(V)], in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$, is predominant in well-oxidized water, while arsenite [As(III)] in the form of H_3AsO_3 and $H_2AsO_3^-$ occurs predominantly in reduced environments [3]. The speciation of inorganic As depends on pH and redox potentials [4]. Anaerobic soil environments caused by prolonged water logging may change soil redox potentials (Eh) to favor As(III) species [5–7].

In recent studies, many scientists have investigated the environmental behavior of As in soils, including immobility and mobility. It is believed that aqueous concentration of As is controlled mainly by sorption and/or mineral dissolution and precipitation [8–10]. Takahashi et al. [11] studied the As behavior in paddy fields during flooded and non-flooded periods. They found that Fe (hydr)oxide was a major sorbent of As in the soils. As in irrigation waters is bound to Fe (hydr)oxide in the soils during non-flooded periods, and As is quickly released from soil to water during flooded periods because of the reductive dissolution of the Fe (hydr)oxide phase and reduction of As from As(V) to As(III). In addition, Pedersen et al. [12] found that the release of As was associated with the reduction and transformation of iron oxides. Generally, iron hydroxide mineral phases play a key role in the biogeochemical cycling of As. Changes in redox conditions should have a significant impact on the behavior of As in water, soil, and plants, since the mobility of As is redox-sensitive [13–15].

Paddy fields have a distinct cycle of drying and wetting periods accompanied by redox changes. Few studies have reported on the immobilization mechanism of As in different Eh soils. Normally, iron oxide reductive dissolution would decrease the number of sorption sites, resulting in less sorption to the soil under anoxic conditions compared with oxic conditions [16–18]. For example, McGeehan et al. [6,19] found that prolonged soil flooding resulted in a decrease in soil redox potential and an increase in dissolved Fe and Mn. Drying the previously flooded soils resulted in an increase in As sorption.

In this study, the influence of iron oxide reductive dissolution on As sorption and Fe fractionation was investigated. Soil was incubated under flooded (anoxic) conditions at different Ehs, and then batch As adsorption experiments on the incubated soils were conducted. The fractionation and distribution of As and Fe in the soil were investigated by using XPS, XAS, μ-XRF and μ-XANES techniques. The objectives of this study were to evaluate iron oxide reductive dissolution under different Ehs, and to reveal mechanism of the immobilization and distribution of As in the soil.

2. Materials and methods

2.1. Soil incubation

The soil used in this study is *Udic Ferrosols* from Jiangxi, China, without As contamination. It was air-dried and ground to pass through a 100-mesh nylon fiber sieve, and stored at room temperature in polyethylene flasks until use. The detailed methods of analysis and physicochemical properties of soil are given in the *Supporting data* (Table S1).

The soils were incubated in three ways at the beginning of the experiments to maintain different soil redox potentials (Eh), including flooded and anoxic soil (S1), flooded soil (S2) and air-dried soil (S3). The air-dried soil was used directly as S3 without any treatment. Briefly, 200 g of air-dried soil and 400 mL deionized water were mixed into a 1 L polyethylene flask. The flooded and anoxic soil (S1) was incubated with the addition of glucose and under N_2 atmosphere. The flooded soil (S2) was incubated without glucose and N_2 atmosphere. The incubation period was 30 days. The Eh, pH, and temperature of the S1 and S2 soil slurries in the incubator were measured every day until Eh and pH were stable. The Eh and pH were measured with a platinum (Pt) electrode and a silver–silver chloride (Ag/AgCl) electrode, and a commercial glass reference electrode (REX, pHS-3B), respectively [20]. The final Ehs were −200 and −100 mV for S1 and S2, respectively. After the incubation, the soil slurries were freeze-dried and stored in the glove box (99.99% N_2 atmosphere).

2.2. Batch sorption experiments

As(V) stock solution was prepared from $Na_2HAsO_4\cdot7H_2O$ (analytical grade, Shanghai reagent company), and As(III) stock solution was prepared from As_2O_3 (analytical grade, Merck). All working standards and solutions for As were prepared by serial dilutions with deionized water. Batch equilibrium experiments were conducted to determine As adsorption isotherms on soils with different treatments. The ionic strength was kept constant at 10 mM in all the experiments by adding NaCl, and pH was adjusted to 5.5 by MES [2-(*N*-morpholino) ethanesulfonic acid hydrate] buffer. Samples of 1.00 g soil were mixed with 25.0 mL aqueous solution of As (initial concentrations ranging from 0 to 10.0 mmol L^{-1}) in polyethylene tubes. After equilibrium for 24 h ($25 \pm 1\,°C$) and centrifugation at 9000 rpm, the supernatant was filtered by using 0.45-μm cellulose filters and stored in the glove box (N_2 atmosphere) until analysis. The solid samples were then freeze-dried for further XPS and XAS characterization. All the adsorption experiments were performed in duplicate. The concentration of As(III) in equilibrium solution was analyzed using hydride generator-atomic fluorescence spectroscopy (HG-AFS Beijing Haiguang) as described by Xu and Zhao [21,22]. The detection limit for As was 0.05 μg L^{-1}. The total concentration of As was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 8000). The concentration of Fe^{2+} in solution was determined by light absorbance measurement at 510 nm using a UV–vis spectrophotometer after reaction with 1,10-phenanthroline [23]. The concentration of total Fe was determined by flame atomic absorption spectrophotometer (Z-2000, Hitachi).

2.3. XPS spectroscopy

The chemical analyses of As sorbed in the soil and species of iron oxides were analyzed by XPS (PHI5000 Versa Probe, ULVAC-PHI, Japan). All the samples were freeze-dried and ground to fine powders prior to the XPS measurement. The XPS spectra were obtained with a monochromatized Al *K*α X-ray source (1486.6 eV) and the pressure in the analytical chamber was below 6×10^{-8} Pa. For wide scan spectra, an energy range of 0–1100 eV was used with the pass energy of 80 eV and the step size of 1 eV. The high-resolution scans were conducted according to the peak being examined with the pass energy of 40 eV and the step size of 0.05 eV. In order to obtain the oxidation status of surface sites and target contaminants, narrow scan spectra for Fe $2p_{3/2}$ and As $3d_{5/2}$ were acquired. The carbon 1s electron binding energy corresponding to graphitic carbon at 284.8 eV was used as a reference for calibration purposes. Narrow scan spectra for Fe $2p_{3/2}$ and As $3d_{5/2}$ were collected in binding energy forms and fitted using a nonlinear least-squares curve-fitting program (XPSPEAK41 software). The XPS spectra were analyzed after subtracting the Shirley background that was applied for transition metals. The full width at half-maximum of those