



Investigation of synthetic ferrihydrite transformation in soils using two-step sequential extraction and the diffusive gradients in thin films (DGT) technique

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ABSTRACT

Ferrihydrite is commonly used as an amendment to remove or stabilize arsenic (As) in water, soils, and sediments due to its high specific surface area ($> 200 \text{ m}^2/\text{g}$). However, its instability under oxic or anoxic conditions sometimes limits its efficiency for arsenic adsorption. This study employed a two-step sequential extraction method and the diffusive gradients in thin films (DGT) technique to investigate the effect of soil properties and water management on ferrihydrite transformation in soils. The results of sequential extraction and DGT indicated that ferrihydrite transformation and dissolution occurred within all treatments in three red soils derived from plate shale (PS), sandstone (SS) and quaternary red clay (QR). Ferrihydrite transformation and dissolution rate under 30% soil water holding capacity (SWHC) treatments were the fastest in PS followed by SS and QR, while in 70% SWHC treatments the order was $\text{SS} > \text{PS} > \text{QR}$. Ferrihydrite in 70% SWHC was transformed about 2–7 times faster than in 30% SWHC for the various treatments. The soil pH may be the main factor controlling ferrihydrite transformation in 30% SHWC, and in 70% SHWC it may work synergistically with Fe(II) as a result of continuous, partial anaerobic conditions formed after about 22 days. Variation among the three soils was controlled by different amounts of soil total organic matter, pH, available Fe, and the content of clay fraction (particulate size $< 0.02 \text{ mm}$). In the present study, SWHC was expected to be the direct factor controlling ferrihydrite transformation and dissolution process. However, the factor controlling these processes was actually variation in soil moisture, which promotes the dissolution of H^+ solutes and formation of Fe(II) in partial anaerobic conditions. The results obtained in this study have demonstrated the potential of using ferrihydrite on contaminated farmland as an amendment for arsenic stabilization.

1. Introduction

Ferrihydrite, a prevalent oxyhydroxide mineral, has been extensively studied in situ and in the lab due to its ability to remove arsenic in water, or to immobilize it in soil and sediment (Kumpiene et al., 2008; Qian et al., 2009; Nielsen et al., 2011). Ferrihydrite has this ability due to its poorly-crystalline structure which has a high binding capacity and large surface area ($> 200 \text{ m}^2/\text{g}$) (Chiang et al., 2012). However, ferrihydrite is generally considered an intermediate phase in the process of forming crystal iron oxides (Johnston and Lewis, 1983; Mazzetti and Thistlethwaite, 2002) and this transformation process

reduces the surface area of ferrihydrite, lowering its ability to adsorb pollutants (Pedersen et al., 2006). Many factors affect the effectiveness of pollutant adsorption by ferrihydrite such as pH, temperature, and abundance of foreign ions (Cornell, 1987; Paige et al., 1996; Das et al., 2010; Bolanz et al., 2013).

Transformation of ferrihydrite at low temperatures takes a long time (10–12 yr) (Schwertmann and Murad, 1983; Schwertmann et al., 2004) while raising the temperature can significantly increase the transformation rate and the reaction may finish in hours or days (Cudennec and Lecerf, 2006; Das et al., 2010). pH is another factor that controls the ferrihydrite transformation rate and formation of products such as

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goethite or hematite. Studies have revealed that under acidic ($\text{pH} \leq 4$) or alkaline conditions ($\text{pH} \geq 10$) the transformation of ferrihydrite to goethite was favored whereas transformation to hematite was favored at the zero point of charge (ZPC) condition ($\text{pH} \sim 7\text{--}8$) (Schwertmann et al., 2004). Existence of ions in solution can also significantly affect ferrihydrite transformation rate. It is widely accepted that most of the inorganic or organic anions (Ford, 2002; Jones et al., 2009; Mikutta et al., 2010; Das et al., 2011; Bolanz, 2013) and some cations (Baltpurvins et al., 1997; Alvarez et al., 2005; Hansel et al., 2011) inhibit ferrihydrite transformation as a function of surface adsorption. The cation Fe(II) has been shown to work in a different way in aqueous solutions and usually acts as a catalyst that strongly promotes ferrihydrite transformation (Pedersen et al., 2005; Hansel et al., 2005; Liu et al., 2007).

In soil environments, the ferrihydrite transformation process is also controlled by pH, temperature, and dissolved ions. Variation in soil moisture and soil characteristics in different soils may also affect the fate of ferrihydrite in soil. Conditions in soil are more complicated than in aqueous solutions and thus more factors may affect ferrihydrite transformation. However, unlike pure aqueous solution, the complicated mineral composition of soil makes it difficult to identify transformation and variation of ferrihydrite that is directly added to soil. This forces researchers to develop new methods to study ferrihydrite transformation in the soil. Nielsen et al. (2014) tested the transformation of ferrihydrite buried in contaminated soil after 4 yr and found that goethite was the most prominent transformation product in contaminated soil. In their study, ferrihydrite was aged in a nylon bag instead of being added directly to soil.

The two step sequential extraction (step A: ferrihydrite phase extraction and step B: well crystalline phase extraction) modified by Nielsen et al. (2014) has proved as a robust method for differentiating amorphous and well crystalline fractionations of iron oxides. The diffusive gradient thin-film technique (DGT) is also accepted as a robust in situ approach for measuring labile elements in waters, sediments and soils (Davison and Zhang, 1994; Gao et al., 2010; Tandy et al., 2011). DGT with Chelex as a binding resin has been widely used for measuring dissolved Fe and can study the process of iron release from a solid phase to a solution phase (Jansen et al., 2003; Naylor et al., 2004; Wu et al., 2011). In the present work, DGT was employed as a novel approach for studying the ferrihydrite dissolution process.

Crystallization of ferrihydrite has been widely studied in aqueous solutions while only limited work has been focused on the ferrihydrite transformation processes in soil due to lack of appropriate methods for soils. Hence, the purpose of this study is to use the newly developed dynamic technique DGT in combination with the established sequential extraction to investigate the factors controlling the transformation/dissolution of ferrihydrite in soils and the kinetics of the crystallization rate of ferrihydrite in soils.

2. Method and materials

2.1. Sites description and soil samples

The arsenic mine (N 29°39'27", E 111°2'20") in Shimen, County of Hunan Province of China had a long time arsenic mining history (over 1000 yr) (Fig. 1). Most of the local soil (over 50%) in this area was derived from parent rock of red soils. The hot spot in regular mine can reach the level as high as $300 \text{ mg}\cdot\text{kg}^{-1}$ (Su et al., 2015). Three sampling sites: Baiyun Town (N 29°41'31", E 111°9'48"), Xinguan Town (29°37'15", E 111°21'60") and Mengquan Town (N 29°24'42", E 111°28'50") labelled in the map were arsenic uncontaminated farmland. Three soils are typical red soils and soil sampled in Baiyun Town is Alliti-Dystric Acrisols derived from plate shale (PS) and soil sampled in Xinguan Town is Hapli-Dystric Acrisols derived from sandstone (SS) and soil sampled in Mengquan Town is Argi-Dystric Acrisols developed from quaternary red clay (QR). Soil samples (0–20 cm) were air-dried,

homogenized, ground, sieved through a 2 mm-mesh and stored in separate polyethylene containers until use. Properties of soils measurement followed the procedures of Du and Gao (2006) and protocols published by Institute of Soil Science, Chinese Academy of Sciences (1978). Particle size composition of the soils was analyzed by aerometer after the dispersing 50 g soil into 0.5 M NaOH solution (finally acquired a 250 mL soil-liquid solution) with pH above 6.0. Soil pH was measured after soaking 10 g soil into 25 mL 1 M KCl solution with 30 min end-to-end shaking. Cation exchange capacity (CEC) was measured by 1 M ammonium acetate exchanging method. Available Fe, Al and Mn were extracted by shaking 10 g of soil in 20 mL of DTPA-TEA-CaCl₃ buffer (pH 7.3) for 2 h at 180 r/min. Total Fe was measured after soil digested in a mixed solution of concentrated HClO₄ and HNO₃ and HF at a ratio 7:9:10. Determination of total-As (concentrated HCl-HNO₃ digestion) and Olsen As (0.5 M NaHCO₃ extraction) were followed the procedures introduced by Wang et al. (2015). The concentration of available Fe, Al, Mn and total Fe were measured by ICP-OES (Thermo Fisher Scientific, 7000 SERIES, USA). The concentration of Olsen-As and total-As were measured by HG-AFS (Ji Tian, AFS-9120, China). (See Table 1.)

2.2. Synthesis of 2-line ferrihydrite

Synthesis of 2-line ferrihydrite was conducted following Cornell and Schwertmann (2003). Iron chloride, FeCl₃·6H₂O, was used as the ferric ion. Briefly, FeCl₃·6H₂O was dissolved in 18.4 Ω MQ water, and the pH of the solution was adjusted to 7–8 by 1 M KOH to obtain the ferrihydrite slurry. A magnetic stirrer was used during the precipitation to make sure FeCl₃ reacted well with KOH. The slurry was washed with MQ water three times and then transferred to a dialysis bag for 10 days of dialysis. After dialysis, the purified ferrihydrite was dried in the oven at 35 °C for 3 days and then ground to a fine powder. The ferrihydrite powder was then sealed in a sample bag and stored in a desiccator at 20 ± 2 °C for further use.

2.3. 2-line ferrihydrite transformation in soils

2-line ferrihydrite powder at concentrations of 0.1% and 1% (w/w) were added to the three soil samples for the ferrihydrite transformation experiment. Each treatment was incubated under 30% and 70% soil water holding capacity (SWHC) to study the effect of soil humidity on ferrihydrite transformation. Treatments without ferrihydrite added incubated under 30% and 70% were set as a control. Soils were sampled at different aging intervals (1 day, 7 days, 15 days, 30 days, 60 days, 90 days, 120 days, 150 days, and 180 days) after adding 2-line ferrihydrite. The three soils were labelled using the following format: Soil number-ferrihydrite concentrations-percentage of SWHC. For example, plate shale soil with ferrihydrite concentrations of 0.1% at 30% of soil water holding capacity is labelled as PS-0.1–30%. There were 18 different treatments in total for the experiments. Ferrihydrite dissolution was measured by Chelex-DGT and the extent of ferrihydrite transformation was determined by sequential extraction. Variance of soil pH was measured from 1–90 days and Fe(II) were measured from 1–30 days respectively.

2.4. Sequential extraction

Procedures for sequential extraction were described by Nielsen et al. (2014). A two-step sequential extraction was employed to differentiate between different iron oxides and distinguish the distribution of contaminants in different phase (Wenzel et al., 2001; Kumpiene et al., 2012). First, poorly crystalline Fe(III)-oxyhydroxides were extracted and second the more crystalline Fe-oxide phase was extracted. A 1 g soil sample reacted with 0.2 M NH₄-oxalate solution at pH 3.25, at a liquid/solid ratio of 25:1. Centrifuge tubes were shaken within an end-to-end shaker for 4 h in the darkness at room temperature and then centrifuged at 3500 r/min after which the supernatant was collected. The remaining

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