

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 absorb 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 (Baltupurins 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- CaCl_3 buffer (pH 7.3) for 2 h at 180 r/min. Total Fe was measured after soil digested in a mixed solution of concentrated HClO_4 and HNO_3 and HF at a ratio 7:9:10. Determination of total-As (concentrated HCl-HNO_3 digestion) and Olsen As (0.5 M NaHCO_3 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, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, was used as the ferric ion. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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 FeCl_3 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 NH_4 -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

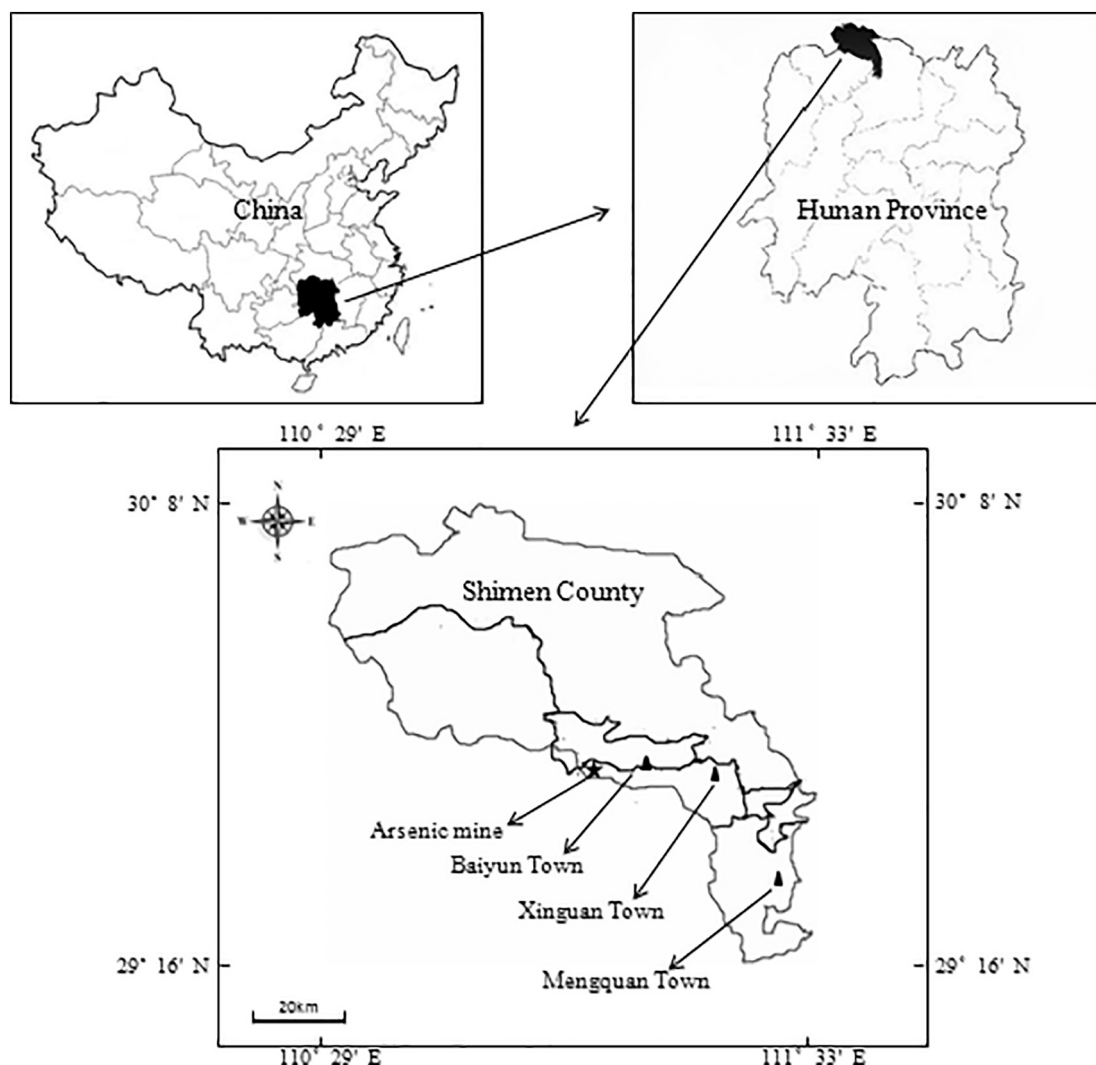


Fig. 1. Location of the study area and samples sites.

Table 1

Chemical and physical properties of the three soils.

Chemical and physical properties of the soils used														
Soil ID	Soil parent material	Particle size (%)				pH	STOM	CEC cmol	Total-As	Olsen-As	Available	Available	Available	Total
		2–0.2 mm	0.2–0.02 mm	0.02–0.002 mm	< 0.002 mm		g/kg	(+)/kg	mg/kg	mg/kg	Fe mg/kg	Al mg/kg	Mn mg/kg	Fe g/kg
PS	Plate shale	34.96	23.79	30.22	11.05	4.00	5.60	14.4	26.03	1.35	19.82	3.84	26.92	36.18
SS	Sandstone	57.42	14.29	19.17	9.12	4.39	6.67	12.2	32.32	1.34	36.11	3.22	10.81	49.43
QR	Quaternary red clay	2.42	16.62	49.88	31.08	4.91	21.55	11.6	14.67	1.35	16.53	3.62	67.67	25.13

Data represent the mean values of duplicate analysis. Values are varied within 0.05.
STOM, soil total organic matter; CEC, cation exchange capacity.

soil was washed by NH_4 -oxalate at a liquid/solid ratio of 12.5:1 for 10 min to acquire a 37.5:1 liquid/solid ratio. Undissolved solids at the bottom were reacted with a 25 mL mixed solution of 0.2 M NH_4 -oxalate and 0.1 M ascorbic acid at pH 3.25 to for obtaining a liquid/solid ratio of 25:1. The centrifuge tube was placed in a water bath at $96 \pm 4^\circ\text{C}$ for 30 min and then centrifuged at 3500 r/min for 5 min. Solutions obtained from step 1 and step 2 of the extraction were then filtered through a $0.45\ \mu\text{m}$ filter membrane and stored at 4°C until ICP-MS analysis (Thermo Fisher Scientific, X SERIES 1, USA).

2.5. DGT

2.5.1. Gel preparation, DGT assembly and deployment

Preparation, assembly, and deployment of DGT followed the method published by Zhang and Davison (1995).

2.5.2. Gel elution and calculation

After soil deployment, DGT were taken out and rinsed with deionized water. The resin gel was removed gently from the sealed DGT and eluted in 1 mL of $1\ \text{mol L}^{-1}\ \text{HNO}_3$ for 24 h. The mass (M) of the target element accumulated on the gel was calculated using Eq. (1),

$$M = \frac{C_e(V_{gel} + V_{acid})}{f_e} \quad (1)$$

where C_e is the concentration of the metal in the elution solution, V_{gel} is the volume of the binding gel, V_{acid} is the acid added for elution (typically 1 mL), and f_e is the elution factor which is normally 0.8 (Zhang and Davison, 1995). The average concentration was determined using Eq. (2),

$$C_{DGT} = \frac{M\Delta g}{DtA} \quad (2)$$

where concentration C_{DGT} ($\mu\text{g/L}$) is calculated based on the mass (M , μg) accumulated on the gel, the thickness of the diffusive path length, diffusive gel and membrane filter (Δg , cm), the diffusive coefficient of the target analyte (D , $\text{cm}^2 \text{s}^{-1}$), the duration of the deployment (t , s), and the area of the sampling window (A , cm^2).

2.6. Measurement of pH and concentration of Fe(II)

pH measurement followed the standard method described by Du and Gao (2006). Fe(II) measurement followed the classic colorimetric ferrozine method (Stookey, 1970). Soil (20 g with water) was centrifuged at 3500 r/min for 10 min and then the supernatant was quickly removed and filtered through a 0.45 μm filter membrane and measured with a UV-spectrophotometer (UV-4802H, Long Nike Instrument Co., Ltd., Shanghai, China).

2.7. QA/QC

All the plastic containers and glassware were washed with MQ water first and then soaked in 10% HNO_3 at least 24 h. They were then thoroughly rinsed with MQ water before use. For Fe(II) UV-spectrophotometer analysis, nitrogen was run through MQ water for 2 h and all the vessels and volumetric flasks to remove oxygen. For ICP-MS analysis, a mixture of Rh, Sc, and Bi was used as the internal standard for calculating recovery.

3. Results

3.1. Physiochemical properties of soils

The texture of PS, SS and QR are loam (41.25% clay, 23.79% silt, 34.96% sand), sandy loam (28.29% clay, 14.29% silt, 57.42% sand) and silty clay loam (81.96% clay, 16.62% silt, 2.42% sand) respectively. Total arsenic contents ranged from 14.67 to 32.32 mg/kg, values that were all lower than the Chinese national standard limit (45 mg/kg at $\text{pH} < 5.5$, CEPA, Chinese Environmental Protection Agency, 1995), which meant the soils were not considered to be arsenic contaminated. The contents of total organic matter ranged from 5.60 to 21.55 mg/kg. pH of three soils varied from 4.00 to 4.91. The concentration of available Fe and total Fe ranged from 16.5 to 36.1 mg/kg and 25.13 to 49.43 g/kg respectively. Among the three soils, SS had the highest concentration of available Fe and total Fe, followed by PS and QR.

3.2. Ferrihydrite transformation process over 180 days

The results of the first extraction step of ferrihydrite from three soils over 180 days are shown in Fig. 2. Ferrihydrite transformation occurred in all treatments of three soils. In PS, it can be clearly observed that ferrihydrite transformed faster in the two 70% SWHC treatments than in the two corresponding 30% SWHC treatments. Ferrihydrite in both 30% SWHC treatments and 70% SWHC treatments experienced a rapid, increasing trend in the first 1–15 days or 1–30 days but had different trends after 30 days. Ferrihydrite in the two 70% SWHC treatments maintained a relatively high, increasing trend until 180 days, while in the 30% SHWC treatments after 30 days the increasing trend of

transformed ferrihydrite slowed down and became stable compared to 70% SWHC treatments. A similar trend was observed in soils SS and QR. In 70% SWHC, ferrihydrite transformed fastest in SS followed by PS and QR, while in 30% SWHC the order was $\text{PS} > \text{SS} \approx \text{QR}$.

3.3. Kinetics of ferrihydrite transformation

Kinetics of the ferrihydrite transformation process in three soils were studied by fitting kinetics parameters obtained in this study using first-order reactions that had been reported in aqueous solutions (Schwertmann and Murad, 1983; Das et al., 2010). Agreement between the experimental data and better fits with the first order reaction (R^2 value; Table 2; Fig. 3) indicated that the ferrihydrite transformation process in soils also followed the first order reaction calculated with a user-defined equation:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]_t$ is the amount of ferrihydrite remaining at time t , $[A]_0$ is initial amount of ferrihydrite to be transformed, k is a rate constant, and t is time.

According to the fitted first order reaction, rate constant k value and half time left $t_{1/2}$ were calculated (Table 2). The k values showed that ferrihydrite transformation was faster in 70% SWHC treatments than in 30% SWHC treatments. The k values in each soil at 0.1% (w/w) ferrihydrite addition with 70% SWHC treatments were 3.49–7.16 times higher than the corresponding 30% SWHC treatments. The k values in each soil at 1% (w/w) ferrihydrite addition with 70% SWHC treatments were 2.27–3.81 times higher than the corresponding 30% SWHC treatments. Comparing the k values of three soils in corresponding treatments, transformation rates in 30% SWHC treatments were highest in the four PS treatments followed by SS and QR, while transformation rates in 70% SWHC treatments were highest in SS followed by PS and QR. These results were consistent with the ferrihydrite transformation process over 180 d discussed above (Fig. 2).

The results of how much ferrihydrite left after $t_{1/2}$ can be used to judge the transformation rate in the three soils with different soil moisture (Table 2). In 30% SWHC treatments, $t_{1/2}$ remaining time was much longer than in the corresponding 70% SWHC treatments. Half transformation of ferrihydrite normally requires thousands of days in 30% SWHC treatments while 70% SWHC treatments may need only hundreds of days for half transformation.

3.4. The process of ferrihydrite transformation to the well crystalline phase iron oxide

Formation of the well crystalline phase and the ferrihydrite transformation process were investigated using 0.1% (w/w) added ferrihydrite because the trends were clearer at this ferrihydrite concentration (Fig. 4). In all three soils as the transformed amount of ferrihydrite increased, the amount of well crystalline phase also increased. The amount of well crystalline phase formed was also related to the amount of ferrihydrite transformed. More ferrihydrite was transformed in SS and the corresponding amount of well crystalline phase formed was also higher than in PS and QR. The amount of well crystalline iron phase formation and ferrihydrite transformation did not follow the approximate 1:1 transformation process as in the aqueous solution (Liu et al., 2007; Das et al., 2010). After 180 days about 48.8% of ferrihydrite transformed in PS-0.1–70% treatment, 60.1% of ferrihydrite transformed in SS-0.1–70% treatment and 36.7% of ferrihydrite transformed in QR-0.1–70% treatment. However, only 26.6%, 32.1%, and 16.6% of the well crystalline phase was formed in the three corresponding treatments respectively. The well crystalline phase was almost half of the amount of transformed ferrihydrite.

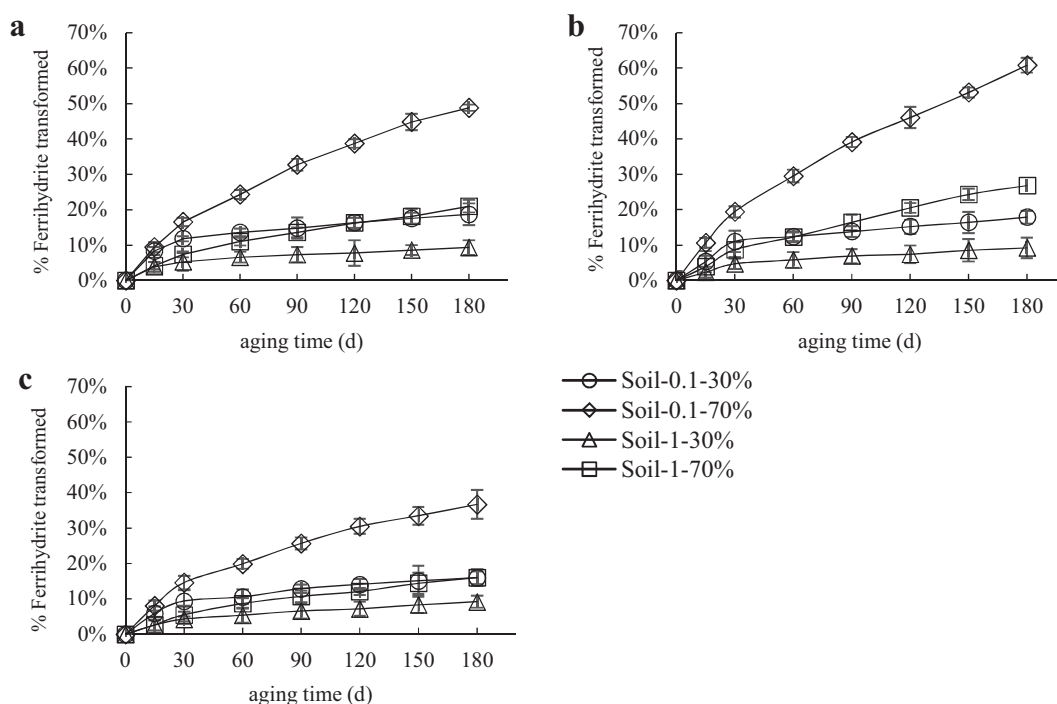


Fig. 2. Relationships of the amount of transformed ferrihydrite with aging time in three soils (a) PS, (b) SS, and (c) QR over 180 days (circle, rhombus, triangle, and square represent soil with 0.1% (w/w) ferrihydrite addition incubated at 30% SWHC, 0.1% (w/w) ferrihydrite addition incubated at 70% SWHC, 1% (w/w) ferrihydrite addition incubated at 30% SWHC, and 1% (w/w) ferrihydrite addition incubated at 70% SWHC, respectively. Error bars represent $\pm$ standard deviation, $n = 3$).

Table 2

First-order reaction rate constants for ferrihydrite transformation in PS, SS, and QR.

Soil ID	k (d) ⁻¹	[A ₁₈₀](%)	$t_{1/2}$ left (d)	R ²	Soil ID	k (d) ⁻¹	[A ₁₈₀](%)	$t_{1/2}$ left (d)	R ²
PS-0.1–30%	7.5×10^{-4}	18.70	924	0.95	PS-1-30%	4.4×10^{-4}	10.60	1575	0.96
PS-0.1–70%	3.4×10^{-3}	48.80	204	0.99	PS-1-70%	1.1×10^{-3}	21.00	630	0.99
SS-0.1–30%	6.7×10^{-4}	17.90	1035	0.95	SS-1-30%	4.2×10^{-4}	9.20	1650	0.98
SS-0.1–70%	4.8×10^{-3}	60.80	144	0.99	SS-1-70%	1.6×10^{-3}	26.80	433	0.99
QR-0.1–30%	6.3×10^{-4}	15.70	1100	0.93	QR-1-30%	3.7×10^{-4}	7.70	1873	0.96
QR-0.1–70%	2.2×10^{-3}	36.70	315	0.98	QR-1-70%	8.4×10^{-4}	16.50	825	0.97

k is transformed rate; [A₁₈₀] is ferrihydrite transform on 180d; $t_{1/2}$ left is time of half ferrihydrite left; R² is the coefficient of determination.

3.5. Variance of labile Fe in soil

DGT results are in Fig. 5. After ferrihydrite addition, the concentration of labile Fe increased to a peak followed by a decreasing trend until the end of the experiment. However, the concentration of labile Fe varied significantly between the two SWHC treatments. For PS (Fig. 5a), the concentration of labile Fe in the two 70% SWHC treatments increased quickly from 105.73 to 179.25 $\mu\text{g/L}$ (PS-0.1–70%) and 110.45 to 222.05 $\mu\text{g/L}$ (PS-1-70%) followed by a gradual increasing trend until the two 70% SWHC treatments reached a peak. After the peak, the concentration of labile Fe decreased gradually until 180 days to 128.62 $\mu\text{g/L}$ and 178.40 $\mu\text{g/L}$ for PS-0.1–70% and PS-1-70%, respectively. Just like 70% SWHC, the concentration of labile Fe in two 30% SWHC treatments also increased quickly in the first 15 days but did not have a gradual increase, instead it directly reached the peaks (160.78 $\mu\text{g/L}$ for PS-0.1–30% and 189.11 $\mu\text{g/L}$ for PS-1-30%) and went down until the end of the aging experiment with the value of 98.28 $\mu\text{g/L}$ for PS-0.1–30% and 109.05 $\mu\text{g/L}$ for PS-1-30%.

The concentration of labile Fe in varied SWHCs of SS (Fig. 5b) and QR (Fig. 5c) experienced a similar trend to PS but there were some differences among the three soils. The concentration of labile Fe in 70% SWHC treatments increased more quickly in SS compared to PS. In contrast, under 30% SWHC treatments, labile Fe increased more quickly in PS compared to SS. In addition, the peak of labile Fe in SS

occurred about one month later than PS. Variance of labile Fe in QR was lower than PS and SS during the whole ferrihydrite dissolution process. No stable, increasing trends were observed in the two 70% SWHC treatments of QR and peaks were much earlier (15 days) than PS and SS. However, the variance of labile Fe in QR in the two 30% SWHC treatments was only slightly lower than SS. The above results indicated that different soil moistures affected the ferrihydrite dissolution process and that differences in some soil properties control ferrihydrite dissolution in various soils.

3.6. Variance of pH, Eh, and Fe(II)

In order to see if pH affects ferrihydrite transformation in soil, the variance of pH values were measured over 90 days during ferrihydrite transformation (Table 3). In the first 15 days, pH values in the three soils increased quickly in 30% SWHC, but after 30 days the pH values stopped increasing. The increasing trend of pH in 70% SWHC was also fast in the first 30 days but different than 30% SWHC in that pH had a slow increasing trend in 70% SHWC until this trend became relatively stable after 60 days. The variance of pH under 30% SWHC in three soils followed the order PS > SS > QR in the first 30 days. Variance of pH in 70% SWHC also followed the order PS > SS > QR in the first 30 days. However, after 30 days, pH of SS increased faster than PS which lead to the final order SS $\approx$ PS > QR at 90 days in 70% SWHC.

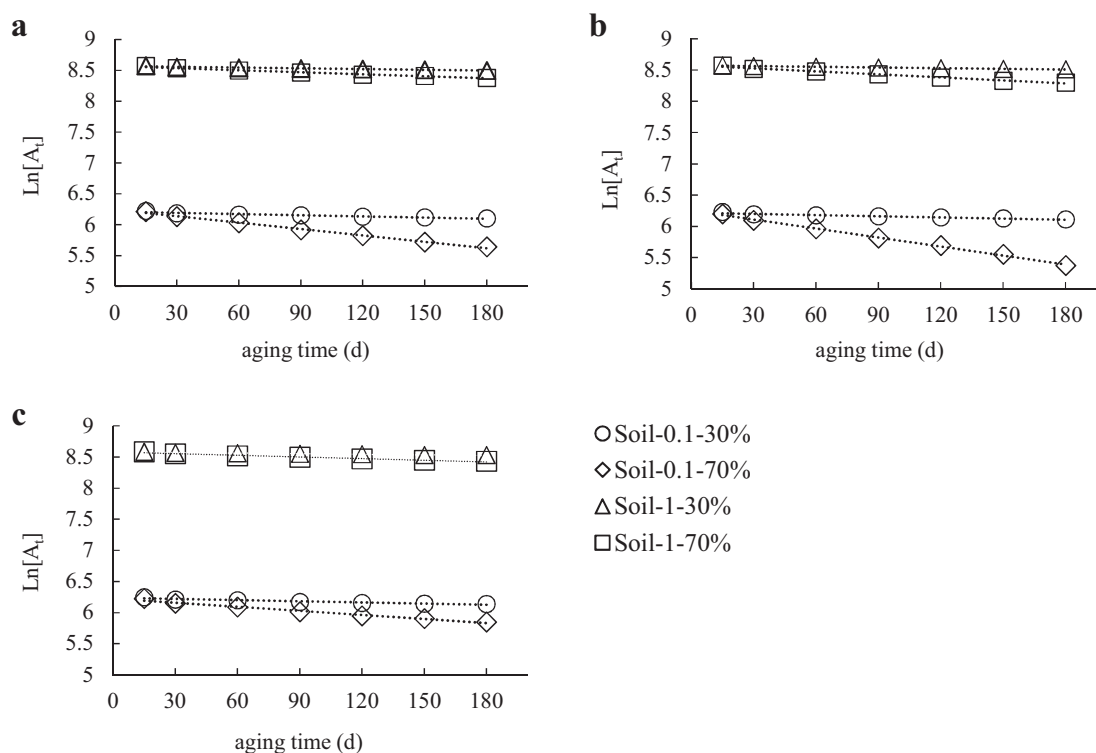


Fig. 3. Ferrihydrite transformation data fitted with a first-order reaction in three soils (a) PS, (b) SS, and (c) QR (circle and rhombus represent soil with 0.1% (w/w) ferrihydrite addition incubated at 30% and 70% SWHC; triangle and square represent soil with 1% (w/w) ferrihydrite addition incubated at 30% and 70% SWHC).

Variances of Fe(II) and Eh in the three soils were measured during the first 30 days (Fig. 6). The Eh values decreased from 433.5 to 279.5 mV (PS), 424.2 to 269.2 mV (SS), and 408.6 to 247.9 mV (QR) after 30 days in 70% SWHC. In contrast, the concentration of Fe(II) increased. From 0 day to 7 days, no Fe(II) was detected in PS and QR

and only a small amount of Fe(II) was detected in SS. This meant that the soils maintained an aerobic condition and were not conducive to formation of Fe(II). From 15 days until 30 days, Fe(II) was detected in all three soils and increased significantly, indicating that the soils gradually stepped into exhibited partial anaerobic condition. The

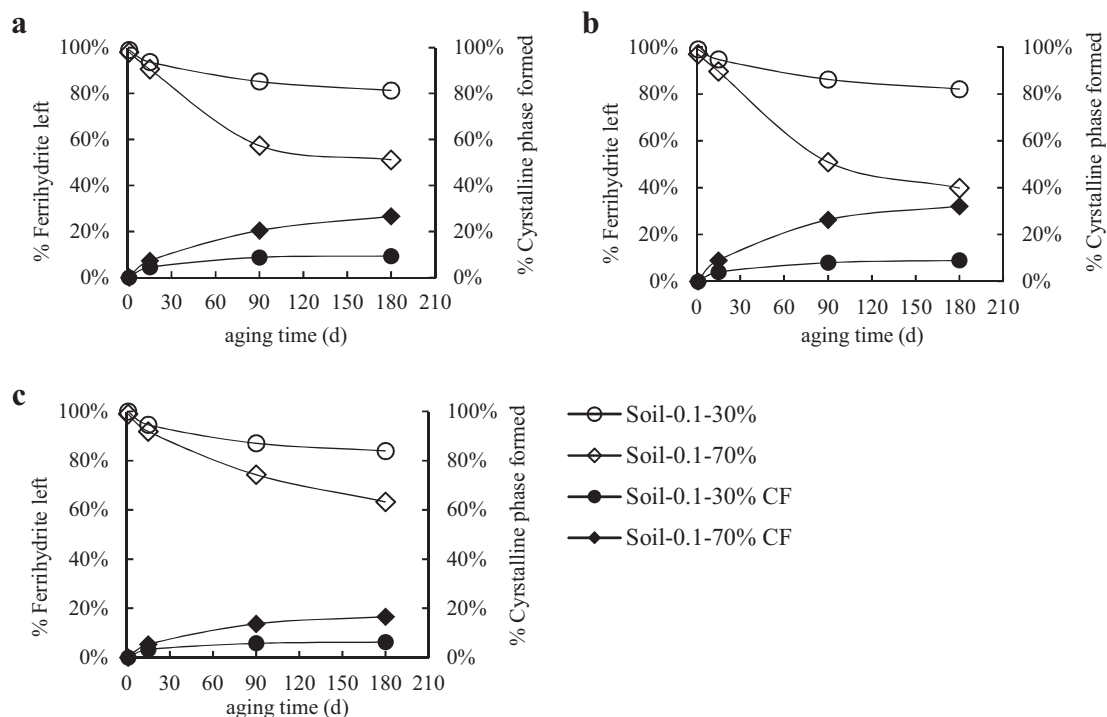


Fig. 4. Ferrihydrite transformation and well crystalline phase formation process in three soils (a) PS, (b) SS, and (c) QR during 180 days aging time (open circle and rhombus represent soil with 0.1% (w/w) ferrihydrite addition incubated at 30% and 70% SWHC; solid circle and rhombus represent the well crystalline phase formation (CF) at the corresponding 30% and 70% SWHC).

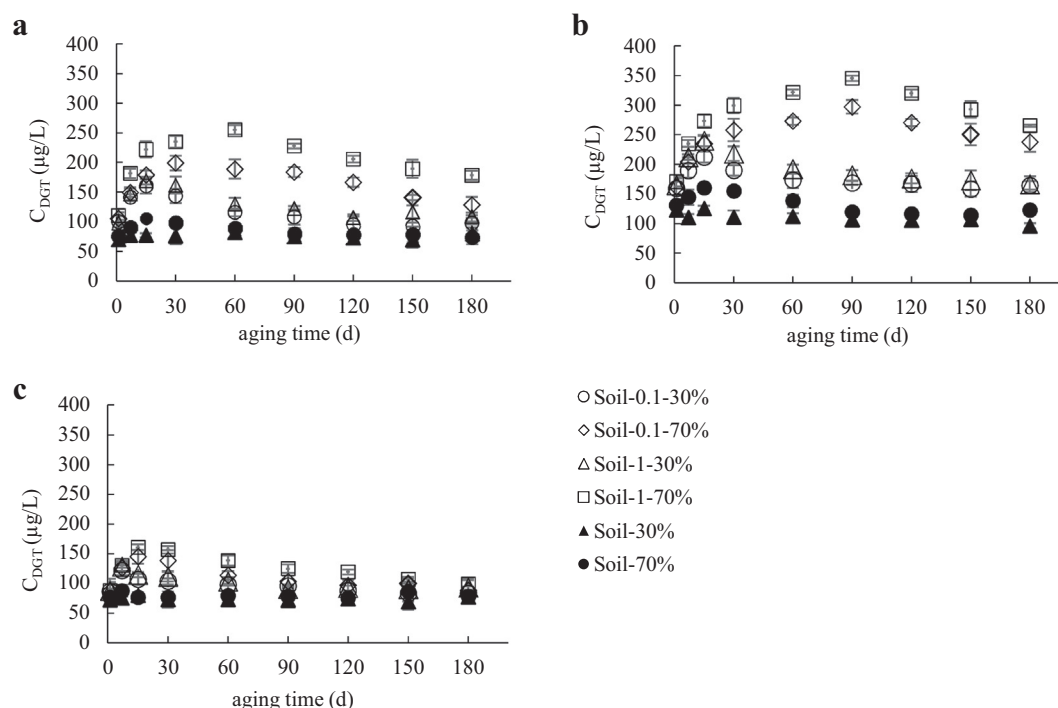


Fig. 5. The variance of labile Fe during the 180-day aging process by DGT measurement in three soils (a) PS, (b) SS and (c) QR (open circle and rhombus stand for the soil with 0.1% (w/w) ferrihydrite addition incubating at 30% and 70% SWHC; open triangle and square stand for the soil with 1% (w/w) ferrihydrite addition incubating at 30% and 70% SWHC; solid triangle and circle stand for the soil with no ferrihydrite addition incubating at 30% and 70% SWHC. Error bars represent $\pm$ standard deviation, $n = 3$).

Table 3
Variation of pH in three soil 30% and 70% SWHC treatments in 90 days.

Soil ID	7 days		15 days		30 days		60 days		90 days	
	30%	70%	30%	70%	30%	70%	30%	70%	30%	70%
PS	4.39	4.55	4.71	5.21	4.90	5.31	4.88	5.50	4.94	5.55
SS	4.50	4.86	4.71	5.19	4.84	5.37	4.92	5.69	4.90	5.88
QR	5.05	5.14	5.16	5.38	5.17	5.46	5.13	5.49	5.12	5.56

concentration of Fe(II) in three soils under 70% SWHC followed the order SS > PS > QR. In 30% SWHC, the Eh values remained stable in the first 30 d and almost no Fe(II) could be detected during this time period in the three soils. This indicated that anaerobic conditions did not form under 30% SWHC.

4. Discussion

4.1. The effect of different SWHCs on the transformation of ferrihydrite in soils

In this study, 30% and 70% SWHC were selected to study the effects of different soil moistures on the transformation of ferrihydrite in soil. The results suggested that higher soil humidity conditions caused a significantly faster reaction rate of Fe(III) transformation in soils. What needs to be taken in consideration is that different soil moisture is not the true factor that affects the ferrihydrite transformation process. Instead, under 70% SWHC treatments, the increased amount of soil solution promotes dissolution of water-soluble solutes in the soil solution, which approaches the characteristics of a pure aqueous solution. Hence, in soil environments with higher SWHC, some solutes like H^+ or Fe(II) that accelerate the transformation process in aqueous solution should play dominant roles in this process in the soil.

4.2. The effect of pH and Fe(II) on the transformation of ferrihydrite in soils

The present study was conducted at room temperature ($25 \pm 2^\circ C$) with soil pH of 4–4.91. Variances of pH in three soils showed that ferrihydrite transformation and the dissolution process were related to depletion of H^+ . Previous studies have acquired similar results of ferrihydrite transformation under acidic conditions (Schwertmann and Murad, 1983; Das et al., 2010). Schwertmann and Murad (1983) concluded that H^+ induces ferrihydrite dissolution under acidic conditions by formation of intermediates. $FeOOH$ was favored to be protonized with H^+ and form an intermediate $Fe(OH)_2^+$ ($pH > 4$, $FeOOH + H^+ \rightarrow Fe(OH)_2^+$) or $Fe(OH)^{2+}$ ($pH < 4$, $FeOOH + 2H^+ \rightarrow Fe(OH)^{2+} + H_2O$). Such Fe(III) intermediates can gradually form the well crystalline iron phase by discharging at the crystal surface. Lindsay and Schwab (1982) pointed out that intermediates of $Fe(OH)_2^+$ may be formed and be the dominant species in solutions under neutral or acidic conditions ($pH < 7.4$). Mohapatra et al. (2005) found that in acidic conditions ($pH 4-6$) release of arsenic occurred from arsenic loaded ferrihydrite due to the dissolution of solid phases by H^+ . Protonation should be the main effect of H^+ on ferrihydrite transformation.

In spite of the function of H^+ , it could be inferred that different results between 70% SWHC and 30% SWHC indicated that other solutes may work synergistically with H^+ to accelerate ferrihydrite transformation in the soil environment. Fe is one of the most abundant elements in the soil, and its ferrous ion can significantly accelerate the transformation of ferrihydrite to the secondary phase even at room temperature (Hansel et al., 2005; Yee et al., 2006; Boland et al., 2014). Fe (II) in the soil may come from three places: natural Fe(II) in soil (very small amount); under partial anaerobic condition, added ferrihydrite may act as an electron receiver and form Fe(II); or soil reductive materials such as organic acids that come from root exudation (Lindsay and Schwab, 1982), activities of microbes (Zachara et al., 2002), or other reductive materials (Lovley and Phillips, 1987; Davidson et al., 2003) may reduce the Fe(III) to Fe(II). In addition, one study showed that both stability and solubility of Fe(II) would be enhanced under acidic conditions and Fe(II) can primarily exist as an aqueous species

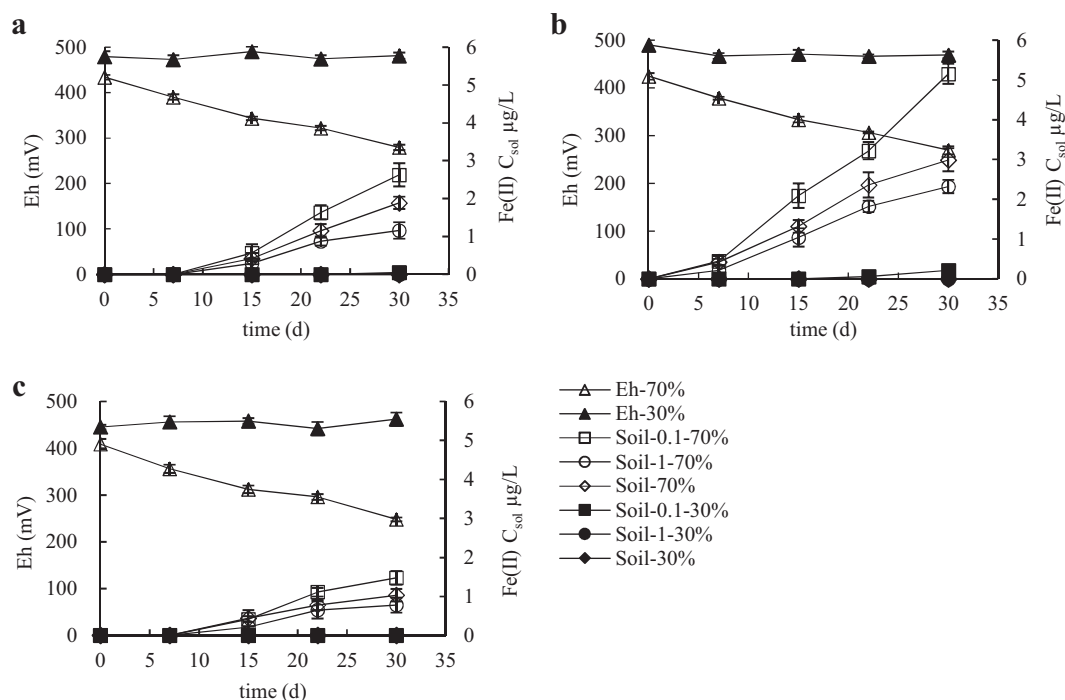


Fig. 6. Variance of Fe(II) and Eh in the first 30 days of three soils (a) PS, (b) SS, and (c) QR (solid triangle, rhombus, square, and circle represent Eh, soil with 0.1% (w/w), 1% (w/w), and no ferrihydrite addition incubated at 30% SWHC, respectively; open triangle, rhombus, square, and circle represent Eh, soil with 0.1% (w/w), 1% (w/w), and no ferrihydrite addition incubated at 70% SWHC, respectively). Error bars represent means $\pm$ standard deviation, $n = 3$).

Table 4

Comparison of clay contents, STOM, pH and available Fe in three soils.

Soil ID	Clay contents < 0.02 mm (%)	pH	STOM g/kg	Available Fe mg/kg
PS	41.25b ^a	4.00c	5.60c	19.80b
SS	28.29c	4.39b	6.68b	36.1a
QR	80.96a	4.91a	21.55a	16.50c

^a Values followed the different letters mean there are significant differences at $p < 0.05$ by Duncan's one-way ANOVA analysis.

even in the presence of oxygen (Weber et al., 2006). This indicated that in partially anaerobic acidic soils, it is possible that dissolved Fe may be gradually reduced in the microsite (these anaerobic microsite normally exists in soil suspensions resulting from the respiration of plant roots or microbes) and formed Fe(II) (Schwab and Lindsay, 1983; Wolf and Russow, 2000). The freshly formed Fe(II) will become the main driving force of the ferrihydrite transformation in soils (Vodyanitskii, 2010; Nielsen et al., 2014). In the present study, the different trends between 30% and 70% SWHC treatments are more likely to be an effect of Fe(II). Soil under 70% SWHC gradually exhibited a partial anaerobic condition after 22 d and the concentration of Fe(II) gradually increased (Fig. 6). The presence of Fe(II) may play a dominant role in catalysing ferrihydrite dissolution while this process was almost impossible in 30% SWHC. This result also explained why in 70% SWHC of three soils, ferrihydrite dissolution process experienced a stable, increasing trend while this did not happen in 30% SWHC.

The products of ferrihydrite transformation in the present study were not measured by an x-Ray Diffractometer (XRD) because peaks in the spectrum results when a small amount of ferrihydrite is added can be easily obscured by peaks from the original existing minerals or iron oxides (hydroxide). Even though it is difficult to measure products in the soil, the categories of products in the present study can still be assumed base on previous studies. The dominant products in the present study are likely to be goethite and lepidocrocite (25 ± 2 °C, pH ~4–5) as a result of the effect of H^+ and Fe(II). Some studies have provided

robust evidence that goethite is more likely to form at pH ~2–5, and that lepidocrocite is a favourable product together with goethite in the presence of Fe(II) during ferrihydrite dissolution and the Fe(III) intermediates reprecipitation process (Schwertmann and Murad, 1983; Liu et al., 2005; Vodyanitskii, 2010; Das et al., 2011; Boland et al., 2014).

4.3. The effect of soil properties on the transformation of ferrihydrite in soils

According to the above discussion, H^+ and Fe(II) can significantly accelerate ferrihydrite transformation. Hence, it is inferred that varied fate of ferrihydrite in the three soils may be related to soil properties including pH and available Fe. Original soil pH values followed the order PS < SS < QR indicating the soil acidity followed the order PS > SS > QR (Table 4). This is consistent with the order of ferrihydrite transformation rate in 30% SWHC and 70% SHWC during the first 15 or 30 days (when partial anaerobic conditions had not formed yet). Available Fe can be understood as a pool for storage of dissolved Fe(III). Available Fe in the three soils followed the order SS > PS > QR (Table 4). This result is consistent with the order of ferrihydrite transformation rate in 70% SHWC treatments, indicating that more dissolved Fe(III) can be reduced to Fe(II) in SS once the soil exhibited the partial anaerobic condition. The result in Fig. 7 provides clear evidence that the concentration of Fe(II) in SS-70% (no ferrihydrite addition) was significantly higher than PS-70% and QR-70%, meaning that in soil with more dissolved Fe, the more Fe(II) could be formed under 70% SWHC.

It had been widely accepted that soil clay minerals and organic matter can hinder ferrihydrite transformation via (1) being adsorbed to the ferrihydrite surface or coprecipitated with ferrihydrite; or (2) adsorbing dissolved Fe(III) or intermediates (Schwertmann, 1966; Tipping et al., 2002; Schwertmann et al., 2005; Bhattacharyya and Gupta, 2008). Based on this, it could be inferred that the two pathways may be related to the decreasing trend of ferrihydrite transformation and the dissolution process present in this work (Fig. 2 and Fig. 5) and varying contents of soil total organic matter (STOM) and clay minerals may finally determine the fate of ferrihydrite in three soils. It was clear that

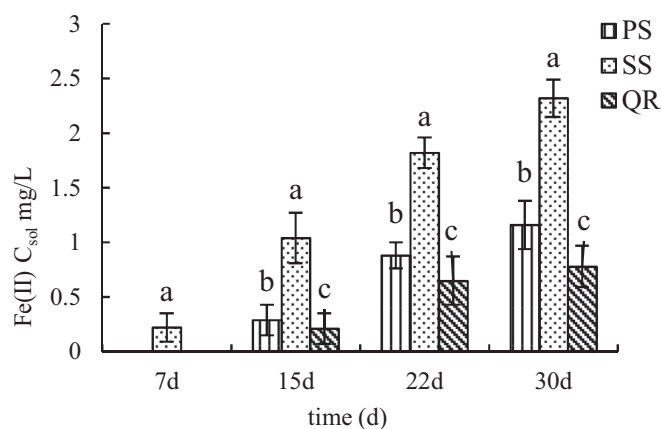


Fig. 7. Comparison of Fe(II) variation in three soils without ferrihydrite addition in 70% SWHC during 30 days (Values followed the different letters mean there are significant differences at $p < 0.05$ by Duncan's one-way ANOVA analysis. Error bars represent means $\pm$ standard deviation, $n = 3$).

the contents of STOM and clay fraction (< 0.02 mm) in QR were significantly higher than SS and PS and this may be the reason that the transformation process was slow in QR (Table 4). In addition to this, because of the adsorptive effect of Fe ions or intermediates, the ratio of formed well crystalline iron oxide/transformed ferrihydrite was lowest in QR (Fig. 4).

5. Conclusions

This study is the first to couple the sequential extraction and DGT technique, and the results have provided a new prospective for understanding iron oxide transformation and the dissolution process in soils. The present study demonstrated the fate of ferrihydrite in three acidic soils and identified some factors that may influence ferrihydrite transformation in the soil environment. Soil moisture is a main factor that influence ferrihydrite transformation while the soil pH and effect of Fe(II) (as a catalyst) are the main driving force that accelerated ferrihydrite transformation in acidic soils. On the contrary, soil organic matter and clay minerals might retard ferrihydrite transformation in the soil environment.

The implication of this study is the potential use of ferrihydrite on contaminated farmland as an amendment for arsenic stabilization and hence reducing arsenic availability and toxicity. There are other mechanisms for arsenic immobilization in soils, especially under reducing conditions with high SHWC or waterlogged farmland, for example, through the formation of As sulphides. Soil maintained at a low or moderate SWHC (such as 30%–50%) can ensure that ferrihydrite is continually effective at absorbing arsenic for over 5–6 yr. In addition, this study has also shown that soil with higher content of organic matter or clay minerals possibly enhances the effectiveness of ferrihydrite for an even longer time.

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