



# Immobilization and release risk of arsenic associated with partitioning and reactivity of iron oxide minerals in paddy soils

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Received: 23 March 2020 / Accepted: 26 May 2020 / Published online: 19 June 2020  
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## Abstract

The consumption of agricultural products grown on paddy soils contaminated with toxic element has a detrimental effect on human health. However, the processes and mechanisms of iron (Fe) mineral-associated arsenic (As) availability and As reactivity in different paddy soil profiles are not well understood. In this study, the fractions, immobilization, and release risk of As in eleven soil profiles from the Changzhutan urban agglomeration in China were investigated; these studied soils were markedly contaminated with As. Sequential extraction experiments were used to analyze fractions of As and Fe oxide minerals, and kinetic experiments were used to characterize the reactivity of Fe oxide minerals. The results showed that concentrations of total As and As fractions had a downward trend with depth, but the average proportions of As fractions only showed relatively small changes, which implied that the decrease in the total As concentrations influenced the changes in fraction concentrations along the sampling depth. Moreover, we found that easily reducible Fe ( $\text{Fe}_{\text{ox}1}$ ) mainly controlled the reductive dissolution of the Fe oxides, which suggest that the reductive dissolution process could potentially release As during the flooded period of rice production. In addition, a high proportion of As was specifically absorbed As (As-F2) (average 20.4%) in paddy soils, higher than that in other soils. The total organic carbon (TOC) content had a positive correlation with the amount of non-specifically bound As (As-F1) ( $R = 0.56$ ), which means that TOC was one factor that affected the As extractability in the As-F1. Consequently, high inputs of organic fertilizers may elevate the release of As and accelerate the diffusion of As.

**Keywords** Arsenic fraction · Iron oxide minerals · Paddy soil profile · Sequential extraction · Reaction kinetics

## Highlights:

- Goethite and hematite played important roles in As immobilization in paddy soil.
- Easily reducible Fe ( $\text{Fe}_{\text{ox}1}$ ) mainly controlled the reductive dissolution of the Fe oxides.
- TOC showed a positive correlation with the amount of As-F1.
- High inputs of organic fertilizers may elevate the release of As.

Responsible editor: Kitae Baek

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s11356-020-09480-y>) contains supplementary material, which is available to authorized users.

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## Introduction

Arsenic (As) is a toxic element that can directly and indirectly affect human health (e.g., cancers, vascular disease, neurological disorders, and skin lesions) (Jain and Ali 2000; Hughes 2002; Naujokas et al. 2013). The terrestrial abundance of As is in the range of 1.5–3 mg kg<sup>-1</sup> (Thornton and Farago 1997; Mandal and Suzuki 2002), while in China, background values of As in soil range from 0.01 to 626 mg kg<sup>-1</sup> (Mandal and Suzuki 2002). In Chenzhou (Hunan province, China), owing to anthropogenic industrial activities, As concentrations of agricultural lands (paddy and vegetable soils) range from 11.0 to 1217 mg kg<sup>-1</sup> and the As contents of the rice grain are high (0.5 to 7.5 mg kg<sup>-1</sup>) (Liao et al. 2005), often exceeding the maximum permissible limit of the Chinese food hygiene standard (0.2 mg kg<sup>-1</sup> dry matter, GB2762-2017).

The release of As to the environment is related to natural phenomena (volcanism, rock weathering, biological activity), and anthropogenic inputs (mining, smelting, agriculture, tanning operations, wood treatment, pesticide manufacturing, coal-burning, and so on) (Alam et al. 2003; Camm et al. 2004). Factors such as climate, organic and inorganic components of the soils, and redox potential status affect As mobility in soils (Mandal and Suzuki 2002). The behavior of As in soils control adsorption reactions (mostly involving iron (Fe) oxides) and the precipitation of secondary minerals (mostly Fe- or Ca-arsenates) (Farquhar et al. 2002; Cancès et al. 2005; Sør et al. 2017). Many studies have been performed on the reactivity of Fe minerals and As in groundwater, aquifer sediments, and soils (Fritzsche et al. 2011; Root et al. 2013; Tong et al. 2014; Park et al. 2016). For example, Cancès et al. (2005) found that more than 65% of the As content was released upon the dissolution of amorphous Fe oxides in soil in Auzon, which indicated that As has a major association with Fe oxide phases. The release of As is correlated to the reductive dissolution of Fe oxide minerals in sediments, and the rate of release is controlled by the availability of reactive organic carbon (Postma et al. 2010).

The presence of natural organic matter (NOM) is an important factor that may influence the fate of As in soils. Numerous studies have demonstrated that competition for the adsorption of NOM could lead to the release of As from minerals and soils (Gustafsson 2006; Weng et al. 2009). Quicksall et al. (2008) found that the degree and rate of organic matter decomposition controlled the localized geochemical parameters for As release and sequestration. Arsenic could also form complexes with NOM and bridge Fe(III)-OM complexes (Redman et al. 2002; Sharma et al. 2010). In addition, As mobilization seemed to be initiated by the reduction of Fe-oxide by sedimentary organic matter (Postma et al. 2007). Hence, the presence of NOM should be considered when assessing As mobilization and release in paddy soils.

The toxicity of As is not only dependent on its total amount but also its chemical form and oxidation state (Hughes 2002). Different As fractions have different physicochemical properties and bioavailability. Therefore, assessments of As fractions in soils are essential. Arsenic sequential extraction procedure (SEP) is a useful method that can be applied to investigate the geochemical partitioning and chemical binding of As in solids; this method is suitable for evaluating the As mobility in a variety of solid environmental samples (Wenzel et al. 2001; Cancès et al. 2008; Costagliola et al. 2013; Kim et al. 2014; Liu et al. 2018). In most cases, As mobilization and release are correlated with the reductive dissolution of Fe oxides (oxyhydroxides) (McArthur et al. 2001; Park et al. 2016); in paddy soils, As distribution is closely associated with iron minerals, and amorphous Fe minerals control the state of As (Yamaguchi et al. 2011; Ji et al. 2019). Therefore, it is necessary to investigate the partitioning of Fe oxides and its reductive dissolution behavior in soils. Sequential extraction of Fe by using different reagents can help to quantify Fe-bearing minerals, and this approach has been successfully applied in soils and sediments (Claff et al. 2010; Shen et al. 2018; Ma et al. 2019). The reductive dissolution and kinetic behaviors of Fe oxides in synthetic minerals and natural sediments can be characterized by using a reactive continuum model for time-dependent reduction rates (Houben 2003; Larsen et al. 2006; Davranche et al. 2013).

Changzhutan is the industrial and economic center of Hunan province, and considerable investigations about As contamination have been conducted in this region. These studies mainly focused on the content of As in paddy soils or As biogeochemical assessment of rice paddies to predict elemental partitioning in rice (Williams et al. 2009; Ma et al. 2016; Yi et al. 2018). Owing to the relationship between As mobilization and Fe-oxide mineral distribution or reactivity in soils (Yamaguchi et al. 2011; Ji et al. 2019), it is essential to investigate the specific relationship between As fractions and partitioning, as well as the reductive dissolution of Fe oxide minerals in different paddy soil profiles. This is of vital importance for assessing As behavior, the safety of agricultural products, and the associated health risks in this region.

## Materials and methods

### Sampling area and soil sampling

Hunan province is located in central China. The sampling area is located in east-central Hunan province, which includes three cities (Changsha, Zhuzhou, and Xiangtan) that form the Changzhutan urban agglomeration. This urban agglomeration lies between a latitude of 26.03° N and 28.41° N and a longitude of 111.53° E and 114.15° E. The climate in this region is of a subtropical moist monsoon type, and the annual

mean rainfall is 1,300 to 1,500 mm, which makes this area preferable for planting subtropical crops (Liao et al. 2005; Liu et al. 2005; Yi et al. 2018). The Hunan province is a major grain-producing region. Crops are cultivated all year round with rice as the predominant crop; crop rotation is scarcely practiced. In order to ensure accurate representation, the sampling sites were selected based on whether local farming habits have been practiced in that site over the past several decades. This study focused on eleven soil profiles from a variety of different paddy fields located in the suburbs; five were collected from Changsha city (CZT1–5), two from Xiangtan city (CZT6 and 8), and four from Zhuzhou city (CZT7, 9–11) (Fig. 1). Both soils were classified as Hydragric Anthrosols in the World Reference Base for Soil Resources (WRB) soil classification (IUSS Working Group WRB 2015). At the time of sampling, first, soil samples were collected from different soil layers at depths of 0–100 cm from each site by using a macro-core soil sampler, when soils were under flooded conditions. Second, the soil samples were dried in air. Finally, the dried soils were crushed with a wooden hammer and passed through a 100 mesh sieve for subsequent analysis.

### Soil physico-chemical properties

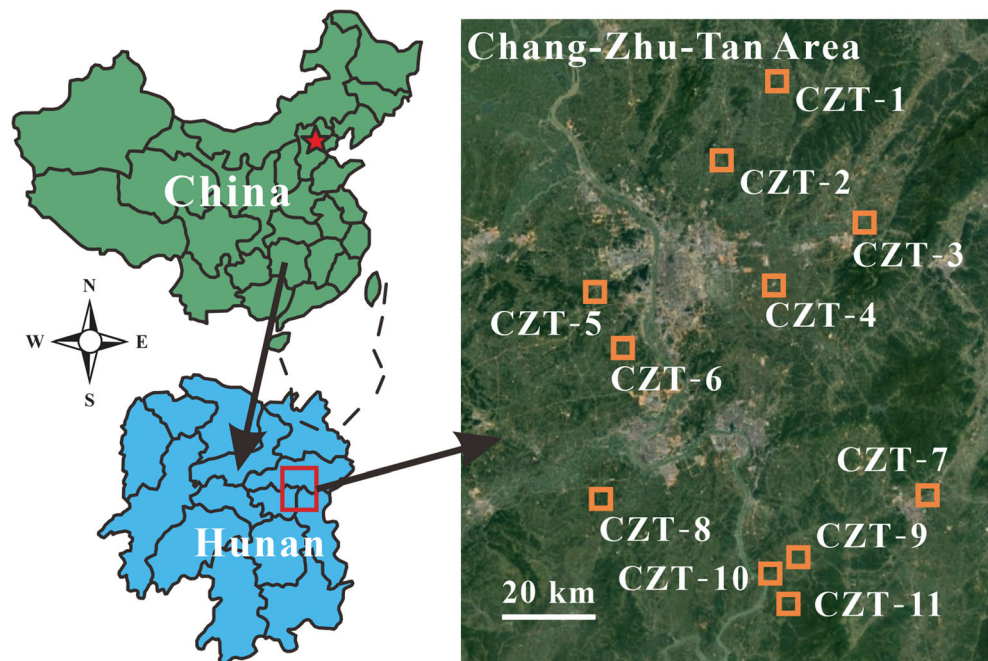
Before analysis, soil samples were freeze-dried, ground to produce a fine powder, sieved ( $< 0.15$  mm), and digested by using  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  (USEPA 1996). Then, As concentrations were detected by using atomic fluorescence spectrometry (AFS, PSA-10.825, PS Analytical), and Fe concentrations

were measured by using atomic absorption spectrometry (AAS, PinAAcle 900T, PerkinElmer). Arsenic and Fe recoveries in reference samples (certified soil GBW07307, Institute of Geophysical and Geochemical Exploration, Langfang, China) were analyzed to be in the range of  $90.9 \pm 3.5$  to  $97.4 \pm 4.9\%$ . The pH of soil samples in a soil suspension containing 10 mM  $\text{CaCl}_2$  (a solid-to-liquid ratio of 1:5) was measured by using a pH/ORP meter (S400 Seven Excellence, METTLER TOLEDO). Hydrochloric acid digestion was used to remove the total inorganic carbon in soil samples, and the total organic carbon (TOC) concentration was detected by using a TOC analyzer (MODEL 1030S, OI Analytical).

### Arsenic fractions

In this study, the As sequential extraction method described by Wenzel et al. (2001) was adopted to investigate As fractions in the soils. Five extraction suspensions identify five As fractions: (I) used 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  to extract non-specifically bound As (As-F1); (II) used 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  to extract the specifically bound As (As-F2); (III) employed 0.2 M  $\text{NH}_4$ -oxalate (pH 3.25) to extract the amorphous Fe hydrous oxides-bound As (As-F3); (IV) employed 0.2 M  $\text{NH}_4$ -oxalate and 0.1 M ascorbic acid (pH 3.25) to dissolve the extraction of As bound to crystalline Fe hydrous oxides (As-F4); (V) employed  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  to digest the residual As (As-F5). The details of As sequential extraction are shown in Table S1. Three replicates of the samples for As fractions were performed. While the accuracy of the sequential extraction procedure was verified by comparison of the difference

**Fig. 1** Locations of the study area and sampling sites



between the sum of each phase concentration and the total concentration of As. The recoveries of Fe and As in sequential extraction ranged from 90 to 110%.

### Partitioning of Fe oxides

Fe oxides were sequentially extracted by different extraction reagents according to the method described by Poulton and Canfield (2005). In brief, the following reagents were used: (1) 1 M MgCl<sub>2</sub> (pH 4.5, extraction time 2 h) to extract exchangeable free Fe<sup>2+</sup> (Fe(II)); (2) 1 M NaOAc (pH 4.5, extraction time 24 h) to extract the Fe associated with carbonate (Fe<sub>carb</sub>), including siderite and ankerite; (3) 1 M hydroxylamine-HCl (extraction time 48 h) to dissolve the extraction of easily reducible Fe (Fe<sub>ox1</sub>), including ferrihydrite and lepidocrocite; (4) 0.28 M sodium dithionite with 0.35 M acetic acid and 0.2 M sodium citrate (pH 4.8, extraction time 2 h) to extract reducible Fe (Fe<sub>ox2</sub>), including goethite, hematite, and akaganeite; (5) 0.2 M ammonium oxalate and 0.17 M oxalic acid (pH 3.2, extraction time 6 h) to extract magnetite (Fe<sub>mag</sub>) (Phillips and Lovley 1987); (6) HNO<sub>3</sub>-HCl-HF mixture to extract the poorly reactive sheet silicate Fe and the residual Fe (Fe<sub>r</sub>). The details of the sequential extraction of Fe oxides are shown in Table S2. Three replicates of the samples for iron fractions were performed, while the accuracy of the sequential extraction procedure was verified by comparison of the difference between the sum of each phase concentration and the total concentration of iron. The recoveries of Fe and As in sequential extraction ranged from 90 to 110%.

### Reaction kinetics of Fe oxide minerals

The method developed by Postma et al. (2010) was used to identify the reaction kinetics of Fe oxide minerals in soils (Raiswell et al. 2010; Zhu et al. 2014; Shen et al. 2018). In this study, two parallel experiments were performed for each soil sample, one in which a 1 mM HCl solution (pH 3) was used as the extractant only for Fe(II) minerals, and another in which a 10 mM ascorbic acid solution adjusted to pH 3 with HCl was used as the extractant for Fe(III) oxides and Fe(II) minerals. Each soil sample and extractant were mixed with a solid-to-liquid ratio of 1:100 in a 50-mL centrifuge tube and stirred at 150 rpm in a thermostatic oscillator for 1–72 h. The suspension was sampled periodically by using 5-mL syringes and filtered using 0.22-μm membrane filters. Filtered liquor was analyzed directly by using the ferrozine method to determine the concentrations of Fe(II) (Hennessy et al. 1984). Three replicates of the samples for reaction kinetics of Fe oxide minerals were performed.

The reactivity of natural Fe oxides was determined by applying a time-dependent reduction rate to a reactive continuum model (Postma 1993; Zhu et al. 2014), and the rate of reduction of Fe oxides is described by Eq. (1).

$$\frac{J}{m_0} = k' \left( \frac{m}{m_0} \right)^\gamma \quad (1)$$

Here,  $J$  is the overall rate of dissolution ( $\text{g s}^{-1}$ ),  $k'$  is the apparent rate constant ( $\text{s}^{-1}$ ),  $m_0$  is the initial amount of reactive Fe oxides (g), and  $m$  is the remaining amount at a given time (g). The parameter  $\gamma$  varies with the crystal structure, particle size distribution, and reactive site density, reflecting the reactivity heterogeneity of dissolved mineral assemblages (Larsen and Postma 2001). The reduction rate (Eq. (1)) is based on the fraction of undissolved Fe oxide ( $m/m_0$ ), while the experimental data produce the dissolved amount of Fe oxides ( $m_t$ ), which is equal to  $m_0 - m$ . Equation (2) was derived by integrating Eq. (1) with  $m_t = m_0 - m$  ( $\gamma \neq 1$ ) (Larsen and Postma 2001; Postma et al. 2010).

$$m_t = m_0 \left[ 1 - \left( 1 - k' (1 - \gamma) t \right)^{\frac{1}{1-\gamma}} \right] \quad (2)$$

Equation (2) contains three fit parameters ( $m_0$ ,  $k'$ , and  $\gamma$ ), whose values can be estimated from the graph of  $m_t$  versus  $t$ .

## Results and discussion

### Soil physicochemical properties

Concentrations of TOC in the soil samples ranged from 7.7 to 39.0  $\text{g kg}^{-1}$ , and the average concentrations of TOC were highest in the topsoil, then values decreased with soil depth (average of 11.6 to 25.2  $\text{g kg}^{-1}$ ) (Fig. S1). By using the conversion coefficient between soil organic matter (SOM) and TOC (SOM/TOC = 1.724) (Rowell 2014), the SOM values of the studied soils were found to be generally consistent with the reported contents of Chinese farmland soils (SOM 10 to 30  $\text{g kg}^{-1}$ , average of 24.65  $\text{g kg}^{-1}$ ) (Yang et al. 2017) and Guangdong province (China) paddy soils (SOM 27–32  $\text{g kg}^{-1}$ ) (Ji et al. 2019).

The soil pH ranged from 4.3 to 6.8 across the site profiles and increased from 5.3 to 6.1 along with the soil depth (Fig. S1). According to the Second National Soil Survey, the pH of the soils ranges from 4.5 to 6.0 in southern China, and fertilization, acid deposition, intensive agriculture, and monoculture can further promote soil acidification (Wu et al. 2013). The negative correlation between TOC and pH along the depth was possibly caused by the release of CO<sub>2</sub> during organic matter decomposition, which tends to decrease the soil pH (Yun et al. 2016). Anoxic conditions prevailed during most of the time of rice growth, during which Eh values of paddy top-soils were around –60 to –160 mV during flooded conditions (Zhang et al. 2014; Kögel-Knabner et al. 2010). Although we did not measure Eh at the time of sampling, there is a general rule that maintains the decrease in Eh with



increasing depth in the paddy soils due to the increasingly anaerobic environment (Otero and Macias 2001; IUSS Working Group WRB 2006).

### Arsenic fractions

The total As concentrations in the studied soil samples ranged from 1.9 to 17.9 mg kg<sup>-1</sup> (Fig. S2a), which is comparable with the reported As contents (9.9–30.4 mg kg<sup>-1</sup>) of paddy field soils in the same region (Xi et al. 2008) and lower than the As limits for paddy soils (30 mg kg<sup>-1</sup> for paddy field soil with pH < 6.5, 25 mg kg<sup>-1</sup> for paddy field soil with pH = 6.5–7.5 (GB 15618-2018 2018)), indicating that the studied soils were uncontaminated with As. Concentrations of As were highest in the topsoil, and values decreased with depth in the soil profiles (average from 12.4 to 9.1 mg kg<sup>-1</sup>) (Fig. S2a).

Arsenic fractions in soil samples were investigated by sequential extraction. Concentrations of As fractions showed a downward trend along soil depth (Figs. 2a and S2b–f), but the average proportion of As fractions showed relatively small changes (Fig. 2b), which implied that the decrease in the total As concentrations influenced the changes in As fraction concentrations along the sampling depth. Specifically, crystalline hydrous oxide-bound As (As-F4) (average of 4.3 mg kg<sup>-1</sup>, 40.0%) showed the highest concentrations, followed by residual As (As-F5) (average of 2.8 mg kg<sup>-1</sup>, 23.5%), specifically absorbed As (As-F2) (average of 2.1 mg kg<sup>-1</sup>, 20.4%), As associated with amorphous hydrous oxide (As-F3) (average of 1.2 mg kg<sup>-1</sup>, 13.9%), and non-specifically bound As (As-F1) (average of 0.2 mg kg<sup>-1</sup>, 2.1%) (Fig. 2). As-F5 concentrations were the highest in CZT-5 soil samples. The average proportion of As-F4 in CZT-9 was the highest for all sites. In this study, the average proportion of AsF4 was similar to that in mining contaminated soils (41.2%), and the average proportion of AsF5 (23.5%) was lower than that in mining contaminated soils (27.4%) (Fig. 2b) (Ma et al. 2018c). Arsenic activity in minerals was generally low but may have increased with mineral weathering and pollution spread (Mandal and Suzuki 2002; Ji et al. 2019), which could have resulted in residual As decreased. The average proportion of As-F3 (13.9%) was lower than that reported in previous studies (approximately 40–59%) (Baroni et al. 2004; Silva Gonzaga et al. 2006). Pedersen et al. (2006) found that adsorbed arsenate was usually released in the aqueous arsenate form during reductive dissolution of amorphous hydrous oxides under anoxic conditions of soils. Thus, the lower As-F3 in our study may have been related to the anoxic conditions during the sampling period, and the released As from amorphous hydrous oxide may have existed as water-soluble form in soils. In addition, the average proportion of As-F2 reached up to 20.4%, which was remarkably higher than that in other soils (approximately 5–15%) (Doušová et al. 2008; Ma et al. 2019), indicating that compared with other soils, the paddy soils in our study pose

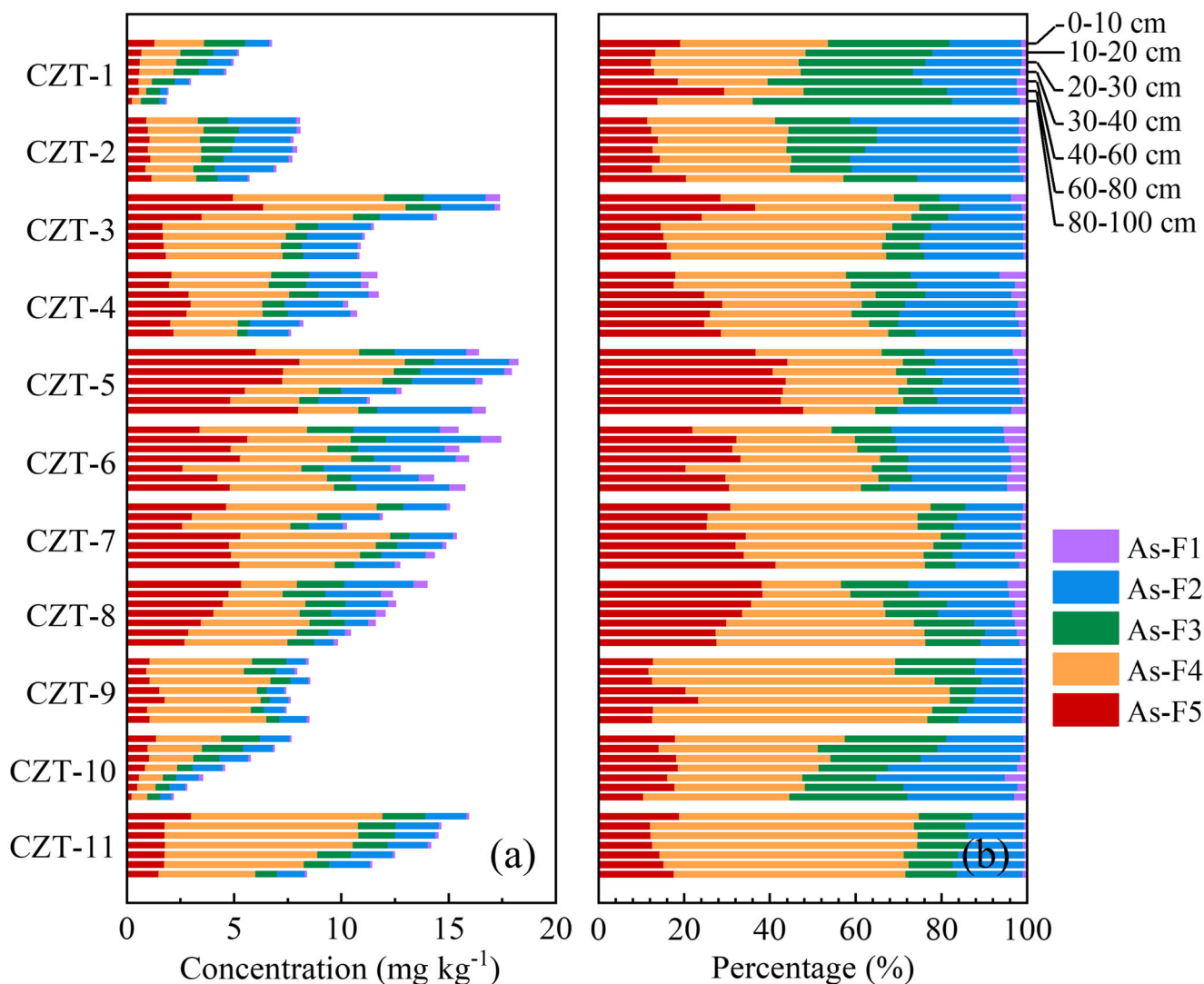
potential environmental risks from As-F2. As the specifically sorbed fraction in soils, As-F2 may be potentially mobilized following changes in pH or P additions (Wenzel et al. 2001). The amount of As-F1 was generally small, but it represents the most important fraction related to environmental risk and has been shown to correlate well with As concentrations in field-collected soil solutions (Fitz and Wenzel 2002; Wenzel et al. 2002).

### Partitioning of Fe oxide minerals

The content of total Fe and Fe fractions varied along with the sampling depth (Fig. S3). Total Fe content ranged from 11.9 to 62.9 g kg<sup>-1</sup> (average ranged from 34.3 to 30.4 g kg<sup>-1</sup> with depth) (Fig. S3a). All Fe fractions across sites revealed a downward trend with depth except Fe<sub>ox2</sub> (Fig. S3b–g). Reducible Fe oxides (Fe<sub>ox2</sub>) (average of 16.5 g kg<sup>-1</sup>, 50.2%) were the highest Fe fraction in soil samples, followed by the poorly reactive sheet silicate Fe and residual Fe (Fe<sub>r</sub>) (average of 11.6 g kg<sup>-1</sup>, 36.3%), easily reducible Fe (Fe<sub>ox1</sub>) (average of 2.2 g kg<sup>-1</sup>, 7.4%), magnetite (Fe<sub>mag</sub>) (average of 1.9 g kg<sup>-1</sup>, 6.1%), Fe associated with carbonate (Fe<sub>carb</sub>) (average of 9.2 mg kg<sup>-1</sup>, 0.030%), and exchangeable free Fe<sup>2+</sup> (Fe(II)) (average of 8.7 mg kg<sup>-1</sup>, 0.030%) (Figs. 3 and S3). However, in the CZT-1 and CZT-8 samples, the concentrations and percentages of Fe<sub>r</sub> were higher than Fe<sub>ox2</sub>, where Fe<sub>r</sub> was also the main Fe fraction (Fig. 3a and b). Concentrations and percentages of the partitioning of Fe oxide minerals showed a barely apparent trend along with the sampling depth in paddy soils (Fig. 3b). Fe(II) and Fe<sub>carb</sub> had low concentrations in soil (Fig. 3a). Although the Fe(II) fraction was active, low concentrations led to a limited effect on As adsorption. Concentrations of Fe<sub>mag</sub> were also low, and their impact on the activity of As was very limited (Fig. 3a and b). Concentrations of Fe<sub>r</sub> were high (Fig. 3a), but this Fe fraction would have been fixed in the sheet silicate mineral lattice and thus could be poorly active (Larsen and Postma 2001). Fe<sub>ox1</sub> and Fe<sub>ox2</sub> were the most important Fe oxide minerals associated with As (Shen et al. 2018). In this study, concentrations of Fe<sub>ox1</sub> (average of 2.2 g kg<sup>-1</sup>) and Fe<sub>ox2</sub> (average of 16.5 g kg<sup>-1</sup>) were lower than those in tailing-contaminated soils (14.6 g kg<sup>-1</sup> for Fe<sub>ox1</sub>, 44.4 g kg<sup>-1</sup> for Fe<sub>ox2</sub>) and smelter-contaminated soils (6.27 g kg<sup>-1</sup> for Fe<sub>ox1</sub>, 51.1 g kg<sup>-1</sup> for Fe<sub>ox2</sub>) (Shen et al. 2018; Ma et al. 2019). However, Fe<sub>ox1</sub> and Fe<sub>ox2</sub> comprised a huge proportion (57.5%) of total Fe, suggesting that they may play important roles in Fe oxide minerals associated with As in paddy soils.

### Reactivity of Fe oxide minerals

Reactivity of Fe oxides and As was more important than their bulk contents (Shen et al. 2018). In this study, Fe oxide dissolution kinetic could be used to characterize the composition,



**Fig. 2** Concentrations (a) and percentages (b) of As fractions in the soil profiles

reactivity, and kinetic behaviors of Fe oxides and associated As in natural soils (Postma 1993). These data were estimated by fitting the rate expression  $J/m_0 = k' (m/m_0)^\gamma$ , where  $J$  represents the overall reduction rate (mol/s). The reactivity was provided by the parameter  $k'$ , which represents the initial reduction rate, and  $\gamma$  which represents a measure of the decrease in the reduction rate owing to changes in factors such as the particle size distribution, crystal geometry, and reactive site density. Based on sequential extraction results, six representative soil sampling sites were selected for kinetic experiments. The representative release patterns of Fe from different soil layers and fitted curves of Fe oxide minerals leached by ascorbic acid and HCl are shown in Fig. 4. In this study, due to low concentrations of Fe(II) and  $Fe_{carb}$ , the concentration of Fe(II)-bearing minerals dissolved by HCl alone was quite low; hence, these data are not shown. In general, the representative releases of Fe oxide minerals were fast, and the times required

for reaching equilibrium were similar (approximately 24 h) (Fig. 4). Initial releases of Fe(II) were quite rapid before slowing down (Fig. 4), which indicated that Fe oxides became more difficult to be dissolved as the reductive process went on. There was a close correlation between the release of Fe and As in the coupled dissolution of As and Fe oxides (Weber et al. 2010). The release of As and Fe during reductive dissolution of Fe oxides was incongruent, in which the release of As was significantly delayed compared to  $Fe^{2+}$  (Pedersen et al. 2006; Yamaguchi et al. 2011). Paige et al. (1997) also observed incongruent release of As and Fe during proton-assisted dissolution of FH with As/Fe ratios between 0.03 and 1.0.

The fitted kinetic parameters are listed in Table S3. The amount of reactive and reducible Fe oxides was expressed as  $m_0$ . The  $m_0$  ranged from 2.08 to 8.83 g kg<sup>-1</sup> (Table S3). The  $m_0$  of reactive Fe oxides decreased with increasing depths.

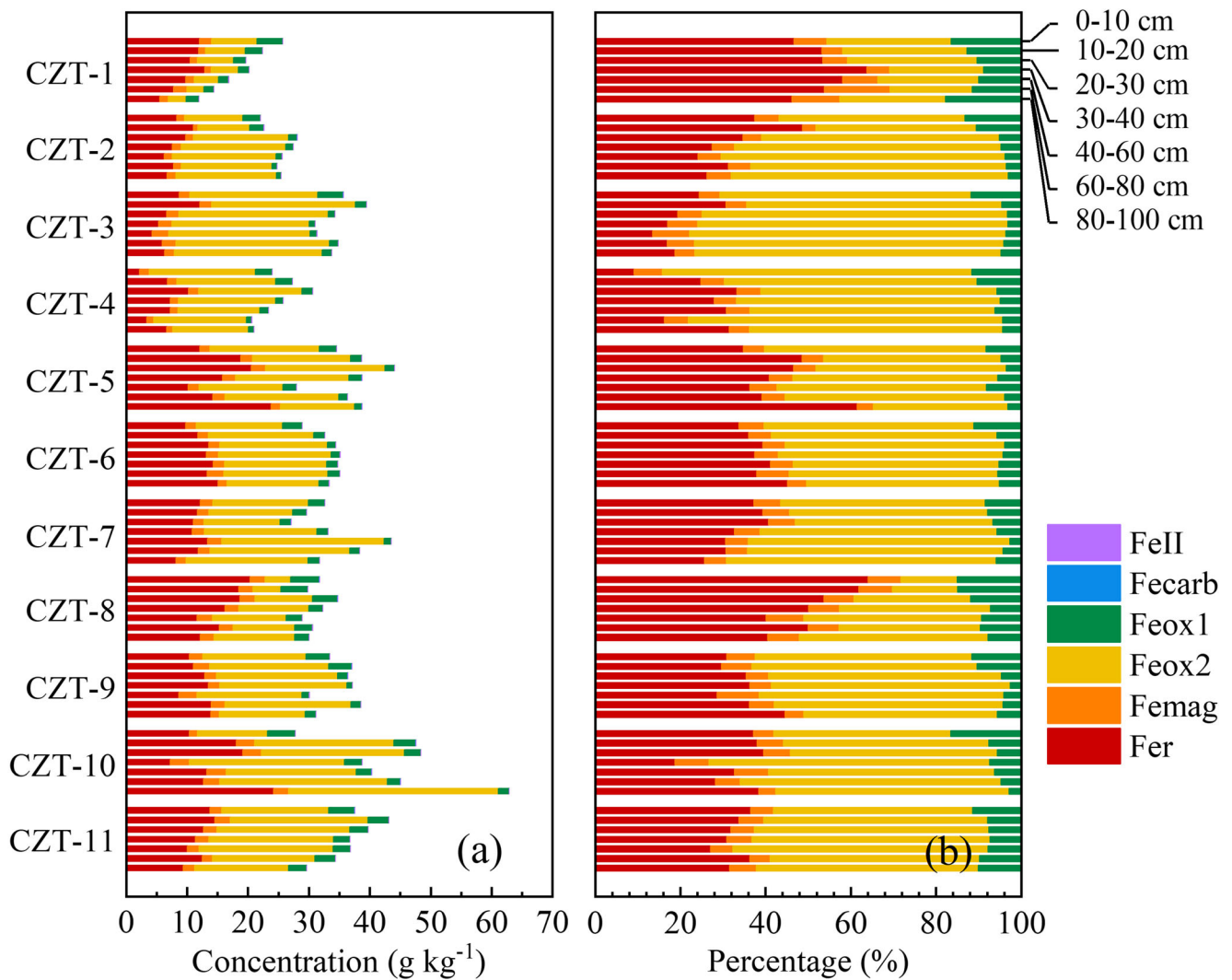


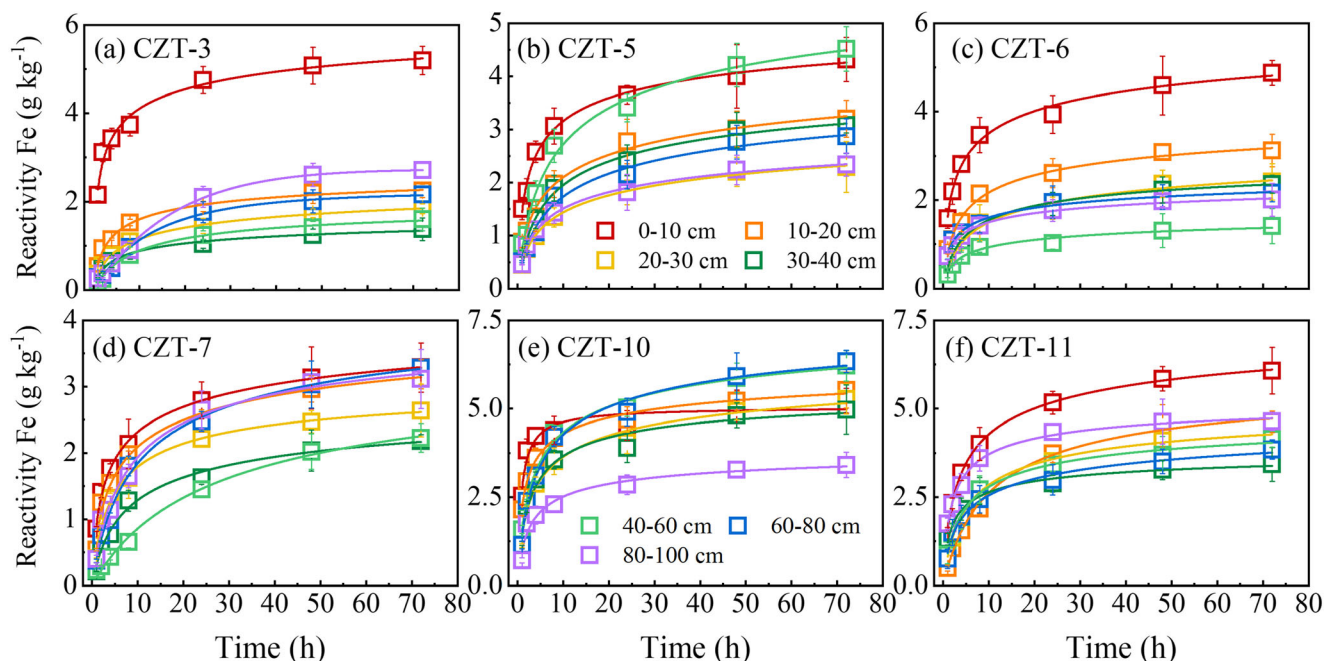
Fig. 3 Concentrations (a) and percentages (b) of partitioning of Fe oxide minerals in the soil profiles

The  $k'$  value reflected the initial reductive dissolution behavior of highly reactive Fe oxides in soils. In this study,  $k'$  ranged from  $0.94 \times 10^{-5}$  to  $34.72 \times 10^{-5} \text{ s}^{-1}$  (Table S3). Although the samples had different  $k'$  values, which were in the same order of magnitude ( $10^{-5} \text{ s}^{-1}$ ) as the typical value for synthesized fresh lepidocrocite (LP) ( $10^{-5} \text{ s}^{-1}$ ) (Larsen and Postma 2001; Pedersen et al. 2005), the values were lower than those for synthesized fresh ferrihydrite (FH) ( $10.3 \times 10^{-4} \text{ s}^{-1}$ ) (Raiswell et al. 2010), indicating that Fe oxides in soils were lower in reactivity than fresh FH and equal to LP. Except for CZT-6 and CZT-11,  $k'$  values decreased along with the sampling depth, which probably occurred because Fe oxides in the surface layer soils had higher reactivity than those in deep soils. The range of  $\gamma$  in paddy soils (0.92–10.81) (Table S3) was higher than that of synthesized fresh FH ( $\gamma = 0.75$ ) (Raiswell et al. 2010) and synthesized fresh LP ( $\gamma = 0.66$ –1.60) (Larsen and Postma 2001; Pedersen et al. 2005), suggesting that most

natural Fe oxide mineral assemblages in paddy soils were more heterogeneous than fresh FH and LP. Additionally, the  $\gamma$  value in paddy soils was much wider than that in estuarine surface sediments ( $\gamma = 1.0$ –3.0) (Zhu et al. 2014). Moreover, the high  $R^2$  values (0.897–1.000) (Table S3) reflected a good performance of the model.

### Relationship between As fractions and partitioning of Fe oxide minerals

In this study, concentrations of As and Fe were significantly and positively correlated ( $R = 0.75$ ), except for CZT-4 (Fig. 5a), and these results are similar to the results from previous studies (Cancès et al. 2008; Fritzsche et al. 2011; Xie et al. 2012; Mikutta et al. 2014; Xu et al. 2017; Ma et al. 2018c). This may have been due to the different geochemical conditions of Fe where Fe concentrations were higher in deep soils

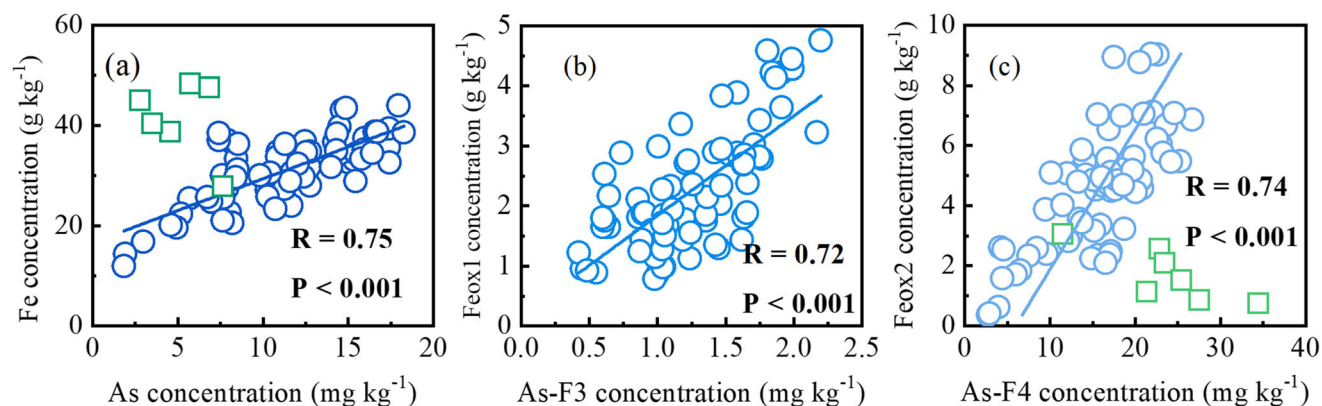


**Fig. 4** Variations and representative dissolution curves of Fe leached from soil profiles (CZT-3, CZT-5, CZT-6, CZT-7, CZT-10, and CZT-11) in different between ascorbic acid (10 mM) and HCl (1 mM)

than top soils. The relationship between As fractions and Fe partitions had been reported in previous studies (Cancès et al. 2008; Hossain et al. 2008). In this study, the relatively active fraction (As-F3) and the relatively stable fraction (As-F4) of As showed remarkable dependency with easily reducible Fe ( $\text{Fe}_{\text{ox}1}$ ) and reducible Fe ( $\text{Fe}_{\text{ox}2}$ ) (Fig. 5b and c). The concentrations of As-F3 and  $\text{Fe}_{\text{ox}1}$  were closely correlated with  $R = 0.72$  (Fig. 5b). Moreover, the concentrations of As-F4 and  $\text{Fe}_{\text{ox}2}$  were also positively correlated ( $R = 0.74$ ), except for CZT-4 owing to the different geochemical background of Fe at those sites (Fig. 5c).

The relatively active fraction of As (As-F3) showed a positive correlation with easily reducible Fe ( $\text{Fe}_{\text{ox}1}$ ), which was similar to that reported in a previous study (Liu et al. 2015). These results indicated that the content of As-F3 increased

with the content of  $\text{Fe}_{\text{ox}1}$  in paddy soils. The relatively stable fraction of As (As-F4) was correlated with reducible Fe ( $\text{Fe}_{\text{ox}2}$ ). Consistent with this result, the study in smelter-contaminated soils indicated that the content of As-F4 was controlled by  $\text{Fe}_{\text{ox}2}$  in soils (Ma et al. 2019). Hence, increasing the content of Fe in the amorphous and well-crystallized Fe oxide fractions can significantly increase the fractions of As in F3 and F4 to control the fates of As-F3 and As-F4 in paddy soils. The transformation between different Fe oxide minerals may lead to the following changes in As forms: the reductive dissolution of FH and LP can result in the release of As from the Fe oxide surface into solution, and this becomes the more active phase of As, while the amorphous Fe (FH) and lepidocrocite (LP) can transform into crystalline Fe(III) oxide phases or magnetite and lead to the incorporation of As into



**Fig. 5** Relationship between As concentrations and Fe concentrations (a), As-F3 and  $\text{Fe}_{\text{ox}1}$  (b), and As-F4 and  $\text{Fe}_{\text{ox}2}$  (c) in the soil profiles. Green squares denote the data from the soil profiles with abnormal Fe concentrations

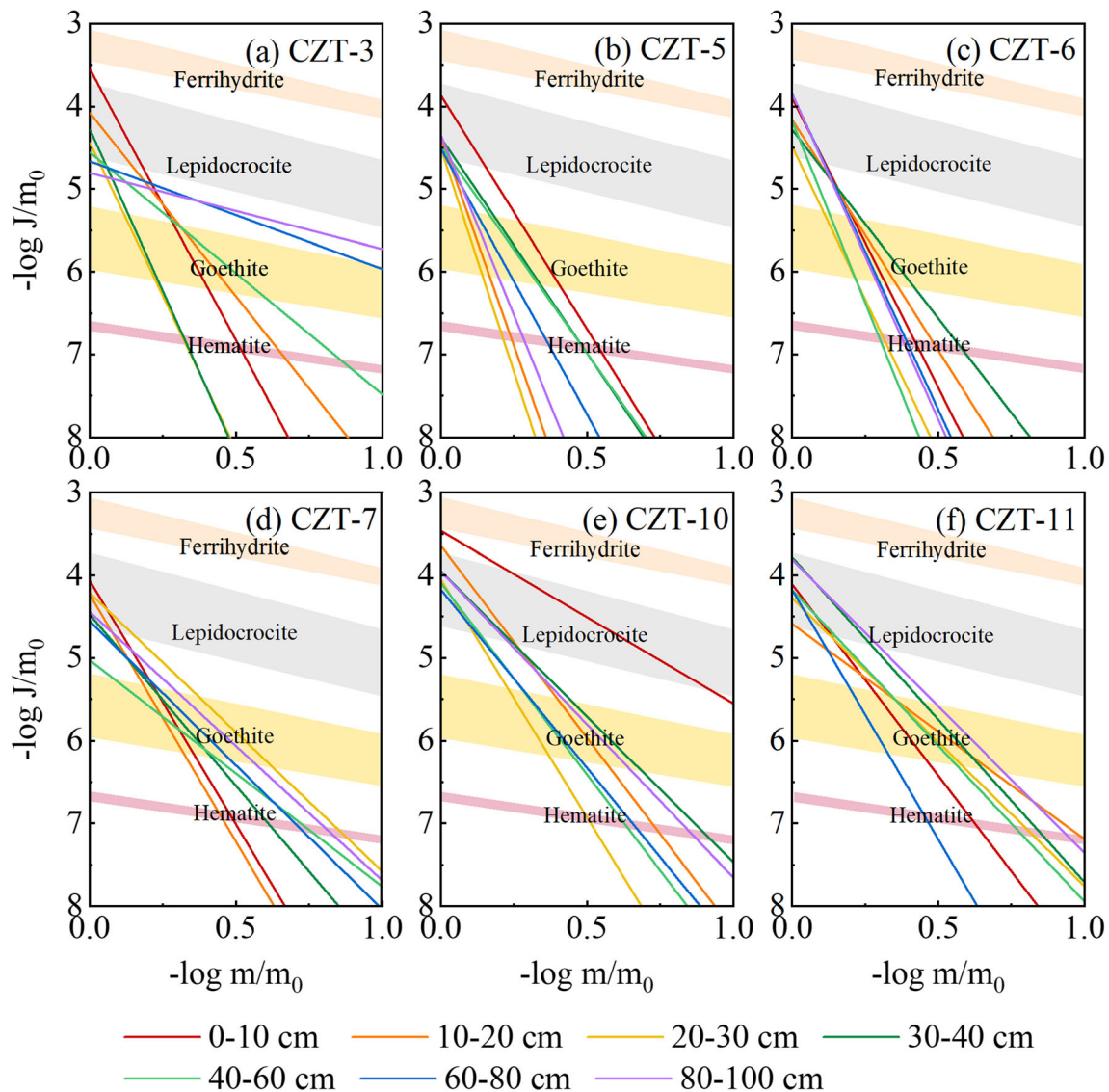


the structure of the crystalline product to become the relatively stable fraction of As (Ona-Nguema et al. 2002; Hansel et al. 2003; Pedersen et al. 2006). Hence, inhibiting the reduction or enhancing the recrystallization of Fe oxides can increase the stable fractions of As in soils. In other words, Fe fractions could influence the proportional distribution of As fractionation and As immobilization in paddy soils.

**Relationship between reaction kinetics of Fe-bearing minerals and As release**

Data for the reactivity of Fe oxide minerals in studied soils compared to that of synthesized Fe oxide minerals are plotted as  $-\log J/m_0$  versus  $-\log m/m_0$  in Fig. 6. Here, the  $y$ -axis intercept was the initial rate  $k'$  and the slope of the line for a given sampling depth corresponded to  $\gamma$ . The results revealed that almost all of the soil samples showed initial rates between

LP and poorly crystalline goethite (GT) (Fig. 6), which were similar to those obtained in previous studies in sediment, river sand, and contaminated soils (Postma et al. 2010; Shen et al. 2018; Ma et al. 2019). The parameter  $\gamma$  was higher than in other soils (Postma et al. 2010; Shen et al. 2018; Ma et al. 2019), suggesting that Fe(III) oxide minerals in paddy soils were more heterogeneous than in other soils. Moreover, the dissolve rates showed a barely apparent trend along the sampling depth in paddy soils, suggesting that minerals had high Fe(III) oxide heterogeneity in the different layers of paddy soils, which coincided with the results of the sequential extraction experiment of Fe(III) oxide minerals showing the percentage of partitioning of Fe oxide minerals in the soil profiles. Because of their high heterogeneity, Fe(III) oxide minerals had high reactivity, and thus, there is a high risk of As release at the beginning of the reaction in the different layers of paddy soils.



**Fig. 6** Comparison of reactivity of Fe(III) oxides in studied soils and synthesized Fe oxide minerals (Pedersen et al. 2005; Pedersen et al. 2006)

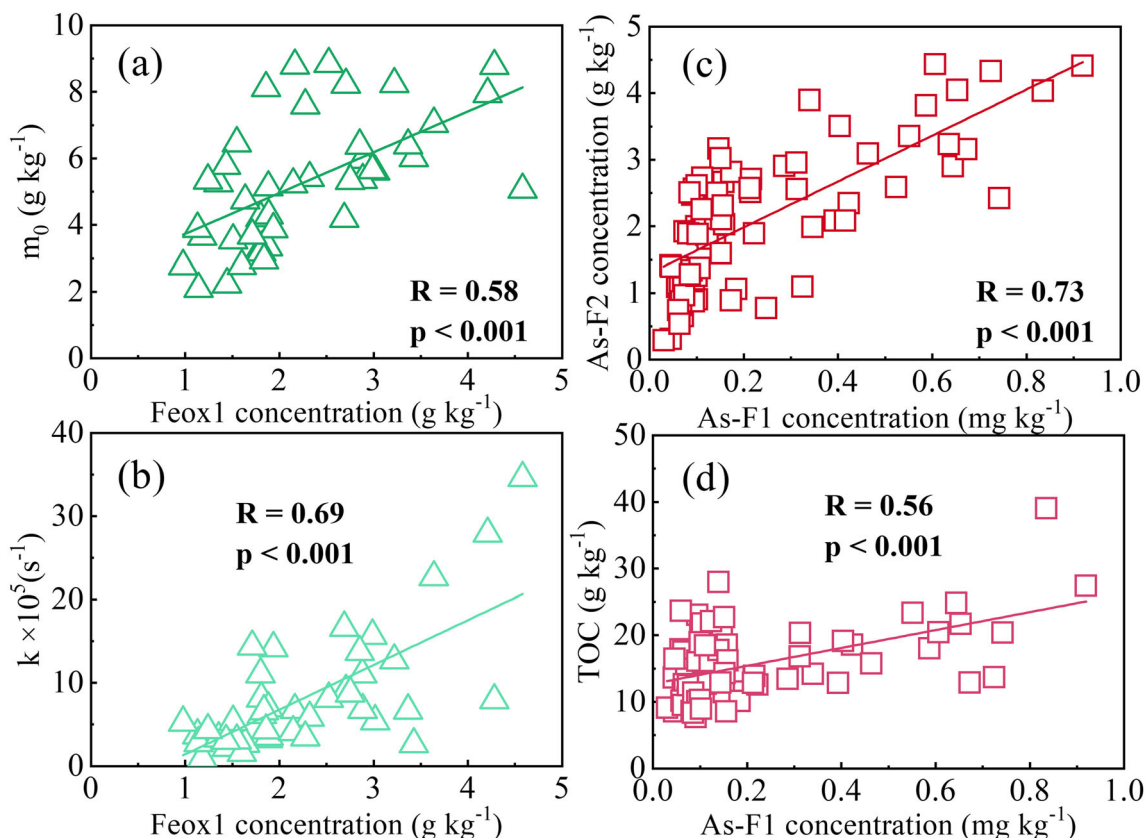
In this study, almost all of the samples passed through the LP, GT, and hematite (HT) zone. For FH and LP, arsenate was mainly associated with the Fe oxide surface, but in GT and magnetite (MT), arsenate was mostly incorporated in the structure, which hindered the desorption of As from GT and led to a more rapid release of As from FH or LP (Pedersen et al. 2006; Gallegos-Garcia et al. 2012). Therefore, GT and HT played important roles in As immobilization owing to their structural stability in soils and hindering the As release from LP became a vital step. In addition, owing to the highly heterogeneous Fe(III) oxide minerals, all soil layers still exhibited a significant risk of As release from the reductive dissolution of Fe(III) oxide minerals.

A positive correlation between  $Fe_{ox1}$  and  $m_0$  in soils ( $R = 0.58$ ) was observed (Fig. 7a). Moreover, concentrations of  $Fe_{ox1}$  correlated strongly with  $k'$  ( $R = 0.69$ ) (Fig. 7b). The correlations between  $m_0$ ,  $k'$ , and  $Fe_{ox1}$  provided evidence that  $Fe_{ox1}$  was likely to control the reductive dissolution of the Fe oxides under reduction conditions. Easily reducible Fe had a larger specific surface area, which could absorb plenty of As (Pedersen et al. 2006). Moreover, arsenic preferentially desorbed from the surface of LP during reductive dissolution and phase transformation of Fe oxides (Pedersen et al. 2006). When paddy soils were under flooded conditions, Fe oxides

were reduced and solubilized, in accompaniment with the release of sorbed As into the solution phase (Weber et al. 2010; Rinklebe et al. 2016; Shaheen et al. 2016; Xu et al. 2017). In addition, experiments under flooded soils also found that the ratios of released As to Fe decreased with flooded time, showing a trend similar to that during the reductive dissolution by ascorbate (Yamaguchi et al. 2011). Hence, combined with the previous conclusion,  $Fe_{ox1}$  mainly controlled the reductive dissolution of the Fe oxides, suggesting that the reductive dissolution process could potentially release As during the flooded period of rice production.

### TOC influence on labile As

A strong relationship between As and TOC in soils has been reported in previous studies (Nickson et al. 2000; Berg et al. 2001; Redman et al. 2002; Islam et al. 2004; Quicksall et al. 2008; Sharma et al. 2010; Xie et al. 2012; Ma et al. 2018b). In this study, the correlation between concentrations of TOC and As fractions in paddy soils were verified. Except for non-specifically bound As (As-F1) and the amorphous Fe hydrous oxides-bound As (As-F3), other As fractions showed no correlations with TOC. TOC and As-F1 showed a positive correlation ( $R = 0.56$ ) (Fig. 7d), which suggested that TOC was



**Fig. 7** Relationship between  $Fe_{ox1}$  concentrations and  $m_0$  (a),  $Fe_{ox1}$  concentrations and  $k'$  (b), As-F1 and As-F2 (c), and As-F1 and TOC concentrations (d) in soil profiles

one factor affecting the As extractability in the As-F1, and OM could have played a role in the adsorption and release of As (Postma et al. 2007; Farooq et al. 2010). Non-specifically bound As (As-F1) has been shown to correlate well with As in field-collected soil solutions and hence could be used for predicting solute As (Wenzel et al. 2001). Therefore, the increase of TOC could increase the As-F1 content and further affect solute As in the soil solution. TOC was correlated with As-F3 ( $R = 0.67$ ) (Fig. S4b), suggesting that As activated by TOC may be reabsorbed onto the mobile amorphous Fe oxides (that is As-F3) (Pedersen et al. 2006; Fritzsche et al. 2011; Ma et al. 2018a; Qian et al. 2020).

A positive correlation between As-F1 and specifically bound As (As-F2) ( $R = 0.73$ ) (Fig. 7c) was found in paddy soils. The NOM structures were the likely redox-active agents affecting As speciation, acting by means of quinone or other functional groups, and As oxyacids in soils interacted with NOM to promote As mobility (Redman et al. 2002). Hence, the transformation between As-F2 and As-F1 could be carried out owing to the redox-active agent-NOM. In another words, organic matter may control the transformation of species of As. Some previous studies reported that the bioavailability of As was significantly correlated with the concentrations of As-F1 or As-F2, which could be considered as available portions of As to plants in soils (Tang et al. 2007; Liu et al. 2012). The amount of labile As fractions (As-F1 and As-F2) may represent the most important fraction related to environmental risks. Therefore, based on our present results, soil organic matter content was an important factor in affecting the distribution and content of As in paddy soils, especially the available portions of As.

## Conclusion

In this study, the fraction distribution, immobilization, and the release risk of As in different soil profiles from the Changzhutan urban agglomerations were investigated. Concentrations of total As and As fractions had a downward trend along depth, but the average proportion of As fractions showed a relatively small change, which implied that the decrease in the total As concentrations influenced the change in As fraction concentrations along the sampling depth. Meanwhile, reactivity of Fe(III) oxides of almost all samples passed through the lepidocrocite (LP), goethite (GT), and hematite (HT) zone. The reductive dissolution rates of Fe(III) oxides had no apparent trend along with the sampling depth in paddy soils, suggesting that Fe oxide minerals had high heterogeneity in the different layers of paddy soils. Because of their high heterogeneity, Fe(III) oxide minerals had high reactivity, and thus, there is a high risk of As release at the beginning of the reaction in the different layers of paddy soils. In addition, easily reducible Fe ( $Fe_{ox1}$ ) mainly controlled the

reductive dissolution of the Fe oxides, suggesting that the reductive dissolution process could potentially release As during the flooded period of rice production. The average proportion of specifically absorbed As (As-F2) reached up to 20.4% in paddy soils, higher than in other soils, indicating that there exhibited a potential environmental risk from the As-F2 in the studied soils. Moreover, the total organic content (TOC) had a positive correlation with the amounts of As-F1 ( $R = 0.56$ ), which means that TOC was one factor affecting the As extractability in the As-F1 fraction. A positive correlation between As-F1 and specifically bound As (As-F2) ( $R = 0.73$ ) was also found in paddy soils. The amount of labile As fractions (As-F1 and As-F2) may represent the most important fraction related to environmental risks. Organic matter was beneficial to the activity of As; high organic matter input may increase the release and diffusion of As, resulting in increased environmental risks. Controlling the input of organic fertilizer and straw turnover in As-contaminated paddy fields may be an effective option to reduce the environmental risks of As.

**Acknowledgments** The study is financially supported by the National Key Research and Development Program of China (2016YFD0800304), the National Natural Science Foundation of China (Nos. 41701262, 41701355, 41601227, and 41771277), and Central Public-interest Scientific Institution Basal Research Fund (Y2020PT03).

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