



# Arsenic availability in rice from a mining area: Is amorphous iron oxide-bound arsenic a source or sink?



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## ABSTRACT

The effect of iron (Fe) redox cycling on the mobility and bioavailability of arsenic (As) in paddy soils has attracted increasing concerns, especially in Asia, where the paddy soil is characteristic of Fe with high abundance and activity. However, whether amorphous Fe oxide-bound As acts as a source or a sink of As in natural field conditions needs to be clarified further. In this study, 73 pairs of soil and rice were collected from paddy fields contaminated by As-containing acid mining drainage. The most significant correlations between the iron fractions and As fractions suggest that Fe redox cycling can directly affect As fractionation in soils, which can then indirectly affect As bioavailability. Significantly negative correlations between amorphous Fe oxide-bound As in soil and As in rice grain were found, indicating that amorphous Fe oxide-bound As acts a sink of As.

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## 1. Introduction

Arsenite and arsenate are the predominant forms of Arsenic (As) in soils and are deemed to be biologically active and more toxic than many organoarsenicals (Caussy, 2003). Under oxidized soil conditions, As is mainly present as arsenate and strongly adsorbed on iron (hydr)oxides (Goldberg, 2002; Dixit and Hering, 2003; Weber et al., 2010). By contrast, under a reducing environment, such as a flooded paddy soil, the sorption sites for As are compromised and the adsorbed As is released into the soil solution because of the reduction of soil Fe(III) (hydr)oxides. As a result, As is mobilized as arsenite in the soil pore water (Islam et al., 2004; Takahashi et al., 2004; Kocar et al., 2006; Pedersen et al., 2006; Yamaguchi et al., 2011). Thus, the bioavailability of As in paddy soils is usually high relative to those in upland soils.

As for the effects of iron redox cycling on As mobility, many previous studies have been conducted under controlled conditions. For example, the anoxic microbial oxidation of ferrous iron (Fe(II)) to produce ferric (Fe(III)) (hydr)oxides can immobilize As (Sun et al., 2009). Furthermore, Fe(II)-activated goethite can catalyze the oxidation of As(III) to As(V) and thus reduce the mobility of As

(Amstaetter et al., 2010). The process of Fe(II)-catalyzed iron oxide recrystallization can release As or incorporate As into the oxide structure (Pedersen et al., 2006; Latta et al., 2012). Additionally, factors such as the types of iron minerals (Dixit and Hering, 2003), microbial species (Kocar et al., 2006), nitrates (Senn and Hemond, 2002), valence states of As (Yamaguchi et al., 2011), pH and Eh (Yamaguchi et al., 2011) can all affect the processes of iron redox cycling coupled to the mobilization of As. Moreover, the results from previous field studies (Takahashi et al., 2004; Yamaguchi et al., 2011) have suggested that the mobilization of As in paddy fields is controlled by the reductive dissolution of iron(III) (hydr)oxide and the reduction of As(V) to As(III). Furthermore, because the total content of As in soil only provides limited information for understanding its availability (Taggart et al., 2004), a sequential extraction procedure has been developed to assess the potential mobilization of As in soil (Wenzel et al., 2001). In particular, As of differential relative lability in soils is extracted with reagents of increasing dissolution strength. Therefore, As fractionation extracted with these different reagents represents the different potentials of mobilization and availability of As. Accordingly, examining the correlations between iron redox cycling and As fractionation in soils is useful for elucidating the mechanism of iron redox cycling coupled to As mobility. However, studies on the effects of iron redox cycling on As fractionation in paddy soils have been limited. Generally, the As fraction bound to amorphous iron

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oxides (F3) is an important portion of As in soils, and thus its availability is an important factor affecting the bioavailability of As in rice (Tang et al., 2007). Compared to exchangeable and carbonate-bound As fractions, As fraction F3 has been considered to be more tightly retained and less labile by some previous studies because of its sequestration by soil oxides (Tang et al., 2007; Du et al., 2008; Liu et al., 2012). However, conflicting results have been reported (Hsu et al., 2012), where it was found that contents of As in F3 were positively correlated with those in rice. It is argued that amorphous iron oxide-bound As exhibits high availability. Hence, for amorphous iron oxide-bound As, the question is whether this system acts as an As source that is available to rice plants or an As sink, making As unavailable to rice. Clearly, further studies are required to elucidate these possibilities, especially

under field conditions.

The Lianhuashan tungsten mine is one of the biggest tungsten mines in China, which lies in Shantou City, in the Guangdong Province of China. The paddy fields downstream to the mining area have received a substantial influx of As from As-containing acid mining drainage. Our previous study (Liu et al., 2010) has shown that the concentrations of As in the agricultural soils of this region ranged from 3.5 to 935 mg kg<sup>-1</sup>, with a mean value of 129 mg kg<sup>-1</sup>. Additionally, the residual level of As in brown rice reached levels up to 1.08 mg kg<sup>-1</sup> (Liu et al., 2010). In the present study, 73 pairs of soil and rice plant samples were collected from rice paddy fields in the area of the Lianhuashan tungsten mine. Arsenic fractionation in soils was determined by a sequential extraction procedure that has been used widely to delineate As fractionation (Wenzel et al., 2001;

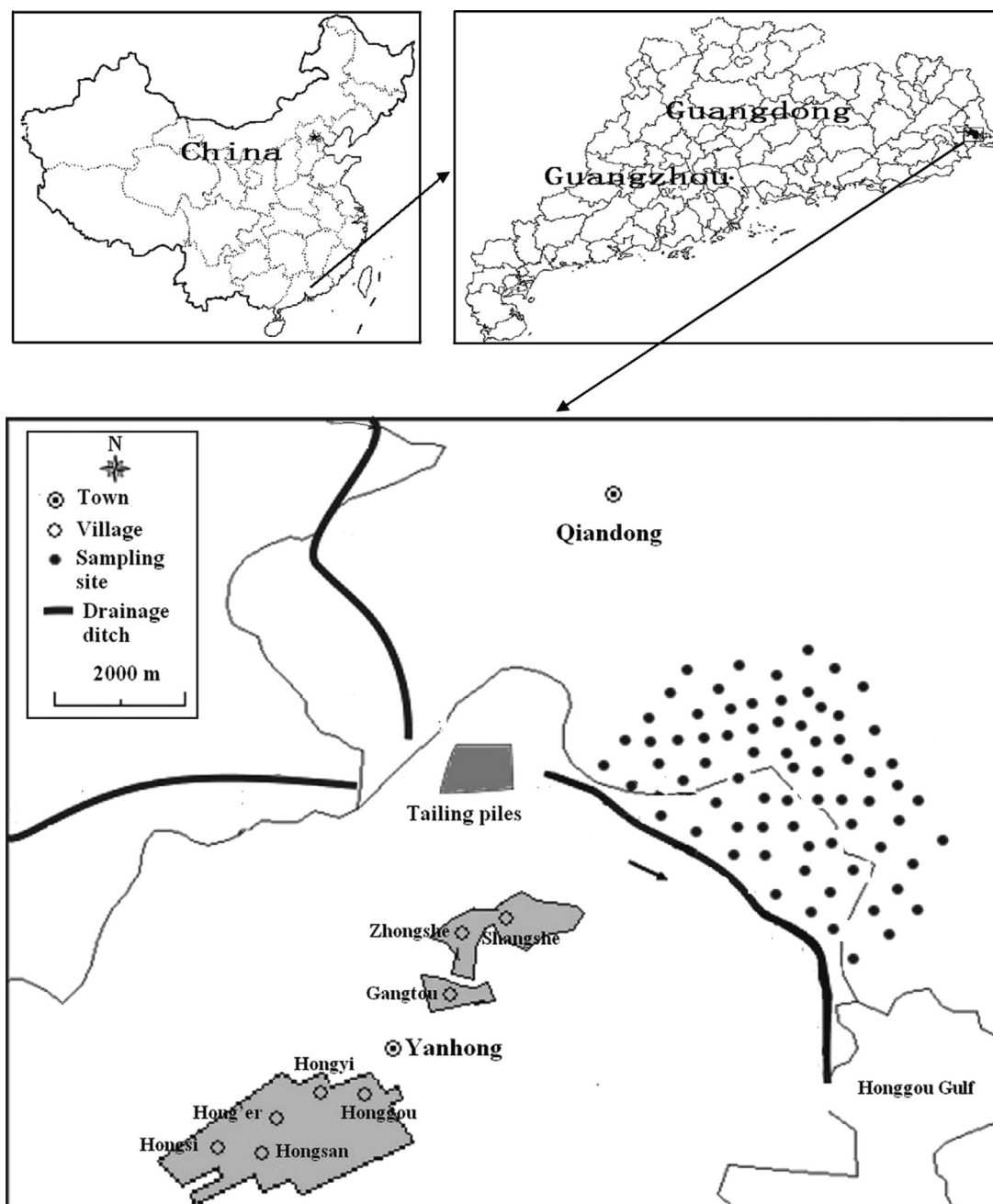


Fig. 1. The map of the study area and sampling sites.

Niazi et al., 2011). Additionally, As loadings in different parts of the rice plants were determined. To delineate the role of iron redox cycling in As availability, the objective of this study is to assess the effects of iron redox cycling on the distribution of As fractionation in soil and As availability to rice plants under field conditions, especially the environmental roles of amorphous iron oxide-bound As.

## 2. Materials and methods

### 2.1. Sampling

Soil and plant samples were collected from 73 different rice paddy fields in the downstream area of the Lianhuashan tungsten mine in November 2010. The sampling area is located in (sub) tropical areas within the Guangdong Province of China (Fig. 1), which is a typical region of red soils. In addition, the sampling area was only contaminated by As-containing acid mining drainage once. In particular, in 2006, a dam burst event occurred in the sampling area, as a result, As-containing acid mining drainage overflowed from mining areas to the surrounding paddy fields and thus the paddy fields were contaminated by As. The diagonal sampling method was adopted and 3–5 sampling points for a field were set according to the sampling area. Then, soil and rice plant samples taken from 3 to 5 sampling points of a field randomly were mixed as composite samples, respectively. During sampling, firstly, we dug a pit with rice plant as the center and 15 cm length as the radius and 30 cm deep to remove the rice plant from soil. Secondly, the rice plants sampled at maturity were separated into roots with soil and the other parts. Finally, all the samples were sealed in polytetrafluoroethylene (PTFE) bags and then transported to the laboratory. In the laboratory, the spikelets of rice were first cut with stainless steel scissors, washed thoroughly with tap water and then rinsed with deionized water more than three times. After being dried at 70 °C in an oven for 72 h, dried spikelets were divided into brown rice and husks with a pestle and mortar. Rice straws were cut at 2 cm above the irrigation water level to avoid contamination by irrigation water. Roots were taken gently from the field to avoid damage. Rice straws and roots were washed and dried using the same procedures described above for the spikelets. All plant materials were ground with a carnelian mortar for further chemical analysis. The soil samples were collected from the root zone of the rice samples and then dried in air. Finally, the dried soils were crushed with a wooden hammer to pass through a 100 mesh sieve for subsequent analysis.

### 2.2. As contents in soil and rice plant

Approximately 0.5 g of each soil sample was digested by 5 mL of HNO<sub>3</sub> and HClO<sub>4</sub> (4:1, v:v) at 140–160 °C. Approximately 1 g of each plant sample was digested with 1.0 mL of HClO<sub>4</sub>, 1.5 mL of H<sub>2</sub>SO<sub>4</sub> and 4.0 mL of HNO<sub>3</sub> at 110–130 °C until a clear solution was obtained. The digested samples were filtered with a 0.45 μm filter, and then analyzed for total concentrations of As with a hydrogen generation-atomic fluorescence spectrometer (AFS-820, Beijing Titan Instruments, China). All reagents were of analytical grade or better. To verify the accuracy of the metal analysis, certified reference materials (GBW(E) 070008 for soils and GBW10014 for plants) from the National Research Center for Standards in China were used. The certified values of GBW(E)070008 and GBW10014 were 75 ± 7 and 0.062 ± 0.014 mg kg<sup>-1</sup>, respectively. The results of our study (n = 12, Table S1) provided mean values of 72 ± 6 and 0.063 ± 0.017 mg kg<sup>-1</sup> for GBW(E)070008 and GBW10014, which were 97% and 102% of the target values, respectively. Reagent blanks and analytical duplicates were also used to ensure accuracy

and precision in the analysis.

### 2.3. As fractionation from the soil

A sequential As fractionation scheme based on a previous method (Wenzel et al., 2001) was employed to determine the following operationally-defined As fractions: (F1) extracted with 0.05 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (non-specification sorbed phase); (F2) extracted with 0.05 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (specifically sorbed phase); (F3) extracted with 0.2 M NH<sub>4</sub><sup>+</sup>-oxalate buffer (amorphous iron oxide-bound phase); (F4) extracted with 0.2 M NH<sub>4</sub><sup>+</sup>-oxalate buffer + ascorbic acid (crystalline iron oxide-bound phase), and (F5) extracted with HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (residual phase). 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 As. The recovery ((fractions sum/total As) × 100%) was 89.2–106.7%, indicating a satisfactory quality control.

### 2.4. Iron fractions in the soil

Free Fe oxides were extracted with dithionite–citrate–bicarbonate (DCB) (Fe<sub>D</sub>) (Mehra and Jackson, 1960) and amorphous Fe oxides were extracted with 0.2 mol L<sup>-1</sup> ammonium oxalate (pH = 3.0) (Fe<sub>O</sub>) (Mckeague and Day, 1966), respectively. Iron in the extracts was analyzed with inductively coupled plasma atomic emission spectrometry (ICP-AES) (PerkinElmer, Inc., America). HCl-extractable Fe(II) was measured with the ferrozine assay after extraction with a 0.5 M HCl solution (Lovley and Phillips, 1988). Briefly, the HCl-extractable Fe(II) was determined by accurately weighing 0.1 g of soil into a 15 mL centrifuge tube, followed by the addition of 5 mL of a 0.5 M HCl solution. After being shaken at 100 rpm for 1 h at room temperature, the samples were centrifuged (at 1700g for 15 min) and 0.05 mL of supernatant was added to 2.45 mL of 50 mM HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid) buffer containing 1 g/L ferrozine at a pH of 7. The concentrations of iron in the samples were then determined using the ferrozine assay. The concentrations of HCl-extractable Fe(III) were obtained by subtracting HCl-extractable Fe(II) from the concentrations of HCl-extractable total Fe. The HCl-extractable total Fe contents in the samples were measured with the ferrozine assay as before, except that 10% hydroxylamine hydrochloride was added to the solution in addition to the HEPES buffer and ferrozine.

### 2.5. Statistical analyses

Statistical analyses of the experimental data were performed using the SPSS® 10.0 (SPSS, USA) software. The statistical significance differences were determined by one-way analyses of variance on ranks followed by the Student multiple comparison t-test with *P* < 0.05. The correlation analysis was conducted by Pearson correlation with a significance level at *P* < 0.05 (two-tailed).

## 3. Result and discussion

### 3.1. Accumulation and distribution of As in rice

High As concentrations were found in rice materials collected from the Lianhuashan mining area (Table S2). The total As concentrations in brown rice, straw and root ranged between 0.03 and 1.04, 1.11–12.7 and 186–2140 mg kg<sup>-1</sup>, with the mean ± SD values of 0.36 ± 0.29, 5.86 ± 3.27 and 1000 ± 355 mg kg<sup>-1</sup>, respectively. Similar to our previous results (Liu et al., 2010), the concentrations of As in brown rice collected from the Lianhuashan mining area were significantly greater than those measured in grains of rice grown in uncontaminated soils (in the range of 0.11–0.20 mg kg<sup>-1</sup>)

(Kabata-Pendias and Pendias, 1984) and the background As concentrations ( $0.001\text{--}0.270\text{ mg kg}^{-1}$ ) measured in rice collected from the Guangdong Province (Liang et al., 2003). Regarding the different tissues of rice plants, the concentration of As followed the order: root > straw > grain; that is, the accumulation of As in rice root was the highest among the three rice plant tissues investigated. It should be noted that As concentration in rice roots may be overestimated, as Fe plaques were not separated from rice roots. Furthermore, the concentrations of As in rice root and straw or brown rice were significantly and negatively correlated with each other ( $r = -0.360$  and  $p < 0.01$  or  $r = -0.281$  and  $p < 0.05$ ; Fig. S1). These results indicate that the accumulation of As in rice root can reduce the amount of As translocating to plant tissues above the ground, which has also been suggested previously (Abedin et al., 2002; Liu et al., 2004; Rahman et al., 2007). Arsenic accumulation in rice root can be partly attributed to the formation of iron plaques around rice roots, which adsorb As and reduce the translocation of As to the above ground tissues of rice (Liu et al., 2004; Garnier et al., 2010; Yamaguchi et al., 2014). The concentrations of Fe in the iron plaques of rice root were not determined in the present study, but the concentrations of As and Fe in the entire root system (Fe coatings in the roots were intact prior to digestion) were significantly correlated with each other ( $r = 0.644$  and  $p < 0.001$ ; Fig. S2). These results are similar to those of Blute et al. (2004), who also attributed significant correlation between the contents of Fe and As in cattail roots grown in As-contaminated sites to the sorption of As to iron plaques formed at the root surface.

### 3.2. Fractionation of As in soil and its implications for the bioavailability of As to rice

The mean  $\pm$  SD concentrations of As in F1 and F2 were  $2.29 \pm 2.03$  and  $7.97 \pm 5.93\text{ mg kg}^{-1}$ , respectively, accounting for 3.0% and 10.3% of the total As content (Table S3). Although the fractions of As in F1 and F2 are quite low, they are important in soil biochemical processes because these two fractions are considered to be the most mobile portions of As in soils (Brandstetter et al., 2000). As shown in Fig. 2, the As in F1 and F2 from the soils were significantly and positively correlated with those in brown rice or straw, which indicates that the fractions of As in F1 and F2 are

available to rice. Tang et al. (2007) and Niazi et al. (2011) also reported that the bioavailability of As was significantly correlated with the concentrations of non-specifically adsorbed As (F1) or specifically adsorbed As (F2). Therefore, fractions of As in F1 and F2 could be considered as available portions of As to plants in soils (Vazquez et al., 2008; Liu et al., 2012). The concentrations of As in F3, F4, and F5 ranged between 3.92 and 59.9, 4.48–59.5, and 1.40–88.8  $\text{mg kg}^{-1}$ , respectively, accounting for 27.7%, 25.1%, and 30.9% of the total As content (Table S3). The concentrations of As in F3 were significantly and negatively correlated with those in brown rice ( $r = -0.555$ ,  $p < 0.001$ ) and straw ( $r = -0.604$ ,  $p < 0.001$ ) (Fig. 2), but no significant correlation was observed between the concentrations of As in any parts of rice and those in F4, F5 or total As (Table S4). Accordingly, fractions of As in F3, F4 and F5 appear to be unavailable to rice in our present study, which is similar to the findings within previous studies (Tang et al., 2007; Du et al., 2008; Liu et al., 2012).

### 3.3. Correlation between iron fractions in soil and As fractionation or bioavailability to rice

Detailed data for iron fractions in soils are provided in Table S5. The concentrations of Fe in the amorphous Fe oxides fraction were positively correlated with the concentrations of As in F3, similar to a previous study (Seyfferth et al., 2014), while they were negatively correlated with the concentrations of As in F1 and F2 (Fig. 3). These results indicate that increasing the content of Fe in the amorphous Fe oxides fraction can significantly increase the fraction of As in F3 and reduce the fractions of As in F1 and F2. By contrast, the concentration of HCl-extractable Fe(II) was significantly and positively correlated with the concentrations of As in F1 and F2, while they were negatively correlated with those in F3 (Fig. 3). Hence, enhancing the reduction of Fe(III) can increase the fractions of As in F1 and F2 and reduce the fraction of As in F3. Therefore, we can conclude that iron fractions affect the proportional distribution of As fractionation in soils and thus affect As mobility. Furthermore, the concentrations of Fe in the amorphous Fe oxides fraction showed a significant and negative correlation with the concentrations of As in brown rice or straw (Fig. 4). The concentrations of DCB-extractable Fe were also found to be significantly and

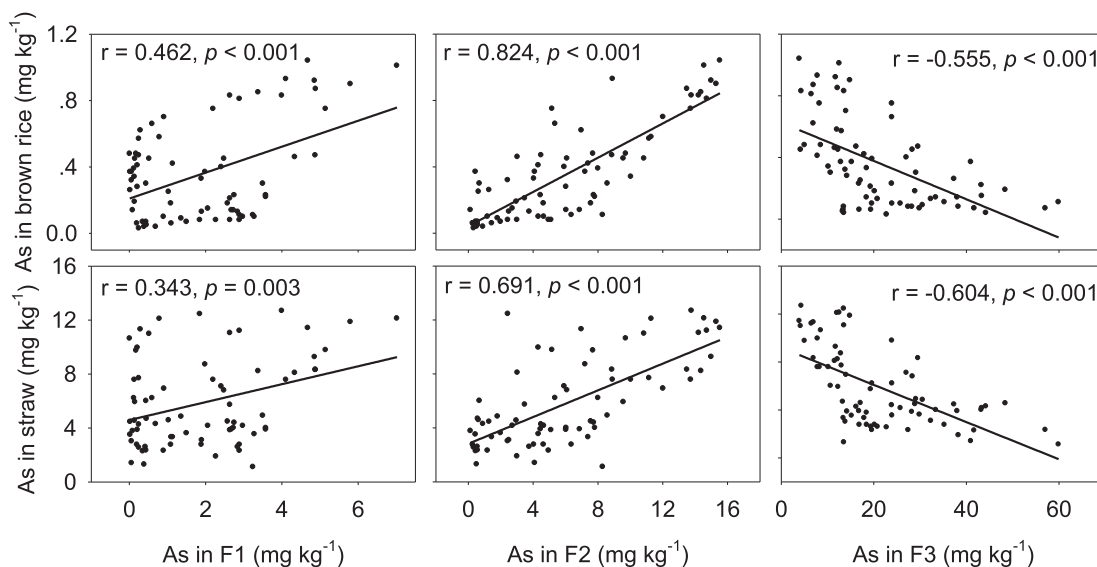
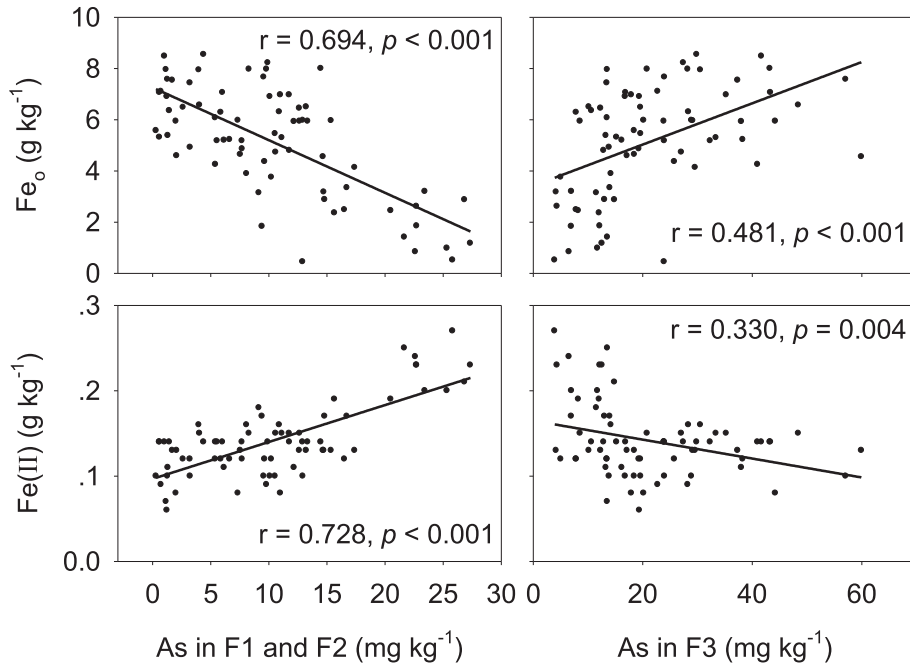


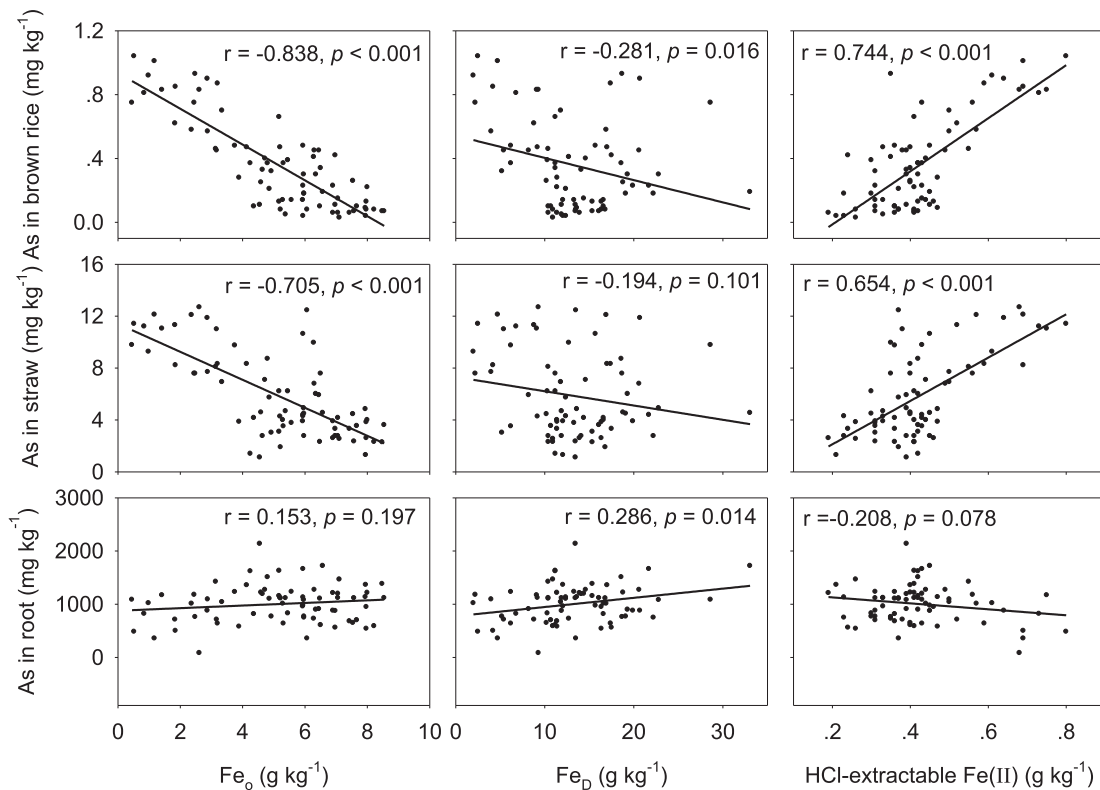
Fig. 2. The correlations between the concentrations of arsenic (As) in rice (brown rice and straw) and As fractions (F1, F2 and F3) in soil. F1: extracted with 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  (non-specification sorbed phase); F2: extracted with 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  (specifically sorbed phase); F3: extracted with 0.2 M  $\text{NH}_4^+$ -oxalate buffer (amorphous iron oxide-bound phase).



**Fig. 3.** The correlations between the concentrations of iron (Fe) fractions in soil ( $Fe_0$  and  $Fe(II)$ ) and As fractions (F1+F2 and F3) in soil.  $Fe_0$ : extracted with  $0.2 \text{ mol L}^{-1}$  ammonium oxalate (pH 3.0);  $Fe(II)$ : extracted with  $0.5 \text{ mol L}^{-1}$  HCl; F1: extracted with  $0.05 \text{ M } (NH_4)_2SO_4$  (non-specification sorbed phase); F2: extracted with  $0.05 \text{ M } NH_4H_2PO_4$  (specifically sorbed phase); F3: extracted with  $0.2 \text{ M } NH_4^+$ -oxalate buffer (amorphous iron oxide-bound phase).

negatively correlated with the concentration of As in brown rice (Fig. 4). These results confirmed that iron oxides play an important role in reducing As bioavailability to rice because of the strong As binding capacity to iron oxides (Bose and Sharma, 2002; Yang et al.,

2002). Therefore, based on our present results, increasing the concentration of Fe in the amorphous iron oxides fraction in paddy soils can efficiently reduce the fractions of As in the soil solution and thus reduce the availability of As. By contrast, no significant



**Fig. 4.** The correlations between the concentrations of arsenic (As) in rice (brown rice, straw and root) and iron (Fe) fractions in soil ( $Fe_0$ ,  $Fe_D$  and  $Fe(II)$ ).  $Fe_0$ : extracted with  $0.2 \text{ mol L}^{-1}$  ammonium oxalate (pH 3.0);  $Fe_D$ : extracted with dithionite–citrate–bicarbonate (DCB);  $Fe(II)$ : extracted with  $0.5 \text{ mol L}^{-1}$  HCl.



correlation was found between As in the root (including Fe plaque) and soil Fe (Fig. 4). This may be attributable to Fe plaque which was not separated from rice root in our study. Additionally, the concentrations of HCl-extractable Fe(II) showed positive correlations with concentrations of As in brown rice or straw (Fig. 4), indicating that HCl-extractable Fe(II) could be used as another indicator of As availability. However, it is noteworthy that the concentrations of HCl-extractable Fe(II) accounted for only 5% of the oxalate soluble Fe and that the similar result has been reported in a previous study (Bogdan and Schenk, 2009). Therefore, the release of As to soil solution as a result of the reduction dissolution of amorphous Fe oxides was not the predominant process in our study.

### 3.4. A proposal for availability of amorphous iron oxide-bound arsenic

All of our results indicate that iron plays a pivotal role in the fate of As. As for the availability of F3, although many previous studies (Tang et al., 2007; Du et al., 2008; Liu et al., 2012) have demonstrated that this fraction is considered to be more tightly retained and unavailable to plants, Hsu et al. (2012) obtained a contrary finding that amorphous iron oxide-bound As was positively correlated with the concentration of As in rice grain. In fact, the availability of F3, the amorphous iron oxide-bound As, depends on soil properties and environmental factors (Hsu et al., 2012). A previous study (Tufano et al., 2008) has examined the fate and transport of As, which is strongly affinitive for iron (hydr)oxides, in laboratory experiments. Their results reveal that substantial differences in As(III) and As(V) desorption occur from ferrihydrite, goethite, and hematite, and that As(III) is desorbed more rapidly and extensively from all of these oxides. Generally, As(III) is more mobile than As(V) and the valence state of As is an important factor affecting As mobility, which have been demonstrated by previous field studies (Takahashi et al., 2004; Yamaguchi et al., 2011).

In the present study, amorphous iron oxide bound-As exhibits low availability as indicated by the significantly negative correlations between the concentrations of As in the amorphous iron oxide-bound fraction in soils and those in brown rice (Fig. 3). Taking the previous reports mentioned above into consideration, the low availability of F3 should be related to the predominance of As(V) in As-bearing Fe(III) minerals of paddy soil in our study (Morin and Calas, 2006; Yamaguchi et al., 2014). Tracing back to the reason why amorphous iron oxide-bound As can be a good indicator of As availability to rice plants in paddy soils according to results from Hsu et al. (2012), while our study showed contrary, this also should be related to the valence state of As. In the study of Hsu et al., As derived from As-containing groundwater most likely existed as As(III) dominantly (Sankar et al., 2014). Of course, there may be some other factors resulting in the difference in the availability of the amorphous iron oxide-bound As, which needs further studies.

### 3.5. Environmental implications

In the actual environment, the effect of iron redox cycling on the fate of As might be more complicated. Notably, contamination of As has become a global environmental problem, especially As contamination of groundwater in South and Southeast Asia (Rodriguez-Lado et al., 2013). Moreover, As contaminated groundwater has caused elevated concentrations of As in rice paddy soil and rice plants (Takahashi et al., 2004; Dittmar et al., 2007). Therefore, it is crucial to explore effective remediation strategies to alleviate the possible health threats derived from As exposure. The paddy fields examined in this work are located in South China and are characterized by their reddish paddy soil containing abundant levels of iron oxides, which exhibit high reactivity and play an

important role in environmental biogeochemistry (Li et al., 2006; Borch et al., 2010). However, as far as we know, studies on the effect of iron redox cycling on the fate of As in South China derived from actual field conditions have been rare. The results from our study provides an indication that the health threat derived from As exposure for people via the uptake of rice contaminated by As-containing acid mining drainage might be mitigated by regulating the content of Fe in the amorphous Fe oxides fraction in soils such as adding iron oxides directly or prolonging the non-flooded period for rice growth (Takahashi et al., 2004) or regulating the content of nitrate (Senn and Hemond, 2002).

### Notes

The authors declare no competing financial interest.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.01.025>.

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