Simultaneous immobilization of arsenic and cadmium in paddy soil by Fe-Mn binary oxide: A field-scale study

Longyong Lin¹,², Junchun Li¹,³, Xiao Yang¹, Xiulan Yan¹,*, Tongtong Feng¹, Zhaoshu Liu¹, Yirong Deng², and Haiyan Zhou²,*

Paddy soil in south China has long been haunted by the co-contamination of arsenic (As) and cadmium (Cd), resulting in the relatively high accumulation of As and Cd in rice, which puts humanity into a food safety dilemma. Therefore, it is paramount to restrain the migration of contaminants from soil to rice grains to cushion their impact on human health. However, the opposite biogeochemical behaviors of As and Cd in paddy soils under flooding condition make it a great challenge to simultaneously immobilize both As and Cd, particularly for the large-scale remediation. In this work, lime, Fe₂O₃, and Fe-Mn binary oxides (FM) were performed for immobilizing As and Cd in paddy soil at a field-scale experiment, and their associated mechanisms were discussed. Results showed that 0.10 wt% of Lime reduced Cd in grain (36.68%), 0.60 wt% of Fe₂O₃ decreased the accumulation of As and Cd (28.32% and 26.91%, respectively), and 0.60 wt% of FM significantly decreased As and Cd (42.42% and 36.49%, respectively). Analytical results of As speciation in rhizosphere soils demonstrated that FM played a dual role in oxidation and adsorption toward As immobilization. The DGT-measured As and Cd concentrations in rhizosphere soils showed that 0.60 wt% of FM significantly reduced the bioavailability of As and Cd in the paddy soil by 65.63% and 52.98%, respectively. Moreover, 0.60 wt% of FM promoted the formation of Fe/Mn-plaque on root surface, which significantly enhanced the adsorption of As and Cd upon Fe/Mn-plaque (44.06% and 32.14%, respectively) and further inhibited the uptake of As and Cd by rice. Hence, the mechanism for As and Cd immobilization by FM can be summarized: (1) oxidation of As(III) to As(V) and transformation and immobilization of As and Cd in rhizosphere soil and (2) promotion of Fe/Mn-plaque formation on root surface to retard the uptake of As and Cd by rice. These efforts attempt to set up a theory-to-practice solution for remediating As and Cd co-contamination in paddy soil.

Keywords: Fe-Mn binary oxides (FM), Trace metals, Speciation, Immobilization, Paddy soil

1. Introduction
Due to large-scale mining and industrial activities, emission of industrial wastes, wastewater irrigation, and pollution of toxic metalloids in farmland around the mining area are becoming the most urgent environmental concerns, particularly the potential toxic elements (PTEs), for example, arsenic (As) and cadmium (Cd; Ye et al., 2018; Liu et al., 2019; Xiao et al., 2020; Zhou et al., 2020). The report on the National Soil Contamination Survey in 2014 shows that As and Cd were recognized as the most serious among the emerging inorganic pollutants, which were ranked third (the exceeding standard rate is 2.7%) and first (the exceeding standard rate is 7.0%), respectively. As and Cd commonly coexist in the paddy fields in south China where farming and mining are codependent, entailing the relatively high accumulation of As and Cd in rice (Wang et al., 2019; Wu et al., 2020). Recent studies have shown that the concentration of As in South China is the highest compared with other regions of China (e.g., North China, Northeast, East China, Northwest, Central China, and Southwest), reaching to 18.8 mg/kg, and the median Cd concentration is 7.9 times higher than other regions of China (e.g., Henan, Hubei, Anhui, Jiangsu, Zhejiang, Fujian, Shandong, Heilongjiang, Jilin, Xinjiang, Liaoning, and Hebei provinces; Chen et al., 2018; Zhou et al., 2018). Meanwhile, rice consumption has been identified as the main exposure route of dietary intake worldwide,
especially in Asia, for example, contributing about 60% of the dietary As intake and 56% of the dietary Cd intake for the general population in China (Chen et al., 2018; Xu et al., 2018). Therefore, it is very urgent to impede the migration of As and Cd from soil to rice, which is of great significance to alleviate the risks of As and Cd in the paddy soil in the main rice producing areas, thereby securing the safe rice (Chen et al., 2018; Carrijo et al., 2019; Zhai et al., 2020).

As and Cd in paddy soil usually exhibit opposite geochemical behavior (Yang et al., 2018). For example, an increase in soil pH will cause a negative surface charge, which may promote the desorption of negatively charged As upon soil surface and increase its bioavailability, while Cd in the soil is often positively charged, giving opposite response when soil pH is increased (He et al., 2020; Kumarathilaka et al., 2018). Nevertheless, rice is typically grown under flooding conditions. Arsenic adsorbed on Fe(III) would be dissolved and released into the soil solution due to the reduction reaction, thereby improving the bioavailability of As. However, a reducing condition enables the soluble Cd(II) to form precipitates, resulting in low bioavailability (Honma et al., 2016; Yu et al., 2017).

Immobilization is considered as an effective way to restrict the toxic metal bioavailability in the soil and prevent their uptake from soil to rice (Liu et al., 2020a; Zhai et al., 2020). Various soil amendments have been developed to increase the mobility and bioavailability of heavy metals, and lime and iron oxides were the most common amendments used in heavy metal-contaminated paddy soils (Chen et al., 2017; Mahar et al., 2017; Xu et al., 2017; Du et al., 2018). Application of lime can sustain the soil pH at a high level (>6.5), which is favorable for Cd immobilization. For the case of As, the situation becomes more complicated because As has two different valences (As(III) and As(V)), taking on a completely different geochemical behavior. Although the iron oxides have been widely used for ameliorating As pollution, their adsorption capacity is highly dependent on the chemical form of As. In general, the interaction between As(III) and iron oxides is normally less effective than that of As(V) (Zhang et al., 2014; Du et al., 2018). Therefore, the synthesis of high-performance soil amendment materials becomes significant for the development of this technology.

Fe-Mn binary oxide (FM) has received considerable attention due to its high effectiveness in immobilizing PTEs (Liu et al., 2020b; Zhang et al., 2020; Zheng et al., 2020). Iron (Fe) and manganese (Mn) oxides, both relatively abundant in soils, are environmentally benign materials. Zhang et al. (2014) reported that the FM binary oxides possessed the oxidation property of manganese dioxide and showed a higher adsorption capacity for As than that of pure iron oxide. Our previous study also confirmed that FM could significantly immobilize As, Pb, and Cd in contaminated soils (Fei et al., 2016; Yan et al., 2020). The FM binary oxide has more pores and thus has a larger specific surface area and more adsorption sites for PTEs capture. For example, the abundant hydroxyl groups on FM surfaces can bind more heavy metal ions, and its adsorption mechanism is superior to conventional pure phase materials (Yan et al., 2020). However, these investigations mainly focused on single heavy metal contaminated soil, rarely in the polymetallic combined pollution soil, and few field-scale experiments were carried out. Therefore, to evaluate the feasibility of immobilizing As and Cd by FM under natural flooding conditions, a series of field experiments were conducted. This work aims to (1) investigate the immobilization efficacy of As and Cd by FM in paddy soils and the accumulation of As and Cd in rice and soil and (2) to reveal the interaction mechanisms between pollutants (As and Cd) and FM in paddy soils.

2. Materials and methods

2.1. Materials and amendments

FM was synthesized using a combined oxidation and co-precipitation method described in our previous studies. The results of mineralogical analysis show that its microscopic morphology is an aggregation of small particles with coarse surfaces, with an Fe/Mn molar ratio of 2.99 and an average particle diameter of 33 μm (Zhou et al., 2019; Yan et al., 2020). Lime (CaO 57.3%, labeled as LE) and Ferric oxide (Fe₂O₃ 99%, labeled as FO) were obtained from the Soil and Fertilizer Institute of Hunan Province (Changsha, China) and Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), with average particle size of 45 μm and 23 μm, respectively.

2.2. Field experiments

The field experiments were performed in the downstream farmland of a large polymetallic mine in Shaoguan city, Guangdong province, China (Figure 1). The mine area has a long history of mineral extraction and processing associated with long-term discharge of acidic wastewater, resulting in widespread pollution of downstream rivers. Flooding and irrigation with the contaminated river water caused serious heavy metal pollution in the surrounding rice fields (Cui et al., 2019).

The field treatments (0.30 and 0.60 wt% for both FM and FO, 0.05 and 0.10 wt% for LE, and the control [CK]) were carried out with five replications, and the area of each experimental plot was 24 m² (4 × 6 m). The average contents of As and Cd in the soil of the seven experimental plots were 68.29 mg/kg and 1.47 mg/kg, respectively. The soil pH ranged from 4.23 to 4.68, the organic matter content was approximately 25.68 to 32.00 mg/kg, the soil sand particle contents were 450.2 g/kg, the soil silt particle contents were 220.5 g/kg, and the soil clay particle content was 265.8 g/kg. The type of studying soil pertains to red soil and lateritic red soil. On February 1, 14, 28, 2017, the surface paddy soil (top 30 cm) was fully agitated by rotary cultivator for 3 times a day and left fallow for a month. On March 30, 2 days before transplanting, compound fertilizer (30 g/m²) and all the amendments were spread evenly for each experimental plot and then mixed with a plow. On April 1, the indica rice seedlings, which have grown for 20 days, were transplanted to each experimental plot with the planting density of about 20 × 20 cm. Urea were applied into the soils by 3.7, 7.5, and 9.0 g/m² on April 6, April 22, and June 1, respectively. Between April 13 and April 22, the paddy field was dried...
for 10 days. The rice plants were harvested and rhizosphere soil was collected on July 20.

The plants were rinsed with deionized water and then divided into two portions. The first portion was heated at 105 °C for 30 min, dried at 65 °C to achieve constant weight and then crushed for As and Cd analysis. The second portion was used for Fe and Mn plaques extraction. Rhizosphere soil samples were also divided into two portions. The first portion was dried in shade, crushed using an agate mortar and then sieved through a 0.85 and a 0.15 mm mesh, respectively, for future analysis. The sieved soils (0.85 mm) were subjected to the analysis of pH, total As and Cd, and available As and Cd. The second portion (0.15 mm) was prefrozen for As speciation analysis.

2.3. Chemical analysis

2.3.1. Total As and Cd analysis
Pulverized plant samples (0.50 g) were slowly heated and digested in 10 ml of HNO₃ and 2 ml of HClO₄ on a hot plate. Till the mixture became transparent, its volume was adjusted to 50 ml with ultrapure water (EPA Method 3010A). 0.50 g of sieved soil (0.15 mm) was digested with 10 ml of HNO₃ and 10 ml of 30% H₂O₂ until the soil turned white and the supernatant solution became slightly yellowish (United States: N. p). The digestion solution was filtered, and the volume was adjusted to 50 ml by deionized water. The extract was filtered through a 0.45 μm membrane for As speciation test using liquid chromatography coupled to atomic fluorescence spectroscopy (LC-AFS, AFS-9130, Titan Instruments, Beijing, China). The physicochemical properties of the soils were determined following SSICA (1980).

2.3.2. Soil As speciation and physicochemical properties
Soil As speciation was determined by the method of previous report (Garcia-Manyes et al., 2002). Freeze-dried soil samples (0.20 g) were extracted with 10 ml mixed solution of 1.0 mol/L phosphoric acid and 0.1 mol/L ascorbic acid. The samples were oscillated for 2 h at 300 r/min and centrifuged at 3,000 r/min for 15 min. After repeating this procedure twice, the supernatants were filtered into a volumetric bottle, and the volume was adjusted to 50 ml by deionized water. The extract was filtered through a 0.45 μm membrane for As speciation test using liquid chromatography coupled to atomic fluorescence spectroscopy (LC-AFS, AFS-9130, Titan Instruments, Beijing, China). The physicochemical properties of the soils were determined following SSICA (1980).

2.4. Available As and Cd in soil measured by the diffusive gradients in thin films (DGT) technique
The Zr-oxide and Chelex DGT (Nanjing Vision Environmental Science & Technology Co., Ltd., Nanjing, China) were used for measurement of DGT-labile As and Cd, respectively (Chen et al., 2017; Zhang et al., 2017). DGT devices were deployed (24 h at 20 ± 1°C) by carefully
pressing them onto the soil paste with gentle pressure to ensure complete contact between the filter membrane of the piston and the soil surface. Upon retrieval, DGT devices were jet-washed with ultrapure water to remove soil particles and then disassembled. The resin gels were removed and immersed in 1 ml of 1 mol/L HNO₃ in micro-centrifuge PVC tubes for at least 24 h at 20 ± 1 °C before As and Cd analysis. The DGT-measured As and Cd concentrations (C_{DGT}) were calculated based on the following equation:

\[ C_{DGT} = \frac{M \cdot \Delta g \cdot D \cdot A \cdot t}{D_g} \]

where
- M: The accumulated mass of As or Cd over the deployment time (ng)
- \( \Delta g \): The thickness of the diffusive layer (cm)
- D: The diffusion coefficient of As or Cd in the diffusive layer (cm²/s)
- A: The area of the DGT exposure window (cm²)
- t: The DGT deployment time (s).

### 2.5. Extraction of Fe/Mn plaques

Fe and Mn plaques were extracted by a dithionite-citrate-bicarbonate (DCB) solution described by Dong et al. (2016). Briefly, the root was incubated for 60 min at room temperature (20–25°C), which is immersing in 15 ml of a solution containing 0.03 mol/L Na₃C₆H₅O₇·2H₂O, 0.125 mol/L NaHCO₃, and 0.144 mol/L Na₂S₂O₄. The root was rinsed 3 times with deionized water, which was then added to the DCB extract. The extracted solution was made up to 25 ml by adding deionized water for As and Cd analysis.

### 2.6. Statistical analysis

Statistical analysis was performed using Microsoft Excel 2010 and Statistic Package for Social Science 13.0 (SPSS Inc. 2004. SPSS 13.0 Base Users Guide. SPSS Inc., Chicago, IL, USA). A significance test was executed.

### 3. Results

#### 3.1. Effect of different amendments on As/Cd accumulation and growth of rice

The effects of different amendments on As and Cd accumulation in different parts of rice are given in Figure 2A and B. The concentrations of both As and Cd in grains were much higher than the maximum allowable limits (As ≤ 0.02 mg/kg, Cd ≤ 0.02 mg/kg) set by the State Environmental Protection Administration in China (GB 2762–2017). Regarding the different tissues of rice plants, concentrations of As followed the order of root > straw > husk > grain, and concentrations of Cd followed the order of root > straw > grain > husk. Both As and Cd are preferentially accumulated in rice roots (Yu et al., 2016).

Compared to the CK, the FM treatments substantially decreased total As and Cd in the grain, husk, straw, and root of rice (P < 0.05). Among them, 0.60 wt% of FM has the most effect, reducing the As and Cd contents in rice grains by 42.42% and 36.49%, respectively. By contrast, in the LE treatment, the total Cd concentrations in rice grain, husk, straw, and root presented a marginal reduction. However, the LE treatment did not decrease As concentration in the four tissues of rice (P < 0.05). The FO treatments substantially reduced total As and Cd in the grain, husk, straw, and root of rice, but the reduction was less than that of FM treatment. Therefore, among the three tested amendments, FM offered a best immobilization performance toward both As and Cd under flooding conditions in paddy fields.

![Figure 2](https://doi.org/10.1525/elementa.2020.094.f2)
Meanwhile, the effects of amendments on rice growth were also investigated in Figure 2C. Application of 0.30 wt% FM increased rice grain yield by 19.51%, but the addition of 0.60 wt% FM slightly decreased the rice grain yield. When LE addition increased from 0.05 to 0.10 wt%, the rice grain yield decreased. In the case of FO, the rice grain yield increased when increasing FO dosage from 0.30 to 0.60 wt%. Meanwhile, the yield of rice husk, straw, and root showed similar trends with rice grain in each treatment. It suggested that the addition of the amendments should be balanced between the rice As and Cd accumulation and the rice yield.

3.2. Available As and Cd in rhizosphere soil measured by DGT

$C_{\text{DGT}}$ (DGT-measured concentrations) of As and Cd in rhizosphere soil by different treatments are given in Figure 3. $C_{\text{DGT}}$ of As and Cd in CK were 419.03 and 13.10 µg/L, respectively. For 0.60 wt% of FM treatment, $C_{\text{DGT}}$ of both As and Cd decreased significantly by as much as 65.63% and 52.98%, respectively ($P < 0.05$). For the LE treatment, although the $C_{\text{DGT}}$ of Cd decreased significantly ($P < 0.05$), however, $C_{\text{DGT}}$ of As showed no significant changes ($P < 0.05$). In the FO treatment, the addition of 0.60 wt% FO can greatly reduce the $C_{\text{DGT}}$ of both As and Cd concentrations by 42.01% and 34.05%, respectively ($P < 0.05$). Therefore, among the three treatments, FM treatment can simultaneously reduce the $C_{\text{DGT}}$ of As and Cd in rhizosphere soils with the greatest reduction rate.

3.3. As speciation in rhizosphere soil

Soil As speciation in different treatments are given in Figure 4. The results showed that As in flooding soil existed in two inorganic speciation, As(V) and As(III), accounting for 72.17% and 27.83%, respectively. For FM treatment, under 0.60 wt% FM, the concentration of As(III) in the rhizosphere soil of rice was significantly reduced, and its proportion dropped to 6.31%. However, the cases of LE and FO treatments had a marginal effect on the distribution of As speciation in the rice rhizosphere soil, with As(III) accounting for 28.96–30.02% and 27.07–26.89% of the total As, respectively ($P < 0.05$). It suggested that As(III), known as more toxic, soluble, and mobile than As(V), was significantly decreased by the addition of FM under the flooding conditions.

3.4. Fe/Mn-plaque formation and As and Cd accumulation

The metal concentrations in the Fe/Mn-plaque of rice roots are given in Figure 5 and analyzed in conjunction with Figure 2. For FM treatment, as FM dosage increased to 0.60 wt%, both Fe and Mn concentrations in the root DCB extracts significantly increased by 32.08% and 29.09%, respectively ($P < 0.05$). Meanwhile, As and Cd in the Fe/Mn-plaque increased, and the total As and Cd in the root reduced, which were much higher than the treatments of adding LE and FO, especially for As. LE did not significantly affect Fe and Mn content in Fe/Mn-plaque, However, after adding 0.10 wt% LE, the total Cd concentration in the roots decreased by 39.82% and the
total As concentration slightly increased (2.34%). For FO treatment, as FO dosage increased to 0.60 wt%, the Fe concentration in the root DCB extracts was significantly increased by 11.21% compared with CK (P < 0.05), but the Mn concentrations remained almost unchanged. Meanwhile, due to the increase in Fe in the Fe/Mn-plaque, the total As and Cd in the root reduced by 28.81% and 12.74%, respectively.

3.5. Characterization of FM
The X-ray photoelectron spectroscopy (XPS) results of Fe2p and Mn2p electron binding energies of FM are illustrated in Figure 6A and B. The XPS peaks at the binding energies of 724.8 and 711.1 eV corresponded to Fe 2p1/2 and Fe 2p3/2 of Fe(III), while the peaks at 653.3 and 642.0 eV are assigned to the Mn 2p1/2 and Mn 2p3/2 of Mn(IV), respectively. The results revealed that the oxidation states of the Fe and Mn in the synthesized FM were Fe(III) and Mn(IV), respectively.

The FTIR spectra of FM (Figure 6C) showed that FM had abundant surface hydroxyl groups (–OH). The peaks at 3,421 and 1,635 cm⁻¹ were due to the stretching vibration of the adsorbed water and surface hydroxyls. The peaks at 1,128 and 977 cm⁻¹ were assigned to the bending vibration of Fe–OH groups, and the peak at 1,340 cm⁻¹ indicated the O-H bending vibrations combined with Mn atoms (Yan et al., 2020). In addition, the peak at 1,538 cm⁻¹ was attributed to the interaction between Mn oxide and Fe oxide (Gao et al., 2007).

4. Discussion
The FM was found to be a highly effective and sustainable soil amendment for simultaneous As and Cd immobilization in paddy soil. At different dosages of FM, total As and Cd in rice grains, husks, straw, and roots all decreased. For As and Cd immobilization, lime was only effective for Cd in rice; Fe₂O₃ had a certain immobilization capacity of both As and Cd.

By comparison, FM exhibited better performance than lime and Fe₂O₃ amendments. The three amendments showed no significant influence on soil pH due to the high acidity (pH 4.23–4.75) and strong pH buffer capacity of the paddy soil. As a strong alkaline material, 0.10 wt% LE elevated soil pH only to 4.68, therefore, exerting no significant effect on the bioavailability of As in this study. FM interacted with As and Cd mainly through adsorption and oxidation processes, with the promotion of Fe/Mn-plaque formation, which resulted in the toxicity reduction of As in both soil and rice. The main processes are schematically shown in Figure 7.

First, FM demonstrated excellent immobilization effectiveness on As and Cd in soil, mainly by oxidation and adsorption processes with As and adsorption processes with Cd. FM has a high specific surface area and pore volume, therefore possessing more adsorption sites and a large number of surface hydroxyl groups (–OH), which were the structural basis for its high adsorption (Fei et al., 2017; Zhang et al., 2007). Monolayer (chemisorption) and multilayer adsorption (physisorption) had occurred on the heterogeneous surface of FM (Yan et al., 2020). In general,
during flooding in paddy fields, the As in soil solution is elevated compared to dryland cultivation systems. The anaerobism would render poorly mobile As(V) to be reduced to highly mobile As(III) (Kumarathilaka et al., 2018). Mn oxides played an important role in the biogeochemical cycle of As in soil because they are strong abiotic oxidants for As(III) (Xu et al., 2017). The Mn(IV) could oxidize As(III) to generate As(V), which was much easier to be adsorbed by FM (Zhang et al., 2007). Zhang et al. (2007) reported that the peak at 1,538 cm−1 disappeared after the reaction with arsenite, possibly because of the changed surface chemistry caused by the redox reaction between As(III) and FM. The As(V) was transferred to the surface of FM from bulk solution and adsorbed through forming an inner spherical bidentate binuclear complex (Zhang et al., 2020). Meanwhile, Mn(IV) was reduced into Mn(II) to form manganese oxide on the surface of FM, which further facilitates the adsorption. Mechanistically, the adsorption active site is mainly centered on the cation vacancy in the octahedral layer inside of MnO₆, and/or the side edge outside of MnO₂ (Wang et al., 2012). There are studies showing that the oxidation of As(III) can occur through two consecutive single electron transfer steps while forming an intermediate Mn(III) product. The product may also be adsorbed on the surface of Mn oxides or replace the surface Mn(IV), leading to further passivation (Lafferty et al., 2010). It was reported that the binary oxides showed higher adsorption capacity for As than that of the pure Fe oxide (Zhang et al., 2014). Zhang et al. (2007) found that FM can efficiently oxidize and adsorb As with a maximum adsorption capacity of 1.77 mmol/g in solution. Therefore, FM played a dual role of oxidation and adsorption for As immobilization; however, the interaction between FM and Cd was only controlled by adsorption process. In contrast, FO provided the adsorption sites for As, and LE had no significant effect on As immobilization.

Second, FM can inhibit the uptake of As and Cd by rice, via promoting the formation of Fe/Mn-plaque. This is because the addition of FM increased the content of Fe²⁺ and Mn²⁺ in the soil, and the presence of As and Cd will promote the formation of O₂ and H₂O₂ in root and shoot tissues, which in turn enhances the release of these free radicals and O₂ from the roots. A large amount of Fe²⁺ and Mn²⁺ is oxidized, and more intensive Fe/Mn plaque is achieved near the root surface (Lee et al., 2012; Dong et al., 2016). Fe plaque, the so-called layer of Fe oxides that is often found on the root surface (Fu et al., 2016), was
generally considered to be a buffer or barrier toward As and Cd (Li et al., 2019). Recent studies validated that Mn is beneficial to the formation of Fe-plaque; therefore, Fe/Mn-plaque of rice has been intensively concerned (Dong et al., 2016). Chen et al. (2019) showed that the addition of Fe(II) and Mn(II) promoted the oxidative precipitation of Fe and Mn on the surface of rice roots. Although the amount of Mn in Fe/Mn-plaque on the root surface was relatively low (Figure 5), the involvement of manganese oxides could enhance the adsorption capacity of heavy metals, owing to their relatively high adsorptive/oxidative activity and abundant OH functional groups that are capable of anchoring the PTEs (Ye et al., 2001; Xu et al., 2015). On the other hand, the introduced exogenous Mn$^{2+}$ would bind to carrier proteins and channel proteins on the cell membrane to antagonize Cd$^{2+}$. This process reduces the amount of Cd$^{2+}$ in the cytoplasm of the root cells and the amount of Cd$^{2+}$ transported to the bud, thereby reducing the physiological toxicity of Cd and mitigating the accumulation of Cd$^{2+}$ in plants (Chen et al., 2019). The uptake of As and Cd by the roots is reduced. It hinders the transport of As and Cd from the root to the organs, including the straw, husk, and grain, thus limiting the accumulation of As and Cd in rice plants. In general, the observed decrease in rice As and Cd by application of FM can be explained by the above proposed interaction mechanisms, which could be further utilized for future design of high-performance soil amendments.

5. Conclusions

Synthetic FM was applied in As and Cd co-contaminated paddy fields in southern China to explore its performance and mechanism for As and Cd immobilization under field and natural flooding conditions. In comparison to lime and Fe$_2$O$_3$, FM showed a higher effectiveness in reducing both As and Cd mobility in paddy soil. The mechanisms found involved two aspects: (1) oxidation of As(III) to As(V) and adsorption of As and Cd worked synergistically in the immobilization of As and Cd in rhizosphere soil and (2) enhanced Fe/Mn-plaque on the root surface effectively inhibited the uptake of As and Cd by rice. Our findings revealed that FM could be considered as useful soil amendment for immobilizing As and Cd from paddy fields under flooding conditions; however, the application rate should be further optimized to balance the grain production and economic merits.

Data accessibility statement

All data are included in the manuscript.
Funding
National Key R&D Program of China (2017YFD0800900) and Guangzhou Science and Technology Program (20180410424, 201707010144) provided financial support.

Competing interests
The authors have declared that no competing interests exist.

Author contributions
Contributed to conception and design: YXL, YX.
Contributed to acquisition of data: LLY, LJC.
Contributed to analysis and interpretation of data: LJC, YX, ZHY.
Drafted and/or revised the article: LLY, LJC, YX, DYR, ZHY.
Approved the submitted version for publication: YXL.

References
Carrijo, DR, Li, C, Parikh, SJ, Linquist, BA. 2019. Irrigation management for arsenic mitigation in rice grain: Timing and severity of a single soil drying. Sci Total Environ 649: 300–307. DOI: https://doi.org/10.1016/j.scitotenv.2018.08.216.

Chen, H, Lei, J, Tong, H, Gu, M, Fang, Y, Wang, X, Tang, C, Li, Z, Liu, C. 2019. Effects of Mn(II) on the oxidation of Fe in soils and the uptake of cadmium by rice (Oryza sativa). Water Air Soil Pollut. 230(8). DOI: https://doi.org/10.1007/s11270-019-4237-3.

Chen, H, Tang, Z, Wang, P, Zhao, FJ. 2018. Geographical variations of cadmium and arsenic concentrations and arsenic speciation in Chinese rice. Environ Pollut 238: 482–490. DOI: https://doi.org/10.1016/j.envpol.2018.03.048.

Chen, TB, Yan, XL, Liao, XY, Xiao, XY, Huang, ZC, Xie, H, Zhai, LM. 2005. Subcellular distribution and compartmentalization of arsenic in Pteris vittata L. Chin Sci Bull 50(24): 2843–2849. DOI: https://doi.org/10.1360/982005-943.

Chen, Z, Tang, YT, Yao, AJ, Cao, J, Wu, ZH, Peng, ZR, Wang, SZ, Xiao, S, Baker, AJM, Qiu, RL. 2017. Mitigation of Cd accumulation in paddy rice (Oryza sativa L) by Fe fertilization. Environ Pollut 231(Pt 1): 549–559. DOI: https://doi.org/10.1016/j.envpol.2017.08.055.

Cui, JL, Zhao, YP, Lu, YJ, Chan, TS, Zhang, LL, Tsang, DCW, Li, XD. 2019. Distribution and speciation of copper in rice (Oryza sativa L.) from mining-impacted paddy soil: Implications for copper uptake mechanisms. Environ Int 126: 717–726. DOI: https://doi.org/10.1016/j.envint.2019.02.045.

Dong, MF, Feng, RW, Wang, RG, Sun, Y, Ding, YZ, Xu, YM, Fan, ZL, Guo, JK. 2016. Inoculation of Fe/Mn-oxidizing bacteria enhances Fe/Mn plaque formation and reduces Cd and As accumulation in rice plant tissues. Plant Soil 404(1–2): 75–83. DOI: https://doi.org/10.1007/s11104-016-2829-x.

Du, Y, Wang, X, Ji, X, Zhang, Z, Saha, UK, Xie, W, Xie, Y, Wu, J, Peng, B, Tan, C. 2018. Effectiveness and potential risk of CaO application in Cd-contaminated paddy soil. Chemosphere 204: 130–139. DOI: https://doi.org/10.1016/j.chemosphere.2018.04.005.

Fei, Y, Yan, X, Liao, X, Li, Y, Lin, L, Shan, T. 2016. Stabilization effects and mechanisms of Fe-Mn binary oxide on arsenic and heavy metal co-contaminated soils. Acta Scientiae Circumstantiae 36(11): 4164–4172.

Fei, Y, Yan, X, Liao, X, Li, Y, Lin, L, Shan, T. 2017. Stabilization effects and ecological impacts on As and heavy metal co-contaminated soils stabilized by Fe-Mn binary oxides. J Agro-Environ Sci 36(1): 57–65.

Fu, Y-Q, Yang, X-J, Ye, Z-H, Shen, H. 2016. Identification, separation and component analysis of reddish brown and non-reddish brown iron plaque on rice (Oryza sativa) root surface. Plant Soil 402(1–2): 277–290. DOI: https://doi.org/10.1007/s11104-016-2802-8.

Gao, TR, Yang, DZ, Zhou, SM, Chantrell, R, Asselin, P, Du, J, Wu, XS. 2007. Hysteretic behavior of angular dependence of exchange bias in FeNi/FeMn bilayers. Phys Rev Lett 99(5). DOI: https://doi.org/10.1103/PhysRevLett.99.057201.

Garcia-Manyes, S, Jimenez, G, Padro, A, Rubio, R, Rauret, G. 2002. Arsenic speciation in contaminated soils. Talanta 58(1): 97–109. DOI: https://doi.org/10.1016/s0039-9140(02)00259-x.

He, Y, Lin, H, Jin, X, Dong, Y, Luo, M. 2020. Simultaneous reduction of arsenic and cadmium bioavailability in agriculture soil and their accumulation in Brassica chinensis L. by using minerals. Ecotoxicol Environ Saf 198. DOI: https://doi.org/10.1016/j.ecoenv.2020.110660.

Honma, T, Obha, H, Kaneko-Kadokura, A, Makino, T, Nakamura, K, Katou, H. 2016. Optimal Soil Eh, pH, and water management for simultaneously minimizing arsenic and cadmium concentrations in rice grains. Environ Sci Technol 50(8): 4178–4185. DOI: https://doi.org/10.1021/acs.est.5b05424.

Kumarathilaka, P, Seneweera, S, Meharg, A, Bundschuh, J. 2018. Arsenic speciation dynamics in paddy rice soil-water environment: Sources, physico-chemical, and biological factors - A review. Water Res 140: 403–414. DOI: https://doi.org/10.1016/j.watres.2018.04.034.

Lafferty, BJ, Ginder-Vogel, M, Sparks, DL. 2010. Arsenite oxidation by a poorly crystalline Manganese-Oxide 1. Stirred-flow experiments. Environ Sci Technol 44(22): 8460–8466. DOI: https://doi.org/10.1021/es102013p.

Lee, C-H, Hsieh, Y-C, Lin, T-H, Lee, D-Y. 2012. Iron plaque formation and its effect on arsenic uptake by different genotypes of paddy rice. Plant Soil 363(1–2): 231–241. DOI: https://doi.org/10.1007/s11104-012-1308-2.

Li, H, Zheng, X, Tao, L, Yang, Y, Gao, L, Xiong, J. 2019. Aeration increases cadmium (Cd) retention by enhancing iron plaque formation and regulating pectin synthesis in the roots of rice (Oryza sativa)
seedlings. Rice (N Y) 12(1): 28. DOI: https://doi.org/10.1186/s12284-019-0291-0.

Liu, J, Li, N, Zhang, W, Wei, X, Tsang, DCW, Sun, Y, Luo, X, Bao, Za, Zheng, W, Wang, J, Xu, G, Hou, L, Chen, Y, Feng, Y. 2019. Thallium contamination in farmlands and common vegetables in a pyrite mining city and potential health risks. Environ Pollut 248: 906–915. DOI: https://doi.org/10.1016/j.envpol.2019.02.092.

Liu, J, Ren, S, Cao, J, Tsang, DCW, Beiyuan, H, Peng, Y, Fang, F, She, J, Yin, M, Shen, N, Wang, J. 2020b. Highly efficient removal of thallium in wastewater by MnFe$_2$O$_4$-biochar composite. J Hazard Mater 410: 123311–123311. DOI: https://doi.org/10.1016/j.jhazmat.2020.123311.

Liu, Z, Huang, Y, Ji, X, Xie, Y, Peng, J, Eissa, MA, Fahmy, AE, Abou-Elwafa, SF. 2020a. Effects and mechanism of continuous liming on cadmium immobilization and uptake by rice grown on acid paddy soils. J Soil Sci Plant Nutr. DOI: https://doi.org/10.1007/s42729-020-00297-9.

Mahar, A, Wang, P, Ali, A, Lahori, AH, Awasthi, MK, Wang, Z, Guo, Z, Wang, Q, Feng, S, Li, R, Zhang, Z. 2017. (Im)mobilization of soil heavy metals using CaO, FA, sulfur, and Na2S: A 1-year incubation study. Int J Environ Sci Technol (Tehran) 15(3): 607–620. DOI: https://doi.org/10.1016/j.ijsst.2017.01.017.1427-7.

Wang, X, Yu, HY, Li, F, Liu, T, Wu, W, Liu, C, Liu, C, Zhang, X. 2019. Enhanced immobilization of arsenic and cadmium in a paddy soil by combined applications of woody peat and Fe(NO3)3: Possible mechanisms and environmental implications. Sci Total Environ 649: 535–543. DOI: https://doi.org/10.1016/j.scitotenv.2018.08.387.

Wang, Y, Feng, X, Villalobos, M, Tan, W, Liu, F. 2012. Sorption behavior of heavy metals on birnessite: Relationship with its Mn average oxidation state and implications for types of sorption sites. Chem Geol 292–293: 25–34. DOI: https://doi.org/10.1016/j.chemgeo.2011.11.001.

Wu, J, Li, Z, Huang, D, Liu, X, Tang, C, Parikh, SJ, Xu, J. 2020. A novel calcium-based magnetic biochar is effective in stabilization of arsenic and cadmium co-contamination in aerobic soils. J Hazard Mater 387: 122010. DOI: https://doi.org/10.1016/j.jhazmat.2019.122010.

Xiao, A, Li, WC, Ye, Z. 2020. Effects of Fe-oxidizing bacteria [FeOB] on iron plaque formation, As concentrations and speciation in rice (Oryza sativa L.). Ecotoxicol Environ Saf 190: 110136. DOI: https://doi.org/10.1016/j.ecoenv.2019.110136.

Xu, C, Zheng, G, Lin, Y. 2018. Brief introduction to research projects on prevention and control of cadmium and arsenic pollution in croplands supported by National Key R&D Program of China in 13th Five-Year Period. J Agro-Environ Sci 37(7): 1321–1325.

Xu, W, Lan, H, Wang, H, Liu, H, Qu, J. 2015. Comparing the adsorption behaviors of Cd, Cu and Pb from water onto Fe-Mn binary oxide, MnO2 and FeOOH. Front Env Sci Eng 9(3): 385–393. DOI: https://doi.org/10.1007/s11783-014-0648-y.

Xu, X, Chen, C, Wang, P, Kretzschmar, R, Zhao, FJ. 2017. Control of arsenic mobilization in paddy soils by manganese and iron oxides. Environ Pollut 231(Pt 1): 37–47. DOI: https://doi.org/10.1016/j.envpol.2017.07.084.

Yan, X, Fei, Y, Zhong, L, Wei, W. 2020. Arsenic stabilization performance of a novel starch-modified Fe-Mn binary oxide colloid. Sci Total Environ 707: 136064. DOI: https://doi.org/10.1016/j.scitotenv.2019.136064.

Yang, X, Igalavithana, AD, Oh, SE, Nam, H, Zhang, M, Wang, CH, Kwon, EE, Tsang, DCW, Ok, YS. 2018. Characterization of bioenergy biochar and its utilization for metal/metalloid immobilization in contaminated soil. Sci Total Environ 640–641: 704–713. DOI: https://doi.org/10.1016/j.scitotenv.2018.05.298.

Ye, X, Li, H, Zhang, L, Chai, R, Tu, R, Gao, H. 2018. Amendment damages the function of continuous flooding in decreasing Cd and Pb uptake by rice in acid paddy soil. Ecotoxicol Environ Saf 147: 708–714. DOI: https://doi.org/10.1016/j.ecoenv.2017.09.034.

Ye, ZH, Cheung, KC, Wong, MH. 2001. Copper uptake in Typha latifolia as affected by iron and manganese plaque on the root surface. Can J Bot 79(3): 314–320. DOI: https://doi.org/10.1139/b01-012.

Yu, HY, Ding, X, Li, F, Fang, X, Zhang, S, Yi, J, Liu, C, Xu, X, Wang, Q. 2016. The availabilities of arsenic and cadmium in rice paddy fields from a mining area: The role of soil extractable and plant silicon. Environ Pollut 215: 258–265. DOI: https://doi.org/10.1016/j.envpol.2016.04.008.

Yu, HY, Yang, X, Li, F, Li, B, Liu, C, Wang, Q, Lei, J. 2017. Arsenic mobility and bioavailability in paddy soil under iron compound amendments at different growth stages of rice. Environ Pollut 224: 136–147. DOI: https://doi.org/10.1016/j.envpol.2017.01.072.

Zhai, W, Dai, Y, Zhao, W, Yuan, H, Qiu, D, Chen, J, Gustave, W, Maguffin, SC, Chen, Z, Liu, X, Tang, X, Xu, J. 2020. Simultaneous immobilization of the cadmium, lead and arsenic in paddy soils amended with titanium gypsum. Environ Pollut 258: 113790. DOI: https://doi.org/10.1016/j.envpol.2019.113790.

Zhang, G, Liu, F, Liu, H, Qu, J, Liu, R. 2014. Respective role of Fe and Mn oxide contents for arsenic sorption in iron and manganese binary oxide: An X-ray absorption spectroscopy investigation. Environ Sci Technol 48(17): 10316–10322. DOI: https://doi.org/10.1021/es501527c.

Zhang, G, Luo, J, Wang, L, Zhang, X. 2020. Polyvinyl alcohol-stabilized granular Fe-Mn binary oxide as an effective adsorbent for simultaneous removal of arsenate and arsenite. Environ Technol 41(20): 2564–2574. DOI: https://doi.org/10.1080/09593330.2019.1575479.

Zhang, G-S, Qu, J-H, Liu, H-J, Liu, R-P, Li, G-T. 2007. Removal mechanism of As(III) by a novel Fe-Mn binary oxide adsorbent: Oxidation and sorption.
How to cite this article: Lin, L, Li, J, Yang, X, Yan, X, Feng, T, Liu, Z, Deng, Y, Zhou, H. 2020. Simultaneous immobilization of arsenic and cadmium in paddy soil by Fe-Mn binary oxide: A field-scale study. *Elem Sci Anth.*, 8: 1. DOI: https://doi.org/10.1525/elementa.2020.094

**Domain Editor-in-Chief:** Steven Allison, University of California Irvine, Irvine, CA, USA

**Associate Editor:** Juan Liu, Guangzhou University, Guangzhou, China

**Knowledge Domain:** Ecology and Earth Systems

**Part of an Elementa Special Feature:** Pan-Pacific Anthropocene

**Published:** December 31, 2020  **Accepted:** October 16, 2020  **Submitted:** July 1, 2020

**Copyright:** © 2020 The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CC-BY 4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited. See http://creativecommons.org/licenses/by/4.0/.

*Elem Sci Anth* is a peer-reviewed open access journal published by University of California Press.