Sustainable removal of soil arsenic by naturally-formed iron oxides on plastic tubes

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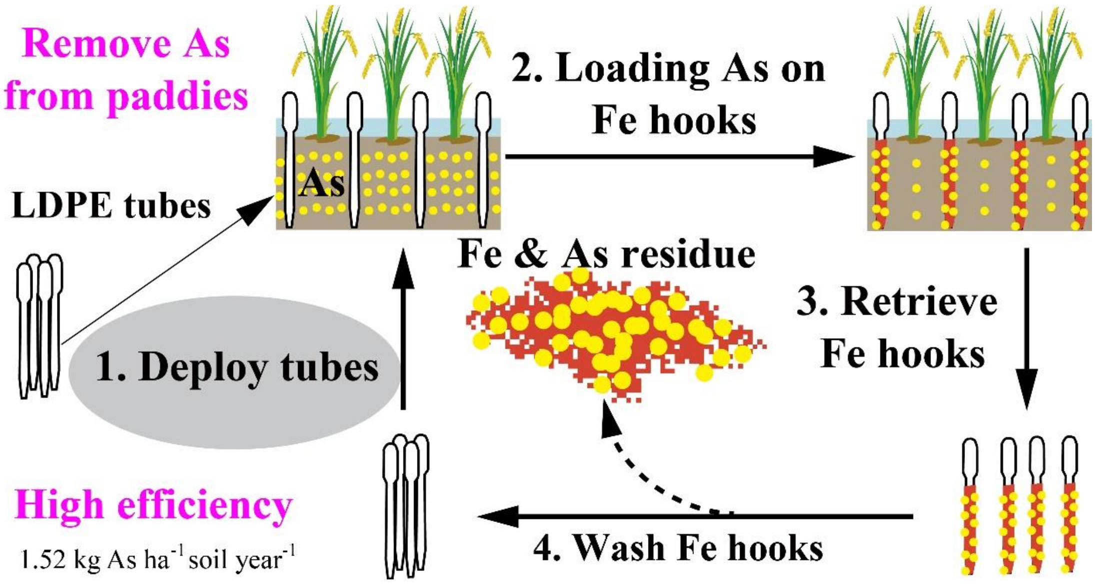
Environmental implication

This work developed a simple method to remove arsenic from soils. During the process, abundant iron minerals were induced on the surface of plastic tubes inserting into paddy soils; the tubes with iron oxides work as “hooks”, which are able to “fish” arsenic out of soils. This provides a new option to remediate arsenic contaminated soils. The results will be relevant for environmental scientists, engineers, land managers, and entrepreneurs as well as rice producers/consumers who are keen on obtaining As-safe rice grains.

Graphical Abstract



Highlights

- A novel As remediation method is able to efficiently remove As from paddy soils
- Massive Fe oxides can be induced on plastic tubes when inserted into flooded soils
- Tube-wall Fe oxides is able to adsorb much soluble As from flooded soils
- Tube-wall Fe oxides can be easily separated from soils and then washed and recycled
- Sustainable As removal from paddy soils is verified in real As contaminated soils

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Abstract

Arsenic (As) pollution in paddy fields is a major threat to rice safety. Existing As remediation techniques are costly, require external chemical addition and degrade soil properties. Here, we report the use of plastic tubes as a recyclable tool to precisely extract As from contaminated soils. Following insertion into flooded paddy soils, polyethylene tube walls were covered by thin but massive Fe coatings of 76.9-367 mg Fe m^{-2} in 2 weeks, which adsorbed significant amounts of As. The formation of tube-wall Fe oxides was driven by local Fe-oxidizing bacteria with oxygen produced by oxygenic phototrophs (e.g., *Cyanobacteria*) or diffused from air through the tube wall. The tubes with As-bound Fe oxides can be easily separated from soil and then washed and reused. We tested the As removal efficiency in a pot experiment to remove As from ~ 20 cm depth / 40 kg soils in a 2-year experiment and achieved an overall removal efficiency of 152 mg As m^{-2} soil $year^{-1}$, comparable to phytoremediation with the As hyperaccumulator *Pteris vittata*. The cost of Fe hooks was estimated at 555 RMB/666.7 m^2/year, and the profit of growing rice (around 1072 RMB/666.7 m^2/year) can be still maintained. The As accumulated in rice tissues was markedly decreased in the treatment (>11.1%). This work provides a low-cost and sustainable soil remediation method for the targeted removal of As from soils and a useful tool for the study and management of the biogeochemical Fe cycle in paddy soils.

Keywords: arsenic remediation, iron oxides, paddy soil, rice, adsorption

Environmental implication

This work developed a simple method to remove arsenic from soils. During the process, abundant iron minerals were induced on the surface of plastic tubes inserting into flooded paddy soils; the tubes with iron oxides work as “hooks”, which are able to “fish” arsenic out of soils. This provides a new option to remediate arsenic contaminated soils. The results will be relevant for environmental scientists, engineers, land managers, and entrepreneurs as well as rice producers/consumers who are keen on obtaining As-safe rice grains.

1. Introduction

Arsenic (As) contamination threatens the health of more than 50% of the global population who rely on rice (*Oryza sativa* L.) as a main staple food. Rice grains accumulate As due to high As availability in flooded paddy soils (Khan et al., 2010; Stroud et al., 2011) and efficient As uptake into rice tissues (Jia et al., 2014; Zhu et al., 2008). Thus, this results in high As concentration in rice grains even when the As concentrations in the paddy soils are below regulated pollution threshold levels (Chen et al., 2019; Chowdhury et al., 2018). As most rice-consuming people live in developing countries, a feasible solution to mitigate As risk in rice must be economically affordable and efficient in real field conditions.

Existing methods to mitigate soil As risk either require continuous external addition or generate undesirable waste. Chemical fixation by using iron (Fe) minerals is intensively studied but it can only temporarily reduce As availability (Qiao et al., 2018; Zhai et al., 2020). Together with the high cost, it is not favored in long-term field use. Chemical washing and phytoremediation are two promising methods that can permanently remove As (Jho et al., 2015; Ma et al., 2001), but both of them affect soil quality too. Phytoremediation is more promising because its impact on soil quality is much smaller than chemical washing (Alka et al., 2021). However, the plants that are able to hyperaccumulate As compete for space, light and nutrients with rice and require special facilities to treat a large amount of high-As bio-waste (Vocciante et al., 2019), which makes it not applicable in paddy fields.

Targeted removal of As, i.e., only removing As with minimal disturbance to soil matrix, was considered impossible because the precise separation always needs huge energy input (Cui et al., 2019). Meanwhile, many studies observed spontaneously-formed hotspots of toxic elements in natural environments. For instance, the As and Fe hotspots are found in Fe-Mn nodules (Chen et al., 2006), soil-water interfaces (SWI) (Mitsunobu et al., 2020; Tong et al., 2019) and the root surface of wetland plants (Chen et al., 2005; Yuan et al., 2021). The formation of As hotspots are fueled by the energy from light and/or biomass (Tong et al., 2019; Xu et al., 2016), and driven by biotic or abiotic activities. Removal of those hotspots looks like a very promising method to precisely extract the target elements from soils, as they are naturally formed with no input of external energy and chemicals. A recent study found removing rice roots and the carried Fe plaque, which accounted for 95% of total As in rice plants, was able to effectively reduce bioavailable As (He et al., 2020). However, those hotspots cannot be easily removed because they are small, unstable, and dispersed in soils.

Except for the naturally-formed hotspots, plastics can induce substantial and stable Fe and Mn oxides formation on the surfaces when inserting plastics into sediments, which was first reported in 1989 (Belzile et al., 1989). This phenomenon was proposed for *in-situ* separation and collection of pure deposits of natural Fe and Mn oxides (Belzile et al., 2001; Couture et al., 2010). Furthermore, similar Fe and Mn bands on plastic containers have been observed on Winogradsky column walls under illumination (Esteban et al., 2015). The Fe coating is usually explained by the effect of phototrophs grown on the walls. However, the formation of Fe oxides is also frequently observed in light-tight conditions (Xu et al., 2017). Although the naturally formed Fe oxides induced by plastics have been noticed by many researchers, the mechanism behind this phenomenon is seldom investigated to date.

Considering the strong coupling of Fe and As in soils, we hypothesized that plastics with self-formed Fe oxides could be a special tool to extract As from the soil porewater and separate it from the soil. Therefore, we proposed an As removal method by mimicking the natural As hotspot formation process and conceptualize it as “fishing” As out of soils by using plastic tubes as “hooks” and the naturally formed Fe oxides as “baits”. To resolve the underlying mechanism behind Fe hooks, we investigated the environmental parameters influencing the formation of Fe oxides on different plastics, including soil properties, light, nitrate input into soils and O_2 diffusion through plastic tubes. Here we present the results of As removal efficiency by the ‘Fe hook’ method from a 2-year pot experiment with growing rice in real As-contaminated soils.

2. Experimental procedures

2.1 Experimental preparation

Twenty-seven typical wetland soils used in this study, including paddy soils and freshwater sediments, were collected from 23 cities and 15 provinces across China. The upper soil layer to a depth of 20 cm of 25 paddies was sampled followed by wet sieving to remove stones and plant debris through a 1.0 mm diameter sieve. The top layer (~ 0-10 cm) of two sediments with reed was sampled and processed by the same method noted above. Geographic information of sampling sites and the selected soil properties are detailed in Supplementary data S1.

Rice (*O. sativa* L.) hybrid, Yliangyou-1, was sterilized and germinated following the previous report (Chen et al., 2012). The seedlings were grown in a Hoagland culture in a glass greenhouse (three-leaf stage) before being transplanted into soils. All the incubation was performed in a glass greenhouse. The greenhouse conditions were set and controlled at 25 °C controlled by an air conditioner.

2.2 Experiment 1: the universality of tube-wall Fe oxide formation

To study self-formed Fe oxides on tube walls, we used a 50 mL transparent polypropylene centrifuge tube to incubate the 27 wetland soils collected. It should be noted that Fe oxides form on tube walls which contacts the saturated soil. The centrifuge tubes were purchased from Minuo Co., Ltd (China). In the centrifuge tube, 50 g water-saturated soil (~ 8 cm depth) was filled, and DI water was added to submerge the soil to mimic flooding soil conditions. The incubated soil column has a diameter and height of 2.5 cm and 7 cm respectively. The tubes were incubated with natural sunlight exposure. There are three replicates for each soil. Brown-red precipitate could be automatically formed on tube sides in several days. After 30 d incubation, soil porewater was sampled by a Rhizon sampler (2.5 cm × 10 cm, MOM, Rhizon, Netherlands). The collected soil porewater was acidified with 6 M HCl to prevent Fe precipitation (Yuan et al., 2021). The centrifuge tubes were washed carefully with DI water until there were no soil particles, 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls (Gerhardt et al., 2005; Yuan et al., 2019).

2.3 Experiment 2: the effect of materials and their different shapes on tube-wall Fe oxide formation

Six common materials (diameter × length=0.8 cm × 10 cm) or tube (diameter × length=0.8-2 cm × 10 cm), including polymethyl methacrylate, polytetrafluoroethylene, nylon, polypropylene, polyethylene and glass, were supplied by Juyayuan Plastic Materials Co., Ltd (China). The plastics in stick or tube shape were inserted into saturated Suzhou (SZ) soils with a depth of 8 cm. The incubation was performed with natural sunlight exposure. After 30 d incubation, the sticks and tubes were taken out from the soil and washed with DI water until there were no soil particles. The formation of Fe oxides on sticks and tubes was recorded and compared.

2.4 Experiment 3: the effect of light conditions on tube-wall Fe oxide formation

The sealed polypropylene and low density polyethylene (LDPE) tubes were selected to assess the effect of light conditions on tube-wall Fe oxide formation in seven soils [i.e., Rugao (RG), Baoding (BD), Ganzhou (GZ), Shaoguan (SG), Kunming (KM), Wuxue (WX), and SZ] with various tube-wall Fe oxide production as determined by using the 27 soils. The ~15 cm length tubes were inserted into saturated soils with a depth of 8 cm, with ~7 cm length tubes above the soil surface. The incubation was performed with natural sunlight exposure or continuous dark conditions. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.5 Experiment 4: the effect of redox conditions on tube-wall Fe oxide formation

Inserting the oxygen-permeable tube into saturated paddies may change the redox conditions around the tube. Hence, the LDPE tube and saturated SZ soil were used to evaluate the effect of redox conditions on tube-wall Fe oxide formation. There are four treatments: i) the inserted LDPE tube without redox disturbance; ii) pump pure nitrogen gas (1.0 L min^{-1}) through the inserted LDPE tube to create an anoxic condition in the tube; iii) pump air (1.0 L min^{-1}) through the inserted LDPE tube to enhance the oxic condition in the tube; iv) add nitrate (500 μM) to the overlying water to enhance the oxic condition outside the tube. Nitrogen gas was provided by a high-pressure tank, air by an air pump. The tightness of the gas blowing system was carefully checked before the experiment to avoid gas leakage. The incubation was performed with continuous dark conditions. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.6 Experiment 5: the involvement of soil microbes in tube-wall Fe oxide formation

Seven soils (i.e., RG, BD, GZ, SG, KM, WX, and SZ) were used to identify whether soil microbes involve in tube-wall Fe oxide formation. 50 g saturated soils were added into a 50 mL centrifuge tube made with polypropylene. There are two treatments: i) without soil sterilization; 2) with soil sterilization by irradiation (50 k Gray, produced from a Co-60 source, Suzhou University). To maintain a sufficient sterile condition, the incubation (in 30 d) was strictly performed within a period (< 40 d) without obvious microbial colonies as reported by Wang et al. (2019). The sterile efficiency was not monitored in this study. There are three replicates for each treatment. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.7 Experiment 6: remediation of As-contaminated paddy soil with Fe hooks

A grey plastic container (width × length × height=30 cm × 40 cm × 23 cm) was used to incubate an As-contaminated (50.7 mg kg^{-1}) Qingyuan (QY) paddy soil. The soil was added to a depth of 20 cm to mimic the plow layer in paddies. Soils were flooded with DI water to maintain a standing water depth of ~ 3 cm above the topsoil surface during the 2-year experiment.

The LDPE tube (diameter × height=0.8 cm × 20 cm) serves as the carrier of tube-wall Fe oxides (also called Fe hooks in this study) and was applied to remediate the QY soil by removing soil As when taking out the tube and Fe hooks from soils. The experimental treatment includes with or without deploying LDPE tubes in soils. There are three replicates for each treatment. The LDPE tube is reusable after deployment. To maximize the removal efficiency by each tube, a short distance (i.e., > 5 cm) without obvious overlapping effect for soluble As and Fe was identified according to a preliminary test (Fig. S1). Accordingly, this equals to a density of < 400 tubes m^{-2} soil. To facilitate the operation, the insertion density is set at 20 tubes per container (~ 200 tubes m^{-2} soil), and the take-out frequency of the LDPE tube is set at every 14 d in warm seasons (annual spring to autumn) and every 30 d in winter according to the preliminary test. Two hills with a distance of 20 cm were grown in each container (Fig. S2). Three identical seedlings were transplanted in each hill on 17th June 2018 and 10th June 2019, respectively. During the experiment, soil porewater was sampled by a Rhizon sampler (one sampler per container). The collected soil porewater was acidified with 6 M HCl to prevent Fe precipitation. When taking out the Fe hooks, two of them were dissolved by 1 M HCl. The As removal rate was calculated by dividing the removed As (mg) by Fe hooks to total As in the soil (50.7 mg As kg^{-1} soil × 40 kg soil= 2028 mg As) and then multiplying 100.

Rice plants were manually uprooted and cut at ground level for determination of As at maturity. Fresh plants were separated into stems, leaves, and grains, followed by oven-drying (60 °C) of sub-samples for the subsequent determination of As accumulation in plants. Plant samples after oven-drying were weighed to measure plant dry matter and rice yield followed by grinding and sieving through a 1.0 mm sieve for chemical analysis. A sample of 0.50 g was digested using a 1:1 mixture of concentrated HNO_3 and H_2O_2 (Gustave et al., 2019). The digested samples were filtered through a 0.45 μm cellulose filter. Certified rice reference materials (GSB-23) were simultaneously processed for quality assurance, and sufficient recoveries (95.5 % to 105%) were obtained.

Potential plastic release of Fe hooks was simulated by continuously recycling plastic tubes's deployment and collection 200 rounds (equal to the operation in 10 years) in real paddy soils. The weight of the plastic tubes was recorded before and after the test, and the plastic surface was also checked with scanning electron microscopy (SEM).

2.8 Analytical measurements

A spectrophotometric method using 1, 10-phenanthroline was applied to determine the total Fe concentration (Tamura et al., 1974). Other elements, such as As, Pb, Sb, Ni, Co, Mn, Cd, Cu, and Cr, were analyzed with NexION 350X ICP-MS (PerkinElmer, Inc., Shelton, CT USA). Total organic carbon and total nitrogen were determined with a TOC/TN analyzer (Shimadzu TOC-VCPH, Japan). The morphology of the tube-wall Fe-oxides was scanned with SEM JSM-7600 (FJEOL Ltd., Japan) and energy dispersive spectroscopy (EDS) (<= 20 kV) under a low vacuum. The mineral structure was characterized by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ=1.5418 Å).

2.9 Microbial analysis

The bulk soil (1.0 cm distance from tube-wall Fe oxides) and soils adjacent to tube walls were sampled from the seven soils (i.e., RG, BD, GZ, SG, KM, and SZ) incubated under natural light or dark conditions. The genomic DNA of the soil was extracted by using the PowerSoil DNA Isolation Kit (MO BIO Laboratories, Inc. Carlsbad, USA) following the manufacturer's instructions.

Extracted DNA was subjected to barcode amplification of the V3–V4 hypervariable region of the 16S rRNA gene at GENEWIZ, Inc. (Suzhou, China). The effective sequences were selected using the same method by Wu et al. (2016). The detailed DNA sequencing and raw data processing information can be found in supplementary files. The average length of the remaining sequences is 450 bp. The effective sequences were grouped into operational taxonomic units (OTUs) at a similarity of >= 97%. The averaged top 15 phyla were analyzed and displayed. To identify the most variable microbe among different soil layers, the linear discriminant analysis (LDA) effect size (LEfSe) method was applied (Segata et al., 2011).

2.10 Statistical analysis

The 16S rRNA gene sequence data have been deposited in NCBI GenBank under the accession number: MF967611-MF968897. All the data were analyzed and plotted in R3.5.0 software unless noted elsewhere. The significance of linear regression and correlation matrix were tested with Fisher least significance difference (LSD) and Standard Student's t tests ($p < 0.05$), respectively.

3. Results

3.1 Iron oxide formation on plastic tube walls with various soils

We investigated whether Fe oxide formation on plastic tube walls is common in flooded soils. In this experiment, 27 soils collected from typical wetlands (mostly rice paddies) over China were used to test the Fe oxide formation on plastic tube walls (Fig. 1).

Plastics-induced Fe oxides were obtained in 22 out of 27 (81.5%) soil samples. Fresh naturally-formed minerals were observed clearly on tube walls under saturated soil incubation (Fig. 2a). When observed by SEM, the brown-red precipitate presented a network-like (Fig. 2b) and particle stacking structure (Fig. 2c). Iron content measured by EDS reached up to 30.3-53.9% of the fresh minerals (Fig. S3), indicating that the naturally formed minerals are mainly composed of Fe oxides. XRD analyses further identified the Fe oxides had low crystallinity (Fig. S4). The Fe oxide density on tube walls ranged from 3.02 to 376 mg Fe m^{-2}, with the porewater Fe from 0.270 to 57.7 mg L^{-1}.

A weak relationship was observed between dissolved Fe and precipitated Fe on tube walls. Fig. 2d clearly showed abundant Fe oxides were formed when porewater Fe was below 10 mg L^{-1}. The high porewater Fe in CZ1 (57.7±10.8 mg L^{-1}) and HA (41.7±14.3 mg L^{-1}) soils did not lead to thick tube-wall Fe coatings (CZ1: 147±54.3 mg Fe m^{-2}; HA: 25.8±6.18 mg Fe m^{-2}). The densest tube-wall Fe oxides were yielded in FS (336±12.6 mg Fe m^{-2}) and SG2 (376±18.4 mg Fe m^{-2}) soils with a moderate porewater Fe (3.21±1.13 mg L^{-1} and 13.8±4.57 mg L^{-1}, respectively).

The tube-wall Fe coatings are hotpots for siderophile elements (Fig. 2e, Table S1). Iron has a significantly positive relationship with As (R^2=0.535), antimony (Sb, R^2=0.186), and lead (Pb, R^2=0.120) (Fig. 2e-f, Table S1). It is worth noting that the elements are tightly bound to the tube-wall Fe oxides, which can be easily separated from soils. Considering the tight coupling between Fe and As, tube-wall Fe oxides could serve as 'Fe hook' for targeted extraction of As from saturated soils.

3.2 Abiotic factors that induce tube-wall Fe oxide formation

Iron oxide formation could be driven by both abiotic and biotic factors. To address the mechanism of Fe coating formation on tube walls, the potential drivers, including tube materials, light, and redox conditions, were investigated.

The common materials (including polymethyl methacrylate, polytetrafluoroethylene, nylon, polypropylene, polyethylene, low density polyethylene (LDPE) and glass) were assessed. Intriguingly, the materials in stick shape did not induce significant Fe oxide formation (Fig. S5a). In contrast, the polypropylene and LDPE materials in tube shape induced abundant tube-wall Fe oxide formation (Fig. S5b-c).

The effect of light on Fe oxide formation on polypropylene and LDPE tubes was investigated with 7 soils (i.e., RG, BD, GZ, SG, KM, WX, SZ). The magnitude of Fe oxide formation varied by 2.70 to 9.28 times under different circumstances (Fig. S6-7). The larger variation of Fe oxide formation was observed on polypropylene tubes no matter under natural light or continuous dark conditions. Generally, natural light induced more (average 29.1%) Fe oxides compared to the continuous dark (Fig. S6). In contrast, the Fe oxide formation on LDPE tubes was consistent under natural light or continuous dark conditions. The results from polypropylene and LDPE tubes indicate natural light facilitates, but is not essential for, Fe oxide formation on tube walls. Furthermore, Fe coating thickness on LDPE tubes was double that on polypropylene tubes, which made LDPE tubes an excellent carrier for making Fe hooks.

Three treatments with nitrogen gas, air, and nitrate addition were applied to study the availability of electron acceptors around the tubes on Fe oxide formation. Pure nitrogen gas and air continuously were pumped through the LDPE tubes, nitrate was added into bulk soils. Blowing gas through the tube would only slightly modify the redox condition around the tube, but not significantly change the reducing condition in bulk soils. Nitrogen gas treatment dramatically inhibited the Fe oxide formation (-70.4% compared to control, Fig. 3). Fe oxide formation was remarkably promoted (109%) when blowing air through the tube. Adding nitrate to soils also markedly accelerated the Fe oxide formation (187%), which might be driven by nitrate-dependent Fe-oxidizing bacteria. The trend of As adsorbed on Fe coating is different from the Fe precipitated on tubes. As shown in Fig. 3, maximum As adsorption was found in the control, both air and nitrate addition treatments significantly decreased the adsorbed As (-33.6%).

3.3 Biotic factors that induce tube-wall Fe oxide formation

We further tested whether microorganisms were involved in tube-wall Fe oxide formation. An initial study found soil sterilization significantly reduced the tube-wall Fe oxides in all the soils (average -67.4%, Fig. S8), but did not fully prevent Fe coating formation on tube wall.

Further study of the major microbial communities in bulk soils and soil adjacent to the tube walls is depicted in Fig. S9. The soil microbial communities were similar between the bulk soils and the soils adjacent to tube-wall in soils under dark conditions. Natural light treatments did not alter the microbial communities in the soils adjacent to tube-wall too, except for the SZ treatment. Light boosted the growth of *Cyanobacteria* in SZ soil. The known oxygenic phototrophic bacteria *FamilyI* (*Cyanobacteria*) and anoxygenic phototrophic bacteria *Chlorobiaceae* (*Chlorobi*) were also significantly promoted by natural light (Fig. 4c).

Strong positive relationships were found between the Fe oxide density and the richness of *Nitrospirae* (r=0.804), *Verrucomicrobia* (r=0.765), *Cyanobacteria* (r=0.699) and *Spirochaetes* (r=0.635). Meanwhile, there are negative relationships with *Rokubacteria* (r=-0.840), *Proteobacteria* (r=-0.679), *Latescibacteria* (r=-0.649) and *Gemmatimonadetes* (r=-0.534) (Fig. 4b). Tube-wall Fe oxide formation might reshape the soil microbial communities. Additionally, the precipitated Fe on tube walls under normal conditions had a strong relationship with the adsorbed As (R^2=0.836, Fig. 4a).

3.4 Remediation of soil As contamination with the Fe hook method

The potential application of using the Fe hook method to remediate As-contaminated paddy soil was tested in a pot experiment. The remediation process consists of 4 steps (Fig. 5a): i) LDPE tubes are inserted into the soil; ii) Fe hooks are naturally formed on the tubes; iii) Fe hooks are retrieved from the soils after 2 week's deployment; iv) the tubes are washed by tap water scrubbing and reused.

The efficiency of Fe hooks for remediating an As-polluted paddy soil was tested in two rice growing seasons (Fig. S2). Without applying Fe hooks, soluble As in soil porewater increased from 41.7 μg L^{-1} at Day 0 (initial soil flooding, 8th April 2018) to as high as 328 μg L^{-1} before rice seedling transplantation (Day 70, Fig. 5b). After five-round As removal by Fe hooks within 70 d, porewater As was only about 60% of the controls. Porewater As in the control group peaked at Day 98 and then decreased to 13.9 μg L^{-1} during the winter without growing rice. Although porewater As with Fe hooks followed a similar pattern, obvious As decline (-35.0%) was achieved during the rice production compared to control (Fig. 5b). Similarly, applying Fe hooks also significantly reduced porewater As in the second year's rice production. Reduction of porewater As by Fe hooks may be due to two causes: i) easily-mobile As pool in soil was significantly decreased; ii) mobile As in porewater was re-immobilized since soil Eh may be elevated by Fe hooks mediated O_2 loss in reducing soils.

The accumulated As removal amount by Fe hooks is presented in Fig. 5c. After two years' remediation, up to 304 mg m^{-2} As was removed by Fe hooks (Fig. S10), and the removal rate of total soil As was estimated to be 1.80% (Fig. 5c). Launching Fe hooks also markedly mitigated As accumulation in rice grain (-11.1%, Fig. S11) and significantly reduced both years' rice stem As (-16.1%, $p < 0.05$, Fig. S11). Meanwhile, the deployment of Fe hooks in 2 years removed 3.16 g C m^{-2} and 0.211 g N m^{-2} in the soil, which only represent 0.07% and 0.05% of total C and N. The results indicate Fe hooks have limited influence on major elements in soils. Additionally, there is no obvious impact of Fe hook deployment on rice biomass and yield.

Nanoplastic particles might be introduced into soils through Fe hooks. Thus, we tested the potential loss of plastic tube weight of deploying Fe hooks in paddy soils (Fig. S12). After 200 cycles of insertion and removal, the tubes were found to have many microscratches on the surface (Fig. S13). The weight loss averaged ~ 0.15%, which equals to a release of < 38 mg plastics m^{-2} soil $year^{-1}$. Moreover, a biodegradable plastic (i.e., polylactic acid) was demonstrated to be more efficient in stimulating tube-wall Fe oxide formation (43.2% higher) and their removal of soil As (55.7% higher) than LDPE (Fig. S14). This indicates Fe hook method could be further optimized to strengthen its performance in removing soil As, and the secondary pollution introduced by Fe hooks could be minimized by employing environmental-friendly materials.

4. Discussion

In this study, we proposed using Fe hooks (LDPE tubes with naturally-formed Fe coatings) for targeted removal of As from paddy soils. The LDPE tubes can induce localized Fe oxidation and As co-precipitation on the tube walls allowing extraction of

As while causing minimum disturbance to the soil. Moreover, this process requires no addition of chemicals, and only a thin layer of Fe and As is removed from the soil. Thus, the Fe hook method can precisely remove As with negligible disturbance to soil matrix.

4.1 Tube-wall Fe oxide formation

The formation of Fe coating on tubes is common in flooded soils and driven by abiotic and biotic factors. The tube-wall Fe-oxides against the soil have a filament-like structure when observed by SEM (Fig. 2b), which is similar to previously reported biogenic Fe-oxides (Kozubal et al., 2012). The Fe-rich filaments were frequently observed in biogenic Fe-oxides. This structure is considered as a robust biosignature of Fe oxidizing bacteria or fungal hyphae (Chan et al., 2011; Limmer et al., 2021). The XRD analysis showed there were no crystalized Fe minerals, so the tube-wall Fe oxides are mainly poorly crystal or amorphous Fe precipitate. The fresh biogenic Fe-oxides with low crystallinity have huge adsorption capacity and fix a large amount of heavy metal(loid)s (Sowers et al., 2017).

4.2 Tube-wall Fe oxide formation driven by abiotic factors

Oxygen diffusion from the atmosphere is the main driver of the Fe coating formation. Crétois et al. (2015) reported polypropylene and polyethylene plastics share a similar O_2 permeability value (50-100 vs. 50-200 cm^3 mm m^{-2} day^{-1} atm^{-1}). But, plastics with low molecular density could produce low intermolecular cohesion and large fractional free volume (Lagaron et al., 2004), thus have a very high O_2 permeability value, which could explain why LDPE tubes induced more Fe oxide formation than polypropylene tubes in this study (Fig. S6). According to reported O_2 diffusion rate in polyethylene plastics (0.4 mm thick, 10.1 cm^3 m^{-2} day^{-1} atm^{-1}) (Buntinx et al., 2014), the diffused O_2 could potentially produce substantial Fe oxides

(101 mg Fe m^{-2} d^{-1}) on tube walls assuming all the O_2 reacted with Fe^{2+}. Our results strongly support abiotic Fe oxidation by O_2 contributes to tube-wall Fe oxide formation, since blowing air through the tube significantly increased tube-wall Fe oxides, while blowing pure nitrogen significantly reduced tube-wall Fe oxides. Due to the O_2 limitation, solid sticks made by plastics were just covered by little Fe-oxide, which was also indicated by utilizing plastic sheets (4-36 mg m^{-2}) (Belzile et al., 1989). Surprisingly, an extra supply of O_2 or other easy-to-use electron acceptors (e.g., nitrate) stimulated Fe oxidation on tube walls and in bulk soils, but didn't increase As accumulation on Fe hooks (Fig. 3). We speculate that the porewater As was immobilized by the Fe oxides formed in bulk soils, rather than by Fe hooks. Thus, the adsorbed As on Fe hooks decreased.

Although Fe coatings on tubes are derived from the oxidation of dissolved Fe^{2+}, soluble Fe is not a determining factor for tube-wall Fe oxide formation (Fig. 2d). For example, in two soils (i. e., CZ1 and HA) with high soluble Fe (> 40 mg L^{-1}, Fig. 2d), no tube-wall Fe oxides were observed. Instead of Fe coating, greenish biofilm was found on the tube wall (Fig. S7b), which indicated there was algae. The phototrophs used light to produce O_2, which would prevent the soluble Fe in bulk soils from diffusing to the tube wall. In addition, the presence of phototrophs could promote reductive dissolution of As-bearing Fe minerals in paddy SWI through elevating the dissolved organic carbon (Guo et al., 2020), then lead to elevated porewater Fe concentration. Thus, the interface process between tube walls and bulk soils plays a vital role in Fe coating formation, especially the spatial distribution of microbial communities along the O_2 gradient.

4.3 Tube-wall Fe oxide formation driven by biotic factors

Soil microbes actively take part in regulating tube-wall Fe oxide formation. The microbial analyses indicated that tube-wall Fe oxides may be stimulated by *Nitrospirae*, *Verrucomicrobia*, *Cyanobacteria*, and *Chlorobi*. *Nitrospirae* is known nitrate-dependent Fe-oxidizing bacteria (Chen et al., 2009; Hedrich et al., 2011), and soil nitrate pool could be replenished by anthropogenic input (Huang et al., 2019) or naturally nitrogen fixation by *Verrucomicrobia* (Khadem et al., 2010). Phototrophic bacteria may contribute to Fe^{2+} oxidation on the transparent plastic tube via four pathways at early growth stage of rice when sunlight is not seriously intercepted by the crop canopy: i) stimulating nitrate-dependent Fe oxidation by offering nitrate substrate via nitrogen fixation (e.g., *Cyanobacteria*) (Ratering and Schnell, 2001); ii) activating microaerophilic Fe oxidizer (e.g., *Zetaproteobacterium*) by providing O_2 (Melton et al., 2014); iii) abiotic Fe oxidation by O_2 produced from oxygenic photobacteria like *Cyanobacteria* (Trouwborst et al., 2007); iv) biotic Fe oxidation by anoxygenic photobacteria like *Chlorobi* (Heising et al., 1999). In contrast, Fe-reducing bacteria, such as some kinds of *Proteobacteria* (Melton et al., 2014) and *Latescibacteria* (Zhang et al., 2019), may provide Fe^{2+} substrate for the tube-wall Fe oxide formation, or consume the formed tube-wall Fe oxides. In this study, the former process dominates under most conditions.

4.4 Advantages and constraints of using Fe hook method to remediate soil As

Iron hook method has its advantages and constraints not only in terms of cost but also in terms of feasibility, efficiency and environmental impact (Table S2). Iron hooks are tightly bound to tube walls. This character makes them easy to separate from soil particles, and not easy to fall off from tube walls. Hence Fe hooks will not cause the transfer of pollutants during the remediation process. And, Fe hooks can be washed with water scrubbing and then reused. This will greatly reduce the secondary pollutants produced during the remediation process. Iron hooks have a low cost (around 555 RMB/666.7 m^2/year) since the plastic tubes used are cheap and recyclable, and can still maintain the profit of growing rice (~1072 RMB/666.7 m^2/year). Compared with soil stabilization (Qiao et al., 2018; Zhai et al., 2020), Fe hooks show a big advantage in permanently remediating soil As contamination by removing As from soils. Compared with phytoremediation (Yang et al., 2020; Ye et al., 2011), Fe hooks do not compete for land with rice production, which may be more easily accepted by farmers. Iron hooks will produce some solid wastes rich in As-bearing Fe oxides, which require proper treatment after the remediation. The solid waste could be stabilized/inertizated with other materials as the bio-waste management of phytoremediation (Vocciante et al., 2019). By contrast, Fe hooks only produce little solid wastes (around 60 g m^{-2} soil $year^{-1}$), hence it is easier to process the waste deposits of Fe hooks than phytoremediation (Vocciante et al., 2019). Iron hooks did not significantly decrease As concentrations in rice grain during the 2-year pot experiment, possibly due to two causes: i) high variability of the measured samples; ii) the relative high porewater As since the experiment was performed under a continuous flooding condition. Iron hooks need further optimization before widespread applications. In addition, it may be difficult to handle Fe hooks at late growth stage of rice in the field, due to the relatively dense rice crop canopy.

The Fe hook method is still in its infancy and there are 2 major concerns of its feasibility in field application. First, intensive labor may require during the remediation, which is estimated of ~ two days' work for each cycle in 666.7 m^2 field. Compared to other remediation technologies, Fe hooks are very flexible and can be integrated into current agriculture machines, for example, rice transplanters may be used to plant a bunch of modified Fe hooks into paddy soils, thus the feasibility could be promoted. Second, the application of Fe hooks may escalate the plastic contamination in the arable lands. Although the microplastic released by Fe hooks (< 38 mg plastics m^{-2} soil $year^{-1}$) is negligible when comparing with the considerable microplastic pollution in farmland in China (2234 mg plastics m^{-2} soil) (Hu et al., 2022), the potential secondary pollution should be avoided considering long-term period is required to perform the soil As contamination. In a supplemental experiment, we verified biodegradable plastic tubes are also able to efficiently make Fe hooks as LDPE tubes (Fig. S14), hence it is a burning issue to test other more environmental-friendly materials for making high-efficiency Fe hooks. Remarkable advance in the relative field will pave the way for the widespread using Fe hook method in paddy fields.

Iron hooks can efficiently remove contaminants. The As removal efficiency (152 mg As m^{-2} soil $year^{-1}$ with a total soil As of 50.7 mg kg^{-1}) by Fe hooks is comparable to phytoremediation by *P. vittata* (29.6-142 mg As m^{-2} soil $year^{-1}$ with total soil As 7.60-74.3 mg kg^{-1}) (Yang et al., 2020; Ye et al., 2011) and rice plants with roots (133 mg As m^{-2} soil $year^{-1}$ with total soil As 39.7 mg kg^{-1}) (He et al., 2020). However, Fe hooks may influence soil properties. When taking Fe hooks out, the tubes bring out Fe oxides, as well as other elements bound with Fe (e.g., Mn, carbon, nitrogen, phosphorus etc.) (Chen et al., 2006; Koopmans et al., 2020; Yuan et al., 2020), with a weight around 60 g m^{-2} soil $year^{-1}$. Although such a rate would pose limited influence on soil major elements (e.g., < 0.1% carbon and nitrogen were removed after 2 years remediation in this study), more studies are essentially required to clarify the influence of Fe hooks on soil properties. Particularly, Fe hooks may deteriorate the phosphorous nutrient provision in the soil after long-term applications, since Fe hooks can remove considerable phosphorous owing to their high-binding affinity for phosphate (Koopmans et al., 2020).

4.5 Future prospect

The proof-of-concept work highlights 4 major areas to further improve the performance of the Fe hook method. First, we explore other environmental-friendly materials, especially biodegradable materials, for making Fe hooks. Second, the contact surface between Fe hooks and bulk soils determines the amount of Fe oxides and As on Fe hooks, thus the removal efficiency could be further enhanced by optimizing the tubes' material and surface topological structure, as well as the configuration of tubes deployment in soils. Third, the Fe and As behavior in the micro-interface between tubes and soils are still unclear, the mechanism is important to optimize the tube deployment pattern and maximize As removal efficiency. Finally, Fe hooks could combine with other strategies and improve the As removal efficiency. For example, external addition of organic matter like rice husk may increase As in the rice grain by enhancing the reductive dissolution of As-bearing Fe oxides. Since Fe hooks can be applied during the whole year, thus combining Fe hooks and organic matter amendment during the non-rice growing reason (e.g., winter and early spring) may be very promising in achieving rapid As reduction in plant tissues and permanent removal of As in soils.

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Conflicts of interest

The authors declare no financial conflict.

Data availability

Data and codes are available from https://doi.org/10.6084/m9.figshare.16836742.v1.

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Abstract

Arsenic (As) pollution in paddy fields is a major threat to rice safety. Existing As remediation techniques are costly, require external chemical addition and degrade soil properties. Here, we report the use of plastic tubes as a recyclable tool to precisely extract As from contaminated soils. Following insertion into flooded paddy soils, polyethylene tube walls were covered by thin but massive Fe coatings of 76.9-367 mg Fe m^{-2} in 2 weeks, which adsorbed significant amounts of As. The formation of tube-wall Fe oxides was driven by local Fe-oxidizing bacteria with oxygen produced by oxygenic phototrophs (e.g., *Cyanobacteria*) or diffused from air through the tube wall. The tubes with As-bound Fe oxides can be easily separated from soil and then washed and reused. We tested the As removal efficiency in a pot experiment to remove As from ~ 20 cm depth / 40 kg soils in a 2-year experiment and achieved an overall removal efficiency of 152 mg As m^{-2} soil $year^{-1}$, comparable to phytoremediation with the As hyperaccumulator *Pteris vittata*. The cost of Fe hooks was estimated at 555 RMB/666.7 m^2/year, and the profit of growing rice (around 1072 RMB/666.7 m^2/year) can be still maintained. The As accumulated in rice tissues was markedly decreased in the treatment (>11.1%). This work provides a low-cost and sustainable soil remediation method for the targeted removal of As from soils and a useful tool for the study and management of the biogeochemical Fe cycle in paddy soils.

Keywords: arsenic remediation, iron oxides, paddy soil, rice, adsorption

Environmental implication

This work developed a simple method to remove arsenic from soils. During the process, abundant iron minerals were induced on the surface of plastic tubes inserting into flooded paddy soils; the tubes with iron oxides work as “hooks”, which are able to “fish” arsenic out of soils. This provides a new option to remediate arsenic contaminated soils. The results will be relevant for environmental scientists, engineers, land managers, and entrepreneurs as well as rice producers/consumers who are keen on obtaining As-safe rice grains.

1. Introduction

Arsenic (As) contamination threatens the health of more than 50% of the global population who rely on rice (*Oryza sativa* L.) as a main staple food. Rice grains accumulate As due to high As availability in flooded paddy soils (Khan et al., 2010; Stroud et al., 2011) and efficient As uptake into rice tissues (Jia et al., 2014; Zhu et al., 2008). Thus, this results in high As concentration in rice grains even when the As concentrations in the paddy soils are below regulated pollution threshold levels (Chen et al., 2019; Chowdhury et al., 2018). As most rice-consuming people live in developing countries, a feasible solution to mitigate As risk in rice must be economically affordable and efficient in real field conditions.

Existing methods to mitigate soil As risk either require continuous external addition or generate undesirable waste. Chemical fixation by using iron (Fe) minerals is intensively studied but it can only temporarily reduce As availability (Qiao et al., 2018; Zhai et al., 2020). Together with the high cost, it is not favored in long-term field use. Chemical washing and phytoremediation are two promising methods that can permanently remove As (Jho et al., 2015; Ma et al., 2001), but both of them affect soil quality too. Phytoremediation is more promising because its impact on soil quality is much smaller than chemical washing (Alka et al., 2021). However, the plants that are able to hyperaccumulate As compete for space, light and nutrients with rice and require special facilities to treat a large amount of high-As bio-waste (Vocciante et al., 2019), which makes it not applicable in paddy fields.

Targeted removal of As, i.e., only removing As with minimal disturbance to soil matrix, was considered impossible because the precise separation always needs huge energy input (Cui et al., 2019). Meanwhile, many studies observed spontaneously-formed hotspots of toxic elements in natural environments. For instance, the As and Fe hotspots are found in Fe-Mn nodules (Chen et al., 2006), soil-water interfaces (SWI) (Mitsunobu et al., 2020; Tong et al., 2019) and the root surface of wetland plants (Chen et al., 2005; Yuan et al., 2021). The formation of As hotspots are fueled by the energy from light and/or biomass (Tong et al., 2019; Xu et al., 2016), and driven by biotic or abiotic activities. Removal of those hotspots looks like a very promising method to precisely extract the target elements from soils, as they are naturally formed with no input of external energy and chemicals. A recent study found removing rice roots and the carried Fe plaque, which accounted for 95% of total As in rice plants, was able to effectively reduce bioavailable As (He et al., 2020). However, those hotspots cannot be easily removed because they are small, unstable, and dispersed in soils.

Except for the naturally-formed hotspots, plastics can induce substantial and stable Fe and Mn oxides formation on the surfaces when inserting plastics into sediments, which was first reported in 1989 (Belzile et al., 1989). This phenomenon was proposed for *in-situ* separation and collection of pure deposits of natural Fe and Mn oxides (Belzile et al., 2001; Couture et al., 2010). Furthermore, similar Fe and Mn bands on plastic containers have been observed on Winogradsky column walls under illumination (Esteban et al., 2015). The Fe coating is usually explained by the effect of phototrophs grown on the walls. However, the formation of Fe oxides is also frequently observed in light-tight conditions (Xu et al., 2017). Although the naturally formed Fe oxides induced by plastics have been noticed by many researchers, the mechanism behind this phenomenon is seldom investigated to date.

Considering the strong coupling of Fe and As in soils, we hypothesized that plastics with self-formed Fe oxides could be a special tool to extract As from the soil porewater and separate it from the soil. Therefore, we proposed an As removal method by mimicking the natural As hotspot formation process and conceptualize it as "fishing" As out of soils by using plastic tubes as "hooks" and the naturally formed Fe oxides as "baits". To resolve the underlying mechanism behind Fe hooks, we investigated the environmental parameters influencing the formation of Fe oxides on different plastics, including soil properties, light, nitrate input into soils and O_2 diffusion through plastic tubes. Here we present the results of As removal efficiency by the 'Fe hook' method from a 2-year pot experiment with growing rice in real As-contaminated soils.

2. Experimental procedures

2.1 Experimental preparation

Twenty-seven typical wetland soils used in this study, including paddy soils and freshwater sediments, were collected from 23 cities and 15 provinces across China. The upper soil layer to a depth of 20 cm of 25 paddies was sampled followed by wet sieving to remove stones and plant debris through a 1.0 mm diameter sieve. The top layer (~ 0-10 cm) of two sediments with reed was sampled and processed by the same method noted above. Geographic information of sampling sites and the selected soil properties are detailed in Supplementary data S1.

Rice (*O. sativa* L.) hybrid, Yliangyou-1, was sterilized and germinated following the previous report (Chen et al., 2012). The seedlings were grown in a Hoagland culture in a glass greenhouse (three-leaf stage) before being transplanted into soils. All the incubation was performed in a glass greenhouse. The greenhouse conditions were set and controlled at 25 °C controlled by an air conditioner.

2.2 Experiment 1: the universality of tube-wall Fe oxide formation

To study self-formed Fe oxides on tube walls, we used a 50 mL transparent polypropylene centrifuge tube to incubate the 27 wetland soils collected. It should be noted that Fe oxides form on tube walls which contacts the saturated soil. The centrifuge tubes were purchased from Minuo Co., Ltd (China). In the centrifuge tube, 50 g water-saturated soil (~ 8 cm depth) was filled, and DI water was added to submerge the soil to mimic flooding soil conditions. The incubated soil column has a diameter and height of 2.5 cm and 7 cm respectively. The tubes were incubated with natural sunlight exposure. There are three replicates for each soil. Brown-red precipitate could be automatically formed on tube sides in several days. After 30 d incubation, soil porewater was sampled by a Rhizon sampler (2.5 cm × 10 cm, MOM, Rhizon, Netherlands). The collected soil porewater was acidified with 6 M HCl to prevent Fe precipitation (Yuan et al., 2021). The centrifuge tubes were washed carefully with DI water until there were no soil particles, 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls (Gerhardt et al., 2005; Yuan et al., 2019).

2.3 Experiment 2: the effect of materials and their different shapes on tube-wall Fe oxide formation

Six common materials (diameter × length=0.8 cm × 10 cm) or tube (diameter × length=0.8-2 cm × 10 cm), including polymethyl methacrylate, polytetrafluoroethylene, nylon, polypropylene, polyethylene and glass, were supplied by Juyayuan Plastic Materials Co., Ltd (China). The plastics in stick or tube shape were inserted into saturated Suzhou (SZ) soils with a depth of 8 cm. The incubation was performed with natural sunlight exposure. After 30 d incubation, the sticks and tubes were taken out from the soil and washed with DI water until there were no soil particles. The formation of Fe oxides on sticks and tubes was recorded and compared.

2.4 Experiment 3: the effect of light conditions on tube-wall Fe oxide formation

The sealed polypropylene and low density polyethylene (LDPE) tubes were selected to assess the effect of light conditions on tube-wall Fe oxide formation in seven soils [i.e., Rugao (RG), Baoding (BD), Ganzhou (GZ), Shaoguan (SG), Kunming (KM), Wuxue (WX), and SZ] with various tube-wall Fe oxide production as determined by using the 27 soils. The ~15 cm length tubes were inserted into saturated soils with a depth of 8 cm, with ~7 cm length tubes above the soil surface. The incubation was performed with natural sunlight exposure or continuous dark conditions. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.5 Experiment 4: the effect of redox conditions on tube-wall Fe oxide formation

Inserting the oxygen-permeable tube into saturated paddies may change the redox conditions around the tube. Hence, the LDPE tube and saturated SZ soil were used to evaluate the effect of redox conditions on tube-wall Fe oxide formation. There are four treatments: i) the inserted LDPE tube without redox disturbance; ii) pump pure nitrogen gas (1.0 L min^{-1}) through the inserted LDPE tube to create an anoxic condition in the tube; iii) pump air (1.0 L min^{-1}) through the inserted LDPE tube to enhance the oxic condition in the tube; iv) add nitrate (500 μM) to the overlying water to enhance the oxic condition outside the tube. Nitrogen gas was provided by a high-pressure tank, air by an air pump. The tightness of the gas blowing system was carefully checked before the experiment to avoid gas leakage. The incubation was performed with continuous dark conditions. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.6 Experiment 5: the involvement of soil microbes in tube-wall Fe oxide formation

Seven soils (i.e., RG, BD, GZ, SG, KM, WX, and SZ) were used to identify whether soil microbes involve in tube-wall Fe oxide formation. 50 g saturated soils were added into a 50 mL centrifuge tube made with polypropylene. There are two treatments: i) without soil sterilization; 2) with soil sterilization by irradiation (50 k Gray, produced from a Co-60 source, Suzhou University). To maintain a sufficient sterile condition, the incubation (in 30 d) was strictly performed within a period (< 40 d) without obvious microbial colonies as reported by Wang et al. (2019). The sterile efficiency was not monitored in this study. There are three replicates for each treatment. After 30 d incubation, the tubes were taken out from the soil, and washed with DI water until there were no soil particles; 1 M HCl was used to dissolve the Fe-oxides adsorbed on tube walls.

2.7 Experiment 6: remediation of As-contaminated paddy soil with Fe hooks

A grey plastic container (width × length × height=30 cm × 40 cm × 23 cm) was used to incubate an As-contaminated (50.7 mg kg^{-1}) Qingyuan (QY) paddy soil. The soil was added to a depth of 20 cm to mimic the plow layer in paddies. Soils were flooded with DI water to maintain a standing water depth of ~ 3 cm above the topsoil surface during the 2-year experiment.

The LDPE tube (diameter × height=0.8 cm × 20 cm) serves as the carrier of tube-wall Fe oxides (also called Fe hooks in this study) and was applied to remediate the QY soil by removing soil As when taking out the tube and Fe hooks from soils. The experimental treatment includes with or without deploying LDPE tubes in soils. There are three replicates for each treatment. The LDPE tube is reusable after deployment. To maximize the removal efficiency by each tube, a short distance (i.e., > 5 cm) without obvious overlapping effect for soluble As and Fe was identified according to a preliminary test (Fig. S1). Accordingly, this equals to a density of < 400 tubes m^{-2} soil. To facilitate the operation, the insertion density is set at 20 tubes per container (~ 200 tubes m^{-2} soil), and the take-out frequency of the LDPE tube is set at every 14 d in warm seasons (annual spring to autumn) and every 30 d in winter according to the preliminary test. Two hills with a distance of 20 cm were grown in each container (Fig. S2). Three identical seedlings were transplanted in each hill on 17th June 2018 and 10th June 2019, respectively. During the experiment, soil porewater was sampled by a Rhizon sampler (one sampler per container). The collected soil porewater was acidified with 6 M HCl to prevent Fe precipitation. When taking out the Fe hooks, two of them were dissolved by 1 M HCl. The As removal rate was calculated by dividing the removed As (mg) by Fe hooks to total As in the soil (50.7 mg As kg^{-1} soil × 40 kg soil= 2028 mg As) and then multiplying 100.

Rice plants were manually uprooted and cut at ground level for determination of As at maturity. Fresh plants were separated into stems, leaves, and grains, followed by oven-drying (60 °C) of sub-samples for the subsequent determination of As accumulation in plants. Plant samples after oven-drying were weighed to measure plant dry matter and rice yield followed by grinding and sieving through a 1.0 mm sieve for chemical analysis. A sample of 0.50 g was digested using a 1:1 mixture of concentrated HNO_3 and H_2O_2 (Gustave et al., 2019). The digested samples were filtered through a 0.45 µm cellulose filter. Certified rice reference materials (GSB-23) were simultaneously processed for quality assurance, and sufficient recoveries (95.5 % to 105%) were obtained.

Potential plastic release of Fe hooks was simulated by continuously recycling plastic tubes's deployment and collection 200 rounds (equal to the operation in 10 years) in real paddy soils. The weight of the plastic tubes was recorded before and after the test, and the plastic surface was also checked with scanning electron microscopy (SEM).

2.8 Analytical measurements

A spectrophotometric method using 1, 10-phenanthroline was applied to determine the total Fe concentration (Tamura et al., 1974). Other elements, such as As, Pb, Sb, Ni, Co, Mn, Cd, Cu, and Cr, were analyzed with NexION 350X ICP-MS (PerkinElmer, Inc., Shelton, CT USA). Total organic carbon and total nitrogen were determined with a TOC/TN analyzer (Shimadzu TOC-VCPH, Japan). The morphology of the tube-wall Fe-oxides was scanned with SEM JSM-7600 (FJEOL Ltd., Japan) and energy dispersive spectroscopy (EDS) (<= 20 kV) under a low vacuum. The mineral structure was characterized by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ=1.5418 Å).

2.9 Microbial analysis

The bulk soil (1.0 cm distance from tube-wall Fe oxides) and soils adjacent to tube walls were sampled from the seven soils (i.e., RG, BD, GZ, SG, KM, and SZ) incubated under natural light or dark conditions. The genomic DNA of the soil was extracted by using the PowerSoil DNA Isolation Kit (MO BIO Laboratories, Inc. Carlsbad, USA) following the manufacturer's instructions.

Extracted DNA was subjected to barcode amplification of the V3–V4 hypervariable region of the 16S rRNA gene at GENEWIZ, Inc. (Suzhou, China). The effective sequences were selected using the same method by Wu et al. (2016). The detailed DNA sequencing and raw data processing information can be found in supplementary files. The average length of the remaining sequences is 450 bp. The effective sequences were grouped into operational taxonomic units (OTUs) at a similarity of >= 97%. The averaged top 15 phyla were analyzed and displayed. To identify the most variable microbe among different soil layers, the linear discriminant analysis (LDA) effect size (LEfSe) method was applied (Segata et al., 2011).

2.10 Statistical analysis

The 16S rRNA gene sequence data have been deposited in NCBI GenBank under the accession number: MF967611-MF968897. All the data were analyzed and plotted in R3.5.0 software unless noted elsewhere. The significance of linear regression and correlation matrix were tested with Fisher least significance difference (LSD) and Standard Student's t tests ($p < 0.05$), respectively.

3. Results

3.1 Iron oxide formation on plastic tube walls with various soils

We investigated whether Fe oxide formation on plastic tube walls is common in flooded soils. In this experiment, 27 soils collected from typical wetlands (mostly rice paddies) over China were used to test the Fe oxide formation on plastic tube walls (Fig. 1).

Plastics-induced Fe oxides were obtained in 22 out of 27 (81.5%) soil samples. Fresh naturally-formed minerals were observed clearly on tube walls under saturated soil incubation (Fig. 2a). When observed by SEM, the brown-red precipitate presented a network-like (Fig. 2b) and particle stacking structure (Fig. 2c). Iron content measured by EDS reached up to 30.3-53.9% of the fresh minerals (Fig. S3), indicating that the naturally formed minerals are mainly composed of Fe oxides. XRD analyses further identified the Fe oxides had low crystallinity (Fig. S4). The Fe oxide density on tube walls ranged from 3.02 to 376 mg Fe m^{-2}, with the porewater Fe from 0.270 to 57.7 mg L^{-1}.

A weak relationship was observed between dissolved Fe and precipitated Fe on tube walls. Fig. 2d clearly showed abundant Fe oxides were formed when porewater Fe was below 10 mg L^{-1}. The high porewater Fe in CZ1 (57.7±10.8 mg L^{-1}) and HA (41.7±14.3 mg L^{-1}) soils did not lead to thick tube-wall Fe coatings (CZ1: 147±54.3 mg Fe m^{-2}; HA: 25.8±6.18 mg Fe m^{-2}). The densest tube-wall Fe oxides were yielded in FS (336±12.6 mg Fe m^{-2}) and SG2 (376±18.4 mg Fe m^{-2}) soils with a moderate porewater Fe (3.21±1.13 mg L^{-1} and 13.8±4.57 mg L^{-1}, respectively).

The tube-wall Fe coatings are hotpots for siderophile elements (Fig. 2e, Table S1). Iron has a significantly positive relationship with As (R^2=0.535), antimony (Sb, R^2=0.186), and lead (Pb, R^2=0.120) (Fig. 2e-f, Table S1). It is worth noting that the elements are tightly bound to the tube-wall Fe oxides, which can be easily separated from soils. Considering the tight coupling between Fe and As, tube-wall Fe oxides could serve as ‘Fe hook’ for targeted extraction of As from saturated soils.

3.2 Abiotic factors that induce tube-wall Fe oxide formation

Iron oxide formation could be driven by both abiotic and biotic factors. To address the mechanism of Fe coating formation on tube walls, the potential drivers, including tube materials, light, and redox conditions, were investigated.

The common materials (including polymethyl methacrylate, polytetrafluoroethylene, nylon, polypropylene, polyethylene, low density polyethylene (LDPE) and glass) were assessed. Intriguingly, the materials in stick shape did not induce significant Fe oxide formation (Fig. S5a). In contrast, the polypropylene and LDPE materials in tube shape induced abundant tube-wall Fe oxide formation (Fig. S5b-c).

The effect of light on Fe oxide formation on polypropylene and LDPE tubes was investigated with 7 soils (i.e., RG, BD, GZ, SG, KM, WX, SZ). The magnitude of Fe oxide formation varied by 2.70 to 9.28 times under different circumstances (Fig. S6-7). The larger variation of Fe oxide formation was observed on polypropylene tubes no matter under natural light or continuous dark conditions. Generally, natural light induced more (average 29.1%) Fe oxides compared to the continuous dark (Fig. S6). In contrast, the Fe oxide formation on LDPE tubes was consistent under natural light or continuous dark conditions. The results from polypropylene and LDPE tubes indicate natural light facilitates, but is not essential for, Fe oxide formation on tube walls. Furthermore, Fe coating thickness on LDPE tubes was double that on polypropylene tubes, which made LDPE tubes an excellent carrier for making Fe hooks.

Three treatments with nitrogen gas, air, and nitrate addition were applied to study the availability of electron acceptors around the tubes on Fe oxide formation. Pure nitrogen gas and air continuously were pumped through the LDPE tubes, nitrate was added into bulk soils. Blowing gas through the tube would only slightly modify the redox condition around the tube, but not significantly change the reducing condition in bulk soils. Nitrogen gas treatment dramatically inhibited the Fe oxide formation (-70.4% compared to control, Fig. 3). Fe oxide formation was remarkably promoted (109%) when blowing air through the tube. Adding nitrate to soils also markedly accelerated the Fe oxide formation (187%), which might be driven by nitrate-dependent Fe-oxidizing bacteria. The trend of As adsorbed on Fe coating is different from the Fe precipitated on tubes. As shown in Fig. 3, maximum As adsorption was found in the control, both air and nitrate addition treatments significantly decreased the adsorbed As (-33.6%).

3.3 Biotic factors that induce tube-wall Fe oxide formation

We further tested whether microorganisms were involved in tube-wall Fe oxide formation. An initial study found soil sterilization significantly reduced the tube-wall Fe oxides in all the soils (average -67.4%, Fig. S8), but did not fully prevent Fe coating formation on tube wall.

Further study of the major microbial communities in bulk soils and soil adjacent to the tube walls is depicted in Fig. S9. The soil microbial communities were similar between the bulk soils and the soils adjacent to tube-wall in soils under dark conditions. Natural light treatments did not alter the microbial communities in the soils adjacent to tube-wall too, except for the SZ treatment. Light boosted the growth of *Cyanobacteria* in SZ soil. The known oxygenic phototrophic bacteria *FamilyI* (*Cyanobacteria*) and anoxygenic phototrophic bacteria *Chlorobiaceae* (*Chlorobi*) were also significantly promoted by natural light (Fig. 4c).

Strong positive relationships were found between the Fe oxide density and the richness of *Nitrospirae* (r=0.804), *Verrucomicrobia* (r=0.765), *Cyanobacteria* (r=0.699) and *Spirochaetes* (r=0.635). Meanwhile, there are negative relationships with *Rokubacteria* (r=-0.840), *Proteobacteria* (r=-0.679), *Latescibacteria* (r=-0.649) and *Gemmatimonadetes* (r=-0.534) (Fig. 4b). Tube-wall Fe oxide formation might reshape the soil microbial communities. Additionally, the precipitated Fe on tube walls under normal conditions had a strong relationship with the adsorbed As (R^2=0.836, Fig. 4a).

3.4 Remediation of soil As contamination with the Fe hook method

The potential application of using the Fe hook method to remediate As-contaminated paddy soil was tested in a pot experiment. The remediation process consists of 4 steps (Fig. 5a): i) LDPE tubes are inserted into the soil; ii) Fe hooks are naturally formed on the tubes; iii) Fe hooks are retrieved from the soils after 2 week's deployment; iv) the tubes are washed by tap water scrubbing and reused.

The efficiency of Fe hooks for remediating an As-polluted paddy soil was tested in two rice growing seasons (Fig. S2). Without applying Fe hooks, soluble As in soil porewater increased from 41.7 μg L^{-1} at Day 0 (initial soil flooding, 8th April 2018) to as high as 328 μg L^{-1} before rice seedling transplantation (Day 70, Fig. 5b). After five-round As removal by Fe hooks within 70 d, porewater As was only about 60% of the controls. Porewater As in the control group peaked at Day 98 and then decreased to 13.9 μg L^{-1} during the winter without growing rice. Although porewater As with Fe hooks followed a similar pattern, obvious As decline (-35.0%) was achieved during the rice production compared to control (Fig. 5b). Similarly, applying Fe hooks also significantly reduced porewater As in the second year's rice production. Reduction of porewater As by Fe hooks may be due to two causes: i) easily-mobile As pool in soil was significantly decreased; ii) mobile As in porewater was re-immobilized since soil Eh may be elevated by Fe hooks mediated O_2 loss in reducing soils.

The accumulated As removal amount by Fe hooks is presented in Fig. 5c. After two years' remediation, up to 304 mg m^{-2} As was removed by Fe hooks (Fig. S10), and the removal rate of total soil As was estimated to be 1.80% (Fig. 5c). Launching Fe hooks also markedly mitigated As accumulation in rice grain (-11.1%, Fig. S11) and significantly reduced both years' rice stem As (-16.1%, $p < 0.05$, Fig. S11). Meanwhile, the deployment of Fe hooks in 2 years removed 3.16 g C m^{-2} and 0.211 g N m^{-2} in the soil, which only represent 0.07% and 0.05% of total C and N. The results indicate Fe hooks have limited influence on major elements in soils. Additionally, there is no obvious impact of Fe hook deployment on rice biomass and yield.

Nanoplastic particles might be introduced into soils through Fe hooks. Thus, we tested the potential loss of plastic tube weight of deploying Fe hooks in paddy soils (Fig. S12). After 200 cycles of insertion and removal, the tubes were found to have many microscratches on the surface (Fig. S13). The weight loss averaged ~ 0.15%, which equals to a release of < 38 mg plastics m^{-2} soil $year^{-1}$. Moreover, a biodegradable plastic (i.e., polylactic acid) was demonstrated to be more efficient in stimulating tube-wall Fe oxide formation (43.2% higher) and their removal of soil As (55.7% higher) than LDPE (Fig. S14). This indicates Fe hook method could be further optimized to strengthen its performance in removing soil As, and the secondary pollution introduced by Fe hooks could be minimized by employing environmental-friendly materials.

4. Discussion

In this study, we proposed using Fe hooks (LDPE tubes with naturally-formed Fe coatings) for targeted removal of As from paddy soils. The LDPE tubes can induce localized Fe oxidation and As co-precipitation on the tube walls allowing extraction of

As while causing minimum disturbance to the soil. Moreover, this process requires no addition of chemicals, and only a thin layer of Fe and As is removed from the soil. Thus, the Fe hook method can precisely remove As with negligible disturbance to soil matrix.

4.1 Tube-wall Fe oxide formation

The formation of Fe coating on tubes is common in flooded soils and driven by abiotic and biotic factors. The tube-wall Fe-oxides against the soil have a filament-like structure when observed by SEM (Fig. 2b), which is similar to previously reported biogenic Fe-oxides (Kozubal et al., 2012). The Fe-rich filaments were frequently observed in biogenic Fe-oxides. This structure is considered as a robust biosignature of Fe oxidizing bacteria or fungal hyphae (Chan et al., 2011; Limmer et al., 2021). The XRD analysis showed there were no crystalized Fe minerals, so the tube-wall Fe oxides are mainly poorly crystal or amorphous Fe precipitate. The fresh biogenic Fe-oxides with low crystallinity have huge adsorption capacity and fix a large amount of heavy metal(loid)s (Sowers et al., 2017).

4.2 Tube-wall Fe oxide formation driven by abiotic factors

Oxygen diffusion from the atmosphere is the main driver of the Fe coating formation. Crétois et al. (2015) reported polypropylene and polyethylene plastics share a similar O_2 permeability value (50-100 vs. 50-200 cm^3 mm m^{-2} day^{-1} atm^{-1}). But, plastics with low molecular density could produce low intermolecular cohesion and large fractional free volume (Lagaron et al., 2004), thus have a very high O_2 permeability value, which could explain why LDPE tubes induced more Fe oxide formation than polypropylene tubes in this study (Fig. S6). According to reported O_2 diffusion rate in polyethylene plastics (0.4 mm thick, 10.1 cm^3 m^{-2} day^{-1} atm^{-1}) (Buntinx et al., 2014), the diffused O_2 could potentially produce substantial Fe oxides

(101 mg Fe m^{-2} d^{-1}) on tube walls assuming all the O_2 reacted with Fe^{2+}. Our results strongly support abiotic Fe oxidation by O_2 contributes to tube-wall Fe oxide formation, since blowing air through the tube significantly increased tube-wall Fe oxides, while blowing pure nitrogen significantly reduced tube-wall Fe oxides. Due to the O_2 limitation, solid sticks made by plastics were just covered by little Fe-oxide, which was also indicated by utilizing plastic sheets (4-36 mg m^{-2}) (Belzile et al., 1989). Surprisingly, an extra supply of O_2 or other easy-to-use electron acceptors (e.g., nitrate) stimulated Fe oxidation on tube walls and in bulk soils, but didn't increase As accumulation on Fe hooks (Fig. 3). We speculate that the porewater As was immobilized by the Fe oxides formed in bulk soils, rather than by Fe hooks. Thus, the adsorbed As on Fe hooks decreased.

Although Fe coatings on tubes are derived from the oxidation of dissolved Fe^{2+}, soluble Fe is not a determining factor for tube-wall Fe oxide formation (Fig. 2d). For example, in two soils (i. e., CZ1 and HA) with high soluble Fe (> 40 mg L^{-1}, Fig. 2d), no tube-wall Fe oxides were observed. Instead of Fe coating, greenish biofilm was found on the tube wall (Fig. S7b), which indicated there was algae. The phototrophs used light to produce O_2, which would prevent the soluble Fe in bulk soils from diffusing to the tube wall. In addition, the presence of phototrophs could promote reductive dissolution of As-bearing Fe minerals in paddy SWI through elevating the dissolved organic carbon (Guo et al., 2020), then lead to elevated porewater Fe concentration. Thus, the interface process between tube walls and bulk soils plays a vital role in Fe coating formation, especially the spatial distribution of microbial communities along the O_2 gradient.

4.3 Tube-wall Fe oxide formation driven by biotic factors

Soil microbes actively take part in regulating tube-wall Fe oxide formation. The microbial analyses indicated that tube-wall Fe oxides may be stimulated by *Nitrospirae*, *Verrucomicrobia*, *Cyanobacteria*, and *Chlorobi*. *Nitrospirae* is known nitrate-dependent Fe-oxidizing bacteria (Chen et al., 2009; Hedrich et al., 2011), and soil nitrate pool could be replenished by anthropogenic input (Huang et al., 2019) or naturally nitrogen fixation by *Verrucomicrobia* (Khadem et al., 2010). Phototrophic bacteria may contribute to Fe^{2+} oxidation on the transparent plastic tube via four pathways at early growth stage of rice when sunlight is not seriously intercepted by the crop canopy: i) stimulating nitrate-dependent Fe oxidation by offering nitrate substrate via nitrogen fixation (e.g., *Cyanobacteria*) (Ratering and Schnell, 2001); ii) activating microaerophilic Fe oxidizer (e.g., *Zetaproteobacterium*) by providing O_2 (Melton et al., 2014); iii) abiotic Fe oxidation by O_2 produced from oxygenic photobacteria like *Cyanobacteria* (Trouwborst et al., 2007); iv) biotic Fe oxidation by anoxygenic photobacteria like *Chlorobi* (Heising et al., 1999). In contrast, Fe-reducing bacteria, such as some kinds of *Proteobacteria* (Melton et al., 2014) and *Latescibacteria* (Zhang et al., 2019), may provide Fe^{2+} substrate for the tube-wall Fe oxide formation, or consume the formed tube-wall Fe oxides. In this study, the former process dominates under most conditions.

4.4 Advantages and constraints of using Fe hook method to remediate soil As

Iron hook method has its advantages and constraints not only in terms of cost but also in terms of feasibility, efficiency and environmental impact (Table S2). Iron hooks are tightly bound to tube walls. This character makes them easy to separate from soil particles, and not easy to fall off from tube walls. Hence Fe hooks will not cause the transfer of pollutants during the remediation process. And, Fe hooks can be washed with water scrubbing and then reused. This will greatly reduce the secondary pollutants produced during the remediation process. Iron hooks have a low cost (around 555 RMB/666.7 m^2/year) since the plastic tubes used are cheap and recyclable, and can still maintain the profit of growing rice (~1072 RMB/666.7 m^2/year). Compared with soil stabilization (Qiao et al., 2018; Zhai et al., 2020), Fe hooks show a big advantage in permanently remediating soil As contamination by removing As from soils. Compared with phytoremediation (Yang et al., 2020; Ye et al., 2011), Fe hooks do not compete for land with rice production, which may be more easily accepted by farmers. Iron hooks will produce some solid wastes rich in As-bearing Fe oxides, which require proper treatment after the remediation. The solid waste could be stabilized/inertizated with other materials as the bio-waste management of phytoremediation (Vocciante et al., 2019). By contrast, Fe hooks only produce little solid wastes (around 60 g m^{-2} soil $year^{-1}$), hence it is easier to process the waste deposits of Fe hooks than phytoremediation (Vocciante et al., 2019). Iron hooks did not significantly decrease As concentrations in rice grain during the 2-year pot experiment, possibly due to two causes: i) high variability of the measured samples; ii) the relative high porewater As since the experiment was performed under a continuous flooding condition. Iron hooks need further optimization before widespread applications. In addition, it may be difficult to handle Fe hooks at late growth stage of rice in the field, due to the relatively dense rice crop canopy.

The Fe hook method is still in its infancy and there are 2 major concerns of its feasibility in field application. First, intensive labor may require during the remediation, which is estimated of ~ two days' work for each cycle in 666.7 m^2 field. Compared to other remediation technologies, Fe hooks are very flexible and can be integrated into current agriculture machines, for example, rice transplanters may be used to plant a bunch of modified Fe hooks into paddy soils, thus the feasibility could be promoted. Second, the application of Fe hooks may escalate the plastic contamination in the arable lands. Although the microplastic released by Fe hooks (< 38 mg plastics m^{-2} soil $year^{-1}$) is negligible when comparing with the considerable microplastic pollution in farmland in China (2234 mg plastics m^{-2} soil) (Hu et al., 2022), the potential secondary pollution should be avoided considering long-term period is required to perform the soil As contamination. In a supplemental experiment, we verified biodegradable plastic tubes are also able to efficiently make Fe hooks as LDPE tubes (Fig. S14), hence it is a burning issue to test other more environmental-friendly materials for making high-efficiency Fe hooks. Remarkable advance in the relative field will pave the way for the widespread using Fe hook method in paddy fields.

Iron hooks can efficiently remove contaminants. The As removal efficiency (152 mg As m^{-2} soil $year^{-1}$ with a total soil As of 50.7 mg kg^{-1}) by Fe hooks is comparable to phytoremediation by *P. vittata* (29.6-142 mg As m^{-2} soil $year^{-1}$ with total soil As 7.60-74.3 mg kg^{-1}) (Yang et al., 2020; Ye et al., 2011) and rice plants with roots (133 mg As m^{-2} soil $year^{-1}$ with total soil As 39.7 mg kg^{-1}) (He et al., 2020). However, Fe hooks may influence soil properties. When taking Fe hooks out, the tubes bring out Fe oxides, as well as other elements bound with Fe (e.g., Mn, carbon, nitrogen, phosphorus etc.) (Chen et al., 2006; Koopmans et al., 2020; Yuan et al., 2020), with a weight around 60 g m^{-2} soil $year^{-1}$. Although such a rate would pose limited influence on soil major elements (e.g., < 0.1% carbon and nitrogen were removed after 2 years remediation in this study), more studies are essentially required to clarify the influence of Fe hooks on soil properties. Particularly, Fe hooks may deteriorate the phosphorous nutrient provision in the soil after long-term applications, since Fe hooks can remove considerable phosphorous owing to their high-binding affinity for phosphate (Koopmans et al., 2020).

4.5 Future prospect

The proof-of-concept work highlights 4 major areas to further improve the performance of the Fe hook method. First, we explore other environmental-friendly materials, especially biodegradable materials, for making Fe hooks. Second, the contact surface between Fe hooks and bulk soils determines the amount of Fe oxides and As on Fe hooks, thus the removal efficiency could be further enhanced by optimizing the tubes' material and surface topological structure, as well as the configuration of tubes deployment in soils. Third, the Fe and As behavior in the micro-interface between tubes and soils are still unclear, the mechanism is important to optimize the tube deployment pattern and maximize As removal efficiency. Finally, Fe hooks could combine with other strategies and improve the As removal efficiency. For example, external addition of organic matter like rice husk may increase As in the rice grain by enhancing the reductive dissolution of As-bearing Fe oxides. Since Fe hooks can be applied during the whole year, thus combining Fe hooks and organic matter amendment during the non-rice growing reason (e.g., winter and early spring) may be very promising in achieving rapid As reduction in plant tissues and permanent removal of As in soils.

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Conflicts of interest

The authors declare no financial conflict.

Data availability

Data and codes are available from https://doi.org/10.6084/m9.figshare.16836742.v1.

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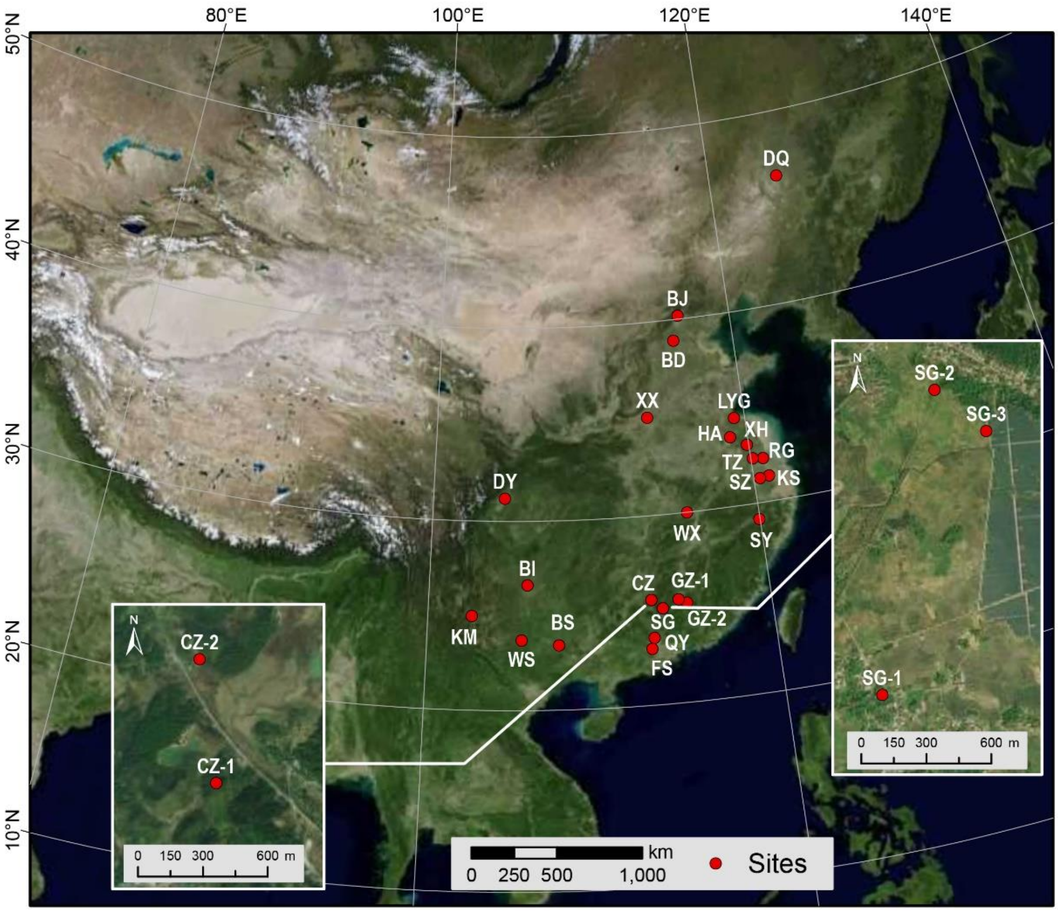

Fig. 1 Geographic map of the sampling sites. A total of 27 wetland soils were sampled from China. Inserts show overlapping sampling sites. Information of the sampling sites and basic soil characteristics can be found in Supplementary Dataset 1.

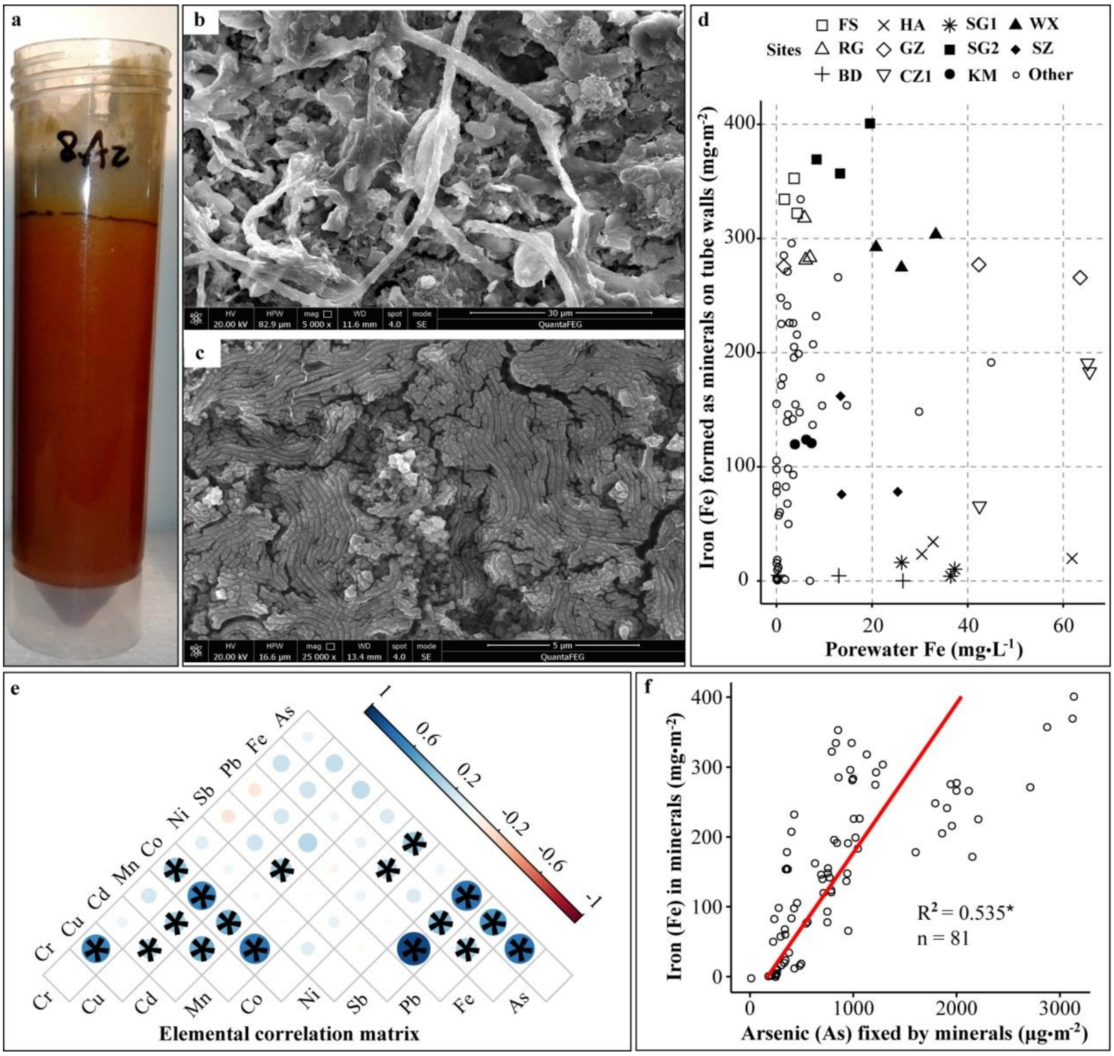

Fig. 2 Minerals formed on tube walls with saturated soil incubation (a-c) and elemental correlation (d-f). a) Fe oxides formed on tube walls; b-c) typical scanning electron microscopy (SEM) images of tube-wall Fe-oxides against the tube wall and soil respectively; d) correlation between porewater Fe with mineral Fe on tube walls; e) correlation matrix of multiple-element in tube-wall minerals; f) regression analysis of Fe and As in tube-wall minerals. The star in panel (e/f) means a significant difference at $p < 0.01$.

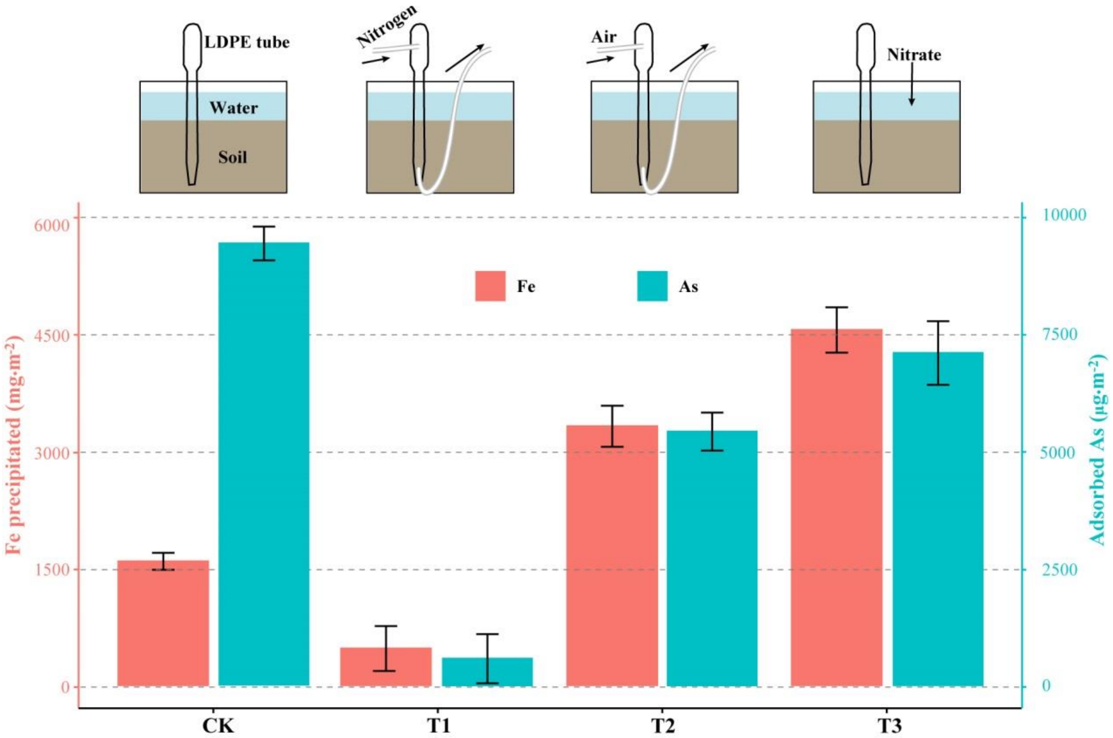

Fig. 3 Fe precipitation and the As adsorbed on low density polyethylene (LDPE) tubes with different electron acceptors supply modes. The incubation was under continuous dark conditions in SZ soils, with a period of 30 days. The redox conditions around the LDPE tubes were modified by blowing pure nitrogen (T1)/air (T2) through the tube (1.0 L min^{-1}) or adding nitrate (T3, 500 μM) into overlying water. The arrows point to the flow direction of the gas, which can only slightly modify the redox condition abound the tube. The error bar is the standard deviation (*n*=4).

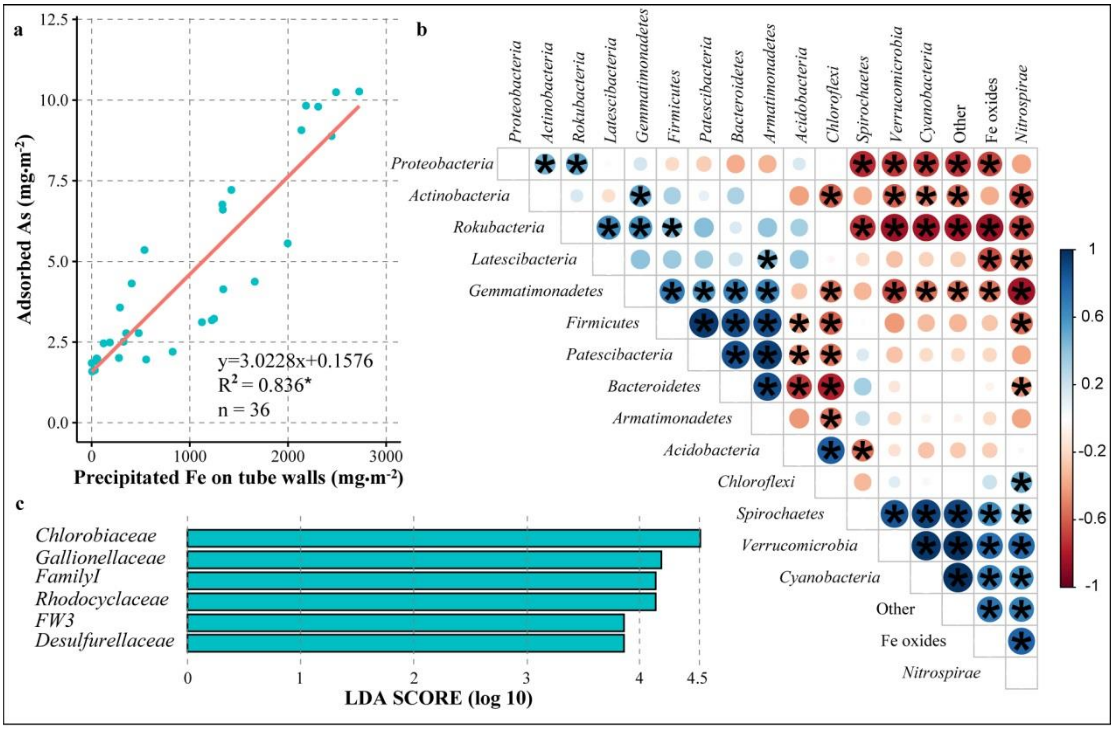

Fig. 4 Correlation between tube-wall Fe oxides and the adsorbed As (a), the correlation matrix of Fe oxides and microbes (b), and linear discriminant analysis (LDA) effect size (LEfSe) analysis between saturated SZ bulk soil and the soil adjacent to tube walls under natural light (c).

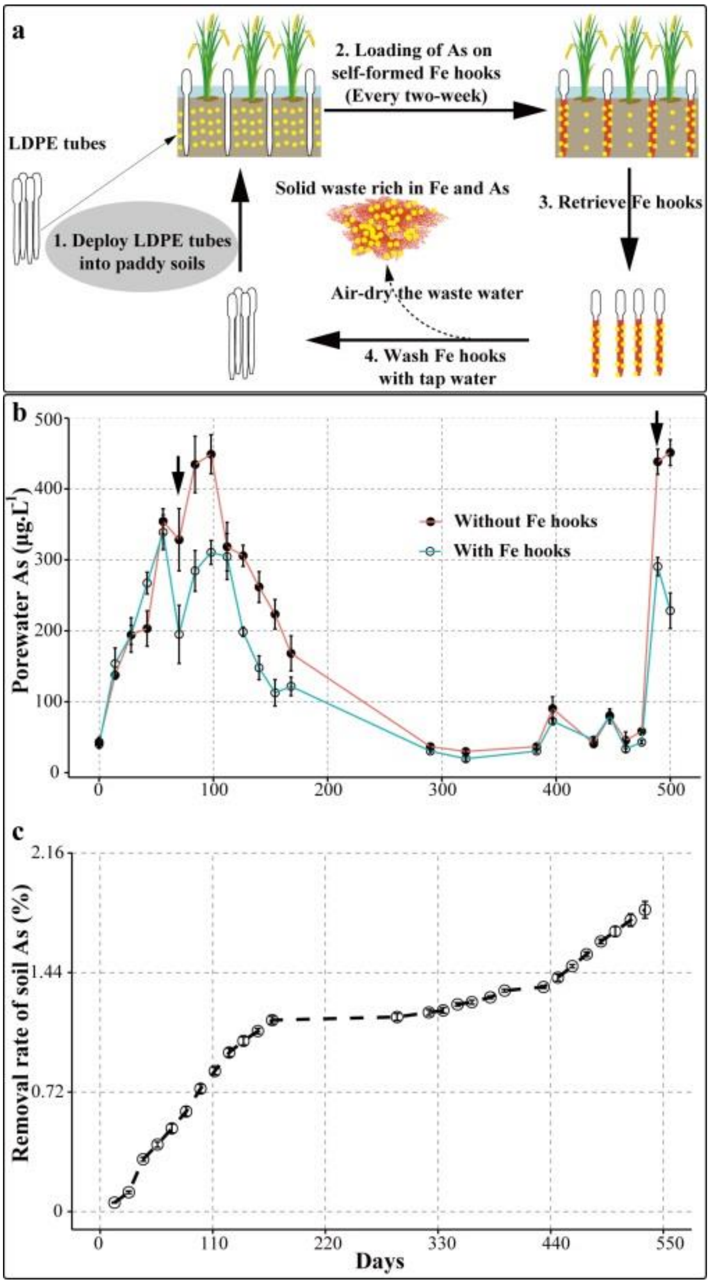

Fig. 5 Conceptual As remediation process with Fe hooks (a) and monitoring of the two-year soil As remediation in paddy soils (b-c). b) dynamic changes of As in soil porewater; c) removal rate of total soil As. An As polluted QY soil (50.7 mg kg^{-1}) was used. LDPE tubes are recycled during the remediation. Arrows in panel (b) indicate the transplantation of rice seedlings. The error bar is the standard deviation (n=3).

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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