

Sustainable Immobilization of Arsenic by Man-Made Aerenchymatous Tissues in Paddy Soil

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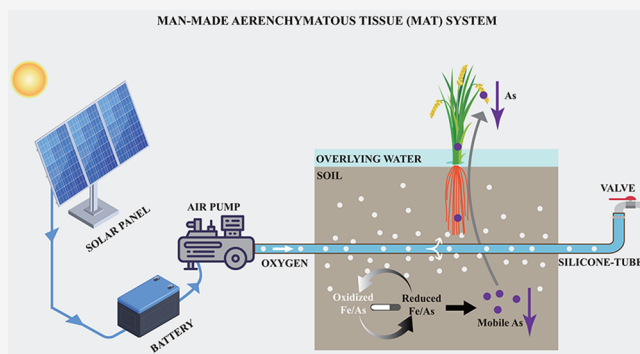
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ABSTRACT: Arsenic (As) is a major environmental pollutant and poses a significant health risk to humans through rice consumption. Elevating the soil redox potential (Eh) has been shown to reduce As bioavailability and decrease As accumulation in rice grains. However, sustainable methods for managing the Eh of rice paddies are lacking. To address this issue, we propose a new approach that uses man-made aerenchymatous tissues (MAT) to increase soil Eh by mimicking O₂ release from wet plant roots. Our study demonstrated that the MAT method sustainably increased the soil Eh levels from −119 to −80.7 mV (~30%), over approximately 100 days and within a radius of around 5 cm from the surface of the MAT. Moreover, it resulted in a significant reduction (−28.5% to −63.3%) in dissolved organic carbon, Fe, Mn, and As concentrations. MAT-induced Fe(III) (oxyhydr)oxide minerals served as additional adsorption sites for dissolved As in soil porewater. Furthermore, MAT promoted the oxidation of arsenite to the less mobile arsenate by significantly enhancing the relative abundance of the *aioA* gene (130% increase in the 0–5 cm soil zone around MAT). The decrease in As bioavailability significantly reduced As accumulation in rice grains (−30.0%). This work offers a low-cost and sustainable method for mitigating As release in rice paddies by addressing the issue of soil Eh management.

KEYWORDS: Arsenic, Oxygen, Iron, Aerenchymatous tissues, Rice



INTRODUCTION

Arsenic (As) is a global environmental pollutant and one of the most toxic heavy metal(loid)s to humans.¹ Four As species (i.e., arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA)) are common in the environment.^{2,3} Among them, As(III) is the most toxic and mobile form, which is frequently detected in saturated soils where dissimilatory As(V)- or iron(III) (Fe(III))-reducing microbes are active.^{4,5} Rice is the only main crop that requires intermittent flooding during its cultivation, which increases As bioavailability in paddy soils even without anthropogenic As pollution.⁶ Additionally, rice is an efficient accumulator of As and can accumulate more than 10 times As than other cereals.⁷ There are considerable food chain concerns about As in rice⁸ since rice provides 23% of the calories for over 50% of the world's population. Therefore, reducing As accumulation in rice is a crucial measure needed to alleviate its threat to human health.

Many methods have been developed to reduce As contamination risk in rice paddies; however, developing a

sustainable remediation technique remains challenging. Chemical washing and phytoremediation are two promising methods that can permanently remove As;^{9,10} however, both methods remove soil nutrients and deteriorate soil quality. Furthermore, plants that can hyperaccumulate As compete with rice plants for space on agricultural fields and require costly disposal methods,¹¹ which makes it hard to convince farmers to use phytoremediation in the field. Chemical stabilization using As passivators (e.g., Fe minerals, nitrate salts, gypsum, and biochar) is considered a cost-effective way of soil remediation.¹² However, the addition of these compounds can only temporarily reduce the As bioavailability.

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In addition to adding stabilization reagents such as Fe minerals to paddy soils, Fe mineral hotspots can also form naturally in soils.¹³ Iron mineral hotspots act as a sink for As as they provide the main adsorption sites for As in soils.^{14,15} For instance, Fe and As hotspots frequently observed at the soil–water interface (i.e., Fe barrier)^{16,17} and at the root surface of wetland plants (i.e., Fe plaque)^{18,19} actively sequester As. The Fe barrier and Fe plaque formation are driven by oxygen (O₂) diffusion from overlying water and radial O₂ loss (ROL) from aerenchymatous tissues, followed by oxidation of dissolved Fe(II) to Fe(III) (oxyhydr)oxide minerals. However, after the Fe barrier and Fe plaque formation, they act as barriers for further O₂ transport.^{20,21} As a result, the Fe barrier and Fe plaque are very thin (e.g., submillimeter), and their efficiency for As immobilization is low.

Similar to aerenchymatous tissues, some synthetic materials are also permeable to O₂, and they can be used to generate Fe hotspots in paddy soils. Previous studies have shown that atmospheric O₂ could diffuse through various plastic tubes inducing Fe(II) oxidation and the formation of Fe(III) (oxyhydr)oxide coatings on the tube walls that come into contact with saturated soil,^{22,23} which is quite similar to Fe plaque formation on wetland plant roots. However, the Fe oxide coating can act as a barrier and significantly inhibits further diffusion of the O₂ from the tube wall to reduced soils, limiting their ability to immobilize As. Among the synthetic materials, silicone tubes are of high O₂ permeability and are water-proof.²⁴ Furthermore, the silicone tube surface does not favor Fe oxide adhesion and thus will not form a barrier for O₂ release, overcoming the limitation of plastics and aerenchymatous tissues of wetland plants. Silicone tubes are considered excellent inert materials and generally have minimal impact on the soil environment, which were successfully utilized to inject or sample methane into/from subsoils.²⁵ We hypothesize that silicone tubes can be used to construct man-made aerenchymatous tissues (MAT) to enhance Fe(III) (oxyhydr)oxide mineral formation in flooded soils. Hence, the MAT approach could be used to sustainably immobilize As in the soil.

The objectives of this study were (i) to investigate whether the use of silicone tube-made MAT can significantly increase the soil redox potential (Eh), (ii) to examine the effectiveness of the MAT method in immobilizing As in paddy soils, and (iii) to verify whether the MAT method can mitigate As accumulation in rice grown in As-contaminated soils. We also examined the impact of MAT on saturated soil chemistry and microbial community composition and activity. Here, we report the findings of our micro- and mesocosm studies on using MAT to immobilize As.

MATERIALS AND METHODS

Man-Made Aerenchymatous Tissue (MAT) Fabrication. In this study, we fabricated a silicone-tube-based MAT, whose working mechanism is depicted in Figure 1. The MAT was designed to oxygenate saturated soils and stimulate Fe and As oxidation. To achieve this, the MAT utilized an air pump or condenser to continuously blow air into the silicone tubes from the atmosphere. When the system is activated, the O₂ from the silicone tube is continuously released into the saturated soil. The silicone tube used in this study (inner diameter × outer diameter = 0.30 cm × 0.50 cm) was obtained from Taobao (Alibaba, Hangzhou, China) and buried at a depth of approximately 8.0 cm in the soil (Figure S1). The basic

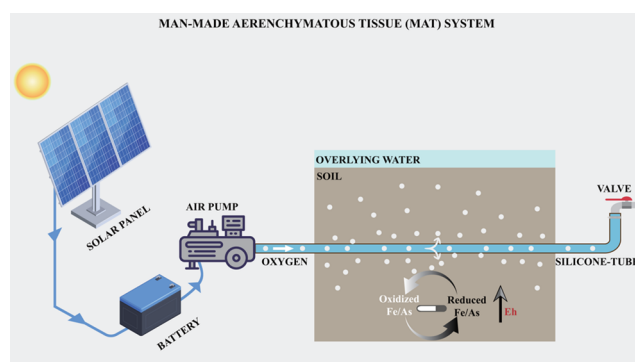


Figure 1. Schematic diagram of the man-made aerenchymatous tissue (MAT) system. The diagram illustrates the procedure for pumping air into the silicone tubes used in MAT. A vertical soil profile illustrates the potential working mechanism of MAT.

physical properties of the silicone tube are given in Table S1. The preliminary test revealed that air pressure in the silicone tube had a linear relationship with the O₂ release rate (Figure S2) and thus can act as an appropriate parameter to control O₂ release from the MAT. We used a 3.5 W portable air pump (Mulongju Co., Ltd., China) to maintain an air pressure of 25 kPa in the MAT, which was estimated to release approximately 5 kg of O₂ per hectare per day (equivalent to 50 kg Fe₂O₃ per hectare per day) when a tube density of 0.2 m² outside tube surface/m² soil was established.

Microcosm Incubation Setup. Soils were taken from an As-contaminated paddy field at Shangyu, Zhejiang, China (29.997 °N, 120.788 °E). The soil was a loam type with total organic C, Fe, Mn, and As concentrations of 9.75 g kg⁻¹, 20.8 g kg⁻¹, 0.381 g kg⁻¹, and 26.1 mg kg⁻¹, respectively. In the lab, 1.0 kg of paddy soil was weighed into each pot (diameter × height = 10 × 15 cm). The soil had a depth of 10 cm and was flooded (3 cm water depth) during the microcosm incubation. The incubation had two treatments: (1) control, in which the silicone tubes were filled with pure nitrogen gas, and (2) with MAT (treatment), in which the silicone tubes were inflated with air. Before the incubation, silicone tubes in the control were flushed by nitrogen gas (provided by a high-pressure tank) for 5 min at a rate of 1.0 mL/min and then sealed on both ends with tight valves (containing ~10 mL of pure nitrogen gas in each control tube). The control setup was expected to completely eliminate any potential impact of the silicone tube itself on the behavior of As in the soil, thus better adhering to the “one variable” principle. For silicone tubes in the treatment (using MAT), an air pump was used to pump air into the tubes during the incubation. Sealing the tube end by a tight valve enabled the maintenance of a specific air pressure within the treatment tubes.

During the 30-day incubation, porewater at two distances (i.e., 1 and 3 cm) from the silicone-tube surface (including the control and treatment group) was sampled using two Rhizon samplers (0.25 cm × 5.0 cm, 0.1 μm pore size, Rhizon, Netherlands), respectively. Every 1–10 days, about 4.0 mL of soil porewater was extracted from each position and acidified with 6 M HCl (1% of the sample volume; the sample pH < 2.0);²⁶ the sample of 4.0 mL porewater represented 0–2 cm and 2–4 cm soil zones around the MAT.²⁷ The acidified porewater sample was used for total elements analysis.

After the 30-day soil incubation, the porewater sample across the silicone-tube surface (0–4.4 cm) was sampled by IPI

samplers (0.20 cm spatial resolution). Each IPI sampler consists of a hollow fiber membrane tube (modified poly(ether sulfone), 20 nm pore size, outer diameter \times inner diameter \times length = 0.20 cm \times 0.10 cm \times 2.0 cm),^{2,28} which serves as the passive sampling component with a spatial resolution of 0.20 cm. Additionally, there are two pipes (PTFE, outer diameter \times inner diameter \times length = 0.10 cm \times 0.05 cm \times 18 cm) through which the porewater sample within the hollow fiber membrane tube is extracted. By assembling a horizontal array of 22 IPI samplers side by side, we can effectively measure a soil distance of 4.4 cm, with a spatial resolution of 0.20 cm at each measurement point. The collected porewater samples were analyzed for total elements and As speciation. Additionally, the Eh profiles (0–6.5 cm) across the soil–water interface and MAT–soil interface were measured using an Eh microelectrode (Unisense ref-RM and RD-N, 0.11 cm spatial resolution; Science Park, Aarhus, Denmark), after the 30-day microcosm incubation. When used, the microelectrode was positioned and advanced with a stepper motor.

After the microcosm incubation, soils across the silicone-tube surface (0–5 cm) were cut into 1.0 cm intervals after the incubation and the soil within each interval was well mixed. Then 0.5 g of well-mixed soil was immediately weighed and extracted by 6 mL of 1 M HCl for 24 h. The extract was filtered through a 0.22 μ m cellulose membrane (Membrana, Germany), and the aqueous samples were preserved in a 4 °C refrigerator before downstream chemical analysis. 0.5 g of sliced soil was taken from each of the five intervals in the control group and thoroughly mixed. Both the mixed soil from the control group and the sliced soil from the treatment group were then subjected to a downstream microbial analysis.

Mesocosm Setup. Rice (*O. sativa* L.) cultivar, Yongyou-15, was sterilized and germinated following a method described in a previous report.²⁹ The seedlings were grown in a Hoagland culture in a greenhouse and transplanted at the four-leaf stage. Well-mixed soils (~5.0 kg) were added into a black plastic pot (length \times width \times height = 15.5 cm \times 15.5 cm \times 20.0 cm) with a soil depth of 15 cm. The soil was flooded during the mesocosm cultivation, with a water depth of 3 cm. Two identical seedlings were transplanted into each pot. The mesocosm incubation had two treatments: (1) control, in which the MAT was filled with pure nitrogen gas, and (2) with MAT, in which the MAT was inflated with air. During the 120-day incubation, porewater around MAT was sampled using Rhizon samplers (0.25 cm \times 10 cm) and acidified with 6 M HCl (1% of the sample volume; sample pH < 2.0). The acidified porewater sample was used for the total elements analysis. Rice plants were harvested at maturity and divided into roots, stems, leaves, and grains. The Fe plaque on rice roots was removed by DCB solution (containing 0.03 M Na₃C₆H₅O₇·2H₂O, 0.125 M NaHCO₃, and 0.06 M Na₂S₂O₄), following the procedure described by a previous study.¹⁹ Plant tissues were dried in an oven (65 °C) until a constant weight. Afterward, the plant tissues were weighed to calculate the plant biomass, and the plant samples were ground and sieved through a 0.10 cm sieve for downstream chemical analysis. A total of 0.25 g of grinded biomass was digested using a 1:1 mixture of concentrated HNO₃ and H₂O₂.³⁰ The digested samples were filtered through a 0.45 μ m cellulose filter for downstream chemical analysis.

Chemical Analysis. For porewater samples collected by Rhizon samplers, before their acidification, the sample pH and

Eh were instantly measured using a PHB-4 portable pH/OPR meter (Leici, Shanghai, China).

The aqueous Fe was determined by the 1,10-phenanthroline method (λ = 510 nm).³¹ Based on our preliminary test, Fe(II) accounts for more than 95% of total Fe in the soil porewater; thus, only Fe(II) was determined in this study. Total solute-phase Mn and As preserved with HCl were measured by inductively coupled plasma-mass spectrometry (ICP-MS, NexION 300X, PerkinElmer, Inc., Shelton, CT USA), under DRC mode (O₂ as the reaction gas). The ⁵⁵Mn⁺ and ⁹¹AsO⁺ counts were recorded. Common As species (including As(III), As(V), MMA, and DMA) were analyzed by high-performance liquid chromatography (HPLC, PerkinElmer, Inc., USA)-inductively coupled plasma mass spectrometry (ICP-MS NEXION300X, PerkinElmer, Inc., USA) under DRC mode (O₂ as the reaction gas), and ⁹¹AsO⁺ counts were recorded. An anion-exchange column (PRP-X100, 25 cm \times 0.41 cm) was used to separate the different As species, and 20 mM NH₄H₂PO₄ with a pH state of 6.5 was used as the mobile phase. The presence of As species in the sample can be determined by comparing their retention time with that of different arsenic species in standard solutions (Figure S3). Peak areas of a series of standards (1.0–20 μ g/L As(III), As(V), MMA, and DMA) were used to create the calibration curves (Figure S3). By inputting the peak areas into the calibration curve, the concentrations of As species in the sample were calculated accordingly.

Dissolved organic carbon (DOC) was quantified by using a TOC analyzer (Shimadzu TOC-VCPH, Japan). The DOC composition was further detected by negative-ion ESI-FT-ICR MS (Bruker Daltonics Inc., Billerica, MA, USA). The aromaticity index (AI_{mod}; eq 1) was calculated in this study and divided into three regions, following the diagram reported previously:^{32,33} AI_{mod} \leq 0.5, organic compounds without aromatic rings; 0.5 < AI_{mod} < 0.7, organic compounds that are likely to be aromatic; AI_{mod} \geq 0.7, organic molecules which contain condensed aromatic rings.

$$\text{AI}_{\text{mod}} = \frac{1 + C - \frac{1}{2}O - S - \frac{1}{2}(N + P + H)}{C - \frac{1}{2}O - N - S - P} \quad (1)$$

Microbial Analysis. Total RNA was extracted from soils using an RNA Isolation Kit (MO BIO Laboratories, Inc. Carlsbad, USA). The extracted RNA was instantly subjected to retrotranscription using a PrimeScript cDNA synthesis kit (TAKARA, China).

The synthesized cDNA was subjected to barcode amplification of the V3–V4 hypervariable region of the 16S rRNA gene at Hangzhou KaiTai Biotechnology Co., Ltd. (Hangzhou, China). The sequencing procedure is described in the Supporting Information. Three As metabolic genes, including *arrA* (As(V) respiratory reductase gene), *arsC* (As(V) reductase gene), and *aioA* (As(III) oxidase gene), were quantified by real-time qPCR. The detailed operation is given in the SI text, and the oligonucleotide primers and qPCR conditions used are summarized in Table S2.

Statistical Analysis. Results are presented as the average \pm standard deviations (SD). The statistical difference was analyzed by SPSS22.0 software (IBM SPSS, Armonk, NY, USA), using the two-tailed Student's *t* test with a significance level of 0.05. All of the data were plotted by R4.1.0 software.

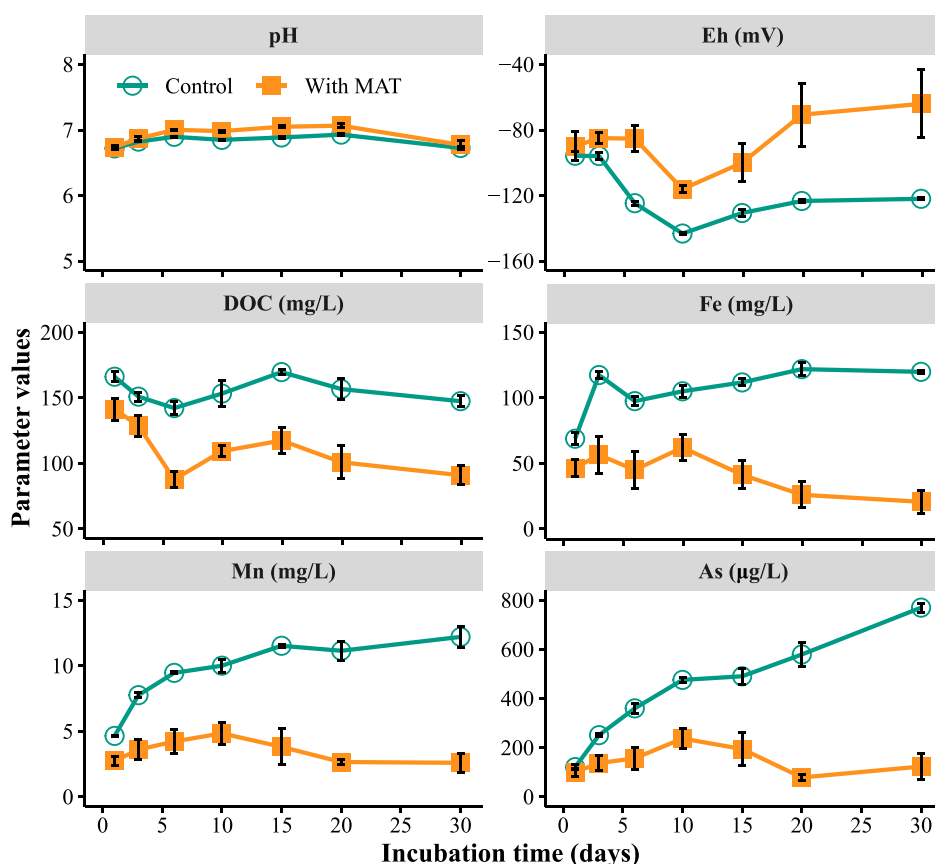


Figure 2. Changes of porewater chemistry with MAT. The porewater was sampled from 0 to 2 cm around MAT. MAT was set at ~8 cm soil depth, with a density and air pressure of 0.2 m² outside tube surface/m² soil and 25 kPa, respectively. The Eh is vs a Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

Performance of Man-Made Aerenchymatous Tissues (MAT). MAT has the ability to efficiently supply O₂ to saturated soil, such as paddy soil, from the atmosphere. For instance, at a MAT density of 0.2 m² outside tube surface/m² soil and an inner air pressure of 25 kPa, it can deliver approximately 5 kg of O₂ per hectare per day. It is supposed that MAT can considerably increase the soil Eh. Similarly, alternative wetting and drying water (AWD) management has also been shown to elevate the soil Eh by transporting O₂ into rice paddies.³⁴ However, its effectiveness largely depends on its operating frequencies.³⁵ By contrast, MAT can continuously input O₂ into paddies, making it more sustainable in a time horizon.

The influences of MAT on soil chemistry (including pH, Eh, DOC, Fe, Mn, and As) are presented in Figure 2. Our results showed that MAT had no obvious influence on soil pH, with values remaining around neutral during the 30-day microcosm incubation, regardless of its deployment. However, MAT had a substantial impact on soil Eh during the incubation. MAT increased the soil Eh by 26.9% over the 30-day incubation period (average Eh from −119 to −87.3 mV) in the 0–2 cm soil zones around MAT during the microcosm incubation. In contrast, the AWD method tends to temporarily increase the soil Eh, and sustainable Eh management can only be achieved by improving the operating frequency. For example, the soil Eh promotion rate with MAT (Figure 2) is in line with the report of the Eh promotion under a high-frequency AWD scenario (i.e., repeated 3 days of flooding + 5/3 days of drainage during

the rice growth; the Eh was promoted from about −170 mV under flooding to −70 mV under high-frequency AWD).³⁵

In addition, MAT tends to sustainably influence other redox-sensitive parameters. For example, MAT significantly decreased the DOC over the 30-day incubation period (−28.5%) and reduced the concentrations of relatively simple organics (i.e., organic compounds without aromatic rings and organic compounds that are likely to be aromatic, Figure S4). The decrease of DOC concentration is most likely due to the adsorption of DOC by newly formed Fe oxides in the soil. Incorporation of organic carbon in Fe oxides has two critical environmental impacts: (i) protect organic carbon from decomposition and enhance their stabilization in the soil³⁶ and (ii) shift Fe oxide crystallization and modulate their adsorption capability for trace elements like As. MAT also significantly decreased porewater Fe, Mn, and As concentrations over the 30-day incubation period, with an average extent of 59.8, 63.3, and 62.2%, respectively. The decrease in these elements was mainly attributed to the increase in soil Eh.^{35,37} The rapid drop in soil Eh is a decisive factor for As mobilization in saturated soils.^{35,38} The increase of soil Eh can help resist two major processes triggered by intermittent flooding in rice production: (i) reductive dissolution of Fe(III) and Mn(IV) (oxyhydr)oxide minerals by stimulating dissimilatory Fe(III)- and Mn(IV)-reducers and (ii) reduction of the immobile As(V) to the more mobile As(III) by stimulating dissimilatory As(V) reducers. For this cause, many attempts have been made to supply oxidants (such as Mn(IV) oxides, nitrate, and O₂) to saturated soils to immobilize As by increasing the soil Eh;^{35,39–41} however, these approaches can

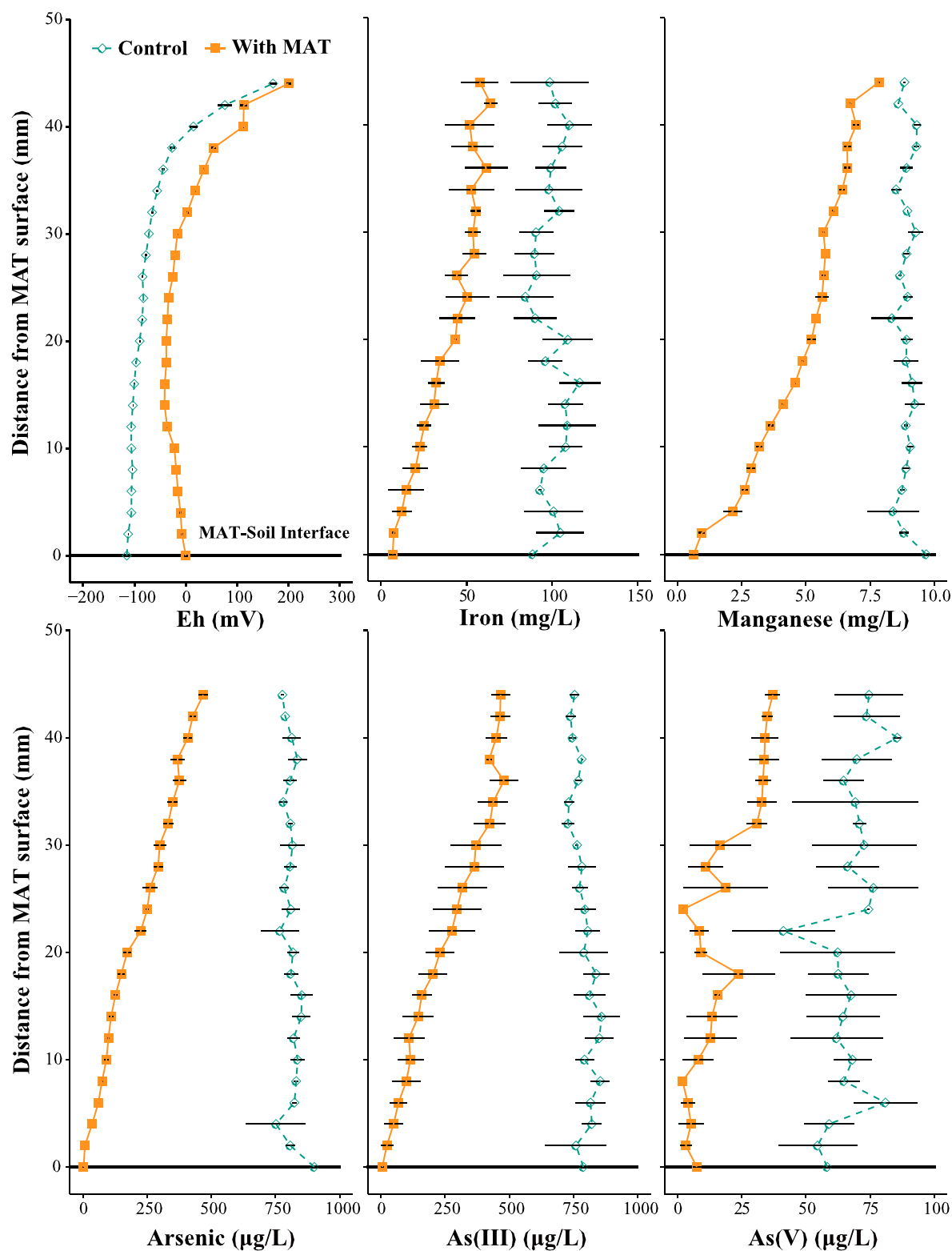


Figure 3. Redox potential (mV; vs a Ag/AgCl reference electrode) and elemental profiles across the MAT–soil interface. The horizontal solid lines at $y = 0$ mean the MAT–soil interface, where the MAT is horizontally deployed. The Eh was measured by a microelectrode across the water–soil interface after 30-day microcosm incubation, while elemental profiles were measured by IPI samplers deployed at the same soil depth as MAT.

only temporarily increase the soil Eh. Although repeated supply can potentially solve this issue, this measure may cause secondary effects on the soil matrix (e.g., acidification of soil, deterioration of soil quality, or loss of soil biodiversity).^{42,43} Previous studies suggested that amending soil with O_2 is an

effective and eco-friendly method since no synthetic chemicals are added to the soil.⁴⁴ As a result, AWD is frequently used in many parts of the world.^{34,45,46} However, the application of AWD has similar unsustainability issues. Additionally, it may bring other problems, such as yield loss⁴⁶ and weed problems

associated with draining a field.⁴⁵ In the present study, the MAT method was demonstrated to continuously supply O₂ to saturated soils at a relatively high efficiency, and the O₂ releasing rate can be easily modulated by adjusting the air pressure in the MAT. Thus, the MAT would be a sustainable method to immobilize As by increasing soil Eh.

Immobilization of As Across the MAT–Soil Interface.

MAT has a high O₂ release rate, suggesting that it may significantly influence a wide range of soil volume. According to the preliminary test, the influence of MAT on redox-sensitive soil parameters can extend to the soil zone 2–4 cm around MAT (Figure S5). For example, MAT increased the Eh over the 30-day incubation period (8.78%) and simultaneously reduced DOC and porewater Fe, Mn, and As concentrations in 2–4 cm soil zones around MAT, to an average extent of 11.8, 23.0, 25.7, and 20.9%, respectively.

To vividly present the process, we measured the soil Eh and porewater Fe, Mn, As, and As species across the MAT–soil interface (~4 cm) in the microcosm after the 30-day incubation. Our results support the notion that the MAT activity (i.e., O₂ release) is also sustainable in a spatial horizon.

Figure 3 illustrates that MAT significantly affected the Eh across the MAT–soil interface (on a centimeter scale). In the control group, a low Eh was observed across the 0–4 cm soil zone from the silicone-tube surface (average –82.1 mV). However, a much higher Eh (i.e., less negative) was observed across the 0–4 cm soil zone from the MAT–soil interface (average –8.43 mV). Similarly, the soil Eh was significantly promoted by ROL from rice roots,⁴⁷ but the influence range of ROL is quite limited, which is usually <1 cm depending on soil properties, rice cultivars, and rice growth stage.^{29,48} In addition, ROL is sensitive to light density and thus has a circadian rhythm, indicating that ROL is extremely weak during nighttime or dark periods. In contrast, the performance of the MAT is less likely to be affected by variations in the surrounding geochemical conditions.

In addition, MAT had a significant impact on the concentrations of dissolved Fe, Mn, and As, as well as the As speciation across the MAT–soil interface (on a centimeter scale; Figure 3). In the control group, porewater Fe, Mn, and As concentrations stayed around 99.7 mg/L, 8.93 mg/L, and 812 μg/L, respectively, across the 0–4.4 cm soil zone from the silicone-tube surface. By contrast, much lower porewater Fe, Mn, and As concentrations were observed across the 0–4.4 cm soil zone from the MAT–soil interface (average 39.0 mg/L, 4.80 mg/L, and 300 μg/L, respectively), especially in the zones adjacent to the MAT (0–1 cm; average 10 mg/L, 2 mg/L, and 217 μg/L, respectively). Additionally, a centimeter-wide brown-red zone with Fe (oxyhydr)oxides was observed across the MAT–soil interface (Figure S6), indicating that the MAT can hold a considerable range of Fe (oxyhydr)oxide minerals in the soil. Iron (oxyhydr)oxides are known to provide the major adsorption sites for As in soils.³⁹ Two inorganic As species (i.e., As(III) and As(V)) were detected across the MAT–soil interface, and As(III) was the predominant redox species in all conditions (As(III) proportion ≥ 92.2%), which is in line with previous studies carried out in reducing environments.^{2,49} Both As species showed a trend similar to that of total As. It should be noted that a higher extent of As(V) (74.1%) was immobilized across the MAT–soil interface than As(III) (67.1%), which is highly plausible because Fe (oxyhydr)oxides exhibit a greater affinity toward As(V) compared to As(III).⁵⁰

Decrease of As Accumulation in Rice. Additionally, we monitored alterations in soil chemistry (including pH, Eh, DOC, Fe, Mn, and As) throughout rice cultivation and observed the accumulation of As in rice plant tissues. MAT considerably increased the soil Eh and influenced other processes sensitive to Eh changes in the soil (Figure S7). During rice cultivation, the MAT had no obvious influence on the soil pH (~6.81). In comparison, MAT significantly increased the soil Eh from –119 to –80.7 mV (32.2%). Meanwhile, DOC, porewater Fe, Mn, and As were noticeably decreased by MAT, with an average extent of 28.0, 37.0, 51.0, and 54.4%, respectively. MAT also significantly decreased As accumulation in the rice plants' roots, stems, leaves, and grains, with an extent of 27.4, 32.2, 24.9, and 30.0%, respectively (Figure 4A), which is in line with the application of high-

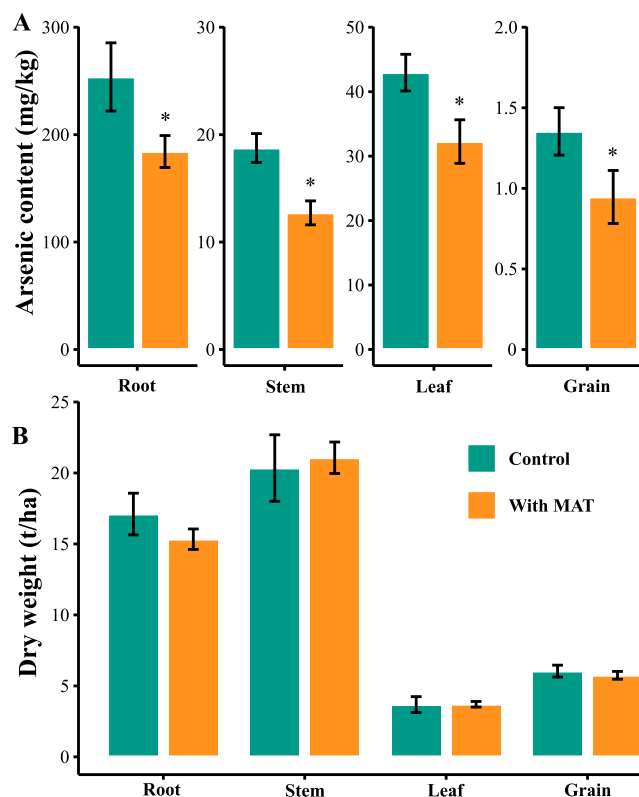


Figure 4. Influence of MAT on As accumulation in different rice tissues (A) and rice plant growth (B). * denotes a significant difference at $p < 0.05$.

frequency AWD.³⁵ MAT showed no significant influence on plant biomass (Figure 4B), indicating that MAT has a limited impact on nutrient uptake in rice. This may be attributed to two causes: (i) MAT does not significantly affect the availability of nutrients in the soil and (ii) the rice root exudates more chelating reagents to liberate nutrients from soil solids.⁵¹ The MAT method may be also applied to remediate other heavy metals that exhibit similar behavior to As, such as lead, cobalt, and vanadium.^{23,52} Nonetheless, certain heavy metals such as cadmium and antimony behave differently from As, thus the persistent rise in saturated soil Eh levels can stimulate their mobilization,³⁵ especially in soils contaminated with multiple heavy metals. Hence, further studies are necessary to optimize MAT's setup in cocontaminated paddy soils. Although the silicone tube of MAT can be retrieved from

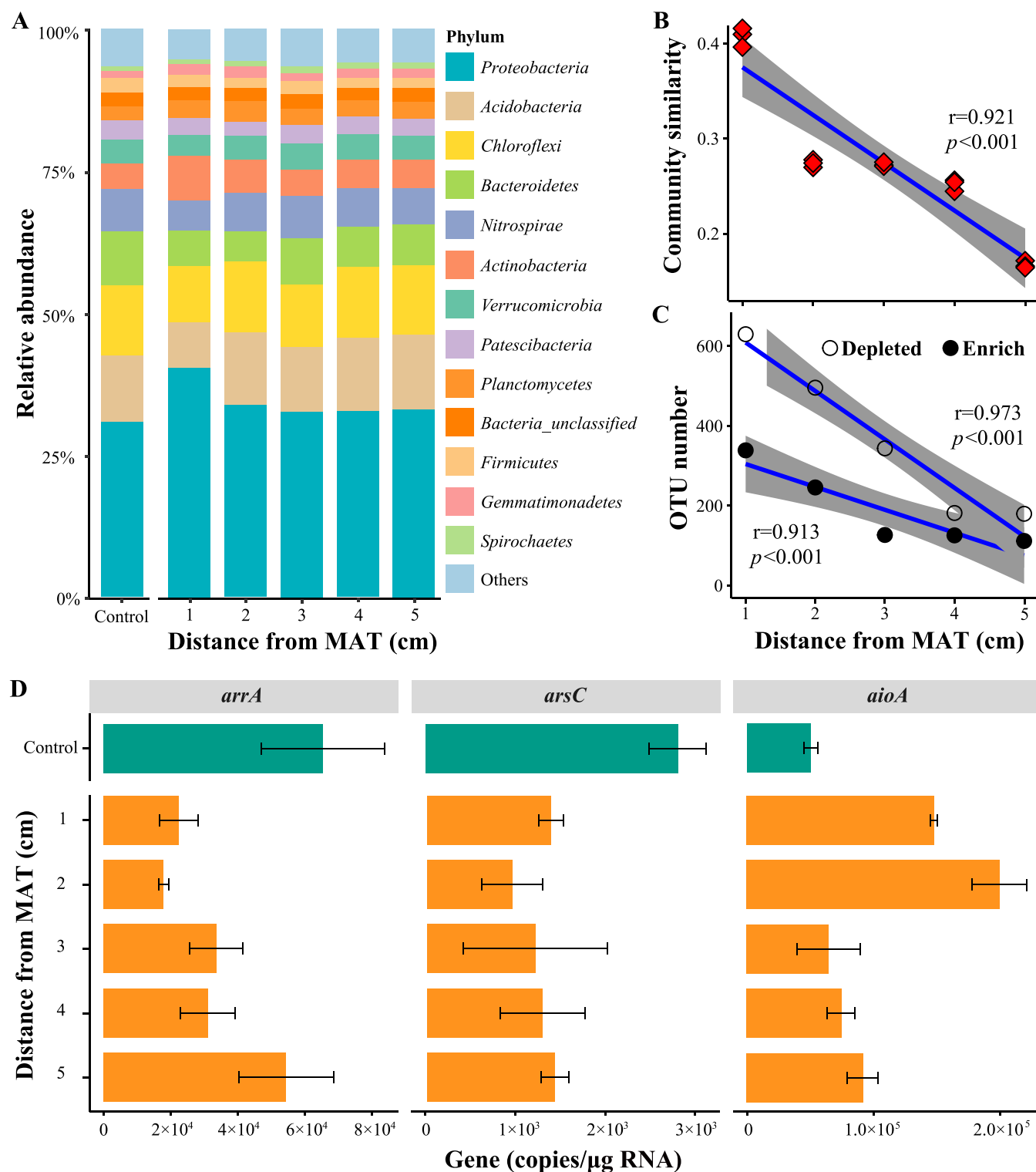


Figure 5. Changes of microbial community composition and abundance of As-metabolic genes. (A) Microbial community distribution in control and at different distances from the MAT surface; (B) community similarity at different distances from the MAT surface; (C) significantly changed OTU numbers at different distances from the MAT surface; (D) As-metabolic genes in control and at different distances from the MAT surface.

the field after rice harvest and can be reused, a significant amount of labor is required for this process. To address this issue, we are currently testing other more environmentally friendly materials to develop a no-side-effect, low-cost, high-efficiency, and disposable MAT system.

The Mechanism of As Immobilization by MAT. The microbial community composition and abundance of As

metabolic genes around MAT were investigated to reveal the potential microbial mechanisms involved in As immobilization (Figure 5).

The major microbial communities are depicted in Figure 5A. The soil microbial communities exhibited notable differences between the MAT and control groups, and they also varied across different distances (1–5 cm) from the MAT surface.

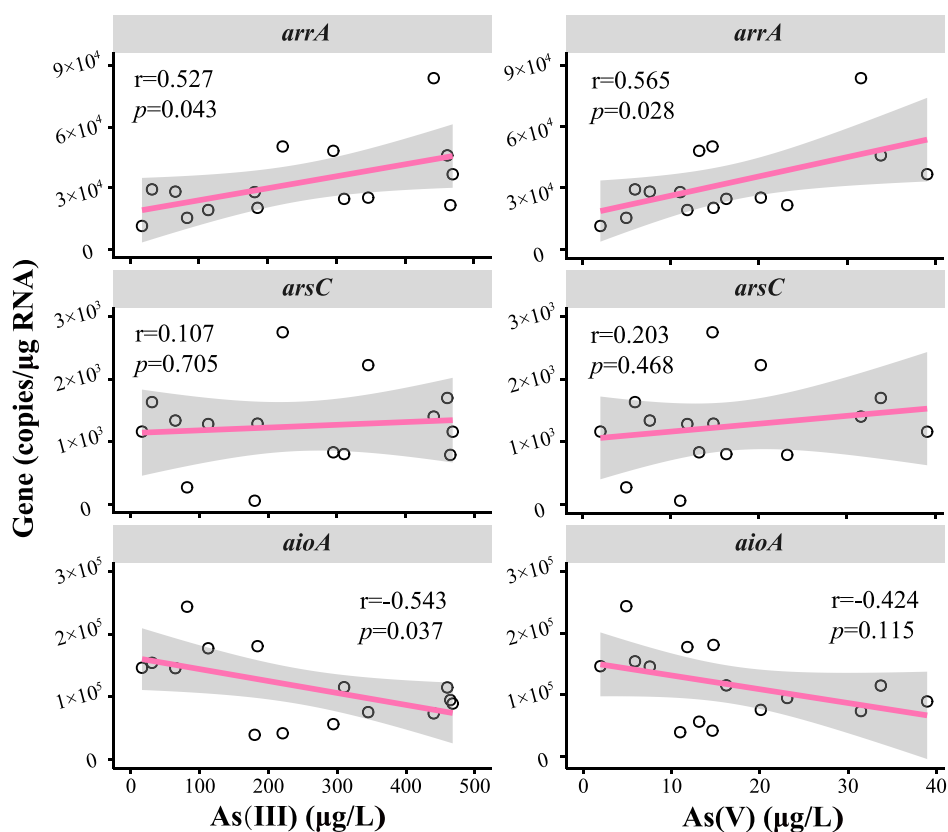


Figure 6. Correlation between As-metabolic gene copies with As speciation around the MAT.

MAT promoted the relative abundance of *Proteobacteria* ($p < 0.001$), especially in soils adjacent to the MAT surface (i.e., 0–1 cm; 31.0% higher than the control). Meanwhile, *Bacteroidetes* were significantly inhibited around the MAT ($p < 0.001$). Both Figure 5B and C demonstrated that MAT had a noticeable impact on microbial communities on a centimeter scale, which is quite similar to the changes of microbial communities across a natural redox gradient (e.g., soil-water interface and rice rhizosphere).^{48,53} Moreover, MAT also affected the distribution of As metabolic genes on a centimeter scale (Figure SD). The As(V)-reducing genes, including *arrA* and *arsC*, were significantly decreased, to extents of -51.1% and -56.6% , respectively. Conversely, the level of the As(III)-oxidizing gene, i.e., *aioA*, was significantly increased (130%). This aligns with previous reports in the rice rhizosphere.^{29,54} The porewater As(III) and As(V) had a significant positive relationship with the *arrA* gene across the MAT–soil interface, which is likely because the *arrA* gene plays a crucial role in As mobilization in a reducing environment.⁵⁵ In contrast, As(III) showed a significant negative relationship with the *aioA* gene (Figure 6), supporting the importance of microbially mediated As(III) oxidation in micro-oxic environments in saturated soils.^{54,56}

The MAT may induce several abiotic or biotic processes and enhance As immobilization when used in saturated soils. First, MAT elevates soil Eh, which inhibits the dissimilatory Fe(III) and As(V) reduction processes. Dissimilatory Fe(III)- and As(V)-reducers prefer more reducing conditions; thus, releasing As under flooded paddy fields has long been a major concern.^{1,7,57} As reported by Honma et al.,³⁵ Eh conditions of ≤ -100 mV tend to activate Fe(III) and As(V) reducers, which finally leads to a rapid increase in porewater As

content. MAT can alter the soil Eh from highly reducing (-150 mV) to mildly reducing (-87.7 mV) conditions (Figure 2), which significantly limits the activities of Fe(III) and As(V) reducers. Second, MAT stimulates biotic/abiotic Fe(II) oxidation and enhances Fe(III) (oxyhydr)oxide mineral formation (Figures S8 and S9), which provides additional adsorption sites for dissolved As. The Fe(III) (oxyhydr)oxide formation driven by O_2 release from aerenchymatous tissues has been observed in many wetlands and was hypothesized to be attributed to radial O_2 loss-driven biotic/abiotic Fe(II) oxidation (i.e., Fe plaque).^{58–60} However, Fe plaques are tightly bound on wet plant roots and would serve as a barrier for further O_2 release from roots to reduced soils.²¹ In contrast, we adopted a material (i.e., silicone) that does not favor the adhesion of Fe (oxyhydr)oxide minerals; thus, the O_2 can be continuously released to the saturated soil and induce the formation of a larger Fe(III) (oxyhydr)oxide mineral pool for sequestering dissolved As. Last, the MAT stimulates the oxidation of As(III) to As(V), which is less mobile. The *aioA* gene mediating As(III) oxidation was observed in this study, which has also been observed in the rhizosphere of many wetland plants.^{29,61} The adsorption of As(V) by Fe(III) (oxyhydr)oxides and other soil solids is much higher than that of As(III),^{50,62} hence oxidation of As(III) to As(V) will aid in reducing the release of As in soils. This shares a similar mechanism as using active oxidants such as Mn oxides and nitrate to immobilize As in soils.^{39,40} Therefore, the immobilization of soil As by the MAT method involves a combination of abiotic and biotic processes. To further enhance the effectiveness of the MAT approach, it is possible to employ strategies that specifically target and enhance the key processes involved in immobilizing As in the soil.

Advantages and Constraints of MAT. The MAT method is still in its infancy and has some advantages and constraints concerning costs, feasibility, efficiency, and environmental impacts (Table S3). MAT is easy to use and requires no additional maintenance after deployment. When used, MAT continuously delivers O₂ to saturated soils from the atmosphere; hence, it has a low cost and a good long-term performance. In contrast, although adding oxidizing chemicals (e.g., O₂, Mn oxides, and nitrate) is easy, each addition can only temporarily immobilize soil As. To achieve a good long-term performance, high-frequency addition is essentially required,^{35,63} but this significantly increases the cost and may cause additional adverse effects (e.g., aggravate the eutrophication of water bodies, degrade soil quality, and cause hazards to living organisms in the soil).^{43,64} By comparison, MAT has a relatively low cost, which is ~50 times lower than the equivalent application of Fe₂O₃ (see calculation in the SI) and MAT causes no negative influence on the soil.

Additionally, the MAT approach is flexible and thus could easily be combined with other strategies to maximize the immobilization of soil As. For example, more efficient As immobilization could be achieved by coupling MAT with the addition of Mn oxides,³⁹ which will trigger Mn cycling in saturated soils and stimulate chemical oxidation of As(III) to As(V) by Mn(IV) oxides.⁶⁵ This indicates that MAT is scalable and can be readily integrated with other techniques to enhance the overall performance.

ENVIRONMENTAL IMPLICATIONS

In this study, we proposed a new method (i.e., MAT) to efficiently and sustainably immobilize As in paddy soils. Maintaining the appropriate Eh levels in flooded paddies has always been a complex issue, but the MAT could offer a potential solution. MAT has the ability to consistently discharge O₂ into saturated soils, increasing soil Eh, thus triggering multiple processes to immobilize As. Our results demonstrate that MAT decreases dissolved As concentrations through three main mechanisms: (i) reducing As dissolution by inhibiting Fe(III) and As(V) reduction; (ii) stimulating Fe(II) oxidation and Fe(III) (oxyhydr)oxide formation, thus generating additional adsorption sites for dissolved As; and (iii) enhancing As(III) oxidation and facilitating As(V) adsorption by Fe(III) (oxyhydr)oxides and other solid phases in soils. It is worth noting that MAT successfully mimics the ROL from wetland roots,^{18,19} and MAT does not suffer the negative effects of Fe plaques, light, and growth stages on ROL.²¹ Moreover, it requires no chemical additives and relies on only blowing air through the MAT device. Therefore, the MAT method can be considered a sustainable approach for saturated soil As immobilization with minimal adverse effects. The MAT has a large potential for simultaneously mitigating methane emissions from rice paddies due to three key factors. First, the MAT-induced Fe oxides have the capability to adsorb a significant amount of DOC (as shown in Figure 2), which in turn can potentially reduce methane generation by limiting the availability of organic substrates for microorganisms including methanogens. Second, the MAT facilitates the diffusion of O₂ into the soil, thereby promoting the aerobic oxidation of methane. This increased availability of O₂ enhances the activity of methane-oxidizing bacteria, leading to a more efficient consumption of methane. Last, the MAT's high inner air pressure (e.g., 25 kPa) acts as a physical barrier, greatly restricting the transportation of methane through the MAT

device. Nevertheless, two primary concerns arise regarding its practical application: (i) developing mechanical equipment for MAT deployment and harvest and (ii) integrating MAT with other As immobilization methods to maximize overall performance.

ASSOCIATED CONTENT

Data Availability Statement

Data and codes are available from the corresponding author upon request.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c03205>.

Details regarding quantitative PCR of genes, 16S rRNA sequencing, microbial data analysis, cost assessment of MAT and other methods, silicone tube properties, qPCR conditions, comparison of MAT with other methods, MAT system in soils, control of O₂ release from MAT, As species detection, DOC composition, porewater chemistry change around MAT, fresh Fe oxides around MAT, Fe speciation in soil solids, and solid–soil chemical changes around MAT (PDF)

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X.T. and Z.Y. designed the research. Z.Y. performed the research. Z.Y., X.T., Y.Z., Z.C., Z.T., W. G., A.K., and J.X. wrote the paper.

Notes

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ABBREVIATIONS

AWD = Alternative wetting and drying

As = Arsenic

DOC = Dissolved organic carbon

MAT = Man-made aerenchymatous tissue

O₂ = Oxygen

Eh = Redox potential

As(V) = Arsenate

As(III) = Arsenite

Fe = Iron

Mn = Manganese

ROL = Radial oxygen loss

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