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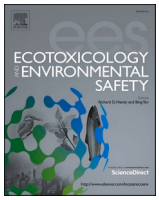

Manganese (II) sulfate affects the formation of iron-manganese oxides in soil and the uptake of cadmium and arsenic by rice

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ABSTRACT

Rice (*Oryza sativa* L.) consumption represents a major route of human exposure to cadmium (Cd) and arsenic (As), especially in Asia. This study investigated the effects of adding $MnSO_4$ (0, 200, 400, and 800 mg kg^{-1-1}) on the formation of soil Fe/Mn oxides and Cd and As uptake in rice. The application of $MnSO_4$ reduced soil pH, increased Eh, increased the contents of Fe/Mn oxides in the soil, and decreased the total Fe and Mn^{2+} contents in the porewater. It also led to lower contents of available Cd and As, higher levels of Cd and As bound to Fe/Mn oxides, and higher abundances of *Thiobacillus* and *Syntrophobacter*. Furthermore, Mn application increased the Fe and Mn contents in the root Fe/Mn plaque and decreased the grain Cd and As contents. Therefore, Mn application may modify the microbial community and porewater composition in soil, resulting in higher levels of Fe/Mn oxides in soil and Fe/Mn plaque at the root surface and in a lower accumulation of Cd and As in rice grains. Thus, Mn application can be a promising strategy for Cd and As stabilization in soils.

1. Introduction

In recent years, because of the influence of human activities (Mining of ores, discharge of municipal sewage, etc.), soil pollution with heavy metals has become more serious. Contamination with heavy metals such as Cd, As, Pb, and Hg can impede agricultural production and, through accumulation in the food chain, poses a risk to human health; the reduction of heavy metal levels in farmland soil is therefore an urgent issue (Iqbal et al., 2023; Turan et al., 2018a, 2018b). Rice is an important food crop in China (Mu et al., 2019), and cadmium (Cd) and arsenic (As) contamination of rice fields in China has become increasingly serious (Shi et al., 2018; Deng et al., 2020), threatening human health (Huang et al., 2019). Therefore, reducing the effectiveness of Cd and As in rice soil, thereby decreasing the accumulation in rice, has become an important research field.

Reducing the bioavailability of Cd and As in soil is an important pathway to control Cd and As accumulation in rice. Binding to soil components may change the speciation of Cd and As, reducing their bioavailable fractions (Lombi et al., 2000; Prokop et al., 2003). Previous studies reported remediation strategies using additional chemical amendments to reduce the bioavailability of heavy metals in paddy soils (Wan et al., 2020). However, the interactions of heavy metals in soil systems are complex, and the physicochemical properties of paddy soils can affect the bioavailability and, thus, accumulation of Cd and As in rice (Wang et al., 2021).

In flooded paddy soils, As(V) can be reduced to As(III), which is highly mobile and toxic and readily absorbed by plants (Mlangeni et al., 2020). In contrast, Cd presents a low bioavailability under anaerobic conditions (Rinklebe et al., 2016). In this context, the simultaneous reduction of the bioavailability of Cd and As in soil systems through the addition of a single amendment is challenging. The remediation of Cd- and As-contaminated agricultural soil can be achieved via the use of biochar biochar, organic amendments (vermicomposting), phytoremediation, microbial fertilizers, and inorganic amendments. Among them, the application of inorganic amendments can both reduce the effectiveness of Cd and As in the soil and provide nutrients for crop growth (Lu et al., 2022; Mubeen et al., 2023; Priya et al., 2023; Pan et al., 2022).

In addition, Fe/Mn can also be used as soil conditioners (Mubeen et al., 2023), and Fe and Mn oxides are common and reactive

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components of soils, which significantly regulate the fate and bioavailability of Cd and As (Tazaki, 2000; Ying et al., 2012; Ehlert et al., 2014; Xu et al., 2017a; Wang et al., 2019). According to previous studies, Mn oxides rapidly oxidize As(III) and Fe(II) under oxic conditions, and Mn oxides and amorphous Fe (oxyhydr) oxides are important factors controlling reductive As mobilization in As-contaminated paddy soils (Ehlert et al., 2014; Xu et al., 2017a; Ying et al., 2012). The surface sites of Fe/Mn oxides can adsorb Cd and, thus, decrease the extractability of Cd in soil (Wang et al., 2019). Furthermore, the rice root plaque, which primarily consists of Fe and Mn oxides, can reduce the uptake of Cd and As by rice (Liu et al., 2010; Hu et al., 2015). There are significant differences in the physicochemical properties of effective Cd and As in soils, and the application of fertilizers to reduce the effectiveness of Cd and As in such contaminated soils is an important issue. As Mn is an essential micronutrient for rice growth, Mn deficiency can lead to reduced yields (Ibrahim et al., 2018) and a reduced Cd uptake by rice (Liang et al., 2022). In a previous study, the lowest As mobilization was observed in soil with significant levels of manganese oxides (Xu et al., 2017b). However, studies on the application of Mn fertilizers in soil contaminated with Cd and As, with the aim to reduce rice Cd and As contamination, are scarce.

In this study, $MnSO_4$ was applied as an Mn fertilizer to rice grown on soil contaminated with a mixture of Cd and As. The morphology of Cd and As in soil, the levels in pore water and the Fe/Mn plaque, as well as the microbial diversity of the rhizosphere soil of rice at maturity were determined. Correlation analysis and structural equation modeling (SEM) were performed based on the Cd and As concentrations of rice plants to explore the mechanism by which Mn fertilization reduces the Cd and As levels in rice by regulating the soil properties. The results provide insight into the development of soil conditioners to mitigate heavy metal pollution in rice.

2. Materials and methods

2.1. Experimental soil

The soil used in this study was collected from a rice paddy (0–20 cm) in Hezhou City, Guangxi Province, China, without heavy metal pollution. The basic physical-chemical properties are listed in Table SI1. The collected soil was air-dried and passed through a 2-mm mesh sieve, followed by mixing with solution containing $Na_3AsO_4{\cdot}12H_2O$ and $CdCl_2{\cdot}1/2H_2O$ and aging under moisture for 6 months. The final total As and Cd levels in the soil were 65.00 and 1.33 mg kg^{-1}, respectively.

2.2. Pot experiments

The pot experiments were conducted in a glass greenhouse. Three rice seedlings (*Oryza sativa* L. cv. *Y Liangyou* No. 2) were planted in each pot, and $MnSO_4{\cdot}H_2O$ was added to the soil at 0.615 g/kg (Mn200), 1.229 g/kg (Mn400), and 2.459 g/kg (Mn800), representing the different treatment groups (Table SI2). The soils without the addition of Mn were regarded as control (CK). Additionally, an extra control was prepared to assess the influence of SO_4^{2-} through adding Na_2SO_4 to the same SO_4^{2-} concentration as Mn400. Table SI2 shows the treatments of soils for the pot experiment. Three replicates were set up for each treatment, with three pots per replicate. To each pot, 6.00 kg of test soil, 1.35 g of CH_4N_2O (base fertilizer: 0.58 g, tillering: 0.77 g), 1.16 g of KH_2PO_4, and 0.92 g of KCl (base fertilizer) were added. Nutrient and water management followed conventional rice cultivation techniques during cultivation.

2.3. Samples collection

Soil and rice samples were collected at the pre-planting, tillering, and maturity stages. Five subsamples from the pot were collected and mixed to obtain a composite soil sample, which then was air-dried and screened for the soil physico-chemical analysis. Rice grains were collected, washed with ultrapure water, dried at 65 ℃ to constant weight, and ground into powder. The water-cleaned root samples were placed into sealed bags and kept at − 20 ℃ for root plaque extraction. Porewater (10 mL) was sampled using a 10 RHIZON MOM (10 cm, Rhizosphere, Netherlands), and the obtained samples were acidified with high-purity concentrated HCl to pH < 1. Rhizosphere samples were collected and stored in a sterile centrifuge tube at − 20 ℃ for microbial analysis. The Fe/Mn plaque on fresh rice roots was extracted using the dithionite-citric acid-bicarbonate (DCB) method (Hu et al., 2020). Briefly, 1 g of fresh roots was mixed with 40 mL of $C_6H_5Na_3O_7$ solution (0.3 mol L^{-1}), 5 mL of $NaHCO_3$ solution (1 mol L^{-1}), and 3 g of $Na_2S_2O_4$, and the mixture was shaken for 3 h.

3. Analytical methods

3.1. Soil pH and Eh

The pH was determined at a water-to-soil ratio of 2.5: 1. The mixture was shaken for 10 min, left to stand for 30 min, and then measured by a calibrated pH meter. The Eh was measured at 10 cm below the soil surface using an automatic redox potential depolarization analyzer.

3.2. Levels of Fe, Mn, Cd, and As in samples

For the soil and grains, 0.2 g of the samples was digested using HNO_3 and milling in a closed-vessel microwave digestion system (CEM MARS 6, USA). The concentrations of total As in the digests were detected via an atomic fluorescence spectrometer (AFS, SA-20, Jitian, Beijing, limit of detection (LOD) of As < 0.01 μg/L). The concentrations of total Cd, Mn, and Fe were detected using an atomic absorption spectrophotometer (AAS, PerkinElmer (PE) PinAAcle 900, USA, limit of detection (LOD) of Cd, Mn, Fe < 0.01 μg/L). As certified reference material, GBW10185 rice cultivar was used. The recovery of As was 98.56 ± 5.81 %, that of Cd was 102.08 ± 10.10 %, that of Mn was 95.34 ± 2.35 %, and that of Fe was 100.56 ± 1.70 %.

The concentrations of Fe(II) and Fe(III) in porewater were measured using the phenanthroline colorimetric method in a Shimadzu UV-2600 (Japan) at 530 nm (Lipson et al., 2010). Colorimetric analysis of Mn (II) in porewater was performed at 540 nm using potassium permanganate colorimetry (Chen et al., 2019). The concentration of Cd was determined by AAS, whereas that of total As was determined by AFS after pre-reduction by ascorbic acid and thiourea.

3.3. Fractionation of Fe, Mn, Cd, and As in soils

To determine free and amorphous Fe/Mn oxides, the methods described in Chen et al. (2019) were applied. The following procedure was used to extract the free Fe/Mn: A 0.5-g aliquot of the soil sample was passed through a 60-mesh sieve and placed in a 50-mL centrifuge tube to which 20 mL of 0.3 mol L^{-1} sodium citrate solution and 2.5 mL of 1 mol L^{-1} sodium bicarbonate solution were added, followed by heating of the tube in a water bath at 80 °C for 5 min. Subsequently, approximately 0.5 g of sodium dithionite was added, and the tube was shaken for 15 min and then centrifuged (10,000 r, 30 min). The following procedure was used to extract amorphous Fe/Mn: 2 g soil of the sample was passed through a 60-mesh sieve and placed into an Erlenmeyer flask. Subsequently, 100 mL (soil-to-liquid ratio of 1:50) of a 0.2-mol L^{-1} ammonium oxalate buffer solution was added at the extractant, and the flask was then covered with a black plastic bag as a light shield. Subsequently, the flask was shaken at a 25 ℃ for 3 h, after which the mixture was transferred to a centrifuge tube and centrifuged (10,000 r, 30 min). The supernatant was stored for later analysis.

The Cd fractions in soils were determined according to Tessier et al. (2002). Exchangeable Cd, Cd bound to carbonates, Cd bound to Fe/Mn oxides, and residual Cd were extracted. To determine the As fractions,

Table 1
Contents of Fe, Mn, Cd, and As in rice plants in maturity (n = 3). Different letters indicate significant differences ($p < 0.05$) between different treatments in the same period.

		CK	Na_2SO_4	Mn200	Mn400	Mn800
Fe (g/kg)	Roots	1.14 ± 0.06b	1.49 ± 0.45b	1.39 ± 0.13b	1.51 ± 0.23b	2.11 ± 0.16a
	Stems	0.28 ± 0.06b	0.21 ± 0.02bc	0.17 ± 0.01c	0.21 ± 0.01c	0.38 ± 0.04a
	Leaves	0.47 ± 0.07d	0.87 ± 0.11a	0.68 ± 0.07bc	0.64 ± 0.07c	0.83 ± 0.09ab
	Grains	7.58 ± 1.49c	14.31 ± 0.42a	8.86 ± 0.59bc	13.25 ± 1.00a	10.54 ± 0.72b
Mn (g/kg)	Roots	9.17 ± 1.97d	8.75 ± 2.5d	22.31 ± 1.54c	46.08 ± 3.27b	168.57 ± 11.92a
	Stems	0.09 ± 0.006d	0.11 ± 0.02d	0.86 ± 0.05c	1.07 ± 0.04b	2.10 ± 0.03a
	Leaves	0.59 ± 0.10d	0.53 ± 0.06d	2.22 ± 0.04c	3.54 ± 0.70b	7.56 ± 0.28a
	Grains	11.59 ± 0.35d	17.42 ± 1.16d	26.37 ± 3.31c	38.89 ± 1.56b	70.17 ± 6.52a
Cd (mg/kg)	Roots	6.24 ± 0.58a	6.00 ± 0.73a	5.43 ± 0.88a	6.53 ± 0.511a	5.95 ± 0.84a
	Stems	2.98 ± 0.17a	2.30 ± 0.17bc	2.47 ± 0.24b	2.24 ± 0.09bc	2.06 ± 0.06c
	Leaves	5.11 ± 0.35a	3.63 ± 0.44b	2.29 ± 0.09d	2.11 ± 0.19d	2.85 ± 0.29c
	Grains	1.93 ± 0.08a	1.59 ± 0.08b	1.34 ± 0.08c	1.24 ± 0.100c	1.03 ± 0.03d
As (mg/kg)	Roots	81.93 ± 2.24a	54.34 ± 6.40bc	48.71 ± 7.69c	58.77 ± 2.12b	43.2 ± 6.18b
	Stems	23.05 ± 0.46a	11.13 ± 0.97e	19.34 ± 0.78b	16.28 ± 0.43c	12.6 ± 0.49d
	Leaves	23.94 ± 0.87b	28.48 ± 3.11a	17.65 ± 2.15c	14.43 ± 0.80c	11.16 ± 0.49d
	Grains	0.73 ± 0.04a	0.66 ± 0.04a	0.69 ± 0.05a	0.51 ± 0.09b	0.39 ± 0.02c

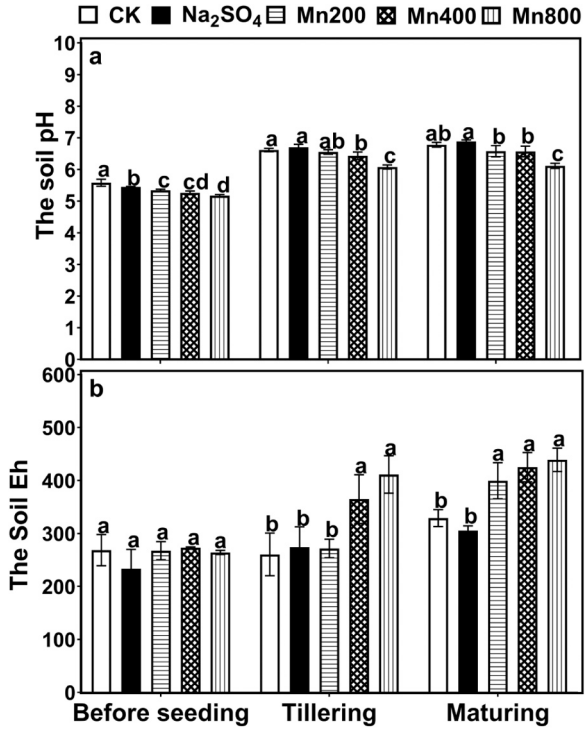

Fig. 1. (a) Effect of $MnSO_4$ application on soil pH. (b) Effect of $MnSO_4$ application on soil Eh. Different letters indicate significant differences ($p < 0.05$) between different treatments in the same period.

the method described in Wenzel et al. (2001) was applied. Non-specific bound As, specific bound As, amorphous Fe/Mn oxide-bound As, crystalline Fe/Mn oxide-bound As, and residual As were determined.

3.4. Microbiological analysis

Rhizosphere soil at maturity was used to determine microbial diversity. The DNA of the soil was measured according to the method described in previously published studies (Chen et al., 2019). Microbiota composition was described using three alpha diversity measures: number of amplicon sequence variants (ASVs; 100 % operational taxonomic units (OTUs)), phylogenetic diversity, Shannon Index. Three indices described microbial richness using the Shannon Index. The OTU table was rarefied to the minimum sample count for subsequent analyses, including the calculation of the alpha diversity measures, beta diversity measures, and species composition. The relative abundance at each level was calculated by collapsing the subsampled OTU table based on seven-level taxonomy strings obtained from the SILVA version 132 database/ UNITE database. Beta diversity metrics (Bray-Curtis, unweighted UniFrac, weighted UniFrac, Jaccard distance) were applied using the QIIME2, and the total genomic DNA extracts were submitted to high-throughput amplicon sequencing at Ecogene-Biotech (Shenzhen, China), targeting the V4–5 region of 16 S ribosomal RNA (rRNA). The PCR amplification of the 16 S r RNA gene fragments was performed using the primers F515 (5′-GTGCCAGCMGCCGCGGTAA-3′) and 926 R (5′- CCGTCAATTCMTTTRAGTTT -3′), with a sample-specific 12-bp barcode added to the reverse primer (Magoc and Salzberg, 2011; Caporaso et al., 2010; Callahan et al., 2016; Quast et al., 2013; Abarenkov et al., 2010; White et al., 2009).

3.5. Statistical analysis

Data are expressed as mean ± standard error. Statistical significance was determined at $p < 0.05$. All statistical analyses were performed using SPSS 24. Figures were obtained using the Prism 7.0 from Origin Software (San Diego, CA, USA). Correlation analysis and structural equation modeling were generated, and the results were plotted using the R software.

4. Results

4.1. Contents of Fe, Mn, Cd, and As in rice plants

Table 1 shows the changes in the Fe, Mn, Cd, and As concentrations in rice plants in maturity. The addition of Na_2SO_4 and Mn did not significantly reduce the Cd content of rice roots, whereas that of both stems and leaves was significantly reduced. In contrast, the addition of Mn significantly reduced the As content of rice roots, stems, and leaves. The application of Na_2SO_4 increased the Fe content of the rice grain, but the addition of Mn reduced this effect. The Mn content in the grain increased with a higher dosage of Mn, but the Cd content decreased with increasing Mn doses. Additionally, Na_2SO_4 application significantly reduced the Cd levels. The application of higher doses of Mn (Mn400 and Mn800) also reduced the As content in the rice grain.

4.2. Changes in pH and Eh with the application of Mn

Fig. 1a, b shows the effects of $MnSO_4$ application on soil pH and Eh. Before seeding, the soil pH was lowest and differed from that of CK in both the Na_2SO_4 and $MnSO_4$ treatment groups. At tillering and maturing stages, the addition of Mn reduced the soil pH more significantly. In

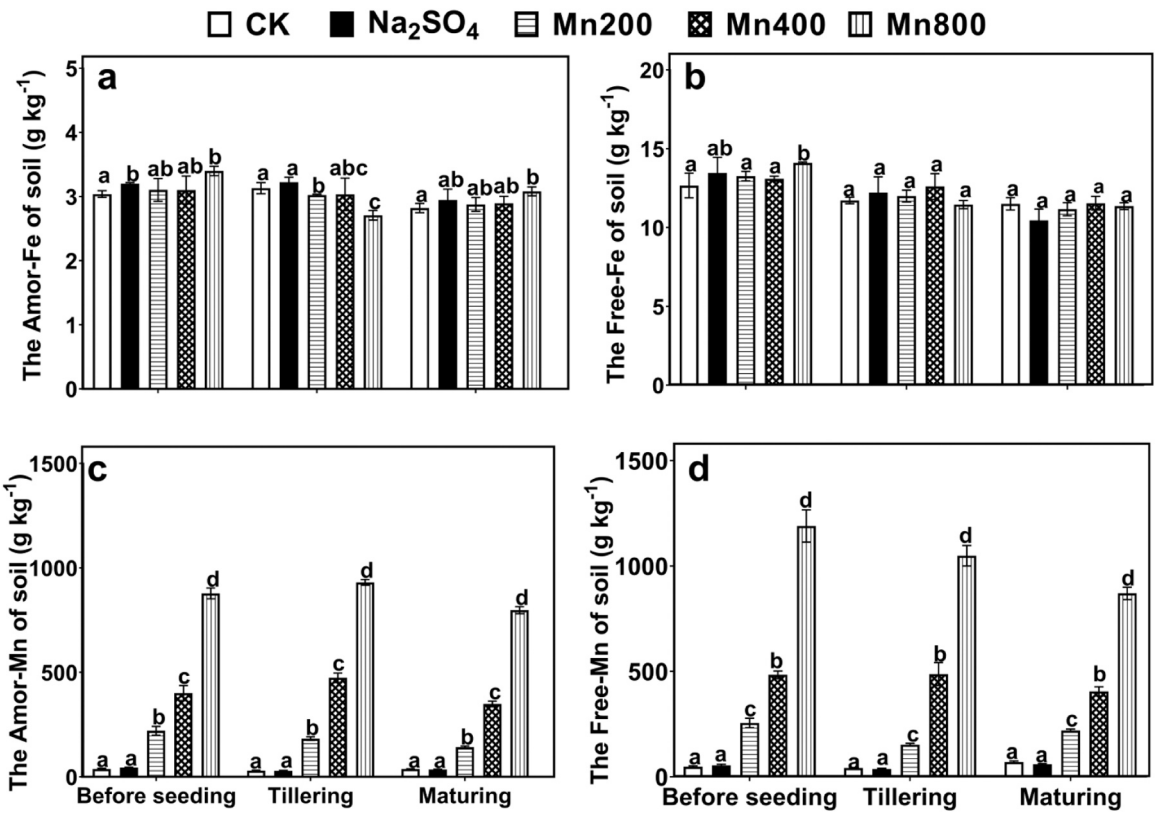

Fig. 2. Effect of $MnSO_4$ application on soil amorphous Fe (Amor-Fe) and free Fe, amorphous Mn (Amor-Mn), and free Mn. (a) Amor-Fe, (b) Free-Fe, (c) Amor-Mn, (d) Free-Mn. Mn200: 200 mg kg^{-1} $MnSO_4$ treatment in soil, Mn400: 400 mg kg^{-1} $MnSO_4$ treatment in soil, Mn800: 800 mg kg^{-1} $MnSO_4$ treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

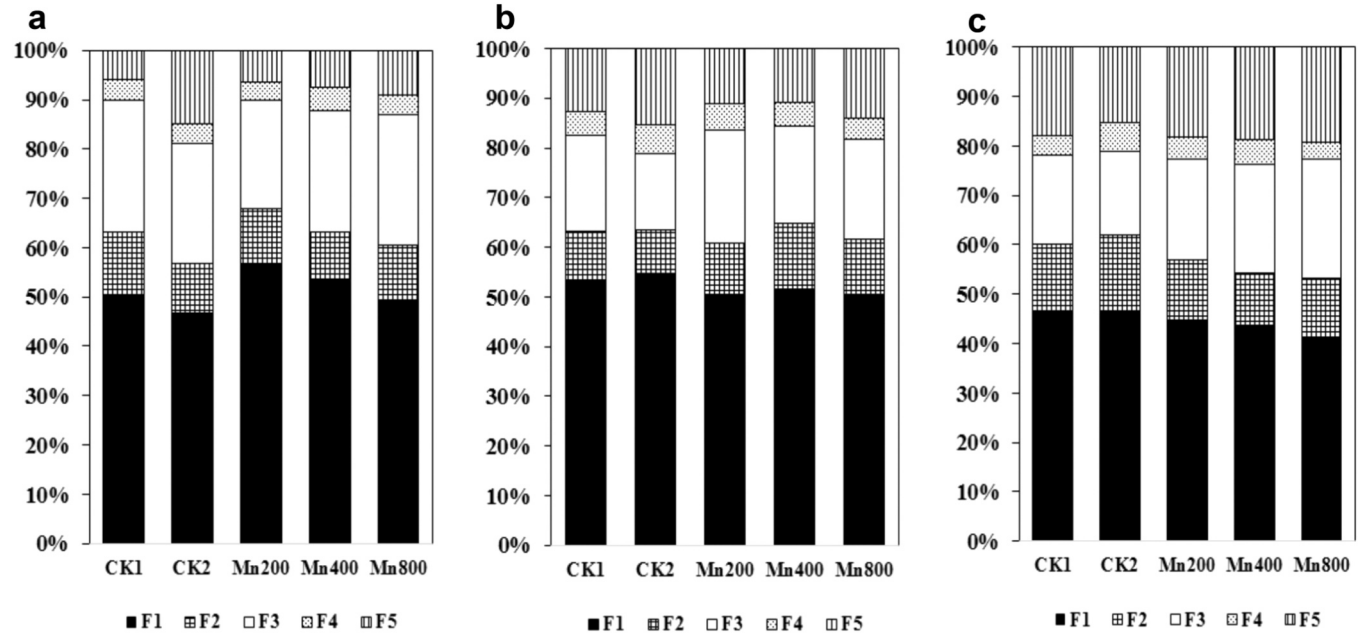

Fig. 3. Effect of Na_2SO_4 and $MnSO_4$ application on soil Cd fractions. F1: Exchangeable Cd, F2: Cd bound to carbonates, F3: Cd bound to Fe/Mn oxides, F4: Cd bound to organic matter, and F5: Residual Cd. A: Before sowing, B: Tillering, and C: Maturity. Mn200: 200 mg kg_{-1} $MnSO_4$ treatment in soil, Mn400:400 mg kg^{-1} MnSO4 treatment in soil, Mn800: 800 mg kg^{-1} MnSO4 treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

contrast, the soil Eh before seeding was not changed by the addition of Na_2SO_4 or $MnSO_4$ but increased in the tillering and maturing stages by $MnSO_4$ addition, particularly in the Mn400 and Mn800 treatments, whereas the treatment Mn200 only resulted in significant differences at maturity.

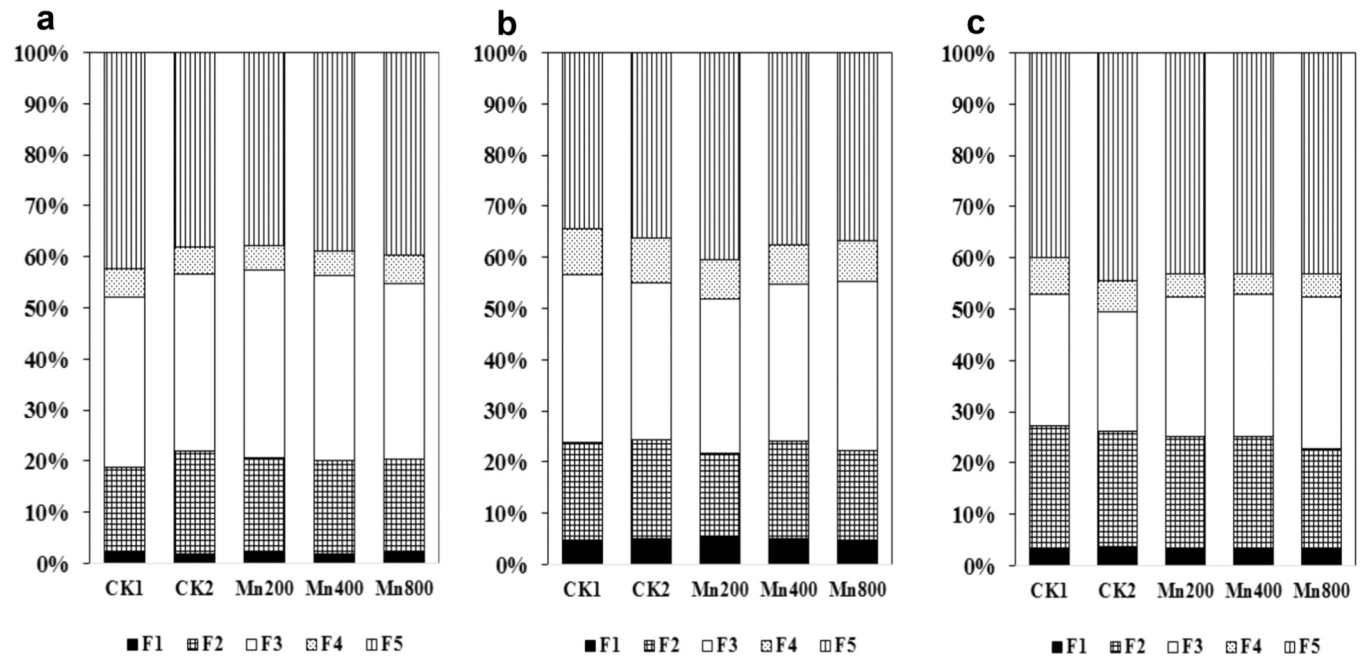

Fig. 4. Effect of Na_2SO_4 and $MnSO_4$ application on soil As fractions. F1: Non-specific bound As, F2: Specific bound As, F3: Amor Fe/Mn oxide-bound As, F4: Crystalline Fe/Mn oxide-bound As, and F5: Residual As. A: Before sowing, B: Tillering, and C: Maturity. Mn200: 200 mg kg^{-1} $MnSO_4$ treatment in soil, Mn400: 400 mg kg^{-1} $MnSO_4$ treatment in soil, Mn800: 800 mg kg^{-1} $MnSO_4$ treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

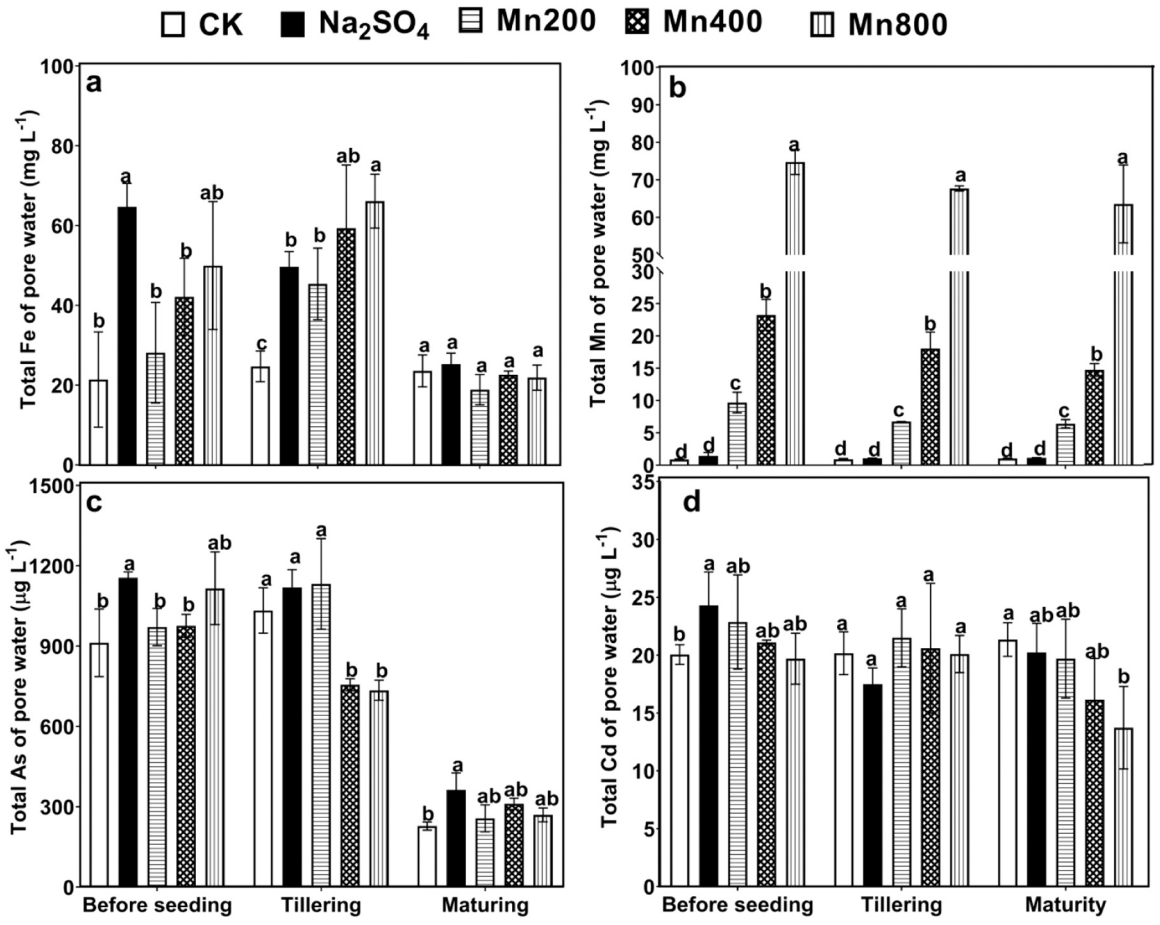

Fig. 5. Changes in Mn, Fe, Cd, and As contents in porewater following Na_2SO_4 and Mn application. A: Total Fe content, B: Total Mn content, C: Total As content, and D: Total Cd content. Mn200: 200 mg kg^{-1} $MnSO_4$ treatment in soil, Mn400: 400 mg kg^{-1} $MnSO_4$ treatment in soil, Mn800: 800 mg kg^{-1} $MnSO_4$ treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

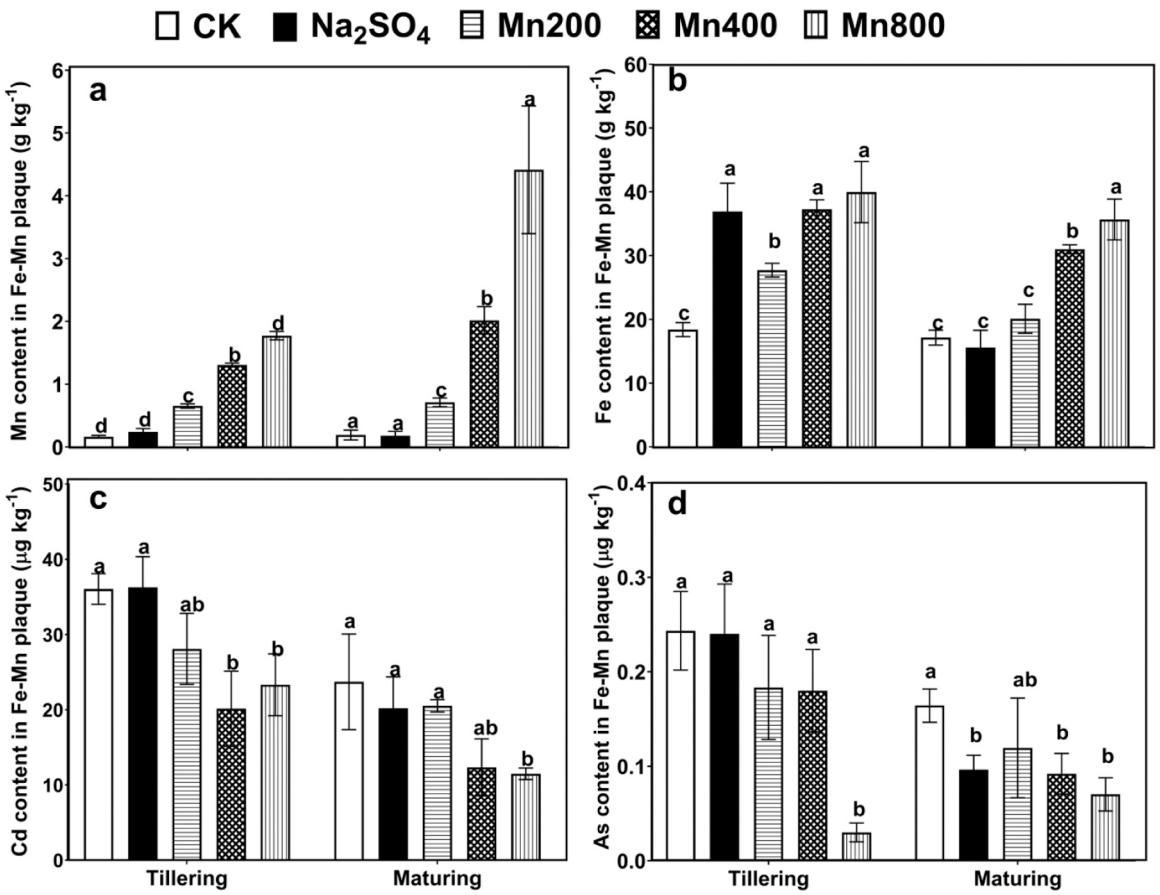

Fig. 6. Effect of Mn addition on the Fe/Mn plaque contents of Fe (a), Mn (b), Cd (c), and As (d) in tillering and maturing. Mn200: 200 mg kg^{-1} $MnSO_4$ treatment in soil, Mn400:400 mg kg^{-1} $MnSO_4$ treatment in soil, Mn800: 800 mg kg^{-1} $MnSO_4$ treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

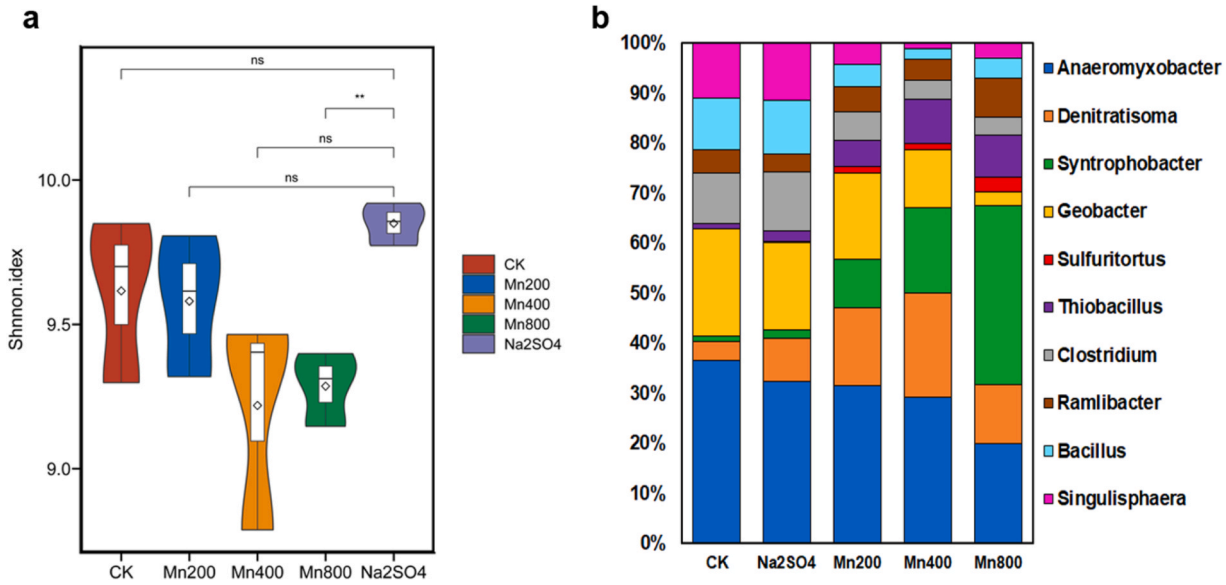

Fig. 7. Analysis of microbial diversity in rhizosphere soils of rice. (a) Shannon index of four groups. (b) Percentage of microbial species on phylum. Mn200: 200 mg kg^{-1} $MnSO_4$ treatment in soil, Mn400: 400 mg kg^{-1} $MnSO_4$ treatment in soil, Mn800: 800 mg kg^{-1} $MnSO_4$ treatment in soil, Na_2SO_4: 400 mg kg^{-1} Na_2SO_4 treatment in soil.

4.3. Changes in Fe and Mn speciation with the application of Mn

Before seeding, the application of both Na_2SO_4 and $MnSO_4$ increased the level of Amor-Fe in the soil, with Na_2SO_4 application increasing the level by 5.36 % and Mn800 by 11.85 %, both with significant differences to the control. However, only when Mn800 was applied, the free-Fe content increased significantly, by 4.75 %. In contrast, at the tillering stage, Mn application reduced the amor-Fe content in soil, which was

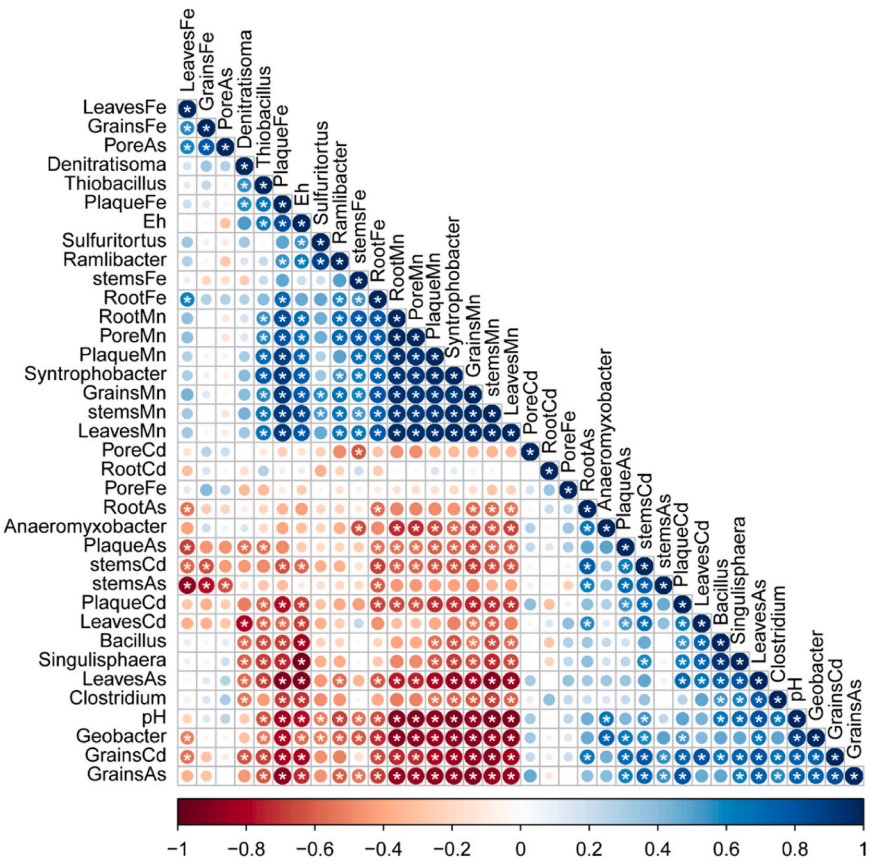

Fig. 8. Correlation analysis of abiotic factors, major phyla of microorganisms, physiological parameters, and contents of Cd and As in rice plants. RootFe, RootMn, RootCd, RootAs: Fe, Mn, Cd, As content of roots; stemsFe, stemsMn, stemsCd, stemsAs: Fe, Mn, Cd, As content of stems; LeavesFe, LeavesMn, LeavesCd, LeavesAs: Fe, Mn, Cd, As content of leaves; GrainsFe, GrainsMn, GrainsCd, GrainsAs: Fe, Mn, Cd, As content of grains; PlaqueFe, PlaqueMn, PlaqueCd, PlaqueAs: Fe, Mn, Cd, As content of Fe/Mn plaque; PoreFe, PoreMn, PoreCd, PoreAs: Fe, Mn, Cd, As content of porewater; AmorFeCd, AmorFeAs: content of As and Cd immobilized by amorphous Fe.

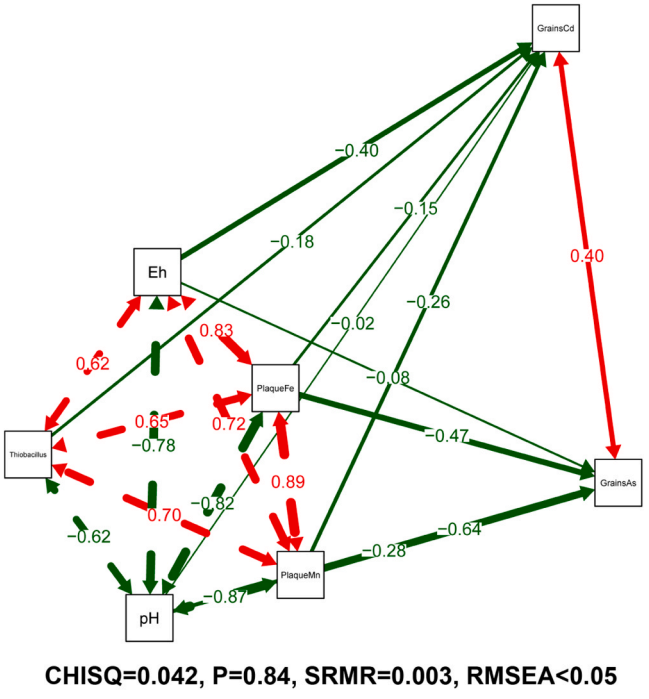

Fig. 9. Structural equation model showing the influences of abiotic and biotic factors on Cd and As accumulation in grains. Red line represents positive correlation, blue line represents negative correlation.

Table 2
Changes in Fe (II) and Fe (III) contents in porewater following Mn application.

	Treatment	Before seeding	Tillering	Maturity
Fe^{2+} (μg L^{-1})	CK	17.24 ± 9.85b	19.91 ± 3.82b	14.85 ± 1.41a
	Na_2SO_4	53.55 ± 5.93a	41.00 ± 3.24a	16.52 ± 1.62a
	Mn200	18.51 ± 10.17b	34.75 ± 7.75a	15.22 ± 3.51a
	Mn400	29.72 ± 7.29b	41.73 ± 11.84a	16.38 ± 2.11a
	Mn800	32.60 ± 10.24b	43.34 ± 4.43a	13.33 ± 1.79a
Fe^{3+} (μg L^{-1})	CK	17.24 ± 9.85b	19.91 ± 3.82b	14.85 ± 1.41a
	Na_2SO_4	53.55 ± 5.93a	41.00 ± 3.24a	16.52 ± 1.62a
	Mn200	18.51 ± 10.17b	34.75 ± 7.75a	15.22 ± 3.51a
	Mn400	29.72 ± 7.29b	41.73 ± 11.84a	16.38 ± 2.11a
	Mn800	32.60 ± 10.24b	43.34 ± 4.43a	13.33 ± 1.79a

most significant in the Mn800 group, whereas the free-iron content of all treatment groups did not differ from that of CK. At maturing, all treatments increased the amor-Fe content; in particular, Mn800 significantly increased the amorphous iron content by 9.22 %, but the free-Fe did not change significantly throughout the maturation period in all treatment groups compared to CK (Fig. 2a, b). The levels of Amor-Mn and Free-Mn in the soil increased with increasing Mn application (Fig. 2c, d).

Table 3
Levels of Cd and As bound by amorphous iron in soils.

	Cd (mg/kg)			As (mg/kg)		
Treatment	Before seeding	Tillering	Maturity	Before seeding	Tillering	Maturity
CK	0.77 ± 0.09b	0.56 ± 0.03ab	0.47 ± 0.02b	19.39 ± 0.60b	14.90 ± 0.62b	28.69 ± 1.62b
Na_2SO_4	0.76 ± 0.01b	0.59 ± 0.09ab	0.32 ± 0.01c	23.25 ± 1.12ab	13.74 ± 1.09b	27.72 ± 2.16b
Mn200	0.79 ± 0.05b	0.53 ± 0.07b	0.42 ± 0.05bc	22.73 ± 3.68ab	14.21 ± 0.94b	32.20 ± 2.94ab
Mn400	0.86 ± 0.05b	0.64 ± 0.10ab	0.53 ± 0.09b	23.61 ± 0.44a	15.28 ± 0.54b	34.46 ± 4.54a
Mn800	1.09 ± 0.05a	0.69 ± 0.05a	0.69 ± 0.08a	25.35 ± 2.35a	17.75 ± 0.78a	36.50 ± 2.23a

4.4. Changes in Cd and As fractions with the application of Mn

Fig. 3a shows the Cd fractions in the soil before seeding. With Na_2SO_4 application, the exchangeable Cd fraction was 93 % for the CK group, and the residual Cd fraction was 2.53 times higher than that in CK. The application of Mn increased the exchangeable Cd fraction when the Mn concentrations were 200 and 400 mg kg^{-1}. All Mn treatments slightly increased the residual Cd proportion. In addition, Na_2SO_4 addition reduced the proportion of Cd-bound Fe-Mn oxides compared to CK (CK: 26.87 %, Na_2SO_4: 24.34 %), which decreased to 21.96 % with the addition of 200 mg kg^{-1} of Mn but increased again to 26.38 % with the application of higher Mn doses. In contract, compared to CK, the exchangeable Cd proportion increased slightly with Na_2SO_4 application at tillering but decreased when Mn was added (CK: 53.43 %, Na_2SO_4: 54.84 %, Mn200: 50.61 %, Mn400: 51.58 %, Mn800: 50.51 %). The application of Mn also increased the Cd bound to carbonates and Fe-Mn oxides but decreased the residual Cd proportion (Fig. 3b). At maturity, exchangeable Cd slightly declined when Na_2SO_4 was added (CK: 46.75 %, Na_2SO_4: 46.34 %) and decreased with increasing Mn concentration (41.34–44.75 %). The proportions of Cd bound to Fe-Mn oxides and residual Cd increased when Mn was applied (Fig. 3c).

Fig. 4 shows the As fractions in soil before seeding (a), at tillering (b), and at maturing (c). The non-specific bound As and crystalline Fe/Mn oxide-bound As proportions were lower in the seeding phase compared to the other stages. The non-specific bound As proportion was not significantly altered by the addition of either sodium or manganese sulphate compared to CK, but the proportion of crystalline Fe/Mn oxide-bound As decreased when Mn was applied at all stages. The proportion of arsenic in the soil decreased most significantly when Mn was applied at a concentration of 400 mg kg^{-1} compared to CK, with decreases by 13.21 %, 14.44 %, and 42.03 % before seeding, at tillering, and at maturity, respectively. Before seeding, the residual As proportion decreased when Na_2SO_4 or Mn was applied. Compared to CK, the group with an Mn concentration of 200 mg kg^{-1} showed the greatest reduction with 11.08 %, followed by the Na_2SO_4 group with 10.61 % reduction. Application of Na_2SO_4 and Mn increased the percentage of As residues at tillering and maturity by 15.01 % with 200 mg kg^{-1} Mn at tillering and 10.47 % with Na2SO4 at maturity compared to CK.

4.5. Effect of Mn application on the levels of Fe, Mn, Cd, and As in soil pore water

The concentration of dissolved Mn^{2+} in porewater increased significantly after the addition of Mn compared to CK, whereas no significant change was observed with the addition of Na_2SO_4. The Mn^{2+} content of the porewater was closely related to the Mn treatment (Fig. 5b). Before seeding and at tillering, Na_2SO_4 application significantly increased the total Fe content significantly compared with CK. The total Fe levels of the CK and Na_2SO_4 groups were 21.38 ± 11.93 mg L^{-1} and 64.71 ± 5.87 mg L^{-1}, respectively. The Fe content decreased with the addition of low Mn doses (Mn200) and only returned to that of the Na_2SO_4 treatment levels with the addition of higher concentrations of Mn (Fig. 5b). The Cd content in porewater decreased after Mn addition, which was more pronounced at maturity (Fig. 5c). Similarly, the total As content in the porewater decreased after applying Mn, especially at higher concentrations, but this reduction was less pronounced at maturity (Fig. 5d).

4.6. Effect of Mn application on the levels of Fe, Mn, Cd, and As in Fe/Mn plaque

The Fe content of the Fe/Mn plaque was significantly higher than that of CK, except for Na_2SO_4 at maturity. The Mn content in Fe/Mn plaque increased with increasing Mn doses, whereas that of Cd decreased after the application of Mn, which was more pronounced at the tillering stage, and significantly reduced at maturity only by the application of higher Mn levels. The As levels in Fe/Mn plaque were lower at maturity than at tillering and were significantly reduced by the addition of Na_2SO_4 and Mn at maturity, whereas only Mn800 significantly reduced the As levels at tillering. The levels of Fe, Mn, Cd, and As in Fe/Mn plaque were closely related to the amount of Mn applied and the growth stage of rice (Fig. 6).

4.7. Effect of Mn application on the soil microbial communities

Microbial diversity was measured using the Shannon index (Fig. 7a). The Shannon index value of the Mn800 group was significantly lower than that of the Na_2SO_4 group. Fig. 7b shows the taxonomic features of rhizosphere soil microbes. The genus *Singulisphaera* was the most abundant one in all samples, and its abundance decreased after Mn application. In contrast, the abundances of *Syntrophobacter*, *Thiobacillus*, and *Sulfuritortus* increased after Mn application.

4.8. Correlation analysis and structural equation modeling on the abiotic factors, microorganisms, and Fe, Mn, Cd, As levels of rice plants

The correlations among abiotic factors (soil pH, Eh, Fe, Mn, Cd, As in pore water, Fe, Mn, Cd, As in Fe/Mn film, Cd and As in amorphous Fe bound), major bacterial genera (*Anaeromyxobacter*, *Denitratisoma*, *Syntrophobacter*, *Geobacter*, *Sulfuritortus*, *Thiobacillus*, *Clostridium*, *Ramlibacter*, *Bacillus*, *Singulisphaera*), and Fe, Mn, Cd, As levels of rice plants are shown in Fig. 8. The Cd and As levels of rice grains were significantly negatively correlated with Eh, plaque-Fe, plaque-Mn, and the Mn content in porewater. Some bacterial genera were significantly associated with the levels of Cd and As in rice grains. *Geobacter*, *Singulisphaera*, *Clostridium*, and *Anaeromyxobacter* were significantly positively correlated with Cd and As in the grains, whereas *Syntrophobacter* and *Thiobacillus* were significantly negatively correlated with Cd and As.

Based on the SEM, the Mn in porewater directly negatively impacted the As concentration in the rice grain, whereas Eh had a negative effect on the accumulation of Cd in the grains (Fig. 9). The abundance of *Thiobacillus* was closely related to the amounts of Fe and Mn in the Fe/Mn film, the amount of Mn in the porewater, and the accumulation of Cd and As in the grains.

5. Discussion

Reducing the availability of Cd and As in the soil could effectively reduce their accumulation in rice. With a decrease in soil pH, the motility of Cd increases, resulting in an increased plant availability; in

addition, the available fraction of As in paddy rice soils increases with decreasing soil pH (Hussain et al., 2021; Huang et al., 2006). However, as the availabilities of As and Cd are differently affected by Eh, the availability of Cd decreases with increasing Eh and pH levels (Li et al., 2021; Rokonuzzaman et al., 2022; Ullah et al., 2020). In the present study, the addition of low concentrations of Mn (200 mg kg^{-1}) at the tillering stage did not result in significant changes in pH and Eh, suggesting that when applying Mn fertilizer, the Mn concentration needs to be taken into account.

According to previous studies, Cd and As uptake by plants can be reduced by the spraying of phytohormones (gibberellins or brassinolide) or deterrents (thiourea or silicon and titanium dioxide nanoparticles, etc) (Li et al., 2023; Srivastava et al., 2021; Rizwan et al., 2019). The use of soil conditioners (such as biochar) to reduce the availability and mobility of heavy metals in the soil is a viable strategy (Turan, 2019, 2020, 2022). The Fe/Mn plaque, which refers to Fe and Mn coatings on the surface of plant roots, can sequester heavy metals and inhibit their uptake and translocation to plants (Hansel et al., 2001; Wei et al., 2021; Zhang et al., 2023). In the present study, the addition of Mn increased the Fe/Mn plaque content on the root surface of rice (Figs. 4–6), indicating that the concentration of Cd bound to Fe/Mn oxides and amorphous Fe/Mn oxide increased significantly. Moreover, Fe/Mn oxides adsorbed and immobilized significant amounts of Cd and As, thus reducing the inter-root migration. According to Suda and Makino (2016), Fe/Mn oxides have large specific surface areas and a strong surface activity; they can also adsorb heavy metals, thereby reducing their bioavailability (Wang et al., 2019). When paddy soils are flooded, poorly crystalline Fe(III)/Mn(III/IV) oxides undergo reductive dissolution, releasing large amounts of Fe and Mn ions into the porewater, which are then re-oxidized to form secondary Fe/Mn oxides (Rinklebe et al., 2016). Under flooding, the Fe oxides in paddy soils undergo a transition from crystalline to amorphous to ionic Fe, and the reduction rate of amorphous Fe oxides in soils is higher than that of crystalline oxides (Tack et al., 2006; Zhang et al., 2016).

Changes in inter-root microorganisms can also affect heavy metal availability (Ma et al., 2016; Turan, 2021), resulting in changes in the microbial community after the addition of soil conditioners. In the present study, Mn application changed the characteristics of the microbial populations in the inter-rhizosphere soil of rice (Fig. 7b), which in turn affected the effectiveness of Fe/Mn oxides in the soil and, consequently, the Cd and As levels. Correlation analysis and SEM analysis showed that *Thiobacillus* was negatively and significantly correlated with Cd and As in the grains (Figs. 8–9); this genus includes Fe-oxidizing species (Cai et al., 2023; Chen et al., 2019). The Fe-oxidizing bacteria (FeOB) can re-oxidize low-valent Fe to high-valent Fe, forming "secondary" iron (hydr)oxides. In contrast, Fe-reducing bacteria (FeRB) can promote the reduction of iron oxide in soil; Fe reduction is usually accompanied by the mobilization of Cd and As (Dai et al., 2020; Qu, Ratering and Schnell, 2004; Wang et al., 2019).

Generally, the oxidation of Mn by oxygen in its natural state is slow, and most of the Mn oxides in nature are produced by microbially mediated processes. Further, Mn is oxidized by manganese-oxidizing bacteria to produce biological Mn oxides, which can oxidize and adsorb metals. The Mn can oxidize some low-valence heavy metals, such as Fe(II) and As(III), and according to Ehlert et al. (2014), Fe(II) oxidation by Mn produces FeOOH precipitation, which enhances the adsorption of heavy metals such as Cd/As. Under certain equilibrium conditions, Mn and Fe oxides can jointly remediate heavy metal-contaminated soils or groundwater (Bai et al., 2017; Liu et al., 2022). Based on the results of the present study, Mn can promote the formation of Fe/Mn oxides after the application of $MnSO_4$ to the soil, but this could change the fugitive form of Cd and As in the soil, thus affecting the biological efficiency of Cd and As. Therefore, the application of Mn fertilizer changed the effectiveness of Cd and As in the soil and drove the Fe-Mn oxidizing bacteria to further produce Fe-Mn oxides, further reducing the mobility of Cd and As and, consequently, reducing their accumulation in rice.

6. Conclusions

The application of Mn reduced the pH and increased the Eh of the soil. It also delayed the reductive dissolution of Fe oxides and promoted the formation of Mn oxides as well as the secondary mineralization of Fe oxides under flooded conditions, resulting in more binding sites for Cd and As adsorption, changing their distribution patterns in soil and, thus, their concentration in porewater. This led to a lower biological availability of Cd and As. In addition, Mn application also increased abundance of Fe-oxidizing bacteria in the rhizosphere, promoted Fe/Mn plaque formation on the rice root surface, and enhanced the binding of Cd and As by Fe and Mn oxides, thereby impeding the transport of Cd and As to the root surface and reducing their accumulation in rice grains .

CRediT authorship contribution statement

Yan Qin: conceptualization, methodology, formal analysis, and writing. Zhiming Li: conceptualization, methodology, formal analysis, and writing. Jing Sun: Formal analysis writing. Meihua Xu: Writing, methodology and formal analysis. Minghua Gu: writing and revision. Yanyan Wei, methodology, formal analysis, writing, and funding acquisition, Jing Lei: writing, and funding acquisition.

Declaration of Competing Interest

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2023.115360.

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