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Quantitative impact of manganese fertilizer across different growth stages on simultaneous reduction of soil arsenic and cadmium accumulation in rice grains

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ABSTRACT

Application of manganese (Mn) fertilizer is a promising strategy to reduce the accumulation of cadmium (Cd) and arsenic (As) in rice grains. However, the quantitative impact of Mn in co-contaminated soils on Cd and As accumulation at different growth stages remains unclear. This study employed controlled pot experiments to investigate the effect of Mn at varying dosages on As and Cd mobility in the soil-root-crop system during booting, heading, and maturity stages. The results revealed that Mn regulated heavy metal uptake in rice throughout its entire growth period, leading to significant reduction in grain Cd and As contents by 30–60 % and 20–25 %, respectively. The relative contribution of Mn to reducing grain Cd was 30.5, 33.9, and 35.6 % at the booting, heading, and maturity stages, respectively, while its contributions to reducing grain As were 37.7, 19.0, and 43.2 %. Mn influences grain total arsenic accumulation by promoting rice growth, enriching Mn in Fe-Mn plaques at the root surface, and reducing available As in soil. For Cd, Mn reduces grain Cd content by promoting growth, modulating root iron- manganese plaques, and adjusting gene expression at maturity. These findings offer new insights into the role of Mn in reducing grain Cd and As at different rice growth stages and aid in developing strategies for remediating As and Cd co-contaminated paddy soils and increasing crop yield.

1. Introduction

Wastewater irrigation, atmospheric deposition, and the widespread use of chemical fertilizers and pesticides have led to the massive influx of toxic elements such as cadmium (Cd) and arsenic (As) in agricultural soils, posing serious threats to global agriculture, ecosystems, and public health (Bandara et al., 2020; Khan et al., 2021). According to the Agency for Toxic Substances and Disease Registry (ATSDR), As and Cd are ranked as the first and seventh most toxic substances, respectively, with high transferability from agricultural soils to crop products (Zhao and Wang, 2020). As a staple food for nearly half of the global population, rice readily accumulates As and Cd compared with other crops, making it a primary dietary source of human exposure (Tsukahara et al., 2003; Su et al., 2010; World Health Organization WHO and Food and Agriculture Organization of the United Nations FAO, 2011; Uraguchi and Fujiwara, 2012; Williams et al., 2012; Zhao et al., 2012; Islam et al., 2021; Wang et al., 2021a). Co-contamination of Cd and As is frequently observed in agricultural soils, particularly in the middle and lower Yangtze River basin, a major rice-producing region in southern China (Yu et al., 2016). Numerous soil amendments, including organic compost, clay minerals, lime, and metal oxides, have been investigated to reduce metal bioavailability and limit their transfer from soil to crops (Li et al., 2021b; Xia et al., 2024). However, the geochemical behavior of Cd and As in soils often differ markedly and even oppose each other, leading most remediation strategies to target one element at the expense of the other (Takahashi et al., 2004; Fulda et al., 2013; Honma et al., 2016; Shen et al., 2020). Consequently, developing effective approaches for remediating soils co-contaminated with Cd and As remains a major scientific and practical challenge (Lin et al., 2024), compared to soils with singular contamination of these elements.

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Manganese (Mn) is an essential trace element for rice growth and is abundant in natural environments and surface soils (Schmidt et al., 2016; Li et al., 2021a). Owing to its high specific surface area, strong reactivity, and dynamic redox behavior, Mn components regulate the fate and behavior of heavy metals (e.g., As and Cd) in soils (Ehlert et al., 2016; Wang et al., 2022a). For instance, the addition of Mn oxides to As-contaminated paddy soils has been shown to oxidize As(III) to the more readily immobilized As(V) (Manning et al., 2002), thereby modulating arsenic speciation and availability through adsorption and precipitation processes (Yu et al., 2017), ultimately reducing As mobility and its accumulation in brown rice (Li et al., 2019; Wang et al., 2020). Unlike redox-variable arsenic, exogenous Mn mainly modulates cadmium through fraction redistribution by promoting the formation of free/amorphous Mn oxide that converts exchangeable Cd to Mn-bound forms, thereby reducing Cd uptake by crop (Wang et al., 2021b; Huang et al., 2022). In Cd-contaminated paddy soil, Mn fertilizer application has also been shown to promote the formation of Mn plaques on the fresh root surface, which exhibit a strong affinity for Cd sequestration (Huang et al., 2021). Moreover, Mn and Cd share the same transport pathways due to their similar ionic radii, enabling Mn to compete for and preferentially occupy carrier or channel proteins, thereby antagonizing Cd uptake (Barberon et al., 2014; Chang et al., 2022). Collectively, these findings indicate that the use of Mn fertilizer represents a promising strategy for simultaneously mitigating Cd and As accumulation in rice grains.

However, the availability of Mn is highly sensitive to changes in soil redox conditions because of its variable chemical valence states (+2, +3, and +4). Under flooded conditions, Mn(IV) is reduced to Mn(II), resulting in increased mobilization that significantly affects the migration of both nutrient and pollutant elements (Borch et al., 2010; Frohne et al., 2011; Ao et al., 2023). Conversely, during drainage, Mn(II) is oxidized back to Mn(IV), precipitating as manganese oxides in the soil (Rinklebe et al., 2016; Van Groeningen et al., 2021). In general, the growth of rice crops primarily involves three major stages: booting, heading, and maturity (Greger and Löfstedt, 2004; Kashiwagi et al., 2009; Yan et al., 2010; Hu et al., 2013; Wang et al., 2013). At the booting stage, flooding lowers soil redox potential (Eh), reducing solid-phase Mn (III/IV) oxides to soluble Mn(II) that enters the porewater (Pan et al., 2016; Wang et al., 2022a). By the heading stage, root-surface Mn(II) is rapidly oxidized under micro-oxic conditions and co-precipitates with Fe (Henry et al., 2012; Williams et al., 2014). After drainage at maturity, re-oxygenation favors the persistence of Mn predominantly as stable oxide minerals (Wang et al., 2022d, 2022c). The redox-driven fluctuations in Mn availability during these stages suggests that its effect on reducing Cd and As uptake by rice plants varies significantly across growth cycle (Maguffin et al., 2020). Moreover, As, as a redox-variable oxyanion, differs significantly from Cd in its chemical properties, including ionic radius and charge (Kubier et al., 2019; Wang et al., 2023). Consequently, the effect of Mn on As uptake by rice is likely distinct from its influence on Cd, and may vary across different growth stages. Understanding how Mn components regulate As and Cd migration and accumulation at different growth stages is therefore critical for developing precise remediation strategies for As-Cd co-contaminated paddy soils through targeted Mn fertilization. Although the mitigating effect of Mn fertilizers on Cd and As uptake at the maturity stage has been relatively well documented, their influence during earlier stages (e.g., booting and heading) remains poorly understood (Fang et al., 2021; Liang et al., 2022; Zhao et al., 2024; Yan et al., 2026). Quantifying the growth stage-specific contributions of Mn to Cd and As reduction will help both the dosage and timing of Mn application, maximizing its benefits for rice growth and food safety.

Herein, Mn oxide was applied at low, medium, and high dosages to evaluate its effectiveness in simultaneously reducing As and Cd uptake by rice plants during the booting, heading, and maturity stages. The effects of Mn addition on soil pH, Fe and Mn components, Cd and As availability, the formation of iron (Fe)-Mn plaques on root surfaces, and the expression of related genes were systematically examined. Furthermore, the bioconcentration and translocation of As and Cd within crop systems at different growth stages were quantified. The specific objectives of this study were threefold: (1) to elucidate the role of Mn in regulating Cd and As uptake in rice through controlled pot experiments; (2) to provide mechanistic insights into how Mn addition influences Cd and As dynamics by tracking the evolution of key parameters in soil, root surfaces, and crop systems throughout the entire growth stages; and (3) to clarify the relative contribution of Mn addition to reducing grain As and Cd accumulation at different growth stages, based on the least squares method, thereby offering guidance for precise remediation of As and Cd co-contaminated paddy soils.

2. Materials and methods

2.1. Cd and As co-contaminated paddy soil sampling

The Cd and As co-contaminated soil used for the pot experiments was collected from a paddy field in Hubei, China (30.18°N 114.87°E), at a depth of 0–20 cm. After air drying, the soil samples were ground to pass through a 20-mesh sieve and thoroughly mixed to ensure homogenization. The soil with pH = 6.01, had total Cd and As concentration determined at 1.19 and 40.52 mg kg^{-1}, respectively. It should be noted that soil environmental quality benchmark values vary considerably among countries due to differences in legislation (Table S1). Since our soil incubation experiments for As and Cd remediation were primarily conducted in China, we adopted the Chinese National Standards for Soil Environmental Quality (GB 15618–2018) as the reference. According to these standards, the concentrations of As and Cd in our collected samples exceed the permissible limits for agricultural soils (As: 30.00 mg kg^{-1}; Cd: 0.40 mg kg^{-1}). Mn oxide is one of the most commonly found Mn fertilizer and was used in this study (Neto et al., 2023; Pei et al., 2023). The detailed synthesis procedure of Mn oxide is presented in the Supplementary Material (Text S1and Fig.S1).

2.2. Pot experiment

The pot experiment was conducted from June to October 2022 under controlled environment in a greenhouse at Huazhong Agricultural University, Hubei Province, China. The rice plant (*Oryza sativa* L., cultivar Huanghuazhan), commonly grown at the sampling site, was used for the experiments. In general, the reported Mn content in paddy soil ranged from 380 to 2800 mg kg^{-1}, where most of Mn content in soils are lower than 1000 mg kg^{-1} (Maguffin et al., 2020). In addition, the field experiments using manganese minerals as soil conditioner for Cd and As remediation typically applied Mn within the range of 0–800 mg kg^{-1} (Fang et al., 2021; Qin et al., 2023; Hu et al., 2024). We therefore designed four Mn fertilizer application treatments as follows: (1) no Mn fertilizer (CK), (2) 200 mg kg^{-1} as low dosage Mn fertilizer (denoted as B200), (3) 400 mg kg^{-1} as medium dosage Mn fertilizer (denoted as B400), and (4) 800 mg kg^{-1} as high dosage Mn fertilizer (denoted as B800). For each treatment, nine replicates were established, and three replicates were randomly selected and destructively sampled at different growth stages of rice. Mn fertilizers were thoroughly mixed and homogenized with 5.0 kg of soil and placed into pots (diameter: 25.50 cm, height: 26.50 cm). Detailed information on rice cultivation management can be found in Text S2.

2.3. Sample collection and preparation

Destructive sampling of potted plants was conducted at the rice booting stage (August 30, 2022), heading stage (September 13, 2022), and maturity stage (October 17, 2022). Soil samples were collected from a depth of 0–20 cm in each treatment pot, air-dried, and ground for subsequent analysis. During sampling, paddy plants were carefully uprooted from the pots with intact root systems and thoroughly washed with deionized water to remove excess soil. The plants were then separated into root, straw, husk, and grain fractions. A portion of the cleaned roots was stored at −20 °C for Fe-Mn plaques (IMPs) extraction. The remaining cleaned roots and aboveground plant parts were blanched in an oven at 105 °C for 30 min, then dried at 65 °C to remove moisture and achieve a constant weight.

2.4. Plant and soil analysis

Soil pH was measured using a pH electrode at a 1:2.5 (soil to water) ratio. The concentrations of available Cd (ACd), available Mn (AMn), and available Fe (AFe) in soil were extracted with DTPA solution (0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$, 0.10 mol L^{-1} triethanolamine, pH 7.30) at a 1:5 (soil to solution) ratio (Wang et al., 2021b). Soil available As (AAs) was extracted with a 0.50 mol L^{-1} $NaHCO_3$ solution at a 1:10 (soil to solution) ratio. Cd concentration was determined by graphite furnace flame atomic absorption spectrometer (GF AAS, Agilent AA 240 Z, Agilent Technologies, USA), Mn and Fe by Inductively coupled plasma-optical emission spectrometry (ICP OES, Agilent 5110 VDV, Agilent Technologies, USA), and As by atomic fluorescence spectrometry (AFS, AFS 830, Jitian, China). To investigate the role of Mn in the formation of IMPs on rice roots and its impact on As and Cd retention, the concentrations of Cd (DCd), As (DAs), Fe (DFe), and Mn (DMn) in the IMPs were determined using a dithionite-citrate-bicarbonate (DCB) extraction method and analyzed by ICP OES (Li et al., 2020). The analytical characteristics of each analytical method and the recovery rates are provided in Supplementary Material (Text S3). Free Mn oxides (Mn_d) and Fe oxides (Fe_d) in soil were extracted using sodium dithionite-citrate-bicarbonate (DCB), while amorphous Mn oxides (Mn_o) and amorphous Fe oxides (Fe_o) were extracted with ammonium oxalate buffer (AO). The details of extraction procedures are shown in Text S4. At maturity, additional root and straw samples were flash-frozen in liquid nitrogen and stored at −80 °C for RNA extraction and subsequent quantitative real-time PCR (qPCR) analysis of Cd-related gene expression. The detailed procedure for subsequent quantitative real-time PCR from rice roots is provided in Supplementary Material (Text S5).

2.5. Data and statistical analysis

All data were analyzed using Tukey's HSD test and Pearson correlation analysis in *R* software, with data fitted using the least squares method. Based on the Pearson correlation results, we identified potential pathways for the main factors influencing Cd and As accumulation and transport across growth stages. The available forms of elements in the soil are directly absorbed and utilized by plants. To better understand As or Cd accumulation in rice, we calculated the bioconcentration factor (BCF) of rice roots relative to the available forms of soil elements. The BCF and translocation factor (TF) for As or Cd in rice tissues were calculated as follows.

$$BCF = R_{As/Cd}/A_{As/Cd} \quad (1)$$

$$TF_{root-straw} = S_{As/Cd}/R_{As/Cd} \quad (2)$$

$$TF_{root-straw} = G_{As/Cd}/S_{As/Cd} \quad (3)$$

where $A_{As/Cd}$ (mg kg^{-1}) refers to the available content of the element in the soil; $R_{As/Cd}$ (mg kg^{-1}) refers to the content of the element in the roots; $S_{As/Cd}$ (mg kg^{-1}) refers to the content of the element in the straw; and $G_{As/Cd}$ (mg kg^{-1}) refers to the content of the element in the grains.

3. Results

3.1. Effect of Mn on the accumulation of As and Cd in the grains and crop yield

Fig. 1a and b illustrate the role of Mn in regulating As and Cd accumulation in rice grains. The result of our pot experiments revealed that the Mn fertilizers application significantly reduced the As and Cd accumulation in rice grains. Compared to the control treatment without Mn fertilizer (CK), the addition of a relatively low dose of Mn fertilizer (200 mg kg^{-1}) has already shown to decreased the grain As and Cd contents from 0.41 and 2.08–0.31 and 1.45 mg kg^{-1}, respectively, indicating a 24.1 % reduction for As and 30.2 % reduction for Cd. With increasing the Mn fertilizer dosage to 400 and 800 mg kg^{-1}, the grain As content did not decrease further as quantified at 0.30 and 0.32 mg kg^{-1}, respectively. However, the Cd content in grain further decreased to 1.23 and 0.75 mg kg^{-1} with Mn fertilizer dosages of 400 and 800 mg kg^{-1}, respectively. In contrast, Mn fertilizer application increased the Mn concentration in rice grains from 20.08 to 23.88–25.25 mg kg^{-1} (Fig. S2a). We employed exposure assessment framework recommended by the U.S. Environmental Protection Agency (U.S. EPA) to evaluate the potential dietary risks for populations consuming rice as a staple food (see Text S6 for details). An age-stratified dietary risk assessment indicated that Mn exposure remained within an acceptable risk range (HQ < 1) across all Mn treatments (Table S2). In addition, Mn application promoted the growth of rice plants (24.7–28.8 %) and significantly increased crop yield (30.0–136.4 %) (Fig. 1c). Representative pot photographs at maturity further illustrate the improved plant growth among treatments (Fig. 1d).

3.2. Evolution of soil pH and Mn / Fe components at different growth stages

Fig. 2a shows the evolution of the available Mn content in the soil under different Mn fertilizer treatments during the rice growth stages. For treatments with the same Mn dosage, the available Mn content (AMn) in the soil gradually decreased from the booting stage to the heading stage, and further to the maturity stage. Compared to the CK treatment, application of Mn fertilizer increased the available Mn content at each growth stage, with the AMn content increased by 1.58–2.98 times at the booting stage, 2.71–3.99 times at heading stage, and 1.06–2.86 times at the maturity stage.

Mn fertilizer treatment also influenced the available Fe content in the soil across different growth stages (Fig. 2b). Similar to the trend for available Mn content, the available Fe content in soil decreased progressively as rice grew under Mn fertilizer treatment with the same dosages. However, the effect of Mn fertilizer on the available Fe content at different rice growth stages differed obviously. Compared to the CK treatment, Mn fertilizer treatment increased the soil available Fe content at booting stage, with an increase ranging from 11.3 % to 16.6 %. For the heading stage, the low-dose Mn fertilizer treatment (e.g., 200 mg kg^{-1}) slightly enhanced the available Fe content in the soil compared to CK treatment, from 140.22 to 149.46 mg kg^{-1}, while at maturity stage there was no obvious change (79.10 vs 79.25 mg kg^{-1}). In addition, we observed that at the booting stage the available Fe content in soil slightly increased with increasing Mn dosage. By contrast, at the heading and maturity stage, the available Fe content at higher Mn dosage decreased compared to the control (Fig. 2b).

To better understand the changes in Fe components in the soil, we used the DCB and AO extraction methods to estimate the content of free Fe (Fe_d) and amorphous Fe oxides (Fe_o) under different treatments and growth stages. As shown in Fig. 2c, application of Mn fertilizer increased the content of Fe_d, although the extent of increase varied slightly across stages. At the same Mn dosages, the Fe_d increased by 5.6–10.2 % at booting stage, 0.8–17.2 % at heading stage, and 0.8–8.5 % at maturity stage. We found that the Fe_d content in the CK treatment was lower than

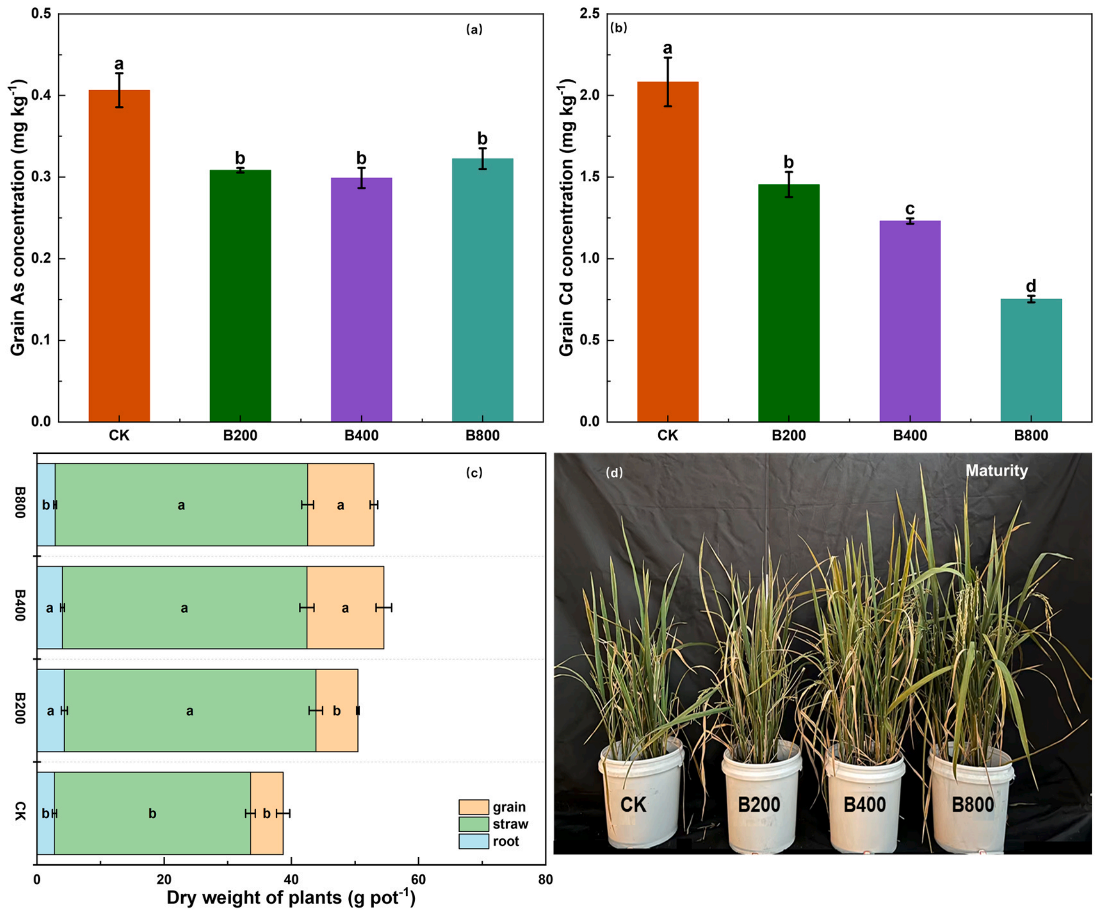

Fig. 1. As (a) and Cd (b) contents in rice grains; dry weight of plant biomass at maturity stage (c) and the photo of rice plant in pots taken at maturity stage (d) harvested from the pots at maturity stage. Error bars represent standard deviations (n = 3). Columns with different letters indicate significant differences according to the Tukey test ($p < 0.05$).

in the Mn treatments; by contrast, the Fe_o/Fe_d ratio was higher in CK (Fig. 2d). Interestingly, the content of free Mn in the soil was positively correlated with Fe_d, but significantly negatively correlated with Fe_o (Fig. 2e-f).

As soil pH significantly influences the availability of heavy metals like Cd and As, we examined the effect of Mn fertilizer treatment on soil pH at different rice growth stages. As shown in Fig. 2g, the Mn fertilizer treatment slightly but significantly increased soil pH (by ~0.20 units) compared to CK at the booting stage. At the heading and maturity stages, the effect on pH was negligible.

3.3. As and Cd availability in soils at different growth stages

Figs. 2h and 2i show the impact of Mn fertilizer on available As and Cd in soil across various growth stages of rice plants. For all Mn fertilizer treatments and the control, the soil available Cd concentrations declined steadily from booting to heading and then to maturity in our experiments. However, compared to CK treatment, the effect of Mn fertilizer on soil available Cd content varied by growth stages. For instance, as booting stage, Mn fertilizer treatments slightly reduced soil available Cd content relative to the control (Fig. 2h). In contrast, Mn fertilizer treatments significantly increased available Cd content during the heading and maturity stages compared to the control, with increase ranging from 12.1 % to 17.4 % and 0.9–13.2 %, at each stage respectively. Moreover, we observed that Mn fertilizer treatments influenced soil available As levels across rice growth stages (Fig. 2i). Compared to control treatment, Mn fertilizer treatments seemingly increased soil available As content at the booting and heading stages, but the increases were not statistically significant. However, at the maturity stage, Mn fertilizer treatments experiment showed significantly reduced soil available As content from 0.39 to 0.28–0.33 mg kg^{-1}.

3.4. Iron and manganese plaque formation on root surfaces

At the root surface, Fe-Mn plaques (IMPs) regulate the chemical behavior of elements, influencing their uptake by rice plants (Dong et al., 2000; Hossain et al., 2009; Yin et al., 2017). In this study, we employed DCB extraction method to determine the content of Mn and Fe in IMPs. Fig. 3a illustrates the dynamic changes in Mn content in the IMPs across different growth stages. After Mn fertilizer application, Mn content in the IMPs significantly increased at the booting, heading, and maturity stages, by 128.7–237.1 %, 13.5–116.8 %, and 150.3–390.7 %, respectively. Notably, Mn fertilizer treatment significantly increased Fe content in the IMPs only at the booting stage (by 123.9–151.9 %; Fig. 3b). While at the heading and maturity stages, the Fe content in the IMPs decreased under Mn fertilizer relative to CK. We further examined Cd and As retention in the IMPs across growth stages. As shown in Fig. 3c, Mn fertilizer affected Cd content in the IMPs, changing by −11.4–20.4 % at the booting stage, −52.0 to −16.2 % at the heading stage, and −33.5 to −6.0 % at the maturity stage. The evolution of As in the IMPs differed from that of Cd. Compared to CK, Mn fertilizer treatment significantly increased As content in the IMPs by 96.9–113.8 % at the booting stage (Fig. 3d). However, at the heading and maturity stages, As decreased by 1.8–18.7 % and 7.7–40.5 %, respectively.

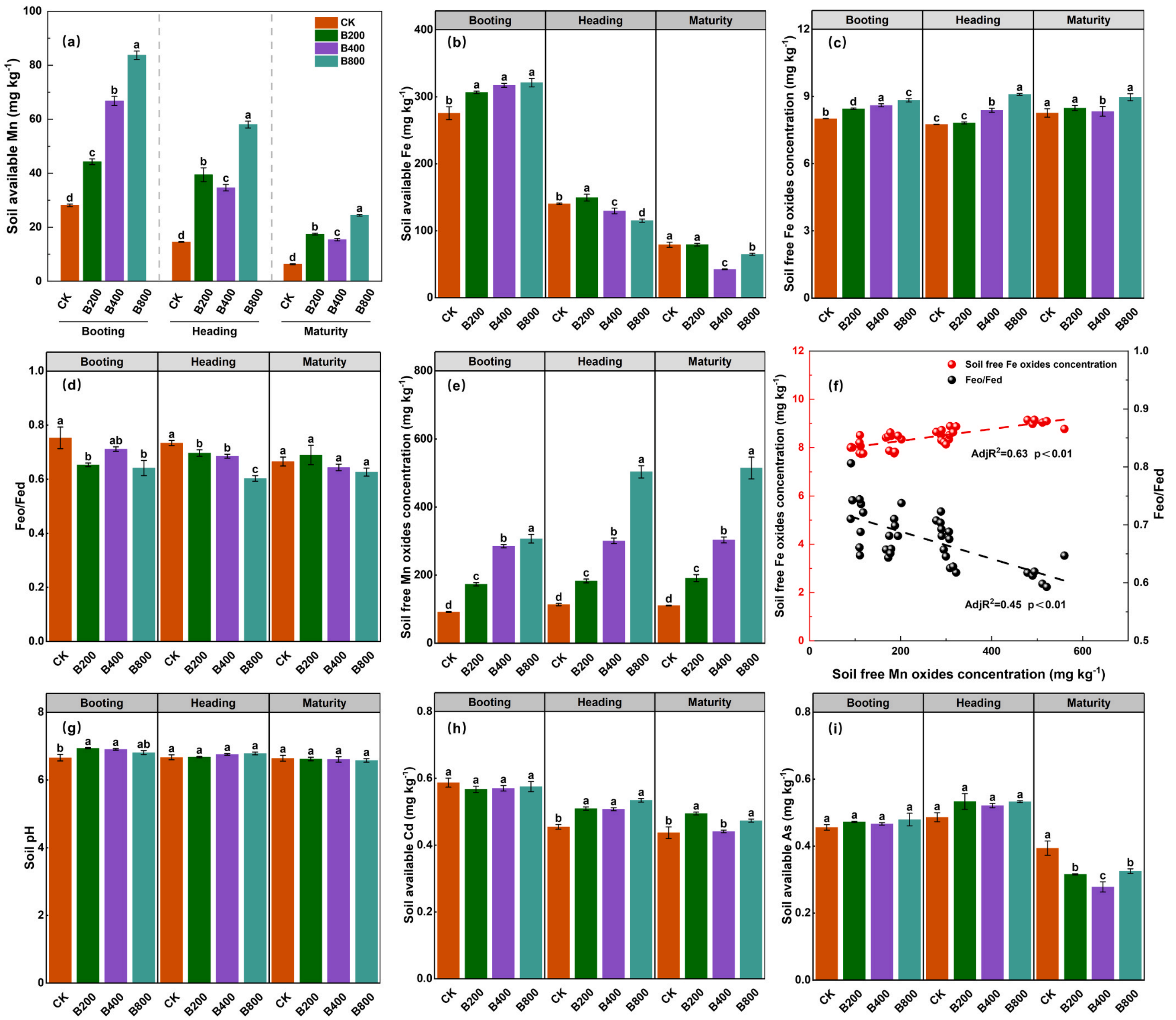

Fig. 2. Effects of Mn amendment across growth stages on soil (a) available Mn, (b) available Fe, (c) free Fe oxides (Fe_d), (d) the Fe_o/Fe_d ratio (amorphous/free Fe), (e) free Mn oxides, (f) correlations among free Mn oxides, Fe_o/Fe_d, and Fe_d, (g) pH, (h) available Cd, and (i) available As. Error bars indicate standard deviations (n = 3). Columns with different letters denote significant differences based on the Tukey test ($p < 0.05$).

3.5. Bioconcentration and translocation of As and Cd in crops at different growth stages

We investigated the effect of Mn on the migration of As and Cd in the soil-root-crop continuum by calculating the bioconcentration factor (BCF) and translocation factor (TF), which indicate the potential movement of As and Cd from the soil to the roots and from the roots to the crops, respectively. Fig. 4 illustrates the changes in the BCF and TF of As and Cd across different growth stages under various Mn fertilization treatments. Compared to the CK (BCF = 79.39), Mn fertilization treatments reduced the BCF of Cd by 7.7–28.0 % at the booting stage (Fig. 4a). In contrast to booting stage, Mn fertilization increased the BCF of Cd by 1.1–22.3 % at the heading stage, and 13.3–44.8 % at the maturity stage. The translocation of Cd from roots to straw is a key step in Cd accumulation in plants (Harris and Taylor, 2013), where a higher $TF_{root-straw}$ indicates a greater accumulation potential of Cd. As shown in Fig. 4b, the $TF_{root\text{-}straw}$ of Cd varied significantly in the CK treatment across growth stages, with the highest value observed at the heading stage (0.15–0.16). However, Mn fertilizer treatments further altered $TF_{root\text{-}straw}$ of Cd across different growth stages. For instance, we observed that Mn fertilizer treatments significantly reduced Cd translocation from roots to straw by 17.5–47.9 % at the booting stage and 37.4–56.1 % at maturity stage, respectively. To further examine the effect of Mn on the translocation of Cd from straw to grains, we calculated the $TF_{straw\text{-}grain}$ at maturity stage. The results showed that Mn fertilizer treatments significantly reduced Cd translocation from straw to grains, with a maximum reduction of 35.7 % (Fig. 4c).

Compared with Cd, Mn fertilizer treatments also affected the BCF and TF of As at different growth stages (Fig. 4). Compared to CK treatment, Mn fertilizer treatments reduced the BCF of As by 14.2–51.3 % at the heading stage, while significantly increasing it by 62.5–97.5 % at the booting stage and 11.4–42.7 % at maturity stage. In addition, following application of Mn fertilizer, the $TF_{root\text{-}straw}$ values of As were changed by −21.4 to −1.2 %, −6.5–53.2 %, and −41.4 to −0.8 % at the booting, heading, and maturity stages, respectively. The $TF_{straw\text{-}grain}$ of As at maturity stage also changed following Mn application, with variations ranging from −26.5–23.8 % (Fig. 4d).

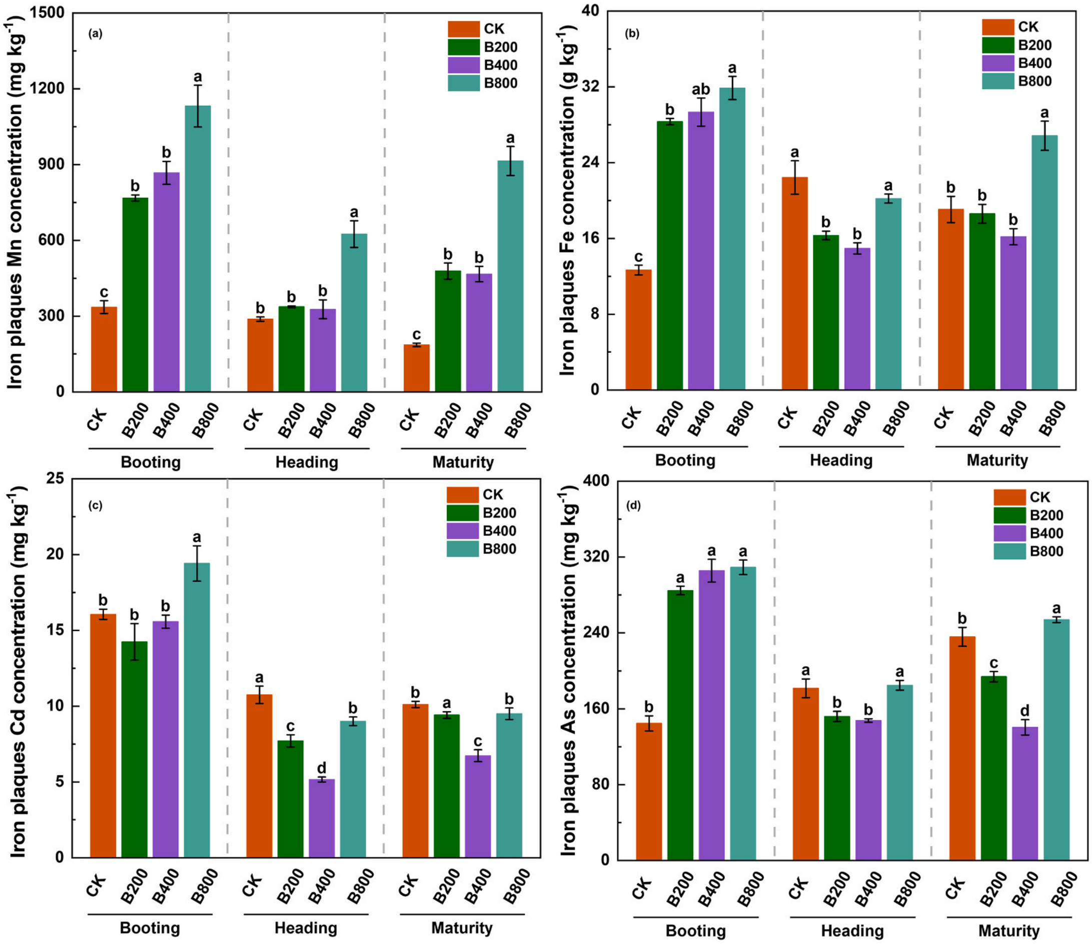

Fig. 3. Effects of Mn amendment on the concentrations of Mn (a), Fe (b), Cd (c), and As (d) in the root surface iron-manganese plaques at three growth stages. Error bars indicate standard deviations (n = 3). Columns with different letters denote significant differences based on the Tukey test ($p < 0.05$).

4. Discussion

4.1. The role of Mn in regulating Cd migration across different growth stages

The application of Mn fertilizers significantly altered soil available Mn (AMn), thereby altering key physicochemical properties such as pH, Fe and Mn availability, and Cd migration (Figs. 2, and 4). To further elucidate these relationships, AMn value as a variable to identify the major factors influencing Cd migration at various rice growth stages (Fig. 5). As shown in Fig. 5a, the BCF of Cd, which reflects its potential for uptake from soil into the crop, had significant positive correlation with the Cd content in the roots (RCd) at the booting stage, whereas no significant correlation was observed with available Cd content in the soil (ACd) or Cd in the IMPs (DCd) ($p > 0.05$). Moreover, we found that the $TF_{root\text{-}straw}$ value, which reflects the potential for Cd accumulation in rice grains, was also influenced by RCd ($p < 0.05$) (Fig. 5a and S3). This suggests that the reduction in Cd accumulation in rice at the booting stage is mainly achieved by regulating Cd concentration in the roots, rather than by altering Cd mobility in the soil. This can be attributed to the rapid vegetative growth of rice at the booting stage, which is further promoted by Mn fertilization (Xu et al., 2015). The enhanced biomass production-particularly the sharp increase in root biomass (DWr) (Fig. S2b), likely diluted the Cd concentration in roots.

For the heading stage, we also observed a significant positive correlation between the BCF of Cd and the Cd content in the roots (RCd). However, unlike at the booting stage, the effect of root biomass (DWr) on RCd shifted from a negative to a positive correlation at the heading stage (Fig. 5b). At this growth stage, IMPs gradually form through the accumulation of free Fe ions from the soil onto the root surface, thereby regulating Cd migration. Studies have shown that when Fe content in the IMPs exceeds 22.50 g kg^{-1}, the IMPs acts as a barrier to Cd entering the roots, reducing Cd migration to the crop; otherwise, a large amount of Cd deposited on the IMPs can serve as a source of Cd for rice roots (Zhang et al., 2020a). At the heading stage, Mn fertilizer treatments further increased root biomass, thereby diluting Fe content in the IMPs and reducing it below 22.50 g kg^{-1} (Fig. 3). This finding helps explain the observed shift in the role of rice roots at the heading stage.

At the maturity stage, the dry weight of roots (DWr) showed significant correlations with both the Cd content in the roots (RCd) and the translocation factor of Cd from roots to straw ($TF_{root\text{-}straw}$). Furthermore, the BCF of Cd was significantly positively correlated with RCd (Fig. 5c). These results suggest that the promotion of crop biomass by Mn fertilizer plays a key role in Cd mobility. Because ion radius of Cd^{2+} is similar to that of Mn^{2+}, the two ions often share transport pathways in plants. In rice, the common transporters reported include *OsNRAMP5*, *OsHMA2*, *OsHMA3*, and *OsLCT1*. Among them, *OsNramp5* is a key transporter for Cd and Mn uptake and translocation in the roots, whereas *OsHMA2* as an efflux transporter involves in the Cd loading and redistribution through the xylem of the nodes (Sasaki et al., 2012; Takahashi et al., 2012; Yang et al., 2014). *OsHMA3* is a P_{1B}-type ATPase predominantly localized to the tonoplast (vacuolar membrane) of root cells and sequesters Cd^{2+} into vacuoles, thereby limiting xylem loading and Cd translocation from roots to shoots (Ueno et al., 2010). Multiple genetic studies show that loss-of-function or weak alleles elevate Cd in shoots and grains, whereas overexpression reduces grain Cd and enhances Cd tolerance (Sasaki

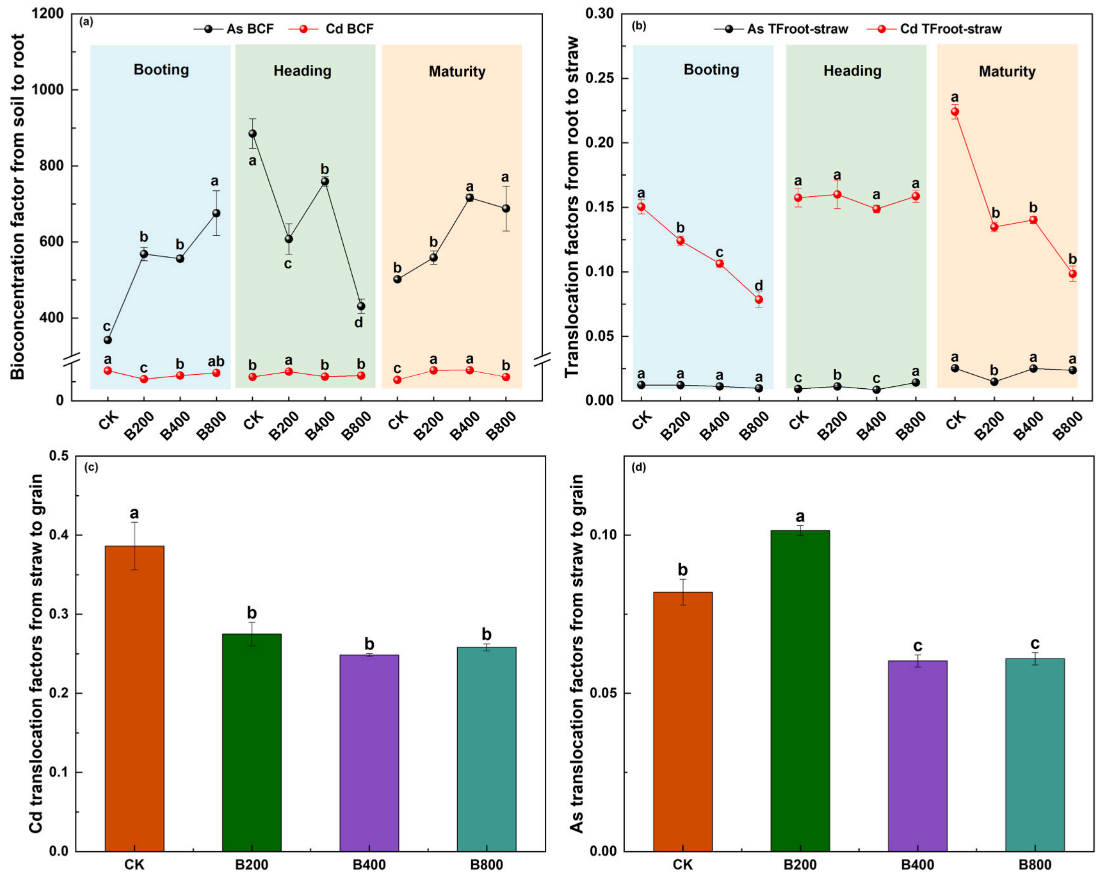

Fig. 4. Effects of Mn fertilizer on the BCF (a) and TF (b-d) of As and Cd at different growth stages. Error bars indicate standard deviations (n = 3). Columns with different letters denote significant differences based on the Tukey test ($p < 0.05$).

et al., 2014; Yan et al., 2016; Cai et al., 2019). *OsLCT1* plays an important role in Cd redistribution via the phloem in the nodes (Tian et al., 2019; Zhang et al., 2020b; Xia et al., 2023). Consequently, Mn^{2+} can markedly influence the uptake and internal transport of Cd^{2+} in crops. This has been corroborated by reports showing that exogenous manganese sulfate not only alters soil Cd availability but also modulates the root expression of *TaNRAMP5*, *TaHMA3*, and *TaHMA2* in wheat (Huang et al., 2022). Notably, Mn fertilizer treatments upregulated the expression of *OsNramp5* in the roots and *OsHMA2* in the straw (Fig. S4). Therefore, Mn fertilizer treatments likely affected Cd uptake in rice roots and its transport from roots to aboveground tissues. We also analyzed the expression of *OsHMA3* and *OsLCT1* with and without Mn fertilizer amendment. As shown in Fig. S4, Mn fertilizer treatment significantly increased the expression of *OsHMA3* in rice roots (by 99.0–157.0 %). Moreover, *OsLCT1* expression significantly decreased (-34.4 %) with increasing Mn fertilizer dosage (e.g., B800). These changes indicate that Mn fertilizer amendment enhances the Cd retention in the vacuole, thereby reducing Cd translocation to the grains.

4.2. The role of Mn in regulating As migration across different growth stages

Similar to Cd, Mn fertilizer treatments also regulated As migration throughout the rice growth stages (Fig. 6 and S5). At the booting stage, Mn application significantly impacted the BCF of As, while its effect on the TF was less pronounced (Fig. 4a and b). Fig. 6a reveals a significant positive correlation between the BCF of As and both As content in roots (RAs) and IMPs (DAs), while no significant correlation observed with the soil available As concentration (AAs) ($p > 0.05$). These findings suggest that Mn fertilizer primarily influences As accumulation in rice plants by regulating As concentrations in roots or at the surface on IMPs, rather than by altering As mobility in the soil. This was primarily due to that Mn fertilizer treatments increased available Mn content and pH value (by approximately 0.20 units) in the soil, while simultaneously inhibited Fe leaching and promote IMPs formation (Figs. 2 and 3). On one hand, Fe components in IMPs have a strong binding affinity for As, and the added Mn provide additional adsorption sites for As (Zhang et al., 2019; Zheng et al., 2021, 2024). On the other hand, Mn fertilizer promotes root growth (Fig. S2b), facilitating the development of more IMPs and thereby increasing As retention in the root system.

At the heading stage, the As BCF was significantly positively correlated with the RAs. However, unlike at the booting stage, the relationship between As BCF and the soil available As concentration (AAs) changed from positive to significant negative at heading stage (Fig. 6b). This suggests that the influence of Mn fertilizer on As migration further extended from root interface to the soil interface in our pot experiments. At this growth stage, Mn fertilizer treatment showed increased content of crystalline Fe-oxides while decreasing the proportion of soil amorphous iron oxides (Fe_o), as indicated by Fe_o/Fe_d ratio (Fig. 2d). Compared to Fe_o, crystalline Fe oxides have a relatively smaller specific surface area, leading to fewer adsorption sites and weaker As adsorption capacity, which can increase the effective As content in soil (Zheng et al., 2023; Liu et al., 2024).

At the maturity stage, our experimental data showed that the As BCF value was significantly positively correlated with both RAs and AAs, consistent with the pattern observed at the heading stage (Fig. 6c). However, in contrast to the heading stage, the negative correlation between As BCF and soil AAs strengthened, while its correlation with RAs weakened. This suggests that Mn fertilizer predominantly affected As mobility through soil interface processes at the maturity stage. On one hand, Fe components in the soil gradually precipitated from dissolved forms to solid iron minerals as oxidation proceeded at the maturity stage

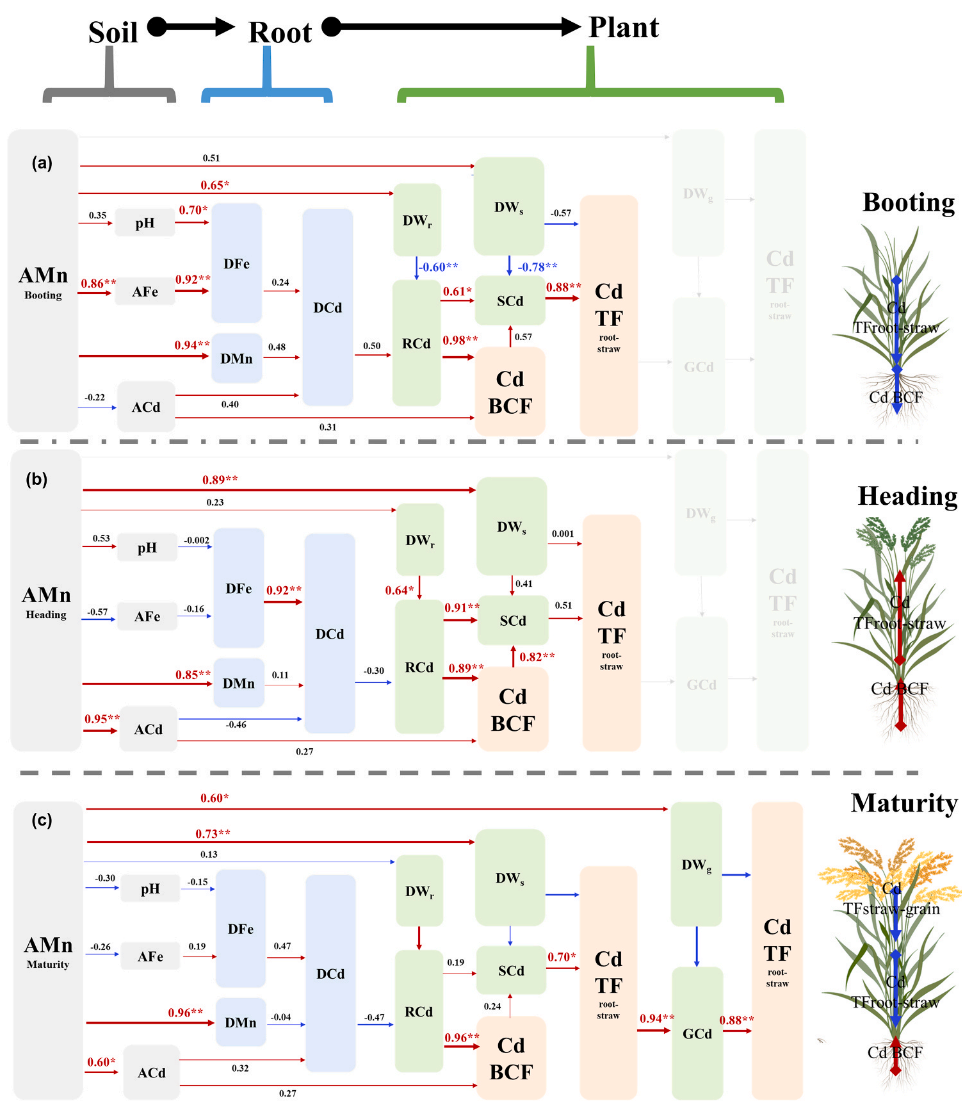

Fig. 5. Pathway analysis of key factors influencing Cd enrichment and transport at the booting (a), heading (b), and maturity (c) stages. In this context, * denotes $p < 0.05$, and ** denotes $p < 0.01$. Red signifies a positive correlation, blue signifies a negative correlation, and the line thickness indicates the magnitude of the correlation coefficient.

(Fig. 2). On the other hand, our previous studies showed that Mn can also accelerate Fe mineral formation via kinetic oxidation processes during simultaneous redox reactions (Zheng et al., 2021). These processes result in an increased number of sites for As immobilization, thereby effectively reducing As activity in the soil and inhibiting its migration to the crop system. Remarkably, RAs were significantly correlated with grain dry weight (DWg). Thus, the reduction in grain As after Mn application could also be attributed to a "dilution effect" resulting from Mn-induced increases in rice biomass. With respect to As transport, As(III) primarily enters roots through silicon channels (e.g., *OsLsi1/OsNIP2;1* for influx and *OsLsi2* for efflux), whereas As(V) is taken up by *OsPHT1* phosphate transporters (e.g., *OsPT1*, *OsPT4*, and *OsPT8*) and subsequently reduced to As(III) by arsenate reductases (*OsHAC1;1*, *OsHAC1;2*, *OsHAC4*). The node-localized *OsABCC1* further sequesters As (III)-phytochelatin complexes into vacuoles, thereby limiting As translocation to grain (Ma et al., 2008; Song et al., 2014; Shi et al., 2016). Given that Mn^{2+} is a divalent cation whereas As species mainly exists as oxyanions, no common transporter shared between Mn and As has been identified to date. Accordingly, we did not further explore As-related transport genes in this study.

4.3. Quantitative contribution of Mn towards reducing grain As and Cd contents across different growth stages

To clarify the relative contribution of Mn at different growth stages in reducing grain Cd and As content, we applied least-squares regression to model the relationship between soil available Mn (AMn) and Cd/As content in brown rice (GCd/GAs) (Fig. 7a-c). The results indicate that the relative contribution of Mn to grain Cd and As accumulation varied by growth stages. We then calculated the average relative contribution of Mn fertilizer treatments to reductions in Cd and As content across the three growth stages. The average relative contribution of Mn to reducing Cd content at the booting, heading, and maturity stages was 30.5, 33.9, and 35.6 %, respectively (Fig. 7d). This suggests that the impact of Mn on Cd migration and transformation at the booting and heading stages was comparable to its effect at the maturity stage. In contrast to Cd, the relative contribution of Mn to reducing grain As differed markedly across the three growth stages. The average relative contribution of Mn at the heading stage (19.0 %) was lower than that at the booting (37.8 %) and maturity (43.2 %) stages, indicating that Mn lowered grain As primarily during the early (booting) and late (maturity) stages. However, previous studies have mainly focused on the migration of heavy metals only at the maturity stage. Our results emphasizes that Cd

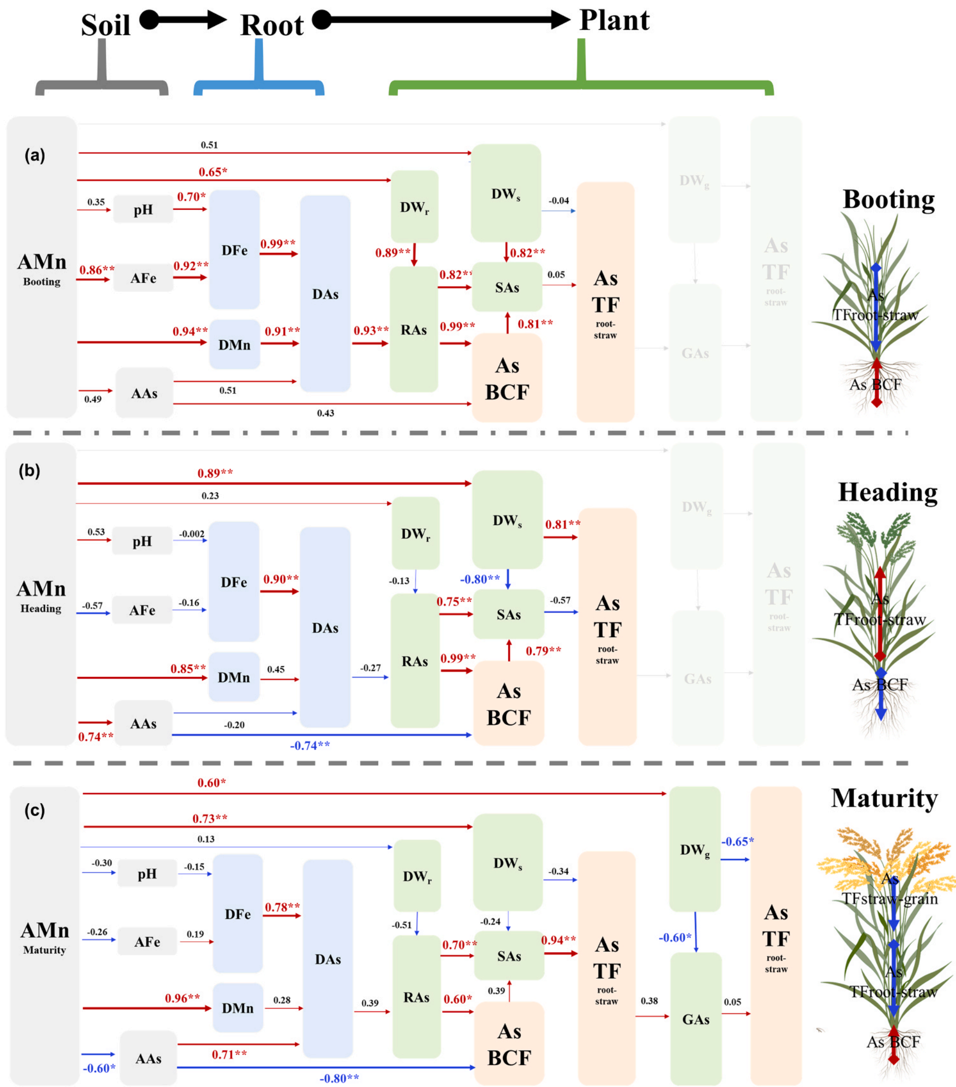

Fig. 6. Pathway analysis of key factors influencing As enrichment and transport during the booting (a), heading (b), and maturity (c) stages in rice. In this context, * denotes $p < 0.05$, and ** denotes $p < 0.01$. Red signifies a positive correlation, blue signifies a negative correlation, and the line thickness indicates the magnitude of the correlation coefficient.

and As migration during other growth stages should not be overlooked.

5. Conclusions

In this study, we conducted, for the first time, an in-depth analysis of the effects and regulatory mechanisms governing Cd and As mobility at three key growth stages: booting, heading, and maturity. We quantified the relative contribution of Mn to reducing grain Cd and As accumulation across growth stages. The results showed that Mn application influenced soil pH, soil Fe-Mn fractions, soil available Cd and As concentrations, and the enrichment of elements in the Fe-Mn plaques. Moreover, Mn application significantly reduced grain Cd and As concentrations by 30.2–63.8 % and 20.6–26.4 %, respectively. Mn also enhanced plant growth (by 24.7–28.8 %) and increased grain yield (by 30.0–136.4 %) without phytotoxic effects. Least squares regression indicated that Mn contributed 30.5 %, 33.9 %, and 35.6 % for Cd reduction, and 37.7 %, 19.0 %, and 43.2 % for As reduction at booting, heading, and maturity, respectively. Path analysis further revealed that Mn regulated As migration in rice mainly by promoting plant growth, altering tissue elemental composition, and lowering soil As availability. In contrast, the reduction of grain Cd accumulation was primarily attributed to Mn-mediated Fe - Mn plaque formation at the root surface, stimulation of plant growth, and modulation of Cd-related gene expression at maturity stage. To sum up, the application of Mn fertilizers for remediating As-Cd co-contaminated soils should not focus solely on the final stage of maturity, but also pay greater attention to the early and middle growth stages, particularly booting and heading. In addition, the role of Mn in reducing heavy metal accumulation in grains should be considered not only from the perspective of soil processes, but within the broader soil-root-crop continuum. The findings of this study not only provide experimental support for the precise remediation of Cd and As co-contaminated soils using Mn fertilizer as conditioners, but also inform strategies to simultaneously reduce toxicity and increase crop yield.

CRediT authorship contribution statement

Jingtao Hou: Writing – review & editing, Visualization, Supervision, Conceptualization. **Mengqing Wang:** Writing – original draft, Methodology, Investigation, Formal analysis. **Andreas Kappler:** Writing – review & editing. **Naresh Kumar:** Writing – review & editing. **Wenfeng Tan:** Supervision. **Mingxia Wang:** Supervision. **Chang Chen:** Formal analysis. **Juan Xiong:** Formal analysis.

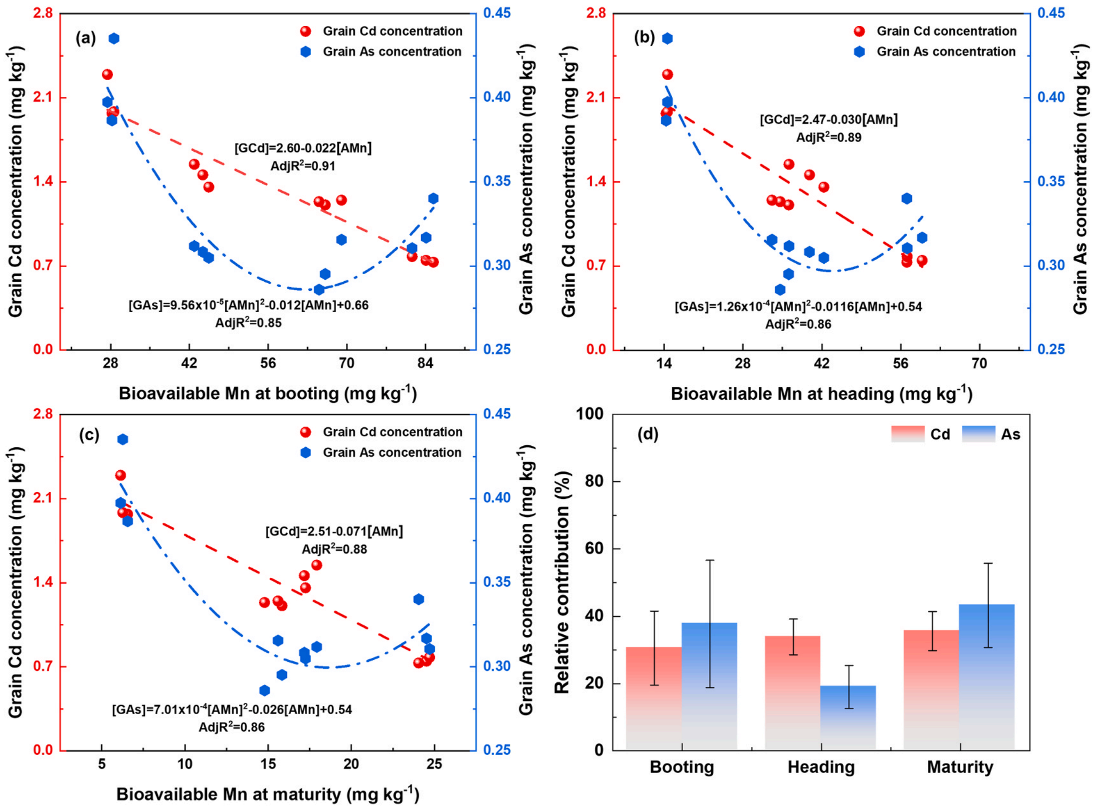

Fig. 7. Relationship between soil Mn and the content of Cd and As in rice grains following Mn fertilizer application at different growth stages: (a) booting, (b) heading, (c) maturity; (d) average relative contribution of manganese fertilizer to the accumulation of As and Cd in grains at each growth stage. Error bars represent standard deviations (n = 3).

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.

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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.2026.119727.

Data availability

Data will be made available on request.

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