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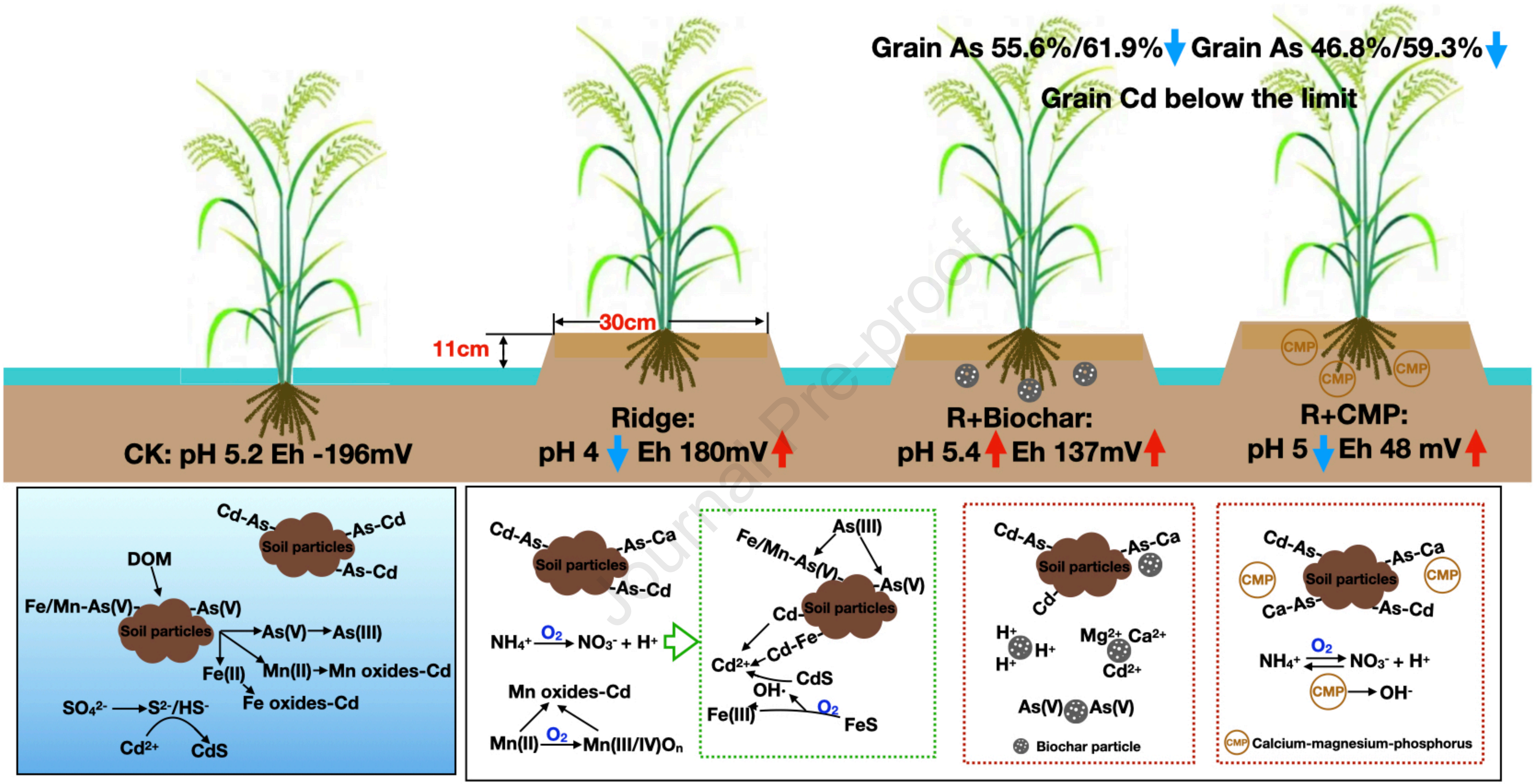
Grain As 55.6%/61.9%
Grain As 46.8%/59.3%
Grain Cd below the limit
30cm
11cm
CK: pH 5.2 Eh -196mV
Ridge:
pH 4 Eh 180mV
R+Biochar:
pH 5.4 Eh 137mV
R+CMP:
pH 5 Eh 48 mV
Cd-As-
Soil particles
-As-Cd
-As-Cd
DOM
Fe/Mn-As(V)-
-As(V)
Soil particles
As(V)→As(III)
Fe(II)
Mn(II)→Mn oxides-Cd
Fe oxides-Cd
SO$_4^{2-}$ → S^{2-}/HS$^-$
Cd^{2+}
CdS
Cd-As-
Soil particles
-As-Ca
-As-Cd
NH$_4^+$ $\xrightarrow{O_2}$ NO$_3^-$ + H$^+$
Mn oxides-Cd
Mn(II) $\xrightarrow{O_2}$ Mn(III/IV)O$_n$
As(III)
Fe/Mn-As(V)-
-As(V)
Cd-
Soil particles
Cd^{2+}
Cd-Fe-
CdS
OH·
Fe(III)
O$_2$
FeS
Cd-As-
Soil particles
-As-Ca
Cd-
H$^+$
H$^+$
H$^+$
Mg^{2+} Ca^{2+}
Cd^{2+}
As(V) As(V)
Biochar particle
Cd-As-
CMP
Soil particles
-As-Ca
CMP
Ca-As-
-As-Cd
NH$_4^+$ ⇄ NO$_3^-$ + H$^+$
O$_2$
CMP → OH$^-$
CMP Calcium-magnesium-phosphorus

Soil ridging combined with biochar or calcium-magnesium-phosphorus fertilizer application: Enhanced interaction with Ca, Fe and Mn in new soil habitat reduces uptake of As and Cd in rice

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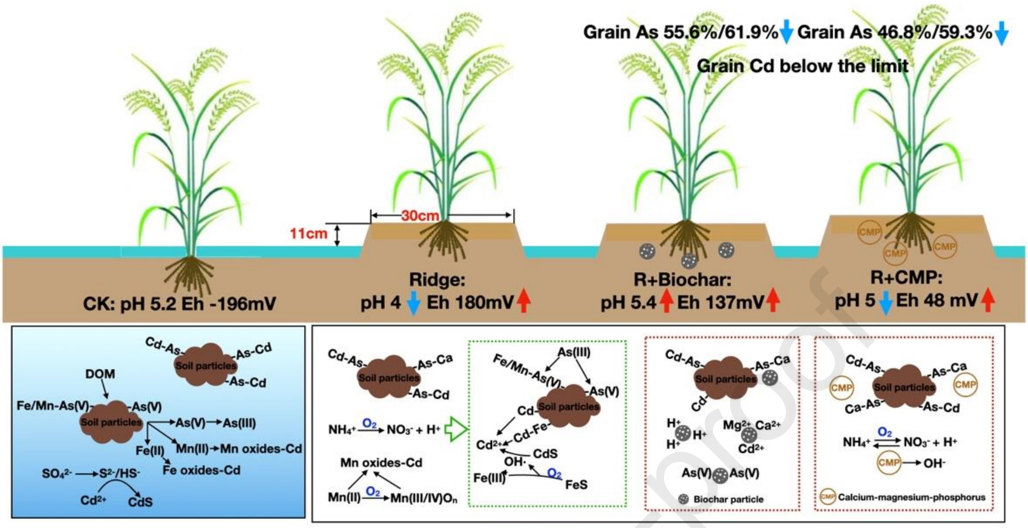
Abstract

Reducing the bioavailability of both cadmium (Cd) and arsenic (As) in paddy fields is a worldwide challenge. The authors investigated whether ridge cultivation combined with biochar or calcium-magnesium-phosphorus (CMP) fertilizer effectively reduces the accumulation of Cd and As in rice grains. Field trial showed that applying biochar or CMP on the ridges was similar to the continuous flooding, which maintained grain Cd at a low level, but grain As was reduced by 55.6%, 46.8% (IIyou28) and 61.9%, 59.3% (Ruiyou 399). Compared with ridging alone, the application of biochar or CMP decreased grain Cd by 38.7%, 37.8% (IIyou28) and 67.58%, 60.98% (Ruiyou399), and reduced grain As by 38.9%, 26.9% (IIyou28) and 39.7%, 35.5% (Ruiyou 399). Microcosm experiment showed that applying biochar and CMP on the ridges decreased As in soil solution by 75.6% and 82.5%, respectively, and kept Cd at a comparably low level at 0.13-0.15 $\mu g \cdot L^{-1}$. Aggregated boosted tree (ABT) analysis revealed that ridge cultivation combined with soil amendments altered soil pH, redox state(Eh) and enhanced the interaction of Ca, Fe, Mn with As and Cd, which promoted the concerted reduction of As and Cd bioavailability. Application of biochar on the ridges enhanced the effects of Ca and Mn to maintain a low level of Cd, and enhanced the effects of pH to reduce As in soil solution. Similar to ridging alone, applying CMP on the ridges enhanced the effects of Mn to reduce As in soil solution, and enhanced the effects of pH and Mn to maintain Cd at a low level. Ridging also promoted the association of As with poorly/well-crystalline Fe/Al and the association of Cd on Mn-oxides. This study provides an effective and environmentally friendly method to decrease Cd and As bioavailability in paddy fields and mitigate Cd and As accumulation in rice grain.

Keywords: arsenic; cadmium; soil amendment; biochar; calcium-magnesium-phosphorus fertilizer; ridge cultivation

TOC/Abstract art



1. Introduction

Soil co-contamination with arsenic (As) and cadmium (Cd) is a growing global concern (Zhao and Wang, 2020). Compared with other corps, rice was found to have efficient pathways for absorbing silicon (Si)/arsenite (As(III)) (Su et al., 2010), phosphate (P)/ As(V) (Kamiya et al., 2013) and manganese (Mn)/Cd (Sasaki et al., 2012), and thus can efficiently absorb As and Cd. Consuming rice as the staple food allows As and Cd to enter the food chain and threatens food safety and human health (Zhao, 2020). Therefore, it is imperative to develop or adapt strategies to reduce the bioavailability of both As and Cd in soil and their accumulation in rice grains. However, the anionic metalloid As and cationic metal Cd in paddy soils exhibit opposite biogeochemical behavior, which makes it challenging to remediate in the As and Cd co-contaminated fields (Zhao and Wang, 2020).

In paddy fields, flooding and drainage are common measures for rice cultivation. As soil moisture changes, soil redox state (Eh) or pe (-log e^- activity, pe = Eh (mV)/59.2 (25 °C)) and pH of the soil changes accordingly (Honma et al., 2016). At low pH and high Eh, the increased positive charge on the soil surface facilitates the desorption of Cd, while high pH and low Eh increases the net negative charge on the soil surface resulting in the desorption of As (Bolan et al., 2013; Yao et al., 2022). The activity of Cd and As in paddy fields are strongly affected by the redox of iron (Fe), manganese (Mn) oxides and sulfate (S). When paddy soil is flooded, As is mobilized by the reductive dissolution of (Fe)-Mn minerals (Shaheen et al., 2020), while soluble Cd forms precipitates, such as CdS, resulting in high As and low Cd bioavailability (Shaheen et al., 2016; El-Naggar et al., 2018). When the paddy field is drained, the transformation of CdS into soluble $CdSO_4$ increases the mobility of Cd (Sebastian and Prasad, 2014), while As is immobilized by the Fe/Mn-(oxy)hydroxides with the oxidation of FeS or Fe^{2+} (Yu et al., 2016). Adjusting water management strategies in paddy soils to the appropriate Eh and pH trade off value can keep As and Cd availability at a low level (Honma et al., 2016). The trade-off value varies with the paddy soil types and the contents of soil As and Cd. It is often difficult to control the Eh and pH at an optimal trade-off state in practice.

Soil ridge cultivation is a traditional agronomic practice in waterlogged paddy fields and has been implemented in China for over 2000 years (Zheng et al., 2014). Ridging prevents the defects caused by high groundwater level, sufficient rainfall, poor drainage, and enrichment of reducing toxic substances in waterlogged fields (Ren et al., 2016). Usually, the height of the ridge is 10-

20 cm, while the width of the ridge surface and furrow adapts to the practical crop production (Xiong et al., 2014). This traditional agronomic practice has been proven to keep As and Cd availability at low levels through the adjustment of the soil Eh and pH to a trade-off situation (Jiku et al., 2022). Due to the elevated Eh, ridge cultivation may increase the risk of Cd for paddy fields, especially with high Cd content (Jiku et al., 2022). Therefore, it may be of added benefit to utilize a form of soil amendments to stabilize Cd on the ridges to reduce Cd release from the soil. However, little information on the effect of soil ridging combined with soil amendments on the As and Cd bioavailability is currently known.

Soil in-situ amendments such as biochar (Rehman et al., 2017), and calcium-magnesium-phosphate (CMP) fertilizers (Jiang et al., 2022; Shi et al., 2022) are effective for Cd immobilization. Both materials are environmentally friendly soil inputs and are compatible with food crops. Due to its negatively-charged surface, biochar increases soil pH and net negative charge on the soil surface and reduces the mobility of metal cations (Beesley et al., 2011; Houben et al., 2013). The increased cation exchange sites may also facilitate the competition or exchange of Cd^{2+} with Ca^{2+} and Mg^{2+} (Harvey et al., 2011). As an alkaline fertilizer, when CMP is applied, the surface hydroxyl groups coordinated with metal cations (such as Fe, Al, etc.) on the soil surface were replaced by P ions, and the soil pH increases (Feng et al., 2013). When P fertilizer was applied, Cd was found to be immobilized as precipitates (Bolan et al., 2003).

With the changes in soil pH, Eh and introduction of exogenous ions after ridge combined with soil amendments, the ions relationship and the chemical process in the rhizosphere may change correspondingly. We hypothesize that a new soil habitat will potentially be formed with this change. The strengthened interaction of Fe, Mn, Ca, Mg with As and Cd as above mentioned might be responsible for the simultaneous decrease of As and Cd bioavailability in paddy soils. The objective of this study was to test the possibility of combining ridging with soil amendments in rice cultivation to simultaneously reduce the accumulation of Cd and As in grains and to explore the importance of ionic interactions in the new soil habitat. We carried out (1) a field trial to investigate the effects of the combination of ridging and biochar or CMP on grain As and Cd concentrations and (2) a soil microcosm experiment with a more controlled environmental condition to investigate whether using paddy soil ridge combined with biochar or CMP can affect the interaction of Fe, Mn, Ca, Mg with As and Cd, and to what extent it plays a role in reducing the bioavailability of As and Cd. The results of this study provide a new method with demonstrated experimental evidence to mitigate Cd and As accumulation in paddy fields to enhance food safety. These findings also expand approached knowledge in the area of mitigating heavy metal contamination in food cropping sites.

2. Materials and methods

2.1 Materials

Two three-line indica hybrid rice cultivars that are widely planted in the rice producing areas in southern China were selected for the field experiment: IIyou 28 produced by Fujian Fengtian Seed Co. Ltd. (Fuzhou, China) and Ruiyou 399 produced by Sichuan Kerui Seed Co. Ltd. (Chengdu, China). Rice straw biochar was obtained from Beijing PhD Union Academy of Agriculture (Beijing, China). The content of Cd and As in the biochar was 0.12 mg·kg^{-1} and 0.5 mg·kg^{-1}. In the given dose of biochar applied to the soil, the content of Cd and As was negligible. CMP fertilizer with the available phosphorus content (P_2O_5) of ≥ 12% and As and Cd content below the detection limit was produced by Phosphate Fertilizer Factory in Liuyang East District (Liuyang, China).

2.2 Field experiment

The field experiment was conducted in a long-term rice-growing field in Shimen County, Hunan province of China (N 29◦38′, E 111◦01′). The area of field plots was 20 m^2 (5 m × 4 m). The soil of the field plot is paddy soil and mainly developed from the Quaternary red clay parent rock. This soil is a common and typical rice cultivating soil in southern China. Due to the long-term mining and smelting of realgar mines nearby, the adjacent farmland was polluted by a large amount of As-containing slag or waste water (Jiku et al. 2022). The total As and Cd contents in the field plot was 66.5 mg·kg^{-1} and 0.41 mg·kg^{-1}, respectively, and the pH value was 5.17, which failed to meet the safety criteria of agricultural land in China: when the soil pH≤5.5, As limit, 30 mg·kg^{-1}; Cd limit, 0.3 mg·kg^{-1} (GB15618-2018).

The experiment treatments included conventional tillage (continuous flooding with a standing layer of ~2cm water, CK) and ridge cultivation above the irrigation level. In order to evaluate the effect of the combination of ridge and soil amendments, ridge cultivation is comprised of ridge without soil amendments (R), ridge with rice straw biochar (R+B), and ridge with CMP (R+CMP). The biochar and CMP were thoroughly mixed and applied to the ridge twice over a month before transplanting rice seedlings. The upper width was 30 cm for all ridges. Our previous work showed that As and Cd contents in rice grains remained at low levels when the soil ridge height was around 11cm (Jiku et al. 2022). Therefore, the ridge height of 11 cm was adopted in this field experiment. Paddy field water and plant management were the same and according to local practices unless otherwise noted, with continuous flooding during rice growth season and drainage 10 days before harvest. Each treatment was repeated three times.

2.3 Microcosm experiment

Microcosms were setup in 100 mL serum bottles. The soil was collected from Shimen field plots. After air drying, sundries were picked out and the soil was ground to pass a 2 mm sieve. Each serum bottle was filled with 60 g dry soil. According to our pre-experimental results, in order to achieve the same redox conditions for conventional tillage and ridging treatments in the above field experiment, the soil moisture content of conventional tillage (mCK) and ridging treatments (mR) in this microcosm experiment was set at 75% and 35% ($w_{water}/w_{dry\text{-}soil}$), respectively. To simulate the treatments of biochar (mR+B) and CMP (mR+CMP) combined with ridge cultivation in this microcosm experiment, the water content was set to 35%, and the dosage of biochar and CMP was 1% ($w/w_{dry\text{-}soil}$) and 0.5‰P ($w/w_{dry\text{-}soil}$), respectively.

Soil and amendments were mixed thoroughly one week in advance. The temperature was set to 37°C, and the cells were incubated in the dark for 40 days. Each treatment was replicated 3 times. The bottles were placed in a randomized, complete block design and weighed every 2 days to keep the soil moisture content the same.

2.4 Sample collection and analysis

Field Experiment: When sampling after rice mature, the Eh and pH of the rhizosphere were preliminary in situ determined by an automated ORP depolarization automatic analyzer (FJA-6; Nanjing Chuan-Di Instrument & Equipment Co. Ltd., Nanjing, China). Subsequently, field pore water was collected in the rhizosphere at a depth of 10 cm through a Rhizon soil moisture sampler (Rhizosphere Research Products, Wageningen, The Netherlands). The porewater was stored in the icebox immediately and shipped to the lab for the analysis of As, Cd, Fe, Mn and S concentrations after having been passed through a 0.45-μm syringe filter. Total As concentration was determined by hydride generation-atomic fluorescence spectrometer (HG-AFS, 9120, Beijing Titan Instrument Co., Ltd.). Total Cd, Fe, Mn and S concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 5300DV; PerkinElmer).

Whole rice plants were collected from each replicate in the field experiment after plant height was measured. All fresh samples were rinsed with tap water and ultrapure water. The plants were separated into husks, grains, straws, and roots without removing the iron plaque on the root surface. All plant organs were oven-dried at 45 °C to constant weight, then weighed, and pulverized for subsequent analysis. Total As concentrations in rice samples were determined by HG-AFS after acid digestion with 4:1:1.5 (v/v/v) HNO_3-$HClO_4$-H_2SO_4 (Yu et al., 2016). Total Cd concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e, Pekin Elmer, USA) after acid digestion with 9:1 (v/v) HNO_3-$HClO_4$ (GB 5009.15-2014).

Microcosm experiment: In situ Eh and pH was tested on the 1st, 7th, 14th, 20th and 40th day. In situ Eh was measured by a redox micro electrode (Mettler Toledo, Columbus, OH, USA) and in situ pH was measured by the micro pH meter (Mettler Toledo) right after the Eh test. Thereafter, soil samples were collected on the 1st, 20th and 40th day to analyze the concentration of ions in the soil solution and the content of As and Cd in the soil.

Soil solutions were extracted by water extractions by shaking 5 g of incubated fresh soil with 50 mL of deionized water for 24 hours. The slurry was centrifuged at 8000 rpm for 10 min, decanted and the solution was filtered with a 0.22 μm syringe filter (Faulkner et al., 2001; Hobson et al., 2020). The dissolved organic carbon (DOC) was determined using carbon and nitrogen analyzer (Multi N/C 3100, Analytik jena, German). The As(III), As(V), SO_4^{2-}, PO_4^{3-}(not detected), Cl^-, CO_3^{2-} and NO_3^- levels were determined using high-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS, PerkinElmer NexION 300X) (Yan et al., 2020). The content of Cd, Fe, Mn, Ca and Mg was analyzed by ICP-OES (Optima 5300DV; PerkinElmer) (Cruz et al., 2015). The analytical results including pH, temperature, DOC, anions and cations were imported into the Visual MINTEQ model 3.1 to calculate the As and Cd species in soil solutions (Gustafsson, 2020).

Two different sequential extraction methods were used to determine the As and Cd fractions in soil samples from the microcosm experiment. A classical Tessier scheme modified by Hobson et al (2020) was chosen for Cd determination (Table S1). The method established by Wenzel et al (2001) was used for As analysis (Table S2). Total As and Cd concentrations in soil samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e, Pekin Elmer, USA) after samples were extracted using HNO_3 and HCl in a ratio of 1:3 (Desrosiers et al., 2008).

2.5 Quality control

For quality control, certified reference material of rice (GBW10045) and soil (GBW07429) were digested at the same time. The recovery of total As and Cd in the standard sample were for As at 88–99 % and Cd at 95–102 % for rice and As at 85–90 % and Cd at 83–106% for soil. The recovery rates in soil sequential extraction were calculated as the sum of each fraction divided by the total content determined by digestion, of which Cd was 102-157% and As was 78-116%. CRM water samples (GBWZ50004-88 for As and 200933 for Cd; Institute for Environmental Reference Materials of the Ministry of Environmental Protection, Beijing, China) were mixed among the blank and digested samples at the beginning of each sample test and intervals of 10 samples analysis for quality control of ICP-MS and AFS.

2.6 Statistical analysis

Basic statistical analysis was performed using Microsoft Excel 2010 and IBM SPSS Statistics 26.0. One way analysis of variance (ANOVA) or non-parametric test was chosen to compare the differences between treatments. Correspondingly, the significant effects were compared by LSD test (*P* < 0.05) or Kruskal-Wallis Test (*P*<0.05). All data are expressed as the means ± standard error (SE). Aggregated boosted tree (ABT) analysis was processed by the "gbmplus" package in *R* (R Development Core Team, Vienna, Austria). Prism 9.1.1 (GraphPad Software, San Diego, CA, USA) and 'ggplot' package in *R* were employed for data plotting.

3. Results

3.1 As and Cd in rice tissues and the biomass change (field experiment)

Ridging alone significantly (*P*<0.05) increased the Cd content of rice grain by 118.3% and 207.0% compared with the control, and similarly, the Cd content of husk, straw and root also increased significantly (*P*<0.05) (Figure 1). With biochar application on the ridge, the Cd contents in grain, husk and root of IIyou28 and all tissues of Ruiyou 399 were at the same lower level as that of the control. With CMP application on the ridge, the content of Cd in rice grain was similar to that of CK. The Cd content in straw and root of IIyou28 and husk of Ruiyou 399 significantly (*P*<0.05) increased compared with the control. Compared with ridging alone, application of biochar and CMP on the ridge significantly (*P*<0.05) decreased the grain Cd by 38.7% (IIyou28), 67.58% (Ruiyou399) and 37.8% (IIyou28), 60.98% (Ruiyou399). However, ridge cultivation significantly (*P*<0.05) decreased the As contents in rice grain, husk, straw and root of IIyou28 and Ruiyou399 compared with the control. Applied biochar and CMP on the ridge decreased (*P*<0.05) grain As by 55.6% (IIyou28), 61.9% (Ruiyou 399) and 46.8% (IIyou28), 59.3% (Ruiyou 399) comparing with the control. The grain As was notably reduced (*P*<0.05) by 38.9% (IIyou28), 39.7% (Ruiyou399) and 26.9% (IIyou28), 35.5% (Ruiyou399), compared with ridging alone.

Application of biochar and CMP on the ridge had a slight effect on the rice thousand kernel weight (Figure S1). The plant heights of IIyou28 grown on the ridges and Ruiyou399 grown on the ridges applied with biochar were significantly (*P*<0.05) decreased by 9.3-11.0% and 18.5%, compared with the control. While the plant height of Ruiyou399 grown on the ridges or ridges applied with CMP were at the same level as that of the control.

3.2 Soil pH, Eh, and levels of As, Cd, Fe, Mn, S in porewater (field experiment)

Soil pH in the control was 5.2 (IIyou28) and 5.0 (Ruiyou 399) (Figure S2). Ridging significantly (P<0.05) decreased the soil pH to 4 (IIyou28) and 3.7 (Ruiyou 399). By applying biochar on the ridge, the soil pH was raised to the control level. With applied CMP on ridge, the soil pH also increased compared with that of ridge alone, but the rhizosphere of Ruiyou399 was still significantly (P<0.05) lower than that of the control. Soil Eh was about -196~-194 mV in the control. Ridging significantly (P<0.05) increased the soil Eh, the Eh values in the ridged treatments were in the following order: R+B>R>R+CMP.

Ridging greatly increased the Cd content in soil porewater when compared with the control (Figure 2). Having been applied with biochar or CMP, the pore water Cd of IIyou28 decreased to a level comparable to that of the control. The As content was similar in each group without significant difference (P>0.05), which were 1.6-2.1 $\mu g \cdot L^{-1}$ (IIyou28) and 2.1-2.2 $\mu g \cdot L^{-1}$ (Ruiyou 399). The content of Mn, Fe and S in soil porewater treated with ridge cultivation were all higher than those of the control, especially Fe and S (P<0.05) (Figure S3). Application of biochar on the ridge further increased the contents of Mn, Fe and S in the porewater. The contents of Mn, Fe and S in R+CMP of Ruiyou399 were significantly (P<0.05) higher than that of R and CK. However, the contents of Mn and Fe in R+CMP of IIyou28 were not significantly (P>0.05) different from that of R, and the content of S was significantly (P<0.05) lower than that of R but still higher (P<0.05) than that of CK.

3.3 Cd and As in soil solution (microcosm experiment)

The Cd content in the soil solution was the highest (0.38-0.66 $\mu g \cdot L^{-1}$) on the 1st day, the lowest (0.07-0.13 $\mu g \cdot L^{-1}$) on the 20th day, which reached the level of 0.13-0.15 $\mu g \cdot L^{-1}$ in each group on the 40th day (Figure 3). Compared with the control, ridging significantly (P<0.05) increased the Cd content in the soil solution, but the increase was gradually weakened with the change of culture time. After applying biochar or CMP, the Cd content was lower than that of ridge alone on the 1st day, but still higher than that of the control, until it dropped to the same level as the control on the 40th day. The analysis result of Visual MINTEQ showed that during the entire process of incubation, the organic complexes (Cd-DOM) were the main fraction of Cd in the soil solution (Figure S4).

The content of As in the soil solution of the control showed a trend of increasing in the first 20 days and then decreasing in the next 20 days (Figure 3). The lowest content was 7.4 $\mu g \cdot L^{-1}$ on the 1st day, and it increased to a maximum of 71.4 $\mu g \cdot L^{-1}$ on the 20th day, then decreased to 38.9 $\mu g \cdot L^{-1}$ on the 40th day. All ridging treatments showed the opposite trend. On the 1st day, the As content was the highest, which was 287.2% (mR), 652.9% (mR+B) and 916.6% (mR+CMP) higher than the control, respectively. On the 20th day, they all decreased to the lowest level and were 97.7% ($P<0.05$) (mR), 87.3% ($P>0.05$) (mR+B) and 93.6% ($P<0.05$) (mR+CMP) lower than the control, respectively. On the 40th day, the As content increased to 6.5-9.2 $\mu g \cdot L^{-1}$, but it was still lower than that of the control by 83.3% ($P<0.05$) (mR), 75.6% ($P>0.05$) (mR+B) and 82.5% ($P<0.05$) (mR+CMP). The analyzing result of Visual MINTEQ showed that the major speciation of inorganic As in the control is H_3AsO_3 and that the major speciation of inorganic As in the ridged treatments are $HAsO_4^{2-}$ and $H_2AsO_4^-$ (Figure S5).

3.4 The pH, Eh and the ions correlated with As and Cd in soil solution (microcosm experiment)

In the microcosm experiment, the soil pH decreased by 9.5%-28.6% after ridging compared with the control (Figure S6). With the application of biochar or CMP on the ridge, the soil pH decreased by 0.1%-34.0% and 0.3%~25.1%, respectively, compared with the control. The soil Eh indicated a distinct increase under all ridging treatments, with the changes of 50.8%-275.5% (mR), 22.0%-233.5% (mR+B) and 51.4%-275.8% (mR+CMP), respectively. The concentrations of all tested ions are listed in Table S3.

The correlation analysis (Figure 4) showed that the content of iAs was positively correlated with Mn^{2+}($P<0.01$), CO_3^{2-}($P<0.01$), pH ($P<0.05$) and negatively correlated with NO_3^-($P<0.01$) and pe ($P<0.01$). The Cd^{2+} content in the soil solution was positively correlated with Mn^{2+}($P<0.01$), Ca^{2+}($P<0.05$),

Mg^{2+}($P<0.05$), SO_4^{2-}($P<0.05$) and negatively correlated with DOC ($P<0.01$) and NO_3^- ($P<0.05$).

Aggregated boosted tree (ABT) analysis was used to analyze the relative importance of ions content, pe and pH in affecting Cd and iAs contents in soil solution. As shown in Figure S7, the main factors contributing to the influence of Cd content in soil solutions were Mn^{2+} and NO_3^-, with relative influence rates of 29.3% and 28.6% respectively, much higher than other indicators. The primary factors affecting iAs were pH, pe, CO_3^{2-} and Mn^{2+}, with relative influence rates of 23.3%, 15.3%, 13.5% and 12.1%, respectively. Further analysis indicated that the primary factors that affected the Cd and iAs contents in soil solutions varied with the treatments (Figure 5 and 6). For Cd, the primary factors in mCK were iAs, Mn^{2+} and SO_4^{2-}, whereas in mR were iAs, NO_3^- and Mn^{2+-}, in mR+B are Ca^{2+}, iAs and Mg^{2+} and in mR+CMP are iAs, Ca^{2+} and NO_3^-. Cd was the primary factor affecting iAs content in mCK. The primary factors affecting iAs were Ca^{2+}, Mn^{2+} and pH in different ridging treatments.

3.5 Cd and As fraction in soil solid phase (microcosm experiment)

Based on Tessier sequential extraction, in the control, Cd was predominant (61.2%) readily exchangeable, followed by that associated with Fe oxide fraction (21.2%) on the 1st day (Figure 7a). While on the 20th and 40th day, the Fe-oxide fraction was the main factor (41%). Ridging significantly increased the exchangeable fraction by up to 102.7% ($P<0.05$) and decreased the carbonate bound or Fe oxide-bound fraction by up to 54.9% or 67.3% ($P<0.05$) on the 20th and 40th day. The Cd associated with Mn-oxide was significantly increased by 36.7% ($P<0.05$) on the 20th day and decreased by 11.0% ($P>0.05$) on the 40th day. With applied biochar on the ridge, the readily exchangeable Cd and Fe oxide bound fraction significantly decreased by up to 45.7% and 61.2%, while the Cd associated with carbonate and Mn-oxide significantly increased by up to 283.9% and 134.0%, compared with the control. CMP application on the ridge increased the readily exchangeable Cd, carbonate bound, Mn oxide-bound and residual fraction by up to 40.1%, 62.1%, 155.3% and 32.8% respectively, and also decreased Fe oxide-bound fraction by up to 62.9%. The organically bound Cd fraction significantly decreased by 79.7% on the 1st day and decreased by up to 33.3% on the 20th and 40th days, but the difference was not significant.

Based on Wenzel sequential extraction, in the control, the portion of non-specifically sorbed As and the specifically sorbed As increased to 3.2% and 23.49%, respectively, on the 20th day and then decreased to 2.83% and 17.5%, respectively, on the 40th day (Figure 7b). However, the non-specifically sorbed As and the specifically sorbed As in all ridging treatments showed a downward trend, and they were significantly (P<0.05) lower than that of the control on the 20th and 40th day. Ridging primarily increased the As associated with poorly-crystalline Fe/Al. The poorly-crystalline Fe/Al was increased by 91.6% when ridging alone, 114.7% when applying biochar on the ridge and 109.8% when applying CMP on the ridge on the 40th day. The As associated well-crystalline Fe/Al also increased after ridging. The change ratio was 30.5% for ridging alone, 23.5% for applying biochar on the ridge and -2.3% for applying CMP on the ridge on the 40th day. Compared with the control, there was no significant difference in the residual fraction As.

4. Discussion

Ridge cultivation is effective in reducing the accumulation of As in rice grains but increases the content of grain Cd (Jiku et al., 2022). In this study, ridge cultivation combined with biochar or CMP showed a great potential for the synergistic decrease in the bioavailability of As and Cd. The pH dropped as Eh rises when ridges were applied. Consequently, the bioavailability of As decreases while that of Cd increases. When applying biochar or CMP on the ridges, their alkaline properties buffer soil acidification, which helps to reduce Cd bioavailability. The strengthened interaction of Ca, Fe and Mn with As and Cd in soil solution was apparently responsible for the decrease in the bioavailability of As and Cd (Figure S8). In addition, the aerobic soil conditions after ridging promoted the association of As with poorly/well-crystalline Fe/Al and Cd with Mn-oxides but reduced the association of Cd with Fe-oxides. Taking together, ridging combined with biochar or CMP can be an effective and low-cost measure to remediate the Cd and As co-contaminated paddy fields.

4.1 Changes in soil pH and Eh after ridging combined with biochar or CMP influence the availability of As and Cd

In this study, with ridging on acidic soil, the pH dropped and Eh increased. After biochar or CMP is applied on the ridge, however, soil pH increased while Eh was lower than that of ridge alone. The biochar and CMP associated pH increase in acidic soils may stimulate the activities of or enrich the soil microorganisms (Tan et al., 2022; Liu et al., 2020). The latter depletes oxygen and whereafter slow down the Eh rise (Marschner, 2021). In this work, the change of pH and Eh in the microcosm experiment was consistent with changes in the field experiment. Decreasing soil pH resulted in an increased in net positive charge on the soil surface (Houben et al., 2013), which accelerated the absorption of negatively charged As and the desorption of positively charged Cd (Yang et al., 2018). As a result, the As content in the soil solution decreased and the content of Cd increased. However, the insignificant difference in porewater As concentration was observed between CK and R in field experiment. This may be resulted from the dilution effect of higher water content in CK. In addition, this study was limited by the low soil Cd content in the selected field plots. Thus, the contents of Cd in rice grains and soil solution were relatively low, which may also be related to the continuous flooding state of the control.

After ridging, the observed increase in the impact of N may be due to its indirect effects on the bioavailability of As and Cd by adjusting soil pH and related microbial activities. Reaeration after soil ridging promotes nitrification, which helps to reduce soil pH (Papirio et al., 2014), resulting in a decrease in As activity and an increase in Cd activity (Zhao and Wang, 2020). In addition to the adsorption of Cd, the addition of biochar can restore the activity of ammonia-oxidizing bacteria (AOB) poisoned by Cd, and promote nitrification by neutralizing the protons generated by nitrification through the lime effect while avoiding more acidification of the soil (Zhao et al., 2020). This effectively addresses the risk of increased Cd bioavailability after ridging. Similarly, alkaline CMP also bufferes soil acidification through the lime effect to reduce the risk of Cd. Furthermore, CMP drives *Thiobacillus* and *Ignavibacteriae* to reduce nitrate to ammonium which affects the Cd uptake by plants (Wang et al., 2021; Cheng et al., 2020). Nitrate promotes the accumulation of Cd in rice more than ammonium (Wu et al. 2018). This may be another reason for the decrease of Cd in rice tissues after CMP application on the ridge.

4.2 Enhanced interaction of Ca, Fe, Mn with Cd and As after ridging combined with biochar or CMP reduces the availability of As and Cd

In this work, the strong contribution of Ca in reducing As and Cd availability in soil solution was observed after ridge cultivation, especially combined with biochar or CMP addition. This could be explained by the following reasons: (I) AsO_3^{3-} and Ca^{2+} can form precipitates in the soil solution and reduce the availability of As (Nazari et al., 2017), especially with the increase in soil pH after applying biochar or CMP on ridges; (II) Calcium ions (Ca^{2+}) and Cd have similar ionic radius and are both divalent cations (Hawkesford et al., 2012). Ca^{2+} and Cd^{2+} may compete for Ca transporters, channels or binding sites on root surface (Wu et al., 2021). Biochar provides more cation exchange sites in soil system, facilitating the exchange of Cd^{2+} with Ca^{2+} (Harvey et al., 2011); (III) Ca has the function of protecting cell membrane stability and cell integrity and may change the negative charge on the membrane surface, thereby hindering the flux of Cd into the plant cell and reducing the Cd in rice grains (Kanu et al., 2019). In addition, although studies have shown that the exogenous input of Mg reduces the Cd content in rice grains (Kikuchi et al., 2008), there is little report on the competition mechanism between Mg and Cd uptake by plants, which may be of future research interest.

Fe and Mn are also involved in the control of Cd and As mobility in paddy fields. When paddy fields are flooded, cation exchange drives the reductive dissolution of Fe/Mn-(hydro)oxides, releasing the absorbed As into soil solution, thereby increasing the mobility of As (Takahashi et al., 2004). At the same time, the dissolved Mn^{2+} may compete with Cd^{2+} for adsorption sites (Zhao and Wang, 2020). In this study, Fe and Mn in porewater of treatments without ridging were lower than those of ridging treatment in field experiment and this could be attributed to the dilution effect of high water. After ridging, the association of As with poorly/well-crystalline Fe/Al increased due to the strong adsorption between Fe-(hydro)oxides and As(V) (Goldberg, 2002). The latter was easily produced from the As(III) oxidation under the oxygenated soil condition (Takahashi et al., 2004). FeS dissolves and generates hydroxyl free radicals (OH·), which may oxidize CdS to mobilize Cd (Huang et al., 2021). Furthermore, our results showed that the transformation of the Cd associated with Fe/Mn-(hydro)oxides into the exchangeable fraction leads to the increase in Cd solubility after soil reoxidation. A similar phenomenon was also observed in the work of Wang et al. (2019). Mn is strong abiotic oxidants of As(III) (Feng et al., 2006). Moreover, Mn oxides can delay the reductive dissolution of As-containing Fe-(hydro)oxides and the release of As into pore water by maintaining the Eh at a relatively higher level (Ehlert et al., 2014). In this work, after ridging, the Cd associated with Mn oxides increased. A large amount of dissolved Mn^{2+} may react with Mn(III/IV)-(oxy)oxides to form heterovalent minerals. Due to its large surface area and strong adsorption affinity for metal ions, secondary Mn minerals can sequester Cd by adsorption or co-precipitation (Wang et al., 2022).

Biochar also has a certain adsorption effect on As and Cd, even though the negatively charged surface makes it weaker to adsorb As than Cd (Wang et al., 2015). CMP brings a large amount of P, which combines with Cd to form $Cd_3(PO_4)_2$ precipitation, thereby reducing the free Cd. Furthermore, with the increase in Cd/As or As/Cd concentration ratio at the mineral interface, the interaction mechanism of Cd and As changes from electrostatic adsorption to the formation of interface-As-Cd ternary complexes, and then becomes the formation of surface co-precipitation (Jiang et al., 2013; Tao et al., 2022). In this study, the co-adsorption between Cd and As was also observed as analyzed by ABT. Since the concentration of As was much higher than that of Cd, As and Cd may interact on soil colloidal particles mainly through the formation of surface precipitation. Further study on this point is needed in the future.

5. Conclusion

In the study, we demonstrated that ridging combined with biochar or CMP can effectively reduce the content of As in rice grains and maintain the content of Cd in grains at a low level. The aerobic soil habitat after ridging promotes the association of As with poorly/well-crystallized Fe/Al and the association of Cd with Mn-(hydro)oxides. Remarkably, the new soil habitat resulting from this new measure changes the soil pH and Eh and enhanced the interaction of Ca, Fe and Mn with Cd and As in the soil solution, which caused a synergistic decrease in the bioavailability of As and Cd. Ridging is not only a traditional agronomic but also an environmentally friendly practice in waterlogged paddy fields. Biochar is a resource-recycling biological material with carbon sequestration potential, and CMP is a commonly used alkaline fertilizer in acidic soils. The proposed strategy is a new use of traditional measures, which has the advantages of economic cost efficiency, environmentally friendly and resource utilization. Although the Cd and As content of the selected field plots exceeded the national risk screening values for soil contamination of agricultural land, they were not severely polluted. Nevertheless, it is clear that combined ridging and soil amendments can effectively reduce soil Cd and As availability. The synergistic remediation effect of the proposed strategy can play an important role in paddy soils with even higher As and Cd content by adjusting the dosage of soil amendments, which still needs to be further evaluated in the future.

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Figure Legends

Figure 1. Contents of total As and Cd of rice grain, husk, straw and root under different treatments. Data are mean ± SE (n = 3). Different letters represent significant differences ($P < 0.05$, LSD test or Kruskal-Wallis test) between the treatments and the control of the same rice variety.

Figure 2. Content of Cd and As in pore water under different treatments (field experiment).

Figure 3. Contents of Cd and As in soil solution of microcosm experiment. Data are mean ± SE (n = 3).

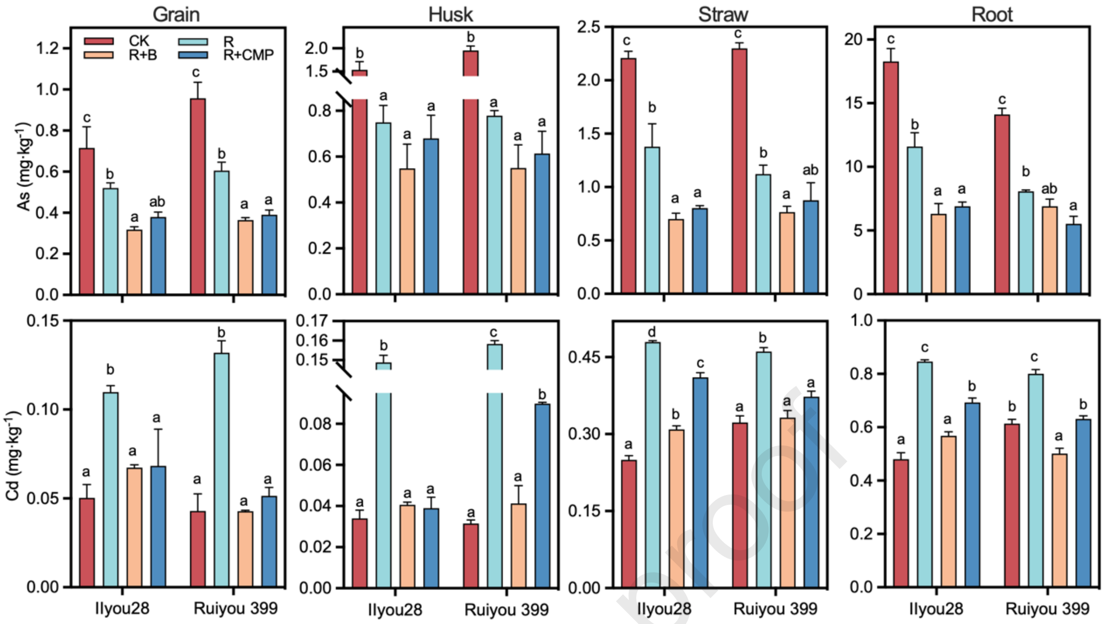
Figure 4. Spearman correlation of iAs and Cd with ions and environmental factors in soil solutions. The size of the bubble represents the correlation levels. The color of the bubble represents the significant levels. Red: positive correlation. Blue: negative correlation.

Figure 5. Aggregated boosted tree analysis for relative importance of elements for (a) Cd and (b) iAs in soil solutions under different treatments.

Figure 6. Aggregated boosted tree analysis for relative importance of elements for iAs in soil solutions under different treatments.

Figure 7. (a) Sequential extraction by Tessier method of Cd on the 1st day, 20th day and 40th day incubation. Total metals are divided into F1: exchangeable, F2: carbonate bound, F3: Mn oxide-bound, F4: Fe oxide-bound, F5: organically bound, and F6: residual fraction. (b) Sequential extraction results by Wenzel method of As on the 1st day, 20th day and 40th day incubation. Total metals are divided into F1: no-specifically sorbed, F2: specifically sorbed, F3: poorly-crystalline Fe/Al, F4: well-crystalline Fe/Al, and F5: residual fraction.

Figure 1


Grain
Husk
Straw
Root
CK
R+B
R
R+CMP
As (mg·kg^{-1})
Cd (mg·kg^{-1})
Ilyou28
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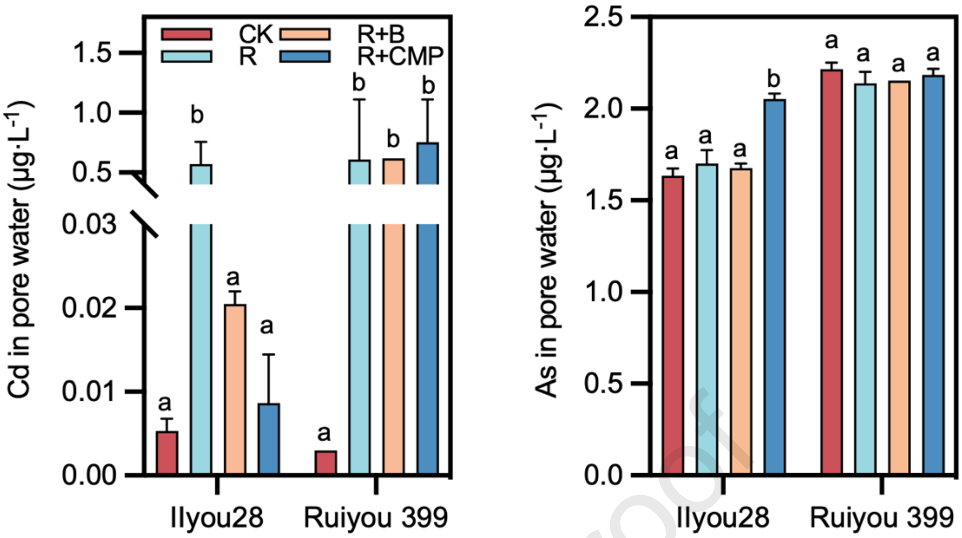
Ruiyou 399

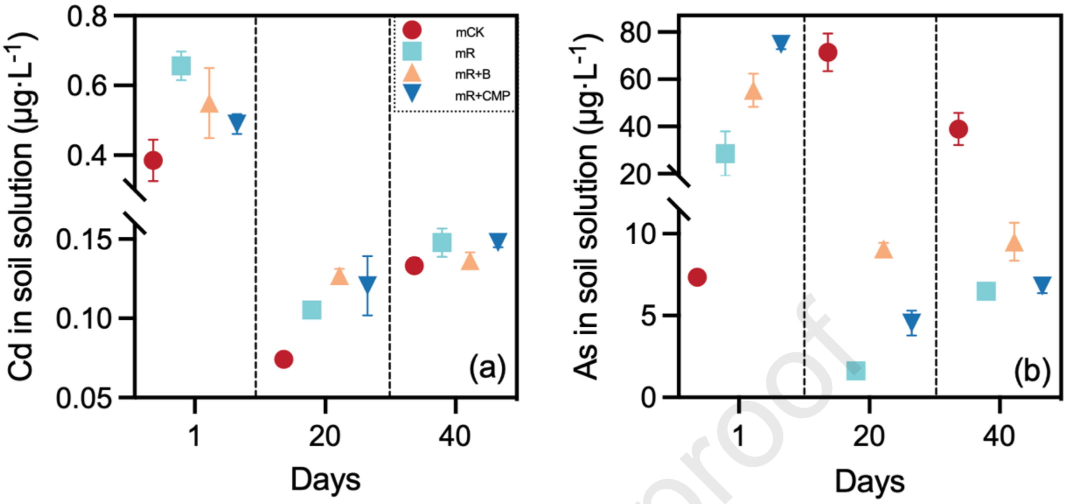
Figure 2


CK
R
R+B
R+CMP
Cd in pore water (µg·L⁻¹)
1.5
1.0
0.5
0.03
0.02
0.01
0.00
a
b
a
a
a
b
b
b
Ilyou28
Ruiyou 399
As in pore water (µg·L⁻¹)
2.5
2.0
1.5
1.0
0.5
0.0
a
a
a
b
a
a
a
a
Ilyou28
Ruiyou 399

836 **Figure 3**

837

838



839

Figure 4

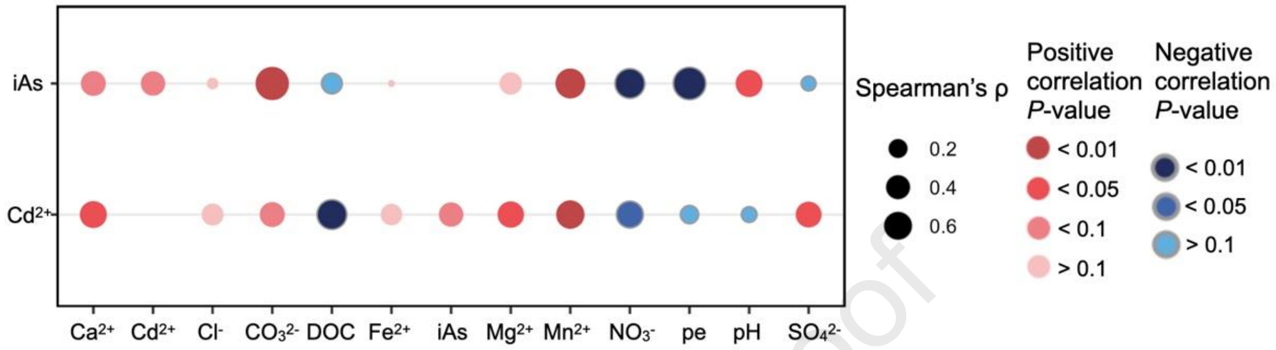

iAs
Cd2+
Ca2+
Cd2+
Cl-
CO32-
DOC
Fe2+
iAs
Mg2+
Mn2+
NO3-
pe
pH
SO42-
Spearman's ρ
0.2
0.4
0.6
Positive correlation P-value
< 0.01
< 0.05
< 0.1
> 0.1
Negative correlation P-value
< 0.01
< 0.05
> 0.1

Figure 5

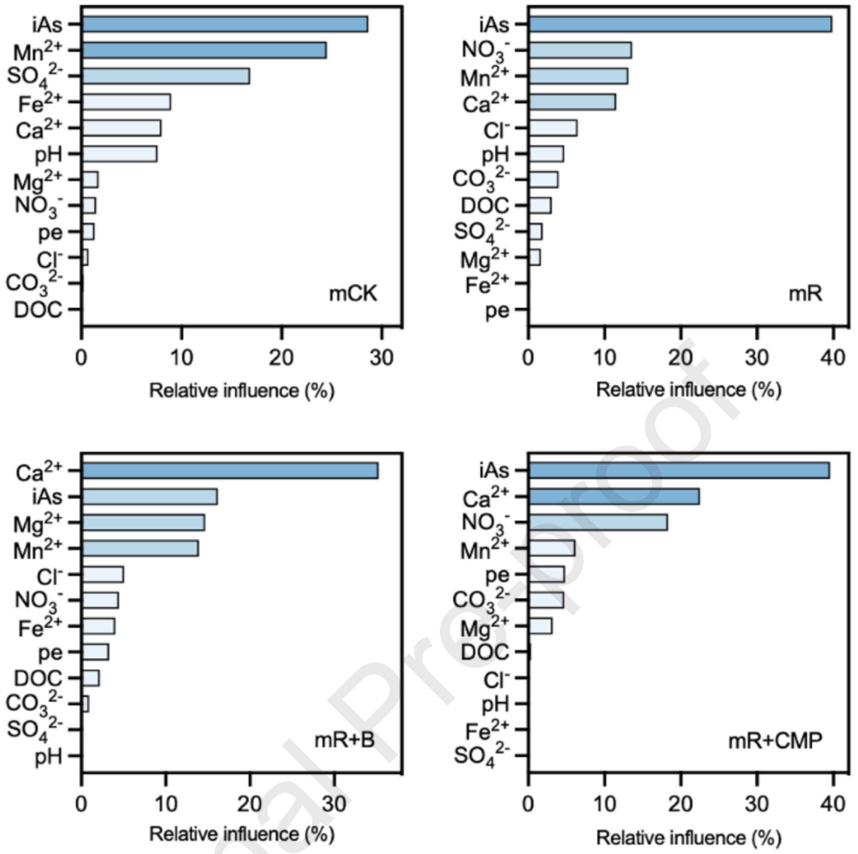

iAs
Mn^{2+}
SO$_4^{2-}$
Fe^{2+}
Ca^{2+}
pH
Mg^{2+}
NO$_3^-$
pe
Cl$^-$
CO$_3^{2-}$
DOC
mCK
0
10
20
30
Relative influence (%)
iAs
NO$_3^-$
Mn^{2+}
Ca^{2+}
Cl$^-$
pH
CO$_3^{2-}$
DOC
SO$_4^{2-}$
Mg^{2+}
Fe^{2+}
pe
mR
0
10
20
30
40
Relative influence (%)
Ca^{2+}
iAs
Mg^{2+}
Mn^{2+}
Cl$^-$
NO$_3^-$
Fe^{2+}
pe
DOC
CO$_3^{2-}$
SO$_4^{2-}$
pH
mR+B
0
10
20
30
Relative influence (%)
iAs
Ca^{2+}
NO$_3^-$
Mn^{2+}
pe
CO$_3^{2-}$
Mg^{2+}
DOC
Cl$^-$
pH
Fe^{2+}
SO$_4^{2-}$
mR+CMP
0
10
20
30
40
Relative influence (%)

Figure 6

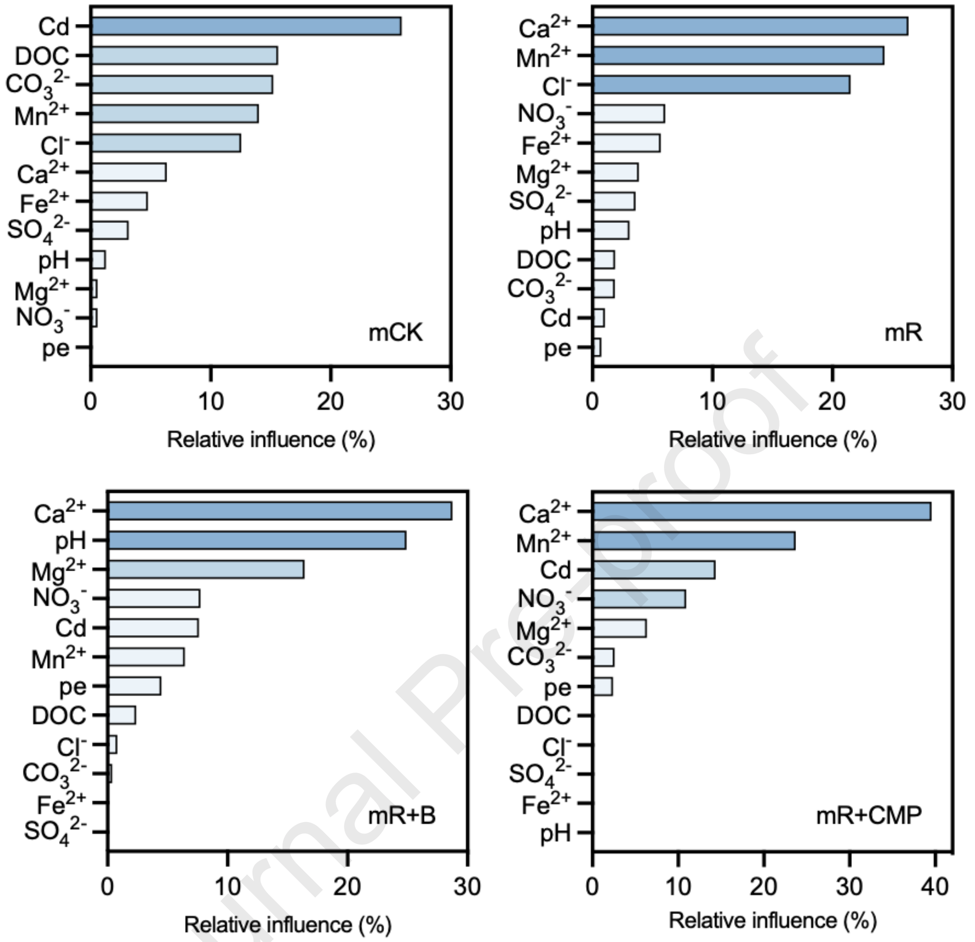
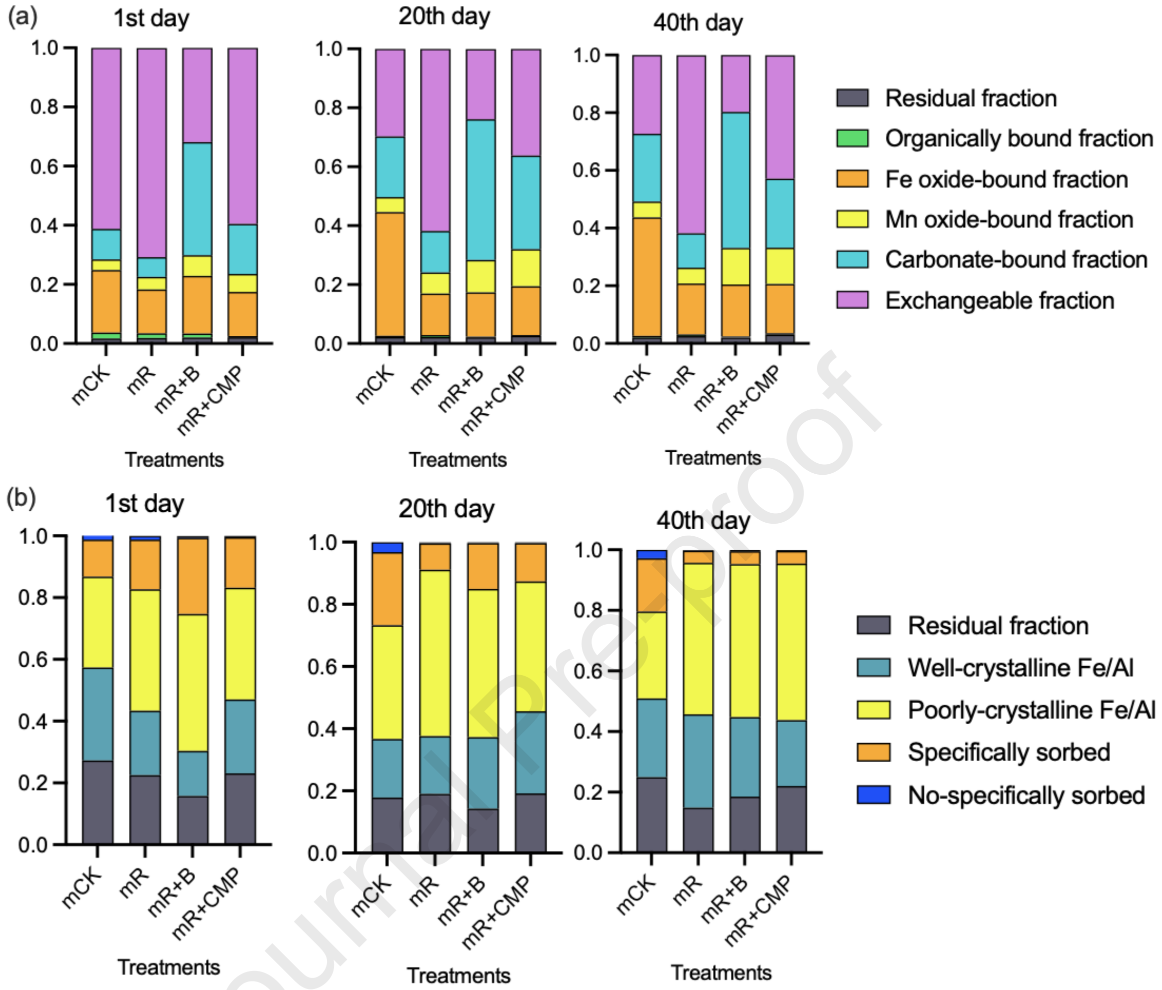

Cd
DOC
CO_3^{2-}
Mn^{2+}
Cl^-
Ca^{2+}
Fe^{2+}
SO_4^{2-}
pH
Mg^{2+}
NO_3^-
pe
mCK
0
10
20
30
Relative influence (%)
Ca^{2+}
Mn^{2+}
Cl^-
NO_3^-
Fe^{2+}
Mg^{2+}
SO_4^{2-}
pH
DOC
CO_3^{2-}
Cd
pe
mR
0
10
20
30
Relative influence (%)
Ca^{2+}
pH
Mg^{2+}
NO_3^-
Cd
Mn^{2+}
pe
DOC
Cl^-
CO_3^{2-}
Fe^{2+}
SO_4^{2-}
mR+B
0
10
20
30
Relative influence (%)
Ca^{2+}
Mn^{2+}
Cd
NO_3^-
Mg^{2+}
CO_3^{2-}
pe
DOC
Cl^-
SO_4^{2-}
Fe^{2+}
pH
mR+CMP
0
10
20
30
40
Relative influence (%)

Figure 7


(a)
1st day
20th day
40th day
1.0
0.8
0.6
0.4
0.2
0.0
mCK
mR
mR+B
mR+CMP
Treatments
Residual fraction
Organically bound fraction
Fe oxide-bound fraction
Mn oxide-bound fraction
Carbonate-bound fraction
Exchangeable fraction
(b)
1st day
20th day
40th day
Treatments
Residual fraction
Well-crystalline Fe/Al
Poorly-crystalline Fe/Al
Specifically sorbed
No-specifically sorbed

Highlights:

- New soil habitat formed by ridging combined with biochar or CMP application.
- Ridging combined with biochar or calcium-magnesium-phosphorus fertilizer reduce grain As and Cd.
- Enhanced interaction with Ca, Fe and Mn promotes reduction of As and Cd bioavailability.
- Fe/Mn-(hydro)oxides absorb As and secondary Mn mineral absorb Cd in soil solid phase.

CRediT author statement

Ting Zhang: Investigation, Methodology, Formal analysis, Visualization, Writing - original draft; **Md. Abu Sayem Jiku:** Investigation, Data curation; **Lingyi Li:** Investigation; **Yanxin Ren:** Investigation; **Lijuan Li:** Investigation; **Xibai Zeng:** Project administration, Funding acquisition; **Gilles Colinet:** Writing - Review & Editing; **Yuanyuan Sun:** Writing - Review & Editing, Funding acquisition; **Lijuan Huo:** Writing - Review & Editing; **Shiming Su:** Conceptualization, Methodology, Supervision, Funding acquisition, Writing-Reviewing and Editing.

Declaration of interests

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

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