# Natural field freeze-thaw process leads to different performances of soil amendments towards Cd immobilization and enrichment

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## Abstract

Cadmium (Cd) soil pollution is a global issue affecting crop production and food safety. Remediation methods involving *in-situ* Cd immobilization have been developed, but their effectiveness can diminish under seasonal freeze-thaw aging processes. In this study, we assessed the field performance of four soil treatments at a seasonally frozen rice paddy. Amendments were applied at 2 wt.%, including: (i) sepiolite (a 2:1 clay mineral), (ii) superphosphate, (iii) biochar (produced by rice husk at 500 °C for 2 h), and (iv) joint application of biochar & superphosphate (1:1 mixture by weight). Immobilization performance was determined as DTPA extractable Cd and plant uptake in various organs.

Overall, the four treatments significantly reduced Cd bioavailability during the plant growth period, with average DTPA-extractable concentrations decreasing by 43%, 34%, 39% and 45% for the four treatments, respectively, relative to untreated soil (control). Rice grain yields from the superphosphate and the joint application treatments increased by 8.0% and 11.8%, respectively, and Cd accumulation within those grains reduced by 14.3% and 48.9%, respectively. During the winter non-growth period, freeze-thaw aging facilitated Cd mobilization, with DTPA-extractable Cd increasing by 16.9% in the control soil, relative to the initial period. However, this reduced to 10.9%, 14.4%, 7.6% and 5.0%, for the sepiolite, superphosphate, biochar and joint application treatments, respectively. Overall, the joint application of biochar and superphosphate provided the best performance in terms of both long-term Cd immobilization and rice production enhancement, offering a green remediation option for risk management at Cd contaminated rice paddies in seasonally frozen regions.

**Keywords**: Soil quality, Soil amendment, Bioavailability, Sustainable remediation, Toxic metal(loid)s

## 1 Introduction

Cadmium (Cd) is a toxic and persistent (WHO, 1992) soil contaminant associated with anthropogenic activities such as mining, metallurgy and electroplating. Plant root systems uptake soil Cd (Antoniadis et al., 2017; Rizwan et al., 2018) causing 'cadmium stress', which is associated with disturbed photosynthesis and metabolic behavior (Bashir et al., 2018a; El Rasafi et al., 2020) and decreased enzymatic antioxidant activity (Abbas et al., 2018). The effect of Cd soil contamination on crops is a threat to food security and food safety, with human consumption of contaminated food a cause of emphysema, itai-itai disease, and kidney damage (Chen et al., 2021; Zeb et al., 2020).

Rice crops are consumed by approximately half of the world's population, with nearly 90% being cultivated in Eastern and Southern Asia (FAO, 2002). Compared with other cereals, rice plants uptake and accumulate high amounts of Cd, especially when grown in acidic contaminated soils (Cwielag-Drabek et al., 2020). This issue is severe in China, where up to 7% of investigated sampling points during a national soil survey contains Cd levels that exceed the relevant national standard (Huang et al., 2020a; MEP, 2014). In Hunan province, for example, 73% of rice grains sampled in a recent study conducted at a Cd contaminated area exceeded the Chinese national food standard (0.2 mg/kg) (Wang et al., 2016), creating a pathway for this element to affect human health (Yin et al., 2016).

The amount of soil Cd that accumulates in plant tissues relates to its 'bioavailability' (Antoniadis et al., 2017; Tian et al., 2021; Wang et al., 2019). Recent remediation efforts have focused on measures for reducing Cd bioavailability in soil (Bashir et al., 2018b; Ouhadi et al., 2021). One promising development is that natural or waste biomass-based materials (e.g. natural minerals or biochar) have shown multifaceted benefits as green and sustainable remediation materials for in-situ Cd immobilization (Hou, 2021a; Jin et al., 2021). For instance, Sun et al. (2016) found that the joint application of sepiolite and bentonite at an application rate of 2.4% decreased exchangeable Cd concentrations by 25.6-23.8% while reducing Cd bioaccumulation in brown rice by 62.1-73.6%, offering a simple yet effective method for the safe use of contaminated agricultural soil. Ran et al. (2019) reported that a mixture of clay minerals, animal manure and calcium-magnesium phosphate fertilizer also effectively decreased bioavailable (DTPA-extractable) Cd by 44.2-51.1%, while enhancing soil enzymatic activities and thus restoring soil health simultaneously. Such research development aligns well with the sustainable remediation principles (Hou, 2021b; Hou and O'Connor, 2020). However, the long-term performance of such soil amendments is not well understood owing to a lack of field studies (Wang et al., 2022a). Chemical, biological or physical aging processes may increase bioavailability levels in treated soils and freeze-thaw cycles in seasonally frozen areas may exacerbate the process (Meng et al., 2020).

Recently, biochar has attracted much attention from the environmental remediation industry (Hou et al., 2020; IBI, 2005; Yang et al., 2022b). This material is typified by an abundance of alkaline minerals that increase pH levels in acidic soils, hence, reducing Cd solubility in soil. Meanwhile, it has a high specific surface area and abundant surface functional groups, which also adsorbs soil Cd in a direct manner (Bandara et al., 2020; Shaheen and Rinklebe, 2015). In addition to biochar, 2:1 clay minerals, such as palygorskite and sepiolite, have shown promise as a soil amendment for metal immobilization (Hamid et al., 2020; Pei et al., 2021). Sepiolite is composed of blocks of two tetrahedral silica sheets sandwiching an octahedral sheet of magnesium oxide/hydroxide, exhibiting a high adsorption capacity towards contaminants due to the high specific surface area, cation exchange capacity, and abundant surface hydroxyl groups (Hamid et al., 2021; Padilla-Ortega et al., 2013). Furthermore, phosphate-containing compounds, such as triple superphosphate, diammonium phosphate, hydroxyapatite and apatite, can also immobilize heavy metals by precipitation, while simultaneously increasing crop yields (Efthymiou et al., 2018; Rehman and Qayyum, 2020; Xu et al., 2019). However, application of a certain type of amendment alone may result in rapidly fading performances in the long run. For clay minerals, ion exchange is a rather weak immobilization mechanism (Rybicka et al., 1995). Although a high immobilization rate may be observed at the initial stage due to high specific surface area of these amendments, loosely-bound metals may in turn release from the clay mineral under rainfall events (Wang et al., 2020a; Wu et al., 2016) . As for biochar, freeze-thaw, wet-dry cycling and chemical oxidation induce disintegration and release of dissolved black carbon, acting as a vehicle for metal migration (Yang et al., 2022a) . For phosphate fertilizers, the leaching loss of soluble phosphorous indicates that this type of amendment should be re-applied to soil for long-term immobilization (Cui et al., 2018).

Hence we attempt to find a solution that can stabilize soil Cd effectively under natural freeze-thaw process. A field trial was setup at a Cd contaminated site in Liaoning Province, China, with treatments of sepiolite, superphosphate, biochar, biochar & superphosphate, as well as a control group (no treatment). Based on the above-mentioned aging processes, it's proposed that joint application may overcome the obstacle of a single type of amendment, thus reducing the bioavailability of heavy metals under natural aging processes. In particular, our recent literature overview and modelling works on biochar-mineral interactions for soil metal(loid) immobilization suggested that assisted long-term immobilization can be achieved theoretically (Wang et al., 2022b; Wang et al., 2022c) , hence shedding light on this joint application design of biochar and superphosphate at field. This work aimed to 1) to assess the Cd bioavailability; 2) to determine the characteristics of soil nutrients and plant biomass; and, 3) to elucidate the uptake and accumulation of Cd in rice plants, and 4) to quantify the effect in response to freeze-thaw induced aging.



## 2 Materials and methods

### 2.1 Study area

The field trial site was located in Shenyang, Liaoning Province (N, 41°39′02″; E, 123°05′16″) where the soil is classified as an Anthrosol (FAO, 2014). The area is located in the Northeast China Plain, which has a temperate monsoon climate characterized by high temperature and rainfall in the summer season, and cold dry weather in the winter. A weather station recorded meteorological conditions during the experiment (Figure 1), revealing a minimum temperature of -16.3 °C and a maximum of 31.7 °C. The average annual precipitation was 821 mm, which mainly occurred during July to September. The annual evaporation was 1620 mm.

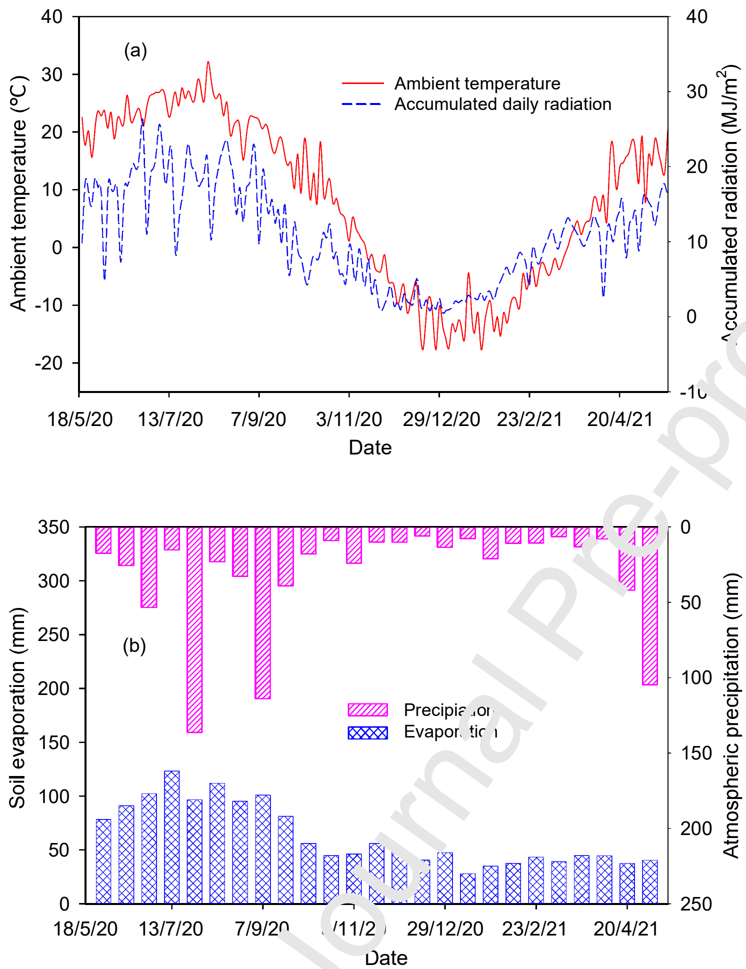



Figure 1. Meteorological indicators during the field experiment (a) ambient temperature and accumulated radiation; (b) soil evaporation and precipitation

## 2.2 Materials

Sepiolite, superphosphate and biochar were applied to the soil as soil amendments. Sepiolite is a magnesium-rich 2:1 clay mineral with layered structure (provided by Lianyungang Huifu Nano New Material Co., Ltd., China), with a high specific surface area being 726 $m^2$/g. Superphosphate is a water-soluble phosphate fertilizer composed of calcium sulfate ($CaSO_4$), calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), and phosphoric acid ($H_3PO_4$) with an effective phosphorus content >18% (provided by Jiangsu Meile Fertilizer Co., Ltd., China). Biochar was produced from rice husk via slow pyrolysis (pyrolysis temperature 500 °C, heating rate 15 °C $min^{-1}$, residence time 2 h), . The specific surface area and total pore volume of the material were 25.38 $m^2 \cdot g^{-1}$ and 0.04 $cm^3 \cdot g^{-1}$. For the joint application treatment, biochar and superphosphate were thoroughly mixed before application. Cd concentration in these amendments were all below 0.01 mg/kg.

A laser particle-size analyser was used to determine the size distribution of soil particles (wet mode). Soil pH was measured using a pH meter at a solid-liquid ratio of 1:5 (ISO, 2005). Electrical conductivity (EC) was similarly recorded using a conductivity meter. Soil organic carbon (SOC) content was measured with a total organic carbon (TOC) analyzer. Soil hydraulic conductivity was measured using a tension infiltration instrument, and the soil field capacity was determined based on the Wilcox method (Lu et al., 2014). Soil metal concentrations (Fe, Mn, Al, Cd) were determined by ICP-MS after $HNO_3$-HCl-HF digestion. The measured soil physicochemical properties for each treatment are shown in Table 1.

Table 1. Physicochemical properties of soils

| Properties | | Treatment | | | | |
|---|---|---|---|---|---|---|
| | | Control | Sepiolite | Superphosphate | Biochar | Joint application |
| Particle Size (%) | Clay (<0.002 mm) | 31.70 ± 1.46 | 27.70 ± 1.62 | 31.40 ± 2.46 | 30.30 ± 2.89 | 29.80 ± 1.56 |
| | Silt (0.002~0.05 mm) | 36.90 ± 1.25 | 35.50 ± 1.88 | 37.90 ± 1.17 | 37.20 ± 1.15 | 37.90 ± 1.73 |
| | Sand (>0.05 mm) | 31.40 ± 1.85 | 36.80 ± 1.19 | 30.70 ± 1.31 | 32.50 ± 1.15 | 32.30 ± 2.11 |
| pH | | 7.31 ± 0.04 | 8.21 ± 0.03 | 6.88 ± 0.04 | 7.87 ± 0.05 | 7.52 ± 0.03 |
| EC ($ms \cdot cm^{-1}$) | | 1.61 ± 0.04 | 1.52 ± 0.04 | 1.84 ± 0.06 | 1.69 ± 0.06 | 1.78 ± 0.05 |
| Soil organic carbon ($g \cdot kg^{-1}$) | | 24.45 ± 1.31 | 22.81 ± 0.94 | 25.69 ± 1.32 | 34.74 ± 1.67 | 31.27 ± 1.48 |
| Saturated hydraulic conductivity ($cm \cdot h^{-1}$) | | 1.63 ± 0.04 | 1.45 ± 0.06 | 1.68 ± 0.04 | 1.42 ± 0.03 | 1.49 ± 0.05 |
| Field capacity ($cm^3 \cdot cm^{-3}$) | | 28.16 ± 1.52 | 31.13 ± 1.26 | 27.11 ± 1.14 | 34.19 ± 1.87 | 32.24 ± 1.54 |
| Total Fe ($g \cdot kg^{-1}$) | | 22.56 ± 1.50 | 23.43 ± 1.67 | 25.12 ± 1.92 | 23.33 ± 1.14 | 24.69 ± 1.39 |
| Total Mn ($mg \cdot kg^{-1}$) | | 958.34 ± 22.13 | 879.45 ±26.47 | 923.45 ± 19.86 | 887.57 ± 27.45 | 925.45 ± 25.17 |
| Total Al ($mg \cdot kg^{-1}$) | | 1874.57 ± 62.81 | 1782.31 ± 35.22 | 1832.12 ± 70.08 | 1833.12 ± 68.44 | 1851.23 ± 46.14 |
| Total Cd ($mg \cdot kg^{-1}$) | | 2.02 ± 0.08 | 1.89 ± 0.09 | 1.86 ± 0.12 | 1.93 ± 0.11 | 1.97 ± 0.15 |
| Available Cd ($mg \cdot kg^{-1}$) | | 1.31 ± 0.06 | - | - | - | - |

## 2.3 Experimental design

The test period was from May 18, 2020 to April 9, 2021. Treatments were established as follows: (i) control (no amendment); (ii) sepiolite; (iii) superphosphate; (iv) biochar; and, (v) joint application. The application rate of amendment was 2% by weight (for the joint application group, the dosage of the 1:1 mixture was also set as 2%). The size of each test plot was 1 × 1 m with a planting density of 25 plants/$m^2$. The amendments were applied on May 8, 2020, and manually mixed into the surface soil layer (0-20 cm). All treatments were conducted in triplicate (n=3). In order to better reveal the characteristics of soil Cd bioavailability corresponding to the nodes of each growth stage of rice, the sampling interval of soil and rice samples was set at 25 d with the experimental period divided into the growth period (18 may 2020 - 15 October 2020) and the non-growth period (November 10, 2020 - April 9, 2021), with natural freeze-thaw event occurring during the latter one (Figure 1).

The rice variety was "Liaojing 433", which was transplanted on May 16, 2021, and harvested on October 7, 2021. A basal NPK (N: $P_2O_5$: $K_2O$ of 11:6:8) fertilizer was applied at a rate of 500 kg/ha to the soil one week before transplanting (Sui et al., 2020). Another 200 kg/ha tillering fertilizer was applied 15 days after transplanting was completed. At sampling event, soil samples were collected manually using a soil drill (sampling depth 0-20 cm). Due to spatial heterogeneity, five soil samples were collected from each plot in an "S-type" pattern (Cappai et al., 2017).

### 2.4 Sample analysis

Soil samples were air-dried and the particle size distribution determined by the wet sieve method *(Elliott, 1986)* and the soil mean weight diameter (MWD) calculated. Available Cd was extracted with diethylenetriaminepentaacetic acid (DTPA) by shaking at constant temperature for 2 h (US EPA, 2012) before Cd analysis by ICP-MS. Soil available N was measured in a closed vessel by the alkali-hydrolysis and diffusion method (Zeng et al., 2018). Available P was determined following extraction with $NaHCO_3$ solution at 25 °C ± 1 °C, and determined by the molybdenum antimony-ascorbic acid colorimetric method (Pansu and Gautheyrou, 2006). Plants sampled from each area were separated into root, shoot, leaf and grain organs, which were washed and dried at 65 °C for 96 h (Lei et al., 2017). The dried plant materials were digested with a mixture of $HNO_3$ and $HClO_4$ (2:1, v/v) before Cd analysis by ICP-MS.

### 2.5 Statistical analyses

The translocation factor (TF), distribution factor (DF), and the bio-concentration factor (BCF) were calculated as follows (Antoniadis et al., 2017):

$$TF_{organ1-organ2} = C_{organ2}/C_{organ1} \quad (1)$$

$$DF_{organ} = T_{organ}/T_{total} \quad (2)$$

$$BCF_{organ} = C_{organ}/C_{soil} \quad (3)$$

Where $C_{organ1}$ is the Cd concentration in the root, $C_{organ2}$ represents a particular organ aboveground (i.e. rice shoot, leaf, and grain), and $C_{soil}$ is the Cd content of the soil. $T_{organ}$ is the accumulation of Cd in all aboveground organs, and the $T_{total}$ represents total Cd in the plant.

Statistical analyses and data visualization were conducted using IBM SPSS 19.0 and Sigmaplot 12.5 software. The Fisher LSD test was used to identify differences in the soil and plants indicators among treatments (significance level $p < .05$).

## 3 Results and discussion

### 3.1 Soil characteristics

The untreated control soil (control) had an average pH value of 7.33 during the initial growth period, whereas the pH values for the various treated soils varied according to the amendments used (Figure 2a). The clay amendment led to an increase in soil pH (Brady and Weil, 2014) and dissolution of biochar ash content also increased soil pH (Kwon et al., 2020). Conversely, superphosphate reduced the soil pH (from 6.95 to 6.57), as this material is prepared from sulfuric acid (Wang et al., 2020c; Wu et al., 2019) and leads to the formation and accumulation of soil organic acids (Wang et al., 2013).

From the initial period (0 d), the superphosphate and joint application treatments increased the amount of soluble salts in the soil, with electrical conductivity (EC) values increasing by 23.49% and 19.26%, respectively, relative to the control. Superphosphate is rich in $Ca^{2+}$, $SO_4^{2-}$, $H_2PO_4^-$ and other soluble ions, which enhance EC values (Xia et al., 2019). The ash content of biochar provides alkaline carbonate, silica, organic and inorganic nitrogen (Nigussie et al., 2012), it also has strong adsorption and cation exchange capacities, which inhibit the release of soil salts (Younis et al., 2020). Similarly, the high adsorption capacity of the sepiolite clay would also have prevented the release of salts (Neaman and Singer, 2004). Therefore, although the EC values in the biochar and sepiolite treatments were slightly higher than the control, they remained relatively stable. It is noticeable that in mid plant growth, the soil EC values decreased and fluctuated in the control and superphosphate treatment. This relates to the rice plants requiring irrigation and subsequent infiltration and evaporation of soil pore water leading to salt migration (Phogat et al., 2020; Yin et al., 2021).

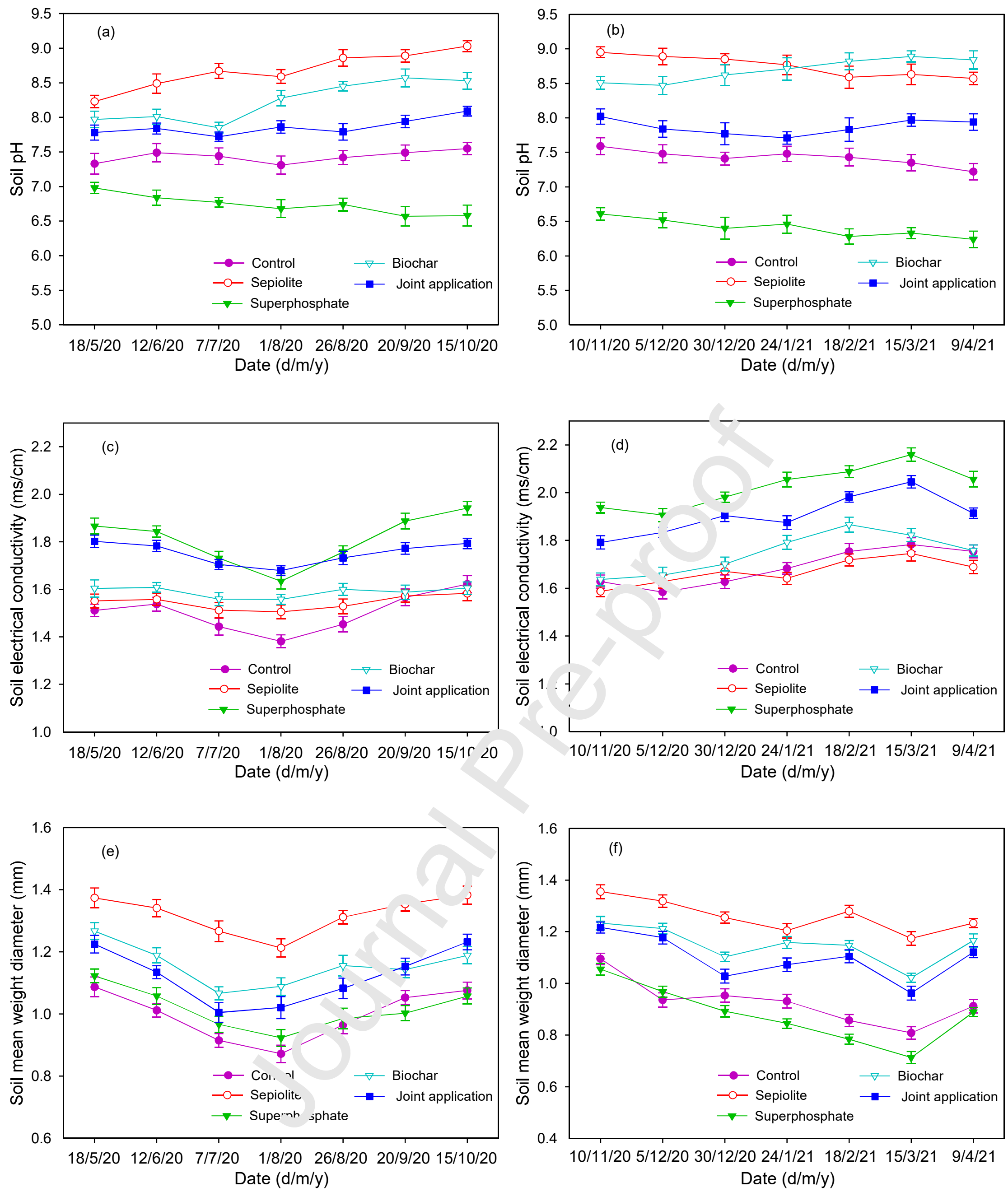



Figure 2. Variation in soil physicochemical properties - error bars show standard error. (a) soil pH in the growth period; (b) soil pH in the non-growth period; (c) soil electrical conductivity (EC) in the growth period; (d) soil EC in the non-growth period; (e) soil mean weight diameter (MWD) in the growth period; (f) soil MWD in the non-growth period



Soil aggregation increased after the addition of the immobilization agents to the soil. For instance, the MWD value for the control was 1.087 mm in the initial growth period, which was 26.41%, 16.56% and 12.69% higher for the sepiolite, biochar and the joint application treatments, respectively. With progression of the growth period, the MWD values displayed a "U" trend. The increased soil MWD relates to biochar derived microbial binding and sepiolite having a micro-fibrous shape and high specific surface area, thus both promoting the aggregation of soil particles (Neaman and Singer, 2004).

### 3.2 Potential “bioavailability” of Cd as determined by chemical extraction

For the control treatment, the average DTPA extractable-Cd content was 1.32 mg/kg in the initial growth period (Figure 3a). In comparison, extractable-Cd for the sepiolite, superphosphate, biochar and the joint application treatments decreased by 43.6%, 33.3%, 39.6% and 42.6%, respectively. Sepiolite elevates soil alkalinity and surface charge negativity, forming precipitation products as hydroxides and carbonates, thus reducing bioavailability (Chen et al., 2020; Yu et al., 2016). As also found by Liang et al. (2016, sepiolite amendment triggered a reduction in the exchangeable Cd geochemical fraction and an increase in the residual form. Biochar contains various functional groups including hydroxyl, carboxyl and carboxyl, which immobilize Cd via surface complexation and other mechanisms (Ahmad et al., 2014). Moreover, biochar reduces dissociation of Cd via electrostatic attraction owing to its negative charge (O'Connor et al., 2018). In addition, the porous carbon matrix of biochar serves well as a habitat for microorganisms including bacteria and fungi to colonize, where microorganisms immobilized onto biochar may also promote the biosorption and immobilization of heavy metals (Cao et al., 2011). Superphosphate amendment leads to the formation of cadmium phosphate via surface polymerization or fixation mechanisms according to Da Rocha et al. (2002. Therefore, the treatments reduced Cd bioavailability to varying degrees. The effects of sepiolite and the joint application groups were significant.

Apart from this, the average DTPA extractable-Cd content of the control treatment showed first a decreasing and then increasing trend accompanied by plant growth. This trend relates to soluble Cd migrating downward through soil pores under irrigation during the initial period (Kakeh et al., 2020), while evaporation mainly occurred during the middle and late period (July and August) (Figure 1b). The result further verifies that the hydrological cycle of irrigated paddy fields affects soluble metal ion levels (Zhang et al., 2020a).

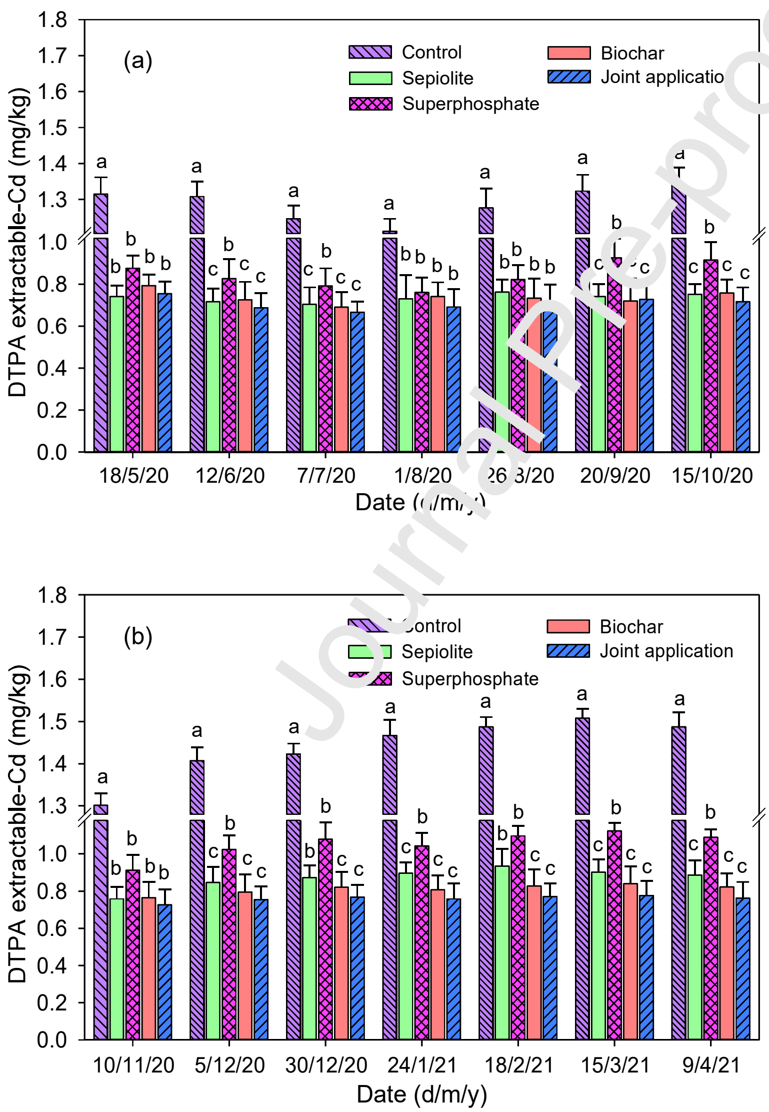



Figure 3. Bioavailability as DTPA extractable Cd – error bars show standard error (a) DTPA extractable-Cd in growth period; (b) DTPA extractable-Cd in non-growth period)

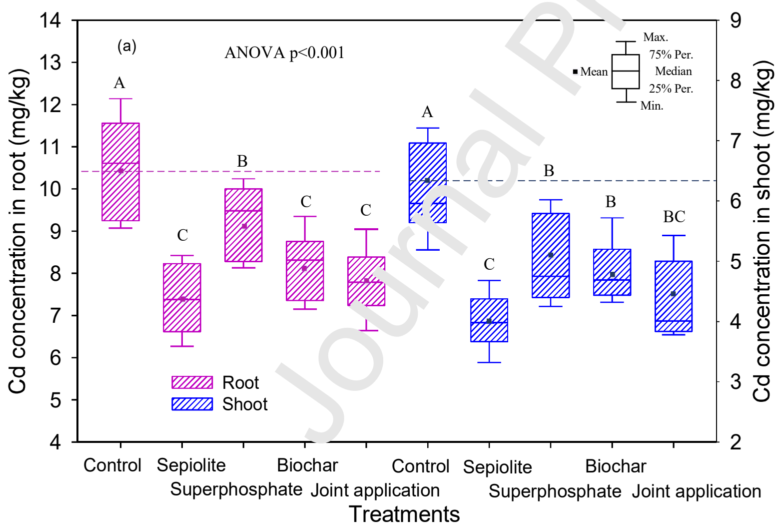
The FTIR spectra demonstrates that biochar contained abundant functional groups (Figure S1). A band was identified at 1684 $cm^{-1}$, which corresponds to the –COOH stretching vibration. The band at 1365 $cm^{-1}$ represents the stretching vibration of C–OH of the alcohol and carboxylic acid groups. In addition, the stretching vibration at 1126 $cm^{-1}$ indicates the superposition of the ester and ether groups. The abundant oxygen-containing functional groups may have contributed to field immobilization performances. As for the sepiolite, the band at 3772 $cm^{-1}$ reveals the stretching vibration peak of octahedral Mg-OH, which will also promote the complexation of Cd. Similarly, the XRD pattern and elemental compositions of immobilized materials are shown in Figure S2&S3.

### 3.3 Plant bioavailability: Cd-in rice tissues

Overall, root Cd concentrations were lower among the treatments than the control (Figure 4). This was most notable for the sepiolite treatment, being 42.4%, 21.1%, 11.3% and 5.3% lower than the control, superphosphate, biochar and joint application treatments, respectively. The mineral composition of sepiolite would have increased the carbonate-bound and residual fractions of soil Cd, which is associated with lower Cd uptake (Liang et al., 2014). Surface complexation with hydroxyls at Si-OH and Mg-OH sites may have also contributed to the high Cd immobilization capacity of the clay mineral (Sheikhhosseini et al., 2013).

The average Cd concentration within the rice grains was 0.56 mg/kg in the control group. Whereas this value decreased by 21.43% ~ 42.78% in the four immobilization treatments (decreased most for the joint application treatment), indicating a synergistic effect of biochar and superphosphate application. It may be attributed to the fact that 1) the porous structure of biochar favors superphosphate adsorption, thus diminishing the leaching loss of phosphate accounting for Cd precipitation (Herath et al., 2020), and that 2) phosphate reduced Cd stress within the plants (Dang et al., 2016). The joint application of biochar and calcium superphosphate also increased soil pH as other single treatments did, contributing to decreased bioavailability of Cd and the enrichment of metals in rice as compared with the control group (Moragues-Saitua et al., 2017).

It's noteworthy that although Cd content in grain decreased after using soil amendments, it still exceeded the limit standard (0.2 mg/kg) of the Chinese standard (GB 2762-2017). It could be that the amendments applied at 2% may not be sufficient to fully come into interact with labile Cd. The alkaline nature and fine texture of soil (Table 1) also hindered the effectiveness of immobilization, as evidenced by previous meta-analyses (Chen et al., 2018; Hu et al., 2020).



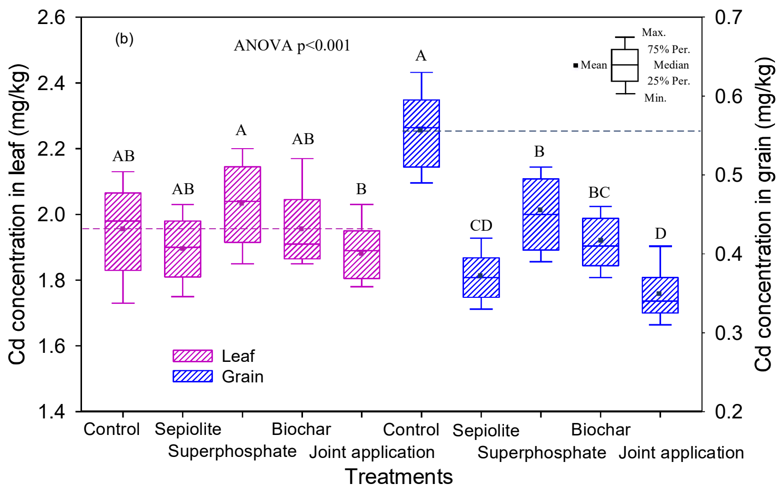



Figure 4. Accumulation of Cd in various plant organs (a) Cd concentrations in roots and shoots; (b) Cd concentrations in leaves and grains

The TF, DF and BCF values for various plant organs were calculated (Table 2). Among the five treatments, the sepiolite and the joint application treatments showed a strong advantage, with the TF of Cd in the shoot being 16.3% and 14.6% lower than the control, respectively. The TF of Cd in the grains was also lowest for the joint application treatment.

All four of the treatments reduced Cd accumulation within the rice grains. The average DF value for grain Cd was 0.062 for the control treatment, which decreased by 16.2%, 8.1%, 11.3% and 32.3% for the sepiolite, superphosphate, biochar and joint application treatments, respectively. The BCF values for Cd in shoot, leaf and grain, reduced by varying degrees following the addition of the immobilized agents. Chen et al. (2020 suggested that sepiolite is an efficient soil amendment to remediate Cd contaminated acid soils. Biochar provides not only causes a reduction of Cd uptake levels but also offers essential nutrients to improve crop yields (Bolan et al., 2013; El-Naggar et al., 2020).

Table 2. Translocation and bio-concentration of Cd in various organs of plants (mean ± standard deviation).

| Index | Plant organ | Treatments | | | | |
|---|---|---|---|---|---|---|
| | | Control | Sepiolite | Superphosphate | Biochar | Joint application |
| Translocation Factor (TF) | Shoot | 0.616 ± 0.034a | 0.516 ± 0.022c | 0.575 ± 0.031b | 0.543 ± 0.025b | 0.526 ± 0.018c |
| | Leaf | 0.258 ± 0.012a | 0.246 ± 0.015a | 0.253 ± 0.015a | 0.248 ± 0.013a | 0.244 ± 0.017a |
| | Grain | 0.069 ± 0.007a | 0.042 ± 0.005b | 0.047 ± 0.007b | 0.049 ± 0.009b | 0.038 ± 0.005b |
| Distribution Factor (DF) | Shoot | 0.698 ± 0.038a | 0.651 ± 0.025b | 0.637 ± 0.037c | 0.675 ± 0.032ab | 0.667 ± 0.029ab |
| | Leaf | 0.241 ± 0.021c | 0.298 ± 0.016ab | 0.306 ± 0.013a | 0.270 ± 0.015b | 0.291 ± 0.018ab |
| | Grain | 0.062 ± 0.008a | 0.052 ± 0.008b | 0.057 ± 0.006ab | 0.055 ± 0.007ab | 0.042 ± 0.006c |
| Bio-concentration Factor (BCF) | Shoot | 1.627 ± 0.065a | 1.103 ± 0.044c | 1.504 ± 0.058b | 1.395 ± 0.056c | 1.183 ± 0.043c |
| | Leaf | 0.593 ± 0.019a | 0.582 ± 0.019a | 0.601 ± 0.021a | 0.595 ± 0.018a | 0.588 ± 0.027a |
| | Grain | 0.154 ± 0.012a | 0.102 ± 0.008c | 0.131 ± 0.007b | 0.118 ± 0.008c | 0.092 ± 0.009c |

Note: Different lower-case letters indicate significant differences of translocation and bio-concentration of Cd in various organs ($p < 0.05$).

## 3.4 Soil nutrients

Biochar and superphosphate treatments increased the soil available nitrogen and phosphorus contents (Figure 5). Available nitrogen gradually decreased throughout the plant growth period, reflecting its role as an essential element. Average available nitrogen for the superphosphate, biochar and control treatments increased by 16.2%, 36.9% and 43.8%, respectively, compared to the control. Biochar applications have been reported to stimulate microbial growth and immobilize plant-available nitrogen (Deenik et al., 2010). Biochars with high H/C ratios may increase N mineralization rates (Liang et al., 2021; Pereira et al., 2015). Meanwhile, an increase in available nitrogen in response to superphosphate application relates to its effect on soil acidity-alkalinity and oxidation-reduction potential (ORP), which regulates nitrogen's state (Curtin et al., 2019). The data supports the hypothesis that N mineralization increases in response to P-fertilization.

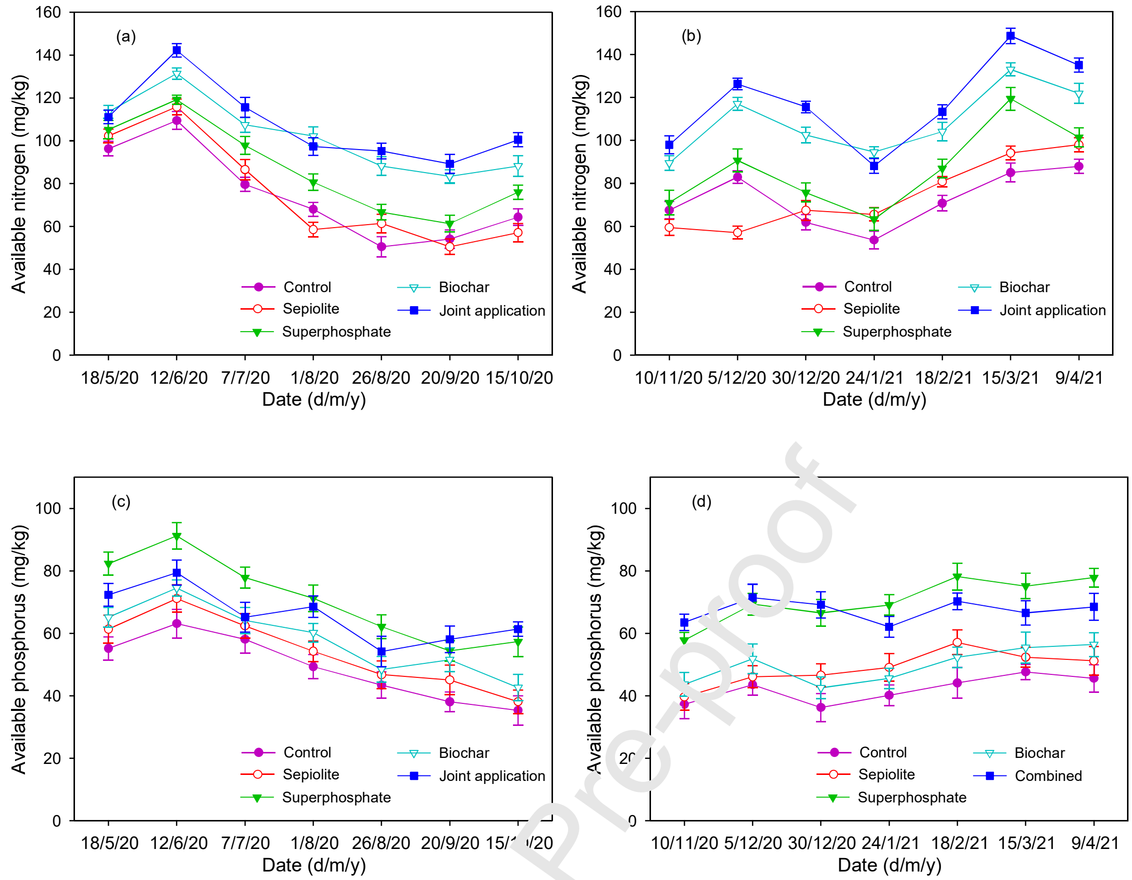



Figure 5. Variation characteristics of soil nutrient content (a) Available N in growth period; (b) Available N in non-growth period; (c) Available P in growth period; (d) Available P in non-growth period (standard error was used to present the error bars).

During the initial growth period, the average available phosphorus content was 61.37 mg/kg for the control treatment, which increased by 11.2%, 49.1%, 18.1% and 31.1% for sepiolite, superphosphate, biochar and the joint application treatments, respectively. Although available phosphorus gradually decreased for all treatments, the superphosphate, joint application and biochar treatments showed the highest levels overall. The available P content in biochar was as high as 21.7 mg/kg, acting as a P source in soil (Gao et al., 2019). In addition, activities of microorganisms that can secrete phosphatase were stimulated by biochar, enhancing the decomposition and mineralization of organic phosphorus (Cleveland and Liptzin, 2007). Meanwhile, sufficient nitrogen supply would increase the microbial P demand and contribute to a net increase in available P (Makoto et al., 2011). It is unsurprising that the superphosphate application elevated available P and enhanced the soil nutrient supply.

### 3.5 Biomass yield

At the mature stage, average root weights increased by 3.1%, 6.6%, 12.5% and 18.8% for the sepiolite, superphosphate, biochar and joint application treatments compared to the control, respectively (Table 3). Shoot weights were highest for plants under the superphosphate and joint application treatments, which increased by 13.1% and 10.6%, respectively. This finding likely owes to the biochar effect on soil water holding capacity and other hydrological properties (Githinji, 2014) while the P-fertilizer provided sufficient nutrient supply to promote root development (Zhang et al., 2016). P-fertilizer also enhances carbohydrate transport within plants, which relates to increased biomass (da Costa et al., 2015).

It is noteworthy that the number of rice grains from plants from the joint application treatment was significantly higher than that of other treatments. This is consistent with the findings of Carneiro et al. (2021), who reported synergistic effects for the application of biochar and P-fertilizer, which promotes N, P, K and other element absorption by plants.



Table 3. Effects of different treatments on biomass of organs in rice plants (mean ± standard deviation, t/ha)

| Treatment | Heading period | | | Mature period | | | |
|---|---|---|---|---|---|---|---|
| | Root | Shoot | Leaf | Root | Shoot | Leaf | Grain |
| Control | 2.11 ± 0.11c | 4.13 ± 0.25c | 1.98 ± 0.15c | 2.88 ± 0.15c | 6.35 ± 0.38c | 2.86 ± 0.13c | 7.46 ± 0.35c |
| Sepiolite | 2.14 ± 0.15c | 4.17 ± 0.27c | 2.09 ± 0.12c | 2.97 ± 0.17c | 6.19 ± 0.34c | 3.11 ± 0.17ab | 7.37 ± 0.23c |
| Superphosphate | 2.23 ± 0.12b | 4.57 ± 0.15a | 2.32 ± 0.18a | 3.07 ± 0.11b | 7.18 ± 0.28a | 3.05 ± 0.15b | 8.06 ± 0.37ab |
| Biochar | 2.45 ± 0.14a | 4.32 ± 0.21b | 2.27 ± 0.14b | 3.24 ± 0.16ab | 6.73 ± 0.34b | 3.12 ± 0.19a | 7.77 ± 0.26b |
| Joint application | 2.29 ± 0.12b | 4.43 ± 0.18ab | 2.39 ± .017a | 3.42 ± 0.15a | 7.02 ± 0.37ab | 3.21 ± 0.17a | 8.34 ± 0.29a |

Note: Different lower-case letters indicate significant differences of organ biomass ($p < 0.05$).

### 3.6 Effect of freeze-thaw aging

### 3.6.1 Soil properties

After the plant growth period had ended, the treatments were exposed freeze-thaw cycles during the winter season. The soil pH for this period is shown in Figure 2b, showing that the pH of the superphosphate treated soil reduced from 6.61 to 6.24, thereby increasing the risk of Cd remobilization. Superphosphate carries free acid, and the freeze-thaw aging would have driven soil particle disintegration and the release of acidic substances (Pegoraro et al., 2018). Conversely, biochar enhanced the soil alkalinity over time owing to the alkaline ash component being gradually released as freeze-thaw cycles broke down the biochar structure (de la Rosa et al., 2018). Therefore, the joint application provided a buffering effect with less change in soil pH observed than other treatments. The pH of the sepiolite treatment showed a decreasing trend, which is attributed to the hydrolysate of CaO contacting $CO_2$ during freeze-thaw aging, resulting in the formation of carbonates and reduced soil pH (Zhang et al., 2019).

Recorded electrical conductivity (EC) values among five treatments generally increased, gradually, during the aging period (Figure 2d). The sepiolite and biochar treatments decreased by 20.2% and 9.1% relative to the control group, respectively. Decreasing EC in biochar treated soils is attributed to frost heave breaking down the biochar structure, thus, increasing its specific surface area and ion adsorption sites, which would suppresses the concentration of free ions (Cui et al., 2021; Wang et al., 2020b). In addition, sepiolite holds colloidal properties, which facilitate soil particle aggregation and, thus, effectively resists the freeze-thaw aging impact on salt ion release (Moreno-Maroto et al., 2017). The EC values for the superphosphate treatment increased relative to the control group. Although freeze-thaw cycles led to phosphate dissolution, which binds with metals through complexation (Zhang et al., 2020b), acid radicals released from soil particles may adversely affect Cd leaching (Zhou et al., 2021).

The soil MWD values showed a decreasing trend with the control group MWD being 0.912 mm at the end of the aging period (Figure 2f). Biochar and sepiolite inhibited the fragmentation of soil particles with MWD values for the sepiolite, biochar and joint application treatments being 26.0%, 21.8% and 18.6% lower than the control group, respectively. Thus may be due to soil particles released from aggregate breakdown re-polymerizing as medium-sized aggregates with the presence of biochar (Hagner et al., 2016). The results also show the advantage of sepiolite on water-stable soil aggregates as discussed by Sheikhhosseini et al. (2014.

### 3.6.2 Cd remobilization

Following the freeze-thaw aging period, DTPA-extractable Cd in the control soil increased by 16.9% relative to the initial period. For the sepiolite, superphosphate, biochar and joint application treatments, it increased by 10.9%, 14.4%, 7.6% and 5.0%, respectively. This is because freeze-thaw aging would have broken down large-size soil particles, resulting in the release of exchangeable Cd (Hou et al., 2021). Compared with fresh biochar, aging affects the particle size, pore diameter and its adsorption capacity. Previous studies have suggested that natural field aging in cold regions can cause the structure of rice husk biochar to collapse (Rafiq et al., 2020). Atmospheric contact during natural aging, on the other hand, would lead to the introduction of additional oxygen-containing functional groups on the biochar surface, which enhance phosphate fixation and, therefore, Cd stabilization increased in the joint application treated soil (Huang et al., 2020b; Zhao et al., 2020). For the sepiolite treatment, the immobilization effect of Cd attenuated with freeze-thaw aging. Nevertheless, the mineral components promoted the conversion of Cd from exchangeable to carbonate-bound and residual fractions, thus limiting the aging effects (Zhu et al., 2010).

### 3.6.3 Nutrient availability

Available nitrogen content in the biochar and superphosphate treated soils improved compared to other treatments (Figure 5b). Interestingly, the trend showed peaks at the beginning and end of the aging period. The reason may be that some small molecular carbon particles were wrapped in porous structure, and freeze-thaw cycles accelerated the mineralization and decomposition of biochar derived dissolved organic carbon (DOC) and generated available nitrogen (Juan et al., 2020). Meanwhile, low temperatures led to the dissociation of microbial cells, releasing inorganic nitrogen and other available elements (Gavrichkova et al., 2020). As the freezing period passes, the soil was in a stable freezing state, and the replenishment effect of available nitrogen was weakened. Whereas the soil denitrifying enzyme still maintains high activity in the coldest month (Pelletier et al., 1999), resulting in a decreasing trend of available nitrogen from 5/12/20 to 24/1/21. Notably, the increase in soil temperature in spring enhanced microbial activity and accelerated the rate of soil nitrogen mineralization (Liu et al., 2021), therefore the content of soil available nitrogen showed an increasing trend from 24/1/21 to 15/3/21. Overall, the synergistic effect of the biochar and superphosphate treatment effectively regulated the carbon-nitrogen cycle with replenished soil available nitrogen content. In contrast, the effect of freeze-thaw aging on soil available phosphorus was relatively weak. Only in the superphosphate treatment was a noticeable effect seen with a variation of 20.08 mg/kg, which indicated that available phosphorus stored in soil aggregates reactivated with aging (Cheng et al., 2018).

## 4 Conclusions

The results revealed that joint application of biochar and superphosphate enhanced both Cd immobilization and nutrient supply in the plant growth period. Importantly, joint application was more effective in inhibiting Cd accumulation in rice organs and increasing the crop yield compared with biochar and superphosphate applications alone. The sepiolite treatment effectively reduced DTPA-extractable Cd, however, the ability to resist Cd enrichment and promote nutrient assimilation was evidently lacking. Additionally, freeze-thaw aging during the winter non-growth period damaged soil aggregates and remobilized soil Cd. However, biochar treatments promoted the formation of medium-sized soil agglomerates. Moreover, the fragmentation of biochar by freeze-thaw cycles created more sorption sites and introduced additional functional groups with binding capacity, which inhibited Cd remobilization. Therefore, we conclude that joint application of biochar and superphosphate suppresses the transfer of Cd in the soil-plant system effectively under freeze-thaw aging with long-term effectiveness. This study confirmed that although clay mineral, biochar and phosphate fertilizer alone immobilized Cd during the experimental period, they had obstacles under a natural freeze-thaw process. Future works may investigate field aging phenomena and mechanisms of various amendments in different regions where other natural events such as wet-dry cycling dominated the aging process, and test whether this joint application treatment still remained effective.



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**Declaration of interests**

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

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

Supplementary data

Supplementary material

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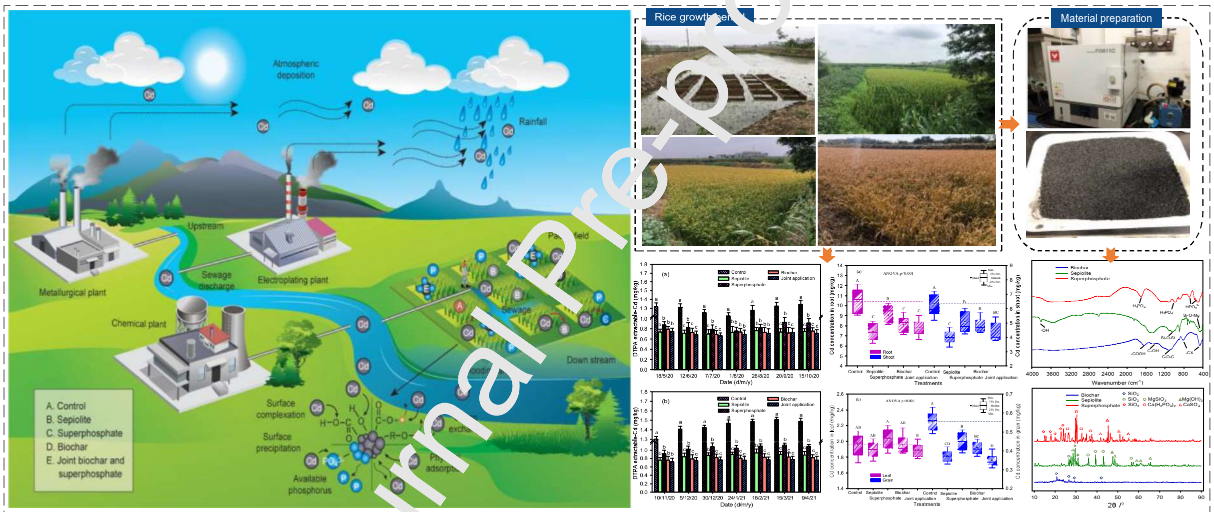
Graphical abstract






Highlights

- Field trial was conducted in Cd contaminated paddy under freeze-thaw process.
- Freeze-thaw aging in non-growth period re-mobilized cadmium in soil.
- Sepiolite, biochar and superphosphate immobilized Cd successfully during aging.
- Joint application of biochar and superphosphate revealed better performance.