

Effects of Aging on The Bioavailability of Cu and Cd Immobilized by Biochars with Varying Endogenous Heavy Metal Concentrations

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Abstract

Biochar is widely used because of its good passivation effect on soil heavy metals; however, the biochar itself may contain heavy metals due to the difference in raw materials, and whether the passivation effect of biochar with high endogenous heavy metals is altered after aging, and whether there is a potential environmental risk should be a concern. In this study, three types of biochar (BB, MB, and HB) with varying endogenous Cu and Cd levels, derived from *Pennisetum giganteum* grown in background, moderately contaminated, and heavily polluted areas, were used as the study objects. The effects of aging on the bioavailability of Cu and Cd in contaminated soil, when subjected to alternating dry-wet and freeze-thaw conditions, were analyzed using the CaCl₂ extraction and the thin-film diffusive gradient (DGT) extraction method. We examined the effects on the bioefficacy of Cu and Cd in contaminated soil by using the BCR sequential extraction method. To analyze the changes in the morphological distribution of soil Cu and Cd. The results showed that the three types of biochar were alkaline, and the contents of Cu in HB and Cd in MB were the highest, being 3.72 and 3.29 times higher, respectively, than those of BB. After 30 days of pre-cultivation, a dosage of 2% to 10% biochar increased the soil pH by 0.32 to 4.50, respectively. All of them significantly reduced soil Cu and Cd bioefficacy, among which a 10% dosage of the three kinds of biochar reduced soil CaCl₂ extraction of Cu and Cd by 98.2%~99.1% and 86.9%~97.0%, respectively, and DGT extraction of Cu and Cd by 80.0%~89.9% and 81.7%~99.0%, respectively. Compared with the control treatment, the addition of biochar significantly reduced the soil acid-soluble Cu content and promoted its transformation to oxidizable, reducible and residual Cu; however, the 5% and 10% MB treatments significantly increased the soil acid-soluble Cd content, which has a substantial potential environmental risk, and thus high endogenous pollutant biochar needs to be paid extra attention to when applied in large quantities. In addition, alternating dry-wet and freeze-thaw aging decreased the CaCl₂- and DGT-extracted soil Cu and Cd contents in each treatment group, which further promoted the transformation of soil Cu and Cd from active to inactive states. Overall, the stabilizing effects of the three types of biochar at the exact dosage were HB > MB > BB for soil Cu, and BB > HB > MB for soil Cd. The results of this study are of great significance for the development of biochar application standards and for evaluating the stability of biochar in long-term passivation and remediation.

Keywords

Biochar; endogenous heavy metals; aging; passivation.

1. INTRODUCTION

Biochar can directly adsorb and immobilize heavy metals in aqueous solution due to its special microcrystalline structure, huge specific surface area, abundant surface-active functional groups, and strong ion-exchange capacity^[1, 2], and it can also indirectly immobilize soil heavy metals by influencing soil pH, cation exchange capacity (CEC), mineral components, and organic matter^[3], and so on. Therefore, it has received wide attention.

Some biochar prepared from biomass feedstock contains endogenous pollutants^[4] (e.g., heavy metals and polycyclic aromatic hydrocarbons (PAHs)). For example, the bioavailability and leaching toxicity of heavy metals in biochar products prepared from sludge are lower than those of the original sludge; however, the leachable content of certain heavy metal elements still exceeds the standard^[5]. The environmental risk of this type of biochar utilization remains, and it poses a significant potential risk if applied in large quantities. Additionally, several foreign organizations, including the International Biochar Initiative (IBI), the European Biochar Certificate (EBC), and the U.S. Environmental Protection Agency (EPA), have issued certificates for the end-use of biochar. They have stipulated the limit values of endogenous pollutants in biochar and formulated relevant standards^[6]. However, there is a lack of pertinent norms of China. Moreover, since China has a large number of heavily contaminated croplands, biomass such as crop residue grown in these areas is likely to be converted into biochar and returned to the field, which may increase the potential environmental risk to the soil.

When biochar is added to the soil, it is bound to interact with the organic and inorganic components of the soil. At the same time, aging will alter the biochar particle size, porosity, and pore structure, causing degradation and transformation of the functional groups and carbon bond structure on the biochar surface^[7], thereby affecting the properties of the biochar and its ability to immobilize heavy metals. Gao Peng et al. demonstrated that aging (chemical, physical, and natural aging) increased the oxidized functional groups of biochar and leached elements such as P, Fe, and Ca from the biochar interior, which in turn contributed to the further stabilization of adsorbed Cd²⁺ in the straw and duckweed biochar^[8]. Chen Yu et al. also demonstrated that the aging effect altered the functional groups on the surface of straw biochar, and the emergence of new functional groups provided additional adsorption sites for Cd, thereby enhancing the adsorption performance of biochar on Cd²⁺^[9]. However, previous studies have shown that dry-wet and freeze-thaw aging increase the risk of endogenous Cu and Cd release from biochar^[10], and the effect of aging on the passivation of soils with endogenous heavy metal-containing biochar remains unclear. Therefore, it is necessary to clarify the impact of aging on the bioefficacy of Cu and Cd in biochar-passivated soils with different endogenous heavy metal contents. Based on this, in this study, we collected different heavy metal contents of Giant Mycorrhiza, prepared three kinds of biochar with different endogenous Cu and Cd contents, and injected them into heavy metal contaminated soils, to clarify the effects of dry, wet, and freeze-thaw aging effects on soil Cu and Cd effective states and chemical activities, with a view to providing theoretical guidance for the safe application of biochar in environmental remediation.

2. MATERIALS AND METHODS

2.1. Preparation of biochar

To obtain biochar from different endogenous heavy metals, we planted *Pennisetum giganteum* in the background area of HongRang Station, ShuiQuan (a moderately polluted area), and JiuniuGang (a heavily polluted area). After harvesting, the fruit is air-dried, washed, and cut into small sections of 1 cm for storage. Then, the stems of *Pennisetum giganteum* were placed into a closed corundum crucible and heated in a muffle furnace with high-purity N₂ (99.99%)

for 0.5 h. The temperature was increased at a rate of 5 °C/min under anoxic conditions, with a pyrolysis temperature of 400 °C. The retention time was two hours. The stems were cooled, removed, and ground through a 0.85 mm (20 mesh) sieve, then stored in a desiccator for future use at room temperature.

Copper and cadmium, the primary pollutants in the region, were the focus of this study^[11]. Biochar prepared from the HongRang station, ShuiQuan, and JiuniuGang giant mycorrhizal grass was labeled as BB (biochar from the background area), MB (biochar from the moderately polluted area), and HB (biochar from the heavily polluted area), respectively. The contents of copper and cadmium in soil, *Pennisetum giganteum*, and biochar from the three regions are shown in Table 1.

Table 1. Copper and cadmium content in soil, *Pennisetum giganteum* and biochar

Area	Soil		<i>Pennisetum giganteum</i>		Biochar	
	Cu(mg·kg ⁻¹)	Cd(μg·kg ⁻¹)	Cu(mg·kg ⁻¹)	Cd(μg·kg ⁻¹)	Cu(mg·kg ⁻¹)	Cd(μg·kg ⁻¹)
HongRang station	32.2±4.58	0.22±0.03	4.08±0.34	1.00±0.09	10.8±1.35	1.92±0.15
JiuQuan	152±16.3	1.10±0.1	5.30±0.31	2.84±0.11	21.4±2.92	6.31±0.39
JiuniuGang	816±55.7	0.98±0.12	7.74±0.96	1.41±0.08	40.2±0.7	5.29±0.03

2.2. Test soil

Soil samples were collected from a contaminated, abandoned rice field (0-20 cm) in the JiuniuGang area, which had heavily polluted soil. The soil was naturally air-dried and then sieved (20 mesh) after removing debris. The specific physical and chemical properties of the test soil are shown in Table 2.

Table 2. Physical and chemical properties of test soil

Sample	pH	Organic matter (g·kg ⁻¹)	CEC (cmol·kg ⁻¹)	Total Cu (mg·kg ⁻¹)	Total Cd (mg·kg ⁻¹)
Soil	5.92	40.7	9.31	981	0.88
Screening value of soil pollution risk of agricultural land (GB15618-2018)	≤5.5	/	/	50.0	0.30
Screening value of soil pollution risk of agricultural land (GB15618-2018)	5.5~6.5	/	/	50.0	0.40

2.3. Experimental design

Plastic beaker. Each biochar was then added at rates of 2%, 5%, and 10% of the soil mass, as per previous studies^[12, 13]. The specific treatments were: control soil (CK); soil +2% of BB (BB-2); soil +5% of BB (BB-5); soil +10% of BB (BB-10); soil +2% of MB (MB-2); soil +5% of MB (MB-5); soil +10% of MB (MB-10); soil +2% of HB (HB-2); soil +5% of HB (HB-5); soil +10% HB (HB-10). All treatments were covered with plastic film (leaving 5 aeration pinholes), and water was maintained at 60% of the soil field water holding capacity using the mass balance method. Water was rehydrated with deionized water approximately every 2 to 3 days during incubation. After 30 days of pre-incubation (IM-30), 50 g of soil samples were taken and stored, and the remaining soil was air-dried for the next stage of the aging test.

2.4. Aging test

(1) Dry-wet alternating aging (DW): take 200 g of pre-cultivated soil into a beaker, add deionized water (to ensure that the soil is 100% water content). 25 °C oven incubation for 16 h, and then 60 °C continue to incubate for 8 h (to ensure that the water content is > 35%), that is, to complete the dry-wet alternating once^[14].

(2) Freeze-thaw alternating aging (FT): Take 200 g of pre-cultured soil into a beaker and add deionized water (to ensure 100% water content of the soil). Cultivate in the refrigerator at 25°C for 5 h, and then continue to cultivate in the oven at 25°C for 19 h, i.e., complete one freeze-thaw alternation^[15].

Both dry-wet and freeze-thaw alternations were carried out for 25 alternation processes, and 20 g of samples were taken after every 5 alternation processes to analyze the soil pH and the effective state of heavy metals. In addition, the effectiveness of Cu-Cd was analyzed using CaCl₂ and diffusive gradients in thin films (DGT) after 30 days of pre-incubation and after the 25th alternation process. The chemical morphology changes of Cu-Cd were analyzed using the BCR continuous extraction method.

2.5. Analyzing methods

Biochar specific surface area was analyzed by a specific surface area analyzer (Auto-sorb-iQA3200-4, QUANTATECH, USA). The pH of biochar was determined using a solid-liquid ratio of 1:20, with mixing and shaking for 1.5 hours, and then measured using a pH meter (PHS-25, Lei Magnetic, China) ^[16]. Soil pH was determined by using carbon dioxide-free water with a water-soil ratio of 2.5:1, stirred vigorously with a glass rod for 1~2 min, and left to stand for 30 min before being determined by a pH meter^[17]. Soil effective state heavy metals were extracted with 0.01 mol·L⁻¹ of CaCl₂ using a solid-liquid ratio of 1:5, and centrifugal filtration was performed after 2 h of oscillatory extraction^[18]. DGT extraction: soil (10 mesh) was incubated for 48 h at 70% of the maximum holding capacity of the field, and 3 g of the soil samples were taken in the DGT, and the samples were allowed to stand for 24 h in a humid environment, after which the soil was removed and washed clean, and the fixation film was removed and washed with 1.8 mL of 1 mol·L⁻¹ nitric acid, and the extract was obtained after 24 h of standing^[19]. Soil heavy metals in acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) states were analyzed by the BCR continuous extraction method proposed by the Community Bureau of Reference^[20]. The samples were determined by an atomic absorption spectrometer equipped with a graphite furnace (A3, Universal Instruments, China). The total heavy metals in soil and biochar were determined using a mixed acid (HF:HNO₃:HClO₄) hot plate digestion method^[17]. A blank control and a soil standard (GBW07445) were set up for the analysis of total soil heavy metals, and the recoveries of copper and cadmium ranged from 85.7% to 113%.

2.6. Data processing

All data were processed by Excel 2016 for data processing, SPSS 25 for ANOVA, and SigmaPlot 12.0 for plotting.

3. RESULTS AND DISCUSSION

3.1. Biochar properties

Biochar prepared from *Pennisetum giganteum* collected from all three regions exhibited an alkaline color (Table 3), with BB biochar having the highest pH, which was 2.09 and 1.73 units higher than MB and HB, respectively. This difference could be attributed to the higher ash content of BB biochar^[21]. HB had the highest specific surface area of 15.1 m²·g⁻¹, which was 2.8 m²·g⁻¹ and 4.5 m²·g⁻¹ higher than BB and MB, respectively. The endogenous Cu content was highest in HB megagrass feedstock and biochar, followed by MB and BB, as influenced by soil Cu

and Cd in the growing area. MB megagrass feedstock and biochar had the highest endogenous Cd content ($6.31 \text{ mg}\cdot\text{kg}^{-1}$), which was higher than that of HB ($1.02 \text{ mg}\cdot\text{kg}^{-1}$) and BB ($4.39 \text{ mg}\cdot\text{kg}^{-1}$), respectively. Previous studies have found that the endogenous Cu in BB and HB biochar is mainly in the oxidizable state (47.6% and 54.7%), followed by the residual state (47.2% and 37.3%). Cd was primarily in the reducible state (42.7% and 42.0%), followed by the residual state (31.8% and 27.3%)^[22].

Table 3. Basic properties of biochar

Sample	pH	Ash content	Specific surface area BET ($\text{m}^2 \cdot \text{g}^{-1}$)	Total Cu($\text{mg}\cdot\text{kg}^{-1}$)	Total Cd($\text{mg}\cdot\text{kg}^{-1}$)
BB	10.1	10.0	12.3	10.8 ± 1.35	1.92 ± 0.15
MB	8.01	8.0	10.6	21.4 ± 2.92	6.31 ± 0.39
HB	8.37	9.0	15.1	40.2 ± 0.7	5.29 ± 0.03

3.2. Effect of aging on pH and effective state of Cu and Cd in biochar passivated soil

After 30 days of pre-incubation, the CK treatment had the lowest pH (4.67). 2% to 10% dosage of BB, MB and HB treatments increased soil pH by 1.32-4.50, 0.36-1.91 and 0.32-2.27, respectively, compared to the control (Fig. 1). Consistent with its own pH, the effect of three kinds of biochar on soil pH at the exact dosage showed that $\text{BB} > \text{HB} > \text{MB} > \text{CK}$. The number of dry-wet and freeze-thaw alternations did not significantly alter the soil pH under the different treatments, indicating that the biochar had good stability in enhancing soil pH. However, previous studies have shown that dry-wet and freeze-thaw aging increase the content of oxygen-containing functional groups on the surface of the biochar and its CO_2 uptake, while significantly decreasing the biochar pH^[23]. This refers to the fact that soil particles are dispersed to the surface and internal pores of the biochar after mixing with soil, which reduces the direct exposure of the biochar to the environment and slows down the aging effect of the biochar.

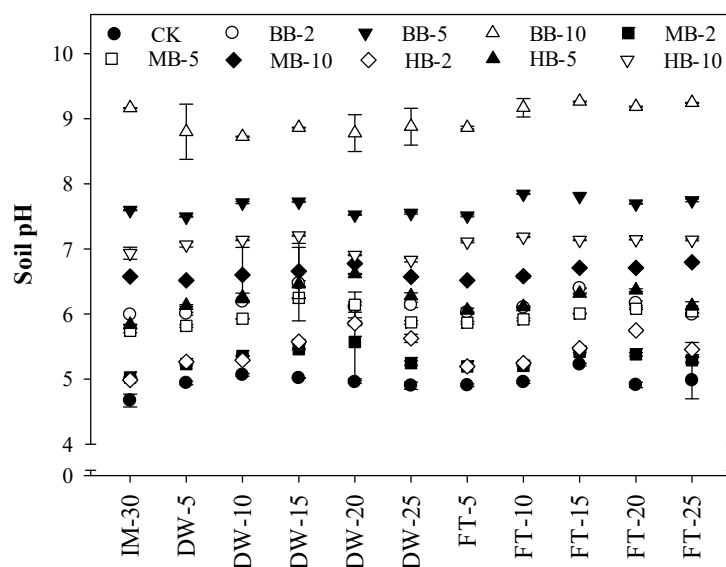


Figure 1. Effect of aging on biochar passivated soil pH

$0.01 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ is an extractant very close to the state of the soil itself, and its extracted heavy metal content in the active state has a good correlation with plant heavy metal uptake^[24, 25]. After 30 days of preincubation, the addition of BB, MB and HB at 2% to 10% dosage resulted in a significant reduction of soil effective state Cu by 75.9% to 98.2%, 70.1% to 98.9% and 79.3% to 99.1% compared with CK (Fig. 2). the passivation effect on effective state Cu at 5% and 10% dosage was $\text{HB} > \text{MB} > \text{BB}$. Compared with preincubation for 30 days, the passivation effect on

effective state Cu at 5% and 10% dosage was HB>MB>BB. Compared with the IM-30, all three biochar treatments at 5% and 10% dosage decreased the effective state Cu, with an increase in the number of dry-wet and freeze-thaw alternating aging cycles.

Similar to the trend of soil effective Cu, soil effective Cd was significantly reduced by 68.7%~97.0%, 1.75%~86.9%, and 25.2%~96.9% in BB, MB, and HB treatments with 2%~10% dosage compared with the control, and the passivation effect of the exact dosage of biochar on soil Cd was as follows: BB>HB>MB>CK. During the alternating aging process of wet and dry, and freeze and thaw, the overall fluctuating trend of soil effective Cd was as follows: it gradually decreased during the 5th-15th aging process and then gradually increased during the 20th-25th aging process. In the alternating dry-wet and freeze-thaw aging process, the soil's effective Cd showed a fluctuating trend, decreasing from the 5th to the 15th aging process and then increasing from the 20th-25th aging process. For example, the effective Cd of HB-2 treated soil gradually decreased from 299 $\mu\text{g}\cdot\text{kg}^{-1}$ before aging to 200 $\mu\text{g}\cdot\text{kg}^{-1}$ after the 5th-15th dry and wet aging, and then increased again to 239 $\mu\text{g}\cdot\text{kg}^{-1}$ after the 25th dry and wet aging. However, the soil effective state Cu and Cd did not show significant differences in both dry-wet and freeze-thaw aging treatments.

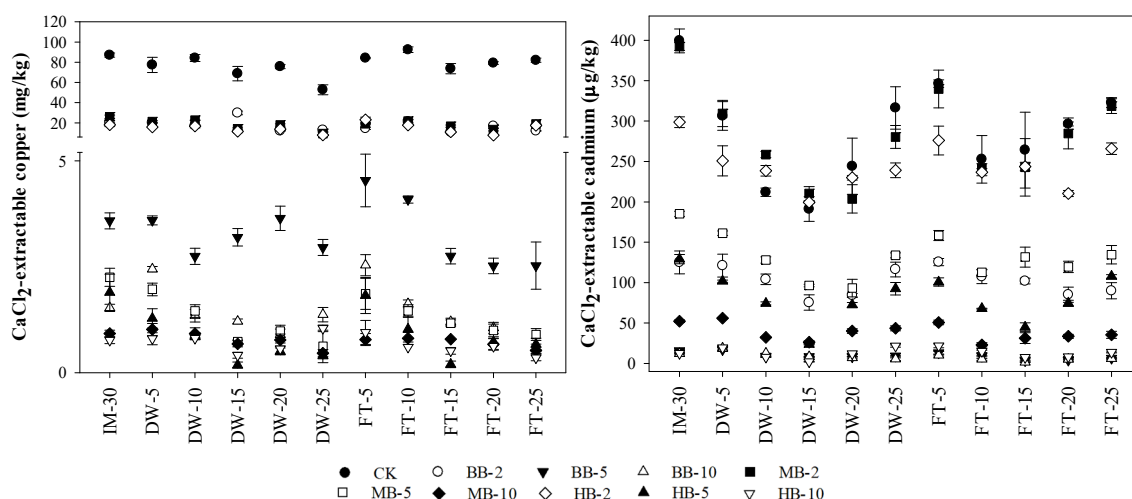


Figure 2. Ageing effects on available copper and cadmium in biochar immobilized soil

The addition of three types of biochar effectively increased the soil pH, and it showed a negative correlation ($P < 0.01$) with the effective states of Cu and Cd, with correlation coefficients of -0.570 and -0.842, respectively. pH elevation could increase the variable charge of the soil surface, enhance cation adsorption capacity, and promote the precipitation of heavy metals^[26]. Meanwhile, biochar promoted passivation of soil heavy metals through electrostatic adsorption, surface complexation, and surface ion exchange^[27, 28]. The better passivation effect of the three biochars on soil effective state Cu may be because the adsorption capacity of biochars on Cu^{2+} is larger than that of Cd^{2+} ^[23], and the content of Cu in the test soil is much higher than that of Cd (Table 2). The large amount of Cu^{2+} present in the soil will compete with Cd^{2+} for adsorption sites.

In addition, the dry-wet and freeze-thaw aging effects further promoted the passivation of soil Cu and Cd by the biochar, probably because the aging effects increased the types and numbers of oxygen-containing functional groups on the surface of the biochar^[29], which provided more Cu^{2+} and Cd^{2+} adsorption sites, and promoted the adsorption and immobilization of Cu and Cd by the biochar.

Meanwhile, the passivation effect of biochar on soil Cu and Cd increased and then decreased during dry-wet and freeze-thaw aging, indicating that the passivation effect of biochar on heavy

metals did not persist well. Similarly, the previous study also found that the passivation effect of biochar on heavy metals under field conditions gradually decreased with time, and could no longer support the growth of ryegrass by the second year^[30]. It is noteworthy that MB-5 and MB-10 significantly reduced the soil effective state Cd compared with the control treatment. Still, the MB-2 treatment was at the same level as the control treatment, which was attributed to the fact that the high additions of MB and HB not only provided more adsorption sites, but also significantly elevated the soil pH (MB-5 and MB-10 were 0.71 and 1.55 units higher than the MB-2 soil pH, respectively), and the soil The elevated pH not only increased the stability of Cu and Cd, but also promoted ion exchange and heavy metal precipitation generation on the biochar surface^[27, 31]. These results suggest a potential environmental risk and poor stability of heavy metal passivation in soil for applications involving higher concentrations of endogenous heavy metals in biochar.

3.3. Effect of aging on the activity of DGT extraction of copper and cadmium from biochar-passivated soil

DGT extraction can simulate the kinetic process of heavy metals resolving from the soil solid phase and recharging into the soil liquid phase under bioturbation^[25, 32, 33]. Therefore, to evaluate the effect of the soil solid phase on the bioavailability of heavy metals more effectively, this study employed the DGT technique to analyze the bioavailability of copper and cadmium passivated by biochar during aging. After 30 days of preincubation, the addition of BB, MB and HB at 5% and 10% dosages resulted in significant reductions of soil DGT-Cu by 47.2% to 80.0%, 73.0% to 86.0% and 84.3% to 89.9% compared to the control (Fig. 3). At the exact dosage, MB and HB reduced soil DGT-Cu more significantly than BB; MB-10 and HB-10 reduced soil DGT-Cu by 121 $\mu\text{g}\cdot\text{kg}^{-1}$ and 200 $\mu\text{g}\cdot\text{kg}^{-1}$, respectively, compared with BB-10. Freezing and thawing reduced soil DGT-Cu more significantly than wet and dry aging at the exact dosage for all three biochar treatments, compared to IM-30.

Similar to soil DGT-Cu, except for MB-2, soil DGT-Cd was significantly reduced by 72.9%-99.0%, 44.7%-81.7%, and 59.8%-98.0% in BB, MB, and HB treatments at different dosages compared to the control. The passivation effect of soil Cd at the exact biochar dosage was BB>HB>MB. Compared with IM-30, dry-wet and freeze-thaw aging tended to reduce soil DGT-Cd content in different treatment groups, but not as significantly as the effect on DGT-Cu, which might also be related to the lower soil Cd content.

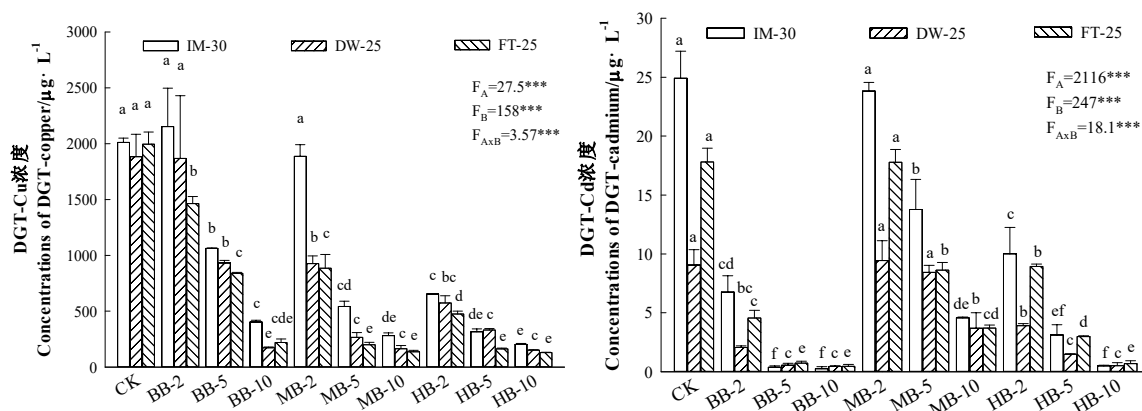


Figure 3. Ageing effects on DGT extraction of copper and cadmium from biochar immobilized soil

In addition, the DGT extracted copper and cadmium were significantly lower than those extracted by 0.01 mol/L CaCl_2 , which was mainly because the CaCl_2 -extracted heavy metals contained both water-soluble and ion-exchangeable states^[31]. Thus, their contents were

considerably higher than those dispersed in the soil solution. Like CaCl_2 , which extracted heavy metals, DGT-extracted Cu-Cd also showed a significant negative correlation ($P < 0.01$) with soil pH, with correlation coefficients of -0.487 and -0.730, respectively.

3.4. Effect of aging on the distribution of Cu-Cd BCR morphology in biochar-passivated soil

Soil pH, soil texture, and organic matter content affect the bioavailability of heavy metals, and the total amount of heavy metals does not accurately reflect their bioactivity^[32]. In this study, we employed the BCR multistage extraction method to assess the impact of biochar passivation on the morphological distribution of Cu and Cd^[34]. After 30 days of preincubation, copper in the control soil was predominantly in the residue state, accounting for 35.3% of the total copper, followed by the acid-soluble state, which accounted for 28.1% of the total copper. The acid-soluble state of Cu in the soil treated with 2% to 10% dosage of BB, MB, and HB was significantly reduced by 29.5% to 57.7%, 18.9% to 54.2% and 36.0% to 52.5%, compared with that of the control (Fig. 4). The addition of biochar minimized the acid-soluble Cu content. It increased the oxidizable, reducible, and residual states in all treatment groups. Both dry-wet and freeze-thaw aging significantly reduced the acid-soluble state Cu content of the three biochar-treated soils (except for HB-2) compared with IM-30; however, no significant differences were observed between the two aging treatments.

Unlike soil BCR graded for Cu extraction, Cd in control soil was dominated by the acid-soluble form, which accounted for 46.0% of the total Cd and was much higher than the other three forms. 2% to 10% dosage of BB, MB, and HB treated soil residue state Cd significantly increased by 0.56-0.75, 0.26-0.91, and 0.48-2.5 fold compared with the control. Still, the content of soil acid-soluble Cd and total Cd also increased with the addition of biochar, in proportion to the amount added. The soil acid-soluble Cd and total Cd contents of the MB-10 group were $178 \mu\text{g}\cdot\text{kg}^{-1}$ and $155 \mu\text{g}\cdot\text{kg}^{-1}$, respectively, higher than those of the blank. The passivation effects of the three biochars on soil Cd at the exact dosage were $\text{BB} > \text{HB} > \text{MB}$. Wet-dry and freeze-thaw aging significantly reduced the acid-soluble Cd content of the three biochar-treated soils and increased the residual Cd content (except for HB-10) compared with the pre-cultivation period of 30 days, but did not show a significant difference between the two aging treatments.

BCR multistage extraction of acid-soluble heavy metals represents bioavailable fractions, reducible and oxidizable states are potentially bioavailable fractions, and residual states are difficult to be utilized by organisms^[35]. The acid-soluble state of Cu-Cd in this study was much higher than $0.01 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 and DGT extracted Cu-Cd content, which was attributed to the fact that the acid-soluble heavy metals included water-soluble, exchangeable, and carbonate-bound states^[36]. In addition, the addition of biochar can promote the conversion of soil acid-soluble Cu-Cd to intermediate and residue states, thereby reducing the activity of soil heavy metals. Dry-wet and freeze-thaw aging further promoted the transformation of acid-soluble Cu-Cd to the residue state. Similarly, we found that the acid-soluble Cd content of the MB biochar treatment was significantly higher than that of the control treatment, which also suggests that higher endogenous heavy metal content of biochar has a substantial potential risk, and its passivation and remediation of soil heavy metals need to be paid extra attention in the application of remediation.

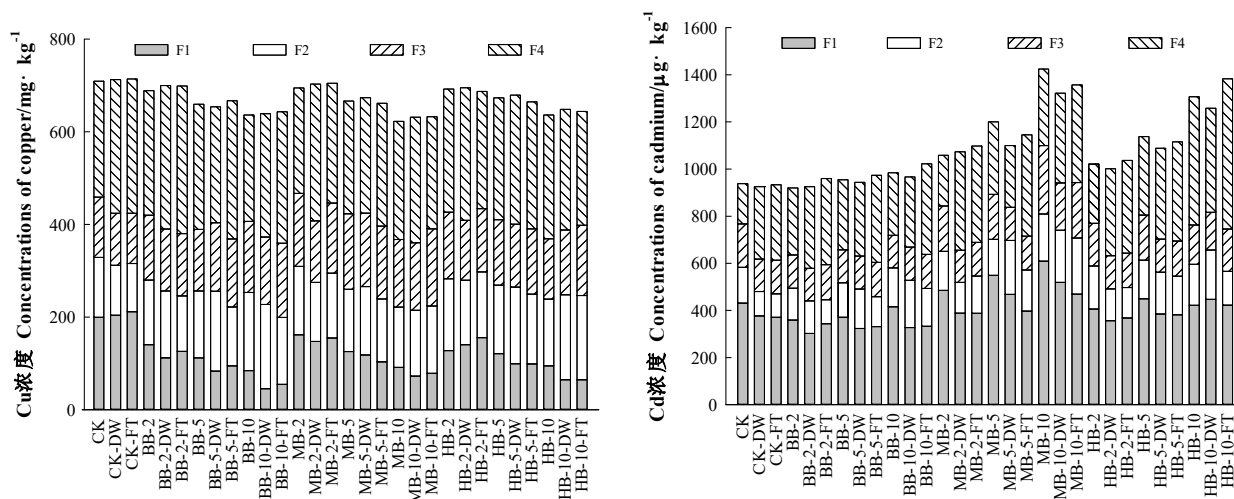


Figure 4. Ageing effects on BCR speciation distribution of copper and cadmium in biochar immobilized soil

4. CONCLUSION

(1) BB, MB, and HB biochar were alkaline, and the soil pH increased significantly with the increase in biochar addition. The effect of the three kinds of biochar on pH was BB > HB > MB. The change in pH was significantly negatively correlated with the CaCl₂ and DGT extracted Cu-Cd, and the soil pH was a key factor influencing the activity of soil heavy metals.

(2) The passivation effect of the three kinds of biochar on Cu is greater than that on Cd, and the passivation effect of the three types of biochar on Cu under the exact dosage is HB>MB>BB; the passivation effect on Cd is BB>HB>MB.

(3) The aging effect can increase the number of oxygen-containing functional groups on the surface of biochar, promote the adsorption and immobilization of soil Cu and Cd by biochar, and reduce the content of soil CaCl₂ and DGT extracted Cu-Cd, as well as promote the transformation of soil acid-soluble Cu to the reducible, oxidizable, and residual states, and promote the transformation of soil acid-soluble Cd to the residual state, which can reduce the bioeffectiveness of Cu and Cd.

(4) The acid-soluble Cd in the MB biochar treatment group was significantly higher than in the control, indicating that the higher endogenous heavy metal content of biochar poses a substantial potential risk, which requires extra attention.

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