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Combined Application of Biochar and Calcium Superphosphate Can Effectively Immobilize Cadmium and Reduce Its Uptake by Cabbage

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Abstract: Biochar and phosphate fertilizer are commonly employed for the mitigation of soil cadmium (Cd) contamination. Nevertheless, there is a dearth of research regarding the mechanism behind their joint implementation. In this study, a combination of corn straw biochar (0 (C_0), 5 (C_5), and 10 (C_{10}) g kg^{-1}) and calcium superphosphate (0 (P_0), 0.1 (P_1), 0.2 (P_2), 0.5 (P_5), and 1.0 (P_{10}) g kg^{-1}) was applied in pot experiments, and the effects of the combined application on Cd bioavailability and its uptake by cabbage were investigated in Cd-contaminated soils. The results demonstrated that the combined treatment of applying biochar and $Ca(H_2PO_2)_2$ yielded a significant decrease in the uptake of Cd by cabbage in alkaline soil, in contrast to the individual treatments of biochar or $Ca(H_2PO_2)_2$. Compared to the CK treatment (C_0P_0), the Cd content in the shoots decreased by 46.26% and in the roots decreased by 24.81%, while the biomass of the cabbage demonstrated a noteworthy increase in C_5P_{10} treatment. Compared to the CK treatment, the content of available phosphate (AP) in the soil increased by 17.57 mg kg^{-1}, residual Cd increased by 22.02%, the exchangeable Cd decreased by 45.86%, and carbonate-bound Cd decreased by 20.55% in the C_5P_{10} treatment. Therefore, it is advisable to use a combination of 5 g kg^{-1} biochar and 1 g kg^{-1} $Ca(H_2PO_2)_2$ for the restoration of soil contaminated with Cd.

Keywords: cadmium; biochar; phosphate fertilizer; immobilization; soil remediation

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1. Introduction

With the progress being made within industrialization, a large amount of industrial waste can pile up on the soil surface, resulting in an increase in heavy metal content in the soil [1]. Heavy metal pollution mainly appears in the soils of cities, industrial mining areas, and agricultural planting areas, exhibiting a regional distribution [2,3]. Cadmium (Cd), a major pollutant, is commonly distributed in the soils of southern China [4]. Wang et al. [5] showed that about 10 million hectares of farmland soil in China were polluted by Cd. Excessive Cd content in plants manifests as yellow leaves and short plants [6]. The excessive accumulation of Cd can damage soil quality and reduce crop yield [7]. Vegetables are the main pathway for humans to ingest Cd [8]. Leafy vegetables are more likely to accumulate Cd [9,10]. The remediation of heavy metals in soil has consistently attracted the interest of numerous researchers. The focus of soil heavy metal remediation is to identify durable and efficient strategies for reducing the availability and mobility of Cd in soil over an extended period.

Remediation technology for soil heavy metal pollution mainly includes physical, chemical, and biological remediation [11]. Passivation has been studied by many researchers due to its simple operation and economic benefits [12]. Common passivators include biochar [13,14], phosphorous materials [15], clay materials [11,16], etc. These materials have different mechanisms and effects on the immobilization of heavy metals in soil [17]. Biochar is the product of agricultural wastes under relatively low-temperature pyrolysis [18]. Biochar has a porous structure and excellent carbon sequestration ability [19,20]. Studies have shown that the application of biochar can reduce the mobility of cadmium in contaminated soil [2]. The various oxygen functional groups on the surface of biochar play an important role in the adsorption and fixation of Cd in soil [21]. In addition, precipitation, electrostatic interactions, and functional group complexation also reduce the effectiveness of Cd [22,23]. An excessive application of biochar will lead to a rise in soil salinity and affect crop growth [24]. At the same time, the production cost of biochar is relatively high, which is a challenge for its practical application.

In Cd-contaminated soil, P fertilizer can reduce the plant uptake of soil Cd through adsorption and precipitation [25]. Heavy metal phosphate precipitation is relatively stable in soil at different pH conditions [26,27]. Additionally, phosphates also fix heavy metals through surface complexation and cation exchange [28,29]. Phosphate materials, such as diammonium phosphate and hydroxyapatite (HAP), are effective in adsorbing and stabilizing Cd and other heavy metals [30,31]. However, the excessive use of P fertilizer will lead to the eutrophication of surrounding water [32]; therefore, the application amount of P fertilizer in soil needs to be controlled.

The combined application of biochar and P fertilizer can effectively immobilize Cd in the soil and improve soil fertility [33]. Biochar effectively immobilizes Cd on its surface through adsorption [34]. The phosphate ions (PO_4^{3-}) in biochar and P fertilizers contribute to the formation of insoluble Cd, such as $Cd_5(PO_4)_3OH/Cl$ and $CdCO_3$ [35]. Among them, Cd orthophosphate and Cd pyrophosphate are the main forms of Cd precipitation with phosphorus [36]. Biochar alleviates nitrogen deficiency after P fertilizer application [37]. The structure of biochar is beneficial for improving the effectiveness of P fertilizer [38]. The cost of biochar is relatively high [17]. It is important to control the amount of P fertilizer and biochar reasonably for the remediation of heavy metals in soil.

Previous studies have mostly focused on the immobilization of Cd in soil by only biochar [39] or P fertilizer [40,41]. Studies on the passivation effect of biochar also focus on acidic soils. However, there are only a few studies on the combined application of biochar and P fertilizer on the Cd forms in the alkaline soil and plant Cd uptake [35]. Studying the effect mechanism of biochar and P fertilizer on the growth and Cd transport of cabbage is beneficial for filling the gap in this area. It was assumed that the addition of biochar helps to reduce P fertilizer loss, while the addition of P fertilizer also promotes the fixation of Cd in the alkaline soil. In this study, different proportions of biochar and calcium superphosphate ($Ca(H_2PO_2)_2$) were added to Cd-contaminated soil (1) to explore the mechanism of combined biochar and $Ca(H_2PO_2)_2$ on the availability of Cd in alkaline soil, (2) to study the impacts of combined biochar and $Ca(H_2PO_2)_2$ on cabbage growth and cabbage Cd reduction, and (3) to investigate the optimal proportion of biochar and $Ca(H_2PO_2)_2$ required to remedy Cd-contaminated soil to ensure food production safety.

2. Materials and Methods

2.1. Materials and Characterization

The testing soil (0–20 cm) was collected from Yangxin county, Huangshi city, Hubei province (N 29°48′40″; E 115°25′53″). The soil is classified as paddy soil. After collection, the soil samples were air-dried and cleared of any loose stones, roots, and other debris. A portion of the samples was passed through a 0.15 mm sieve to determine the basic physical and chemical parameters, while the other half was passed through a 2 mm sieve for the subsequent pot experiment. The Supplementary Materials include instructions for determining soil pH, organic carbon (OC), total nitrogen (TN), total phosphorus (TP), available phosphorus (AP), and total Cd (Method part 1). The soil pH, OC, TN, TP, AP, and total Cd levels were 8.13, 13.71 g kg^{-1}, 1.63 g kg^{-1}, 0.50 g kg^{-1}, 11.63 mg kg^{-1}, and 3.61 mg kg^{-1}, respectively (Table S1).

The biochar used for treating contaminated soil was obtained from Henan Lize Environmental Protection Technology Co. (Zhengzhou, China). This biochar was produced from corn stover through pyrolysis at 500 °C. Before use in the experiment, the biochar samples were dried at 40 °C for 48 h, ground using a mortar and pestle to pass through a 2 mm sieve, and stored in a sealed nylon bag. The manufacturer provided the main physical and chemical characteristics of the biochar, which are presented in Table S1. The biochar exhibited pH, OC, TN, TP, and AP values of 9.17, 404.78 mg kg^{-1}, 8.45 mg kg^{-1}, 5.29 g kg^{-1}, and 122.69 mg kg^{-1}, respectively. The total Cd content was below the detection limit (0.003 mg kg^{-1}) (Table S1).

The phosphate fertilizer used was calcium superphosphate ($Ca(H_2PO_2)_2$) with chemical purity, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Some physical and chemical properties of $Ca(H_2PO_2)_2$ were provided by the manufacturer (Table S1). The pH of the $Ca(H_2PO_2)_2$ compound was 2.78, the P_2O_5 concentration was 15.0%, and the Cd concentration was less than the detection threshold (0.003 mg kg^{-1}) (Table S1).

The cabbage (*Brassica rapa* L.) used was purchased from Hunan Hezhiyuan Seed Industry Co., Ltd. (Changsha, China), and the variety was Hua'nai Shanghaiqing.

2.2. Experiment Design and Methods

The pot experiment was conducted in a completely randomized design in the greenhouse of Huazhong Agricultural University in summer 2021. In this experiment, the Cd content of soil is 3.61 mg kg^{-1}. Each plastic pot (diameter 12 cm, height 11.5 cm) received a 1 kg air-dried soil sample. Then, three levels of biochar treatment (0, 5, 10 g kg^{-1}), denoted as C_0, C_5, and C_{10}, and five levels of $Ca(H_2PO_2)_2$ treatment (0, 0.1, 0.2, 0.5, and 1.0 g kg^{-1}), denoted as P_0, P_1, P_2, P_5, and P_{10}, were added in combination to the pot. A control treatment (CK) with no biochar material or phosphate fertilizer was added. In total, there were 13 treatments, and each treatment was replicated three times, which were as follows: (1) CK, (2) C_0P_5, (3) C_0P_{10}, (4) C_5P_0, (5) C_5P_1, (6) C_5P_2, (7) C_5P_5, (8) C_5P_{10}, (9) $C_{10}P_0$, (10) $C_{10}P_1$, (11) $C_{10}P_2$, (12) $C_{10}P_5$, and (13) $C_{10}P_{10}$. The pots were placed in the greenhouse at random. In each pot, 0.15 g kg^{-1} urea and 0.06 g kg^{-1} potassium chloride were added as recommended by Wang et al. [42]. In each pot, ten cabbage seeds (*Brassica rapa* L.) were sowed. After 10 days, three cabbage plants with the same growth were selected and kept, while the other seedlings were removed. During the growing season in summer, water was given on a daily basis up to 60–70% of field capacity.

The cabbage plants were harvested after 50 days of sowing. The cabbage samples were cleaned with deionized water, separated into roots, stems, and leaves, and their fresh weight was determined. Half of the plant samples were frozen with liquid nitrogen and stored in a refrigerator at −80 °C. The second half was oven-dried at 105 °C for 30 min before heating at 60 °C until it attained a steady weight. Then, their dry weight was determined, and the grind-dried cabbage sample was passed through 100 sieves.

To determine the Cd concentrations in the plant roots and shoots (stems + leaves), they were digested with HNO_3-$HClO_4$ (3:1) [33]. The concentrations of Cd in the extracts were determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Agilent 5110, Santa Clara City, CA, USA). The detailed steps of digestion were described in the Supplementary Materials (Methods part 1).

The levels of antioxidative enzymes (superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT)) in the plant leaves were measured following the methods reported in the Supplementary Materials (Methods part 4).

After harvesting the plants, 100 g of soil was collected from each pot. The samples were then mixed, air-dried, ground, and sieved by 0.25 mm and 1 mm to determine the soil chemical properties and Cd fractions, respectively. The pH, AP, and enzyme activity (phosphatase, urease, and catalase) of the post-harvest soil were measured as the same methods of pH, AP, and enzyme activity of the studied soil (Method parts 1 and 3 in the Supplementary Materials).

The mobile Cd in the soil was determined by extracting the soil with a diethylenetriamine pentaacetate acid (DTPA) solution, as described by Lahori et al. [43]. The Tessier sequential extraction procedure [44] was adopted to classify soil Cd into five forms, namely exchangeable Cd, carbonate-bound Cd, Fe–Mn oxides Cd, organic matter-bound Cd, and residual Cd. The detailed methods of Cd speciation in the soil are described in the Supplementary Materials section (Method part 2 and Table S2).

2.3. Data Analysis

All values were processed in triplicate and expressed as the mean ± standard deviation using Excel 2010. In all tests, a $p < 0.05$ test was considered statistically significant. The analysis of variance (ANOVA) among different treatments was proceeded by SPSS 21 software and Duncan's method. The Origin 2018 software was used for drawing.

3. Results

3.1. Cd Uptake by Cabbage Under Amendment Application

The application of the C_5P_{10} treatment resulted in a 40.0% decrease in Cd levels in the shoots and a 17.2% decrease in Cd levels in the roots compared to the C_5P_0 treatment (Figure 1). The shoots and roots of cabbage had 0.30 and 0.80 mg kg^{-1} of Cd, respectively, when treated with 10 g kg^{-1} of biochar ($C_{10}P_0$). Comparing the $C_{10}P_{10}$ treatment to the $C_{10}P_0$ treatment, the Cd concentrations in the shoots and roots decreased by 32.7% and 17.8%, respectively. The concentration of Cd in the shoots and roots of cabbage exhibited an inverse relationship with the application amount of $Ca(H_2PO_2)_2$ while keeping the biochar application quantity constant. Furthermore, the concentration of Cd in the roots was greater than that in the shoots.

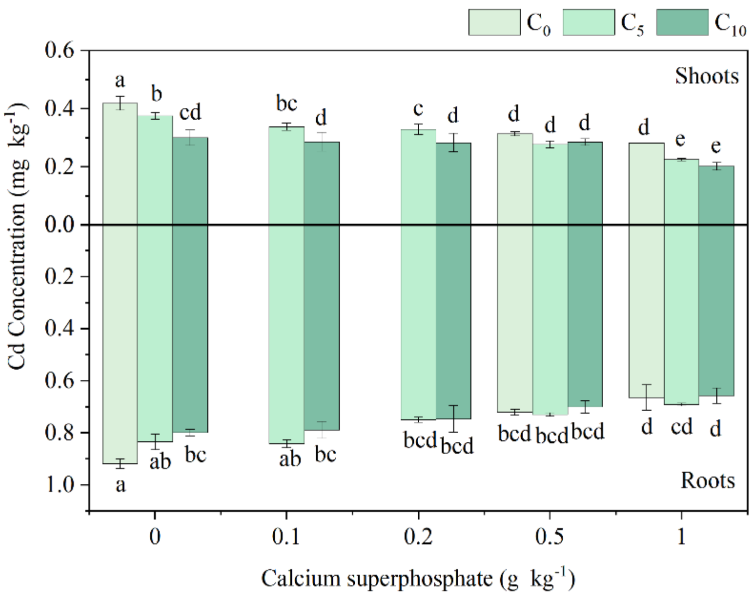


Figure 1. Effect of the combined application of biochar and calcium superphosphate on the Cd content of cabbage at 50 days of growth. Data are mean ± SE (n = 3) (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}. Different lower case letters above columns indicate statistical differences at $p < 0.05$).

3.2. Plant Biomass Under Amendment Application

In comparison to the CK treatment, the fresh weight of the cabbage shoots increased by 1.03 g under the C_0P_{10} treatment and by 1.65 g under the $C_{10}P_0$ treatment (Figure S2). The impact was most pronounced when subjected to the $C_{10}P_{10}$ treatment, resulting in a 5.19 g rise in shoot fresh weight and a 0.50 g increase in root fresh weight. Compared to the CK treatment, the fresh weight of the cabbage shoots and roots increased by 4.56 g and 0.35 g in the C_5P_{10} treatment, respectively.

Under the $C_{10}P_{10}$ treatment, the dry weights of the cabbage shoots and roots were 0.95 g and 0.062 g (Figure 2). Compared to the CK treatment, the dry weight of the cabbage shoots and roots increased by 0.80 g and 0.053 g in the C_5P_{10} treatment, respectively. The dry weight of the cabbage roots showed a favorable correlation with the amount of phosphorus applied when the cabbage was planted for 50 d using the same amount of biochar application. The combined treatment significantly promoted the growth of cabbage.

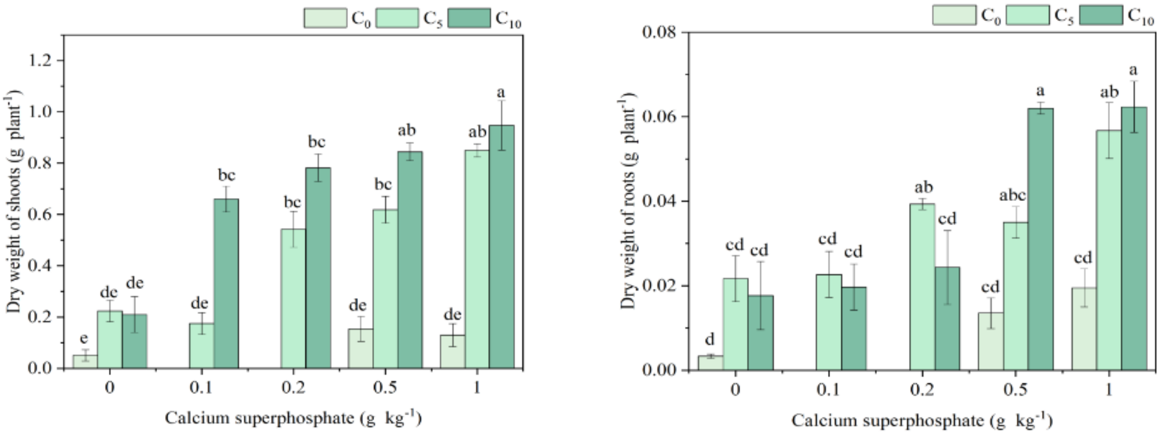


Figure 2. Effect of the combined application of biochar and calcium superphosphate on the dry weight of cabbage at 50 days of growth. Data are mean ± SE (n = 3) (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}. Different lower case letters above columns indicate statistical differences at $p < 0.05$).

3.3. Physiological Indexes and Phosphorus Content of Cabbage Under Amendments Application

Under the condition of 10 g kg^{-1} biochar application, the SOD, CAT, and POD activities decreased to 92.43, 0.32, and 3.39 U g^{-1} (Table 1). Under the treatment of 0.5 g kg^{-1} phosphate fertilizer, the SOD activity in cabbage leaves increased to 108.8 U g^{-1}. After biochar application, the SOD, CAT, and POD activity in cabbage leaves decreased, and the CAT and POD activity was negatively correlated with the biochar application amount. When the application amount of biochar was constant, the SOD content in cabbage leaves was positively proportional to the application amount of $Ca(H_2PO_2)_2$, while the CAT and POD contents were inversely proportional.

Table 1. Effect of the combined application of biochar and calcium superphosphate on the enzymes of cabbage leaves.

Treatment	SOD (U g^{-1})	CAT (U g^{-1})	POD (U g^{-1})
CK	103.89 ± 6.15abc	0.96 ± 0.030a	5.86 ± 0.88a
C_0P_5	108.78 ± 2.79ab	0.04 ± 0.001h	5.31 ± 0.82ab
C_0P_{10}	115.27 ± 7.35a	0.04 ± 0.018h	5.44 ± 0.55ab
C_5P_0	98.64 ± 9.58bcd	0.12 ± 0.002ef	4.84 ± 0.21b
C_5P_1	109.24 ± 7.48ab	0.15 ± 0.038de	2.25 ± 0.44def
C_5P_2	115.69 ± 7.48a	0.16 ± 0.017d	1.78 ± 0.47def
C_5P_5	99.19 ± 8.10bc	0.09 ± 0.011fg	1.49 ± 0.24f
C_5P_{10}	89.67 ± 6.98cd	0.06 ± 0.023gh	2.00 ± 0.29def
$C_{10}P_0$	92.43 ± 9.27cd	0.32 ± 0.048b	3.39 ± 0.37c
$C_{10}P_1$	85.07 ± 10.25de	0.22 ± 0.013c	2.58 ± 0.40d
$C_{10}P_2$	92.36 ± 10.98cd	0.23 ± 0.020c	3.42 ± 0.04c
$C_{10}P_5$	16.78 ± 4.45f	0.06 ± 0.027gh	2.48 ± 0.20de
$C_{10}P_{10}$	72.82 ± 6.31e	0.04 ± 0.001h	1.65 ± 0.46ef

Different lower case letters above columns indicate statistical differences at $p < 0.05$.

Applying just $Ca(H_2PO_2)_2$ and biochar significantly boosted the phosphorus concentration in the cabbage, as shown in Figure 3. Applying 10 g kg^{-1} biochar resulted in a significant increase in the cabbage's ability to absorb phosphorus. The cabbage exhibited the highest phosphorus level under the $C_{10}P_{10}$ treatment, with a 16.46% increase compared to the phosphorus content under the C_5P_{10} treatment. An increase in the application of biochar resulted in a decrease in the phosphorus content of cabbage, assuming that the amount of $Ca(H_2PO_2)_2$ remains constant.

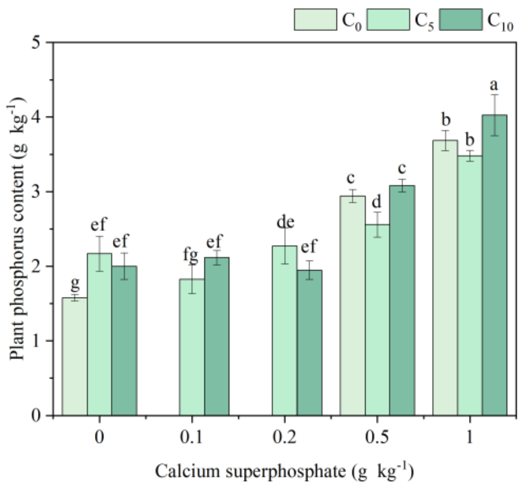


Figure 3. Effect of the combined application of biochar and calcium superphosphate on the shoot phosphorus content of cabbage at 50 days of growth. Data are mean ± SE (n = 3) (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}. Different lower case letters above columns indicate statistical differences at $p < 0.05$).

3.4. DTPA-Cd and Cd Fractionation for Contaminated Soil Under Amendments Application

Within the CK treatment, 11.94% of the Cd was exchangeable, 22.90% was bound to carbonate, 10.21% was associated with Fe-Mn oxides, 4.43% was linked to organic material, and 50.53% remained as residual Cd (Figure 4). Compared to the CK treatment, the exchangeable Cd decreased by 9.38%, the carbonate-bound Cd increased by 4.91%, and the Fe-Mn oxides bound Cd increased by 2.13% in the $C_{10}P_0$ treatment. When biochar was added to the soil, the amount of exchangeable Cd went down, but the amounts of carbonate-bound Cd and Fe-Mn oxides bound Cd went up. Compared to the CK treatment, with the C_0P_{10} treatment, we observed that the exchangeable Cd in the soil decreased by 2.18%, the carbonate-bound Cd decreased by 5.28%, and the residual Cd increased by 8.76%. The use of $Ca(H_2PO_2)_2$ facilitated the transformation of exchangeable Cd and carbonate-bound Cd into residual Cd inside the soil.

Compared to the CK treatment, the exchangeable Cd decreased by 45.86%, the carbonate-bound Cd decreased by 20.55%, and the residual Cd increased by 22.02% in the C_5P_{10} treatment. When biochar and $Ca(H_2PO_2)_2$ were applied together, increasing the amount of $Ca(H_2PO_2)_2$ resulted in a drop in the proportion of exchangeable Cd and Fe-Mn oxides bound Cd. Meanwhile, the proportion of residual Cd increased and the proportion of organic matter Cd initially increased and subsequently decreased. The ratio of carbonate-bound Cd to Fe-Mn oxides bound Cd in the soil increased in direct proportion to the biochar application amount, whereas the exchangeable Cd decreased in an inverse proportion to the biochar application rate when the phosphate application rate remained constant.

The application of either biochar or phosphate to the soil after cabbage planting resulted in a considerable reduction in the concentration of DTPA-Cd in the soil (Figure 5). Compared to the CK treatment, the DTPA-Cd content decreased by 16.80% in the C_5P_{10} treatment. The DTPA-Cd content in the soil decreased when the application amounts of $Ca(H_2PO_2)_2$ increased.

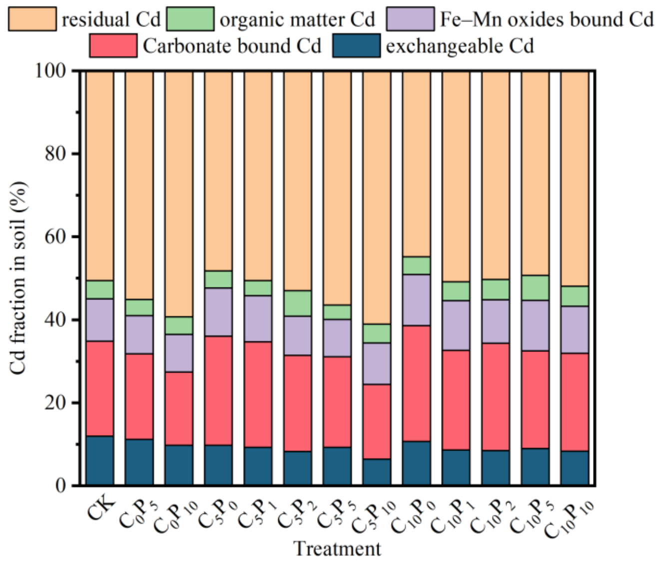


Figure 4. Effect of the combined application of biochar and calcium superphosphate on the Cd content of different forms of soil after cabbage planting. Data are mean ± SE (n = 3) (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}; P_0, P_1, P_2, P_5, P_{10} represent calcium superphosphate application amounts of 0, 0.1, 0.2, 0.5, 1.0 g kg^{-1}).

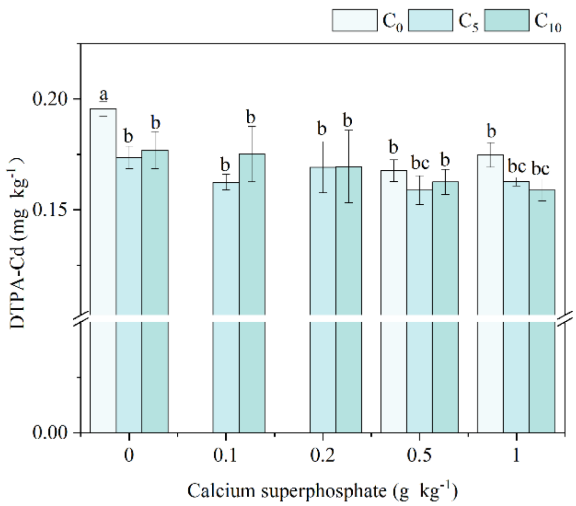
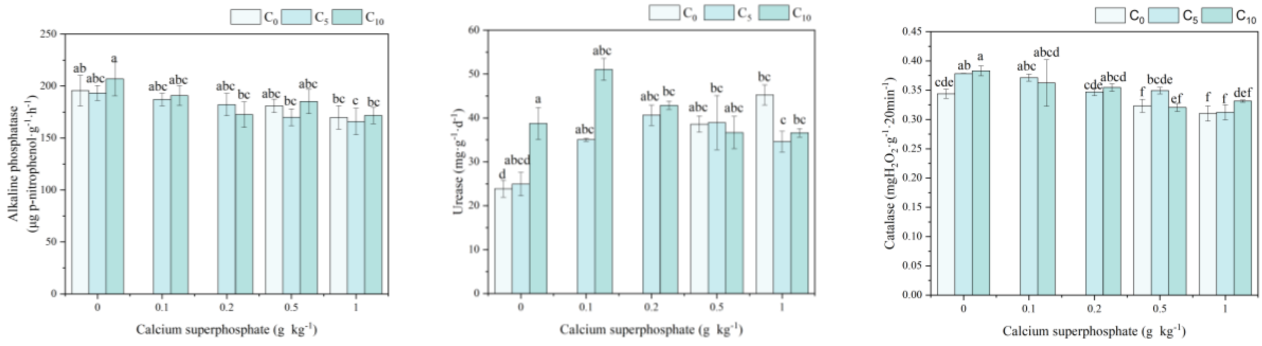


Figure 5. Effect of the combined application of biochar and calcium superphosphate on the DTPA-extractable Cd of soil after cabbage planting. Data are mean ± SE (n = 3). (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}. Different lower case letters above columns indicate statistical differences at $p < 0.05$).

3.5. Chemical Properties of Soil Under Amendments Application

In the soil after cabbage planting, the alkaline phosphatase activity showed a decreasing trend with the increase in $Ca(H_2PO_2)_2$ application (Figure 6a). Compared to CK, the alkaline phosphatase activity increased by 4.44% in $C_{10}P_0$. At a 10 g kg^{-1} biochar application amount, the alkaline phosphatase activity in the $C_{10}P_{10}$ treatment was significantly decreased by 17.0% compared to the $C_{10}P_0$ treatment. The alkaline phosphatase activity was positively correlated with the biochar application amount under the same phosphate fertilizer content.

The soil urease activity increased by 4.44% in C_5P_0 and 61.64% in C_0P_{10} (Figure 6b). The application of $Ca(H_2PO_2)_2$ and biochar also significantly increased the activity of urease in the soil. When the biochar application amount was the same, the urease activity increased first and then decreased with the phosphorus application amount.



(**a**) (**b**) (**c**)

Figure 6. Effect of the combined application of biochar and calcium superphosphate on the alkaline phosphatase (**a**), urease (**b**), and catalase (**c**) of soil after cabbage planting. Data are mean ± SE (n = 3). (C_0, C_5, and C_{10} represent biochar application amounts of 0, 5, 10 g kg^{-1}. Different lower case letters above columns indicate statistical differences at $p < 0.05$).

The catalase activity increased by 5.8% under the $C_{10}P_0$ treatment compare to CK (Figure 6c). This meant that the application of biochar increased the catalase activity in the soil. Under the same application amount of biochar, the catalase activity in the soil was inversely proportional to the application amount of phosphate fertilizer.

Table 2 shows that the addition of biochar and $Ca(H_2PO_2)_2$ significantly increased the content of AP in the soil. After the addition of biochar, the gap in AP between different phosphorus application levels decreased, which may be caused by the fact that biochar application promoted the growth of cabbage and uptake of phosphorus from the soil.

Table 2. Effect of the combined application of biochar and calcium superphosphate on the pH and available phosphorus of soil after planting.

Treatment	pH	Available Phosphorus (mg kg^{-1})
CK	8.24 ± 0.01ab	6.50 ± 0.49g
C_0P_5	8.24 ± 0.05ab	20.36 ± 1.43b
C_0P_{10}	8.21 ± 0.05ab	25.83 ± 1.88a
C_5P_0	8.24 ± 0.03ab	8.99 ± 0.25f
C_5P_1	8.25 ± 0.03ab	11.38 ± 0.65def
C_5P_2	8.25 ± 0.07ab	11.94 ± 0.86de
C_5P_5	8.28 ± 0.04ab	15.18 ± 0.51c
C_5P_{10}	8.23 ± 0.05ab	24.07 ± 0.57a
$C_{10}P_0$	8.24 ± 0.06ab	9.65 ± 0.54ef
$C_{10}P_1$	8.23 ± 0.06ab	12.43 ± 0.24d
$C_{10}P_2$	8.18 ± 0.05ab	12.05 ± 1.06d
$C_{10}P_5$	8.17 ± 0.02b	17.19 ± 0.93c
$C_{10}P_{10}$	8.14 ± 0.03b	21.17 ± 2.56b

Different lower case letters above columns indicate statistical differences at $p < 0.05$.

In this experiment, the effect of biochar on soil pH was not significant (Table 2). This may be due to the high pH of the soil. Compared with the CK treatment, the soil pH increased insignificantly after 5 g kg^{-1} biochar was applied. At a 10 g kg^{-1} biochar application amount, the soil pH decreased with the increase in the amount of phosphorus applied. At a biochar application amount of 5 g kg^{-1}, there was no significant change in the soil pH with the increase in the $Ca(H_2PO_2)_2$ application.

A significant positive relationship was found between organic matter-bound Cd and carbonate-bound Cd (Figure 7). Applying biochar to the soil can lead to an increase in organic carbon and carbonate-bound Cd content. This increase in carbonate-bound Cd content helped to decrease the bioavailability of Cd. In Figure 7, there was a substantial negative association between the available phosphorus and Cd contents in the shoots and roots. A strong positive correlation was seen between the DTPA-Cd content and the Cd content in both the shoots and roots of cabbage. This suggest that the simultaneous use of $Ca(H_2PO_2)_2$ and biochar could mitigate the toxicity of Cd by enhancing the concentration of available phosphorus in the soil.

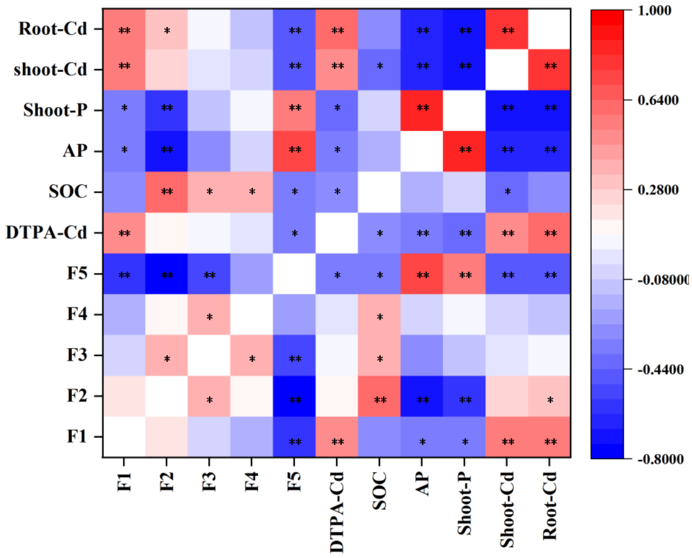


Figure 7. Correlation between Cd content in cabbage, soil chemical properties, and Cd forms (** significant at level $p < 0.01$; * significant at level $p < 0.05$. F1, F2, F3, F4, and F5 represent exchangeable Cd, carbonate-bound Cd, Fe-Mn oxides bound Cd, organic matter-bound Cd, and residual Cd).

4. Discussion

The phytotoxicity of Cd on plants primarily relied on the concentration of DTPA-Cd present in the soil [42,43]. The incorporation of biochar and phosphate fertilizer resulted in a significant decrease in DTPA-Cd levels in the soil and facilitated the conversion of mobile Cd into more stable fractions within the soil [27,28]. The biochar treatment resulted in a decrease in the amount of exchangeable Cd in the soil compared to the CK treatment. Additionally, there was a significant increase in the content of carbonate-bound Cd and Fe-Mn oxides bound states in the soil. The addition of biochar to soil contaminated with Cd resulted in a negligible increase in the concentration of Cd bound to organic matter in the soil. There was a positive correlation between the amount of biochar applied and the content of carbonate-bound Cd [45].

$Ca(H_2PO_2)_2$ greatly decreased the amount of exchangeable Cd in the soil and dramatically increased the amount of residual Cd. Phosphates facilitate the conversion of heavy metals into stable forms primarily by causing metal phosphate precipitation and ion exchange [28,31]. Nevertheless, many investigations had yielded opposite findings about the impact of P fertilizer on the bioavailability reduction in Cd in soil [46]. This could be attributed to the competition between Ca^{2+} and Mg^{2+} ions present in the P fertilizer and Cd ions in the soil for adsorption sites [43]. The impact of P fertilizer on cadmium was dependent on the quantity of phosphate application, soil characteristics, and features [32].

There was a decrease in the levels of carbonate-bound Cd and Fe-Mn oxides bound Cd in the soil as the application amount of $Ca(H_2PO_2)_2$ applied increased. Meanwhile, the residual Cd increased (Figure 4). Adding biochar and P fertilizer to cadmium-contaminated soil would form $Cd_5(PO_4)_3OH/Cl$ on the surface of biochar [35]. Chen et al. [47] found that the abundant surface groups of biochar, such as hydroxyl and amino, can adsorb nanohydroxyapatite (nHAP) and prevent the polymerization of nHAP. Meanwhile, the presence of nHAP also enhanced the adsorption capacity of biochar [31,48]. Therefore, the combined application of biochar and $Ca(H_2PO_2)_2$ improved the immobilization capacity. When $Ca(H_2PO_2)_2$ application was low, the use of $Ca(H_2PO_2)_2$ increased the amount of organically bound Cd in the soil. Conversely, when phosphorus application was high, it decreased the amount of organic matter Cd in the soil. Under high $Ca(H_2PO_2)_2$ treatment, the content of residual Cd was higher than that under low phosphorus treatment, and exchangeable Cd was lower than that under low phosphorus treatment [36]. Combined application led to the transformation of mobile Cd in the soil into an insoluble state [49].

The exchangeable state had a direct impact on the plants' ability to absorb heavy metals, with the residue state being the most stable [20]. Under appropriate conditions, the carbonate-bound state and organic matter state could undergo a transformation into exchangeable states, and then they would be assimilated by plants [50]. The impact of the quantity of biochar applied on the levels of exchangeable and residual Cd was found to be insignificant in alkaline soil. The combined use of biochar and $Ca(H_2PO_2)_2$ resulted in a notable increase in the concentration of AP in the soil. This, in turn, facilitated the conversion of free Cd into phosphate precipitation within the soil [51]. The utilization of both phosphate fertilizer and biochar exhibited a heightened level of stability and a long-lasting impact on the immobilization of Cd in soil, as demonstrated by Li et al. [36].

Some studies showed that biochar can change the accumulation of organic carbon in soil [52]. Biochar can promote soil fertility and crop growth [3]. Cd promoted oxidative loss in plants by increasing the production of reactive oxygen species (ROS) [53], and plant cells reduce ROS levels through a variety of protective mechanisms, including the antioxidant enzyme system. Under high Cd stress, the activity of antioxidant enzymes in plants increased, and the contents of SOD, POD, CAT, and other stress-resistant indexes increased [54]. The addition of biochar alleviated the toxicity of soil Cd to plants. The application of biochar significantly increased the biomass of cabbage and reduced the content of Cd in cabbage, which was the same as the findings of Bian et al. [55]. The synergistic effect of combining biochar with $Ca(H_2PO_2)_2$ on plant growth surpassed that of applying phosphate fertilizer or biochar alone, and it exhibited a certain level of stability.

5. Conclusions

The concurrent utilization of biochar and phosphate fertilizer resulted in a significant decrease in the DTPA-Cd concentration in the soil, suppressed the uptake of Cd by cabbage, and enhanced the growth of cabbage. Furthermore, the application of biochar and phosphate fertilizer enhanced the transformation of exchangeable Cd into more enduring forms such as carbonate-bound and residual Cd, hence diminishing the availability of Cd for plants. Therefore, to address heavy metal contamination in soil, it is recommended to use a combination of 5 g kg^{-1} of corn stalk biochar and 1.0 g kg^{-1} of superphosphate. This treatment has been found to have a positive impact on the environment and provide economic advantages. Moreover, the suggested application quantities were evidently reduced in comparison to prior reports. Nevertheless, it is imperative to take into account long-term investigations in forthcoming assessments. Furthermore, the presence of Cd in phosphate fertilizer might exacerbate Cd contamination. Conducting field studies is crucial to accurately assessing the impact of biochar and phosphate fertilizer on soil Cd rehabilitation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14112538/s1. Figure S1. Effect of the combined application of biochar and phosphate fertilizer on the growth of cabbage at 50 days of growth. Figure S2. Effect of the combined application of biochar and phosphate fertilizer on the fresh weight of cabbage at 50 days of growth. Figure S3 Effect of the combined application of biochar and phosphate fertilizer on the photosynthetic pigment in cabbage leaves at 50 days of growth. Table S1. Some physical and chemical properties of soil, biochar, and $Ca(H_2PO_2)_2$ used in the experiment. Table S2. Sequential fractionation of Cd in soils [56,57].

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