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Effect of Organic and Inorganic Soil Amendments on Cadmium Immobilization and Bioaccumulation in Chinese Cabbage

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Abstract: Chemical immobilization, as a cost-effective and environmentally friendly technique, has been widely researched in the remediation of cadmium (Cd)-contaminated soil. The key is to find appropriate amendments and optimize their use. In this study, the effects of the application of an inorganic material (phosphorus slag (PS)) and organic materials (biochar (BC) and beer lees (BL)), individually or combinedly on the immobilization of Cd in contaminated soil and subsequent bioaccumulation in Chinese cabbage were investigated. The results showed that PS and PS+BL were more effective in decreasing exchangeable Cd (EX-Cd) than other treatments, decreased by 91.2% in the PS treatment and by 64.0% in the PS+BL treatment. However, the soil enzyme activity and soil microbial activity decreased in the treatment with PS alone. In contrast, the combination use of PS and BL could increase soil enzyme activity, soil microbial activity, and functional diversity, and decrease EX-Cd as well. Moreover, the PS+BL treatment reduced the accumulation of Cd in Chinese cabbage most effectively, 81.5% in roots and 72.5% in shoots. This treatment could also increase the aboveground height and chlorophyll content of Chinese cabbage while reducing the content of malondialdehyde (MDA). Thus, the PS + BL treatment is highly recommended for Cd immobilization, as it can improve soil quality and reduce Cd accumulation in Chinese cabbage at the same time and hence promote plant growth.

Key words: cadmium (Cd); metal pollution; soil amendments; vegetable

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0 Introduction

Cd is one of the most hazardous elements in the environment. According to statistics, about 10 million hectares of agricultural soils have been contaminated by Cd in China[1]. Moreover, the Cd-contaminated soils are also generally accompanied by the deterioration of physical, chemical, and biological properties[2,3], threatening the

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long-term soil productivity—the main hindrance to achieving the goal of sustainable ecosystem development[4]. Cd in soil can result in Cd accumulation in crops, which may exceed the Cd threshold, thereby increasing the risk of human exposure to Cd[5]. Thus, the remediation of Cd-contaminated soils in China has become urgent. Considering the widespread distribution of Cd-contaminated soil and the sustainable development of agriculture, it is necessary to reduce the cost of remediation and to improve soil quality simultaneously.

The techniques for the remediation of Cd-contaminated soils can be classified as physical, chemical, and biological methods[6]. Physical remediation methods include surface capping, encapsulation, soil isolation, and nitrification, which can efficiently alleviate the risk of exposure to the contaminated soil[7]. However, these are not truly soil "remediation" techniques, as the heavy metal contaminants are only isolated in situ[8]. Biological remediation includes phytoextraction, phytovolatilization and microorganisms, which are evaluated as low-cost techniques and are easy to implement in-situ[9, 10]. In total, 721 hyperaccumulator plants were researched[11] regarding their ability to accumulate metals or metalloids. Obviously, only heavy metals with a low concentration can be treated, and the time required is very long, which limits the wide use of bioremediation. Chemical immobilization represents a cost-effective and environmentally compatible technique in reducing the mobility and bioavailability of Cd in soil, as well as its transfer to plants[12]. The aim of chemical immobilization relies on adding an amendment to the contaminated soil to change the valence state or form of metals to reduce their migration rather than total removal[13].

So far, much work has been done regarding the effect of materials used as amendments on the remediation of heavy metals in soil. Various amendments materials have been verified as effective in reducing the bioavailability of heavy metals in soils, including inorganic, organic and microorganismic materials[14]. Inorganic materials, such as phosphate- and carbonate-containing materials, have a higher immobilization ability because of their high alkalinity[2]. However, the large input of inorganic materials would lead to the deterioration of soil quality due to a reduction in soil organic carbon (SOC) and negative effects on the soil microaggregates[15]. Organic amendments can be used as one of the major carbon source[16]. Several studies have reported that organic amendments can significantly increase soil microbiological properties, such as bacterial diversity and the microbial community structure, and can improve soil enzyme activity[17]. Microorganisms can also be used to assimilate, precipitate, oxidize, or reduce heavy metal toxicity. Moreover, microorganisms can degrade organic matters into nutrients available to plants and in turn improve the soil microbial status[18]. For example, Cd-tolerant *Saccharomyces cerevisiae* was used for the removal of Cd from contaminated soil[19]. However, the amount of organic amendment used for heavy metal remediation is usually quite large. Therefore, it is of great interest in developing a highly efficient environmentally compatible soil amendments with a combination of various materials for the remediation of Cd-contaminated soils and improving soil quality as well.

In this study, an inorganic material, phosphorus slag (PS), and organic materials, biochar (BC) and beer lees (BL), were evaluated in the remediation of Cd-contaminated soil. PS, a byproduct from the production of yellow phosphorus, is a kind of good fixing material because of its good adsorption property and strong fixing ability to cadmium. BL is the main byproduct from the beer industry, a residue of fermented barley after soluble carbohydrates extract, which contains abundant organic matters. BC made from different raw materials as a promising amendment material has been demonstrated to be effective in reducing the bioavailability of heavy metals as well as improving soil quality. Therefore, pot trials were conducted to compare the effects of PS, BC, and BL applied alone or together on the immobilization of Cd and the soil quality. Chinese cabbage was planted in treated and untreated soil to understand the effects of the amendments on the accumulation of Cd in plants to provide some theoretical and practical bases for rational application of amendments for sustainable agricultural development.

1 Materials and Methods

1.1 Experimental Materials

Soil was collected at a depth of 0-20 cm from a hill at China Three Gorges University (CTGU) in Yichang, Hubei Province, China (105.75° E, 29.56° N). After the removal of gravel and plant residues, the soil was air-dried, thoroughly mixed, and passed through a 2 mm nylon sieve for later analyses. The cadmium-contaminated soil (CS-H) used in the experiment was prepared by spraying $Cd(NO_3)_2·4H_2O$ solution into the original soil sample with 70% of the relative water content (*W*/*V*). The soil was then aged at room temperature for one month, and dried and ground to pass through a 2-mm nylon sieve. Finally the as-obtained CS-H was kept in a desiccator for later use. There were three soil amendments utilized in this study. PS was obtained from Hubei Xingfa Chemicals Group Co., Ltd., Hubei Province, China, and was pretreated as in previous study[20]. BL were provided by CHEER®BEER Group (Jingmen, Hubei Province, China). BL powder was used directly or as BC raw materials after air drying, grinding and passing through a 1.5 mm nylon sieve. BC was produced by BL powder pyrolysis at 450 ℃ in a nitrogen atmosphere. The main physicochemical properties of the soil, BL and BC are shown in Table S1.

1.2 Pot Trial

The pot trial was conducted in a glasshouse located in the Three Gorges University campus. The average temperature in the glasshouse ranged from 27 to 35 ℃, and relative humidity ranged from 70% to 90%. The soil (9.5 kg) was mixed with amendments in plastic pots (39 cm×29 cm×12.5 cm). The treatments included the following: i) control (CK); ii) 2% BC; iii) 2% BL; iv) 2% PS; v) 1% PS+1% BL; vi) 1% PS+1% BC, where the percentage represents the percentage of certain amendment materials applied to the soil on a mass basis. Each treatment was set up with three replicates.

Chinese cabbage pot trials were also performed to demonstrate the accumulation of Cd in plants and to evaluate the effects of remediation with different treatments. Thirty Chinese cabbage seeds were planted in each pot and then reduced to fifteen seedlings after germination. Deionized water was added daily to the pots to maintain the soil content at approximately 70% in all treatments.

1.3 Sampling and Analysis

1.3.1 Sample collection and preparation

Chinese cabbage was harvested at 90 days after planting, and roots and leaves were collected separately. All these plant parts were washed with deionized water. Fresh plants were used to analyze the content of chlorophyll and malondialdehyde (MDA) activity, while the remaining samples were dried in an oven at 70 ℃ for Cd content analysis.

The rhizospheric soil samples were immediately collected from each pot and divided into two subsamples. The fresh rhizospheric soil samples were analyzed using BIOLOG ECO plates, and the remaining samples were air-dried and passed through a 2 mm sieve for analysis of chemical properties, Cd content and soil enzyme activities[21].

1.3.2 Soil chemical properties

Soil pH was measured with a glass electrode at a water-to-soil mass ratio of 2.5: 1. Soil organic matter (SOM) was determined by hydrothermal potassium dichromate colorimetry.

1.3.3 Cd analysis

The content of Cd in soil and plant samples was determined by ICP-MS (X Series 2, Thermo Co., Ltd., USA). To measure the total Cd content, soil samples were first digested with HNO_3 and HCl (1:3, *V*/*V*; aqua regia). For exchangeable, reducible, oxidizable, and residual Cd fractions in soil, the modified Community Bureau of Reference (BCR) sequential extraction procedure was applied to pretreat the soil[22]. In a typical plant sample pretreatment process, a 0.5 g plant sample was digested with a mixed solution of HNO_3 and H_2O_2 (1:1, *V*/*V*) in a digestion tank at 140 ℃ for 14 h. All the solutions were measured with ICP-MS after passing through a 0.45-μm filter membrane. The results were validated using standard samples (GNM-SCD-002-2013) from Guobiao (Beijing) Testing & Certification Co., Ltd. An analytical blank from the pretreatment process was also used to calibrate the results.

1.3.4 Soil enzyme activity analysis

Soil catalase, saccharase, urease, and alkaline phosphatase activities were determined by the potassium permanganate titration method, 3, 5-dinitrosalicylic acid colorimetry, the disodium phenyl phosphate colorimetric method[23], and the phenol sodium hypochlorite colorimetric method, respectively[24].

1.3.5 BIOLOG analysis

Soil microbial function was estimated by the BIOLOG ECO plate method. Average well color development (AWCD) was employed to measure general microbial activity[25].

$$\mathrm{AWCD} = \left[\sum (C_i - R) \right] \Big/ n \tag{1}$$

where C_i is the absorbance value of each reaction well at 590 nm, R is the absorbance value of the control well, and n is the number of wells.

The metabolic functional diversity of microbial microorganisms was reflected by the Shannon index, Simpson index, and McIntosh index, which represents the richness, diversity, and evenness of the species in the community, respectively[26-28].

$$\text{Shannon index, } H = \sum (P_i \cdot \ln P_i) \quad (2)$$

$$\text{Simpson index } (1/D),\ D = \sum \frac{n_i(n_i - 1)}{N(N-1)} \quad (3)$$

$$\text{McIntosh index, } E = \sqrt{\sum n_i^2} \quad (4)$$

where P_i represents the ratio of the relative absorption value of the i-th well to the total relative absorbance value of all wells, n_i represents the relative absorption value of the i-th well, and N represents the total relative absorbance value of all wells.

1.3.6 Plant characteristic property analysis

MDA activity and chlorophyll contents (SPAD) in plant samples were measured using the thiobarbituric acid (TBA) reaction and spectrophotometry, respectively[29, 30].

1.3.7 Statistical analysis

The data obtained were subjected to analysis of variance (ANOVA) of means with Duncan's multiple range test by using SPSS 19.0. Figures were prepared with Origin 9.0. Data are presented as the mean±error bar with statistical significance at p<0.05.

2 Results and Discussion

2.1 Effects of Amendments on Soil pH, SOM, and Cd Fractions in Soils

As illustrated in Fig. 1(a), soil pH increased significantly (p<0.05) with the addition of amendments except in the BC treatment. The highest pH was observed in the PS treatment, increasing by 1.7 units compared with the CK. This can be explained by the PS alkaline properties and the relatively higher contents of Ca and Mg and the dissolution of their respective carbonates and oxides[31]. The addition of BL significantly (p<0.05) increased the content of SOM by 103.65% compared with the CK (Fig. 1(b)) due to its different chemical nature. As a pure inorganic material, PS can increase the bulk density of soil, which may account for the decrease of SOM by 4.15% in the PS treatment. This necessitates organic amendments for maintaining or improving soil quality. In fact, the combined application of PS and BL significantly (p<0.05) increased SOM by 43.12%.

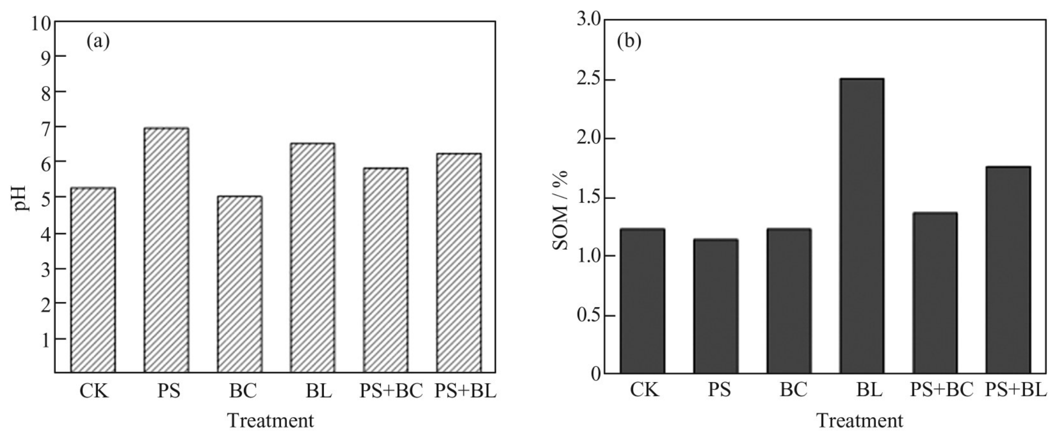

Fig. 1 Effects of different treatments on soil pH (a) and SOM (b)

Of all the fractions of Cd, the exchangeable fraction is the most toxic to plants and can be considered as the bioavailable state; the reducible and oxidizable fractions (RE-Cd, OX-Cd) are potentially bio-available; the residual fraction (RS-Cd) is hardly absorbed/utilized by plants and can be considered as the stable state[32]. The fractions of Cd in soils of different treatments are shown in Fig. 2. In the CK treatment, the highest fraction was EX-Cd, followed by RE-Cd, RS-Cd, and OX-Cd, indicating that EX-Cd and RE-Cd dominated the Cd fractions in soil.

In all treated soil samples, EX-Cd was significantly (p<0.05) decreased while the RE-Cd, OX-Cd, and RS-Cd fractions increased. The EX-Cd in soil followed the

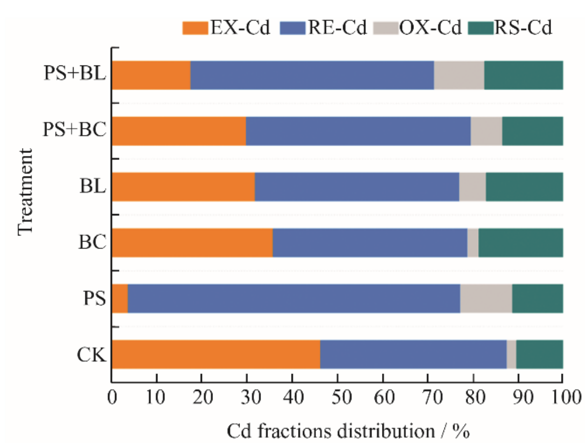

Fig. 2 The percentage of Cd fractions in soil with the addition of different amendments

order of PS<PS+BL<PS+BC<BL<BC<CK. The EX-Cd level in the PS treatment was decreased by 91.21%. Previous studies reported that the heavy metal exchangeable form is affected by soil pH and SOM, especially soil pH, which significantly influences metal bioavailability. Bashir *et al*[33] also reported that the hydrolysis and dissolution of these alkaline substance could increase soil pH and induce precipitation of Cd as $CdCO_3$ and $Cd_3(PO_4)_2$, which could increase the residual Cd portion in soil. Therefore, it is postulated that the addition of alkaline PS increases the pH value of the soil and inturn forms of Cd precipitates of phosphate, carbonate and hydroxide in the PS treatment. Compared with a 3% addition of sepiolite, BC, zeolite (ZE) and rock phosphate (RP) in previous studies[34,35], PS was quite effective in reducing RE-Cd.

It has been reported that the interaction between Cd and organic matter containing functional groups such as hydroxyl groups, phenols, carbonyl groups, and carboxyl groups can significantly reduce EX-Cd in soil[36]. Chen *et al*[37] found that the application of compost produced from poultry manure and chaff in Cd-contaminated soils transformed 47.8%-69.8% of EX-Cd to the organic-bound fraction. Liu *et al*[38] showed that chicken manure compost application resulted in a decrease of soluble/exchangeable Cd by 71.8%-95.7%. In our study, BL was more effective than BC in reducing EX-Cd due to its higher organic matter content. In this study, the application of BL and BC did reduce the fraction of EX-Cd as expected. But, it is worth noting that by combining BL or BC with PS, the reduce of EX-Cd was much more significant than that in the BL+PS treatment (the reduction is 64.0%). In general, PS and PS+BL could reduce the bioavailability of Cd in soil. The proportions of OX-Cd and RS-Cd changed correspondingly with the decrease in EX-Cd and RE-Cd.

2.2 Effects of Amendments on Soil Enzyme Activity

Soil enzymes such as catalase, urease, alkaline phosphatase, and saccharase play critical roles in catalyzing biochemical reactions during the decomposition of microorganisms, plants, and animals, which form the basis of soil metabolism and have been considered as appropriate indexes of soil quality[39,40]. The effects of amendments on soil enzyme activities in Cd-contaminated soil are listed in Table 1. All four soil enzyme activities were enhanced significantly (p<0.05) with the addition of various amendments except for PS, which decreased soil urease and saccharase activities. The highest catalase (increased by 222.06%), alkaline phosphatase (increased by 1 281.72%), saccharase (increased by 161.30%), and urease (increased by 173.84%) activities were observed in the BL treatment, followed by the PS+BL treatment. Previous studies have reported that enzyme activities were highly correlated with SOM[17]; therefore, the addition of organic amendments with high organic matter causes an increase in soil enzyme activities. In our study, therefore, BL was more capable of increasing enzyme activities in soil than PS+BL. Similarly, organic fertilizer, rice-straw compost and manure has been reported to increase urease and alkaline phosphatase activities significantly[15,39,41].

In addition, the single application of PS led to a dramatic (p<0.01) increase in catalase activity, which may be due to the increase in soil pH and the decrease in EX-Cd, as it was demonstrated that catalase activity was positively correlated with soil pH and negatively correlated with EX-Cd[42]. Microhydroxyapatite and inorganic

Table 1 Effects of different amendments on the activity of soil enzymes

Treatment	Catalase activities /($mg\cdot g^{-1}\cdot(30\ min)^{-1}$)	Urease activities /($mg\cdot g^{-1}\cdot(24\ h)^{-1}$)	Alkaline phosphatase activities /($mg\cdot g^{-1}\cdot(24\ h)^{-1}$)	Saccharase activities /($mg\cdot g^{-1}\cdot(24\ h)^{-1}$)
CK	0.457 4±0.026 39^{d}	0.234 3±0.059 61^{bc}	0.074 4±0.005 51^{c}	5.036 1±0.054 06^{c}
PS	0.856 2±0.093 36^{c}	0.130 7±0.039 78^{c}	0.142 3±0.017 04^{c}	1.439 8±0.317 87^{d}
BC	0.903 8±0.043 14b^{c}	0.325 5±0.045 66^{b}	0.094 7±0.012 26^{c}	6.028 3±1.175 37^{c}
BL	1.473 1±0.014 62^{a}	0.641 6±0.077 14^{a}	1.028±0.177 75^{a}	13.159±0.448 51^{a}
PS+BC	0.479 3±0.009 68^{d}	0.243 8±0.007 47^{bc}	0.111 4±0.018 59^{c}	2.841 1±0.649 5^{cd}
PS+BL	1.039 2±0.031 26^{b}	0.388 6±0.04727^{b}	0.567 5±0.018 36^{b}	9.537 8±2.160 85^{b}

Note: The different letters represent significant difference (p<0.05)

P fertilizer were also proved to be satisfactory in increasing catalase activity[43].

The alkaline phosphatase enzyme activity was reported to be positively correlated not only with SOM and microbial activity[44] but also with available phosphorus (AP). This may be responsible for the increase in alkaline phosphatase enzyme activity in the PS treatment, although not significant. However, a single application of PS had a negative effect on soil urease and saccharase activities, decreasing by 44.21% and 71.41%, respectively, considering their close relationship with SOM, microbial action, and soil pH[45,46].

It is worth noting that Cd has a beneficial effect on soil enzyme activities[39]. The dramatic decrease in soil Cd content in the PS treatment group did lead to a decrease in soil enzyme activity.

2.3 Effect of Amendments on Microbial Activity and Diversity

2.3.1 Average well color development

AWCD is an important indicator of the capability of microorganisms to utilize carbon sources, reflecting the soil microbial activity[28]. The AWCD of all treatments increased with incubation time (Fig. 3), which increased rapidly after 1 day, slowed down after 5 days, and gradually stabilized after 8 days. Similar AWCD changes during incubation were reported by Ge *et al*[28]. In 8 days, the increase in the AWCD values followed the order of BL>PS+BL>BC>PS+BC>CK>PS. The result suggests that BL can be recognized as a suitable material in increasing soil microbial activity[4]. It is known that the application of BL increased SOM and soil enzyme activities. Enzymes promote the decomposition of organic matter into a C source and then speed the growth and reproduction of microorganisms[47].

BL is rich in *Saccharomyces cerevisiae*, which improves the metabolic activity of microorganisms. By contrast, PS reduced microbial activity, as AWCD in the PS treatment decreased significantly by 49.00%, which may result from the sensitivity of microorganisms to the pH of the environment[4,48] offered by PS. The microbial activity also significantly (p<0.05) increased in the PS+BL treatments, and no significant (p<0.05) differences were observed between the BL and PS+BL treatments, indicating that PS with the addition of BL can counteract the inhibitory effect of PS on soil microbial activity.

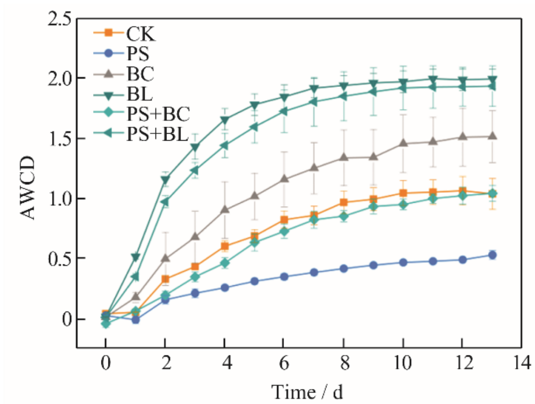

Fig. 3 The AWCD of different carbon sources with incubation time in different treatments

2.3.2 The diversity indices

The metabolic functional diversity of soil microbial communities is reflected by functional diversity indices. A higher diversity index indicates that the metabolic functional diversity of the soil microbial community is quite high[28]. The Shannon diversity index (H), Simpson index ($1/D$) and McIntosh index (E) for all treatments are provided in Table 2.

Table 2 The metabolic functional diversity indices of the soil microbial communities under different amendments

Treatment	Shannon index	Simpson index	McIntosh index
CK	2.585 8±0.110 55^{d}	33.969 0±2.886 41^{b}	4.884 6±0.461 34^{c}
PS	2.371 2±0.067 76^{d}	25.892 2±0.792 97^{d}	4.718 4±0.076 90^{c}
BC	3.141 1±0.084 17^{bc}	43.416 9±3.071 91^{b}	8.991 3±1.026 00^{b}
BL	3.380 0±0.004 70^{a}	52.852 8±1.032 27^{a}	11.425 8±0.390 19^{a}
PS+BC	2.932 6±0.058 44^{c}	35.719 3±3.013 99^{bc}	7.191 1±0.258 56^{b}
PS+BL	3.230 8±0.071 15^{ab}	40.808 4±2.607 89^{bc}	11.842 1±0.781 33^{a}

The different letters represent significant difference (p<0.05)

All treatments except PS increased the soil diversity index. It is worth noting that the Shannon index and Simpson index reached the highest level in the BL treatment, and the McIntosh index reached the highest level in the PS+BL treatment. It is reasonable that the higher SOM in BL and BL+PS treatments help to create a virtuous circle between the activity of enzymes and microorganism diversity[16, 49]. The effect of PS on the diversity indices in soil is similar to that of phosphate fertilizer[24], which influenced the nutrient balance and the biological properties of soil, thereby reducing the soil diversity index. Further studies are needed to explain the increase in the McIntosh index in the PS+BL treatment that was even greater than the total increase in the BL treatment and PS treatment.

2.3.3 Carbon utilization pattern

According to the biochemical properties of the carbon sources, the 31 carbon sources in the BIOLOG ECO microplates were divided into six categories: carbohydrates, carboxylic acids, amino acids, amines, polymers and phenolic compounds[50]. The AWCD value on day 9 was selected to calculate the utilization rate of different carbon sources by microbial communities (Fig. 4).

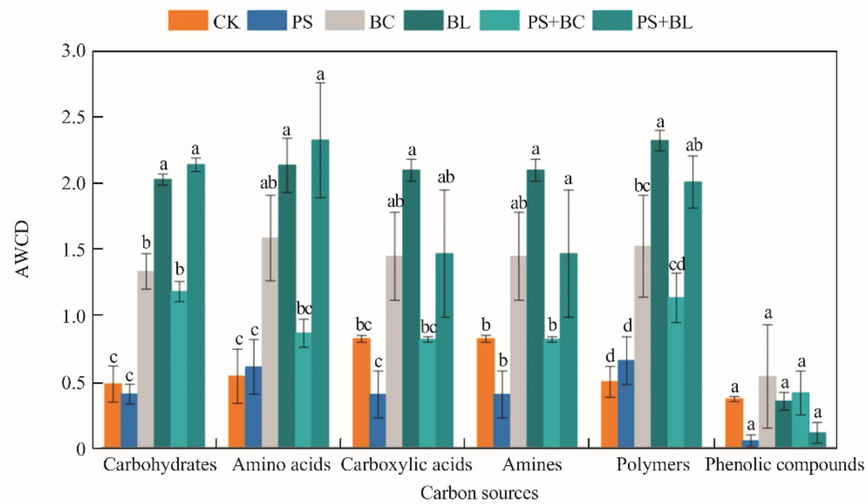

Fig. 4 Utilization of different carbon sources by soil microbial communities in different treatments

The different letters represent significant difference (p<0.05)

The lowest degree of metabolic utilization was phenolic compounds in all treatments. In the PS treatment, all carbon sources were subjected to a utilization level no higher than those in the control. The result indicated that PS application was likely to hinder the growth and metabolism of soil microorganisms by decreasing the utilization capacity of the carbon source. The AWCD values of the five carbon sources for the BL and PS+BL treatments were the highest, corresponding to the highest enzyme actives and prosperous microorganism communities.

2.3.4 Principal component analysis (PCA)

The absorbance on day 8 was used to quantify the carbon source utilization. The PCA results of carbon substrate utilization revealed that the two PCs (PC1 and PC2) explained 56.1% and 19.6%, respectively, of the variance in AWCD. The cumulative contribution ratio was 86.1% (>85%), which was sufficient to represent the information on the original variables. The load factor analysis showed that the largest loading (>0.60) on PC1 was from polymer, followed by carbohydrates, acid, amino acids, amines, and the largest loading (>0.60) on PC2 was from phenolic acids.

In PCA (Fig. 5), the distance between the samples represents the degree of similarity between samples, which in this case reflects differences in the metabolic functions of the microbial community between samples: the closer distance, the smaller the metabolic function differences. From Fig. 5, it is clear that soil samples of different treatments were relatively dispersed, which indicates that the addition of different amendments cause obvious changes in the metabolic function of the soil microbial community. Significant difference between CK and other samples indicates that the application of these amendments contributed to the change in the soil microbial community. The separation between BL, BL+PS

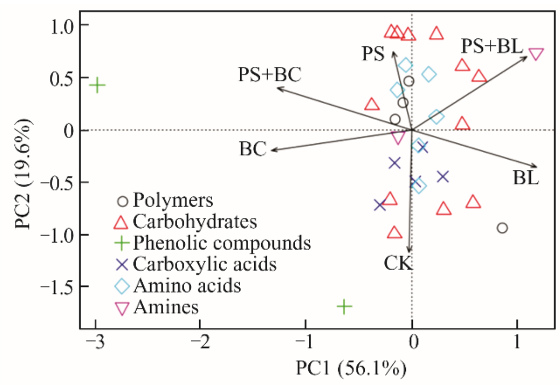

Fig. 5 PC analysis of the functional diversity of soil microbes in different amendments

and PS, BC, and BC+PS demonstrates that BL has a certain influence on the soil microbial community. Different amendments had different effects on the utilization of the carbon sources. In CK, carbohydrates and carboxyl acids were the most utilized. The addition of PS, PS+BC, or PS+BL increased the utilization of amino acids, while carbohydrates were still the most utilized. The application of PS+BL dramatically increased the utilization of amines.

2.4 Effects of Amendments on Growth and Accumulation of Cd in Chinese Cabbage

Cd accumulation in Chinese cabbage and its growth characteristics in all treatments are shown in Table 3. With the reduction of EX-Cd in soils after the application of different amendments, the content of Cd in shoots and roots of Chinese cabbage was significantly ($p<0.05$) reduced. In PS and PS+BL treatments, Chinese cabbage had the lowest Cd in shoots and roots. Although the Cd contents of Chinese cabbage from the PS and PS+BL treatments did not differ significantly, the growth characteristics of Chinese cabbage from those two treatments were quite different. A significant greater plant height and higher chlorophyll content were observed in the BL+PS treatment, indicating that Chinese cabbage was more prosperous in this treatment (Fig. S1).

Table 3 Effect of amendments on the height, root length, and chlorophyll content of Chinese cabbage

Treatment	Root /(mg/kg)	Leaf /(mg/kg)	Plant height /cm	Chlorophyll (a+b) /(μg /mL)	MDA /(nmol/g FW)
CK	57.26±1.56^{a}	58.71±0.72^{a}	10.26±0.23^{c}	0.63±0.07^{c}	5.73±0.22^{a}
PS	9.62±1.47^{d}	15.73±2.40^{c}	10.44±0.26^{c}	1.01±0.21^{ab}	3.88±0.17^{c}
BC	50.55±1.77^{b}	53.60±1.06^{a}	10.21±0.31^{c}	0.63±0.12^{c}	4.94±0.51^{b}
BL	24.16±2.81^{c}	38.55±0.98^{b}	10.86±0.25^{bc}	0.82±0.19^{abc}	4.38±0.07^{bc}
PS+BC	19.24±0.50^{c}	28.77±3.32^{b}	11.54±0.20^{b}	0.69±0.15^{bc}	4.83±0.20^{b}
PS+BL	10.60±1.34^{d}	16.14±2.96^{c}	14.68±0.25^{a}	1.05±0.27^{a}	3.89±0.72^{c}

The different letters represent significant difference ($p<0.05$)

The MDA content is usually regarded as one of the indicators of membrane lipid peroxidation[51]. In our study, the highest MDA content was observed in the CK, and it was decreased significantly ($p<0.05$) in all treatments compared with that of the control. The minimum MDA content was found in the PS and PS+BL treatments, which decreased by 32.286% and 32.112%, respectively, compared with the control. This suggested that the toxicity of Cd to plant growth was alleviated with the application of amendments at the same level.

3 Conclusion

In conclusion, all the amendments selected in this study can reduce EX-Cd in soil and then reduce the transference from soil to plants, thus significantly decreasing the accumulation of Cd in the shoots and roots of Chinese cabbage. Moreover, the combined application of inorganic waste, PS, and organic waste, BL, can improve soil quality by enhancing SOM, enzyme activity, and the diversity of microorganisms in soil and can improve plant quality by decreasing MDA, reducing the accumulation of Cd, boosting the vigor of plants, and providing desirable immobilization of Cd. The deterioration of soil quality by PS was more than offset by the addition of BL. At the same time, wastes were made the most use of. Thus, the combined application of inorganic and organic amendments, especially PS and BL, is highly recommended in the remediation of Cd-contaminated soil to improve soil quality and the safety of agricultural products.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Supplemental Information

Supplemental information can be found online at http://wujns.whu.edu.cn/en/article/doi/10.1051/wujns/2024296600/.

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有机无机复合土壤调理剂对污染土壤中Cd的固定和小白菜中Cd的生物累积的影响

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摘要：化学修复技术因为成本低效果好等优点，在修复镉(Cd)污染土壤中得到了广泛研究，其关键在于开发和应用优异的土壤改良剂。在本研究中，研究了无机材料(磷渣PS)和有机材料(生物炭BC和啤酒糟BL)单独或联合应用对受污染土壤中Cd的固定以及在小白菜中的生物积累的影响。结果表明，PS和PS+BL可显著降低土壤中的可交换镉(EX-Cd)，PS处理组降低了91.2%，PS+BL处理组降低了64.0%。然而，单独使用PS使土壤酶活性和土壤微生物活性明显降低。相比之下，PS+BL的联合使用不但增加了土壤的pH值也增加了其有机质含量，还增加了土壤酶活性、土壤微生物活性和功能多样性。同时，PS+BL处理组有效地减少了小白菜中镉的积累，其中根部减少81.5%，茎叶减少72.5%。PS+BL还可以增加小白菜的地上高度和叶绿素含量，同时减少丙二醛(MDA)的含量。因此，PS+BL的有机无机复合镉修复剂可有效固定污染土壤中的镉，从而减小镉在小白菜中的生物累积，同时改善土壤质量，促进植物生长。

关键词：Cd；重金属污染；土壤修复；蔬菜

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