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RESEARCH ARTICLE

Effect of peanut shell and wheat straw biochar on the availability of Cd and Pb in a soil–rice (*Oryza sativa* L.) system

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Abstract Soil amendments, such as biochar, have been used to enhance the immobilization of heavy metals in contaminated soil. A pot experiment was conducted to immobilize the available cadmium (Cd) and lead (Pb) in soil using peanut shell biochar (PBC) and wheat straw biochar (WBC), and to observe the accumulation of these heavy metals in rice (*Oryza sativa* L.). The application of PBC and WBC led to significantly higher pH, soil organic carbon (SOC), and cation exchange capacity (CEC) in paddy soil, while the content of $MgCl_2$-extractable Cd and Pb was lower than that of untreated soil. $MgCl_2$-extractable Cd and Pb showed significant negative correlations with pH, SOC, and CEC ($p < 0.01$). The application of 5% biochar to contaminated paddy soil led to reductions of 40.4–45.7 and 68.6–79.0%, respectively, in the content of $MgCl_2$-extractable Cd and Pb. PBC more effectively immobilized Cd and Pb than WBC. Sequential chemical extractions revealed that biochar induced the transformation of the acid-soluble fraction of Cd to oxidizable and residual fractions, and the acid-soluble fraction of Pb to reducible and residual fractions. PBC and WBC clearly inhibited the uptake and accumulation of Cd and Pb in rice plants. Specially, when compared to the corresponding concentrations in rice grown in control soils, 5% PBC addition lowered Cd and Pb concentrations in grains by 22.9 and 12.2%, respectively, while WBC addition lowered them by 29.1 and 15.0%, respectively. Compared to Pb content, Cd content was reduced to a greater extent in grain by PBC and WBC. These results suggest that biochar application is effective for immobilizing Cd and Pb in contaminated paddy soil, and reduces their bioavailability in rice. Biochar could be used as a soil amendment for the remediation of soils contaminated with heavy metals.

Keywords Biochar · Bioavailability · Contaminated paddy soil · Heavy metals · Rice

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Introduction

Soil heavy metal contamination is a global environmental problem, with this problem being extremely even more serious in China. The results of national soil pollution surveys showed that 19.4% of the total agricultural soil was contaminated by heavy metals (approximately 2.0×10^7 ha of agricultural soil) in China, with cadmium (Cd) and lead (Pb) being the major pollutants of heavy metals in the soil (Zhao et al. 2015). Cd and Pb are one of the most harmful heavy metals for human health. The accumulation of Cd and Pb in crop grains harvested in these agricultural soils is of great concern because of the enhanced dietary exposure through food chain transfer, affecting human beings who consume the grain (Khan et al. 2015). The Cd and Pb concentrations in food crops that exceed the national standard for food safety is more prevalent in southern China compared to other regions because of the acidity of the soils, which increases the phytoavailability of Cd and Pb in the soil (Zhao et al. 2015; Zhu et al. 2016). Therefore, it is necessary to reduce the bioavailability of Cd and Pb in acidic agricultural soils to ensure food security and human health (Mahar et al. 2015; Zhao et al. 2015).

Biochars are porous, low-density, and rich carbon materials produced by biological residues under low-oxygen combustion (Beesley et al. 2011). Recent studies have examined the applicability of biochar for the remediation of soil contaminated with heavy metals via the reduction of the mobility and availability of heavy metals, such as Cd and Pb, thereby reducing their accumulation within plants (Park et al. 2011; Puga et al. 2015; Zheng et al. 2015; Cui et al. 2016). The application of chicken manure- and green waste-derived biochars significantly reduces Cd and Pb accumulation by Indian mustard (*Brassica juncea*) through the immobilization of the metals (Park et al. 2011). Similarly, sugarcane straw biochar decreases the available concentrations of Cd and Pb in soil contaminated by mine waste and reduces their uptake by two leguminous plant species (Puga et al. 2015). However, the effect of biochar on heavy metal bioavailability is related to the plant source, application rate, and the type of heavy metal (Fellet et al. 2014; Lu et al. 2014; Yin et al. 2016). Bean stalk biochar and rice straw biochar significantly decrease Cd concentrations in rice grains, but the two biochars do not significantly affect the uptake of Pb (Zheng et al. 2015). In contrast, Lu et al. (2014) reported that rice straw biochar is effective in decreasing the shoot Pb concentration of *Sedum plumbizincicola*, while bamboo biochar is effective in decreasing Cd in the same plant. However, few studies have examined the influence of biochar feedstock on the bioavailability of Cd and Pb in contaminated agricultural soil–crop systems.

Rice (*Oryza sativa* L.) is a major staple crop in eastern and southern China; however, industrial production, mining operations, and metal processing have led to the contamination of paddy soils (Zhao et al. 2015). Some studies have demonstrated that biochar significantly reduces the mobility of Cd and Pb in contaminated paddy soil (Bian et al. 2014; Zheng et al. 2015; Li et al. 2016; Yang et al. 2016; Yin et al. 2016). However, studies investigating how different biochars affect the uptake of Cd and Pb by rice plants remain equivocal (Khan et al. 2013; Bian et al. 2014; Zheng et al. 2015; Li et al. 2016). Sewage sludge biochar significantly reduced the accumulation of Pb, but increased that of Cd in rice (Khan et al. 2013). Wheat straw biochar significantly reduced Cd concentration in rice roots, shoots, and grain, whereas Pb concentration was only reduced in rice roots, and no differences have been observed in rice grain and shoot Pb concentrations between amended and control plots (Bian et al. 2014). Cd concentrations in rice roots, shoots, and grain were significantly reduced after applying rice straw biochar and bean stalk biochar. However, only rice straw biochar significantly reduced Pb concentrations in the roots, and neither biochar significantly changed Pb concentrations in the shoots and grains (Zheng et al. 2015). In contrast, Pb concentrations in the stems, leaves, husks, and grains were significantly reduced by the addition of 5% (*w*/*w*) rice straw biochar (Li et al. 2016). Thus, a reduction in Cd and Pb has not been consistently demonstrated in response to soil biochar amendment. Furthermore, information is still limited regarding the effectiveness of biochar for Cd and Pb immobilization and accumulation in rice tissues. Therefore, detailed studies on how different types of biochar affect the bioavailability of Cd and Pb in contaminated paddy soils are required. The objectives of this study were to (1) study the effects of biochar addition on the mobility of Cd and Pb in contaminated paddy soil and the accumulation of these metals in rice plants, (2) compare the effects of different biochar sources (wheat straw and peanut shell) on Cd and Pb accumulation, and (3) determine the correlation between Cd and Pb concentrations in rice plants and their transformation in paddy soil after biochar application.

Materials and methods

Experimental materials

Soil

Surface soil (0–15 cm) was collected from a paddy field in Shangba Village, Xinjiang Town, which is located 6 km from the Dabao Mountain mining area in Shaoguan City, Guangdong Province, South China. The Dabao Mountain mine is a polymetallic sulfide deposit. Large quantities of mine waste materials and acidic mine drainage (AMD) have been produced by the mining process for more than 40 years, which are discharged into the Hengshi River. Large areas of agricultural soils are irrigated with the AMD-contaminated water, which has low pH and high heavy metal concentrations (Cd, Pb, Cu, and Zn) (Gu et al. 2011). The soil was collected using spades, and was subsequently stored in polyvinylchloride bags. Soil samples were thoroughly mixed, air-dried, crushed, and passed through a 2-mm nylon mesh before the pot experiment. Soil properties are presented in Table 1.

Biochar

Two types of biochar—peanut shell biochar (PBC) and wheat straw biochar (WBC)—were obtained from Sanli New Energy Company, Henan Province, China; these were produced at a pyrolysis temperature of 350–500 °C. The black carbon content was 30–35%. The biochars were ground and passed through a 1-mm sieve before the pot experiment. The pH of biochar was measured in water at a 1:25 (*w*/*v*) ratio after

Table 1 Physico-chemical properties of the paddy soil and biochar used

Property			Soil	Peanut shell biochar	Wheat straw biochar
pH (H_2O)			5.04	9.95	9.90
Organic C (g kg^{-1})			9.30	–	–
Total C (g kg^{-1})			–	133.7	144.8
Total N (g kg^{-1})			1.06	5.21	6.93
Total P (g kg^{-1})			0.22	2.76	1.72
Surface oxygenic functional groups (mmol g^{-1})	Acidic groups	Carboxyl	–	0.10	0.11
		Lactone	–	0.15	0.24
		Phenolic hydroxyl	–	0.12	0.33
		Total content	–	0.37	0.68
	Basic groups		–	1.17	1.13
Total Cd (mg kg^{-1})			0.507	0.123	0.281
Total Pb (mg kg^{-1})			267.5	9.9	5.6

mixing for 5 min and equilibration for 1 h (Gaskin et al. 2008). The pH was then measured using a PHS-3C pH meter (Shanghai INESA Analytical Instrument Co., Ltd., Shanghai, China). The total carbon content of the biochar was analyzed using a previously described method to measure soil organic matter (Liu 1996). The surface functional groups in the biochar were analyzed using Boehm titration (Boehm 1994). Total N concentrations were determined using the semi-micro Kjeldahl method, and total P was determined using Mo-Sb antispetrophotography method (DSH-UV755B UV-Vis Spectrophotometer, Guangzhou SH Biological Technology Co., Ltd., Guangzhou, China), after digestion with H_2SO_4–H_2O_2 (Lu 2000). The total heavy metal concentration in the biochar was measured using flame atomic absorption spectrophotometry (FAAS) (Hitachi Z-2300, Japan) after digestion with HCl–HNO_3–$HClO_4$ (*v*/*v*/v = 15:5:1) (Lu 2000). The basic properties of PBC and WBC are presented in Table 1.

Rice plants

The rice cultivar Boyou 998 was used in the experiment. Seeds were obtained from the Rice Research Institution, Guangdong Academy of Agricultural Sciences. This cultivar is widely cultivated in Guangdong Province, China.

Pot experiment

Plastic pots 25 cm in height and 20 cm in diameter were used for the pot trials. There were three treatment groups with three replicates each: (1) control (without biochar, designated CK), (2) soil amended with 5% (*w*/*w*) peanut shell biochar (designated PBC), and (3) soil amended with 5% (*w*/*w*) wheat straw biochar (designated WBC). Five kilograms of dried soil was placed in each pot. Urea, potassium dihydrogen phosphate, and potassium chloride were applied to each pot as basal fertilizer to achieve an N application rate of 200 mg kg^{-1} and P and K equivalent to 150 mg kg^{-1} P_2O_5 and 200 mg kg^{-1} K_2O. The fertilizers were added to the soil as solids, and the soil was mixed thoroughly before watering with tap water to produce a 3-cm water layer above the soil surface. The pots were then incubated for 60 days (May 5 to July 4, 2013) in a greenhouse at room temperature with a natural day/night regimen. Tap water was added every day to maintain the 3-cm submergence layer throughout the incubation period.

Sowing

Rice seeds were surface sterilized with 0.1% H_2O_2 for 20 min, rinsed thoroughly with deionized water, and soaked overnight in sterile water at room temperature. The seeds were then allowed to germinate in sterilized moist sand in a greenhouse. When the seedlings reached the three-leaf stage, five uniformly grown seedlings were transplanted to each prepared pot. Tap water was added daily to maintain the 3-cm submergence layer throughout the experimental period. All pots were arranged randomly outside a greenhouse at South China Agricultural University from July 5 to October 13, 2013. Rice plants were harvested 100 days after transplanting.

Harvest and sampling

Plants

After harvest, the rice plants were separated into roots, straws, husks, and grains. The plant parts were rinsed thoroughly, first with tap water and then with deionized water, and were oven-dried at 105 °C for 30 min and then at 60 °C until a constant weight was attained, after which dry weights were recorded. All dried tissue samples were ground using an electric steel mill. The powder was passed through a 1-mm sieve and was homogenized before chemical analysis.

Soil

Soil sample was collected from each pot and air-dried at room temperature. Plant debris was removed. The soil was then ground with a wood grinder and passed through a 1-mm nylon sieve. The sieved soil samples were collected, and the bulk of each sample was stored in plastic bags for the measurement of pH, cation exchange capacity (CEC), and available heavy metals. A small subsample was ground further, passed through a 0.149-mm nylon sieve, and stored in plastic bags for the determination of soil organic carbon (SOC) and heavy metals extracted by a sequential extraction procedure for soil.

Sample analysis

Soil

Soil pH was measured in a 1:2.5 suspension of soil to water using a PHS-3C pH meter. The mixture was shaken for 2 min and then allowed to settle for 30 min before measurements. Total N and P concentrations were determined using the semi-micro Kjeldahl and molybdenum colorimetry methods. Available P was extracted using 0.5 mol L^{-1} $NaHCO_3$ and estimated using colorimetry (DSH-UV755B UV-Vis spectrophotometer). SOC was determined using the potassium dichromate oxidation ($K_2Cr_2O_7$–H_2SO_4–H_2O) spectrophotometric method (DSH-UV755B UV-Vis Spectrophotometer). Soil CEC was extracted with 1 mol L^{-1} ammonium acetate (pH 7) and determined by FAAS. All methods described above followed Lu (2000).

Soil samples were digested with HCl–HNO_3–$HClO_4$ (*v*/*v*/*v* = 15:5:1), and the total heavy metal concentrations were then determined by FAAS. Available Cd and Pb in the soils were extracted with 1 mol L^{-1} $MgCl_2$ (pH 7): 2.50 g of soil sample was added to 20 mL 1 mol L^{-1} $MgCl_2$ (pH 7) solution and shaken at 150 rpm for 1 h (Tessier et al. 1979). The extracts were separated from soil samples by filtration through a 0.45-μm membrane. Cd and Pb concentrations in the filtrates were determined by FAAS.

The redistribution of Cd and Pb in soil was determined using the BCR sequential extraction method (Jiang et al. 2012). Cd concentrations in the acid-soluble, reducible, oxidizable, and residual fractions of soil samples were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS) (Hitachi Z-2700, Japan). Pb concentrations in the acid-soluble, reducible, oxidizable, and residual fractions of soil samples were determined by FAAS.

Plant tissues

The Cd and Pb concentrations in plant tissues was determined using FAAS after digestion with HNO_3–$HClO_4$ (*v*/*v* = 20:3) (Lu 2000).

Data analysis

All data were analyzed by one-way analysis of variance. Tukey's honest significant difference test was used to assess the statistical significance effect; the level of significance was set at $p < 0.05$. Bivariate correlations and Pearson's correlation coefficients (significance set at $p < 0.05$ and $p < 0.01$) were also determined. Statistical analysis was performed using SPSS version 16.0 (SPSS Inc., USA).

Results

Plant growth and heavy metal accumulation

No significant difference was observed in the dry weight of grains between the two biochar treatments and the control; however, the application of WBC led to significantly lower straw dry weight (by 32.3%) than that of the control (Fig. 1).

The Cd concentrations in the roots and grains and Pb concentrations in the roots and straw were significantly reduced by the addition of biochar; however, the type of biochar source material had no significant effect on the uptake and accumulation of Cd and Pb by rice. PBC and WBC application led to significantly lower concentrations of Cd and Pb in rice roots compared to the control ($p < 0.05$) (Table 2). For instance, Cd and Pb concentrations in rice roots were lower by 50.8 and 22.6% using PBC, and 48.9% and 19.4% using WBC, respectively. Biochar addition had no significant effect on Cd concentrations in the straw, but both PBC and WBC application led to significantly lower Pb concentrations in the straw ($p < 0.05$) (Table 2). Biochar application led to lower Cd and Pb concentrations in the grains compared to control (Table 2), with Cd concentrations being significantly lower (by 22.9% for PBC and 29.1% for WBC; $p < 0.05$). While Pb concentration was lower in the grains (by 12.2% for PBC and 15.0% for WBC), this difference was not significant (Table 2).

Effect of biochar on soil properties

Biochar addition led to significantly higher soil pH, SOC, and CEC (Table 3). Soil pH values in the PBC and WBC treatments were significantly higher than those in the control ($p < 0.05$). Soil pH was 5.96 with PBC and 5.80 with WBC, as against 5.32 in CK (Table 3). PBC and WBC treatments led to significantly higher soil SOC concentrations than those in

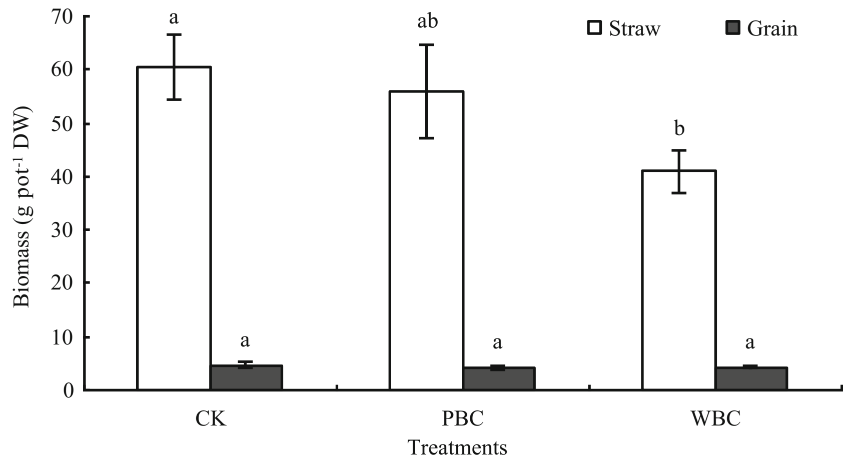

Fig. 1 Effect of biochar application on the weight of straw and grain dry matter of *Oryza sativa* L. Treatments: CK, control (no biochar applied); PBC, peanut shell biochar applied at 5% (*w*/*w*); WBC, wheat straw biochar applied at 5%. Error bars indicate the standard deviation from the means ($n = 3$). Different letters above the columns indicate significant differences between treatments ($p < 0.05$)

the control ($p < 0.05$), but no significant difference was observed between the two treatments (Table 3). PBC and WBC treatments significantly increased soil CECs compared to the control ($p < 0.05$), but there was no significant difference between PBC and WBC (Table 3).

$MgCl_2$-extractable concentrations of Cd and Pb

The application of the two types of biochar led to significantly lower Cd and Pb in both $MgCl_2$ extracts compared to the control (Fig. 2). Cd and Pb concentrations in the $MgCl_2$ extracts were lower by 45.7 and 79.0% for PBC and by 40.4 and 68.6% for WBC, respectively, than in the control. The addition of PBC was more effective than WBC in reducing extractable Cd and Pb. Furthermore, $MgCl_2$–Cd and $MgCl_2$–Pb concentrations differed significantly between PBC and WBC (Fig. 2).

Sequential extraction of Cd and Pb

The application of biochar altered the fraction distributions of Cd and Pb in paddy soil (Fig. 3). The acid-soluble fractions of Cd and Pb were significantly reduced by 27.76 and 48.71% for PBC, and by 21.03 and 41.68% for WBC, respectively ($p < 0.05$). The application of PBC and WBC significantly increased the reducible fraction of Pb by 19.04 and 24.44% ($p < 0.05$), respectively. PBC and WBC also led to significant increases in the oxidizable fractions of Cd, by 37.24 and 44.66% ($p < 0.05$), respectively. The residual fraction of Cd and Pb was increased by 37.87 and 8.68% by PBC, and by 24.88 and 2.98% by WBC, respectively. Some of the acid-soluble heavy metal fractions were transformed into reducible and residual fractions, indicating a decrease in their bioavailability.

Correlation between Cd and Pb bioavailability and soil chemical characteristics

The Cd and Pb concentrations in $MgCl_2$ extracts showed strong and significant negative correlations ($p < 0.01$) with pH, SOC, and CEC (Table 4).

Correlation between Cd and Pb bioavailability in the soil and accumulation in rice

Correlation coefficients of Cd and Pb concentrations in different parts of the rice plants and the concentration of $MgCl_2$-extractable Cd and Pb in the soil were calculated (Table 5). Concentrations in the $MgCl_2$ extracts were significantly positively correlated with concentrations in rice roots and grains for Cd ($p < 0.05$) and with concentrations in roots and straw for Pb ($p < 0.05$) (Table 5).

Table 2 Concentrations of Cd and Pb in root, straw, husk, and grains of *Oryza sativa* L.

Treatment	Cd concentration (mg kg^{-1})				Pb concentration (mg kg^{-1})			
	Root	Straw	Husk	Grain	Root	Straw	Husk	Grain
CK	2.311 ± 0.032 a	0.480 ± 0.047 a	0.450 ± 0.090 a	0.227 ± 0.025 a	149.3 ± 4.3 a	12.06 ± 1.31 a	2.41 ± 0.17 a	1.80 ± 0.15 a
PBC	1.13 6 ± 0.146 b	0.439 ± 0.003 a	0.421 ± 0.038 a	0.175 ± 0.022 b	115.5 ± 4.4 b	9.39 ± 0.79 b	2.57 ± 0.31 a	1.58 ± 0.14 a
WBC	1.182 ± 0.120 b	0.429 ± 0.057 a	0.425 ± 0.035 a	0.161 ± 0.008 b	120.3 ± 3.6 b	6.92 ± 0.77 b	2.28 ± 0.04 a	1.53 ± 0.22 a

Treatments: CK, control (no biochar applied); PBC, peanut shell biochar applied at 5% (*w*/*w*); WBC, wheat straw biochar applied at 5% (*w*/*w*). Each value represents the mean of three replicates ± standard deviation, and different letters on a column against the same element indicate a significant difference at $p < 0.05$ according to Tukey's HSD multiple range test

Table 3 Effect of biochar on soil pH, soil organic carbon (SOC), and CEC

Treatment	pH	SOC (g kg^{-1})	CEC(cmol kg^{-1})
CK	5.32 ± 0.02 b	10.73 ± 1.17 b	7.95 ± 0.38 b
PBC	5.96 ± 0.03 a	14.95 ± 1.53 a	9.85 ± 0.50 a
WBC	5.81 ± 0.02 a	16.18 ± 0.92 a	9.16 ± 0.52 a

Treatments: CK, control (no biochar applied); PBC, peanut shell biochar applied at 5% (*w*/*w*); WBC, wheat straw biochar applied at 5% (*w*/*w*). Each value represents the mean of three replicates ± standard deviation, and different letters on a column against the same element indicate a significant difference at $p < 0.05$ according to Tukey's HSD multiple range test

Discussion

The aim of this study was to examine the effect of different biochar types on the availability and accumulation of Cd and Pb in paddy soil and rice plants. The application of both PBC and WBC led to a significant increase in the pH of the acidic soil (Table 3). Biochars have high pH and have a liming effect when applied to acidic soils (Beesley and Marmiroli 2011; Bian et al. 2014), which increases soil pH. In the process of pyrolysis to produce biochar, the basic cations (mainly Ca, Mg, K, and Na) in biomass are converted to different alkaline substances (such as oxides, hydroxides, and carbonates, such as ash) during the pyrolysis process, and are then mixed with biochar (Houben et al. 2013b). The dissolution of these alkaline substances increases soil pH and CEC. Here, the application of organic carbon-rich biochar led to significantly higher SOC in paddy soil, similar to observations by Kelly et al. (2014) and Zhang et al. (2017). We also found that the application of biochar significantly increased soil CEC (Table 3), corresponding with previous studies (Fellet et al. 2011; Houben et al. 2013a; Puga et al. 2015; Yin et al. 2016). The content of CEC of PBC and WBC was 17–19 times higher than that of the soil used in the experiment (Table 1).

Soil pH, SOC, and CEC are important factors affecting Cd and Pb availability in soil (Rieuwerts et al. 2006; Park et al. 2011; Moon et al. 2013). In the present study, we found that $MgCl_2$-extractable Cd and Pb concentrations were significantly negatively correlated with soil pH ($p < 0.01$). Zheng et al. (2012) observed that NH_4NO_3-extractable concentrations of soil Cd and Pb were significantly negatively correlated with soil pH ($p < 0.01$) in a multielement-contaminated paddy soil supplemented with bean stalk and rice straw biochars. Similarly, Yang et al. (2016) reported significant negative correlations between $CaCl_2$-extractable Cd and Pb concentrations and soil pH ($p < 0.01$) in a heavy metal-contaminated soil to which bamboo biochar and rice straw biochar had been added. Biochar enhanced soil pH, which led to the precipitation of Cd as $CdCO_3$ (Xue et al. 2012) and of Pb as $Pb_5(PO_4)_3OH$ (Cao et al. 2011). In addition, with increasing pH, the density of cation exchange sites on the biochar surface increases, which improves metal adsorption on the biochar particles themselves (Harvey et al. 2011). Uchimiya et al. (2011) and Houben et al. (2013a) reported that cation exchange played a role in reducing the availability of Cd and Pb under biochar addition by increasing the CEC of the soil. Therefore, in our study, the decrease in extractable Cd and Pb concentrations might have also contributed to increasing soil CEC because CEC and $MgCl_2$-extractable Cd and Pb were significantly negatively correlated ($p < 0.01$) (Table 5). The formation of stable organic matter complexes with heavy metals could enhance the immobilization of heavy metals with increasing SOC (Namgay et al. 2010; Cui et al. 2016; Zhang et al. 2017). The retention ability to metals enhanced with increasing SOC (Park et al. 2011). The oxygen-containing functional groups (e.g., carboxylic, alcohol, and hydroxyl groups) on the surfaces of biochars form strong complexes with Cd and Pb, thus increasing the adsorption of Cd and Pb on biochars (Uchimiya et al. 2011; Jiang et al. 2012; Xu and Zhao 2013). Moreover, biochars serve as sources of P (Table 1), which might be available to precipitate metals in soil (Ahmad et al. 2014).

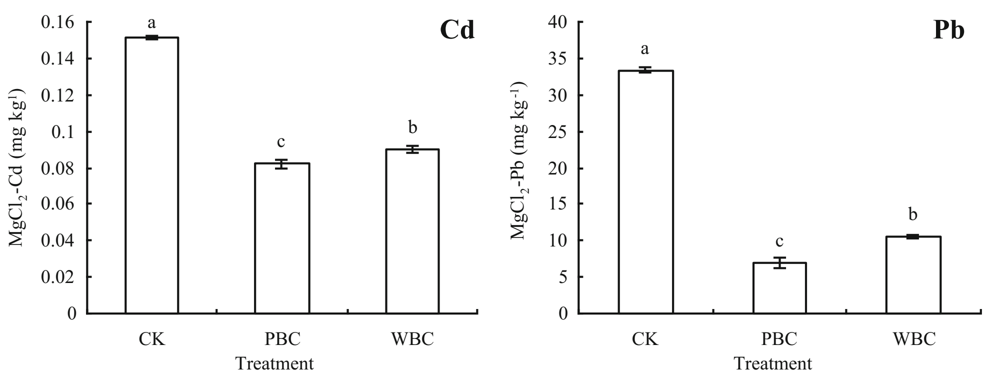

Fig. 2 Effect of biochar application on heavy metal concentrations in $MgCl_2$ extracts in Cd- and Pb-contaminated paddy soil. Treatments: CK, control (no biochar applied); PBC, peanut shell biochar applied at 5% (*w*/*w*); WBC, wheat straw biochar applied at 5%. Error bars indicate the standard deviation from the mean ($n = 3$). Different letters above the columns indicate significant differences between treatments ($p < 0.05$)

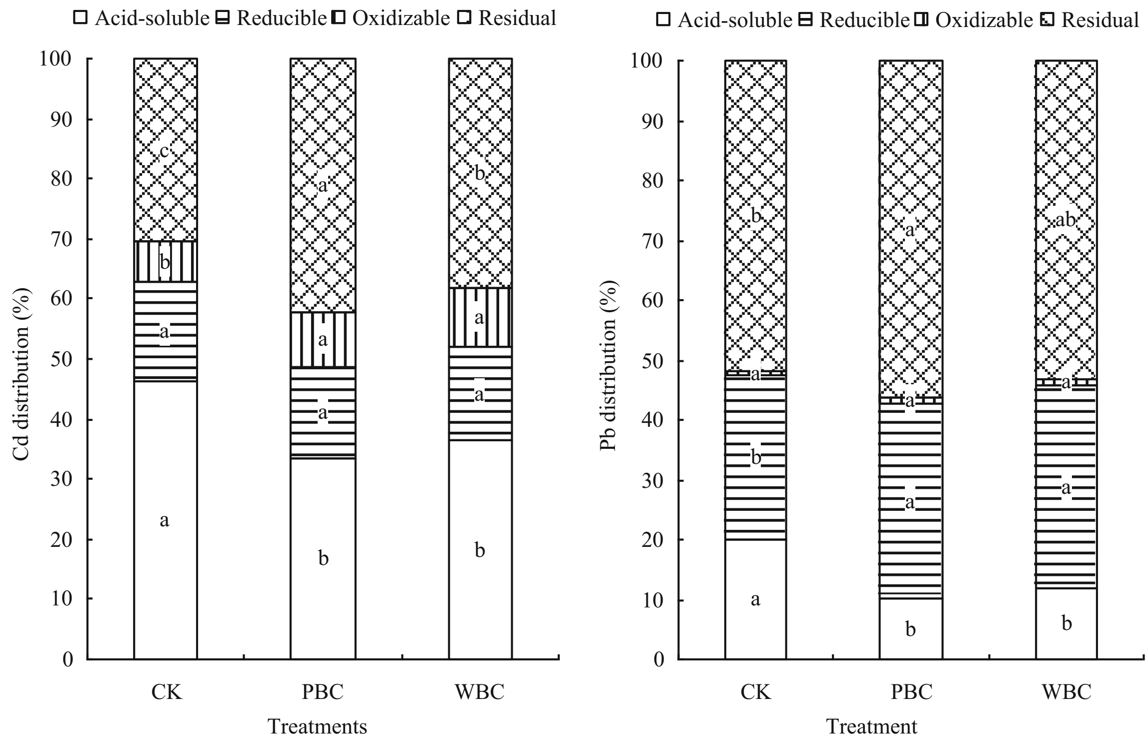

Fig. 3 Proportions of Cd and Pb in different fractions following sequential extraction. Treatments: CK, control (no biochar applied); PBC, peanut shell biochar applied at 5% (*w*/*w*); WBC, wheat straw biochar applied at 5%. Data are the means of three replicates

We observed that the application of PBC and WBC led to a significantly lower acid-soluble fraction of Cd and Pb and a higher residual fraction than that observed in the control (Fig. 3). Therefore, PBC and WBC promote the conversion of easily available forms of Cd and Pb to relatively stable forms. The difference in Cd and Pb distribution between the various fractions of the control and PBC and WBC treatment groups has considerable implications for the mobility and/or bioavailability of Cd and Pb following biochar application to paddy soil. Similar to our results, Zhu et al. (2015) and Cui et al. (2016) found that biochar application led to a significantly lower acid-soluble fraction of Cd and Pb and a higher residual fraction in acidic paddy soil. The application of biochar increases the residual fraction of Cd and Pb mainly because biochar particles have strong inner-sphere complexation with these metals (Bian et al. 2014). The reducible fraction of Pb significantly increased after the addition of PBC and WBC (Fig. 3). Li et al. (2016) also found that acid-soluble Pb transformed to reducible Pb in paddy soil supplemented with rice straw biochar addition, in supporting our finding that the residual fraction of Pb was significantly higher after biochar application than in the control soil. Liu et al. (2015) also observed that adding rice straw biochar to contaminated paddy soil improves the transformation of Pb from the acid-soluble fraction to reducible and oxidizable fractions. This increase in the reducible fraction of Pb following biochar application could be attributed to the adsorption on Fe/Mn oxides (Fang et al. 2016) and bonds with the mineral phase of Fe, Al, and P on, around, and inside biochar particles (Bian et al. 2014; Ahmad et al. 2017). Fe and Mn oxides in soils are amphoteric colloids, the adsorption of which depends mainly on the surface negative charge. Biochar might improve soil pH value by decreasing H^+, Fe^{3+}, Al^{3+}, and Mn^{2+} concentrations in soil solution. In turn, this action weakens the competitive adsorption of Cd and Pb and further increases the adsorption of Cd and Pb on Fe and Mn oxides (Li et al. 2013). Metals probably bound to Fe/Mn

Table 4 Correlation coefficients between soil chemical characteristics and extractable Cd and Pb

	$MgCl_2$-extractable heavy metals	
	Cd	Pb
pH	− 0.990*	− 0.993*
SOC	− 0.852*	− 0.854*
CEC	− 0.877*	− 0.868*

*Correlation is significant at the 0.01 level

Table 5 Correlation coefficients between concentrations of Cd and Pb in extracts and rice tissues

	Root–Cd	Straw–Cd	Husk–Cd	Grain–Cd
$MgCl_2$–Cd	0.979**	0.528	0.257	0.829**
	Root–Pb	Straw–Pb	Husk–Pb	Grain–Pb
$MgCl_2$–Pb	0.975**	0.758*	− 0.071	0.600

*Correlation is significant at the 0.05 level; **correlation is significant at the 0.01 level oxides in the soils, because biochars and fertilizers contain very small amounts of Fe, Mn, and Al (Shen et al. 2015; Shen et al. 2016). Furthermore, P entering the soil with biochar application might react with Pb to form hydroxypyromorphite (Cao et al. 2011). Biochars have much more P than soil and fertilizer (Table 1); therefore, Pb was probably immobilized with P in biochars. The significant increase in the oxidizable fraction of Cd after biochar addition might contribute to the increase of SOC after biochar application, which could make more metals form highly stable metal-organic complexes (Zhang et al. 2017). Furthermore, the reducing condition in the soil formed by the decomposition of organic matter helps with the formation of CdS (Covelo et al. 2007).

The Cd and Pb concentrations in different tissues of rice plants, with and without biochars addition, decreased in the order root > straw > husk > grain (Table 2), supporting previous studies (Bian et al. 2014; Zheng et al. 2015; Li et al. 2016). After PBC and WBC application, Cd and Pb concentrations in the roots, Pb concentrations in the straw, and Cd concentrations in the grains were significantly lower than those in the control (Table 3). The reduction in Cd and Pb concentrations in rice tissues might be attributed to the immobilization of Cd and Pb in the soil, as strong and significant positive correlations were noted between Cd and Pb concentrations in rice tissues and the concentrations of these metals in $MgCl_2$ extracts ($p < 0.05$) (Table 5).

The effects of biochar on the immobilization and phytoavailability of Cd and Pb differed in this study. PBC and WBC reduced $MgCl_2$-extractable metal concentrations in the order Pb > Cd (Table 3), while PBC and WBC reduced grain metal concentrations in the order Cd > Pb (Table 2). This difference could be attributed to the following: (1) the amount of Pb(II) precipitates formed on biochars was much higher than that of Cd(II) because the ability of Pb(II) to form metal-hydroxyl and metal hydroxides was greater than that of Cd(II) (Xu and Zhao 2013); or (2) the transport of Pb in plants is largely restricted because it is blocked by the Casparian strip in the endoderm, adsorbed by the negatively charged pectins in the cell wall, precipitated in intercellular spaces with insoluble oxalate and phosphate, and subjected to complexation with organic acid and phytochelatin in the vacuoles (Shahid et al. 2012).

Our study showed that both PBC and WBC significantly reduce Cd and Pb concentrations in the roots, Pb concentrations in the straw, and Cd concentrations in the grains (Table 3). Zheng et al. (2015) found that Cd concentrations in rice roots, shoots, husks, and grains significantly decreased following bean stalk biochar and rice straw biochar addition in a field experiment; however, only root Pb significantly decreased following the application of rice straw biochar. Therefore, Cd and Pb concentrations in different rice tissues respond differently to the addition of biochar from different feedstocks and to different soil environments. However, further data are needed to validate this conclusion.

Conclusions

We demonstrated that the application of 5% PBC and WBC significantly increased soil pH, SOC, and CEC, and effectively immobilized Cd and Pb in contaminated paddy soil, thus reducing Cd and Pb uptake by paddy. The improved soil pH, SOC, and CEC following biochar treatment played an important role in reducing the mobility and availability of Cd and Pb in the soil. Sequential extraction tests showed that biochar induced the transformation of the acid-soluble fraction of Cd to the oxidizable and residual fractions, and that of Pb to the reducible and residual fractions. Both PBC and WBC were effective in decreasing the Cd concentration in grain, but had no significant effects on Pb concentration. PBC and WBC could be used to enhance the immobilization of Cd and Pb in contaminated paddy soils. The effect of biochar application differed for Cd and Pb accumulation in different rice tissues and also varied with feedstock. Further experiments are needed to investigate the influence of biochar on the mobility and bioavailability of Cd and Pb in contaminated paddy soils under field conditions.

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