

Effects of Different Biochars on Cd Immobilization in Rice Paddy Soil: A Two-year Field Study

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This study addressed the efficiency of different biochars in Cd immobilization in soil. An acidic sandy loam paddy contaminated with Cd was selected for the field trial, which was continued for three rice-growing seasons. Rice straw biochar (BR), wheat straw biochar (BW), and maize straw biochar (BM) were pyrolysed as pellets at 450 °C and applied at 0 t/ha (BC0), 10 t/ha (BR1/BW1/BM1), and 20 t/ha (BR2/BW2/BM2). Compared to BC0, BR and BW were more effective in decreasing Cd accumulation in rice grains, and BR2 achieved the highest reduction, averaging 43.4% over three rice seasons. The Cd contents in rice roots with BR2 treatment decreased by 15.2 to 55.3% compared with BC0. The bioconcentration factors for grains (BCF_{Grain}), shoots (BCF_{Shoot}), and (BCF_{Root}) of BR2 treatment were averagely decreased by 53.3%, 27.4%, and 19.0% over BC0, respectively. There was a negative correlation between soil CaCl_2 -Cd and soil pH. FTIR analysis demonstrated that Cd complexed with SiO_2 on aged BR2 particles. During the natural aging process, BR2 significantly and sustainably inhibited rice uptake Cd through co-deposition. Therefore, the BR was judged to be an effective soil amendment with high Si content and alkalinity for Cd immobilization in paddy soil.

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INTRODUCTION

Agricultural soil contaminated by heavy metals is a global dilemma, especially in China, which supports 22% of the global population with only 7% of the world's farmlands (Zhao *et al.* 2015). Cadmium (Cd) contamination, especially in paddy soil, has drawn wide attention as a major contaminant. Annually, approximately 1.3×10^4 ha of cultivated soil is polluted by Cd, and the production of Cd-contaminated rice amounts to approximately 5.0×10^4 t (Gu and Zhou 2002). Rice accumulates Cd mainly from roots and partly leaf; thus, the amount of Cd accumulation in rice is determined by the availability of Cd in soil. The Cd in water-soluble fraction, ion exchange fraction, and carbonate fraction is generally considered as the available or potentially available Cd fraction in soil (Zhang *et al.* 2018; Jia *et al.* 2020). Because the Cd fraction in soil is affected by soil pH, soil pH is a determinant of Cd availability to rice (Zou *et al.* 2021; Ning *et al.* 2019).

Biochar is generally derived from the wastes from agricultural production, such as crop straws, containing abundant organic and inorganic components, which are beneficial for both plant growth and heavy metal immobilization (Wang *et al.* 2018; Jeffery *et al.* 2015). Multiple field studies with different scale in many provinces of China have demonstrated that the reductions of metals availabilities could reach up to 20 to 70% in soil, and the concentrations in rice grains decreased by 20 to 60% (Pan and Li 2013; Huang *et al.* 2013). The primary mechanism underlying the immobilization of metals by biochar is largely attributed to its properties of high pH value, notable ash content, large specific surface area, and numerous surface functional groups (Li *et al.* 2016; Jing *et al.* 2020; Meng *et al.* 2022).

The immobilization of Cd by biochar is generally affected by the biochar aging process. Once applied to soils, biochar will undergo natural aging, which can cause biochar properties changes, including the decomposition of labile fraction in biochar, disturbing of biochar pore structure, and a reduction in pH (Li *et al.* 2019; Yuan *et al.* 2021). Ke *et al.* (2023) found that artificial aging treatments, including dry-wet, freeze-thaw cycle, and oxidation, reduced the Cd adsorption capacity of biochar. However, Liu *et al.* (2024) suggested that the aging process with freeze-dried treatment improved the adsorption capacity of biochar for Cd. Presumably, the immobilization effect of aged biochar on Cd in field soil varies with aging treatment. This has been proved by the study reported by Meng *et al.* (2022), which indicated that individual aging achieved a certain superimposition effect when combined.

Therefore, when elucidating the mechanism of Cd immobilization by biochar, especially in field studies, the aging effect must be taken into account. The natural aging of biochar is generally caused by multiple environmental factors. This study was carried out in a field trial with three different biochars for three rice seasons. The availability of Cd in soil, the concentrations of Cd in rice plants, and the corresponding bioconcentration factors (BCFs) were comprehensively analyzed across three rice seasons, to verify the effects of naturally aged biochars on Cd fixation in paddy soil. The hypothesis of this study is that the mineral fraction and surface functional groups in different biochars are the determined factors for the efficiency and sustainability of Cd stabilization. Moreover, this mechanism might be weakened by the natural aging process of biochar.

EXPERIMENTAL

Biochars

Three biochars applied in this study were purchased from Nanjing Qinfeng Zhongcheng Novel Bio-Material Co., Ltd (Nanjing, China). The raw materials, including rice straw, wheat straw, and maize straw were pyrolyzed under special conditions with limited oxygen. The pyrolysis temperature was set at 450 °C and kept for 1 h. The produced rice straw biochar (BR), wheat straw biochar (BW) and maize straw biochar (BM) were ground and passed through a 2 mm sieve before the application in field, and the particle size of the applied biochar was mainly 1 to 2 mm. The basic properties of three biochars are listed in Table 1.

Experimental Design

With a Cd contaminated rice paddy, the study lasted for two late rice seasons and one early rice season during 2016 to 2017 to verify two effects: first, the effects of biochars,

derived from different feedstocks, on the Cd immobilization; second, the effects of different biochar on Cd immobilization during the aging process in natural environment. Biochar was applied at levels of 0 (BC0), 10 t/ha (BR1, BW1, BM1), and 20 t/ha (BR2, BW2, BM2). The application levels of biochar were referred to “Technical Specifications or the application of biochar-based soil conditioners,” which ruled the application amount of biochar should less than 30t/ha. Before the transplantation of rice seedlings in the summer of 2016, biochar was first applied and with no further application during the three rice seasons. Every treatment with three replications, and each treatment plot was 30 m² in area. A randomized block design was applied for the treatment plots organization.

Table 1. The Basic Properties of Three Biochars

	pH	OC (g/kg)	Available Si (mg/kg)	Cd (mg/kg)
BR	10.55	406.37	760	0.82
BW	10.24	409.89	518	0.71
BM	8.56	315.79	178	0.27
Soil	5.59	26.13	85	0.85

BR: rice straw biochar; BW: wheat straw biochar; BM: maize straw biochar. SOC: soil organic

The field operation details followed the demonstration in Sui *et al.* (2020). Biochar was applied on the surface of the rice paddy, and the 0 to 15 cm surface layer was plowed to mix biochar and soil thoroughly. Three rice growing seasons were operated with two late rice seasons and one early rice season. In detail, Xiang Wanxian 12 was grown in the late rice season, and Xiang Zaoxian 45 was chosen as the early rice crop; both of the cultivars were local rice crops. The application of base fertilizer was the same for both late and early rice seasons. Base fertilizer was used at a level of 375 kg/ha with N: P₂O₅: K₂O of 11:6:8, and base fertilizer was applied one week before rice seedlings were transplanted in both late and early rice seasons. The topdressing was carried out one week after transplanting with 37.5 kg urea per hectare and 22.5 kg potassium chloride per hectare, respectively.

In every rice season, the rice paddy was kept flooded most of the time except one week ahead of the harvest. Across the three rice seasons, soil irrigation, fertilization and plant protection, and all other farming managements all followed local conventional practices and were kept consistent across these treatments. The dates for rice seedlings transplantation were at July 22, 2016, April 18, 2017 and July 22, 2017, and the rice was harvested on October 23, 2016, July 25, 2017, and October 26, 2017, for late rice 2016 (2016L), early rice 2017 (2017E), and late rice 2017 (2017E), respectively. The field experimental plots left land uncultivated in winter from October 24, 2016 to April 17, 2017.

Sampling and Analysis

The samples of every rice season included rhizospheric soil and rice plant samples. The rhizospheric soil sample of every plot contained three randomly selected samples. In detail, the rhizospheric soil was obtained by vigorously shaking rice root to detach the soil that attached loosely to the root. Thus, in every rice season, each treatment contained in total nine samples. The rhizospheric soil samples without any plant detritus and other

fragments were transported to the laboratory with sealing in plastic bags. Soil pH, available silicon, and CaCl_2 extractable Cd concentrations were analyzed with the air-drying soil samples, which were ground thoroughly to pass through a 2 mm sieve. Moreover, part of the ground soil samples were separated and continually ground to pass a 0.15 mm sieve to be analyzed with for soil organic matter (SOC), Cd fractions, and total content of Cd.

The method applied for plant Si contents was followed by the description from Liu *et al.* (2014). The basic properties of soil were analyzed followed the method proposed by Lu (2000). The concentrations of total and available Cd were analyzed by the same methods used by Cui *et al.* (2011) and Chen *et al.* (2016). Cd fractions were analyzed with the method of BCR; this procedure has been described elsewhere (Golia *et al.* 2007).

Each plot was harvested with three rice plants, the rice plants were analyzed separately as grains, shoot and root tissue samples. The unpolished rice grain was treated by a thresher to detach with the grain ears. The analysis procedures for plants followed the method described as Chen *et al.* (2016).

To guarantee the credibility of the analysis, three standard reference materials (SRM) were applied in each batch of soil and plant samples analysis process. SRM of GBW07401 was chosen and analyzed along with soil sample. The recovery percentages of GBW07401 ranged from 90 to 106% for Cd. SRMs for rice leaves and grains were bush twigs and leaves (GSV-1, GBW07602) and rice flour (GBW08511), respectively. The recovery percentages of GSV-1, GBW07602 and GBW08511 were 85 to 110% and 99 to 112%, respectively. The SRMs mentioned above were provided by the National Research Center for Standards in China.

Statistical Analysis

Results from both plant and soil samples analysis in this study were expressed as mean plus or minus one standard deviation (mean $\pm$ S.D., $n=3$). Three-way ANOVA analysis was applied to distinguish the effect of different biochar and rice seasons on Cd accumulation in rice tissues. Duncan analyses were used to determine the significance among different treatments. SPSS 23.0 (USA 2013) was applied for all the analysis conducting.

The calculation for total amount of Cd contents in rice plant followed the process of total Cd contents in rice tissues, including rice grain, shoot and root, multiplied the total corresponding biomass. Equation 1 was applied for the calculation of bio-concentration factors (BCF),

$$\text{BCF} = \frac{C_{\text{crop}}}{C_{\text{soil}}} \quad (1)$$

where C_{crop} (mg/kg) is Cd concentrations of grains, shoots and roots, respectively, and C_{soil} (mg/kg) represents the total content of Cd of rhizospheric soil.

RESULTS

Rice Grain Yield

Figure 1 shows the changes in rice grain yields. For all treatments, rice grain yields decreased across the three rice seasons. In 2017E, compared with BC0, only the treatment with BR2 significantly increased rice grain yields by 21.0%.

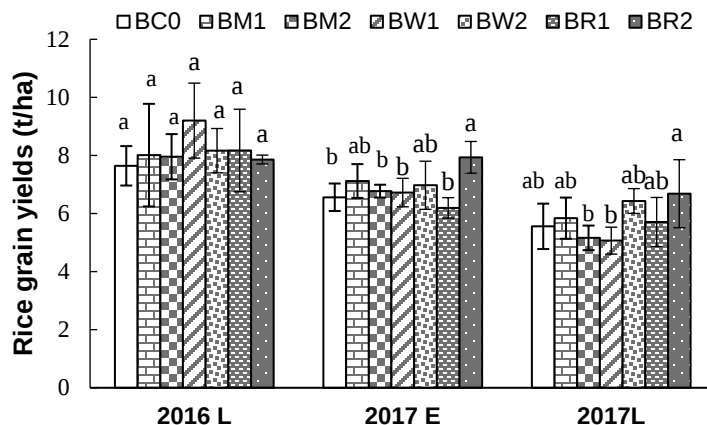


Fig. 1. Effects of soil amendments on rice grain yields (mean $\pm$ S.D., $n=3$). 2016 L (2016 late season rice), 2017 E (2017 early season rice), 2017 L (2017 late season rice). The different lower-case letters indicate a significant difference between biochar treatments for each treatment in one season ($p<0.05$). The same notations are also used in Figs. 2 to 7.

Cd Accumulation in Rice

Figure 2 displays the Cd uptake in rice grains and roots. Compared to BC0, within 2016L and 2017E, all biochars treatments significantly decreased Cd concentrations of rice grains (GCd), except for BM2 and BW2 treatment in 2016L. In 2016L, the reductions in GCd under biochars treatments ranged from 12.7 to 47.9%, and the highest reduction was BR2 treatment. Comparatively, biochars treatments decreased GCd by 45.0 to 60.7% in 2017E. However, in 2017L, only BR2 significantly reduced GCd by 32.1%, compared with BC0.

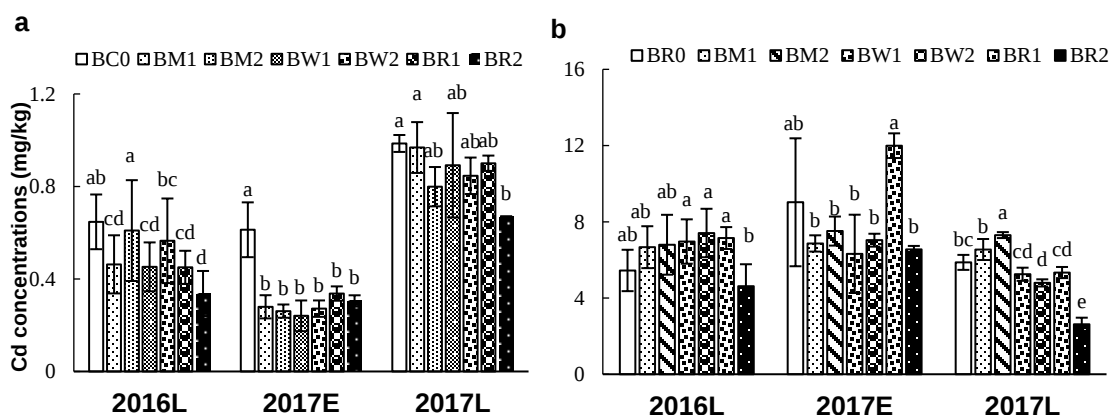


Fig. 2. Effect of soil amendments on rice grains (a) and roots (b) Cd concentrations

Compared with BC0, biochars treatments made no significant differences to RCd in 2016L, except for BR2 treatment. However, in 2016L, treatments with BR2 significantly reduced RCd by 55.3% compared to BC0. There were no obvious changes for the RCd in 2017E under different treatments. Especially, in 2017L, BW2 and BR2 significantly decreased RCd by 18.3% and 55.3%, respectively.

Figure 3 presents the bio-concentration factors (BCFs) of Cd in rice plant tissues. Nearly all biochar treatments, except for BM2, inhibited Cd uptake in rice grains and the average reductions in BCF_{Grain} was 39.5% (25.1 to 51.2%) (Fig. 3a). Moreover, BM1 and BR2 significantly decreased BCF_{Shoot} by 25.4% and 34.6% compared with BC0 in 2016L,

respectively (Fig. 3b). Especially in 2016L, nearly all biochar treatments failed to reduce BCF_{Root} or even increased BCF_{Root} compared to BC0 (Fig. 3c). Similar results also showed in 2017E, compared to BC0, only BR2 significantly decrease BCF_{Root} by 53.7% (Fig.3c). However, there were no differences between biochar treatments and BC0 in 2017L. Cd uptake in rice tissues increased largely in 2017L, especially in rice shoots and grains.

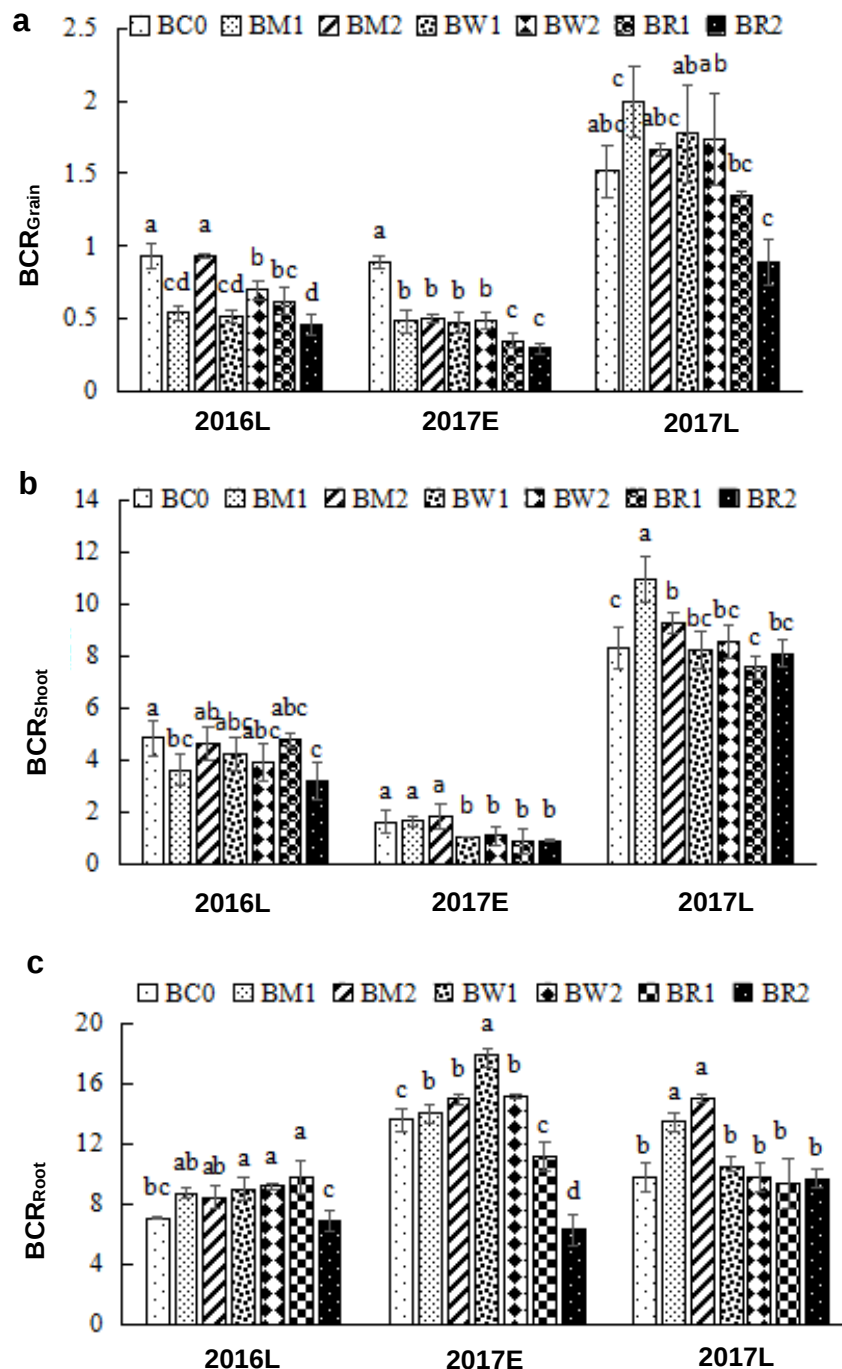


Fig. 3. Changes of bio-concentration factors of Cd in plant grain(a), shoot(b) and root(c),

Changes of Cd Mobility in Soil

Figure 4 shows the concentrations of CaCl_2 extractable Cd ($\text{CaCl}_2\text{-Cd}$) in soil. In 2016L, except for BW2, all other biochar treatments reduced $\text{CaCl}_2\text{-Cd}$ concentrations in soil by 33.1% to 73.3% compared to BC0. In 2017E, except for BW treatments, BM and BR reduced, on average, $\text{CaCl}_2\text{-Cd}$ 45.2% and 35.8% compared to BC0, respectively. On average, BM, BW and BR reduced $\text{CaCl}_2\text{-Cd}$ by 61.6%, 53.9%, and 53.3% over BC0 in 2017L, respectively.

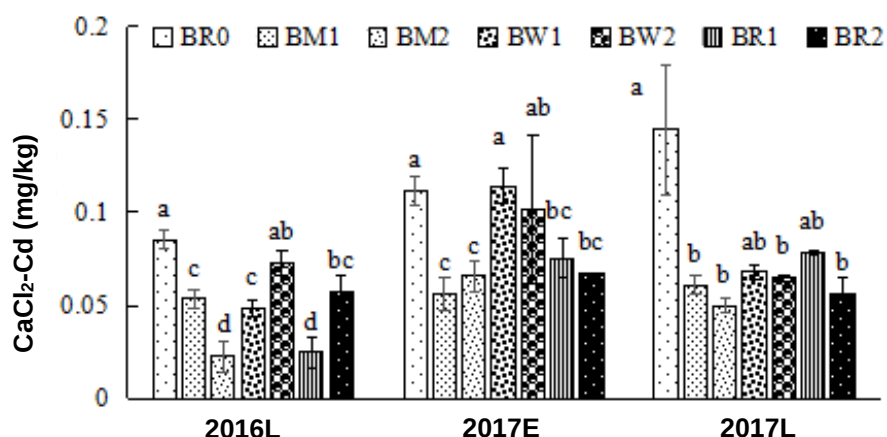


Fig. 4. Changes of CaCl_2 extractable Cd concentrations in soil with different biochar treatments

The Cd fractions were analyzed with BCR, and the results presented in Fig. 5. Accordingly, Cd mainly were present as F1 (Exchangeable and water-soluble) and F2 [Fe and Mn (hydr)oxide-bound or reducible]. Across the three rice seasons, the proportion of F1 showed a decrease and F2 increased with biochar application compared with BC. In 2017L, compared to BC0, treatments with BM, BW and BR on average increased F2 by 4.9%, 9.4% and 7.8%, respectively. Notably, compared with 2017E, the proportions of F3 (Organically bound) and F4 (Residual) decreased with treatments of BM1, BM2 and BW1 in 2017L.

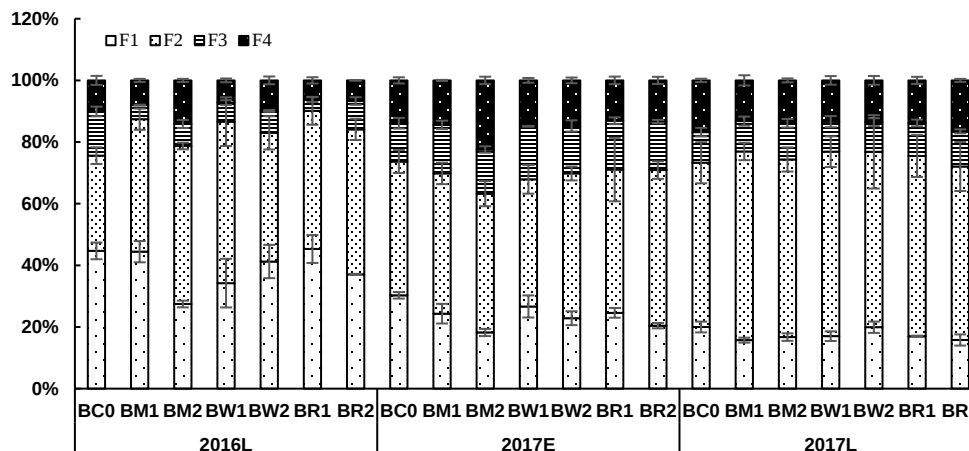


Fig. 5. Changes of different Cd fractions in soil with different biochar treatments (mg/kg). F1: Exchangeable and water-soluble, F2: Fe and Mn (hydr)oxide-bound or reducible, F3: Organically bound, F4: Residual

Changes in Soil Properties

Figure 6 lists the data of soil pH across the three rice seasons. In 2016L, biochar treatments effectively increased soil pH by 0.09 to 9.0% compared with BC0. Especially, treatments with BM1, BW1 and BR1 significantly increased soil pH by 5.1%, 9.0%, and 7.7%, respectively. In 2017E, all biochar treatments increased soil pH in the range of 3.7% to 5.8%, except for BM2. Biochar treatments sustainably increased soil pH in 2017L by 5.5% to 10.9%.

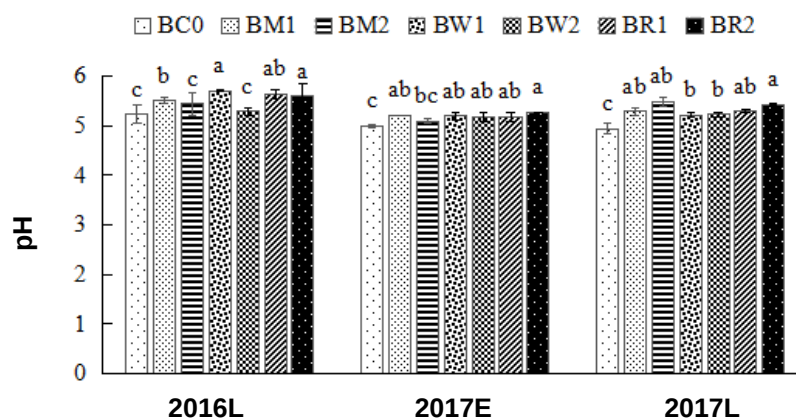


Fig. 6. Changes of soil pH with different biochar treatments in three rice seasons.

The contents of soil available Si across the three seasons are shown in Fig. 7. Compared to BC0, the BM1, BW1, and BR1 treatments increased soil available Si by 10.8%, 26.5%, and 27.0% on average across the three rice seasons, respectively. In comparison, the average increments in soil available Si contents over the three rice seasons were 10.9%, 32.6%, and 31.5% following BM2, BW2, and BR2, respectively.

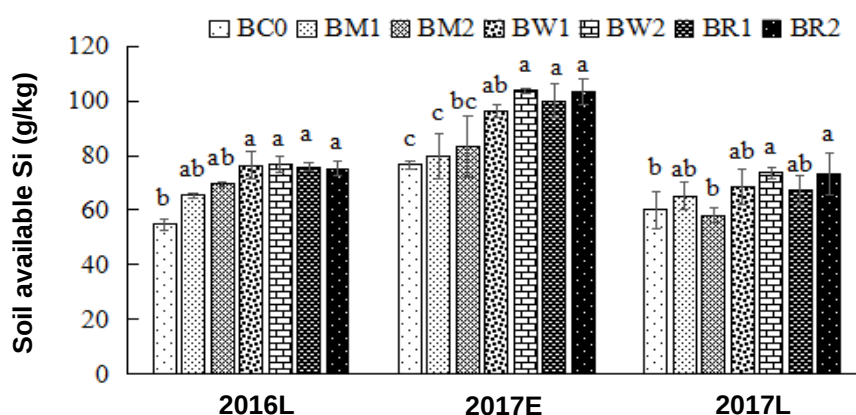


Fig. 7. Changes of soil available silicon concentrations with different biochar treatments

DISCUSSION

Effects of Biochar Application on Rice Grain Yield

Generally, biochar application was found to be beneficial for rice growth. Some field studies have shown that biochar can efficiently increase rice yield (Bian *et al.* 2014; Chen *et al.* 2016; Sui *et al.* 2020). Based on a meta-analysis with different soil texture and

biochar treatment, the increment in rice yield under biochar amendment can reach 10.7% (Liu *et al.* 2022). In this study, compared with other biochars, BR showed a greater potential for enhancing rice growth. Moreover, the increment of rice yield was higher under BR2 treatment than under the BR1 treatment, indicating that rice yield increased with an increase in biochar application amount. This finding is consistent with reported studies (Chen *et al.* 2021; Bian *et al.* 2014). Biochar applications could alleviate soil acidity, thus improving the availability of soil nutrients, especially for the Si (Zhang *et al.* 2018). Furthermore, the high content of organic carbon (OC) in biochar is also beneficial for rice growth. In this study, both BR and BW contained higher OC (Table 1), which probably contributed significantly to the high rice yields in 2017E and 2017L with the BR2 and BW2 treatments. Moreover, an increase in soil pH could enhance Si availability to rice. Specially, the input of BR with inherent Si has been proven effective in improving the available Si content in soil (Wang *et al.* 2019). Therefore, treatment with BR2 maintained a high rice yield across three rice seasons might be due to the high pH, high content of OC, and the inherent Si content.

However, the rice yields across three seasons under BR2 were 7.86 t/ha, 7.93 t/ha, and 6.68 t/ha respectively, indicating that the impact of biochar varied over time. As demonstrated by Chen *et al.* (2021), during the aging process in natural soil, dissolution components within biochar, such as alkaline substances and dissolved organic matter (DOM), will leach out. This leaching phenomenon leads to a decrease in soil pH and organic matter content. Additionally, soil microbes are capable of degrading and mineralizing the organic matter present in the soil organic matter (SOM). In this study, as the biochar underwent the natural aging process, soil organic carbon and available silicon (Si) decreased over time, as shown in Figs. 7 and 8. Consequently, this led to a reduction in the yield - enhancing effect of biochar.

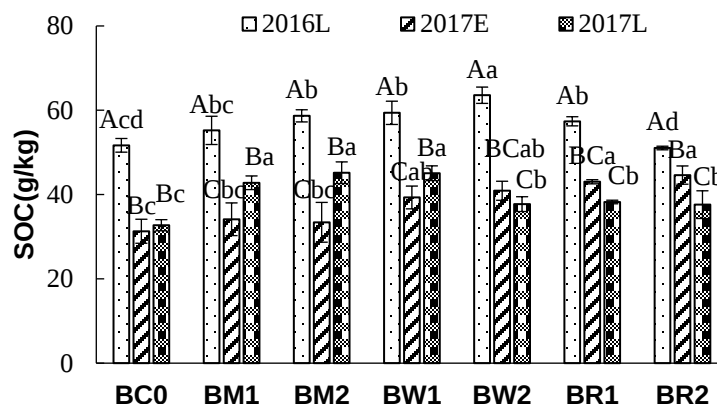


Fig. 8. Variations in soil organic matter (SOC) under distinct biochar treatments. Different capital letters signify the differences among different seasons under the same treatment, while lowercase letters denote the differences among different treatments within the same rice season.

Effects of Biochar Application on Cd Uptake in Rice

Typically, the effect of biochar on inhibiting Cd uptake in rice could be enhanced by increasing biochar application rates (Chen *et al.* 2018). However, compared with BW1 and BM1, BW2 and BM2 increased the concentrations of Cd in rice grains in 2016L (Figs. 2 and 3a). This may be due to the dissolved organic matter (DOM) derived from biochar. DOM which could form soluble complexes with Cd^{2+} , thus promoting Cd release from

biochar and elevating Cd mobility (Borggaard *et al.* 2019; Tian *et al.* 2020). The content of dissolved components in biochar decreased with the extension of application time (Joseph *et al.* 2010). In this study, the content of DOM derived from biochar might be higher in the first season, which could induce higher Cd bioavailability with higher biochar application rate.

Even though with high OC content (Table 1), BR2 effectively and sustainably inhibited Cd bioavailability compared with BR1 across the three seasons (Fig. 3). This may be attributed to the high Si concentration in biochar. Si could mediate toxic metal ions uptake in higher plants by co-precipitation, immobilization, and compartmentation, thus inhibiting toxic metal ions accumulation in plants (Liang *et al.* 2007). Xiao *et al.* (2021) found that compared to the organosilicone fertilizer, Si in the mineral silicon fertilizer was available to rice, thus decreasing Cd uptake in rice by inducing Cd immobilization in both soil and root-to-shoot transport pathway. Notably, the inorganic fractions in biochar also contains available Si, especially in rice straw biochar, which has been addressed as Si-rice biochar (Sichar) (Xiao *et al.* 2014; Wang *et al.* 2019). The application of Sichar could improve Si dissolution in soil and increase Si accumulation in rice and reduce Cd upward translocation from rice root. Moreover, the carboxyl groups of biochar could enhance Cd immobilization in soil through surface complexation (Wang *et al.* 2020).

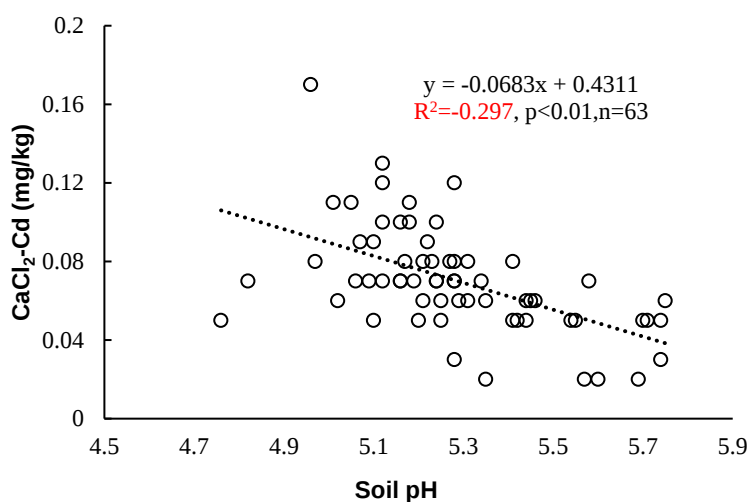


Fig. 9. Correlation between soil pH and soil CaCl₂ extractable Cd

In this study, both BR and BW effectively increased soil available Si content (Fig. 7), while only BR showed sustainable and significant effect on inhibiting Cd uptake in rice. This may be attributed to the obvious increase in soil pH induced by BR. Results in this study suggested that soil pH increment was negatively correlated to soil exchangeable Cd (Fig. 9). Intriguingly, although the coefficient of determination (R^2) having a value of 0.297, the p -value was less than 0.01. This indicates that the decrease in the available Cd content in the soil may be partially influenced by the increase in soil pH. Additionally, apart from soil pH, another factor, the rise in soil available Si, could also contribute to the reduction of Cd availability (Zhao *et al.* 2020).

Effects of Aged Biochar on Cd Immobilization

The results in this study suggested that BR2 treatment could sustainably impede Cd accumulation in rice tissues during the aging process. Further FTIR analysis of aged BR2

showed new stretching bands of -OH, -NH₂, and Si-O-Si on the aged BR particles (Fig. 10). Moreover, the stretching bands of O-H and C=C changed to lower frequencies. These low electron density on the aged BR2 particles might be induced by Cd adsorption. This evidence showed that the oxygenated functional groups contributed to Cd fixation on biochar surface area during the aging process. This conclusion was also proposed in another study (Uchimiya *et al.* 2011). Except for the contribution from oxygenated functional groups, the insoluble mineral fraction in the aged BR2 particles also facilitated Cd immobilization. This inference was supported by the results from FTIR, which demonstrated lower frequencies (800 and 700 cm⁻¹) on the aged BR particles. Moreover, BR contained a high concentration of Si, the high contents of Si in biochar could induce Cd bounding with insoluble SiO₂ (Xu and Chen 2015). Quan *et al.* (2022) found that biochar could immobilize Cd(II) by precipitation reaction, in which process, Cd-silicate might precipitate on the biochar-attapulgite as Cd₂SiO₃. These might be the main reasons for Cd immobilization during BR2 aging process.

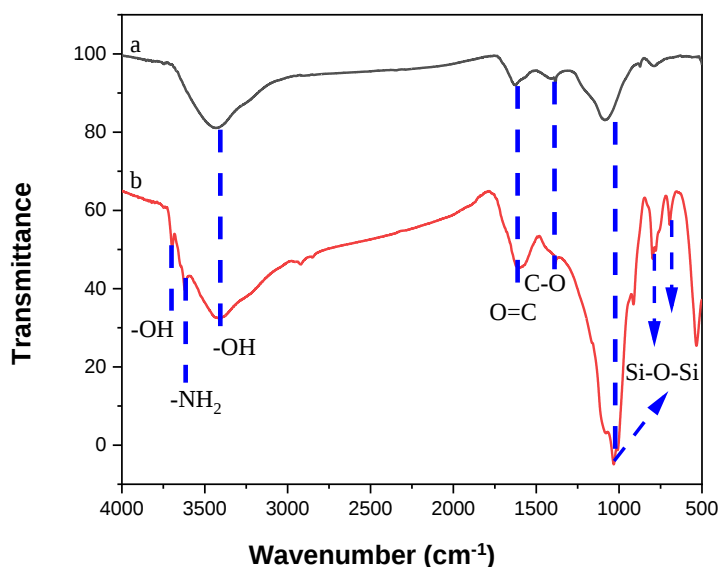


Fig. 10. FTIR spectra of (a) fresh rice straw biochar, (b) aged rice straw biochar particles from treatment of BR2. The arrows refer to three different chemical transformation of the same binding site.

Moreover, BR2 significantly and sustainably increased soil pH across the three rice seasons. The concentrations of Cd in both soil and rice root demonstrated that there was no significant increase in the bioavailability of Cd in soil (Figs. 2b and 4), especially under BR2 treatment. Above all, throughout the three rice seasons, the aged BR effectively and sustainably immobilized soil Cd by rising soil pH and surface complexation with Si-O-Si.

The uptake of Cd in rice straw was higher than that in rice root in 2017L, which probably accumulate exogenous Cd in leaf. The exogenous heavy metals may come from exhaust gas, acid rain, or fertilizer could entry to the amended soil and plants amended by biochar (Wang *et al.* 2018). In this study, the high Cd concentration in rice straw might have been caused by the exhaust gas with atmosphere deposition. This can be further shown by the report from Yi *et al.* (2018), which found that the atmosphere deposition could contribute about 83.8% to the total Cd input fluxes in the study area.

CONCLUSIONS

1. Fresh biochar with high available Si contents effectively inhibited Cd accumulation in rice grains by decreasing Cd upward translocation from rice root in condition 2016L.
2. The rice straw biochar (BR) significantly increased soil pH over the three rice seasons, which induced obvious Cd immobilization in soil.
3. The highly soluble Si contents in BR and labile fraction Si complexed with Cd, thus facilitating Cd fixation within the study period.
4. The natural aging process enhanced the effect of BR on Cd immobilization in rice paddy soil.
5. The exogenous Cd, especially from atmosphere deposition, probably affected Cd uptake in rice plants.

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