Environ Geochem Health (2019) 41:43–52
https://doi.org/10.1007/s10653-018-0120-1

Biochar reduces cadmium accumulation in rice grains in a tungsten mining area-field experiment: effects of biochar type and dosage, rice variety, and pollution level

Min Zhang · Shengdao Shan · Yonggen Chen · Fang Wang · Deyi Yang · Jikai Ren · Haoyu Lu · Lifeng Ping · Yanjun Chai

Received: 30 December 2017 / Accepted: 7 May 2018 / Published online: 8 June 2018

Abstract Cadmium (Cd)-contaminated rice (*Oryza sativa*) in Southern China is a great threat to food security, and the paddy soil remediation is urgently needed to reduce Cd accumulation in rice. Application of biochar could effectively immobilize soil Cd and reduce Cd uptake by rice. Fields that were applied with soil treatments including control and 15 and 30 t ha^{-1} each hickory nut shell-derived biochar (KC) or maize straw-derived biochar (MC), and grown with two rice varieties (hybrid rice and late japonica rice) were selected for this study. The long-term effect of biochars on decreasing Cd bioavailability in paddy soils was evaluated. The results showed when MC was applied at 15 t ha^{-1}, DTPA-Cd (soil cadmium extracted by diethylenetriamine pentaacetic acid) was reduced by 20.0 and 34.5% in Field A (slightly Cd pollution) and B (moderately Cd pollution), respectively. In Field B, soil DTPA-Cd concentrations with application of 30 t ha^{-1} biochars were all lower than that of 15 t ha^{-1} biochar, but there were no significant differences between the two types of biochars. Cd concentration in rice grains and straws of hybrid rice are two times more than those of late japonica rice. Cd bio-concentration factor both of grains and straw was significantly increased by biochar application, which in Field A was higher than that in Field B. Our results suggest that biochars reduce Cd accumulation in rice grains by immobilizing soil Cd. KC has a higher potential in lowering Cd bioavailability than MC. Hybrid rice should be prohibited to cultivate in these areas.

Keywords Biochar · Cadmium · Immobilization · Rice variety · Soil remediation · Tungsten mine wastewater

M. Zhang · S. Shan (✉) · J. Ren · H. Lu · L. Ping · Y. Chai
Zhejiang Key Laboratory of Recycling and Eco-treatment of Waste Biomass, Zhejiang University of Science and Technology, Hangzhou 310023, China
e-mail: shanshd@vip.sina.com

M. Zhang
e-mail: Zhangmin524@163.com

Y. Chen
School of Landscape Architecture, Zhejiang A&F University, Lin'an 311300, China

F. Wang
Lin'an A&F Bureau, Hangzhou 311300, China

D. Yang
Jinhua Integrated Supervision and Inspection Center of Agricultural Products Quality, Jinhua 321000, China

Introduction

In the rice production area of the Yangtze River Delta, soil heavy metal contamination is a serious issue, especially paddy soils (MEP & MLP 2014; Chen et al. 2015). Of the total area of contaminated lands, 64.8%

is polluted by heavy metal (of which 46.7% is slightly polluted), with lands contaminated by Cd taking up the largest area. Compared to other toxic heavy metals, Cd is readily mobile metal and is toxic even at lower concentration (He et al. 2015; Rizwan et al. 2016; Ran et al. 2016). It is recognized that Cd could be the key factor behind unavailability of safe food on a sustainable basis (Ran et al. 2016). This causes a concern for rice cultivation as it is known that rice readily accumulates Cd. Therefore, major effort should be on the proper remediation of slightly polluted agricultural soils, especially paddy soils, aiming to break the bottle neck of remediation cost and technology so as to have the agricultural production capacity recover as soon as possible.

Heavy metal mining is one of the major reasons for soil heavy metal pollution, and acidic mine wastewater is a worldwide environmental problem causing a broad concern (Natarajan et al. 2006). Due to disorderly exploitation and unregulated mine wastewater emission, nearby water bodies used for irrigation have been contaminated. Consequently, a large area of downstream agricultural lands shows very high concentrations of heavy metals, causing a concern on agricultural product security and severely constraining local agricultural production. China is a major tungsten production and consumption country. High concentrations of Cd, Cu, Zn, and Pb were found in the agricultural soils close to the Dayu Tungsten Ore in Jiangxi, which is the largest reserve and the longest exploiting history in China; the Cd had the largest accumulation factor of up to 4.0 (Shao et al. 2013). Thus, there is an urgent need to employ remediation techniques to reduce Cd availability and uptake by crops in such area.

Various remediation techniques have been proposed for reduction in Cd contents and availability in polluted agricultural soils (Shaheen and Rinklebe 2015; Antoniadis et al. 2017). To employ low Cd-accumulating rice varieties in combination with amendments for Cd decontamination, as an efficient remediation technique, is mainly used for slightly contaminated agricultural soil especial dealing with large area and sustainable agricultural outputs (Yu et al. 2006; Qayyum et al. 2017). Biochar has extremely large surface area, rich carboxyl groups and minerals, and high pH and cation exchange capacity (CEC). Therefore, it can not only improve soil fertility and structure, but also effectively immobilize toxic elements, contributing to low plant accumulation and significant efficacy in Cd-contaminated paddy soil remediation (Beesley et al. 2011; Zhang et al. 2013; Bian et al. 2014; Yan et al. 2014; Li et al. 2016). Previous field studies by others showed that application of biochar (at 20 and 40 t ha^{-1}) sharply reduced the bioavailability of heavy metals and the Cd concentration in rice grains to safe levels (Bian et al. 2013, 2014). Up till now, most studies on heavy metal immobilization were carried out via pot experiments, and pollutants were artificially added. Few field studies have been conducted to compare the effects of biochar on Cd uptake by different rice varieties, and the remediation potential of different types of biochars under different soil Cd contamination level. Therefore, in this study, slightly and moderately Cd-contaminated agricultural fields irrigated with tungsten mine wastewater were chosen and cultivated with super high yield hybrid rice and conventional late japonica rice. Biochars derived from two different raw materials were applied at different dosages to investigate their effects on soil Cd immobilization and Cd accumulation in rice grains.

Materials and methods

Site and soil

The field trail was conducted in the site (N29°56′, E119°13′) locating approximately 8 km downstream a tungsten ore in the northwest of Zhejiang Province, China. The ore was discovered in 1960s and used to be the largest tungsten ore in Zhejiang Province. The area has a subtropical monsoon climate and an altitude of 400 m a.s.l. Disorderly mine exploitation and unregulated emission of mine wastewater have led to heavy metal pollution of nearby water bodies and downstream agricultural soils. As a result, the safety of agricultural products has been a concern and local agricultural production has been restricted. In this study, two fields (Fields A and B) in a same irrigation system using river water were about 300 m apart from each other. Traditionally in rice–wheat (oilseed rape) rotation, the two fields were of the same landform and had close soil properties (Table 1) except for heavy metal concentrations (Table 2). Soils were Ferralic Acrisols.

Table 1 Soil properties of the two study fields

Field	Available nitrogen (mg/kg)	Available phosphorus (mg/kg)	Available potassium (mg/kg)	Total N (g/kg)	Total P (g/kg)	Total K (g/kg)	Total C (g/kg)	pH
A	129.4 ± 12.7	40.7 ± 20.6	36.3 ± 10.1	1.48 ± 0.10	0.36 ± 0.5	11.9 ± 0.7	24.1 ± 1.7	4.87 ± 0.1
B	168.7 ± 20.3	32.6 ± 7.9	44.2 ± 3.5	1.95 ± 0.15	0.26 ± 0.03	12.2 ± 0.2	31.2 ± 2.5	5.02 ± 0.1

Table 2 Soil heavy metal concentrations (mg/kg) of the two study fields

Field	Cd	Pb	Ni	Cr	Zn	Cu
A	0.70 ± 0. 1	16.59 ± 3.2	7.10 ± 1.4	21.76 ± 3.5	81.98 ± 10.2	15.95 ± 2.3
B	2.04 ± 0.7	29.47 ± 4. 3	9.78 ± 0.7	24.87 ± 2.0	50.57 ± 6.2	34.94 ± 9.3

Biochar for soil amendment

The two types of biochars, MC and KC, used in this study were derived from maize straw and hickory nut shell, respectively. For the production of MC, maize straws were pyrolyzed at 550 °C, for KC, hickory nut shells were pyrolyzed at 500 °C. The specific surface area of MC and KC was 57.68 and 93.46 $m^2\ g^{-1}$, respectively. The SEM images in Fig. 1 show the microstructures of MC and KC.

Experimental design

In this study, two rice varieties, high yield single cropping hybrid rice (Zhongzheyou#1) and conventional late japonica rice (Xiushui#9), were cultivated. In Field A, hybrid rice was planted and two biochar treatments were set up: 0(CK) and 15 t ha^{-1} (MC1). In Field B, five biochar treatments were set up: 0, 15 t ha^{-1} (MC1 and KC1), and 30 t ha^{-1} (MC2 and KC2), and each biochar treatment was further divided into two for cultivation of hybrid rice and japonica rice, respectively. The treatments were performed in triplicate, and the individual treatment plots were arranged in a complete randomized block design. Each plot of 2 m × 20 m in area was separated with surrounding protection rows 0.5 m in width and with separated irrigation inlets and drainage outlets. In Field A, there were three biochar treatments and total nine individual plots. In Field B, there were five biochar treatments and total 15 individual plot. The biochars were applied and mixed with the soils when

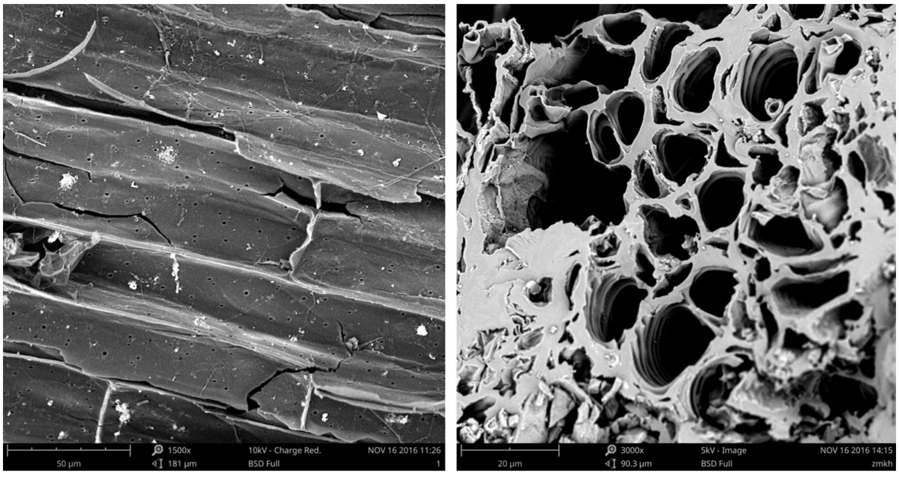

Fig. 1 SEM images of the maize straw-derived biochar (MC, left) and the hickory nut shell-derived biochar (KC, right)

the paddy soil were turn over in April before the rice transplanting in June 21. The plow depth is 20 cm. When the rice was harvested in October 24, 30 clusters of rice plants were randomly selected from each plot for productive ear counting and then the straws and grains of 3 clusters were oven-dried and weighed. Meanwhile, soil was sampled from each plot by collecting 3 randomly selected cores (0–10 cm deep), which were mixed to yield one composite sample per plot. Soil was air-dried and ground to pass through a 2-mm sieve for the detection of pH and through 150 µm for DTPA-Cd contents.

Chemical analysis

Soil pH was measured with a pH meter (FE28-Standard, Mettler Toledo). For Cd determination, soil samples were digested with HNO_3-HF-H_2O_2, while brown rice and straw were digested with HNO_3-H_2O_2, Soil DTPA-Cd was extracted using DTPA extraction method, and then Cd concentration of was measured with an ICP-MS (ICPMA8300, Perkin-Elmer).

Calculation of Cd bio-concentration factor (BCF)

A plant's BCF of heavy mental is an important parameter for plant's potential in remediating soil heavy metal contamination. The Cd BCF in rice straw or grain = Cd concentration in rice straw or grain/soil available Cd (i.e., DTPA-Cd) (Sun et al. 2009; Arao et al. 2010; Tang et al. 2015).

Statistics

Statistical analysis was performed using SAS 8.0 (SAS Institute, Cary, NC, USA); means were separated by LSD test at $P < 0.05$; and graphs were plotted using SigmaPlot 10 (Systat software Inc., San Jose, USA).

Results and analysis

The effects of biochar type and dosage on soil DTPA-Cd

Two-way ANOVA results showed that DTPA-Cd in the MC1 treatment of Field A was decreased by an average of 20.0% (from 0.44 ± 0.17 to 0.35 ± 0.07 mg kg^{-1}) compared to CK (Fig. 2). In Field B, DTPA-Cd was reduced by 34.4–50.4% in the MC treatments while by 42.4–53.6% in the KC treatments (Fig. 3). Particularly, DTPA-Cd in the MC1 treatment of Field B was significantly reduced by 34.4% on average from 1.26 ± 0.12 to 0.82 ± 0.14 mg kg^{-1}, a much higher percentage than that in MC1 of Field A. The larger dosage (30 t ha^{-1}) reduced DTPA-Cd more than the less dosage. However, for the same dosage, there were no significant differences in soil DTPA-Cd between treatments of different biochar types. That is, there was no significant difference in DTPA-Cd between MC1 and KC1 or between MC2 and KC2. Biochar slightly increased the soil pH value, which ranged from 4.7 to 5.6.

Effects of biochar application on Cd accumulation of the two rice varieties

The results showed that the severer the soil contamination, the higher the Cd accumulation in the rice. The Cd concentration in the straws and grains of the hybrid rice was significantly higher than that of the late japonica (Table 3). For the hybrid rice, its grain Cd concentration was 3.57 ± 0.51 mg kg^{-1} and up to 8.06 ± 0.18 mg kg^{-1} in CK of Field A and B, respectively; and its straw Cd concentration in Field B was 2.2 times that in Field A. Biochar application significantly reduced grain and straw Cd concentration by 21.3 and 28.3%, respectively, for the hybrid rice in Field A, while 18.1 and 26.5%, respectively, in Field

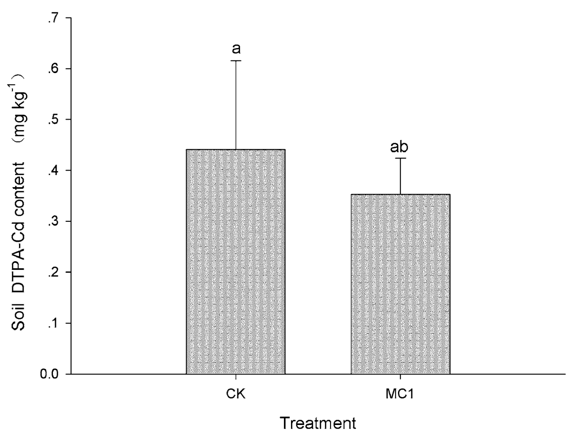

Fig. 2 Effects of biochar application on soil DTPA-Cd in Field A. MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}. Different letters indicate significant difference between treatments at $P \leq 0.05$

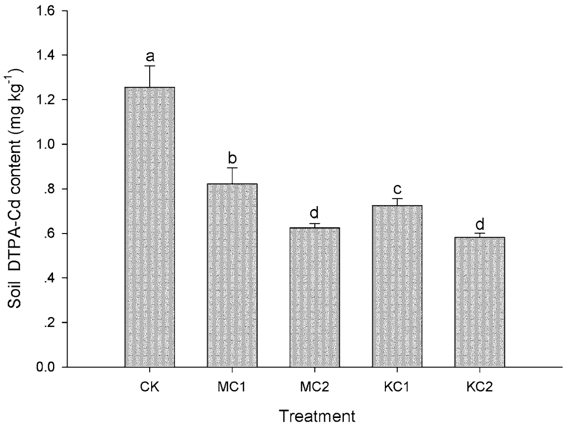

Fig. 3 Effects of biochar type and dosage on soil DTPA-Cd in Field B. MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}; MC2: MC applied at 30 t ha^{-1}; KC1: hickory nut shell-derived biochar (KC) applied at 15 t ha^{-1}; KC2: MKC applied at 30 t ha^{-1}. Different letters indicate significant difference between treatments at $P \leq 0.05$

Table 3 The effects of biochar application on Cd concentration in the brown rice grains and straws of the hybrid rice

Field	Treatment	Brown rice grain (mg kg^{-1})	Straw (mg kg^{-1})
A	CK	3.57 a[1]	14.56 a
	MC1[2]	2.81 b	10.43 b
B	CK	8.06 a	32.05 a
	MC1	6.60 b	23.57 b

[1]Different letters in a same column indicate significant differences at $P < 0.05$ between treatments in a same field

[2]MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}

B. In Field B (Fig. 4), grain Cd concentration of the late japonica rice under CK was 3.23 ± 0.25 mg kg^{-1}, 38.0% that of the hybrid rice, while straw Cd concentration of the former was 65.6% that of the latter. Through all treatments in Field B, the ratio of grain to straw in Cd concentration of the late japonica rice was 0.13–0.17, while that of the hybrid rice was 0.26–0.40. Results showed biochar can decreased the Cd concentrations both in the hybrid rice and late japonica rice. As for the late japonica rice, grain and straw Cd concentrations under treatments of MC2 and KC2 were lower than those of MC1 and KC1. As for the hybrid rice, grain and straw Cd concentration under treatments of KC2 was lower than that KC1, and they had no significant difference between treatments of MC1 and MC2. Above results showed that after biochar application, straw Cd concentration was decreased by a larger percentage than grain Cd concentration, which led to increase in the grain/straw ratio in Cd concentration or increase in the transfer coefficient (TC) of Cd from straw to grain.

The effects of biochar application on rice growth and Cd BCF

The Cd BCF values of brown grain and straw of the hybrid rice were 7.75–9.25 and 25.50–38.55, respectively (Table 4). Values in Field A were significantly higher than those of Field B. Biochar application lowered Cd BCF values in Field A, but not significantly, compared to no biochar application (CK). In

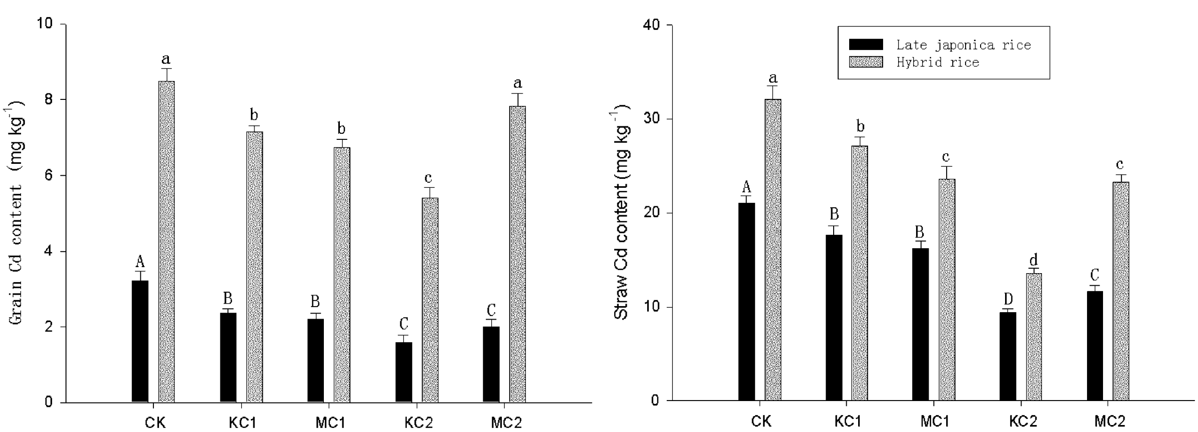

Fig. 4 The effects of biochar type and dosage on Cd concentration of the brown rice grains and straws in Field B. MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}; MC2: MC applied at 30 t ha^{-1}; KC1: hickory nut shell-derived biochar (KC) applied at 15 t ha^{-1}; KC2: MKC applied at 30 t ha^{-1}. Different letters indicate significant difference between treatments at $P \leq 0.05$

Field B, Cd BCF of the hybrid rice was higher than that of the late japonica rice, 140–270 and 20–90% higher for brown grains and straws, respectively (Fig. 5). ANOVA results (Table 5) showed that biochar application significantly raised Cd BCF of rice grain and straw; for Cd BCF increase, grain > straw and the hybrid rice > the japonica rice. The Cd BCF value was higher in KC1 than in KC2, while the opposite was true for MC.

Table 4 Effects of biochar application and Cd pollution level on the Cd BCF of grain and straw of the hybrid rice

Field	Treatment	Brown rice	Straw
A	CK	9.25a[2]	38.55a
	MC1[1]	9.05a	32.00a
B	CK	7.75b	25.50b
	MC1	8.19b	28.64b

[1]MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}

[2]Different letters in a same column indicate significant differences at $P < 0.05$ between the treatments

The influence of biochar on rice yield index, such as productive ear count and rice per spike, is not significant both in field A and field B. Yield composition analysis showed that there were no significant differences in productive ear count of the hybrid rice between the treatments with it being 15.9 ± 1.2 and 15.9 ± 0.8 in Field A and B, respectively. In Field A, the unhusked rice biomass the hybrid rice took up 1.49 ± 0.53 and 1.88 ± 0.64 of the straw biomass (aboveground) in CK and MC1, respectively. In Field B, the unhusked rice biomass of the hybrid rice took up 0.38–0.87 of the total straw biomass under various treatments. Generally, the hybrid rice grew obviously better in Field A than in Field B, but biochar application did not make significant differences in the ratio of unhusked rice biomass to aboveground biomass. In Field B (Table 6), the late japonica rice

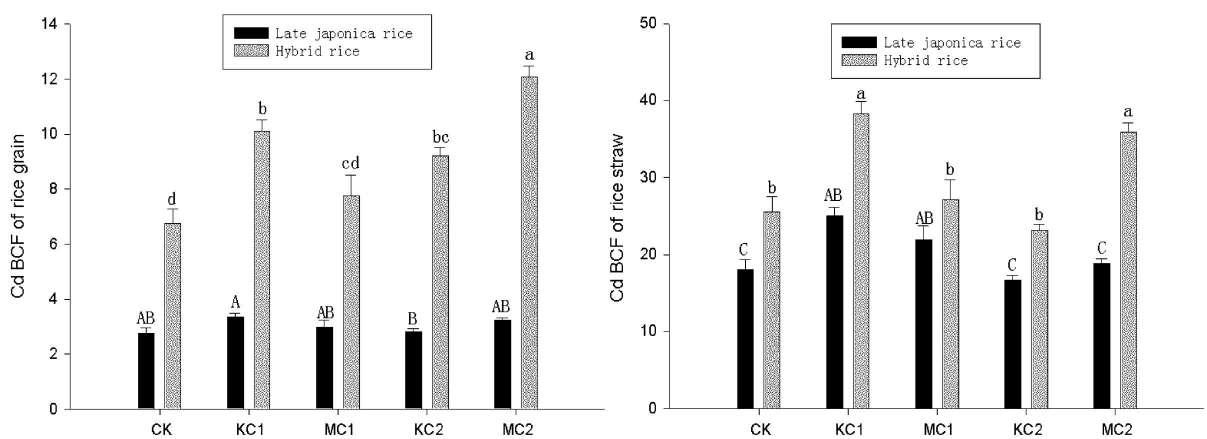

Fig. 5 Cd bio-concentration factor (BCF) of brown rice grain and straw in Field B. MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}; MC2: MC applied at 30 t ha^{-1}; KC1: hickory nut shell-derived biochar (KC) applied at 15 t ha^{-1}; KC2: KC applied at 30 t ha^{-1}. Different letters indicate significant difference between treatments at $P \leq 0.05$

Table 5 Two-way ANOVA on the effects of biochar type and dosage on Cd bio-concentration factor (BCF) of rice grain and straw

Factor	Conventional late japonica rice		Hybrid rice	
	Brown rice	Straw	Brown rice	Straw
Biochar dosage	0.86	< 0.0001	0.0005	0.012
Biochar type	0.66	0.12	0.067	0.015
Cross effect	0.0008	0.0002	< 0.0001	< 0.0001

Table 6 Rice yield composition in Field B

Treatment[1]	Unhusked rice weight (g)/ear		Productive ear number/cluster	
	Late japonica rice	Hybrid rice	Late japonica rice	Hybrid rice
CK	2.85 ± 0.7	1.92 ± 0.2	12.80 ± 0.5	15.20 ± 0.8
MC1	2.96 ± 0.6	2.36 ± 0.7	13.40 ± 0.8	16.00 ± 1.2
KC1	2.20 ± 0.6	1.46 ± 0.1	13.00 ± 0.6	15.00 ± 0.7
MC2	2.46 ± 0.3	1.92 ± 0.5	15.60 ± 0.9	16.90 ± 1.1
KC2	3.19 ± 0.5	1.73 ± 0.1	13.40 ± 0.7	15.89 ± 0.9

[1]MC1: maize straw-derived biochar (MC) applied at 15 t ha^{-1}; MC2: MC applied at 30 t ha^{-1}; KC1: hickory nut shell-derived biochar (KC) applied at 15 t ha^{-1}; KC2: KC applied at 30 t ha^{-1}

weighed 2.2–3.2 g per spike, higher than the hybrid rice. But with a count of 12.8–15.9 per cluster, the former had fewer productive ears per cluster than the latter. Assuming a rice plant density of 240,000 clusters per ha, theoretical rice yield in the different treatments ranged 5258 to 10,245 kg ha^{-1}, close to the yield level in the local region. Biochar application did not exert a significant effect on rice yield, due to large soil heterogeneity in this field experiment.

Discussion

Immobilization of soil Cd by biochars in paddy fields

In this study, 7 months after biochar application, soil DTPA-Cd decreased by over 20%, and plant Cd concentration also decreased significantly. The severer the soil pollution was, by a larger percentage soil DTPA-Cd and rice grain Cd concentration were decreased, indicating that after a crop growing season, heavy metal adsorption by the biochars was not yet to reach equilibrium and heavy metal immobilization would continue. It is pointed out by previous studies that the heavy metal immobilization ability of biochar is mainly attributed to its surface functional groups, which interact with heavy metal via chelation, precipitation, redox, electrostatic attraction, etc.(Beesley et al. 2011). Short-term adsorption experiments demonstrated that Cd^{2+} adsorption by an MC can be well described by a Langmuir equation, and the adsorption capacity was 23.52–23.59 mg/g at 25–35 °C (Kołodyńska et al. 2012; Xu et al. 2014). Findings of 1–3-year field experiments on agricultural soil remediation showed that biochar has a long-term immobilizing effect on Cd, Pb, and Cu and improves the uptake of Si, P, and K by rice and wheat (Bian et al. 2014; Li et al. 2016; Abbas et al. 2017). The alternate wetting and drying water management and fertilization in paddy fields lead to continuous increase in the surface organic and inorganic layers of biochar, which could be one of the major reasons for biochar's long-term adsorption effect. Another reason might be that the reaction of the iron oxides on the surface and in the nano-pores of heavy metal-loaded biochar would increase the surface functional group density of biochar. Consequently, heavy metal nano-particles are continuously adsorbed and react with the surface inorganic and organic compounds.

Though biochar application slightly raised soil pH, soil pH was not significantly related to soil DTPA-Cd due to high heterogeneity in soil heavy metal concentration in this study. This implies that soil pH increase was not the major reason for heavy metal immobilization by biochar. It was in line with the result from Rinklebe et al.(2016) which found that biochar addition for 1 year into a flooding soil has little effects on soil E_H/pH and while decreased concentrations of dissolved heavy metals under dynamic redox conditions. Biochar have abundant binding sites and a large surface area and thus can reduce cadmium mobilization, while El-Naggar et al. (2018) found short-term addition of biochar into aerobic soil, exhibited a wider range of E_H and a lower pH than the non-treated soil, biochar addition had increased the dissolved concentrations of Cd, which might be due to the lower pH values under oxic conditions. In addition, MC and KC biochars differed in the function of soil Cd immobilization. Soil DTPA-Cd was reduced by a larger percentage by KC than by MC. It is attributed to the more abundant pore structure and binding sites in KC than MC and thus had higher heavy metal immobilization capacity. Li et al. (2016) found that corn straw-derived biochar (CB) had more O-bearing groups than hardwood-derived biochar (HB) and in turn more adsorbing sites for Cd and Cu. Lignin content is an important factor influencing the oxidation degree of biochars and in turn the sustainability of heavy metal immobilization. In this study, it was found that soil DTPA-Cd was lower with KC application than with MC application, which might be due to the high porosity and high lignin content in KC.

Grain Cd accumulation characteristics and responses to biochar application of the two rice varieties

The results of this study showed that grain Cd concentration of the hybrid rice in Field B was twice that in Field A. Meanwhile, for the same biochar treatment, grain Cd concentration was reduced by a larger percentage in Field B than in Field A, which was directly related to the larger decrease in soil DTPA-Cd in Field B. It is believed that biochar reduces Cd accumulation in rice grains by reducing Cd mobility. Bian et al. (2013) found grain Cd concentration of both super rice and conventional rice decreased significantly to 0.4 mg kg^{-1} with 40 t ha^{-1} biochar in Cd-contaminated soil and the brown grain Cd concentration was positively and significantly related to soil exchangeable Cd. Biochar addition improve the rice tiller number in this study. It improved rice growth in the slightly polluted field, while in the moderately polluted field, its effect was not so prominent. In rhizosphere, significant soil–rice plant interaction occurs, explaining plant behavior in remediated contaminated soils. In biochar remediation soil, Cd photoavailability and accumulation in rice plants were altered by changed microflora and root exudates in rhizosphere with biochar amendments, and strategies were employed for Cd uptake and translocation of different rice varieties (Antoniadis et al. 2017). Long-term biochar addition can improve the microliving environment, such as increasing soil pH, moisture, active nutrients and the C/N ratio, and indirectly strong influence on microbe compositions, especially fungals in paddy soil, as well as increased root growth and raised plant biomass (Dai et al. 2016; Zheng et al. 2016).

Liu et al. (2016) found that the BCF of Cd, Cu, Pb, and Zn of the underground part and aboveground part of lettuce (*Lactuca sativa* L. var. *capitata* L.) tended to decrease with increasing biochar application dosage. However, the transfer coefficient of Cd, Cu, and Zn in the aboveground part tended to increase, demonstrating that biochar can significantly lower heavy metal accumulation in plant tissues but increase heavy metal upward transfer. It was also found in this work that the higher the biochar application dosage, the higher the grain Cd/straw Cd ratio was, and the more Cd was transferred from straw to grain. Chen et al. (2016) found that biochar works better in lowering Cd uptake by low Cd-accumulating rice varieties than by high Cd-accumulating rice varieties. The results from this work shows that biochar can significantly raise the Cd BCF of the straws and grains for the hybrid rice, but not significantly for the conventional late japonica rice. Additionally, Cd BCF responded differently to the two types of biochars. Compared to in KC1, soil DTPA-Cd was lower, less Cd was accumulated by rice plants, and Cd BCF was lower in KC2. Similar to KC, soil DTPA-Cd was lower in MC2 than in MC1. However, Cd accumulation by rice plants was not significantly reduced with higher MC application dosage. This indicates that KC has a higher potential than MC in lowering Cd bioavailability.

Grain Cd concentration of different rice varieties can differ by several times due to their different strategies employed for Cd uptake and translocation (Zhou et al. 2013; Zhang et al. 2015; Cai et al. 2016). Cd accumulation in rice plants mainly differ in its accumulation and transfer in stems and leaves (Liu et al. 2007; Uraguchi et al. 2009; Yang et al. 2015; Cai et al. 2016), as they are one of the paths for Cd to reach rice grains and also an important regulating factor. Many protein families involving in metal transfer and playing important roles in Cd transfer, such as gene $OsHMA_2$ was found to involve in the transfer of metals from the underground parts to the aboveground parts, facilitating the loading of Cd and Zn in xylem (Takahashi et al. 2012; Yamaji et al. 2013). It is also suggested the accumulation of Cd in rice roots should be attributed to the sequestration of intense Fe plaque in rhizosphere of paddy soil (Yu et al. 2016; Li et al. 2017). The results from this work show that whether for the hybrid rice or the conventional rice, Cd BCF of straw was higher than that of grain and Cd BCF in Field A was higher than in Field B. In addition, Cd BCF of rice straw was more sensitive to rice variety and pollution level than that of grain, confirming that straw Cd accumulation is an important factor regulating grain Cd accumulation. Grain Cd accumulation in hybrid rice was more sensitive to soil Cd contamination than that in late japonica rice, and Cd BCF in the straws and grains of the hybrid rice was higher than that of the japonica rice. In terms of the ratio of grain Cd concentration to straw Cd concentration, the hybrid rice was also twice the japonica rice, indicating a stronger Cd-transferring capacity of the former. This may be a major reason for high Cd accumulation in the high yield hybrid rice. Therefore, it is suggested that caution should be taken when choosing high yield single cropping hybrid rice for Cd-contaminated fields.

Conclusions

Results of the field experiment showed biochar had significantly decreased the soil Cd mobilization and reduced Cd uptake by rice and accumulation in rice grains. More biochar inputs, less soil DAPT-Cd concentration. With application of larger dosage, hickory nut shell-derived biochar led to larger reduction both of plant Cd accumulation and soil DAPT-Cd concentration than maize straw-derived biochar. The hybrid rice variety commonly grown by local people accumulated much more Cd in its grains than the conventional late japonica rice, so it is not suggested to be grown in area with Cd-contaminated soil or high environmental original value of cadmium.

Acknowledgements This work was financially supported by the Key Science and Technology Special Project of Zhejiang Province (2015C02037), Science and Technology Development Planning Programme of Hangzhou City (20140533B68), Science and Technology Planning Programme of Jinhua City (2016-2-015), Public Welfare Technology Application Research Project of Zhejiang Province (2016C33102) and the Key Research and Development Project of Zhejiang Province (2017C03010). The authors thank Drs. Bin Guo and Junmin Wang with the Zhejiang Academic of Agricultural Sciences for their suggestions and supports in the selection of rice varieties and studied fields.

References

Abbas, T., Rizwan, M., Ali, S., Zia-Ur-Rehman, M., & Qayyum, M. F. (2017). Effect of biochar on cadmium bioavailability and uptake in wheat (*Triticum Aestivum L.*) grown in a soil with aged contamination. *Ecotoxicology and Environmental Safety, 140,* 37–47.

Antoniadis, V., Levizou, E., Shaheen, S. M., Ok, Y. S., Sebastian, A., Baum, C., et al. (2017). Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation—A review. *Earth-Science Reviews, 171,* 621–645.

Arao, T., Ishikawa, S., Murakami, M., Abe, K., Maejima, Y., & Makino, T. (2010). Heavy metal contamination of agricultural soil and countermeasures in Japan. *Paddy and Water Environment, 8,* 247–257.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution, 159,* 3269–3282.

Bian, R. J., Chen, D., Liu, X. Y., Li, L. Q., Pan, G., Xie, D., et al. (2013). Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment. *Ecological Engineering, 58,* 378–383.

Bian, R. J., Joseph, S., Cui, L., Pan, G., Li, L., Liu, X., et al. (2014). Three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment. *Journal of Hazardous Materials, 272,* 121–128.

Cai, Q., Lin, D., Wang, G., & Wang, D. (2016). Differences in cadmium accumulation and transfer capacity among different types of rice cultivars. *Journal of Agro-Environment Science, 35,* 1028–1033.

Chen, D., Guo, H., Li, R., Li, L., Pan, G., Chang, A., et al. (2016). Low uptake affinity cultivars with biochar to tackle Cd-tainted rice—A field study over four rice seasons in Hunan, China. *Science of the Total Environment, 541,* 1489–1498.

Chen, H., Teng, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. *Science of the Total Environment, 512–513,* 143–153.

Dai, Z., Hu, J., Xu, X., Zhang, L., Brookes, P., He, Y., Xu, J. (2016). Sensitive responders among bacterial and fungal microbiome to pyrogenic organic matter (biochar) addition differed greatly between rhizosphere and bulk soils. Scientific Report, Nov 8–6, 3610.

El-Naggar, A., Shaheen, S. M., Ok, Y. S., Rinklebe, J. (2018). Biochar affects the dissolved and colloidal concentrations of Cd, Cu, Ni, and Zn and their phytoavailability and potential mobility in a mining soil under dynamic redox-conditions. *Science of the Total Environment*, *624*, 1059–1071.

He, S., He, Z., Yang, X., Stoffella, P. J., & Baligar, V. C. (2015). Soil biogeochemistry, plant physiology, and phytoremediation of cadmium-contaminated soils. *Advances in Agronomy, 134,* 135–225.

Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapińskib, W., & Hubickia, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal, 197,* 295–305.

Li, H., Luo, N., Li, Y. W., Cai, Q. Y., Li, H. Y., Mo, C. H., et al. (2017). Cadmium in rice: Transport mechanisms, influencing factors, and minimizing measures: A Review. *Environmental Pollution, 224,* 622–630.

Li, H., Ye, X., Geng, Z., Zhou, H., Guo, X., Zhang, Y., et al. (2016). The influence of biochar type on long-term stabilization for Cd and Cu in contaminated paddy soils. *Journal of Hazardous Materials, 304,* 40–48.

Liu, C., Liu, X., Wu, W., Cai, X., Liang, Y., & Nan, Z. (2016). Effect of biochar and biochar based fertilizer on growth of *Lactuca sativa* L. and absorption of heavy metals. *China Environmental Science, 36,* 3064–3070. **(in Chinese with English abstract)**.

Liu, J. G., Qian, M., Cai, G. L., Liang, X., Li, Y., & Nan, Z. (2007). Uptake and translocation of Cd in different rice cultivars and the relation with Cd accumulation in rice grain. *Journal of Hazardous Materials, 143,* 443–447.

Ministry of Environmental Protection, Ministry of Land and Resources. (2014). Report on the national general survey of soil contamination [R/OL]. (2014-04-17) [2014-04-20]. http://www.zhb.gov.cn/gkml/hbb/qt/201404/t20140417_270670.htm.

Natarajan, K. A., Subramanian, S., & Braun, J. J. (2006). Environmental impact of metal mining—Biotechnological aspects of water pollution and remediation—An Indian experience. *Journal of Geochemical Exploration, 88,* 45–48.

Qayyum, M. F., ur Rehman, M. Z., Ali, S., Rizwan, M., Naeem, A., Maqsood, M. A., et al. (2017). Residual effects of monoammonium phosphate, gypsum and elemental sulfur on cadmium phytoavailability and translocation from soil to wheat in an effluent irrigated field. *Chemosphere, 174,* 515–523.

Ran, J., Wang, D., Wang, C., Zhang, G., & Zhang, H. (2016). Heavy metal contents, distribution, and prediction in a regional soil–wheat system. *Science of the Total Environment, 544,* 422–431.

Rinklebe, J., Shaheen, S. M., & Frohne, T. (2016). Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil. *Chemosphere, 142,* 41–47.

Rizwan, M., Meunier, J. D., Davidian, J. C., Pokrovsky, O. S., Bovet, N., & Keller, C. (2016). Silicon alleviates Cd stress of wheat seedlings (*Triticum turgidum* L. cv. Claudio) grown in hydroponics. *Environmental Science and Pollution Research, 23,* 1414–1427.

Shaheen, S. M., & Rinklebe, J. (2015). Impact of emerging and low cost alternative amendments on the (im)mobilization and phytoavailability of Cd and Pb in a contaminated floodplain soil. *Ecological Engineering, 74,* 319–326.

Shao, X., Cheng, H., Duan, X., & Lin, C. (2013). Concentrations and chemical forms of heavy metals in agricultural soil near the world‘s largest and oldest tungsten mine located in China. *Chemical Speciation and Bioavailability, 25,* 125–132.

Sun, Y. B., Zhou, Q., Liu, W., An, J., Xu, Z. Q., & Wang, L. (2009). Joint effects of arsenic and cadmium on plant growth and metal bioaccumulation: A potential Cd-hyperaccumulator and as-excluder *Bidens Pilosa* L. *Journal of Hazardous Materials, 165,* 1023–1028.

Takahashi, R., Ishimaru, Y., Shimo, H., Ogo, Y., Senoura, T., Nishizawa, N. K., et al. (2012). The OsHMA2 transporter is involved in root-to-shoot translocation of Zn and Cd in rice. *Plant, Cell and Environment, 35,* 1948–1957.

Tang, H., Li, T., Zhang, X., & Chen, G. (2015). Screening of rice cultivars with high cadmium accumulation and its cadmium accumulation characteristics. *Ecology and Environmental Sciences, 24,* 1910–1916. **(in Chinese with English abstract)**.

Uraguchi, S., Mori, S., Kuramata, M., Akira, K., Tomohito, A., & Satoru, I. (2009). Root-to-shoot Cd translocation via the xylem is the major process determining shoot and grain cadmium accumulation in rice. *Journal of Experimental Botany, 60,* 2677–2688.

Xu, N., Lin, D., Xu, Y., Xie, Z., Liang, X., & Guo, W. (2014). Adsorption of aquatic Cd^{2+} by biochar obtained from corn stover. *Journal of Agro-Environment Science, 33,* 958–964. **(in Chinese with English abstract)**.

Yamaji, N., Xia, J., Mitani-Ueno, N., Yokosho, K., & Feng, M. J. (2013). Preferential delivery of zinc to developing tissues in rice is mediated by P-type heavy metal ATPase OsHMA2. *Plant Physiology, 162,* 927–939.

Yan, M., Cheng, K., Luo, T., & Pan, G. (2014). Carbon footprint of crop production and the significance for greenhouse gas reduction in the agriculture sector of China. In S. S. Muthu (Ed.), *Assessment of carbon footprint in different industrial sectors* (Vol. 1, pp. 247–264). Singapore: Springer.

Yang, F., Tang, M., & Zhu, Y. (2015). Molecular mechanism of cadmium absorption and transport in rice. *Hybrid rice, 30,* 2–8. **(in Chinese with English abstract)**.

Yu, H.-Y., Liu, C., Zhu, J., Li, F., Deng, D.-M., Wang, Q., et al. (2016). Cadmium availability in rice paddy fields from a mining area: The effects of soil properties highlighting iron fractions and pH value. *Environmental Pollution, 209,* 38–45.

Yu, H., Wang, J., Fang, W., Yuan, J., & Yang, Z. (2006). Cadmium accumulation in different rice cultivars and screening for pollution-safe cultivars of rice. *Science of the Total Environment, 370,* 302–309.

Zhang, B., Luo, L., Wei, Y., Zhang, X., & Nie, G. (2015). Analysis of cadmium accumulation dynamics in rice with distinct genotypes. *Chinese Agricultural Science Bulletin, 2015*(31), 25–30. **(in Chinese with English abstract)**.

Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., et al. (2013). Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science and Pollution Research, 20,* 8472–8483.

Zheng, J., Chen, J., Pan, G., Liu, X., Zhang, X., Lianqing Li, L., et al. (2016). Biochar decreased microbial metabolic quotient and shifted community composition four years after a single incorporation in a slightly acid rice paddy from southwest China. *Science of the Total Environment, 571,* 206–217.

Zhou, X., Zhou, H., Hu, M., & Liao, B. (2013). The difference of Cd, Zn and As accumulation in different hybrid rice cultivars. *Chinese Agricultural Science Bulletin, 29,* 145–150. **(in Chinese with English abstract)**.