Effects of Biochar on Cadmium Accumulation in Rice and Cadmium Fractions of Soil: A Three-Year Pot Experiment

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A three-year rice pot experiment was conducted to investigate the effects of biochar on cadmium (Cd) accumulation in rice and Cd fractions of soil. The biochar was derived from farmland waste and applied to contaminated paddy soil at various application rates (0, 1, 2, and 4%). The dry matter accumulations in rice, Cd contents of various rice organs, and fraction distributions of Cd in soil were measured. In a 3-year experiment, the results indicated that biochar treatments reduced the exchangeable Cd concentrations by 28.5 to 59.4% in soil, the total Cd accumulations in rice by 2.7 to 23.8%, and promoted rice growth by 0.7 to 3.9%. The application rates of 2% to 4% were considered to be reasonable for both rice growth and remediation of Cd-contaminated soil. Meanwhile, the Cd-contaminated biochar and straw were studied in the above manner for two years. Contaminated biochar reduced the Cd content of individual rice plants and ensured the normal growth of rice, but it had little effect on the Cd contents in specific organs of rice and Cd fractions of soil. However, this indicated that contaminated biomass materials have the possibility to be reused after pyrolysis for remediation of contaminated paddy soil.

Keywords: Tessier; Fractions; Application rate; Contaminated biochar; Straw

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INTRODUCTION

Heavy metal pollution is a global environmental problem (Arunakumara *et al*. 2013; Tóth *et al*. 2016) and causes concern in China regarding food security and public health (Duan *et al*. 2016; Li *et al*. 2016; Wu and Sun 2016). Cadmium (Cd) is considered the most toxic of the heavy metals (Wu *et al*. 2016). Liaoning province is one of three provinces in Northeast China, which is the main grain-producing area of China; however, with the rapid development of industry in the last century, large areas of paddy soil have been contaminated by heavy metals because of sewage irrigation and rice is the most planted crop in this contaminated soil (Jalali and Hemati 2013; Ke *et al*. 2015). Rice is a staple food for nearly 60% of China's population and has very important planting status in China. However, in recent years, it is not uncommon to find the reports that the cadmium content of rice has exceeded the standard due to soil pollution (Liu *et al*. 2016a). This study is from the perspective of practical production and application. Thus, local contaminated soil and a local rice variety were selected as experimental materials to test the biochar effects on Cd bioavailability of soil and Cd accumulation in rice.

In recent years, many studies have shown that biochar can affect plant growth (Major *et al*. 2010; Liu *et al*. 2013; Coumar *et al*. 2016; Ding *et al*. 2016). Novak *et al.* (2016) pointed out that the effects of biochar on crop yield can be both positive and negative because of differences in the initial soil properties. In addition, various articles mention that biochar can reduce the phytoavailability of heavy metals in soil effectively (Park *et al*. 2011; Zhang *et al*. 2013; Bian *et al*. 2014; Puga *et al*. 2015). In either plant growth promotion or contaminated soil remediation, the application rate of biochar is considered one of the key factors (Cui *et al*. 2011, 2012; Jeffery *et al*. 2011). This study focuses on the biochar application rates for both rice production and remediation of Cd-contaminated soil as a means to find a reasonable application rate range to ensure the normal growth of rice, or even increase production, and to reduce the phytoavailability of Cd in soil and Cd uptake by rice effectively.

The large amount of contaminated straw produced year after year from heavy metal contaminated paddy soil is still an issue, even if biochar could effectively remediate contaminated soil and reduce crop uptake. Previous studies have suggested pyrolysis as a promising method for contaminated biomass disposal (Sas-Nowosielska *et al.* 2004; Stals *et al*. 2010; Fletcher *et al*. 2014). Břendová *et al.* (2015) confirmed that the metal sorption ability of biochar derived from contaminated biomass was not significantly different from uncontaminated biomass; however, another study pointed out that biochar made from waste wood increased concentrations of available Cu in soil and led to significant uptake by crop (Jones and Quilliam 2014). Therefore, another research focus of this study was the utilization of Cd-contaminated straw, to explore whether contaminated straw can be charred to biochar and returned to the local soil for heavy metal pollution management.

The bioavailability of heavy metals in soil depends not only on their total contents but also on their forms (Hu *et al*. 2014). Heavy metals exist in various forms having different bioavailabilities in soils (Jalali and Hemati 2013). The Tessier sequential extraction method is commonly used to determine the forms of heavy metals in soil (Wang *et al*. 2013); this method divides the total metals into five fractions: exchangeable fraction (EXCH), carbonate-bound (CARB), Fe-Mn oxide bound fractions (Fe-Mn), organic bound fraction (OM), and residual fraction (RES) (Tessier *et al*. 1979). Many researchers have attempted to assess the phytoavailability of heavy metals in contaminated soils using a sequential extraction procedure (Kashem *et al*. 2010). Thus, in this study, the Tessier scheme is used for evaluating the effects of biochar on Cd bioavailability in soil.

For studies of biochar affecting crop growth, the results of short-term and seeding experiments tend to have good regularity, but they lack practical and instructive value. Jeffery *et al*. (2011) suggested that pot experiments should be designed to summarize laws and evaluate mechanisms in the long-term. Therefore, this experiment was designed for three years, to allow a comprehensive determination of the effects of biochar on Cd fractions in soil and rice Cd uptake.

In summary, this pot experiment lasted three years, and the main objective was to use Cd contaminated soil to plant rice. The first part of treatment concerns various biochar application rates, and the other part is about comparison of contaminated biochar and straw. The main research method is to analyze the Cd forms in soil, as well as the Cd contents and dry matter accumulation in rice. The purpose of this research is to make a scientific evaluation of the effects of biochar on the process of Cd bioavailability changes in soil and Cd uptake by rice.

EXPERIMENTAL

Materials

Biochar for the experiment was provided by Liaoning Jinhefu Agriculture Development Co., Ltd. Raw materials for pyrolysis were mixed farm residuals including corn stalk, peanut hull, and rice hull. The pyrolysis condition was 450 °C for 1 to 2 h, and the detailed charring method can be found in a China patent (publish number: CN 102092709 B) .

Yellow-brown surface soil (0 to 20 cm) was collected from a Cd-contaminated site in Shenyang City, Liaoning Province, China, which was subjected to a long-term irrigation by industrial waste water.

Shennong 265 (*Oryza sativa* L.) is a new variety of rice, planted widely as classical super-high-yield japonica in northeast China.

The characteristics of the soil and biochar are shown in Table 1. The pH, CEC, total and available element contents, and texture of soil were determined by referring to Lu (2000). Total carbon, nitrogen, and sulfur contents of soil and biochar were determined by dry combustion analysis using an Elementar (vario MACRO CNS; Elementar, Germany). The specific surface area, total pore volume, and average pore diameter of biochar were analyzed using a surface area and pore size analyzer (V-sorb 4800, JINAIPU, China).

Table 1. Characteristics of Soil and Biochar

Properties		Soil	Biochar
Cd (mg kg^{-1})		3.98 ± 0.09	-
pH (H_2O)		5.26 ± 0.07	8.94 ± 0.06
CEC (cmol kg^{-1})		11.89 ± 0.49	21.20 ± 0.77
Total C (%)		1.54 ± 0.02	42.85 ± 1.52
Total N (%)		0.14 ± 0.01	1.40 ± 0.02
Total P (%)		0.05 ± 0.00	0.12 ± 0.00
Total K (%)		0.13 ± 0.00	0.08 ±0.01
Total S (%)		0.09 ± 0.01	0.30 ± 0.00
C/N		11.00 ± 0.67	30.61 ± 0.69
Available N (mg kg^{-1})		144.75 ± 4.17	-
Available P (mg kg^{-1})		30.42 ±1.00	-
Available K (mg kg^{-1})		89.15 ±1.50	-
Texture (%)	Silt	33.52 ± 1.00	-
	Clay	35.92 ± 1.33	-
	Sand	30.56 ± 0.83	-
Specific surface area (m^2 g^{-1})		-	28.14 ± 0.46
Total pore volume (ml g^{-1})		-	0.05 ± 0.00
Average pore diameter (nm)		-	10.90 ± 0.14

Experimental Design and Procedure

The three-year pot experiment from 2012 to 2014 was set up at Shenyang Agricultural University.

The first part of the study was about biochar applications at different rates and primarily examined the effects of the biochar application rate on the dry weights and Cd contents of rice organs and the Cd fractions in soil. In 2012, biochar was incorporated into the soil at five levels before rice transplantation: CK: 0%, C1: 0.5%, C2: 1%, C3:

2%, and C4: 4%, and each pot contained 15 kg soil. Rice seedling culture was carried out in a green house on April 28, 2012, and seedlings were transplanted to pots on May 23, 2012. Each pot contained four holes, with one rice seedling in each hole. Chemical fertilizers were applied with 1 g of KH_2PO_4 pot^{-1} and 1 g of $CO(NH_2)_2$ pot^{-1} three times: 3 d before transplantation, 20 d after transplantation, and 5 d before heading. Water layer depths were maintained at approximately 2 cm during the whole growth period. In 2013 and 2014, no more biochar was applied to the above treatments; the soil of each treatment was remixed before rice transplantation, roots and residuals were eliminated, and rice cultivation procedures were repeated. Soil and rice plant samples were collected after rice harvests from 2012 to 2014.

The second part of the study was about contaminated biochar and primarily examined the effects of biochar derived from Cd-contaminated rice straw on the dry weights and Cd contents of rice organs, as well as the Cd fractions in soil. Contaminated straw was obtained from the first part of the experiment after the rice harvest in 2012, including leaf, sheath, and stem, and was dried and crushed before application and pyrolysis. Contaminated biochar was prepared at the highest treatment temperature (HTT) of 500 °C for 1 h. No application was named CK, contaminated biochar applied treatment was CB, and contaminated straw applied treatment was CS; the application rates of CB and CS were both 2%. The detailed cultivation methods were the same as in the first part. Soil and rice plant samples were collected after rice harvests in 2013 and 2014.

All treatments were performed in a complete randomized design with three replicates.

Sampling and Analysis Methods

For both parts, soil samples (0 to 20 cm) were collected after harvest each year. Each pot took three points, mixed into one soil sample, and each treatment took soil samples from three pots. Soil samples were ground after being air dried, then passed through a 2-mm sieve for further analysis (Chen and Zheng 2000); plant detritus and any visible fragments were removed. Three whole plant samples were collected randomly from each treatment each year and oven-dried at 105 °C for 30 min, then further dried at 80 °C for 48 h. Rice plant samples were divided into leaf, stem, sheath, hull, and brown rice, then crushed for further analysis.

The dry matter weights of rice organs were measured using an electronic balance (BSA4202S, Sartorius, Germany) after plant samples were air dried completely.

The Cd contents of different rice organs were determined by graphite method atomic absorption spectrophotometer (AA-7000, Shimadzu Inc., Japan) after digestion, and the total accumulation of Cd in rice organs was obtained by multiplying the dry matter weight and the corresponding Cd content.

The Cd fractions in soil samples from the pot experiment were analyzed using a sequential extraction technique. The detailed procedure is found in Tessier *et al*. (1979).

Statistical Analysis

Data were summarized as means and standard deviation (SD) of the means using Excel 2013 software (Microsoft, Redmond, WA). One-way analysis of variance (ANOVA) was performed to determine the statistical significance ($p \leqslant 0.05$; $n = 3$) of the treatment effects using SPSS version 13.0 (SPSS Institute, USA).

RESULTS

Effects of Biochar on Dry Matter Accumulation in Rice

Figure 1A shows the effects of biochar application rate treatments on the total dry weights of individual rice plants.

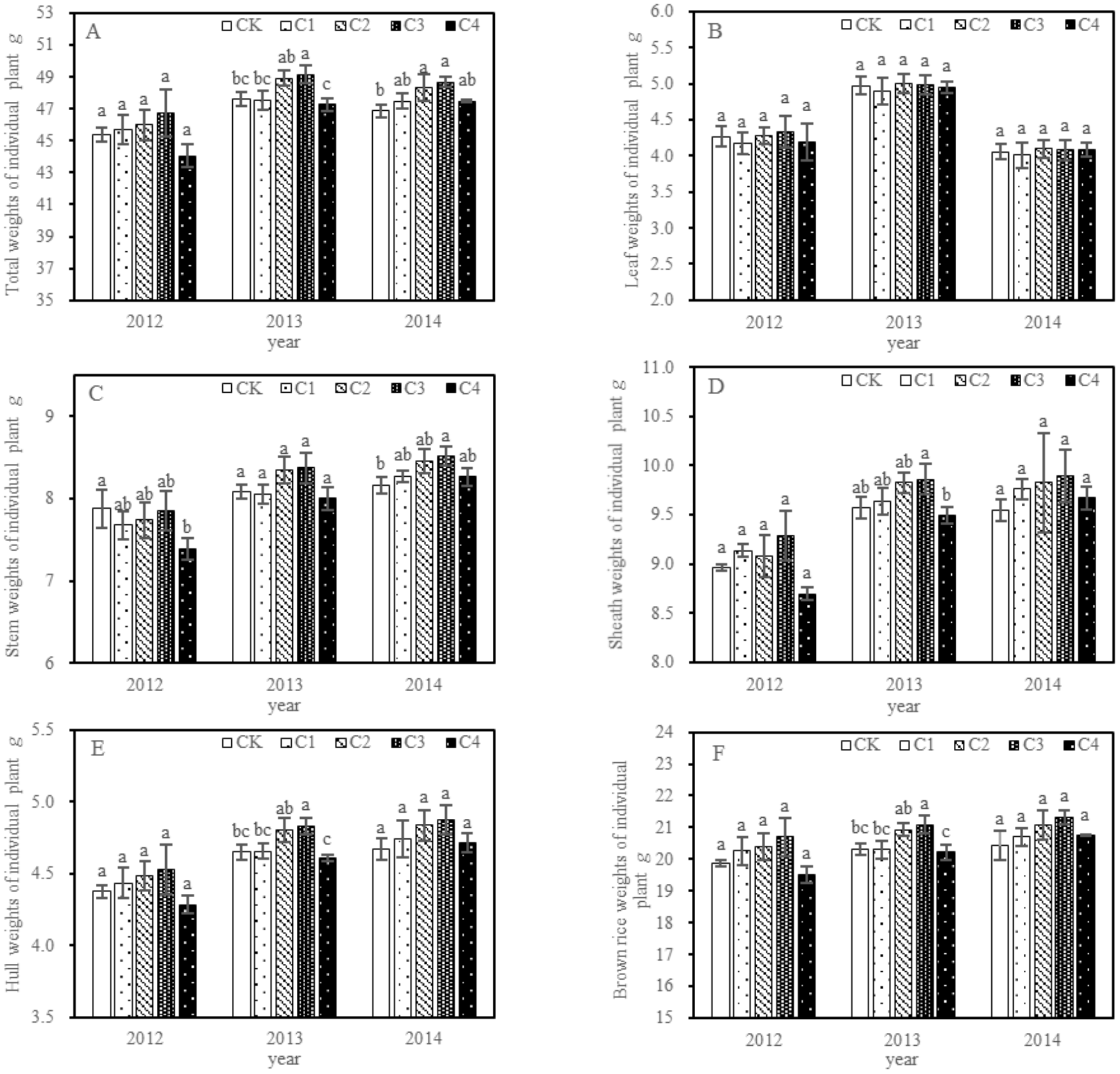


Fig. 1. Effects of biochar application rate on dry matter accumulation in (A) individual plants, (B) leaf, (C) stem, (D) sheath, (E) hull, and (F) brown rice. Different lower case letters represent significant differences between the treatments in a single year ($p \leqslant 0.05$; n=3); the same below.

In general, the total dry weights of rice increased gradually with increasing biochar application; the total dry weight of C3 was the highest, while the total dry weight of C4, as the highest amount of treatment, showed a decreasing trend. Specifically, in 2012, although the results of C1, C2, and C3 were higher than CK, and showed a gradually increasing trend, the differences were not significant. The total dry weight of C4 was lower than that of CK, but showed no significant difference either. In 2013, the trend of results was similar to 2012, but the difference between the total dry weights of C3 and CK reached significant levels; the total dry weight of C3 was significantly higher than those of C1 and C4, and the total dry weight of C2 was also significantly higher than that of C4. In 2014, the total dry weights of C2 and C3 were both significantly higher than that of CK.

Figure 1B shows the results for the leaf. The trend of results in each year showed slight fluctuations, but the results were very similar, and there was no significant difference among all treatments.

Figure 1C shows the results for the stem. In 2012, the total stem dry weight of C4 was significantly lower than that of CK. In 2013, the total dry weights of C2 and C3 were slightly higher than that of CK, the total dry weights of C1 and C4 were close to that of CK, and there was no significant difference among all treatments. In 2014, the total dry weight of C3 was significantly higher than that of CK.

Figure 1D shows the results for the sheath. In 2012 and 2014, there was no significant difference among all treatments. In 2013, the total dry weight of C4 was significantly lower than that of C3, and there were no significant differences among the other treatments.

Figure 1E shows the results for the hull. In 2013, the total dry weight of C3 was significantly higher than that of CK, and the total dry weights of C2 and C3 were significantly higher than that of C4.

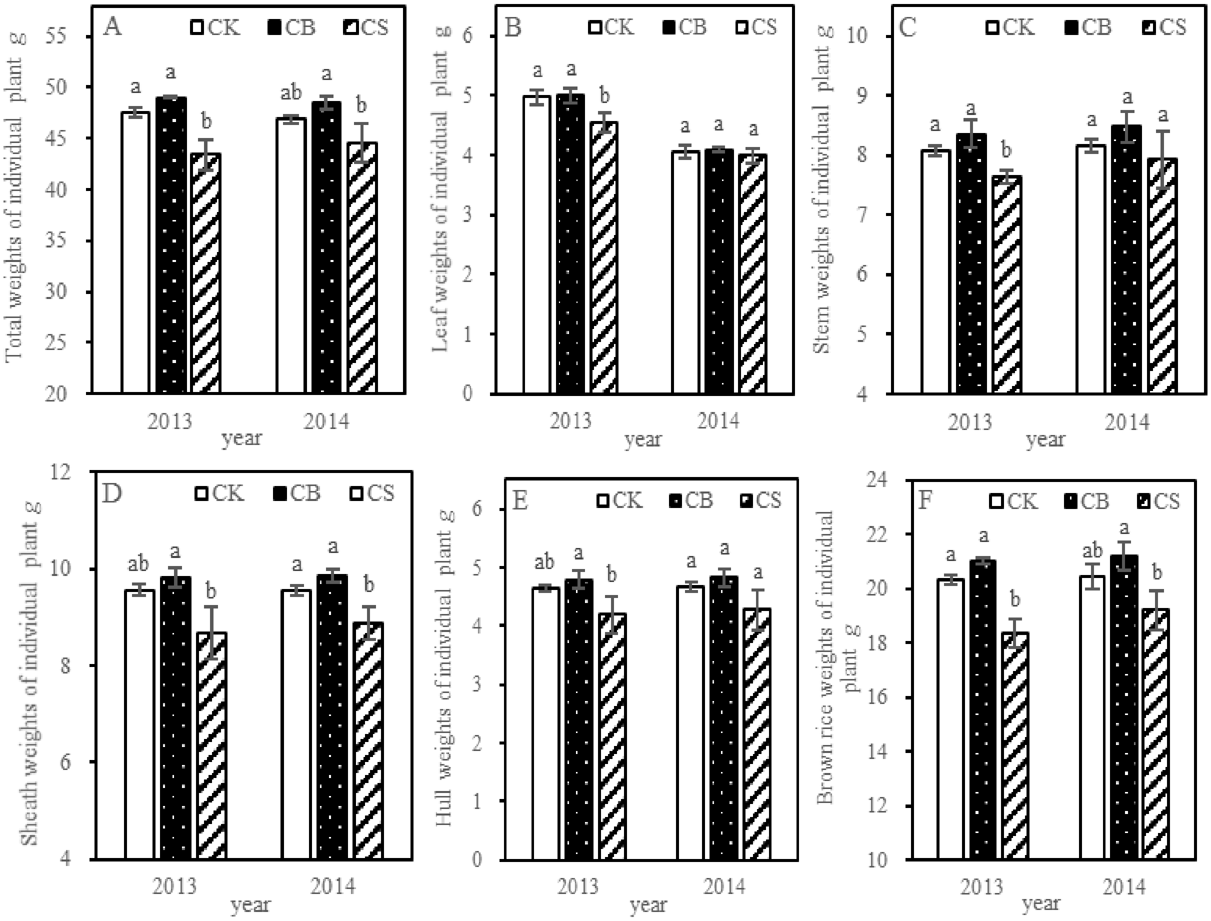


Fig. 2. Effects of various contaminated material treatments on dry matter accumulation in (A) individual plants, (B) leaf, (C) stem, (D) sheath, (E) hull, and (F) brown rice

Figure 1F shows the results for brown rice. The dry weights of brown rice increased gradually with increasing biochar application in general, but the highest amount for treatment C4 decreased. However, the difference between each treatment did not reach significance in 2012 and 2014. In 2013, the total dry weight of C3 was significantly higher than that of CK, and the total dry weights of C2 and C3 were significantly higher than that of C4; the total dry weight of C4 was the lowest, but differences with CK and C1 were not significant.

Figure 2A represents the effects of contaminated biomass material treatments on dry weight of single plant. In 2013, CK and CB were higher than CS significantly. In 2014, CB was higher than CS significantly.

Figure 2B represents the result of leaf. In 2013, CB was similar to CK, CS was the lowest, there was no significant difference between CK and CB, but they were both higher than CS significantly. In 2014, the results of three treatments were similar, and the difference between each treatment did not reach significant level.

Figure 2C represents the result of stem. In 2013, CK and CB were significantly higher than CS. In 2014, the differences among treatments were not significant.

Figure 2D is the result of sheath. In 2013, CB was higher than CS significantly. In 2014, CS was lower than CK and CB significantly.

Figure 2E represents the result of hull. In 2013, CB was significantly higher than CS. The differences among the three treatments did not reach a significant level in 2014.

Figure 2F is the result of brown rice. In 2013, CK and CB were significantly higher than CS. In 2014, CB was higher than CS significantly.

Effects of Biochar on Cd Concentration and Total Uptake of Rice

Table 2 shows the effects of biochar application rate on the Cd concentrations and Cd accumulation in rice from 2012 to 2014. Cd concentration means the Cd content in a unit weight of rice, and Cd accumulation means the total Cd content uptake by a single plant or organ of rice.

Table 3 shows the effects of contaminated biomass material treatments on the Cd contents and Cd accumulation in rice.

Table 2. Effects of Biochar Application Rate on Cd Concentration and Uptake by Rice

		Cd concentration *mg kg^{-1}*				Cd uptake *μg plant^{-1}*		
		2012	2013	2014		2012	2013	2014
Plant	CK	2.23±0.05a	2.18±0.04a	2.16±0.07a		100.98±2.09a	103.89±2.59a	101.04±2.54a
	C1	2.12±0.05ab	2.09±0.08a	2.07±0.06ab		96.84±4.03ab	99.41±5.29ab	98.35±3.09a
	C2	2.04±0.06b	2.03±0.05a	2.00±0.05bc		93.71±1.60bc	99.54±3.23ab	96.47±1.51ab
	C3	1.88±0.02b	1.88±0.02b	1.89±0.03cd		87.68±2.57c	92.30±1.84bc	91.80±1.30b
	C4	1.75±0.03c	1.76±0.05b	1.76±0.01d		76.95±0.27d	83.16±2.10c	83.44±0.44c
Leaf	CK	1.17±0.03a	1.11±0.06a	1.09±0.04a		4.99±0.10a	5.5±0.23a	4.39±0.26a
	C1	1.11±0.08ab	1.02±0.08a	1.08±0.16a		4.64±1.00ab	5.00±0.54a	4.11±0.83a
	C2	1.03±0.21ab	1.10±0.21a	1.03±0.11a		4.4±0.28ab	5.51±1.1a	3.77±0.51a
	C3	0.93±0.03ab	0.95±0.05a	0.92±0.03a		4.03±0.29ab	4.72±0.2a	3.63±0.02a
	C4	0.86±0.04b	0.92±0.04a	0.89±0.04a		3.61±0.32b	4.54±0.16a	3.64±0.25a
Stem	CK	3.22±0.1a	3.15±0.06a	3.11±0.12a		25.36±1.08a	25.4±0.68a	25.36±1.25a
	C1	3.17±0.11a	3.13±0.11a	3.01±0.08ab		24.32±0.86a	25.25±1.22a	24.91±0.47a
	C2	3.11±0.03ab	3.04±0.11ab	2.88±0.09abc		24.07±0.58a	25.35±0.96a	24.32±0.37a
	C3	2.88±0.11bc	2.87±0.05bc	2.76±0.12bc		22.62±1.4ab	24.02±0.57ab	23.47±1.13ab
	C4	2.75±0.08c	2.75±0.08c	2.62±0.07c		20.32±0.88b	21.99±0.94b	21.63±0.83b
Sheath	CK	4.11±0.10a	4.05±0.11a	4.00±0.11a		36.8±1.04a	38.71±1.38a	38.23±1.44a
	C1	3.88±0.07b	3.83±0.12ab	3.82±0.12ab		35.42±0.93a	36.95±1.05ab	37.28±0.77a
	C2	3.68±0.07bc	3.65±0.06bc	3.68±0.08bc		33.42±0.17a	35.85±0.38ab	36.15±1.64a
	C3	3.53±0.08cd	3.52±0.13c	3.54±0.07cd		32.79±0.92a	34.70±1.80bc	34.98±0.39ab
	C4	3.35±0.06d	3.34±0.10c	3.31±0.10d		29.08±0.51b	31.69±1.19c	31.98±1.08b
Hull	CK	1.19±0.03a	1.18±0.06a	1.11±0.09a		5.22±0.18a	5.47±0.32a	5.19±0.35a
	C1	1.15±0.04a	1.09±0.07ab	1.05±0.09ab		5.10±0.29a	5.09±0.31ab	4.95±0.3ab
	C2	1.11±0.06ab	1.14±0.13a	1.07±0.04ab		4.95±0.14a	5.48±0.64a	5.16±0.23a
	C3	0.95±0.07bc	0.95±0.03ab	0.97±0.08ab		4.33±0.45a	4.59±0.18ab	4.74±0.31ab
	C4	0.90±0.05c	0.90±0.07b	0.89±0.03b		3.87±0.20a	4.16±0.32b	4.21±0.17b
Brown rice	CK	1.44±0.07a	1.42±0.05a	1.36±0.07a		28.62±1.20a	28.81±1.19a	27.83±0.78a
	C1	1.35±0.09ab	1.33±0.13ab	1.3±0.09a		27.35±2.10a	27.12±3.1a	26.85±1.98a
	C2	1.32±0.10ab	1.31±0.08ab	1.26±0.08ab		26.88±1.58a	27.35±1.76a	26.63±1.41a
	C3	1.16±0.08bc	1.15±0.06bc	1.17±0.05ab		23.91±1.35ab	24.28±1.07ab	24.86±0.92ab
	C4	1.03±0.08c	1.03±0.10c	1.06±0.05b		20.07±1.29b	20.78±1.76b	21.98±1.08b

Different lower case letters represent significant differences between the treatments in a single year ($p \leqslant 0.05$; n = 3); the same below.

Table 3. Effects of Contaminated Biomass Treatment on Cd Concentration and Uptake of Rice

		Cd concentrations *mg kg^{-1}*			Cd uptake *µg plant^{-1}*	
		2013	2014		2013	2014
Plant	CK	2.18±0.04b	2.16±0.07b		103.88±2.59a	101.04±2.54a
	CS	2.19±0.06b	2.08±0.1b		107.26±3.06a	100.64±3.7a
	CB	2.47±0.08a	2.42±0.06a		107.43±3.84a	107.94±3.84a
Leaf	CK	1.11±0.06ab	1.09±0.04ab		5.5±0.23a	4.42±0.26ab
	CS	1.08±0.08b	1.01±0.03b		5.4±0.38a	4.14±0.08b
	CB	1.26±0.06a	1.15±0.04a		5.7±0.1a	4.7±0.07a
Stem	CK	3.15±0.06b	3.11±0.12a		25.4±0.68a	25.36±1.25a
	CS	3.15±0.06b	3.08±0.19a		26.36±0.53a	26.16±1.91a
	CB	3.44±0.06a	3.37±0.11a		26.25±0.42a	26.76±2.44a
Sheath	CK	4.05±0.11b	4±0.11ab		38.71±1.37a	38.23±1.44a
	CS	4.1±0.11b	3.66±0.41b		40.28±1.87a	36.11±4.35a
	CB	4.63±0.08a	4.54±0.06a		40.18±2.93a	40.29±1.03a
Hull	CK	1.17±0.06b	1.11±0.09b		5.46±0.33a	5.19±0.35a
	CS	1.2±0.11ab	1.16±0.17ab		5.74±0.46a	5.59±0.84a
	CB	1.46±0.11a	1.44±0.07a		6.09±0.14a	6.15±0.21a
Brown rice	CK	1.42±0.05ab	1.36±0.07ab		28.81±1.19a	27.83±0.78a
	CS	1.4±0.09b	1.35±0.07b		29.48±1.99a	28.63±1.06a
	CB	1.59±0.06a	1.55±0.07a		29.21±1.26a	30.04±0.78a

Effect of Biochar on Contents and Distribution of Cd Fractions in Soil

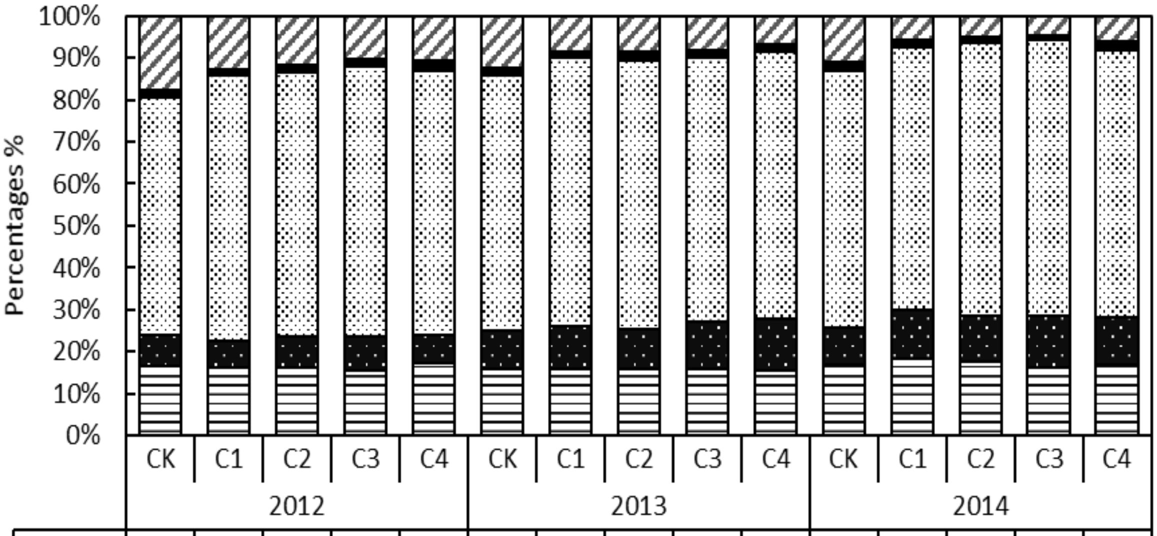
Table 4 shows the effects of biochar application rate treatments on the contents of Cd fractions in soil. Figure 3 shows the Cd contents of various fractions in soil; it is a supplementary figure with specific data to facilitate understanding of Table 4.

For exchangeable fraction, except C1 in 2012, the results of biochar applied treatments were all significantly lower than CK in three years. For carbonate bound fraction, there was no significant difference among treatments in three year. For Fe-Mn oxide bound fraction, the results of biochar applied treatments were all higher than CK in three years, however, only the difference between C3 and CK in 2014 reached significant level. For organic bound fraction, in 2012, C2 and C3 were higher than CK, and the difference of C3 reached significant level; in 2013, the results of biochar applied treatments were all higher than CK, in which C3 and C4 were significantly higher than CK; in 2014, all biochar applied treatments were significantly higher than CK. For residual fraction, there was no significant difference among treatments in three years.

Table 4. Effects of Biochar Application Rate on Contents of Cd Fractions (mg/kg)

Fraction	Treatment	2012	2013	2014
EXCH	CK	0.69±0.14 a	0.48±0.06a	0.43±0.07a
	C1	0.50±0.03ab	0.32±0.02b	0.22±0.03b
	C2	0.46±0.04 b	0.33±0.04b	0.2±0.01b
	C3	0.40±0.04 b	0.31±0.01b	0.17±0.04b
	C4	0.42±0.03 b	0.26±0.03b	0.23±0.06b
CARB	CK	0.07±0.01 a	0.07±0.03 a	0.08±0.00 a
	C1	0.06±0.00 a	0.05±0.01 a	0.06±0.01 a
	C2	0.07±0.01 a	0.08±0.03 a	0.05±0.00 a
	C3	0.07±0.01 a	0.07±0.02 a	0.05±0.00 a
	C4	0.09±0.01 a	0.06±0.03 a	0.08±0.03 a
Fe-Mn	CK	2.23±0.20 a	2.34±0.12a	2.35±0.04b
	C1	2.46±0.12 a	2.47±0.07a	2.40±0.09ab
	C2	2.44±0.11 a	2.46±0.15a	2.49±0.05ab
	C3	2.51±0.06 a	2.42±0.08a	2.53±0.07a
	C4	2.44±0.13 a	2.44±0.09a	2.44±0.04ab
OM	CK	0.28±0.01ab	0.36±0.03 b	0.35±0.04 b
	C1	0.25±0.03 b	0.4±0.01ab	0.45±0.02 a
	C2	0.29±0.02ab	0.37±0.01 b	0.42±0.01 a
	C3	0.31±0.01 a	0.44±0.01 a	0.46±0.02 a
	C4	0.27±0.02ab	0.46±0.01 a	0.44±0.01 a
RES	CK	0.65±0.13a	0.61±0.13a	0.61±0.08a
	C1	0.63±0.09a	0.61±0.06a	0.7±0.09a
	C2	0.63±0.12a	0.61±0.08a	0.68±0.06a
	C3	0.61±0.10a	0.6±0.05a	0.63±0.09a
	C4	0.67±0.08a	0.59±0.09a	0.65±0.05a

Different letters in the table denote significant difference at 0.05 level; the same below.



	2012 CK	2012 C1	2012 C2	2012 C3	2012 C4	2013 CK	2013 C1	2013 C2	2013 C3	2013 C4	2014 CK	2014 C1	2014 C2	2014 C3	2014 C4
▨ EXCH	17.6	12.7	11.7	10.3	10.7	12.5	8.38	8.65	8.16	6.70	11.0	5.86	5.12	4.50	6.04
■ CARB	1.75	1.46	1.87	1.84	2.34	1.71	1.40	2.12	1.75	1.70	2.03	1.49	1.42	1.30	2.15
░ Fe-Mn	56.7	63.1	62.7	64.3	62.7	60.7	64.1	63.7	63.0	63.9	61.0	62.5	64.8	65.8	63.4
▣ OM	7.25	6.53	7.39	7.86	6.92	9.23	10.2	9.62	11.3	12.1	9.04	11.7	11.0	12.0	11.4
⊟ RES	16.6	16.1	16.2	15.6	17.2	15.7	15.8	15.9	15.7	15.5	16.8	18.3	17.6	16.3	16.9

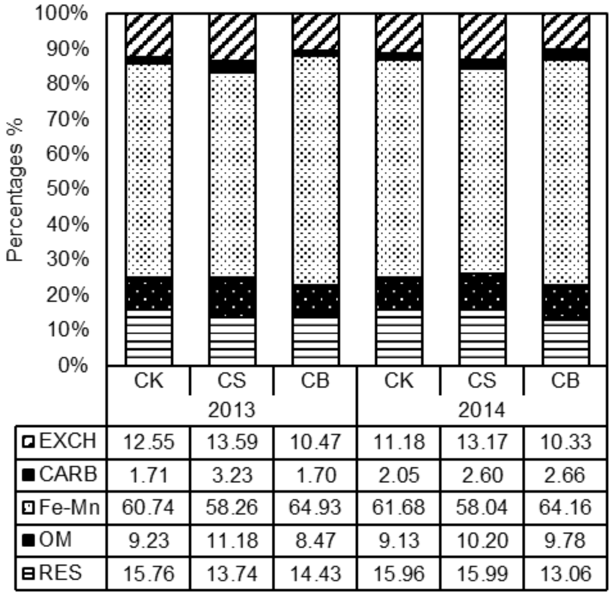
Fig. 3. Effects of biochar application rate on distribution of Cd fractions in soil

Table 5 shows the effects of contaminated biomass on Cd fractions in soil. Figure 4 is the Cd contents of various fractions in soil; it is a supplementary figure with specific data to facilitate understanding of Table 5.

For the exchangeable fraction, CS was the highest, CK was the second and CB was the lowest, but only the difference between CB and CS in 2013 reached a significant level. For carbonated bound fraction, only CS was significantly higher than CK in 2013, and there was no significant difference among other treatments. For Fe-Mn oxide bound fraction, CB was the highest, the results of CS and CK were close, and there was no significant difference among treatments in two years. For organic bound fraction, CS was the highest in two years, CB was lower than CK in 2013, while CB was higher than CK in 2014, but there was no significant difference among treatments in two years. For residual fraction, the results of treatments were close and had no significant difference.

Table 5. Effects of Contaminated Biomass Materials on Contents of Cd Fractions (mg/kg)

			2013		2014
EXCH	CK		0.48±0.06ab		0.42±0.07a
	CS		0.54±0.05a		0.51±0.06a
	CB		0.41±0.02b		0.4±0.05a
CARB	CK		0.07±0.03b		0.08±0a
	CS		0.13±0.04a		0.1±0.02a
	CB		0.07±0.02ab		0.1±0a
Fe-Mn	CK		2.34±0.12a		2.32±0.04a
	CS		2.30±0.05a		2.27±0.07a
	CB		2.53±0.10a		2.48±0.14a
OM	CK		0.36±0.03a		0.34±0.04a
	CS		0.44±0.07a		0.4±0.02a
	CB		0.33±0.04a		0.38±0.04a
RES	CK		0.61±0.13a		0.6±0.08a
	CS		0.54±0.06a		0.62±0.06a
	CB		0.56±0.06a		0.50±0.10a



	CK 2013	CS 2013	CB 2013	CK 2014	CS 2014	CB 2014
▨ EXCH	12.55	13.59	10.47	11.18	13.17	10.33
■ CARB	1.71	3.23	1.70	2.05	2.60	2.66
░ Fe-Mn	60.74	58.26	64.93	61.68	58.04	64.16
■ OM	9.23	11.18	8.47	9.13	10.20	9.78
▤ RES	15.76	13.74	14.43	15.96	15.99	13.06

Fig. 4. Effects of contaminated biomass treatments on distribution of Cd fractions in soil

DISCUSSION

Changes in Dry Matter Accumulation in Rice, Cd Uptake by Rice, and Cd Fractions in Soil

The total dry weight of rice increased gradually with increasing biochar application; this result is similar to Liu *et al*. (2016b). Their study suggested that the application of rice straw biochar can enhance soil properties, improve rice yield, and improve crop nutrient uptake in paddy soils. However, in this study, the highest biochar application treatment decreased the total dry weight of rice (Fig. 1). This result suggested that the dry matter accumulation of rice could not always be promoted by increasing biochar application; this may be due to the fact that biochar application had a negative impact on the uptake of soil nutrients by rice (Peng *et al*. 2007; Qiao *et al*. 2013; Ye *et al*. 2013).

Suitable soil pH is necessary for rice growth (Figueiredo *et al*. 2015; Minasny *et al*. 2016); we measured the pH of soil samples from three years (Fig. 5) and found that the biochar application increased soil pH effectively, while the increase in soil pH by biochar could affect the supply of soil nutrients to plants indirectly (Liu *et al*. 2016b). Xu *et al.* (2016) indicated that biochar amendments may decrease the availability of nutrients other than metals, which could result in plant deficiency. Thus, we suggest that excessively high biochar application inhibited the growth of rice because of the high pH and adsorption capacity of biochar.

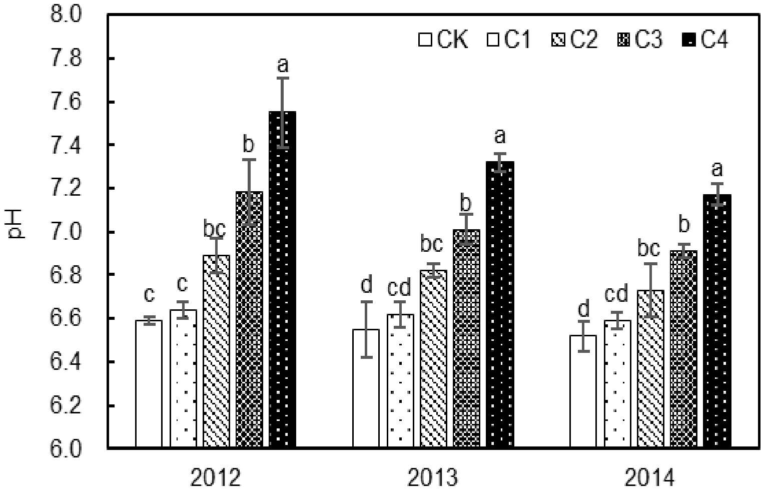


Fig. 5. Effects of biochar application rate on pH of soil

The rice Cd uptake decreased gradually with increasing biochar application. This result is similar to that of Bian *et al*. (2013), who indicated that biochar effectively immobilized Cd and greatly reduced rice Cd uptake in long-term contaminated rice paddies; biochar amendment at 40 t ha^{-1} could even allow rice Cd levels to meet the guideline limit of 0.4 mg/kg suggested by the CAC (Codex Alimentarius Commission), FAO (Food and Agriculture Organization of the United Nations), and WHO (World Health Organization) (2005).

In this study, carbonate-bound fractions and residual fractions were changed slightly by biochar application. The residual fraction is a fraction that may be held by crystal structure, and this fraction is not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Tessier *et al*.

1979), so it is believed to be the most stable fraction in soil (Huang *et al*. 2012; Quan *et al*. 2014; Lee *et al*. 2015). The variation tendency of the Fe-Mn oxide bound fraction is increasing, and part of the results in the final year reached significance (Table 4). In the Fe-Mn oxide fraction, it is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as coatings on particles, and these oxides are excellent scavengers for heavy metals and are thermodynamically unstable under anoxic conditions (Tessier *et al*. 1979). The exchangeable fractions of biochar treatments were all significantly lower than that of CK (Table 4); this reflected the ability of biochar to adsorb and retain heavy metal cations in soil (Beesley *et al*. 2015). It is noteworthy that there were no significant differences among biochar treatments. One possible reason is rice cultivation; the soil samples were collected after the rice harvest. The rice uptake and root exudates can both affect the Cd content of the exchangeable fraction in soil during the whole growth season, which may reflect the fact that the exchangeable Cd content in soil cannot completely indicate the rice Cd uptake. Cd may be bound to various forms of organic matter (Tessier *et al*. 1979). The Cd content of the organic bound fraction increased gradually during the three years of the study (Table 4), reflecting the long-term stability of the strong specific adsorption of biochar.

Reasonable Amount of Biochar Application

There is more than one way to evaluate a reasonable biochar application rate (Janoš *et al*. 2010; Yang *et al*. 2012; Mahar *et al.* 2015, 2016) for remediation of Cd-contaminated paddy soil. In this study, we evaluated the suitable application rate from three points of view: the first is Cd accumulation in rice, the second is dry matter accumulation in rice, and the third is Cd fractions in soil. We suggest that these three points have certain reference values; the first consideration is whether the biochar application rate can reduce the Cd accumulation in rice effectively, because no matter what soil amendments are used, reduced plant uptake of heavy metals is the ultimate objective (Chen *et al*. 2014; Yang *et al*. 2014), and it is also an important indicator to verify whether the amendment works (Hashim *et al*. 2011; Yao *et al*. 2012; Venegas *et al*. 2016). The second consideration is dry matter accumulation in rice, dry matter accumulation is related to the growth and development of rice, and we suggest that a suitable application rate should ensure good growth and development of rice, which proves that the amendment can alleviate the toxicity of heavy metals and also show that the amendment itself has no significant inhibitory effect on plant growth. In addition, in China, rice is an important food crop (Che *et al*. 2015), and farmland is very scarce (Zhang *et al*. 2015; Liang *et al*. 2015). Even though the rice fields are slightly polluted, agricultural production is still being carried out (Hu *et al*. 2016); therefore, the guarantee of rice growth by the amendment can achieve better ecological, social, and economic benefits. Finally, the changes in the Cd fractions in soil, and the harm of Cd to plants, does not depend on the total amount, but the content of the available part in soil (Lee *et al*. 2015), so a reasonable application rate of biochar should be able to not only reduce available Cd content, but also ensure the stability of total Cd in soil (Beesley *et al*. 2011). We suggest that evaluation of Cd fractions in soil could achieve this objective.

From the perspective of Cd accumulation in rice, for the purposes of this study, we suggest that higher biochar application rates are better for reducing Cd accumulation in rice. As shown in Table 2, almost all the results of the Cd contents and accumulations in rice were gradually reduced with increasing biochar application: 2% and 4%

applications could more effectively reduce the Cd content and accumulation in rice compared with CK, especially the 4%.

With respect to dry matter accumulation in rice, this study suggests that 0.5% application of biochar affected rice dry matter accumulation weakly, 1% to 2% application of biochar was suitable for increasing dry matter accumulation, and 4% application of biochar inhibited accumulation slightly. Specifically, the results of 0.5% application were all similar to CK, and the changes were weak and showed no significant difference; the results for 1% and 2% were above CK in general, and part of the differences reached significant levels (for instance, the total dry weight of 2% application in 2013). Although 4% showed some inhibitory effect, the gap between it and CK was very small, and only the dry weight of the stem in 2012 and total dry weight in 2013 were significantly lower than those in CK.

Regarding the Cd fractions in soil, as mentioned above (Fig. 3 and Table 4), biochar application could reduce the exchangeable fraction, increase the Fe-Mn oxide and organic bound fractions, and affect the carbonate bound and residual fractions weakly. However, the changes in these fractions did not have a set trend with respect to the increase in biochar application, and there were no significant differences among biochar applications. Therefore, we suggest that 0.5% to 4% application rates are all reasonable for reducing available Cd content and ensuring the stability of whole Cd in soil.

In summary, taking the intersection of these three suitable ranges, we suggest that 2% to 4% applications of biochar are reasonable rates for remediation of Cd contaminated paddy soil. The 2% application, under the premise of a guarantee of both reducing Cd uptake by rice and positive changes in the Cd fractions in soil, is more conducive to dry matter accumulation, and 4% application can achieve better effects of reducing Cd accumulation in rice and stabilizing the Cd fractions in soil, while slightly inhibiting rice dry matter accumulation.

Evaluation of the Utilization of Cd Contaminated Biomass Materials

Similar to the evaluation of a reasonable biochar application rate, we evaluate the utilization of Cd-contaminated biomass materials from the same three viewpoints.

For the dry matter accumulation, the result of contaminated biochar was higher than CK, but the difference did not reach significant levels, while contaminated straw reduced dry matter accumulation in rice significantly in the main. Visibly, contaminated biochar has the potential to promote the dry matter accumulation of rice (Nzihou and Stanmore 2013), and contaminated straw has an inhibitory effect on dry matter accumulation of rice.

For Cd uptake by rice, contaminated straw increased the Cd content in rice significantly; we suggest that this is due to the additional Cd brought by contaminated straw returning, and we also think that contaminated straw inhibited rice dry matter accumulation, hence the total Cd accumulation amounts did not increase significantly. Contaminated biochar has no significant effects on Cd contents and accumulation in rice.

The effects of contaminated biomass materials on Cd fractions are focused on the exchangeable Cd fraction. In 2013, contaminated biochar reduced the exchangeable fraction significantly compared with contaminated straw; in 2014, this difference did not reach a significant level. This condition has been mentioned above, and there are some different changing trends between the results in rice Cd uptake and Cd fractions in soil; here, we also suggest the effects of rice growth.

In general, the performances of contaminated biochar are better than straw as both soil amendments. That is to say, pyrolysis is a potential way to deal with contaminated farm residuals. The ultimate goal is to use contaminated biochar as an ideal amendment to reduce the bioavailability of Cd in the soil and ensure or promote crop production. However, the results of this experiment were promising but not optimal. Biochar properties should be modified through some creative ways either before, during, or after a pyrolysis process, and such materials can be applied to other crops, in order to achieve better results.

Deficiencies of this Study and Suggestions for Future Research

In this article, we primarily studied the effects of biochar on Cd fractions in soil and Cd accumulation in rice, and through the analysis of the above data, we attempted to analyze a reasonable biochar application rate, which could not only ensure rice growth, but also remedy the Cd-contaminated soil. Although we have tried to make a detailed analysis, we recommend using these results as reference under certain conditions, as only one kind of biochar and one kind of soil were used in this study, and it was a pot experiment. The test results could be complicated by the variety of soil, biochar, environment, *etc*. (Jeffery *et al*. 2011; Omondi *et al*. 2016), and under the same test conditions, the results for a pot experiment and field experiment may vary (Friesl *et al*. 2006). In future studies, we propose that a wide variety of representative biochar and soils should be used, meaning the results would have better guiding significance.

This is only a preliminary and exploratory study on whether or not Cd-contaminated biomass materials can be used in the field after pyrolysis. This part of the research is related to the utilization of contaminated materials (Sas-Nowosielska *et al*. 2004; Chen *et al*. 2012; Šyc *et al*. 2012) and the evaluation of biochar environmental safety (Stals *et al*. 2010; Fletcher *et al*. 2014; Břendová *et al*. 2015). Therefore, in future studies, we suggest that more contaminated bioresources should be used, the process of preparing biochar from contaminated biomass materials should be studied and optimized, the stability of heavy metals in contaminated materials should be evaluated, and reasonable application rates should be set and discussed.

CONCLUSIONS

1. Biochar application reduced the bioavailability of Cd in soil, primarily through reducing the exchangeable fraction and increasing the organic bound fraction.
2. Biochar application reduced the Cd accumulation in rice, and the dry matter accumulation in rice did not always increase with increasing biochar application rate; 2% to 4% was determined to be a suitable application rate for biochar.
3. Contaminated biochar reduced the Cd content of individual rice plants and ensured the normal growth of rice, but had little influence on the Cd fractions in soil.

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