Earth Surface Processes and Environmental Sustainability in China

Long-term effects of biochar on rice production and stabilisation of cadmium and arsenic levels in contaminated paddy soils

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ABSTRACT: Heavy metal contamination in the paddy soils of China is a serious concern because of its health risk through transfer in food chains. A field experiment was conducted in 2014–2015 to investigate the long-term effects of different biochar amendments on cadmium (Cd) and arsenic (As) immobilisation in a contaminated paddy field in southern China. Two types of biochar, a rice-straw-derived biochar (RB) and a coconut-by-product-derived biochar (CB), were amended separately to determine their impacts on rice yield and their efficacy in reducing Cd and As in rice. The two-year field experiment showed that biochar amendments significantly improved the rice yields and that CB is superior to RB, especially in the first growth season. Using a large amount of biochar amendment (22.5 t ha^{-1}) significantly increased soil pH and total organic carbon, and concomitantly decreased the Cd content in rice grains over the four growth seasons, regardless of biochar type and application rate. Arsenic levels in rice were similar to the control, and results from this study suggest that there was a sustainable effect of biochar on Cd sequestration in soil and reduction of Cd accumulation in rice for at least two years. Biochar amendment in soil could be considered as a sustainable, reliable and cost-effective option to remediate heavy metal contamination in paddy fields for long periods.

KEY WORDS: dissolved organic matter, immobilisation, pH value, remediation, total organic carbon.

Toxic elements such as cadmium (Cd) and arsenic (As) often co-contaminate paddy soils (Wang *et al.* 2016) and pose a risk to human health through the soil–plant–food chain. Rice (*Oryza sativa* L.) is the world's dominant staple food, especially in some Asian countries like China (Sun *et al.* 2012). A large area of Chinese paddy soil has been contaminated with heavy metals, especially in Southern China, due to mining and/or irrigation with polluted water (Williams *et al.* 2009). Human exposure to As and Cd through daily rice consumption has been of great concern due to rice grown in heavy metal contaminated fields (Williams *et al.* 2009; Sun *et al.* 2012).

In comparison with other remediation methods such as chemical washing (Abumaizar & Smith 1999; Makino *et al.* 2007), the *in-situ* immobilisation of heavy metals in contaminated arable fields is an effective and cost-effective remediation technology (Beesley & Marmiroli 2011), especially for large areas of contaminated agricultural land (Bian *et al.* 2014; Zheng *et al.* 2015; Li *et al.* 2016). Biochar has been proved to be particularly effective for the sequestration of heavy metals in soils and their accumulation in edible parts of plants (Zheng *et al.* 2012, 2013; Khan *et al.* 2014). However, the long-term effects of different biochars on the immobilisation of different heavy metals in fields have not been well studied (Cui *et al.* 2011; Bian *et al.* 2014; Li *et al.* 2016). Wheat-straw-derived biochar reduced the Cd content in rice plant tissues (Cui *et al.* 2011; Bian *et al.* 2014) and the lead (Pb) content in plant roots in a three-year field experiment (Bian *et al.* 2014). The three-year pot-culture experiment showed that hardwood-derived biochar substantially reduced the concentration of Cd and copper (Cu) in rice tissues in the first year, whereas these values increased in the following two years. Corn-straw-derived biochar decreased these values steadily year by year (Li *et al.* 2016). A field experiment is necessary to confirm the effects of different biochars on heavy metal immobilisation for a long period, especially in paddy fields with many contaminants.

In this study, two biochars (rice-straw-derived biochar (RB) and a coconut-by-product-derived biochar (CB)) were chosen to investigate their capacities for reducing Cd and As

concentrations in rice. The aims of the present study were to: (1) research the effect of biochars in reducing Cd and As concentrations in rice over two years (four growth seasons); and (2) determine the effects of two biochars in reducing Cd and As concentrations using different amendment rates.

1. Materials and methods

1.1. Experiment site and rice
A two-year field experiment was conducted in the spring of 2014 at Beiyue village, Shaoguan, Guangdong Province, S China, where the cropping regime is dominated by the double rice-cropping systems. Early and late rice were both grown in the same field each growth season (early rice from early April to July and late rice from July to late October). Most paddy fields at Beiyue village had been contaminated with heavy metals (especially Cd). The average concentrations of Cd and As were 0.42 ± 0.06 and $35.4 \pm 1.2 \, mg \, kg^{-1}$, respectively, which can be considered as slight pollution based on the Chinese environmental quality standards for soils (GB15618–1995, Grade II). The pH value was 4.76 ± 0.2. A local eugenic rice cultivar (*Oryza sativa* L.), was chosen for the early (spring) and late (summer) rice cropping in the experiment.

1.2. Experiment treatments
In this two-year field experiment, a randomised block experiment with three replicates was established, with four different levels of biochar treatments (2.25, 6.75, 11.25, 22.5 t ha^{-1}). No biochar application was set as a control. Each field plot was $4.0 \times 5.0 \, m^2$.

To understand the role of biochar type on heavy metal stabilisation, two types of biochar – RB and CB – were purchased from Qinfeng Straw Technology Co. Ltd., Nanjing, and utilised in the experiment for their sequestration of Cd and As in soils.

Applied basal fertilisers in each season were urea for nitrogen (N) ($225 \, kg \, ha^{-1}$), calcium superphosphate for phosphous (P) ($225 \, kg \, ha^{-1}$), and potassium chloride for kalium (K) ($150 \, kg \, ha^{-1}$). The basal fertiliser, together with biochar, were applied two days before rice transplanting in the early season of 2014 (first growth season), and was well incorporated into the soil by manual ploughing to a depth of 10–20 cm. In the following three growth seasons the biochar treatments were ploughed by machine. The basal fertiliser was applied but no biochar was amended.

1.3. Sample preparation
The early and late rice-cropping seasons were from early April (planted) to July (harvested) and from July (planted) to October (harvested), respectively. Three grains of rice were randomly collected from each plot during harvesting. These were air-dried in the laboratory until constant weight was reached. The grain was dehulled in a motorised dehusker (JLGJ4.5, TZYQ, Zhejiang, China), and the resultant brown rice was milled to fine powder using a blender (Langjia, China). GBW 07602 (GSV-1) rice flour was used as the standard reference material (SRM) for the rice samples. The recoveries of Cd and As from rice grains were 104–121 % and 106–118 %, respectively. The recoveries of Cd and As in soil were 115 % and 103 %, respectively.

1.4. Digestion and analysis
The digestion procedure for all rice samples followed the method of Sun *et al.* (2010). Subsamples of rice powder (0.2 g) were weighed into pre-acid-washed 50 mL polyethylene centri-

fuge tubes with HNO$_3$ (2 mL) added, and then the tubes were kept overnight at room temperature ($\sim 25 \, °C$). Three SRM samples of rice flour (GSV-1) and three blanks were prepared simultaneously for quality control. All samples were microwave-digested (MARS, Matthew Inc., USA) using the same temperature program (Sun *et al.* 2010). The temperature was increased to 55 °C within 5 min and maintained for 10 min, then increased to 75 °C within 5 min and maintained for 10 min, and finally increased to 95 °C within 5 min and maintained for 30 min. After digestion, the samples were cooled and then diluted to 50 mL with Millipore ultrapure water (Millipore Milli-Q).

The samples were analysed for total Cd and As concentrations using inductively coupled plasma mass spectrometry (ICP-MS, 7500, Agilent Technologies). Cd isotopes Cd^{111} and Cd^{114}, as well as indium (In) as an internal standard, were measured simultaneously. All samples were randomised prior to analysis.

1.5. The pH value and dissolved organic matter (DOC) in soil and biochar
Soil pH was measured following Wang *et al.* (2016). Soil samples (2 g) and Millipore ultrapure water (5 mL) were mixed in a 10 mL centrifuge tube. After agitation (150 rpm) at room temperature for 20 min, tubes were left to stand for 30 min. The pH was tested using a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). Biochar pH was measured with the modified method (GB/T 12496.7-1999). Biochar samples (0.25 g) were weighed into a 10 mL centrifuge tube, added to carbon dioxide-free water (5 mL) and kept for half an hour. The supernatant was obtained by filtering the mixture and tested with the pH meter. The pH for RB and CB were 9.3 ± 0.1 and 10.4 ± 0.1, respectively.

A total of 4 g of soil was weighed into acid pre-washed 50 mL polypropylene centrifuge tubes and 20 mL of extracting solution was added (1:5 weight/volume ratio). All tubes were shaken for 15 min at 200 rpm at 20 °C, the soil suspensions were then centrifuged for 10 min at 7900 *g* at a temperature of 20 °C. Supernatants were filtered through a 0.45 μm filter, and DOC was determined using a total organic carbon (TOC) analyser (Liquic TOC, Elementar, Germany). The contents of organic matter for RB and CB were 22.1 % and 38.6 %, respectively.

1.6. Statistical analysis and quality control
All statistical analyses were conducted using SPSS 17.0 software. One-way analysis of variance (ANOVA) was used to identify significant differences ($P < 0.05$) between Cd or As concentrations.

2. Results and discussion

2.1. Rice yields
No significant differences in grain yields were observed between different biochar amendments and their dosages (Fig. 1). The average grain yields among different amendment levels were calculated, and a weak but significant increase in the rice grain yields was observed in the presence of CB compared to the corresponding control ($P < 0.05$) for all four growth seasons (Table 1). The amendment with RB increased the average rice yield as well, but not significantly (Table 1). The greatest improvement in rice yield was exhibited in the first growth season: up to 10.3–16.1 % higher than that in other seasons (2.1–5.6 %) (Table 1). The nutrients from amended biochars were probably utilised at the first growth season and fewer nutrients were
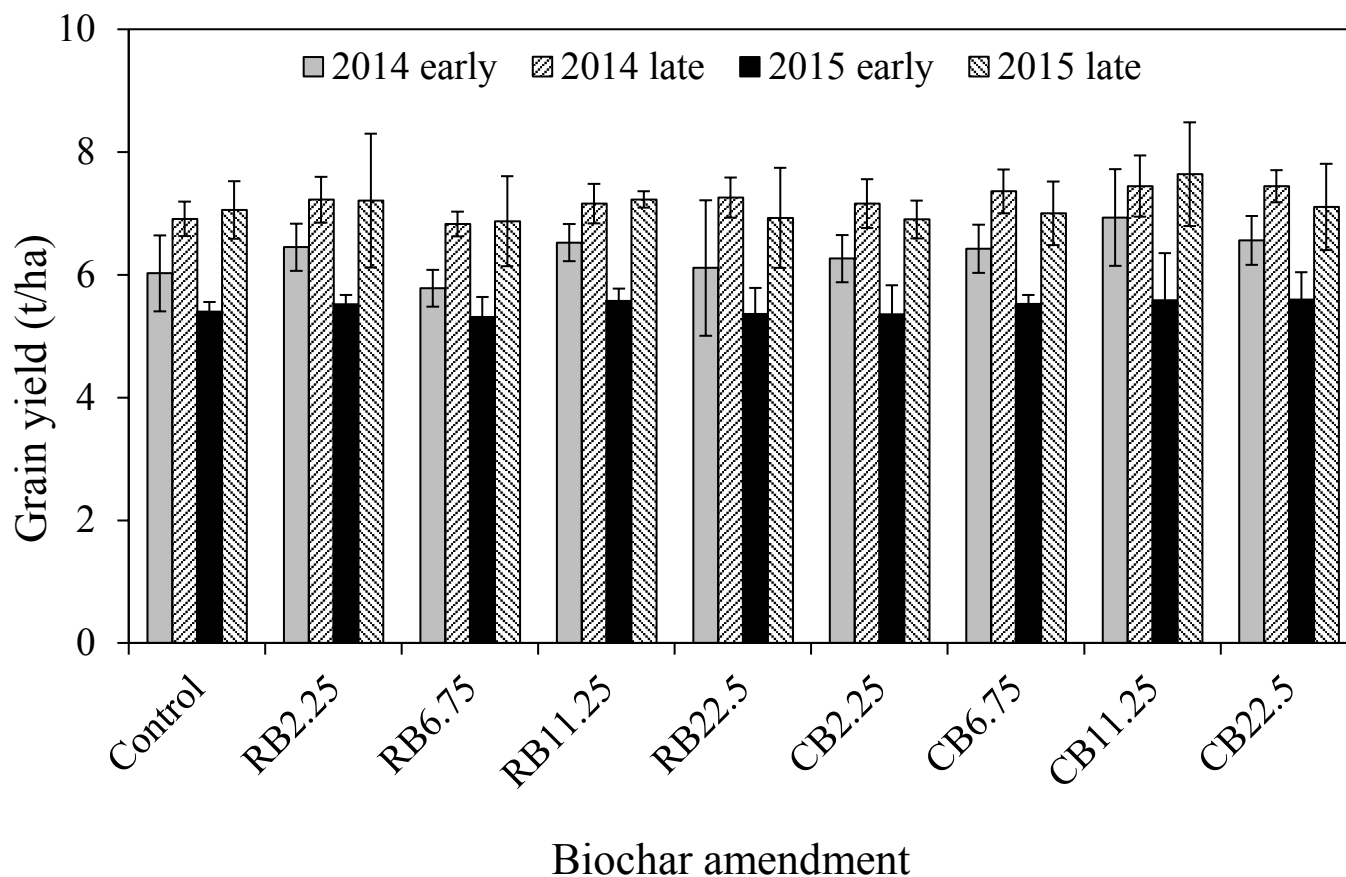
Figure 1 Grain yields of rice with amendments of RB and CB in contaminated paddy soil, respectively, at various levels of biochar treatments (2.25, 6.75, 11.25, 22.5 t ha^{-1}).

Table 1 The average grain yields (t ha^{-1}) for the amendment of different biochars and the percentage (%) for increased average rice yield.

|	**2014 early**	**2014 late**	**2015 early**	**2015 late**
Control (t ha^{-1})	5.64 ± 0.62a	6.97 ± 0.28a	5.22 ± 0.16a	6.77 ± 0.47a
Average RB (t ha^{-1})	6.22 ± 0.34ab	7.12 ± 0.20ab	5.44 ± 0.12ab	7.06 ± 0.19ab
Average CB (t ha^{-1})	6.55 ± 0.29a	7.35 ± 0.13b	5.52 ± 0.11b	7.16 ± 0.33b
Average RB (%)	10.3	2.1	4.2	4.1
Average CB (%)	16.1	5.4	5.6	5.4

derived from biochars in the following ones. It has been reported that some biochars derived from various feedstock could improve rice yield. For example, the addition of sewage-sludge-derived biochar significantly increased grain yield in a pot experiment (Khan *et al.* 2014) and rice yield was enhanced under the treatment of wheat straw biochar in a one-year field experiment (Zhang *et al.* 2012). Some studies have shown that there was no mean effect on rice yield with biochar amendments from wheat straw (Bian *et al.* 2013; Huang *et al.* 2013), although some nutrient levels had been substantially improved (Utomo *et al.* 2011). Many factors can affect the improvement of plant growth, such as nutrients, pH, cation exchange capacity (CEC) of biochar, the biochar amount amended, soil properties and decreased accumulation of toxic metals. It is likely that more nutrients were contained in CB than RB because the large silicon content (20%) contained in rice husks causes less nutrients in this biochar (Kumar *et al.* 2013).

During the two-year experiment, the crop yields in the late season (summer season) were always greater than those in the corresponding early season (spring season), regardless of biochar addition (Fig. 1; Table 1), although the growth period

of early rice was longer (110 days) than that of late rice (100 days). It was reported that average temperature and rainfall were the main climatic factors influencing rice yield, and the seasonal average maximum temperature adversely affected rice yield for the two growing seasons (Chung *et al.* 2015), having a strong influence on rice yield from the flowering stage to the full-ripe stage (about 30 days). During this period the local average maximum temperature for early rice was 32 °C and higher than that for late rice (28 °C). Perhaps this is one of the reasons for a higher rice yield from late rice.

2.2. Cd and As concentrations

The average Cd content in rice samples of the control was 0.39–0.49 mg kg^{-1} in all four seasons, which markedly exceeded the national food standard limit of 0.2 mg kg^{-1} Cd for rice in China (GB2762-2012). The Cd concentration in rice grain was significantly reduced by amending biochar in the soil, regardless of the biochar types, compared with the corresponding control for the two years (Fig. 2; Table 2). However, the decreases of Cd in rice were not related to the amount of biochar amendments. For example, the addition of biochar at
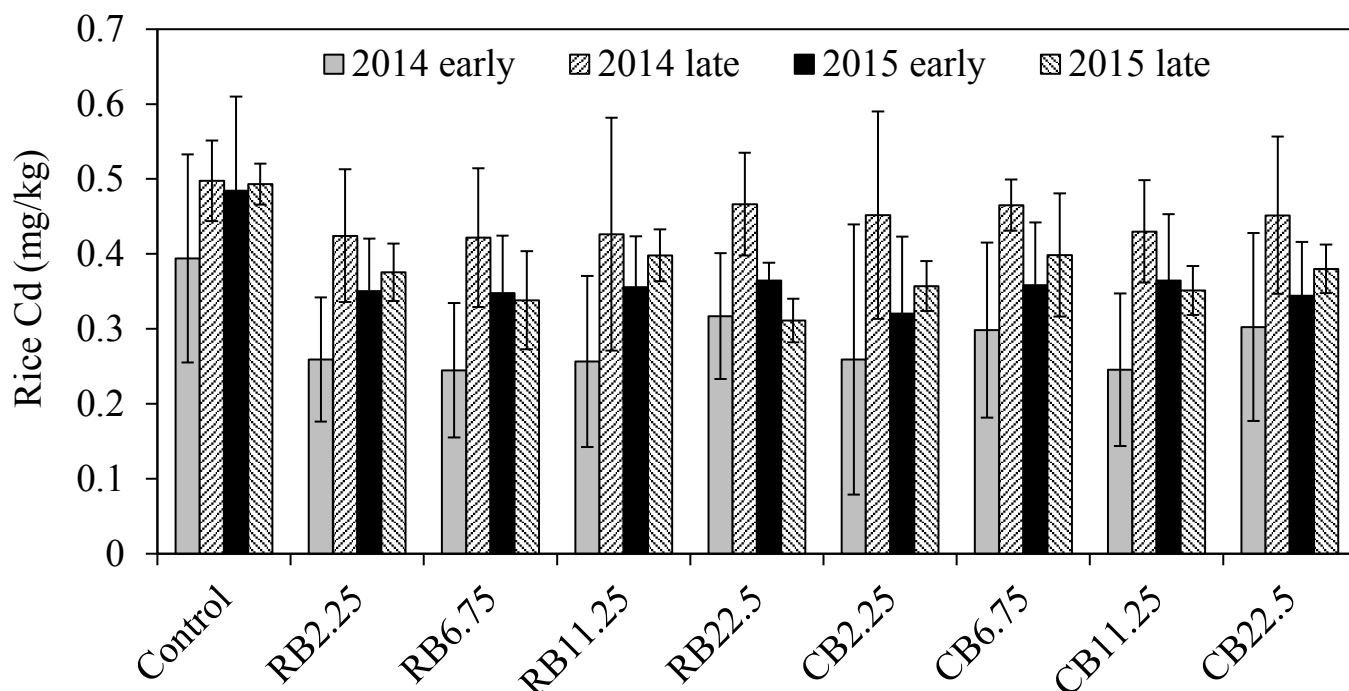
Figure 2 The concentrations of rice Cd with the addition of RB and CB in contaminated paddy soil, respectively, at various levels of biochar treatments (2.25, 6.75, 11.25, 22.5 t ha^{-1}).

Table 2 The Cd removal (%) in rice grain in the paddy field with the amendment of different biochars at various dosages.

|	2014 early	2014 late	2015 early	2015 late
Control	–	–	–	–
RB2.25	34.2	14.7	27.7	23.9
RB6.75	37.8	15.2	28.2	31.4
RB11.25	34.9	14.3	26.5	19.3
RB22.5	19.5	6.2	24.7	36.9
CB2.25	34.2	9.2	33.8	27.6
CB6.75	24.3	6.5	26.0	19.2
CB11.25	37.7	13.6	24.8	28.8
CB22.5	23.2	9.2	28.9	22.9
Average RB	31.6	12.6	26.8	27.9
Average CB	29.9	9.6	28.4	24.6

2.25 t ha^{-1} has a similar effect on Cd reduction in rice with the addition of 22.5 t ha^{-1} (Fig. 2; Table 2), even for the long-term growth season (2015 late season). No difference was observed in reducing Cd in rice with different biochars and different dosages. The long term effects of the two biochars were similar on Cd immobilisation over the two years (Table 2). A smaller removal of Cd was observed in the second season (2014 late rice), up to 9.6–11.1 % of the control (Table 2), and the reasons for this are unclear. In other growing seasons with biochar amendments, rice Cd concentration was reduced by 24.6–31.6 % in two years of the experiment, indicating the long-term effect of biochars on the sequestration of Cd in paddy soils.

The biochar had no effect in mitigating As in rice (Fig. 3), as reported previously (Zheng *et al.* 2012, 2015). Most concentrations of As in rice with biochar treatments were similar or slightly greater than the controls, although no significant difference was observed (Fig. 3). Similar As levels in rice during the four growth seasons after biochar application suggested that biochar amendment did not release As or increase As accumulation in the long-term experiment.

2.3. pH and DOC in soil

The soil pH in the control treatment remained unchanged throughout the experiment (Table 3). The biochar-amended soil showed no significant difference with control after two years of the experiment. Large amounts of biochar (22.5 t ha^{-1}) substantially increased soil pH from 4.76 to 4.83 in RB and to 5.05 in CB at the first growth season ($P < 0.05$) (Table 3); this is probably due to the higher pH for CB (10.37) than that for RB (9.30), reflecting the alkaline nature of the biochar. There was little change in soil pH during the four growth seasons. This result is supported by other reports, which evidence the increase of pH with the addition of biochar to paddy soil (Cui *et al.* 2011; Li *et al.* 2016). Base cations in biomass were transformed into oxides, hydroxides or carbonates in the biochar during pyrolysis at high temperature (Yuan *et al.* 2011). The dissolution of these alkaline substances in biochars improved the soil pH (Houben *et al.* 2013). With the increase in soil pH, the hydrolysis of metal cations such as Cd^{2+} promoted precipitates of metal(oxy)hydroxide forms. The enhancement of soil pH facilitated the immobilisation of Cd in soil. However, As existed as a hydro anion in an aquatic environment. The enhancement of pH decreased the number of positively charged sites on soil minerals, which lowered the sorption capacity of negatively charged oxyanions of As and increased As mobilisation and release from soil (Wilson *et al.* 2010). Phosphorus and silicon released from biochar competed with As for binding sites at iron oxide surfaces in soils to improve As solubility in pore water (Jain & Loeppert 2000; Waltham & Eick 2002; Zheng *et al.* 2012).

The concentrations of DOC in late rice fields were greater than those in corresponding early rice fields. The roots were left in the field after the early harvest and ploughed directly into the soil. After a week, the late rice was transplanted and the roots were left to decompose during summer growth (Huang *et al.* 2012). This suggests that the enhanced DOC was derived from root decomposition. The contents of DOC were not significantly changed in the soil treated with different amounts of RB ($P > 0.05$). The DOC in CB-treated soil decreased with the increase in CB amendments (Table 4). There was a positive relationship between Cd concentrations in rice
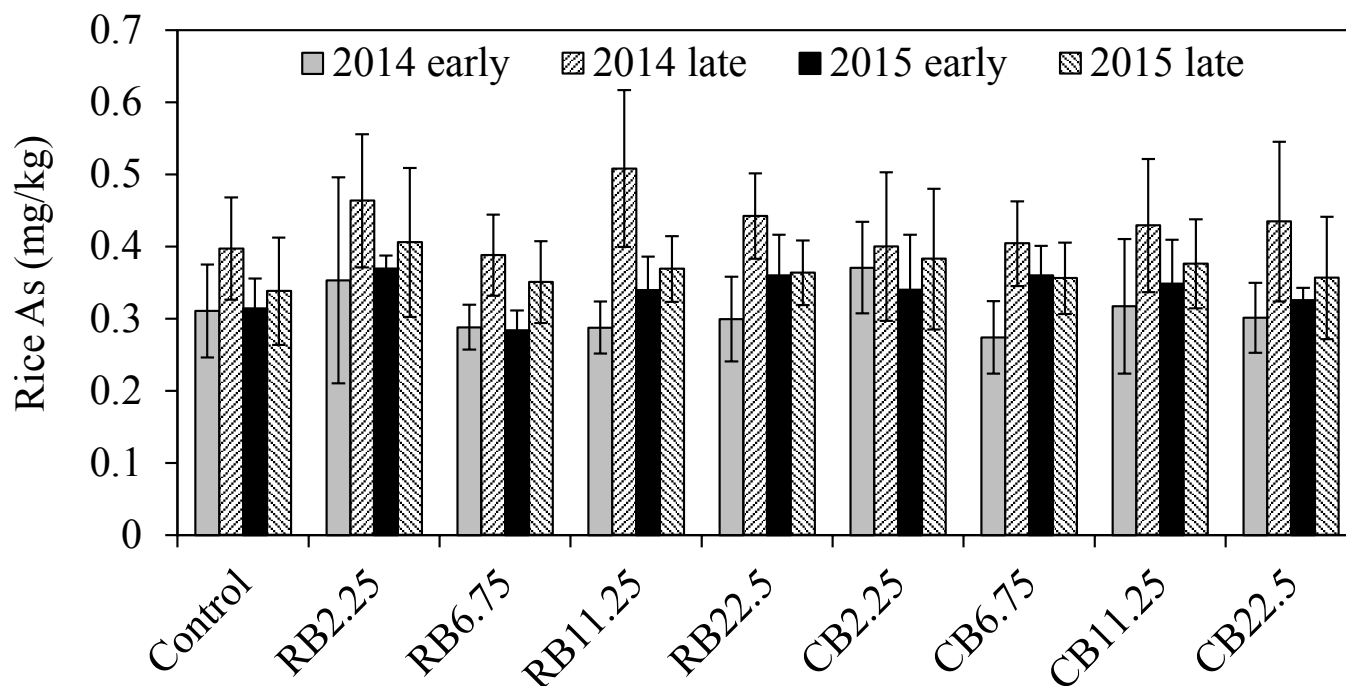
Figure 3 The concentrations of rice As with the addition of RB and CB in contaminated paddy soil, respectively, at various levels of biochar treatments (2.25, 6.75, 11.25, 22.5 t ha^{-1}).
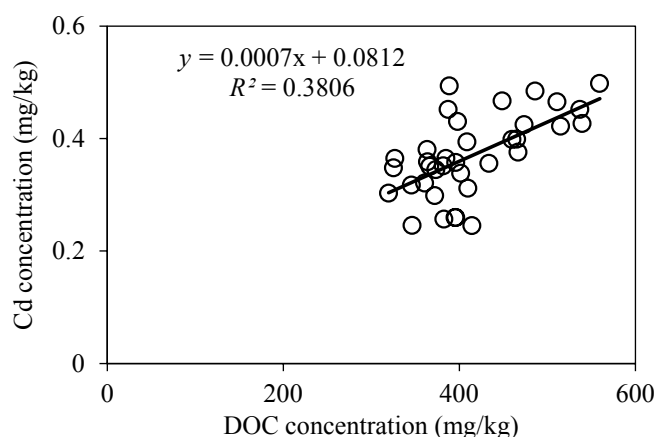
Table 3 The soil pH for the amendment of different biochars at different growth seasons.

	2014 early	**2014 late**	**2015 early**	**2015 late**
Control	4.76 ± 0.20	4.64 ± 0.07	4.85 ± 0.02	4.70 ± 0.12
RB2.25	4.66 ± 0.11	4.76 ± 0.06	4.84 ± 0.24	4.76 ± 0.10
RB6.75	4.68 ± 0.11	4.77 ± 0.08	4.74 ± 0.19	4.76 ± 0.04
RB11.25	4.62 ± 0.30	4.70 ± 0.03	4.82 ± 0.03	4.80 ± 0.06
RB22.5	4.83 ± 0.06	4.75 ± 0.06	4.84 ± 0.14	4.82 ± 0.11
CB2.25	4.76 ± 0.03	4.71 ± 0.11	4.84 ± 0.12	4.75 ± 0.04
CB6.75	4.83 ± 0.04	4.73 ± 0.05	4.93 ± 0.13	4.82 ± 0.18
CB11.25	4.90 ± 0.02	4.79 ± 0.07	4.94 ± 0.14	4.82 ± 0.06
CB22.5	5.05 ± 0.38	4.95 ± 0.05	4.92 ± 0.10	4.93 ± 0.05

Table 4 The DOC contents (mg kg^{-1}) for the amendment of different biochars at different growth seasons.

	2014 early	**2014 late**	**2015 early**	**2015 late**
Control	408.9 ± 25.0	559.6 ± 107.4	486.3 ± 54.9	388.8 ± 74.2
RB2.25	395.4 ± 53.4	473.7 ± 79.8	366.5 ± 45.4	466.8 ± 95.2
RB6.75	414.5 ± 38.3	515.2 ± 40.1	325.5 ± 15.5	401.8 ± 51.2
RB11.25	382.6 ± 11.7	539.6 ± 39.7	433.8 ± 34.7	460.1 ± 35.8
RB22.5	345.8 ± 21.2	448.9 ± 107.9	327.0 ± 55.7	409.9 ± 97.6
CB2.25	396.1 ± 7.6	537.1 ± 147.2	360.8 ± 33.6	396.1 ± 68.1
CB6.75	372.3 ± 17.7	511.1 ± 51.0	364.1 ± 2.4	465.3 ± 12.5
CB11.25	346.5 ± 18.3	398.1 ± 47.9	384.9 ± 75.8	381.8 ± 41.3
CB22.5	319.7 ± 9.4	387.5 ± 32.9	373.4 ± 54.0	296.9 ± 34.9

Figure 4 The relationship of rice Cd levels with the DOC contents in soil.

such as Cd and As (Liu *et al*. 2004; Chen *et al*. 2005; Hu *et al*. 2005). The iron plaque was dissolved during the decay of the rice roots (Wang *et al*. 2009; Huang *et al*. 2012), accompanied by the release of As and Cd during root decomposition and iron plaque reduction, all mediated by microorganisms in the paddy (Zhu *et al*. 2014). The released Cd and As were bioavailable and easily absorbed and accumulated in rice grains. This explains why in late rice the average concentrations of Cd and As were greater than those in the corresponding early rice (Figs 2, 3).

3. Conclusions

Rice yields were significantly increased after the application of CB during the four growth seasons (two-year) experiment, especially during the first growth season. The amendment RB increased the average rice yield but not to a significant level. CB proved superior to RB in improving rice yield over two years. The Cd content in rice was reduced by both biochars, regardless of the biochar application rate, in a long-term contaminated paddy field for at least two years. There were

and DOC content (Fig. 4), indicating that large amounts of DOC in soil enhanced the accumulation Cd in rice. Organic matter can exist in soluble complexes with Cd to reduce metal adsorption onto soil particles and promote metal availability for plants (Antoniadis & Alloway 2002; Cornu *et al*. 2011). It has been reported that high Cd–DOM complexes in the rhizosphere soil solution improve Cd accumulation in plants (Li *et al*. 2013). This can explain why most average Cd levels in late rice were always greater than those in early rice (Fig. 2). In addition, iron plaque on the root surfaces of rice can also accumulate a variety of heavy metals and metalloids

no significant variations in As in rice after biochar addition. Biochar has been shown to have significant and sustainable potential in Cd sequestration for reducing Cd accumulation in rice when applied to paddy soils. Biochar amendment offers a sustainable strategy for mitigating heavy metal pollution in agricultural fields.

4. Acknowledgements

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