

## BIOCHAR AMENDMENT GREATLY REDUCES RICE Cd UPTAKE IN A CONTAMINATED PADDY SOIL: A TWO-YEAR FIELD EXPERIMENT

Liqiang Cui,<sup>a</sup> Lianqing Li,<sup>a</sup> Afeng Zhang,<sup>a</sup> Genxing Pan,<sup>a,\*</sup> Dandan Bao,<sup>a</sup> and Andrew Chang<sup>b</sup>

A field experiment was conducted on the effect of biochar (BC) amendment on Cd uptake by rice (*Oryza sativa* L.) in a contaminated paddy in 2009 and 2010. BC was applied as a basal soil amendment before rice transplantation in 2009 at rates of 0, 10, 20, 40 t ha<sup>-1</sup>, and rice yield and Cd uptake were monitored in both 2009 and 2010. The BC amendment significantly increased soil pH by 0.15-0.33 units in 2009 and 0.24-0.38 units in 2010, and decreased CaCl<sub>2</sub> extracted Cd in soil by 32.0%-52.5% in 2009 and 5.5%-43.4% in 2010, respectively. Under BC amendment at 10, 20, 40 t ha<sup>-1</sup>, rice grain Cd concentration was observed to be reduced by 16.8%, 37.1%, and 45.0% in 2009 and by 42.7%, 39.9%, and 61.9% in 2010, while the total plant Cd uptake was found to decrease by 28.1%, 45.7%, and 54.2% in 2009 and by 14.4%, 35.9%, and 45.9% in 2010, respectively. Such effect of BC amendment on reducing Cd plant uptake has profound implications among those using bioresources for field application. Finally, BC amendment in combination with low Cd cultivars may offer a basic option to reduce Cd levels in rice as well as to reduce greenhouse gas emissions in rice agriculture in contaminated paddies.

*Keywords:* Biochar; Cd; Rice paddy; Contaminated soil; Metal mobility; Soil amendment

*Contact information:* a: Institute of Resources, Ecosystem and Environment of Agriculture, Nanjing Agricultural University, 1 Weigang, Nanjing, 210095-China; b: Department of Environmental Sciences, University of California Riverside, CA92521, USA.

\*Corresponding author: [gspan1@hotmail.com](mailto:gspan1@hotmail.com)

### INTRODUCTION

As a toxic element, cadmium (Cd) can cause serious dysfunctions in human organs, especially in liver and kidney (Recatalá et al. 2010). The bioavailability of Cd in agricultural soils has been a great health concern due to the potential risk through exposure of agro-food produced in Cd-contaminated fields (Chaney et al. 2004). In particular, this may become severe in acid soil areas with marginal deficiencies of the essential nutrients such as Zn, Fe, and Ca. This may lead to enhancement of Cd absorption, organ accumulation, and retention of dietary Cd intake (Reeves et al. 2008). Countermeasures for reducing Cd availability and plant Cd uptake and balancing mineral nutrition with Zn, Ca, and Fe in food as well as phytoremediation have been recommended for preventing potential Cd risks from food exposure in agricultural soils (Chaney et al. 2007; Reeves et al. 2008).

Rice has been of particular concern as a Cd health risk through food exposure by subsistence diet consumers (Chaney et al. 2005). Potential adverse consequences would be magnified under cultivation of high-yielding super-rice cultivars grown in contaminated acid rice paddies under intermittent moisture conditions, which may allow high Cd release from Cd-bound sulfides upon drainage due to higher biomass production, thick and sturdy stems, a vigorous root system, increased harvest index, and high productive tiller percentage (Gong et al. 2006; Zhang et al. 2009c). A large area of China's croplands has been reported to have Cd contamination in a recent soil pollution survey, which raised particular critical for South China (Zhang et al. 2000; Teng et al. 2010). In fact, excessive levels of Cd in rice grains sampled from South China rice areas were already reported (Zhang et al. 2009a). Yet, rice paddies subject to Cd contamination appear to have expanded for the last decade due to irrigation with waste water from municipal sewage and mining tailing as well as chemical fertilization in South China (Du et al. 2009). This is supposed to raise the uptake and rice grain accumulation of Cd and, in turn, the already existing health risks for subsistence diet farmers of South China.

Therefore, reducing Cd mobility and plant uptake would be an urgent demand for safe rice production in China. Phytoremediation of Cd-contaminated fields, generally considered as a low input technique to remove, transform, or assimilate toxic chemical from contaminated site, would need a long time before low-Cd rice could be produced (Peng et al. 2009). Other physico-chemical extraction techniques are costly and have had limited use in seriously contaminated soil without practical crop production, and mainly at the scale of lab experiments (Chen et al. 1995; Peters, 1999; Di Palma et al. 2005; Kuo et al. 2006; Udovic et al. 2009; Zhang et al. 2010b).

Techniques for stabilizing metals may be more effective in reducing Cd mobility and plant uptake in rice paddies with low-level of Cd contamination, as they are generally cost-effective and beneficial for improving physico-chemical and biological properties of contaminated soil (Mench et al. 2003; Madejón et al. 2006). There have been a number of reports of field trials to reduce Cd availability and plant Cd uptake using physico-chemical approaches. These may lead to removal of available metals or transformation of less harmful speciation at a significant amount of amendment input and/or period of time of application (Zhou et al. 2004; Aboulroos et al. 2006; Mulligan et al. 2001; Chen et al. 2006). Alkaline amendments used as stabilizing agents in moderately and slightly contaminated soil may have good effects on reducing metal mobility by increasing the soil pH and enhancing metal binding to soil particles, but such approaches are not always cost-effective for the large amount used for amelioration (Filius et al. 1998; McBride. 1989). In a recently study, Zhang et al. (2009b) reported that use of calcium magnesium phosphate in amounts 0.7, 1, and 1.3 t ha<sup>-1</sup> significantly decreased grain Cd concentration, while soil pH was increased and rice yield was not affected under amendment treatments compared to no treatment. However, the Cd level of rice grain under the treatments in high amount was still beyond the state guideline limit.

Recently, application of biochar in agriculture soil has been adopted as an option for enhancing soil C stock and mitigating greenhouse gas emission from world cropland (Roberts et al. 2010). BC contains a large amount of highly recalcitrant organic material in more or less alkaline reaction (Lehmann et al. 2006; Hossain et al. 2010), which would benefit reduction in metal mobility in soils. Experiments using BC as a soil amendment

in contamination soils have been reported. In a short lab incubation study, Gomez-Eyles et al. (2011) observed a significant reduction in available Cd and Cu and an increase in soil pH after BC amendment for 1-2 months, and Namgay et al. (2010) also found significantly decreased availability of Cd and Pb with BC application in a pot experiment. Likewise, in a microcosmic study, Beesley et al. (2011) could trace the reduction in Cd and Zn concentration in the leachates from the soil column amended with biochar. Similarly, Beesley et al. (2010) reported significantly decreased Cd and Zn concentrations in pore water after the soil was mixed with BC. Therefore, there may be a potential of using BC to reduce Cd availability in contaminated soils. However, there have not yet been any reports of field study in contaminated rice paddies.

Therefore, the alleviation of excessive Cd in rice grains due to contaminated soil has become a major concern of rice agriculture in South China. The purpose of this study is to address the efforts of biochar amendment on soil Cd availability, plant uptake, and grain Cd level in a contaminated rice paddy and discuss the potential application of BC in rice agriculture in Cd-contaminated rice areas.

## EXPERIMENTAL

### Field Experiment Site

A field experiment for alleviation of Cd uptake in rice grain using biochar as soil amendment was initiated in 2009. The experimental site was located in Yifeng village (31°24.434'N, 119°41.605'E), Yixing Municipality, Jiangsu, China and was conducted in a rice farm that had been contaminated with heavy metals from a metallurgy plant in that vicinity since the 1970s. The status of multi-metal contaminated and high grain Cd level of the rice grown in the field was already reported by Liu et al. (2006). The paddy soil of the farm belongs to Ferric-accumulic Stagnic Anthrosols (Gong 1999). The local climate was humid subtropical with a mean annual temperature and precipitation of 22°C and 1100 mm, respectively. The rice farm had been cultivated traditionally under rotation of rice and winter wheat.

### Experiment Design

Four treatments of biochar amendment were designed as C0, C1, C2, and C3 at application rates of 0 (as control), 10, 20, and 40 t ha<sup>-1</sup>, respectively. Biochar as soil amendment was spread on the surface and then thoroughly mixed by manual plowing after the wheat harvest in May of 2009. The biochar treatments were plowed by machine in 2010. Treatment plots with an area of 4 m × 5 m each were laid out in a randomized complete block design. For rice production, seed of a traditional local rice cultivar, Wuyunjing-19 in 2009 and Wuyunjing-23 in 2010, were directly seeded in each plot in late May, and calcium biphosphate, potassium chloride, and urea were applied as basal fertilizers at 125 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> and 125kg K<sub>2</sub>O ha<sup>-1</sup>, 120 kg N ha<sup>-1</sup> respectively. Total N fertilizer at 300 kg N ha<sup>-1</sup> was applied both in 2009 and 2010. The water regime and N fertilization management were performed following conventional practices by the local farmers. The experiment was performed in triplicates.

Biochar used in the field experiment was produced from wheat straw by the Sanli New Energy Company, Henan, China. The biochar was produced by pyrolysis at 350 to 550°C using a vertical kiln made of refractory bricks, with which 35% of straw biomass was converted to biochar. The produced biochar was ground to pass a 2 mm sieve. The basic property of biochar used and soil are listed in Table 1.

**Table 1.** Basic Properties of Topsoil (0 to 15 cm) of the Studied Rice Paddy before Experiment and Biochar Amended

	pH (H <sub>2</sub> O)	SOC (g kg <sup>-1</sup> )	Total N (g kg <sup>-1</sup> )	Total P (g kg <sup>-1</sup> )	Total K (g kg <sup>-1</sup> )	CEC (cmol kg <sup>-1</sup> )	Total Cd (mg kg <sup>-1</sup> )
Topsoil	6.07	20.71	3.19	0.82	11.4	18.05	21.84
Biochar	10.35	467.2	5.90	14.43	11.5	217.0	1.18

### Soil Sampling and Analysis

Topsoil samples were randomly collected for basic property analysis before the field experiment in 2009 and after the rice harvest both in 2009 and 2010. For sampling, three undisturbed core samples at depth of 0 to 15 cm were collected in an S shaped way, respectively, from each plot using an Eijkelkamp core sampler (Netherlands). After shipping to the lab, all soil samples were removed of plant detritus and any visible fragments, ground, and sieved to pass 2 mm sieve after air-drying at room temperature at lab.

All soil analysis was conducted following the procedures described by Lu (2000). Soil pH was measured using a Mettler Toledo Seveneasy precision pH meter (Switzerland) in a soil-to-solution ratio of 1:2.5. Total Cd contents were determined by digesting the 0.5000 g soil (further ground and sieved to pass 0.15 mm sieve) with a mixed solution of HF, HNO<sub>3</sub>, HClO<sub>4</sub> (10: 2.5: 2.5, V: V: V) at 100 °C for 60 min and further at 250 °C until the sample was concentrated to an approximate volume of 2 mL in the PTFE (polyfluortetraethylene) crucibles. Three reagent blank samples were also digested in each batch of digestion. A certified reference material of sediment GBW 07406 (0.13 ± 0.04 mg kg<sup>-1</sup> Cd) from the National Centre for Certificate Reference Materials, China was used as internal standard in each patch of digestions, and the Cd recovery was between 81.2% and 125.5%. Soil available Cd was analyzed by extracting with 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. Cd concentration in these solutions was determined with a Flame Atomic Absorption Spectrophotometer (FAAS, TAS-986, Persee, China).

### Plant Sampling and Analysis

On harvest, rice yield was directly measured by weighing all the grains harvested in each plot. Three composite plant samples were randomly collected from each plot at the ripening stage on the 23rd of October in both years. After shipping to the lab, the samples were washed to remove soil particles first with tap water and further with deionized water. Each plant sample was then separated into roots, shoots, and grain. They were first dehydrated in an air-convection oven at 105 °C for 30 min and further dried to constant weight at 60 °C for another 48 h (Lu 2000). The dried samples were crushed, mixed, and homogenized, then stored in air-tight polyethylene bags prior to chemical analysis. A portion of 0.5000 g of a plant sub-sample was digested in a 100 mL digestion

flask with 10 mL mixed solution of HNO<sub>3</sub> and HClO<sub>4</sub> (8:2, V:V), then heated to complete the digestion on an electric heating plate digester. Three reagent blank samples and three certified plant reference materials GBW 07602 (0.14 ± 0.06 mg kg<sup>-1</sup> Cd) and GBW 10010 (0.087±0.005 mg kg<sup>-1</sup> Cd) from the National Centre for Certificate Reference Materials, China were inserted in each bath used for digestion. Cd in the digest was determined with Graphite Furnace Atomic Absorption Spectrometry (GFAAS; SpectrAA 220Z, Varian, USA). The recovery of Cd was in the range of 86.5% to 122.1%.

### Data Processing and Statistics

All data were expressed as means plus or minus one standard deviation. Differences between the treatments were examined using a two-way analysis of variance (ANOVA). All statistical analyses were carried out using SPSS, version 13.0 (SPSS Institute, USA, 2001).

## RESULTS AND DISCUSSION

### Soil Cd Mobility

Data of soil pH changes under biochar treatment are presented respectively in Table 2. As result of the alkaline reaction of biochar used, compared to the soil itself, biochar amendment significantly increased soil pH over the control in a similar rate of 0.01 unit per ton of amended BC in both years. Meanwhile, soil organic carbon (SOC) content was consistently increased at a rate of 0.42 g kg<sup>-1</sup> per ton of amended BC in both years.

**Table 2.** Changes in Soil pH and SOC Following BC Amendment

Treatment	Soil pH (H <sub>2</sub> O)	SOC (g kg <sup>-1</sup> )
2009		
C0	6.07±0.01c	21.25±0.31d
C1	6.22±0.01b	23.44±0.41c
C2	6.29±0.09ab	28.81±0.60b
C3	6.40±0.05a	33.50±1.24a
2010		
C0	5.89±0.04c	21.55±0.36c
C1	6.13±0.01b	23.70±3.04bc
C2	6.24±0.01a	29.03±4.96ab
C3	6.27±0.02a	33.83±2.51a

Different low case letters represent significant difference between the treatments in a single year.

As shown in Table 3, soil Cd mobility was much decreased under biochar application in both years. The concentration of CaCl<sub>2</sub> extracted Cd in soil was significantly decreased by 32.0%, 39.2%, and 52.5% in 2009 and by 5.3%, 43.4%, and 39.8% in 2010 respectively under C1, C2, and C3 treatments. As a relatively small pool of the total Cd, exchangeable Cd did show significant difference between two years under a single BC treatment. However, DTPA extracted Cd exerted a similar large pool of total Cd across the BC treatments in the contaminated soil. While the extractability of DTPA seemed a function of the stability of metal-DTPA chelate, it did become smaller in a

single BC treatment, especially under high rate of 40 t ha<sup>-1</sup>, in 2010 than in 2009 following the BC application. This may indicate existence of some tightly bound Cd by BC material, which could not be identified with CaCl<sub>2</sub> extraction.

**Table 3.** Change in Cd Mobility in Soil Following BC Amendment

Treatments	CaCl <sub>2</sub>		DTPA	
	2009	2010	2009	2010
C0	1.73±0.22aA	1.52±0.21aA	14.00±1.92Aa	15.02±2.03aA
C1	1.17±0.24bA	1.44±0.15aA	13.64±2.45Aa	11.20±1.46bA
C2	1.05±0.31bA	0.86±0.20bA	13.98±3.65Aa	11.78±0.35bA
C3	0.82±0.09cA	0.91±0.05bA	11.78±2.17Aa	7.73±0.01cB

Different low case and capital letters represent significant difference between the treatments in a single year and between the years for a single treatment, respectively.

### Cd Uptake and Partitioning in Plant Tissues

Table 4 lists the total plant Cd uptake, Cd concentration, and partitioning in plant tissues under biochar amendment treatments. Total plant Cd uptake ranged from 152.9 g ha<sup>-1</sup> and 171.2 g ha<sup>-1</sup> under BC amendment at 40 t ha<sup>-1</sup> to 296.2 g ha<sup>-1</sup> and 241.7 g ha<sup>-1</sup> under no BC amendment in 2009 and 2010, respectively. Compared to no BC amendment, total plant Cd uptake was significantly decreased by 28.1%, 45.7%, and 54.2% in 2009 and by 14.4%, 35.9%, and 45.9% in 2010, respectively under C1, C2, and C3 treatments. Ranging from 39.5 mg kg<sup>-1</sup> to 71.5 mg kg<sup>-1</sup>, root Cd concentration was multiple-fold as much as the soil total and showed a smaller decreasing trend with BC rates than total plant Cd uptake. However, there were no significant differences in Cd partitioning (at mostly 40%) in underground tissues between BC treatments or between the years. These indicated no profound effect of BC treatment on Cd translocation from root to shoots.

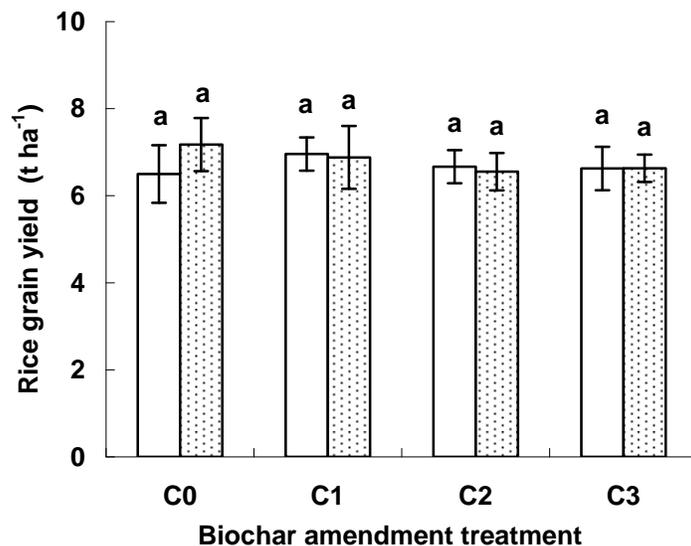
**Table 4.** The Cd Plant Uptake, Cd Concentration, and Partitioning in Plant Tissues under Biochar Amendment (n =3, mean ± S.D.).

Treat ment	Year	Total Cd uptake (g ha <sup>-1</sup> )	Cd in plant tissue (mg kg <sup>-1</sup> ) and the partitioning (% in bracket)	
			Underground	Aboveground
C0	2009	296.17±13.66aA	71.53±9.50aA (34.5)	15.20±0.63aA (65.5)
	2010	241.71±25.92aB	66.39±4.83aA (40.1)	9.42±0.77aB (59.9)
C1	2009	241.87±12.48bA	54.29±7.44bA (44.7)	9.00±0.79bA (55.3)
	2010	201.81±5.89abB	48.63±1.69bA (43.3)	8.30±0.50abA (56.7)
C2	2009	180.97±31.02cA	48.05±11.97bA (44.2)	6.34±0.80cA (55.8)
	2010	195.56±16.24bA	48.89±8.28bA (38.7)	7.68±1.82abA (61.3)
C3	2009	152.94±27.28cA	39.49±2.63bA (40.5)	5.40±1.70cA (59.5)
	2010	171.24±12.84bA	52.03±0.85bA (45.3)	6.99±1.04bA (54.7)

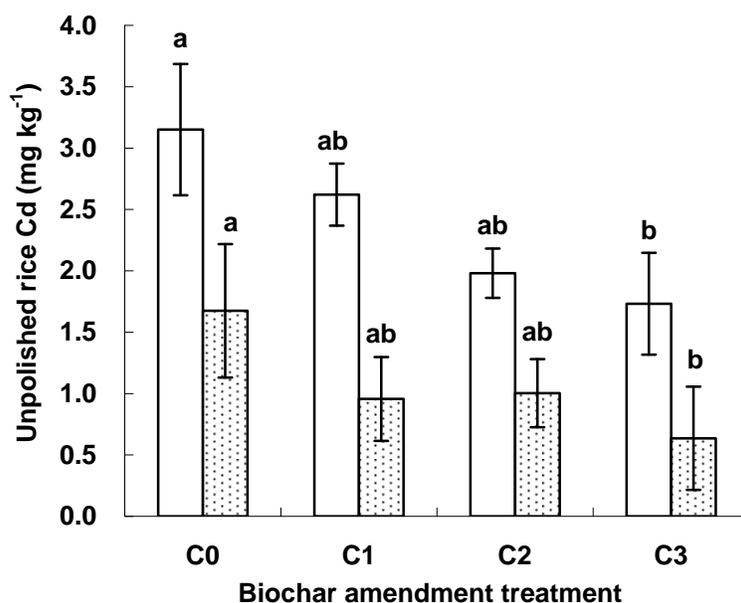
The different letters in a column indicate a significant difference between the treatments in a single year ( $p < 0.05$ ).

### Rice Grain Yield and Grain Cd

Data in Fig. 1 showed no significant differences in rice grain yield between the treatments in a single year or between the years, though the grain yield of  $7 \text{ t ha}^{-1}$  on average was a little lower in the contaminated field compared to that reported by Zhang et al. (2010a) in an uncontaminated adjacent field.



**Fig. 1.** Change in rice yields with biochar treatment (Blank, in 2009; Shaded, in 2010). The bar above the block represents the standard deviation of three replicates, different letters above the blocks indicate significant differences ( $p < 0.05$ ) between the biochar treatments.



**Fig. 2.** Change in Cd concentration of unpolished rice with biochar treatment (Blank, in 2009; Shaded, in 2010). The bar above the block represents the standard deviation of three replicates, different letters above the blocks indicate significant differences ( $p < 0.05$ ) between the biochar treatments.

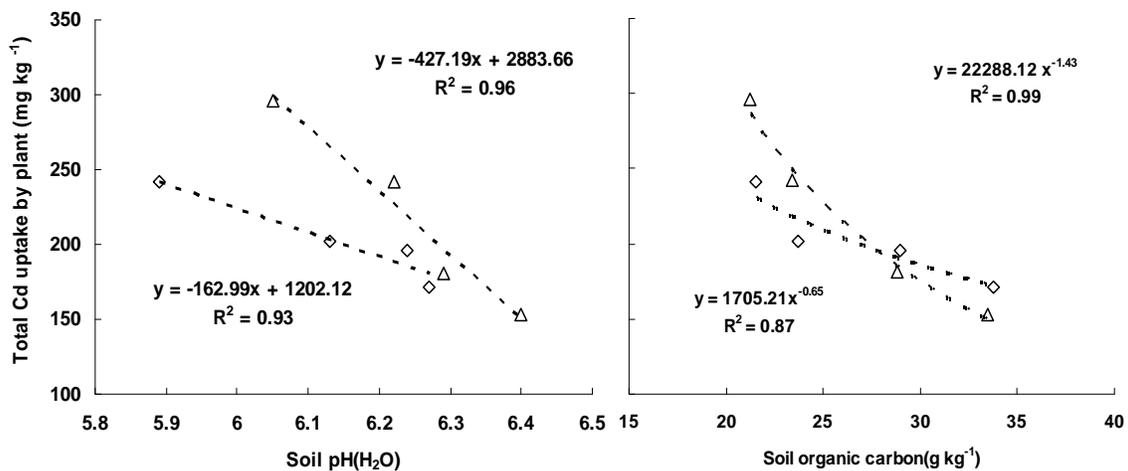
Figure 2 presents data for unpolished rice Cd concentration of the harvested rice in both years. Rice grain Cd concentration under no BC amendment was as high as 3.15 mg kg<sup>-1</sup> and as 1.67 mg kg<sup>-1</sup> in 2009 and 2010, respectively. However, it was reduced to 2.62, 1.98, and 1.73 mg kg<sup>-1</sup> in 2009 and to 0.96, 1.00, and 0.64 mg kg<sup>-1</sup> in 2010, respectively under C1, C2, and C3 treatments compared to no BC amendment. On average, grain Cd was decreased at a rate of 0.035 g kg<sup>-1</sup> in 2009 and 0.022 g kg<sup>-1</sup> in 2010 per ton of BC amendment. A great reduction in grain Cd calculated in contrast to no amendment is seen at 16.8%, 37.1%, and 45.0% in 2009 and at 42.7%, 39.9%, and 61.9% in 2010 under BC amendment of 10, 20, and 40 t ha<sup>-1</sup> respectively. In addition, a more profound effect of biochar application in reducing grain Cd level was observed in the subsequent year of 2010 with a different cultivar.

## DISCUSSION

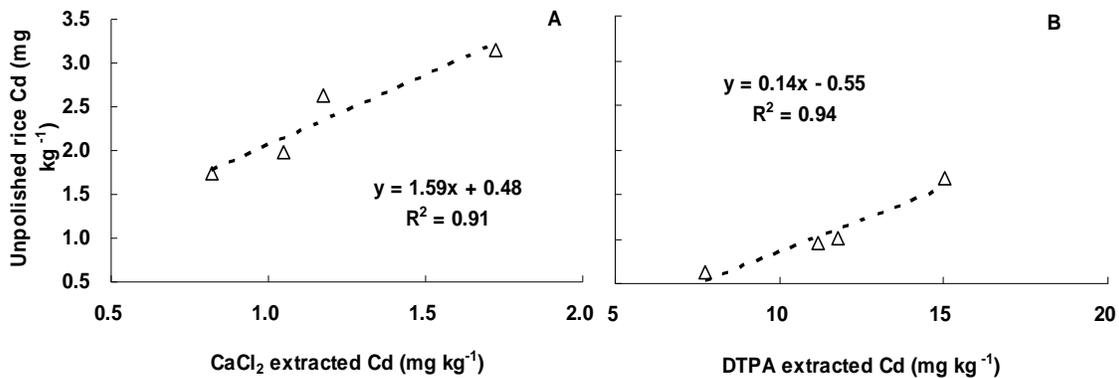
This experiment showed significant effects of biochar amendments on reducing rice grain Cd uptake in the contaminated acidic rice paddy. In an adjacent similar field, Zhang et al. (2009b) reported a large range of decrease in rice grain Cd by 16.6%, 22.6%, and 66.6% under application of calcium-magnesium phosphate (CMP) of pH (H<sub>2</sub>O) 9.3 at 0.67, 1.00, and 1.33 t ha<sup>-1</sup>, respectively. Comparatively, BC effects on reducing rice Cd (Fig. 2) were seen to be much greater than CMP at rates beyond 1 t ha<sup>-1</sup>. However, Gray et al. (2006) reported that plant Cd uptake by a metal tolerant plant was reduced by 68.5% and 69.8%, and by 73.8% and 60.7% in the first year and the subsequent year after application of alkaline red mud at high rates of 60 and 100 t ha<sup>-1</sup>, respectively. Using pot experiments, cyclonic ashes (CA) at very high rate of 5% (ca. 150 t ha<sup>-1</sup>) were seen to reduce Cd uptake by a phytoaccumulator at 52% (Ruttens et al. 2010). In a field study using poultry compost with pH (H<sub>2</sub>O) 7.1, Sato et al. (2010) reported a reduction in leaf Cd at 37% under a high rate of 75 t ha<sup>-1</sup>. Comparatively, BC effect on reducing Cd uptake could be seen to be very profound and convincing among the relevant technologies using recycled bioresource materials.

Plant Cd uptake is generally controlled by Cd mobility in soil, which is in turn highly dependent on soil pH and organic matter content (Sauve et al. 2000). As in the case of red mud (Gray et al. 2006), of cyclonic ashes (Ruttens et al. 2010), and of CMP (Zhang et al. 2009b), the effects of amendments on reducing metal mobility and plant uptake were mainly attributed to the increased soil pH as result of the alkaline reaction of the material added in large amount. In this study, total plant Cd uptake as a measure of Cd bioavailability was found correlating both with soil pH and organic carbon content for the individual years (Fig. 3). While there existed a significant negative correlation of CaCl<sub>2</sub>-extractable Cd with pH for both years (data not shown), the correlation of rice Cd with CaCl<sub>2</sub>-extractable Cd was valid only in 2009, the first year of BC amendment (Fig. 4A). Notably, in the subsequent year after BC amendment a significant strong correlation was observed with DTPA (Fig. 4 B). These results exerted strong interactive effects of pH and SOM on Cd mobility, and plant uptake. DTPA extraction was tentatively proposed to measure the pool of a metal to release from soil solid phase into solution through forming chelates, which was generally accepted as indicative of accessibility to

plant root uptake (Amacher 1996). Accordingly, higher DTPA extractability refers to a smaller fraction of bound metals. In this study, the great increase in SOC (Table 2) following BC amendment could have enhanced the binding and aging capacity for mobile Cd, thus exerting a stronger control on Cd bioavailability to rice in the subsequent year. BC contains a large amount of such functional groups as  $-\text{COO}^-(-\text{COOH})$  and  $-\text{O}^-(-\text{OH})$  with large organic molecules, which are responsible for binding metal and then stabilized in solid phase (Yuan et al. 2011). Such capacity could be greatly enhanced as total SOC was increased to 28.8 and 33.5  $\text{g kg}^{-1}$  under BC amendments at high rates of 20 and 40  $\text{t ha}^{-1}$ . On the other hand, the exchangeable pool of Cd was strongly affected by the pH increase under BC amendment, and this would account for the dominant decrease in Cd uptake and rice grain concentration in the first year. Therefore, the present study demonstrates a sustaining effect of BC amendments on reducing rice grain Cd concentration in the contaminated field, which involves decreasing Cd chemical mobility through increased soil pH mainly in the first year and strongly enhancing metal stabilization through greatly increased SOM in soil mainly in the subsequent year following BC amendments.



**Fig. 3.** Correlation of total plant Cd uptake with soil pH and organic carbon content ( $\Delta$ , 2009;  $\diamond$ , 2010)



**Fig. 4.** Unpolished rice Cd as a function of  $\text{CaCl}_2$  extracted Cd in 2009 (A) and of DTPA extracted Cd in 2010 (B)

The observed decrease in rice grain Cd concentration was more profound in the subsequent year with alternative cultivars, though rice grain yield was not affected. There was no significant difference observed in Cd partitioning between BC treatments in a single year, suggesting no remarkable BC effect on decreasing Cd partitioning between root and grain. This seems to disagree with Harris et al. (2001), who suggested that Cd translocation from root to shoot can be restricted under BC treatment, thus limiting Cd accumulation in grain by controlling the size of root and shoot Cd pools able to remobilize to the grain. By contrast, the Cd ratio of root to grain (calculated from data in Table 4 and Fig. 2) ranged from 20.7 to 24.3 in 2009 and from 40.0 to 81.3 in 2010, being much greater in 2010 than in 2009. Moreover, Cd partitioning in root and shoot was 91.8% and 91.6% in 2009 and 96.3% and 97.5% in 2010 under BC amendment at 20 t ha<sup>-1</sup> and 40 t ha<sup>-1</sup>, respectively. Thus, decreased partitioning of Cd in rice grain may partly explain the greater extent to which rice grain Cd was reduced while the total plant uptake of Cd was increased in the subsequent year of 2010 with an alternative cultivar. The effect of cultivars on Cd uptake and partitioning were well demonstrated in our previous studies (Li et al. 2005; Shi et al. 2007). With this low Cd partitioning, in cultivars Wuyunjing-23 rice grain Cd was reduced under BC amendment at 40 t ha<sup>-1</sup> as low as 0.6 mg kg<sup>-1</sup> compared to 3.15 mg kg<sup>-1</sup> with Wuyunjing-19 under no BC treatment. Thus, BC amendment in combination with low Cd cultivars breeding would offer a basic option to grow low Cd rice in contaminated paddies; this has been identified as an urgent need with regard to China's rice agriculture and risks to human health due to Cd (Gong and Pan 2006).

It has been widely recognized that BC amendment can benefit agricultural production through improving soil quality and soil health, as well as by decreasing N<sub>2</sub>O emissions in agriculture (Lehmann and Rhodon.2006), as shown in a number of field studies (Asai et al. 2009; Rondon et al. 2007; Major et al. 2010). Our previous studies with BC amendment showed significant beneficial effects on rice yield, greenhouse gases mitigation, and N use efficiency in uncontaminated rice fields (Zhang et al. 2010a). It is already well known that biochar application in agriculture would have a net C negative effect by conversion of the crop residue into recalcitrant C form, thus offsetting greenhouse gas (GHGs) emission from N consumption and avoiding burning (Roberts et al. 2010). The present study further evidenced a remarkable effect of BC amendment on reducing rice grain Cd in a contaminated rice paddy. Therefore, it is urged to adopt BC amendment as a key option to reduce rice Cd as well as to reduce net GHGs emission in rice agriculture of China, a particular need for those areas with Cd contamination in South China.

## CONCLUSIONS

Biochar showed high efficiency to reduce rice Cd content in a long-term contaminated paddy for at least two years, while grain yield was not observed to be affected. Combination of BC amendment with low Cd cultivar breeding can offer a basic option to reduce rice Cd content as well as reduce GHGs emission in rice agriculture, particularly in the acidic Cd-contaminated fields. Of course, long term effects on soil health and potential off-setting effects under BC amendment deserve further field monitoring studies.

## ACKNOWLEDGMENTS

This study was partially supported by the Ministry of Science and Technology of China under grants 2008BAD95B13-1 and 2006BAD17B06, and an oversea partnership program from the Ministry of Education of China (MS2010NJND046).

## REFERENCES CITED

- Aboulroos, S. A., Helal, M. I. D., and Kamel, M. M. (2006). "Remediation of Pb and Cd polluted soils using in situ immobilization and phytoextraction techniques," *Soil Sediment. Contam.* 15, 199-215.
- Amacher, M.C. (1996). "Nickel, cadmium and lead," In: *Methods of Soil Analysis, Part 3-Chemical Methods*, Soil Science Society of America, Inc., Madison, Wisconsin, USA. 752-754.
- Asai, H., Samson, B. K., Stephan, H. M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T., and Horie, T. (2009). "Biochar amendment techniques for upland rice production in Northern Laos: 1. Soil physical properties, leaf SPAD and grain yield," *Field Crop Res.* 111, 81-84.
- Beesley, L., and Marmiroli, M. (2011). "The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar," *Environ. Pollut.* 159, 474-480.
- Beesley, L., Moreno-Jiménez, E., and Gomez-Eyles, J. L. (2010). "Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil," *Environ. Pollut.* 158, 2282-2287.
- Chaney, R. L., Angel, J. S., McIntosh, M. S., Reeves, P. G., Li, Y. M., Brewer, E. P., Chen, K. Y., Roseberg, R. J., Perner, H., Synkowski, E. C., Broadhurst, C. L., Wang, S., and Baker, A. J. M. (2005). "Using hyperaccumulator plants to phytoextract soil Ni and Cd," *Z. Naturforsch* 60C, 190-198.
- Chaney, R. L., Angle, J. S., Broadhurst, C. L., Peters, C. A., Tappero, R. V., and Sparks, D. L. (2007). "Improved understanding of hyperaccumulation yields commercial phytoextraction and phytomining technologies," *J. Environ. Qual.* 36, 1429-1443.
- Chaney, R. L., Reeves, P. G., Ryan, J. A., Simmons, R. W., Welch, R. M., and Angle, J. S. (2004). "An improved understanding of soil Cd risk to humans and low cost methods to phytoextract Cd from contaminated soils to prevent soil Cd risks," *BioMetals* 17, 549-553.
- Chen, S. B., Zhu, Y. G., and Ma, Y. B. (2006). "The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils," *J. Hazard. Mater.* 134, 74-79.
- Chen, T. C., and Hong, A. (1995). "Chelating extraction of lead and copper from an authentic contaminated soil using N-(2-acetamido) iminodiacetic acid and S-carboxymethyl-L-cysteine," *J. Hazard. Mater.* 41, 147-160.
- Di Palma, L., Ferrantelli, P., and Medici, F. (2005). "Heavy metals extraction from contaminated soil: Recovery of the flushing solution," *J. Environ. Manage.* 77, 205-211.

- Du, Q., Chen, M., Zhou, R., Chao, Z., Shao, G., and Wang, G. (2009). "Cd toxicity and accumulation in rice plants vary with soil nitrogen status and their genotypic difference can be partly attributed to nitrogen uptake capacity," *Rice Sci.* 16, 283-291.
- Filius, A., Streck, T., and Richter, J. (1998). "Cadmium sorption and desorption in limed topsoils as influenced by pH: Isotherms and simulated leaching," *J. Environ. Qual.* 27, 12-18.
- Gomez-Eyles, J. L., Sizmur, T., Collins, C. D., and Hodson, M. E. (2011). "Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements," *Environ. Pollut.* 159, 616-622.
- Gong, W., Li L., and Pan, G. (2006). "Cd uptake and accumulation in grains by hybrid rice in two paddy soils: Interactive effect of soil type and cultivars," *Environ. Sci.* 21, 1647-1653 (in Chinese).
- Gong, W., and Pan, G. (2006). "Issues of grain Cd uptake and the potential health risk of rice production sector of China," *Sci. Technol. Rev.* 24, 43-48 (in Chinese).
- Gong, Z. T. (1999). *Chinese Soil Taxonomy*, China Science Press, Beijing, 109-192 (in Chinese).
- Gray, C. W., Dunham, S. J., Dennis, P. G., Zhao, F. J., and McGrath, S. P. (2006). "Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud," *Environ. Pollut.* 142, 530-539.
- Harris, N. S., and Taylor, G. J. (2001). "Remobilization of cadmium in maturing shoots of near isogenic lines of durum wheat that differ in grain cadmium accumulation," *J. Exp. Bot.* 52, 1473-1481.
- Hossain, M. K., Strezov, V., Chan, K. Y., Ziolkowski, A., and Nelson, P. F. (2010). "Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar," *J. Environ. Manage.* 92, 223-228.
- Kuo, S., Lai, M. S., and Lin, C. W. (2006). "Influence of solution acidity and CaCl<sub>2</sub> concentration on the removal of heavy metals from metal-contaminated rice soils," *Environ. Pollut.* 144, 918-925.
- Lehmann, J., Gaunt, J., and Rondon, M. (2006). "Bio-char sequestration in terrestrial ecosystems – A review," *Mitig. Adapt. Strateg. Global Change* 11, 403-427.
- Lehmann, J., and Rhodon, M. (2006). "Biochar soil management on highly-weathered soils in the humid tropics," In: *Biological Approaches to Sustainable Soil Systems*, Uphoff, N. (Ed.), CRC Press, Boca Raton, FL, 517-540.
- Li, Z. W., Li, L. Q., Pan, G. X., and Chen, J. (2005). "Bioavailability of Cd in a soil-rice system in China soil type versus genotype effects," *Plant Soil* 271, 165-173.
- Liu, H., Li, Y., Li, L., Jin, L., and Pan, G. (2006). "Pollution and risk evaluation of heavy metals in soil and agro-products from an area in the Taihu Lake region," *J. Saf. Environ.* 6, 60-63 (in Chinese).
- Lu, R. K. (2000). "Methods of inorganic pollutants analysis," In: *Soil and Agro-chemical Analysis Methods*, Agricultural Science and Technology Press, Beijing, 205-266.
- Madejón, E., Mora, A. P., Felipe, E., Burgos, P., Cabrera, F. (2006). "Soil amendments reduce trace element solubility in a contaminated soil and allow regrowth of natural vegetation," *Environ. Pollut.* 139, 40-52.

- Major, J., Rondon, M., Molina, D., Riha, S. J., and Lehmann, J. (2010). "Maize yield and nutrition during 4 years after biochar application to a *Colombian savanna oxiso*," *Plant Soil* 333, 117-128.
- McBride, M. B. (1989). "Reactions controlling heavy metal solubility in soils," *Adv. Soil Sci.* 10, 1-56.
- Mench, M., Bussiere, S., Boisson, J., Castaing, E., Vangronsveld, J., Ruttens, A., De Koe, T., Bleeker, P., Assuncao, A., and Manceau, A. (2003). "Progress in remediation and revegetation of the barren Jales gold mine spoil after in situ treatments," *Plant Soil* 249, 187-202.
- Mulligan, C. N., Yong, R. N., and Gibbs, B. F. (2001). "An evaluation of technologies for the heavy metal remediation of dredged sediments," *J. Hazard. Mater.* 85, 145-163.
- Namgay, T., Singh, B., Singh, B.P. (2010). "Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (*Zea mays L.*)," *Aust. J. Soil Res.* 48, 638-647.
- Peng, S., Zhou, Q., Cai, Z., and Zhang, Z. (2009). "Phytoremediation of petroleum contaminated soils by *Mirabilis Jalapa L.* in a greenhouse plot experiment," *J. Hazard. Mater.* 168, 1490-1496.
- Peters, R. W. (1999). "Chelant extraction of heavy metals from contaminated soils," *J. Hazard. Mater.* 66, 151-210.
- Recatalá, L., Sánchez, J., Arbelo, C., and Sacristán, D. (2010). "Testing the validity of a Cd soil quality standard in representative Mediterranean agricultural soils under an accumulator crop," *Sci. Total Environ.* 409, 9-18.
- Reeves, P. G., and Chaney, R. L. (2008). "Bioavailability as an issue in risk assessment and management of food cadmium: A review," *Sci. Tot. Environ.* 398, 13-19.
- Roberts, K. G., Gloy, B. A., Joseph, S., Scott, N. R., and Lehmann, J. (2010). "Life cycle assessment of biochar systems: Estimating the energetic, economic, and climate change potential," *Environ. Sci. Technol.* 44, 827-833.
- Rondon, M., Lehmann, J., Ramírez, J., and Hurtado, M. (2007). "Biological nitrogen fixation by common beans (*Phaseolus vulgaris L.*) increases with biochar additions," *Biol. Fertil. Soils*, 43, 699-708.
- Ruttens, A., Adriaensen, K., Meers, E., De Vocht, A., Gebelen, W., Carleer, R., Mench, M., and Vangronsveld, J. (2010). "Long-term sustainability of metal immobilization by soil amendments: Cyclonic ashes versus lime addition," *Environ. Pollut.* 158, 1428-1434.
- Sato, A., Takeda, H., Oyanagi, W., Nishihara, E., and Murakami, M. (2010). "Reduction of cadmium uptake in spinach (*Spinacia oleracea L.*) by soil amendment with animal waste compost," *J. Hazard. Mater.* 181, 298-304.
- Sauve, S., Hendershot, W., and Allen, H. E. (2000). "Solid solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter (TOC)," *Environ. Sci. Technol.* 34, 1125-1131.
- Shi, J., Li, Z. W., Gong, W. Q., and Pan, G. (2007). "Uptake and partitioning of Cd and Zn by two non-hybrid rice cultivars in different growth stages: Effect of cultivars, soil type and Cd spike," *Asian J. Ecotoxicol.* 2, 32-40.

- Teng, Y., Ni, S., Wang, J., Zuo, R., and Yang, J. (2010). "A geochemical survey of trace elements in agricultural and non-agricultural topsoil in Dexing area, China," *J. Geochem. Explor.* 104, 118-127.
- Udovic, M., and Lestan, D. (2009). "Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching," *Chemosphere* 74, 1367-1373.
- Yuan, J. H., Xu, R. K., and Zhang, H. (2011). "The forms of alkalis in the biochar produced from crop residues at different temperatures," *Bioresour. Technol.* 102, 3488-3497.
- Zhang, A., Cui, L., Pan, G., Li, L., Hussaina, Q., Zhang, X., Zheng, J., and Crowley, D. (2010a). "Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China," *Agric. Ecosyst. Environ.* 139, 469-475.
- Zhang, J., and Huang, W. (2000). "Advances on physiological and ecological effects of cadmium on plants," *Acta Ecol. Sinica.* 20, 514-523 (in Chinese).
- Zhang, L., Li, L., and Pan, G. (2009a). "Variation of Cd, Zn and Se contents of polished rice and the potential health risk for subsistence-diet farmers from typical areas of South China," *Environ. Sci.* 30, 2792-2797.
- Zhang, L., Li, L., Pan, G., Cui, L., and Hu, Z. (2009b). "Effects of phosphorus and foliar zinc fertilizers on reducing grain Cd concentration of rice grown in a polluted paddy," *Ecol. Environ. Sci.* 18, 909-913 (In Chinese).
- Zhang, Y., Tang, Q., Zou, Y., Li, D., Qin, J., Yang, S., Chen, L., Xia, B., and Peng, S. (2009c). "Yield potential and radiation use efficiency of "super" hybrid rice grown under subtropical conditions," *Field Crops Res.* 114, 91-98.
- Zhang, W., Huang, H., Tan, F., Wang, H., and Qiu, R. (2010b). "Influence of EDTA washing on the species and mobility of heavy metals residual in soils," *J. Hazard. Mater.* 173, 369-376.
- Zhou, Q. X., and Song, Y. F. (2004). *Remediation of Contaminated Soils: Principles and Methods*, Science Press, China, Beijing (In Chinese).

Article submitted: March 20, 2011; Peer review completed: May 8, 2011; Revised version received and accepted: May 14, 2011; Published: May 17, 2011.