Modest amendment of sewage sludge biochar to reduce the accumulation of cadmium into rice(Oryza sativa L.): A field study*

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Abstract

Much research has considered the influence of biochars on the availability and phytoaccumulation of potentially toxic elements (PTEs) from soil. However, the vast majority of these studies use, what are arguably, unrealistic and unpractical amounts of biochar (10, 50 and even up to 100 t/ha). To offer a more realistic insight into the influence of biochar on PTE partitioning and phytoaccumulation, a field study, using modest rates of biochar application (1.5, 3.0 t/ha), was undertaken. Specifically, the research investigated the influence of sewage sludge biochar (SSBC) on the accumulation of Cd into rice (Oryza sativa L.) grown in Cd contaminated (0.82 ± 0.07 mg/kg) paddy soil. Results indicated, Cd concentrations in rice grains to significantly ($p < 0.05$) decrease from 1.35 ± 0.09 mg/kg in the control to 0.82 ± 0.07 mg/kg and 0.80 ± 0.21 mg/kg in the 1.5 t/ha and 3.0 t/ha treatments, respectively. Accordingly, the hazardous quotient (HQ) indices for Cd, associated with rice grain consumption, were also reduced by ~40%. SSBC amendment significantly ($p < 0.05$) increased grain yields from 1.90 ± 0.08 g/plant in the control to 2.17 ± 0.30 g/plant and 3.40 ± 0.27 g/plant in the 1.5 t/ha and 3.0 t/ha treatments, respectively. Thus, the amendment of SSBC to contaminated paddy soils, even at low application rates, could be an effective approach to mitigate Cd accumulation into rice plants, to improve rice grain yields, and to thereby improve food security and protect public health.

Introduction

Cadmium (Cd) is one of the most toxic heavy metal pollutants to humans (WHO, 1992). Cd is readily transfer, via food, into humans and it has a long biological half-life (WHO, 1992). The intensification of human activities, including mining and ore processing, has resulted in severe soil Cd contamination around the world (Oporto et al., 2012; Li et al., 2014); and this has brought with it an increased risk to crop safety and public health (Zhao et al., 2012; Robson et al., 2014). As the dominant Chinese staple food, rice (Oryza sativa L.) is widely cultivated in China. The safety of rice production plays an important role in the social and economic development of China. In some area of China, including Guangdong and Hunan, Cd concentrations, particularly in paddy soils, have become elevated due to the mining activities and the use of mining wastewater in field irrigation (Zhai et al., 2008;Wang et al., 2014). Rice produced under these circumstances has been shown to have greater accumulation of Cd and as a consequence consumption of this ‘tainted’ rice results in much greater exposure to Cd (Simmons et al., 2005; Meharg et al., 2013). In southern China, for example in Guangdong, the dominant soils are acidic and of low organic carbon content; here, Cd is more mobile, has higher bioavailability and is more readily accumulated into rice grain (Zhao et al., 2010). A survey conducted in Youxian, in Hunan province (southern China), indicated that 73% of rice grain samples obtained from mine impacted paddy soils exceeded the Chinese national food standard for Cd; of 0.2 mg/kg (Wang et al., 2016). In light of the issue, there is a need to develop techniques for the remediation of Cd contaminated soil.

In that last decade, pyrolysis has emerged as a cost-effective strategy to deal with the treatment of municipal sewage sludge. Pyrolysis converts the municipal sewage sludge into biochar, a carbonaceous solid product that is enriched surface functional groups and has a well-developed pore structure (Agrafioti et al., 2013; Yuan et al., 2015). Pyrolysis treatment of sewage sludge has been shown to decrease extractable concentrations of organic pollutants, such as PAHs (Zielinska and Oleszczuk, 2015), and the bioavailable fractions of toxic elements (Khan et al., 2014; Lu et al., 2015) present within it. Thus, pyrolysis represents a treatment approach that can reduce the chemical risks associated with sewage sludge. Biochar, including biochar produced form sewage sludge, has been proposed as a useful soil amendment that has been shown to manipulate soil pH and water retention capacity, to enhance soil fertility, and to promote the growths of plants (Mendez et al., 2012; Song et al., 2014; Liu et al., 2014). Of significance to the focus of this manuscript, biochar has been shown to decrease the bioavailability of potentially toxic elements (PTEs) in soils and, as a consequence, suppress the uptake and translocation of these contaminants by plants (Khan et al., 2015; Waqas et al., 2015). For instance, Khan et al. (2013) reported the amendment of SSBC to reduce the bioaccumulation of PTEs (including Cd and Cu), and that increasing biochar dosage (up to 10%) led to sustained decrease in PTE bioaccessibility. These finding suggests that SSBC may be a promising material for the restoration of Cd contaminated soil and by extension a mean through which to improve crop safety.

To date, research regarding the utilization of biochars as soil amendments for PTE remediation is limited with the majority of studies being conducted at in pot experiments, rather than at field scales. Significantly, the effects of biochar, and specifically SSBC, amendment on the bioaccumulation of different PTEs are inconsistent. Mendez et al. (2012) found the amendment of SSBC decreased the plant availability of Ni, Zn, Pb and Cd in soils comparing to the soils amended with sewage sludge. Waqas et al. (2015) found the bioaccumulation of Cd, Cu, Zn and As into tomato were decreased following SSBC application, but in his another study, with cucumber (Waqas et al., 2014), the bioaccumulation of Cd was reported to increase in the SSBC amended treatments. The amendment of SSBC has been reported to decrease the bioaccumulation of Cr and Pb into rice plants but increased that of Cd (Khan et al., 2013). Therefore, further research is required to obtain a better understanding of the effect of SSBC amendment on PTE bioavailability and bioaccumulation from contaminated soils.

It is salient to note, that many studies use applications of biochar that are unrealistic in a practical sense. A few studies have used biochar application rates of ~100 t/ha (Rajkovich et al., 2012; Joseph et al., 2013) and many more studies application rates in the range 10-50 t/ha (Hossain et al., 2010; Liu et al., 2013; Chen et al., 2016). Such large application rates are, arguably, unrealistic given the availability of resources to make biochar, the physical effort required to incorporate such large volumes of biochar into the soil and the cost that would be associated with such endeavors. Thus, there is pressing need to establish the influence biochar has on PTE availability and hytoaccumulation when applied to soil at more modest and practicable application rates (<5 t/ha).

To address current knowledge gaps, a field trial was set up in a Cd-contaminated paddy soil, in Hunan province, China, wherein SSBC were applied at modest application rates of 1.5 and 3 t/ha. The present study was conducted (i) to evaluate the effect of modest SSBC amendment on the growth of rice plant and the accumulation of Cd into rice plants from contaminated paddy field; (ii) to calculate the changes in metal intake and quotients (HQ) associated with rice consumption.

Materials and methods

Location of field trial site

The field trial was conducted on a rice farm located in Feilongqiao village (27_43.9730N, 112_56.9400E), Hunan province in southern China. The mean annual temperature was 16.7e18.3 _C, and the average annual precipitation was 1300 mm (subtropical monsoon moist climate). Due to the production and discharge activities of industries including mining and smelting factories, local paddy soils were contaminated with PTEs with Cd being the primary contaminant. Soil properties are provided in Table 1.

Sewage sludge biochar(SSBC)

The SSBC was prepared at the Institute of Urban Environment, Chinese Academy of Sciences. Municipal sewage sludge, which was collected from a wastewater treatment plant of Xiamen city; it was hydrothermal carbonized at 160 _C for 1 h, and then pyrolyzed at 500 _C for 3 h under oxygen-limited condition. For the field trial, the SSBC was ground to pass through a 2 mm sieve and then mixed thoroughly before application to the soil. SSBC properties are provided in Table 1.

Set-up of field trial

Three treatments were used to investigate the effect of SSBC amendment on the accumulation of PTEs by rice (Oryza sativa L.), in which the rates of SSBC application were 0 (CK), 1.5 (C1) and 3.0 t/ha (C2), respectively. For each treatment, a large experimental area (approximately 1000 m2) was used. Before rice transplantation in April 2015, the surface soils in the 0e25 cm layer were firstly plowed and broken up. Then, the SSBC was spread on the surface, and thoroughly mixed with the surface soils. Thereafter, the land was flattened. Xiangwanxian-13, a traditional local rice cultivar, was chosen as the experimental cultivar. The water management was performed according to the conventional practices of the local farmers (detail information is provided in the Supporting materials).

Plant sampling and analysis

In July 2015, the rice plants were harvested. Six composite plant samples, each consisting of 10 whole plant samples randomly selected from each treatment were obtained. Following their transfer to the laboratory, the plant samples were washed with deionized water and oven-dried at 90 _C for 48 h. Thereafter, each plant sample was separated into four parts (shoot, root, grain and husk), and stored dry until their analysis.

The measurement of plant height and tiller number were conducted after the sampling. The dry weight of shoot, root, grain and husk of the rice plants were measured. For the analysis of PTE concentration, subsamples of shoot, root, grain and husk were crushed, ground, and passed through a 0.2 mm sieve. Samples of shoot, root, grain and husk were then digested with HNO3(65%, Merck, EMSURE®) using a Microwave oven (Mars 5, CEM Incorporation, Matthews, NC, USA) according to the protocol developed by Williams et al. (2007). Plant reference materials (GBW10010 and GBW10015; purchased from the National Research Center for Standards in China) were digested and analyzed, as were reagent blanks, for quality control of the data. The concentrations of Cd, Cu, and Zn in the digestates were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500cx, Agilent Technologies Incorporation, Santa Clara, CA, USA). The recovery rates of metals from the reference materials ranged from 78 to 110%.

Soil sampling and analysis

On harvest, six soil samples at the depth of 0e15 cm were collected from each treatment. Following their transfer to the laboratory, soil samples were air-dried, at room temperature, and sieved (2 mm). Subsamples of soils were then ground and passed through the 0.149 mm sieve and taken forward for PTEs quantification.

The pH of soil samples was measured using a pH meter (UB-7, Denver Inc., USA) at the ratio of 1 g soil:2.5 mL deionized water. The content of organic matter was determined by wet oxidation using dichromate (Schulte, 1995). The content of C, N and S of the soil samples were measured using a Vario Max CNS Analyzer (Elementar incorporation, Hanau, Germany). In order to determine available nitrate-nitrogen (NO3_N) and ammonium-nitrogen (NH4_N) soil samples (1 g) were extracted with 2 mol/L KCl (Khan et al., 2013), while available P (Olsen-P) was determined using 0.5 mol/L NaHCO3 (20 mL) solution for the extraction of soil samples (1 g) (Olsen and Sommers, 1982). The total PTE concentrations of soils were analyzed using HNO3-HClO4 digestion-ICP-MS measurement (Li et al., 2004). Available PTE concentrations were determined using 1 mol/L NH4NO3 (20 mL) for the extraction of soil samples (1 g) (Gryschko et al., 2005).

Calculation of estimated daily intake (EDI) and hazard quotient (HQ) indices of PTEs in rice grains The calculation of estimated daily intake (EDI) of PTEs (Cd, Cu and Zn) through consumption of rice grains was conducted using the following equation (Eq. (1)) (Zheng et al., 2015):

EDI ¼ IRGrain _ Conmetal

BW

(1)

where IRGrain, Conmetal, and BW represented the rice grain intake rate (0.218 kg/day; Meharg et al., 2009), metal concentrations in rice grain (mg/kg), and average body weight (BW of 56.8 kg; MEP China, 2014), respectively.

The hazard quotient (HQ) indices for the metals in rice grain were determined using the following equation (Eq. (2)):

HQ ¼ EDI

RfD

(2)

where RfD represented the oral reference dose. RfD for Cd, Cu and Zn; these were 1, 40 and 300 mg/kg/day, respectively (MEP China, 2014).

Statistical analysis

Statistical analysis was performed using the SPSS 22.0 software (SPSS Inc., USA). One-way analysis of variance (ANOVA) was conducted to evaluate the differences among treatments, in which significant effects were compared using the Turkey's test ($p < 0.05$).

Results

Effect of SSBC amendment on the biomass and grain yields of rice plants

The growth of rice plants was enhanced by the amendment of SSBC (Fig. 1). The average plant height of rice plants grown in the paddy soils, amended with 1.5 t/ha SSBC, in the C1 treatment, was significantly ($p < 0.05$) increased to 75.7 ± 4.9 cm/plant compared to 68.2 ± 5.1 cm/plant in the CK treatment (Fig. 1a). Where the rate of SSBC amendment was increased to 3.0 t/ha, in the C2 treatment, the average plant height was increased to 77.3 ± 2.9 cm/plant. In addition, SSBC amendment resulted in a significant ($p < 0.05$) increase in the average tiller number of rice plants in the C1 (2.6 ± 0.7) and C2 (3.0 ± 1.0) treatments with respect to the CK treatment (1.9 ± 0.6).

Accordingly, rice plant biomass also significantly increased in SSBC amended treatments ($p < 0.05$) (Fig. 2). In the C1 treatment, the average dry weight of shoots and roots of rice plants were 6.10 ± 0.83 g/plant and 1.70 ± 0.44 g/plant, respectively. These values being approximately 1.1 and 1.4 fold greater than the control values (5.44 ± 0.54 g/plant and 1.24 ± 0.44 g/plant). When the rate of SSBC amendment was increased to 3.0 t/ha, the average dry weight of shoots and roots of rice plants in the C2 treatment were increased to 7.06 ± 1.04 g/plant and 2.25 ± 0.64 g/plant, respectively.

These values being approximately 1.3 and 1.8 fold greater than the control value. The grain yield of rice plants also increased in the SSBC amended treatments (Fig. 2c). In the C1 treatment, the average grain yield of rice plants was insignificantly ($p > 0.05$) increased to 2.17 ± 0.30 g/plant comparing to 1.90 ± 0.08 g/plant in the control treatment. As the rate of SSBC amendment was increased to 3.0

t/ha, the average grain yield of rice plants in the C2 treatment was significantly increased to 3.40 ± 0.27 g/plant ($p < 0.05$). In addition, in the CK treatment, the average dry weight of rice husk was 1.22 ± 0.01 g/plant, while in the C1 treatment, the average dry weight was insignificantly ($p > 0.05$) increased to 1.26 ± 0.25 g/plant. As the rate of SSBC amendment was increased to 3.0 t/ha, in the C2 treatment, the average dry weight of rice husk was significantly ($p < 0.05$) increased to 1.43 ± 0.40 g/plant (Fig. 2d).

Effect of SSBC amendment on Cd accumulation in rice plants

The accumulation of Cd by rice plants was significantly ($p < 0.05$) decreased by SSBC amendment (Fig. 3). In the C1 treatments, applied with 1.5 t/ha SSBC, the concentration of Cd in the grain was 0.82 ± 0.07 mg/kg, which was approximately 60%, and significantly ($p < 0.05$) lower, to that of the CK treatment (1.35 ± 0.09 mg/kg). With increasing SSBC amendment in the C2 treatment, the Cd concentration of the grain decreased further, to 0.80 ± 0.21 mg/kg (the C2 value being significantly lower than the control value but not significantly different to that of the C1 treatment).

The Cd concentrations of shoots and roots in the CK treatment were 4.80 ± 1.06 mg/kg and 3.37 ± 0.36 mg/kg, respectively. With the C1, 1.5 t/ha SSBC, amendment the Cd concentrations of the shoots and roots were not significantly different to those in the CK treatment. However, in the C2 treatment, the Cd concentrations of the shoots and roots were significantly decreased to 4.01 ± 0.42 mg/kg and 2.54 ± 0.63 mg/kg, respectively ($p < 0.05$).

For the rice husk, the Cd concentration in the CK treatment was 1.50 ± 0.29 mg/kg. This significantly decreased to 1.48 ± 0.24 mg/kg and 1.43 ± 0.29 mg/kg in the C1 and C2 treatments, respectively.

Estimated daily intakes and hazard quotient indices of metals in rice grains

The EDI and HQ of Cd are listed in Table 3. In all treatment, with or without SSBC amendment, the EDI of Cd was higher than RfD (1 mg/kg/day) recommended by the MEP China (2014). The HQs of Cd were observed to be in the range 3.07e5.20. These HQs, being greater than 1, indicate the Cd levels in rice grain to be in excess of the recommended limit. SSBC was effective in reducing EDI from 5.20 in the CK treatment to 3.13 and 3.07 in the C1 and C2 treatments, respectively. Accordingly HQ in the C1 and C2 treatments fell by approximately 40%. These calculations indicate that while SSBC was effective in reducing the dietary exposure to Cd it did not mitigate the risks to below safe limits.

Changes of NH4NO3 extracted PTEs in soils

As shown in Fig. 4, the concentration of NH4NO3 extracted Cd in soils were changed in the SSBC amended treatments. In the CK treatment, the concentration of NH4NO3 extracted Cd in soil was 0.33 ± 0.06 mg/kg. In contrast, with SSBC amendment, the concentrations of NH4NO3 extracted Cd were significantly ($p < 0.05$) decreased to 0.24 ± 0.07 mg/kg (C1) and 0.22 ± 0.05 mg/kg (C2) ($p < 0.05$).

Discussion

It is well-known that amendment of biochar to croplands can enhance crop productivity (Zhang et al., 2012; Bakar et al., 2015). As showed in Figs. 1 and 2, the plant height, tiller number and grain yield were all increased in the treatments containing SSBC. Similar increases in biomass were also observed in the dry weight of shoots and roots of rice plants. Grain yields of rice plants were 1.1 times (C1) and 1.8 times (C2) greater than in the CK treatment. It has been reported that biochar, derived from different organic solid wastes, can indirectly enhance plant growth through improving soil fertility and increasing the supply of nutrients and trace elements to plants (Hossain et al., 2010). In this study, as showed in Table 2, the concentration of available NH4, NO3 and P of soils as well as soil organic matter were all increased with increased SSBC amendment. Thus, the improvement of soil fertility associated with SSBC amendment would have supported improved rice plant growth and grain yields.

Metal bioaccumulation in rice grains, shoots, roots and husks were influenced by the SSBC amendment to varying extents. SSBC amendment reduced the concentrations of Cd in grain, shoots and roots (Fig. 3). Only in the case of Cd in grain did both C1 and C2 SSBC treatments result in a significant decrease in metal accumulation relative to the control (there were no significant difference between C1 and C2 values). In addition, although the grain yield and biomass of rice plant were both increased in the treatments containing SSBC, the total metal mass in rice grains, shoots and husks were not significantly increased (Table S1). Only in the rice roots, were the total mass of Cd increased with increased SSBC amendment. Thus, while the growth of rice plant was prompted by the SSBC amendment, the uptake of PTEswas suppressed. Regarding the co-existing PTEs Cu and Zn, SSBC amendment significantly decreased Cu accumulation into grains and shoots (Fig. S1), and more markedly reduced Zn accumulation in the shoots (Fig. S2). Thus, these results suggested that the SSBC amendment could affect accumulation of PTEs, other than Cd, in rice plant and result in lower accumulation and therefore lower concentrations of PTEs in rice grain. A probable reason for the decreased PTE accumulation into rice plants observed was the decrease in the bioavailable fractions of metals in the SSBC amended soils.

The SSBC prepared from municipal sewage sludge contained 0.42 ± 0.10 mg/kg for Cd. However, the pyrolysis process lead to the stabilization of PTEs in SSBC, resulting in lower amounts of NH4NO3 extractable PTEs (i.e. 0.10 ± 0.01 mg/kg Cd). So, with modest amendment of SSBC, the input of available PTEs into soils were limited. Furthermore, with the interaction of PTEs with the soil biochar matrix, the total amounts of NH4NO3 extractable PTEs were not increased; but in this study they were significantly decreased (Fig. 4 and Fig. S3). Several manuscripts have considered pH conditions, created by SSBC amendment, could have contributed to lower PTE availability; these then underpinning the decrease in the accumulation of Cd and Cu observed.

In particular, the SSBC amendment decreased the metal accumulation in rice grain and as a consequence, reduced its potential hazardous to human health via rice grain consumption. A decrease of Cd concentration in rice grain (40e41%) was observed (Fig. 3), while the concentration of Cu or Zn in rice grain was 5.5e19% lower than that in the CK treatment (Figs. S1 and S2). In addition, the EDIs and HQs for metals in grains were decreased (Table 3 and Table S2).

The HQs for Cd were most markedly reduced; decreasing from 5.20(CK) to 3.13(C1) and 3.07(C2), respectively. Similar result had been reported by Cui et al. (2011) in which the decrease in rice grain Cd concentration (16.8e61.9%) was found following amendment of wheat straw derived biochar (at 10e40 t/ha) to a paddy soil. In our study, the rate of SSBC application was far less than in Cui et al. (2011); nonetheless, reductions in PTE concentrations in grain were still observed. Thus, the results suggested SSBC amendment applied at a more feasible rate could also be an effective approach for the mitigation of PTE phytoaccumulation from soil. Furthermore, since municipal sewage sludge is more readily available in larger quantities (compared to other organic solid waste, such as wheat straw (Cui et al., 2011)), the utilization of SSBC amendment could be more cost-effective.

Regarding the HQs for metals associated with the consumption of rice grain, it is apparent that rice grownin the control CK soil had a very high potential to damage human health (Cd HQ > 5), and while SSBC did not completely abate this issue (to yield a HQ < 1), significant improvement was observed in the SSBC amended treatments.

HQs of 3.13 and 3.07 were calculated for rice grown in the C1 and C2 treatments, respectively. The results of present study indicated the potential for SSBC amendment, at modest application rates (1.5 and 3 t/ha) to reduce dietary Cd intake via rice consumption.

Conclusions

With the amendment of SSBC into paddy soils, the biomass and grain yield of rice plants were increased, while the bioaccumulation of Cd in rice grain, shoot, root and husk were reduced. In particular, the Cd concentrations in grains were decreased following SSBC amendment, and the EDIs and HQs for metals associated with rice consumption were reduced as a consequence. Collectively, the results of this study suggest SSBC, applied to soil at very modest application rates (1.5e3 t/ha), could deliver an effective approach for the remediation of Cd polluted soils. Such application rates are realistically achievable, and therefore, this research points towards a potential solution to the acute issue of finding a practicable approach to mitigate the transfer of Cd from polluted soils into rice.

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Figures and Tables

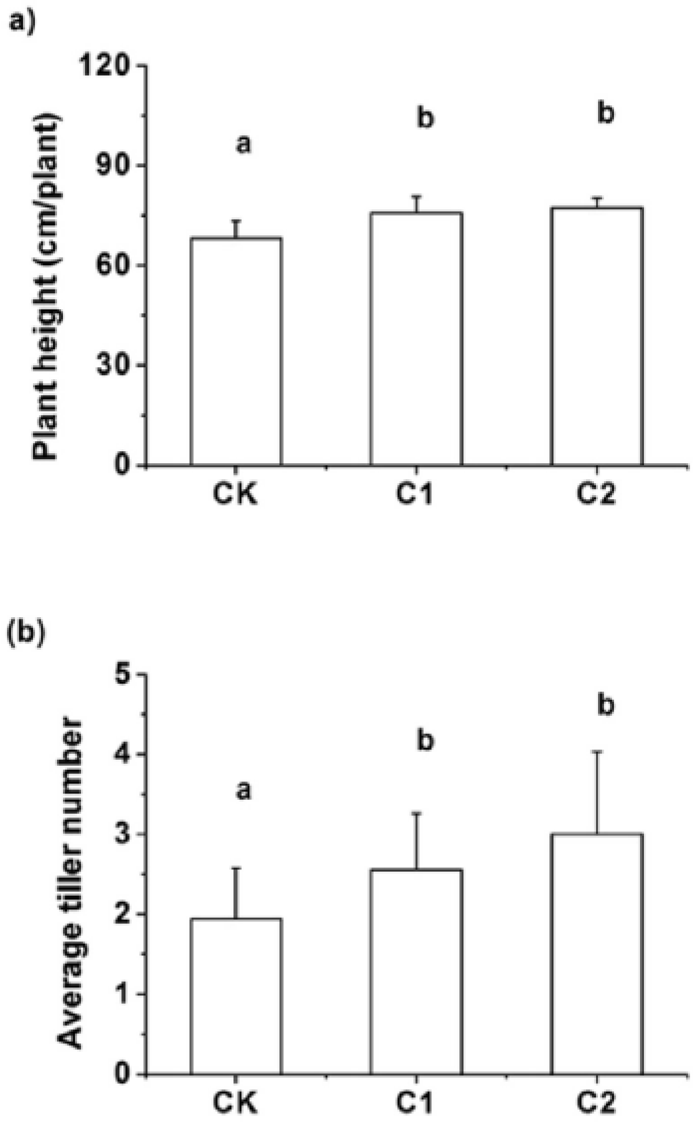
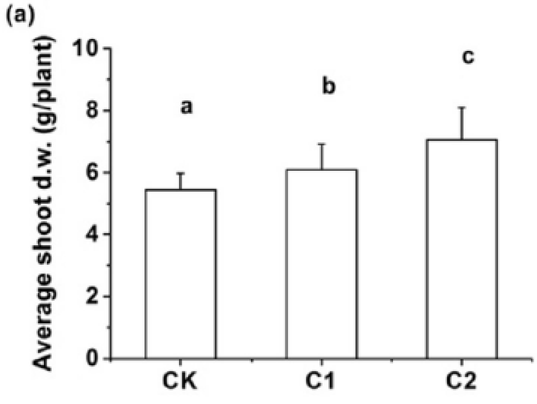
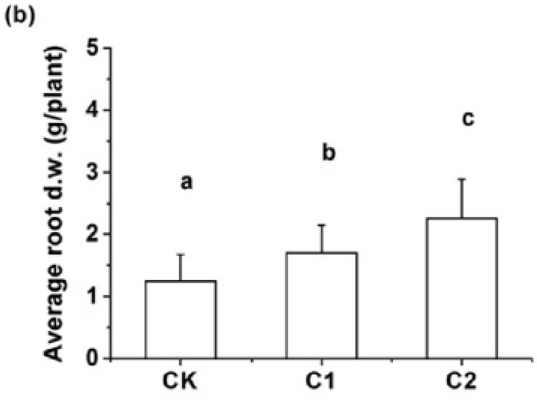
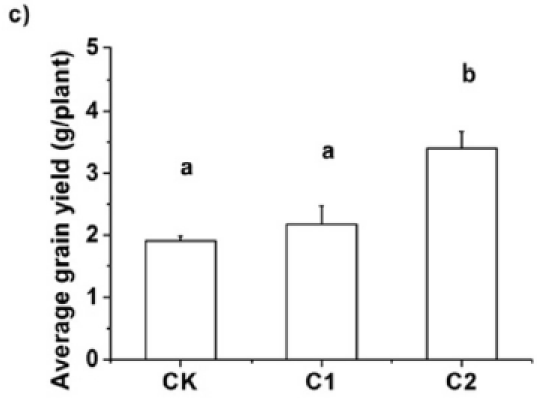


Fig. 1. Effect of biochar amendment on the plant height and tiller number in control soil 0 t/ha (CK) and soil amended with SSBC at application rates of 1.5 t/ha (C1), and 3.0 t/ha (C2). The different lower case letters indicate a significant difference between biochar treatments ($p < 0.05$).


(a)
Average shoot d.w. (g/plant)
0
2
4
6
8
10
a
b
c
CK
C1
C2


(b)
Average root d.w. (g/plant)
0
1
2
3
4
5
a
b
c
CK
C1
C2


c)
Average grain yield (g/plant)
0
1
2
3
4
5
a
a
b
CK
C1
C2

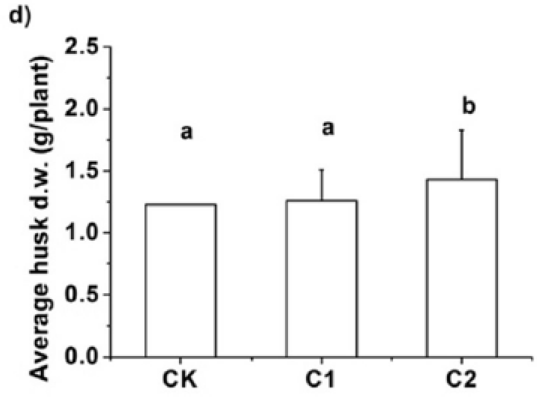
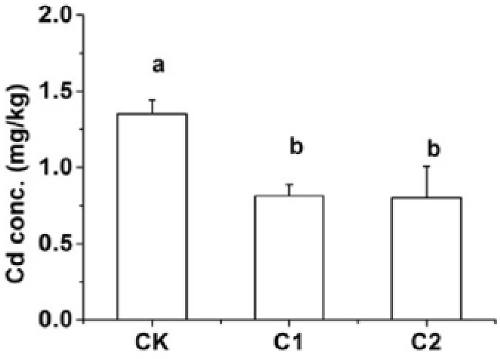
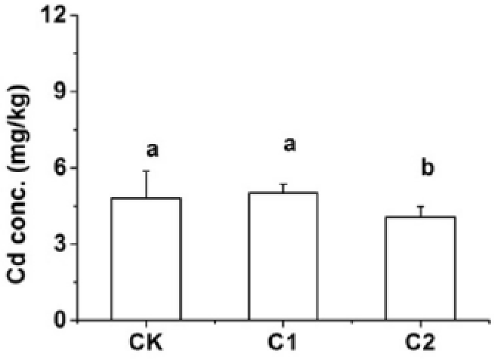

d)
Average husk d.w. (g/plant)
0.0
0.5
1.0
1.5
2.0
2.5
a
a
b
CK
C1
C2

Fig. 2. Effect of biochar amendment on the biomass of rice plant and grain yield in control soil 0 t/ha (CK) and soil amended with SSBC at application rates of 1.5 t/ha (C1), and 3.0 t/ha (C2). The different lower case letters indicate a significant difference between biochar treatments ($p < 0.05$).

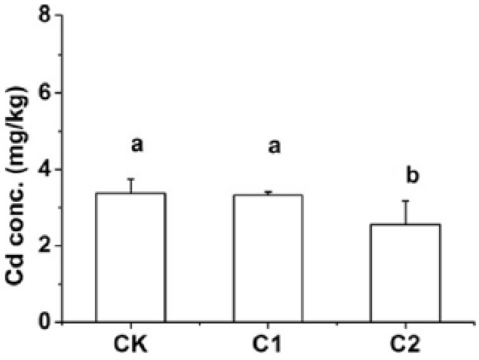
a) grain Cd



b) shoot Cd



c) root Cd



d) husk Cd

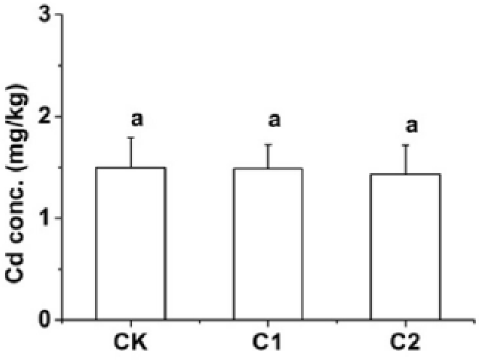


Fig. 3. Effect of biochar amendment on the accumulation of cd in the rice plants grown in control soil 0 t/ha (CK) and soil amended with SSBC at application rates of 1.5 t/ha (C1), and 3.0 t/ha (C2). Different lower case letters indicate a significant difference between biochar treatments ($p < 0.05$).

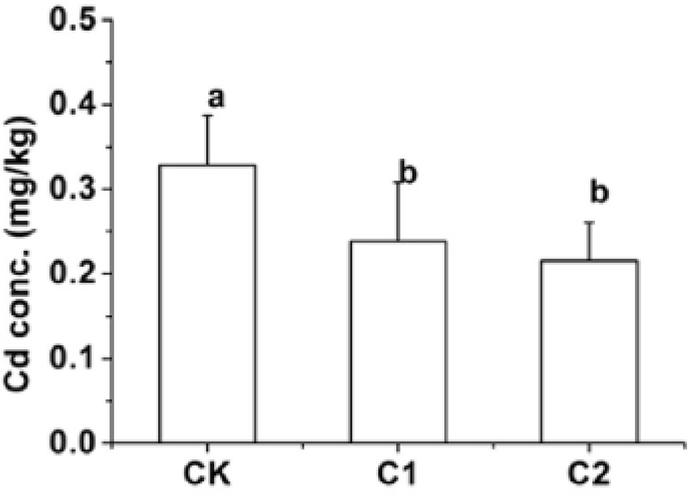


Fig. 4. NH_4NO_3 extracted amounts of Cd in control soil 0 t/ha (CK) and soil amended with SSBC at application rates of 1.5 t/ha (C1), and 3.0 t/ha (C2). The different lower case letters indicate a significant difference between biochar treatments ($p < 0.05$).

Table 1
Properties of soil and biochar.

	Soil	Sewage sludge biochar
pH	4.50 ± 0.05	7.19 ± 0.37
Organic matter (%)	3.34 ± 0.71	13.39 ± 0.39
C (%)	1.69 ± 0.04	12.38 ± 0.04
N (%)	0.21 ± 0.002	0.52 ± 0.01
S (%)	0.35 ± 0.004	1.59 ± 0.14
Available NH_4^+ (mg/kg)	39.1 ± 0.3	79.4 ± 16.4
Available NO_3^- (mg/kg)	26.7 ± 0.3	29.3 ± 0.1
Available P (mg/kg)	3.30 ± 0.55	9.74 ± 2.96
Total Cd (mg/kg)	0.82 ± 0.07	0.42 ± 0.10
Total Cu (mg/kg)	29.9 ± 0.9	2750 ± 39
Total Zn (mg/kg)	122.1 ± 8.4	3341 ± 133
Available Cd (mg/kg)	0.30 ± 0.01	0.10 ± 0.01
Available Cu (mg/kg)	0.16 ± 0.01	285 ± 7
Available Zn (mg/kg)	10.7 ± 0.3	38.3 ± 3.3

Table 2
Properties of soils in different treatments after cultivation.

	CK	C1	C2
pH	4.50 ± 0.06^{a}	4.79 ± 0.08^{b}	4.83 ± 0.17^{b}
Organic matter (%)	3.41 ± 0.68^{a}	3.71 ± 0.96^{a}	4.67 ± 1.44^{a}
C (%)	1.66 ± 0.08^{a}	1.79 ± 0.09^{ab}	1.86 ± 0.03^{b}
N (%)	0.20 ± 0.01^{a}	0.21 ± 0.02^{a}	0.22 ± 0.01^{a}
S (%)	0.35 ± 0.01^{a}	0.35 ± 0.01^{a}	0.34 ± 0.02^{a}
Available NH_4^+ (mg/kg)	41.4 ± 5.0^{a}	43.3 ± 1.6^{ab}	48.9 ± 3.9^{b}
Available NO_3^- (mg/kg)	33.2 ± 4.2^{a}	41.8 ± 1.2^{b}	44.6 ± 0.4^{b}
Available P (mg/kg)	3.52 ± 0.54^{a}	3.96 ± 1.24^{a}	4.22 ± 0.93^{a}

Note: The different lower case letters indicate a significant difference between biochar treatments ($p < 0.05$).

Table 3
RfD (μg/kg/day), EDI (μg/kg/day) and HQ for individual metal associated with the consumption of rice grain.

	RfD	EDI			HQ		
		CK	C1	C2	CK	C1	C2
Cd	1	5.20	3.13	3.07	5.20	3.13	3.07