Mitigating heavy metal accumulation into rice (*Oryza sativa* L.) using biochar amendment — a field experiment in Hunan, China

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Abstract A field experiment was conducted to investigate the effect of bean stalk (BBC) and rice straw (RBC) biochars on the bioavailability of metal(loid)s in soil and their accumulation into rice plants. Phytoavailability of Cd was most dramatically influenced by biochars addition. Both biochars significantly decreased Cd concentrations in iron plaque (35–81 %), roots (30–75 %), shoots (43–79 %) and rice grain (26–71 %). Following biochars addition, Zinc concentrations in roots and shoots decreased by 25.0–44.1 and 19.9–44.2 %, respectively, although no significant decreases were observed in iron plaque and rice grain. Only RBC significantly reduced Pb

concentrations in iron plaque (65.0 %) and roots (40.7 %). However, neither biochar significantly changed Pb concentrations in rice shoots and grain. Arsenic phytoavailability was not significantly altered by biochars addition. Calculation of hazard quotients (HQ) associated with rice consumption revealed RBC to represent a promising candidate to mitigate hazards associated with metal(loid) bioaccumulation. RBC reduced Cd HQ from a 5.5 to 1.6. A dynamic factor's way was also used to evaluate the changes in metal(loid) plant uptake process after the soil amendment with two types of biochar. In conclusion, these results highlight the potential for biochar to mitigate the phytoaccumulation of metal(loid)s and to thereby reduce metal(loid) exposure associated with rice consumption.

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Introduction

Biochar is receiving increasing attention due to its benefits in agricultural and environmental contexts. There is growing evidence that the application of biochar to soil has the potential to mitigate global warming (Lehmann 2007), improve soil quality (Fellet et al. 2011), reduce the bioavailability of organic contaminants (Li et al. 2013), increase nutrient and water retention capacity of soil (Abel et al. 2013; Zheng et al. 2013a), and thereby increase crop yield (Zhang et al. 2012).

Rice is recognized as a staple global food with over 400 million metric tons of milled rice being consumed each year. Approximately half of the world's population is reliant upon rice for sustenance (Zhu et al. 2008). Several studies have reported enhanced plant growth and rice grain yield following

biochar addition to soil (Dong et al. 2013; Khan et al. 2013). These findings are clearly important in the context of food security and provisioning for an increasing global population. However, rice is also recognized as a major dietary source for metal(loid) exposure (Zhu et al. 2008; Williams et al. 2009). Many studies, from various countries, have reported metal(loid) concentrations that exceed guidance values (Herawati et al. 2000; Wang et al. 2001; Cheng et al. 2006b; Meharg et al. 2009; Rogan et al. 2009). The exposure to metal(loid)s through the consumption of contaminated rice brings elevated risk to human health. Given the global importance of rice as a food stuff there is a pressing need to establish means or technologies to mitigate the phytoaccumulation of metal(loid)s into rice. With biochar amendments expected to become commonplace, to sequester carbon and increase crop yield, there stands the possibility of ancillary benefits in terms of reduced metal(loid) levels in rice grain and, as a consequence, reduced dietary metal(loid) exposure associated with rice consumption. Such a proposition is not unfounded; several studies have already established the ability of biochar to immobilize metals, such as Cd, Zn, Cu, and Pb, in the soil and to thereby reduce their accumulations within plants. Incorporation of biochars into soil caused significant immobilization of Cd, Cu, and Pb in a shooting range soil and thereby reducing the accumulation of these metals in Indian mustard (Park et al. 2011). Further to these studies, large decreases in Cd, Zn, and Pb accumulation in rice plant grown in a historically contaminated soil after biochar additions were observed in our previous pot study (Zheng et al. 2012). Biochar amendment to soil has recently been reported to reduce Cd accumulation in rice plant from Cd-contaminated rice paddies (Cui et al. 2011; Bian et al. 2013). However, not all metal(loid)s have shown such positive response to biochar amendment to soil. Arsenic concentrations in porewater following biochar addition to soil (Beesley et al. 2010) were shown to increase >30-folds, while our previous pot study (Zheng et al. 2012) indicated considerable (threefold) increase in phytoaccumulation of As into rice shoots.

Although many studies have reported the effect of biochar on the immobilization of heavy metals in soils, information is still lacking regarding the effectiveness of biochar amendment for multielemental immobilization and accumulation into edible plant parts under field conditions. The intention of this research was to consider the potential of biochar to afford dual benefits of improved grain yield and improved food safety (through the reduction in metal(loid) phytoaccumulation). Thus, the present study was conducted (i) to investigate the influence of biochar additions on the mobility of metal(loid)s in a multielemental contaminated paddy field soil; (ii) to investigate their accumulations in rice plants; (iii) to calculate changes in metal(loid) intake and hazard quotients (HQ) associated with rice consumption; and (iv) to compare the effects of biochars made from different parent materials (bean stalk and rice straw).

Materials and methods

Study area and biochar description

The field experiment was carried out at a rice field in Xinma Town, Zhuzhou, Hunan Province, China (N27°50', E113°02') and was initiated in 2011. The paddy field soil was historically contaminated with metal(loid)s, due to inundation with waste water, over the course of about 50 years, from a nearby galvanizing mill.

Biochar was made from bean stalk (BBC) and rice straw (RBC). Each type of biomass was charred in a kiln at 500 °C for 8 h and then ground to pass through sieves with 2-mm mesh. Selected physicochemical properties of the field soil and biochars are presented in Table 1.

Experimental design

There were three treatments in this experiment: control (no addition of biochar) and addition of BBC or RBC. Three plots (1.2 × 1.2 m) were produced for each treatment type. BBC and RBC (<2 mm) were added into the soil at a rate of 20 tons ha⁻¹, respectively, and mixed thoroughly with top soil (0–20 cm depth) via manual plowing. Synthetic fertilizers were applied as basal fertilizers at 150 kg P₂O₅ ha⁻¹, 150 kg K₂O ha⁻¹, and 150 kg N ha⁻¹. Following a period of 2 weeks, rice seedlings (*Oryza sativa* L.), which had been raised for 4 weeks in clean soil were transplanted into experimental plots. Rice used here was a traditional local cultivar named Zhongyou 978. Urea was supplied (100 kg ha⁻¹) 2 weeks after transplanting of the rice seedlings. The water management was as follows: at tillering stage, a regime of shallow water

Table 1 Physicochemical properties and elemental concentrations in soil, BBC, and RBC

	Soil	Background soil	BBC	RBC	Regulatory limits
pH	6.1		9.2	10.5	
CEC	12.5		27.5	32.1	
TC (%)	1.4		44.5	27.4	
TN (%)	0.15		1.85	1.26	
Cd (μg g ⁻¹)	4.7	0.126 ^a	0.15	0.10	0.3 ^b
Zn (μg g ⁻¹)	360	94.4 ^a	265.7	255.4	200 ^b
Pb (μg g ⁻¹)	124	29.7 ^a	14.0	12.8	250 ^b
As (μg g ⁻¹)	34	15.7 ^a	0.14	0.79	30 ^b
K (%)	—		5.0	7.9	
P (%)	—		0.37	0.46	

CEC cation exchange capacity (cmol kg⁻¹)

^a Concentrations in background soil of Hunan, China (CNEMC 1990).

^b Environmental quality standard for agricultural soils of China, GB15618-1995

submerged irrigation and humid irrigation was alternated. Afterwards, the flooded land was drained for about a week before the jointing stage. Thereafter, an intermittent shallow water submerged, irrigation regime was used during the jointing-booting stage and the filling stage, and the land was unwatered for a week before harvest.

Sampling and chemical analysis

Samples including top soil and roots, shoots, and ears of mature rice were taken after 4 months growth. Soil samples were taken at five random points (away from the edge of experimental plot) in each of the replicated plots. These five samples were combined to give a composite sample for the plot. Soil samples were air-dried, crushed, and sieved with 2-mm mesh. Shoots were cut at the soil surface, washed with deionized water; fresh weight were recorded and dried at 70 °C for 48 h. The corresponding root samples (0–20 cm depth) with attached soil were taken and washed gently with deionized water through a sieve to dislodge soil from the roots. The clean-washed root samples were stored at 2 °C for further treatments. The corresponding ear samples were washed with deionized water, dried at 70 °C for 48 h, and then separated into husk and rice grain using a rice sheller.

Iron plaque was extracted from fresh root surfaces using dithionite–citrate–bicarbonate (DCB) solution containing 0.03 M sodium citrate and 0.125 M sodium bicarbonate, with the addition of 0.02 g sodium dithionite per milliliter (Taylor and Crowder 1983; Liu et al. 2004). The root sample per cluster was immersed in DCB solution (200 ml) at 25 °C for 60 min, and then rinsed three times with deionized water. Rinse water was poured into the DCB extracts and the total volume was made up to 250 ml with deionized water. The final solution was passed through a 0.45-μm nylon filter and refrigerated at 2 °C until analysis (Liu et al. 2004). After extraction by DCB solution, fresh roots were oven-dried at 70 °C for 48 h.

Metal(loid) concentrations in dried plant samples were determined as follows. Samples were ground to a fine powder, weighed into 50 ml polyethylene centrifuge tubes, and digested with concentrated HNO₃ (2 ml) in a microwave digester (Sun et al. 2008).

Finely ground (<0.149 mm) soil and biochar samples were digested with HNO₃–HCl–HClO₄ (3:1:1) for determination of total element concentrations. Available metal(loid) concentrations in the soil were assessed using 1 M NH₄NO₃ as an extractant (1:2.5 w/v). 1 M NH₄NO₃ (25 ml) was added to soil samples (10 g) contained within 50 ml flask and shaken for 2 h. Elements in dissolved samples and extracts were determined using inductively coupled plasma mass spectroscopy (ICP-MS, 7500a, Agilent Technologies, USA) for Cd, Zn, Pb, and As with indium isotopes (In115) as internal standards

(10 μg l⁻¹), and ICP optical emission spectroscopy (ICP-OES, Optima 2000, Perkin-Elmer, USA) for P and K. Certified reference material (CRM) GBW07603 (bush twigs and leaves), GBW10010 (GSB-1; rice), spikes, and blanks were used for quality control. The recovery of the elements determined ranged from 82 to 115 %.

The cation exchange capacity (CEC) was determined referring to modified barium chloride compulsive exchange method (Lee et al. 2010). Total carbon (TC) and nitrogen (TN) analyses of soil and biochar were conducted on a solid TC/TN analyzer (Vario EL III, Elementar Analysen systeme, Germany).

Daily intake of metal(loid)s and hazard quotient (HQ)

The estimated daily intake (EDI) of metal(loid)s through consumption of rice was determined using the following equation (Eq. 1):

$$EDI = \frac{IR_{\text{Rice}} \times C_{\text{PTEs}}}{BW} \quad (1)$$

where IR_{Rice} , C_{PTEs} , and BW represent the rice intake rate (kg day⁻¹; 218 g day⁻¹; Meharg et al. 2009), metal(loid) concentrations in rice, and average body weight (70 kg).

The hazard quotient (HQ) indices for the metal(loid)s in rice was calculated using the equation detailed by the U.S. Environmental Protection Agency (USEPA 2014).

$$HQ = \frac{EDI}{RfD}$$

where RfD represents the oral reference dose. RfD for Cd, Zn, Pb, and As were 1, 300, 3.5, and 0.3 μg kg⁻¹ day⁻¹, respectively (USEPA 2014).

Dynamic factor (DF) of metal(loid) bioavailability (BIO_{dyn}) and bioaccumulation (BA_{dyn})

The DF of metal(loid) bioavailability (BIO_{dyn}) in soil and that of metal(loid) bioaccumulation (BA_{dyn}) in rice roots (BA_{dyn_roots}), shoots (BA_{dyn_shoots}), and grain (BA_{dyn_grain}) were calculated using the following Eq. 2, Eq. 3, Eq. 4, and Eq. 5, respectively, referring to Baltrėnaitė et al. (2012, 2015):

$$BIO_{\text{dyn}} = \frac{[M]_{\text{bav}} \text{ in BBC or RBC treatment}}{[M]_{\text{soil}} \text{ in BBC or RBC treatment}} \times \frac{[M]_{\text{soil}} \text{ in control}}{[M]_{\text{bav}} \text{ in control}} \quad (2)$$

$$BA_{\text{dyn_roots}} = \frac{[M]_{\text{root}} \text{ in BBC or RBC treatment}}{[M]_{\text{soil}} \text{ in BBC or RBC treatment}} \times \frac{[M]_{\text{soil}} \text{ in control}}{[M]_{\text{root}} \text{ in control}} \quad (3)$$

$$BA_{\text{dyn_shoots}} = \frac{[M]_{\text{shoot}} \text{ in BBC or RBC treatment}}{[M]_{\text{soil}} \text{ in BBC or RBC treatment}} \times \frac{[M]_{\text{soil}} \text{ in control}}{[M]_{\text{shoot}} \text{ in control}} \quad (4)$$

$$BA_{\text{dyn_grain}} = \frac{[M]_{\text{grain}} \text{ in BBC or RBC treatment}}{[M]_{\text{soil}} \text{ in BBC or RBC treatment}} \times \frac{[M]_{\text{soil}} \text{ in control}}{[M]_{\text{grain}} \text{ in control}} \quad (5)$$

where $[M]_{\text{bav}}$ and $[M]_{\text{soil}}$ represent NH_4NO_3 -extractable metal(loid) concentration and total metal(loid) concentration in soil, respectively. $[M]_{\text{roots}}$, $[M]_{\text{shoots}}$, and $[M]_{\text{grain}}$ represent metal(loid) concentration in roots, shoots, and grain of rice plant, respectively. All data used were means of four replicates for each treatment, and the concentration units were consistent in milligrams per kilogram.

Statistical analysis

All data were subjected to one-way analysis of variance (ANOVA). Significant effects were compared using the Tukey's test ($p < 0.05$). Statistical analysis was performed using the SPSS 16.0 software (SPSS, USA).

Results

Characteristics of the soil and biochars

The soil used in this study was moderately acidic (pH 6.1). Concentrations of metal(loid)s in the soil were elevated with respect to background soil concentrations: Cd ($\times 37.3$), Zn ($\times 3.8$), Pb ($\times 4.2$), and As ($\times 2.2$) (Table 1). Concentrations of Cd, Zn, and As also elevated by factors of 15.7, 1.8, and 1.1, respectively, above guidance values for agricultural soil regulations of China (GB15618-1995). Only Pb concentrations were lower (50 %) than the agricultural soil regulation value.

BBC and RBC had high pH and CEC and also high carbon levels (Table 1). These were in agreement with other studies

(Atkinson et al. 2010; Hale et al. 2011; Yuan et al. 2011). In addition, BCs used here also contained nutrients such as K (5.0–7.9 %), P (0.4–0.5 %), and N (1.3–1.9 %) (Table 1). Properties of biochar varied depending on the feedstock material (Table 1). RBC was more alkaline (pH 10.5) than BBC (pH 9.2). CEC ($32.1 \text{ cmol kg}^{-1}$), K (7.9 %), and P (0.46 %) concentrations of RBC were 16.7, 58, and 24.3 % higher than that of BBC, respectively, whereas TC (27.4 %) and TN (1.26 %) concentrations of RBC were 38.4 and 31.9 % lower than that of BBC. The difference in properties between BBC and RBC are consistent with reports that account chemical constituents in BCs to vary with feedstock and pyrolysis conditions used (Atkinson et al. 2010).

Concentrations of Cd, Pb, and As in both RBC and BBC were much lower than in the soil used in this study (Table 1). However, concentrations of Zn in RBC and BBC were similar to those in soil. While there are no regulatory limits in place for biochar, the concentrations of all four metal(loid)s were much lower than the Chinese regulation limit set for sludge to be used for agriculture (GB18918-2002). Cd concentration in RBC and BBC were an order of magnitude lower than maximum values reported for a range of biochars (Freddo et al. 2012), while Zn, Pb and As fell within a factor of 3.

Influence of biochar on biomass yield

The essential plant nutrients in biochar (Table 1) are usually conducive to crop production (Park et al. 2011; Uzoma et al. 2011). In our present study, shoot weights were increased though not significantly ($p > 0.05$). Grain weights were increased and decreased in BBC and RBC treatments by 57.5 and 7.4 %, respectively, but these changes were also not significant ($p > 0.05$; Table 3). RBC addition significantly increased K and P concentrations of rice shoot by 20.3 and 29.6 %, respectively, but this outcome was not observed in the BBC treatment. These results indicate the potential to improve plant growth is dependent on type of BC applied.

NH_4NO_3 -extractable concentrations of metal(loid)s

NH_4NO_3 extractable fractions of metal(loid)s represented a very small portion of the total metal loadings: Cd (< 3 %), Zn (< 0.6 %), Pb (< 0.1 %), and As (< 0.1 %). Biochar addition significantly decreased initial NH_4NO_3 -extractable concentrations of soil Cd, Zn, and Pb (0.14 , 2.03 , and $0.15 \text{ } \mu\text{g g}^{-1}$) by 66.0–90.1 %, 73.1–92.2 %, and 74.1–91.0 %, respectively (Fig. 1). Given the concentrations of Cd, Zn, and Pb in BBC, RBC, and soil (Table 1) and the rate of application these changes cannot be attributed to a dilution effect. Rather they reflect biochar induced changes to metal(loid) partitioning (see “Discussion”). In contrast to Cd, Zn, and Pb, extractable As concentration ($0.02 \text{ } \mu\text{g g}^{-1}$) increased by up to 73.3 % (Fig. 1). Again, these changes are proposed to reflect

Fig. 1 NH_4NO_3 -extractable concentrations of Cd, Zn, Pb, and As in un-amended soils (white), BBC treatments (grey), and RBC treatments (black). Different letters above bars indicate significant difference at $p < 0.05$ between treatments ($n = 4$)

biochar-induced changes to As partitioning (the As concentrations in BBC and RBC were 242 and 42 times lower than that in the receiving soil). RBC treatment resulted in the largest decrease in NH_4NO_3 -extractable concentrations of soil Cd, Zn, and Pb and the largest increase in that of As. There was no significant change in As concentration following BBC addition. These changes in metal(loid) extractability are attributed, in part, to changes in pH following BC amendment to soil. Soil pH (6.2) was increased to 6.7 (BBC) and 7.4 (RBC) after biochar additions (Table 2). The greater increase in pH associated with RBC amendment is suggested to have underpinned the greater reduction in Cd, Zn, and Pb and the greater increase in As extractability (see later “Discussion”).

Metal(loid) and nutrient uptake by rice plant

The formation of iron plaque on the root surface of rice plants was reduced by up to 49.0 % following RBC amendment, but it was not significantly influenced by BBC amendment (Table 2). Concentrations of Cd and Pb in iron plaque were decreased significantly by up to 81.4 and 65.0 %, respectively,

after BC (especially RBC) amendment, whereas neither BC treatments had a significant effect on concentrations of Zn and As in iron plaque (Fig. 2).

Biochar amendment decreased concentrations of Cd and Zn in rice root by 29.6–74.9 % and 25.0–44.1 %, respectively ($p < 0.05$). The largest decrease was observed in the RBC treatment. Root Pb was significantly decreased by RBC (40.7 %) but not by BBC. Root As concentrations were not changed significantly after BC addition (Fig. 2).

Shoot concentrations of Cd and Zn were decreased significantly by 42.9–79.3 % and 19.9–44.2 %, respectively ($p < 0.05$), most noticeably in the case of RBC (Fig. 2). Neither of BC additions caused significant reductions in shoot Pb concentration with respect to the control, although shoot Pb concentration in RBC treatment was significantly lower than in BBC treatment. An increase in shoot As concentration (34.2 %) occurred in the BBC treatment but not in RBC treatment.

Regarding rice husk and grain, biochar additions significantly decreased Cd concentrations, but had no significant effects on the concentrations of Pb and As (Fig. 2; Table 3).

Table 2 Influence of biochar additions on: soil pH, iron plaque formation (DCB-Fe), shoot K and P concentrations, and shoot fresh weight (FW) of rice plants

Treatment	Soil pH	DCB-Fe (mg g^{-1} RDW)	Shoot K concentration (mg g^{-1} DW)	Shoot P concentration (mg g^{-1} DW)	Shoot weight (kg FW m^{-2})
Control	6.2±0.06c	30.3±3.0a	16.8±1.7b	1.5±0.2b	2.60±0.28a
BBC	6.7±0.06b	27.8±3.6a	18.4±0.7ab	1.5±0.1b	2.78±0.27a
RBC	7.4±0.06a	15.5±1.9b	20.3±1.4a	2.0±0.1a	3.40±0.79a

Different letters in a same column represent significant difference between treatments ($p < 0.05$; $n = 4$)

Fig. 2 Concentrations of Cd, Zn, Pb and As in iron plaque, root, shoot and husk of rice plant (*Oryza sativa* L.). Un-amended soil (white), BBC treatments (grey), and RBC treatments (black). Different letters above columns indicate significant difference at $p < 0.05$ between treatments for the same tissue of rice plant ($n = 4$)

Cd concentrations were decreased by 70.6 and 46.2 % for husk ($3.9 \mu\text{g g}^{-1}$ initially) and by 70.9 and 25.8 % for rice grain ($1.8 \mu\text{g g}^{-1}$ initially) after RBC and BBC amendments, respectively ($p < 0.05$). RBC addition caused larger decreases in Cd concentration in rice husk and grain than BBC. For Zn, the influence was dependent on BC type. An increase ($p < 0.05$) in Zn concentration (25.1 %) in rice grain was observed following RBC addition, yet no effect was observed in the BBC treatment. BBC addition significantly decreased Zn concentration in husk by 12.5 %, but no significant effect was observed following RBC amendment. Cd concentrations in rice grain were 1.6 to 8.0 factors higher than the Chinese regulation limit set for food ($0.2 \mu\text{g g}^{-1}$), but grain As concentrations were below the maximum limit ($0.2 \mu\text{g g}^{-1}$) (Table 3).

For nutrient elements, shoot K and P concentrations were increased significantly by 20.3 and 29.6 %, respectively, in RBC but not in BBC treatment (Table 2). Also, BCs increased

shoot weights although the increases were not significant statistically ($p > 0.05$).

Estimated daily intake of metal(loid)s and hazard quotients

EDIs and HQs of metal(loid)s are listed in Table 4. EDIs of Zn in soil and both BC treatments ($87\text{--}115 \mu\text{g kg}^{-1} \text{ day}^{-1}$) were all below the RfD ($300 \mu\text{g kg}^{-1} \text{ day}^{-1}$) set by the USEPA, and as a consequence, their HQs were < 1 (Table 4). After BC addition, Zn HQ decreased by 5.4 % in the BBC treatments and increased by 25 % in the RBC treatments, but HQs remained well below 1 ($0.29\text{--}0.38$). EDI for Pb in the control soil ($0.21 \mu\text{g kg}^{-1} \text{ day}^{-1}$) much lower than its RfD ($3.5 \mu\text{g kg}^{-1} \text{ day}^{-1}$) and, as a consequence, Pb HQ was very small (0.06). The addition of BBC and RBC did not alter the EDI or the HQ for Pb. EDI for As in the control soil ($0.48 \mu\text{g kg}^{-1} \text{ day}^{-1}$) was higher than RfD ($0.3 \mu\text{g kg}^{-1} \text{ day}^{-1}$), and as a consequence, As HQ (1.6)

Table 3 Influence of biochar additions on concentrations of Cd, Zn, Pb, and As in rice grain and grain yield [dry weight (DW)]

	Metal(loid) in rice grain ($\mu\text{g g}^{-1}$ DW)				Grain weight (kg DW m^{-2})
	Cd	Zn	Pb	As	
Control	$1.78 \pm 0.29\text{a}$	$29.5 \pm 1.9\text{b}$	$0.069 \pm 0.01\text{a}$	$0.154 \pm 0.01\text{a}$	$0.41 \pm 0.07\text{a}$
BBC	$1.32 \pm 0.08\text{b}$	$27.9 \pm 2.8\text{b}$	$0.067 \pm 0.01\text{a}$	$0.161 \pm 0.01\text{a}$	$0.64 \pm 0.18\text{a}$
RBC	$0.52 \pm 0.03\text{c}$	$36.9 \pm 2.9\text{a}$	$0.067 \pm 0.01\text{a}$	$0.168 \pm 0.01\text{a}$	$0.38 \pm 0.08\text{a}$
CML	≤ 0.2	—	≤ 0.2	≤ 0.2	

Different letters in a same column represent significant difference between treatments ($p < 0.05$; $n = 4$).

CML Chinese maximum allowable limit of heavy metals in food set by Ministry of Health of the People's Republic of China and Standardization Administration of China (MHPRC and SAC 2012), $0.2 \mu\text{g g}^{-1}$ for As represents the limit of inorganic arsenic in rice grain

Table 4 RfD ($\mu\text{g kg}^{-1} \text{ day}^{-1}$), EDI ($\mu\text{g kg}^{-1} \text{ day}^{-1}$), and HQ for individual metal(loid)s associated with the consumption of rice grown in control soils and soils amended with BBC and RBC

	RfD	EDI			HQ		
		Control	BBC	RBC	Control	BBC	RBC
Cd	1	5.5	4.1	1.6	5.54	4.11	1.62
Zn	300	92	87	115	0.31	0.29	0.38
Pb	3.5	0.21	0.21	0.21	0.06	0.06	0.06
As	0.3	0.48	0.50	0.52	1.60	1.67	1.74

Where HQ was <2, this has been indicated in italics

exceeded acceptable limits. The addition of BBC and RBC increased EDI (to 0.50 and $0.52 \mu\text{g kg}^{-1} \text{ day}^{-1}$, respectively) and HQ (to 1.67 and 1.74, respectively), but these increases were only trivial (of the order 4.5–9.1 %). The most dramatic changes to EDI and HQ were observed for Cd. Cd EDI in the control soil ($5.5 \mu\text{g kg}^{-1} \text{ day}^{-1}$) was greatly in excess of the RfD ($1 \mu\text{g kg}^{-1} \text{ day}^{-1}$), and as a consequence, the Cd HQ (5.5) was well in excess of acceptable levels. Addition of BBC and RBC resulted in EDI decreases of 25.8 and 70.8 %, respectively. In light of this, Cd HQ saw a modest decrease (to 4.1) in the BBC treatment and a very pronounced decrease (to 1.6) in the RBC treatment.

Calculated DF of metal(loid) bioavailability and bioaccumulation

Dynamic factor of metal(loid) bioavailability in soil was showed in Fig. 3a. The BIO_{dyn} of soil Cd, Zn, and Pb in BC

treatments were all below 1 (0.26–0.34) though not for that of As (1.08–1.73). The BIO_{dyn} of soil Cd, Zn, and Pb in RBC treatment were 70.9, 71.0, and 65.1 % lower than that in BBC treatment, respectively, whereas that of As in RBC was 60.3 % higher than in BBC amendment. $\text{BA}_{\text{dyn_roots}}$ of Cd, Zn, Pb, and As were lower than 1 (0.70–0.87) in BBC treatment, and only that of As in RBC treatment was 1.04 (>1; Fig. 3b). The $\text{BA}_{\text{dyn_roots}}$ of Cd, Zn, and Pb were 64.4, 25.5, and 31.4 % lower in RBC versus BBC treatment, but that of As was 29.5 % higher in RBC. After RBC addition, $\text{BA}_{\text{dyn_shoots}}$ of Cd, Zn, Pb and As were all lower than 1 following the sequence of $\text{Cd} < \text{Zn} < \text{As} < \text{Pb}$ (Fig. 3c). The $\text{BA}_{\text{dyn_shoots}}$ of Cd and Zn were below 1 versus higher than 1 for that of Pb and As in BBC treatment. Comparing with BBC amendment, $\text{BA}_{\text{dyn_shoots}}$ of Cd, Zn, Pb, and As in RBC treatment were dramatically lower by 63.8, 30.4, 39.0, and 46.5 %, respectively. Regarding rice grain, $\text{BA}_{\text{dyn_grain}}$ of Cd and Pb were lower than 1 in both BC treatments, especially for that of Cd (0.29–0.74; Fig. 3d). Only a slight reduction compared to 1 occurred in BBC treatment for $\text{BA}_{\text{dyn_grain}}$ of Zn (0.95). The $\text{BA}_{\text{dyn_grain}}$ of As were larger than 1 in both BC treatments.

Discussion

To our knowledge, this is the first investigation of the influence of BC upon the accumulation of multiple metal(loid)s in rice plants under field conditions. The paddy field herein was historically tainted by multiple metal(loid)s including Pb, As, Zn, and Cd. NH_4NO_3 -extractable concentrations of soil Cd,

Fig. 3 Dynamic factors of metal(loid) bioavailability in soil (a), and dynamic factors of metal(loid) bioaccumulation in roots (b), shoots (c), and grain (d) of rice plant. BBC treatments (grey) and RBC treatments (black). The dashed line indicates the area below which the bioavailability of metal(loid) in soil and concentration of metal(loid) in plant tissues [root (b), shoots (c), and grain (d)] are not higher than those in the control soil

Zn, and Pb decreased significantly following biochar addition, this was particularly true for RBC (Fig. 1). However, RBC also increased NH_4NO_3 -extractable concentrations of As (Fig. 1). Potential toxic elements (PTEs; except As) concentrations in rice plant changed by varying degrees after biochar additions; decreases in phytoaccumulation was especially noticeable for Cd (Fig. 2; Table 3).

Soil pH and P are suggested to be key factors influencing the decrease in NH_4NO_3 -extractable concentrations of soil Cd, Zn, Pb and the increase in that of As after biochar addition. The biochar-induced pH increase (0.5–1.2 units) was very important for the immobilization of Cd, Zn, and Pb (Fig. 1), which is further supported by a significant correlation existed here between pH and NH_4NO_3 -extractable concentrations of soil Cd, Zn, and Pb (Fig. 4). Because the number of negatively charged surface sites in soil increases with increasing pH, and the sorption capacity of soil to cationic metals correspondingly increases (Bradl 2004). The pH increase subsequent to the application of biochar can also reduce metal extractability through promoting metal (co)precipitation as well as metal adsorption on specific biochar mineral phases (Houben et al. 2013; Rees et al. 2014). Finally, there are also other studies showing that metal mobility is reduced in the presence of biochar due to adsorption on the biochar surface (especially on carboxylic and phenolic groups; Uchimiya et al. 2011a, b). On the other hand, a probable increase in the silicon (Si) concentration of soil solution after biochar addition may also contribute to metal immobilization via the formation of silicate precipitates (Houben et al. 2014; Zheng et al. 2012; Gu et al. 2011). A significant increase in Si concentration of soil pore water after biochar (made from rice straw) addition was obtained in our recent study (Zheng et al. 2012). However, Si

solubility is not systematically increased in the presence of biochar. Biochar can increase or decrease Si solubility depending on several factors, including feedstocks, application rate, etc. (Houben et al. 2014). The effect of Si on metal immobilization in biochar-amended soils is worth studying. Regarding As, existing as negatively charged oxy-anions, an increase in pH can decrease the number of positively charged sites in soil and, consequently, lower the sorption capacity (Wilson et al. 2010). Thus, it was reasonable that biochar addition increased NH_4NO_3 -extractable concentration of As, especially the RBC treatment (Fig. 1; Fig. 4). In addition to an increase in soil pH, P entering into soil with biochar application (especially RBC) may also have been a contributing factor in immobilizing Cd, Zn, and Pb via the formation of phosphate precipitates (McGowen et al. 2001; Tang et al. 2004) and activating As via competing adsorption onto soil surface with arsenate (Jain and Loeppert 2000). Arsenate retained in soil particles can be desorbed by phosphate and released into soil solution. This process could also accelerate the reduction of arsenate and accordingly increase arsenite concentration in soil solution. Thus, because RBC contained higher P levels than BBC, it may have brought about higher NH_4NO_3 -extractable concentrations of As (Fig. 1).

The high levels of Cd, Zn, Pb, and As contained in iron plaque supports the general consensus that iron plaque has a high adsorption capacity for metal(loid)s (Liu et al. 2006; Lei et al. 2011). However, iron plaque sequestered less Cd and Pb after BCs amendment though Zn and As concentrations in iron plaque were not significantly influenced (Fig. 2). This was likely attributable to the immobilization of Cd and Pb in soil as indicated by the decreased NH_4NO_3 -extractable concentrations (Fig. 1), thus undergoing less transport to the roots.

Fig. 4 Relationship between soil pH and NH_4NO_3 -extractable concentrations of Cd, Zn, Pb, and As in un-amended soils and BBC and RBC treatments

It was hard to explain the insignificant influence on Zn concentrations of iron plaque despite the decrease of NH_4NO_3 -extractable Zn concentration following BC addition. One possibility was that the adsorption of iron plaque to Zn was always in a maximum adsorption state due to the particularly high Zn levels in soil solution. Less iron plaque was formed on root surface after additions of biochar than the control (Table 2). This may be due to the elevated P concentration following BC addition. An increase in P concentration may result in an enhancement of iron phosphate precipitation formation lowering iron mobility in soil solution and/or a reduction in root-oxidizing capacity of rice and retarding the development of iron plaque accordingly (Geng et al. 2005; Fu et al. 2014). The iron plaque may have prevented these metal(loid)s entering into rice plants, although its development was reduced.

Furthermore, biochar can also participate in a variety of biotic and abiotic redox-mediated reactions in soil. Some other studies showed that biochar-derived dissolved organic matter could increase Fe/Mn oxide solubilization from soils via reductive dissolution, enhance Cr(VI) reduction, but promote As(III) oxidation (Dong et al. 2014; Graber et al. 2014; Tong et al. 2014). These redox reactions caused by biochar addition play a considerable role in soil metal(loid)s availability due to potential formation of sulfide precipitation, loss of iron plaque, release of As from Fe/Mn oxide, etc.. These redox process induced by biochar addition and the relevant mechanisms require further studies.

Regarding metal(loid) in plant, Cd, Zn, and Pb concentrations in root, shoot, and husk were reduced significantly after biochar addition, RBC caused the largest decrease (Fig. 2). Plant As was slightly influenced by biochar amendment, only shoot As concentration increased in BBC treatment. Reductions in Cd and Pb accumulation by Indian mustard after biochar amendment were observed by Park et al. (2011). Similar changes in concentrations of Cd, Zn, and Pb in rice shoot influenced by biochar amendment were also observed in our pot experiments previously, yet not in that of As (Zheng et al. 2012). The increased NH_4NO_3 -extractable concentration of As herein was not translated into the increased As level in rice plant (Fig. 2). This was likely attributed to elevated Si level in rhizosphere competing with As for transporters and preventing As entering into rice root. Arsenite is taken up by rice roots mainly through the Si uptake pathway (Ma et al. 2008; Zheng et al. 2013b). The only increase in shoot As concentration in BBC indicated the influenced translocation of As in plant by biochar amendment in keeping with our previous study (Zheng et al. 2012). However, the pathway of As translocation in rice plant involving As sequestration in vacuoles, loading and unloading in xylem and phloem, and reduction or methylation responsible by enzymes remains poorly understood (Zhao et al. 2010). Much further research needs to be undertaken to unravel the mechanisms influencing As translocation in plants.

For concentrations in rice grain, different metal(loid)s had different responses to BCs addition (Table 3). Grain Cd concentration decreased markedly in both BC treatments; Pb and As concentrations were not affected significantly; while Zn concentration slightly increased and decreased in RBC and BBC treatments, respectively. A decrease in rice grain Cd concentration (by 16.8–61.9 %) was also reported under biochar amendment at 10–40 tons ha^{-1} in a field experiment (Cui et al. 2011). In the present study, grain Cd concentration reached up to $1.8 \mu\text{g g}^{-1}$ in rice grown in the control soils; this value being eight times higher than the Chinese maximum allowable limit (CML) of $0.2 \mu\text{g g}^{-1}$ set by the Ministry of Health of the People's Republic of China and Standardization Administration of China (Table 3). Although still higher than the maximum allowable limit, Cd concentrations in grain (about $0.5 \mu\text{g g}^{-1}$) biochar additions had decreased grain Cd concentration by up to 71 %. This decrease was greater than that reported by Cui et al. (2011). Grain As concentrations (0.154 – $0.168 \mu\text{g g}^{-1}$) in all treatments were lower than the CML of $0.2 \mu\text{g g}^{-1}$ (Table 3). Furthermore, BC addition resulted in no significant ($p < 0.05$) changes to grain As concentration. This outcome was observed even though available As concentrations in the RBC treatments were observed to significantly ($p < 0.05$) increase (Fig. 1). Linkage between available Pb concentrations [which change significantly ($p < 0.05$) following BC addition (Fig. 1)] and grain/husk Pb concentrations [which did not change significantly (Table 3, Fig. 2) following biochar addition] are likely attributable to the alteration of elemental translocation in plant by biochar treatment (Zheng et al. 2012). Biochar additions, which influenced soil pH, ionic strength, CEC, nutrient level, and microbial activity, can play a key role in plant physiological metabolism indirectly and subsequent elemental translocation. There are abundant Zn transporters dedicated to Zn uptake and translocation throughout rice plants (Ishimaru et al. 2011). For Pb, its translocation in plant is restricted to a great extent due to immobilization by the negatively charged pectins within cell wall, precipitation in intercellular space, accumulation in plasma membrane, or sequestration in the vacuoles (Shahid et al. 2012). Thus, only a small fraction of Pb absorbed by roots can enter into grain.

HQs less than one indicate daily intake of metal(loid)s to be less than the reference dose; this implies an absence of unacceptable risk to human health. The influence of BC upon EDIs and HQs was not standard across the range of metal(loid)s tested. Cd HQ was the most markedly influence by BC decreasing by up to 70.8 %, from 5.5 to 1.6 following RBC addition. Taking an overall average HQ of all metal(loid)s tested suggested a 49 % decrease in HQ following RBC addition. Significantly, the overall HQ was decreased from 1.88 to <1 (0.95; Table 4).

The values of BIO_{dyn} and BA_{dyn} below 1 in the present study implied that there were positive effects of reduction on

metal(loid)s bioavailability in soil and metal(loid)s accumulation in rice roots, shoots, and grain, respectively, caused by BC additions. The lower BIO_{dyn} and BA_{dyn} became, the larger effect of reduction biochar treatments made, and vice versa. According to these calculated DFs, the following information can be obtained. Both BC treatments reduced bioavailability of Cd, Zn, and Pb by 66.0–90.1 %, 73.1–92.2 %, and 74.1–91.0 %, respectively, and increased that of As by 8.1–73.3 %, especially in RBC treatment (Fig. 3a). RBC and BBC treatments had positive effects on reduction of metal(loid)s accumulation in roots (except for As in RBC case). The reduction extent in Cd, Zn, and Pb were 153.5, 76.2, and 201.3 % larger in RBC treatment than in BBC treatment (Fig. 3b). RBC addition reduced accumulations of Cd, Zn, Pb, and As in shoots by 79.3, 44.2, 25.0, and 28.2 %, respectively, and had higher effect of shoots metal(loid)s accumulation reduction than BBC. Only Cd and Zn accumulation in shoots were reduced under BBC amendment than control (Fig. 3c). Only a marked reduction occurred in grain Cd accumulation under both BC treatments. RBC treatment had a larger reduction effect on grain Cd accumulation than BBC (by 173.9 %; Fig. 3d). These dynamic factors are dimensionless, thus it is conducive to making comparisons between different treatments easily, or between our data and others in the dynamic factor's way.

The results obtained in the present study are significant as they show potential for BC to improve food (specifically rice) safety through its ability to mitigate the transfer of metal(loid)s from paddy soil to plant tissues. EDIs and HQ associated with rice consumption can be reduced as a consequence. Considering the important contribution of liming effect to metal immobilization after biochar addition, the interesting results may therefore be limited over time (Houben et al. 2013). Further study is needed to inquire into a long-term effect of biochar on metal immobilization and relevant mechanisms including factors of pH, functional groups, biotic and abiotic surface oxidation in the aging process (Cheng et al. 2006a; Houben et al. 2013; Uchimiya et al. 2011a).

Conclusions

Both biochar RBC and BBC additions effectively immobilized Cd, Zn, and Pb in historically multielemental contaminated paddy soil under field conditions. While these additions increased the mobility of soil As, there was no significant increase in concentrations of As in rice grain. Mechanisms affecting plant translocation of As, one of the major contaminants in rice, are badly in need of more research. Of the metal(loid)s considered, BC showed the greatest influence over Cd availability and its subsequent phytoaccumulation. Grain Cd concentration decreased by up to 71 % after BCs addition. Of the two BCs assessed RBC showed the greater potential to reduce Cd, Zn, and Pb accumulations in rice plant.

RBC additions successfully decreased overall HQ from 1.9 to an acceptable level (<1). Given that rice straw is a readily available agricultural residue, we suggest that its conversion to biochar and incorporation into metal(loid), particularly Cd, contaminated soil could be an achievable and cost-effective approach to mitigate metal(loid) exposure associated with rice consumption. In addition, the dynamic factor of metal(loid)s bioaccumulation in plant can be considered as a simple evaluation method to compare effects in chemical element uptake by plants between treatments.

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