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Effect of bamboo and rice straw biochars on the bioavailability of Cd, Cu, Pb and Zn to *Sedum plumbizincicola*

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ABSTRACT

Soil contamination with heavy metals has become a global concern because of its adverse effects on ecosystem health and food security. Soil amendments including biochar can reduce the bioavailability of heavy metals in contaminated soils and reduce their risk of entering the food chain. A pot experiment was conducted to investigate the effects of biochars derived from bamboo and rice straw on bioavailability and plant growth in a sandy loam paddy soil naturally co-contaminated with Cd, Cu, Pb and Zn. The soil was moderately acidic (pH = 5.7) and low in organic carbon content (8.7 g kg^{-1}). Bamboo and rice straw biochars, pyrolyzed at temperatures $\geq 500\,^{\circ}C$ and with two mesh sizes (< 0.25 mm and < 1 mm), were applied at three rates (0, 1% and 5%, w/w). A metal-tolerant plant, *Sedum plumbizincicola* X. H. Guo et S. B. Zhou sp. nov. was used in the plant growth experiment to examine the bioavailability of these metals. The addition of biochars to soil significantly ($p < 0.05$) increased the above-ground biomass of *S. plumbizincicola*. By the end of the experiment, soils amended with biochar had pH values significantly ($p < 0.05$) higher, this effect being more accentuated at the high biochar dose and small particle size. The solubility of Cd, Cu, Pb, and Zn as measured by Toxicity Characteristic Leaching Procedure (TCLP) was significantly lower ($p < 0.05$) in the biochar-amended soils than in the control soil. This was paralleled by significant reductions in Cd, Cu, Pb and Zn accumulated in the above-plant biomass of amended soils. Rice straw biochar reduced the concentration of Cu and Pb in the shoots by 46 and 71%, while bamboo biochar reduced concentration of Cd in the shoot by 49%. Finer biochar was more effective on reducing the concentrations of Zn in shoot than the coarse ones, while particle size had no effect on the concentrations of Cd, Cu and Pb in the shoot of *S. plumbizincicola*. In conclusion, the influence of biochar on heavy metal bioavailability varied not only with the feedstock and application rate of biochars, but also with the metal species. Therefore, biochar should be carefully designed to maximize the reduction of the bioavailability of a given heavy metal in soil.

1. Introduction

In recent decades, rapid industrial development has resulted in elevated levels of heavy metals in soils in Eastern and Southern China, which have resulted in great public health and environmental contamination concerns (Hu et al., 2007). Cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) often coexist in contaminated soils and there is currently no effective means for their concurrent removal (Jiang et al., 2012). Concerns about their mobility and bioavailability have increased because of food safety, potential health risks and its detrimental effects on the ecosystems (Uchimiya et al., 2010a). The application of soil amendments that bind or precipitate contaminants whilst promoting plant growth can reduce environmental risk (Vangronsveld et al., 2009; Beesley et al., 2011; Bolan et al., 2014).

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Biochar is the solid product derived from the pyrolysis of waste biomass, such as residues from agricultural and forestry production (Wang et al., 2010; Liu et al., 2011). Most biochars have a highly porous structure and contain various functional groups that are effective in the adsorption of metals (Wu et al., 2012). Numerous studies showed that, typically, the application of biochar to soil can potentially enhance the long term soil carbon pool (Lehmann, 2007), improve soil properties and crop yield (Jeffery et al., 2011; Kookana et al., 2011; Matovic, 2011), and reduce greenhouse gas emissions including N_2O, CH_4 and CO_2 (Dong et al., 2013; Zhang et al., 2013a). It has been demonstrated that biochar could bind and/or precipitate contaminants in soil and minimize the risk of entering the human food chain (Zhang et al., 2010; Uchimiya et al., 2012). Unlike other soil amendments, the longevity of biochar reduces the need for repeated applications and the potential introduction of new contaminants derived from these amendments (Zhang et al., 2013a).

While a number of studies have shown that biochar could significantly remove heavy metals from wastewaters (Chen et al., 2011; Lu et al., 2012; Xu et al., 2013), few studies have quantified the effect of adding biochar to contaminated soil systems. Recently, biochar from pyrolysis of different wastes has been used in various soil remediation experiments (Fellet et al., 2011; Karami et al., 2011). Many studies indicated that biochar could significantly contribute to the immobilization of certain heavy metals such as Cd, Pb and Zn in the soil (Beesley et al., 2010; Cao et al., 2011). However, the soils used in these studies were usually freshly spiked with heavy metals. Relatively few studies investigate the influence of biochar on the bioavailability of heavy metals in aged field contaminated soils.

The properties of biochar depend on the type of the feedstock and pyrolysis conditions (Wu et al., 2012). The selection of a specific type of feedstock is to a great extent determined by the availability of this material in the region where the biochar is likely to be produced, as this reduces the cost of transport while decreasing the carbon footprint of the biochar technology. Large quantities of crop residues (e.g., rice straw) are produced in China annually. In addition, bamboo, as a fast-growing timber crop commonly grown in this country, is an attractive feedstock for biochar production (Liu et al., 2011). A number of studies show that biochar addition can reduce the bioavailability of organic contaminants (Beesley et al., 2010), whereas less attention has been given to determining the effectiveness of biochar on bioavailability of heavy metals in soils (Park et al., 2011; Méndez et al., 2012). Therefore, the objective of this study was to evaluate the influence of biochar feedstock and particle sizes on immobilizing of heavy metals in soil, thereby reducing their accumulation in a metal-tolerant plant, *Sedum plumbizincicola* X. H. Guo et S. B. Zhou sp. nov. The effectiveness of immobilization was evaluated by determining the availability of Cd, Cu, Pb and Zn based on Toxicity Characteristic Leaching Procedure (TCLP) in a naturally co-contaminated soil. The bioavailability of the heavy metals was evaluated by the uptake of *S. plumbizincicola*.

2. Materials and methods

2.1. Soil and biochars

Soil was collected from an abandoned paddy field in Fuyang County, southwest of Hangzhou City, Zhejiang Province, China. The sandy loam soil developed from alluvial material was classified as paddy soil according to the Chinese soil classification (Gong, 1999). The dominant clay mineral was illite. This site received dust emitted from a copper smelter and the soil has been co-contaminated with Cd, Cu, Pb and Zn, which severely reduced crop plant growth (Liu et al., 2010), thereby leading to the abandonment of this site for cultivation. Topsoil (0–20 cm) was taken for the pot experiment. The bulk soil sample was thoroughly mixed, air-dried and passed through a 2-mm stainless steel sieve prior to the pot experiment. Selected soil properties are presented in Table 1.

Table 1
Physicochemical properties of the sandy loam paddy soil and biochars used in the experiment.

Property	Soil	Bamboo biochar	Rice straw biochar
Sand (%)	51.5	–	–
Silt (%)	38.9	–	–
Clay (%)	9.6	–	–
Olsen-P (mg kg^{-1})	18	–	–
Total P (g kg^{-1})	–	2.3	2.6
Electrical conductivity (ds m^{-1})	0.02	0.08	0.18
pH (H_2O)	5.7	9.5	10
Total C (g kg^{-1})	8.7	860	508
Total N (g kg^{-1})	2.5	4.5	16.6
Total H (g kg^{-1})	–	14.9	17.2
C_{org} (g kg^{-1})	8.7	839	470
C_{org}/N	–	186	28
Atomic H/C_{org}	–	0.21	0.44
Ash (%)	–	11.9	42.7
Cation exchange capacity (cmol kg^{-1})	5.3	15	45
Surface area (BET) (m^2 g^{-1})		907.4	36.7
Alkalinity (cmol kg^{-1})	–	123	152
Total Cd (mg kg^{-1})	1.4	Not detected	Not detected
Total Cu (mg kg^{-1})	693	19	47
Total Pb (mg kg^{-1})	527	Not detected	4.8
Total Zn (mg kg^{-1})	1471	33	197

Two biochar samples, a bamboo biochar and a rice straw biochar, were used in the experiment. Bamboo biochar was a commercial product from a local producer using a batch pyrolysis facility with a retention time of 3 h. Although its final temperature was not measured, it was suggested that the pyrolysis temperature would be approximately 750 °C. The straw biochar was produced using a continuous slow pyrolysis at a final temperature of 500 °C with a retention time of 30 min. Biochar samples were ground and sieved, yielding two different size fractions, fine (<0.25 mm) and coarse (<1 mm).

2.2. Pot experiment

In the pot experiment, the naturally co-contaminated paddy soil was used to evaluate the effect of bamboo and rice straw biochars on the bioavailability of mixed metal contaminants. Plastic pots (18 cm in diameter and 14 cm in height) were filled with 2 kg of soil, and amended with 0, 1% (w/w, equivalent to 15.6 t ha^{-1}) and 5% (w/w, equivalent to 78 t ha^{-1}) of bamboo or rice straw biochar. Each pot was fertilized with a basal dose of N, P and K at 156, 125 and 156 kg ha^{-1}, respectively. Each treatment was replicated four times. Once all the experimental units received the amendments, the pots were irrigated with deionized water to 70% of the field water holding capacity, and allowed to equilibrate for 2 weeks. The soil was severely contaminated with heavy metals (Table 1) and most plants could not survive in this soil. Therefore, *S. plumbizincicola*, a metal-tolerant plant, was chosen as an indicator plant to evaluate the effect of biochars on the bioavailability of the heavy metals. Four *S. plumbizincicola* per pot were transplanted in mid July 2012, and the number of plants was later thinned to 3 per pot after 4 weeks when all plants appeared to be established. The trial was carried out in a plant growth facility with a transparent roof to prevent rain from entering to the pots. The facility has no side walls. The average temperature during the period was 26 °C, with the maximum of 38 °C and minimum of 10 °C during the experimental period. Regular watering (2 to 4 times a week) with deionized water was maintained to prevent drought stress to the plants.

After 3 months of growth, the aboveground biomass of the plants was harvested. The harvested shoots were thoroughly washed with deionized water then oven-dried at 65 °C in paper bags until a constant weight was reached. Dried samples were ground with a stainless steel mill and stored for chemical analysis. The soil from each pot was air-dried and thoroughly mixed. The air-dried soil was passed through a 2-mm sieve to remove any visible roots.

2.3. *Chemical analysis*

The pH of biochar in water solution was measured at 1:20 (w/v) ratio after occasionally stirring over 1 h. The electrical conductivity (EC) of biochar was measured at 25 °C after suspending in water (1:10 w/w). The cation exchange capacity (CEC) was measured using 1 M ammonium acetate (pH 7) method (Lu, 1999). Ash content was determined using the ASTM D1762-84 method (ASTM International, 2013). The alkalinity of biochar was determined using the back titration method (Yuan and Xu, 2011). Briefly, 0.2 g of bamboo or rice straw biochar was weighed into plastic bottles. 40 mL of 0.03 M HCl solution was added into each bottle and shaken for 2 h at 25 °C. After the samples were left standing for 24 h, residual HCl was titrated to pH 7.0 with 0.5 M NaOH. The acid uptake of the biochar was converted to its alkalinity content (Yuan and Xu, 2011). Total C, H and N contents in biochars were determined by an elemental analyzer (Flash EA1112, Thermo Finnigan, Italy). Inorganic C was analyzed by determination of CO_2-C content with 1 M HCl treatment, as outlined in ASTM D4373-02 (ASTM International, 2007). Organic C was calculated as Total C subtracting Inorganic C, following the methods described in the IBI (2013) Biochar Standards. Surface area was determined by nitrogen sorption at 77 K in a surface analyzer (TristarII 3020, Micromeritica Instrument Corporation, USA). Before measurement, samples were thoroughly degassed at the out-gassing stations of the instrument at 573 K, 10^{-4} mbar for 8 h. The Brunauer–Emmett–Teller (BET) surface area of the biochars was calculated at the relative pressure of 0.05–0.30. Chemical analysis of the biochar particles was carried out with energy dispersive X-ray spectrometry (EDS) elemental mapping. The total phosphorous was measured with the molybdate–ascorbic acid procedure at 700 nm according to the method described by Lu (1999).

Soil pH was measured in a soil/water slurry at a 1:2.5 (w/v) ratio and the electrical conductivity (EC) was measured in a soil/water slurry at a ratio of 1:5 (w/v). Total N was measured by semi-micro Kjeldhal method, and available phosphorus (P) was extracted with 0.5 M $NaHCO_3$ and determined by colorimetry (UVA 132122 spectrophotometer, Thermo electron corporation, England). Organic C (OC) was determined by Walkley–Black method, and soil texture was determined using the pipette method, and the cation exchange capacity (CEC) of the soils was measured by the ammonium acetate (pH 7.0) method. All methods described above followed Lu (1999). Physicochemical properties and elemental analysis of the experimental soil and the biochars used are shown in Table 1. The total N, P concentration in the shoot of the plant was analyzed using H_2SO_4–H_2O_2 digestion, following the methods described by Lu (1999). The uptake of N, P by the shoot of each pot was calculated as follows: the content (mg pot^{-1}) = the concentration in the shoot × the dry weight of the shoot in each pot.

The solubility of heavy metals in the soil from each pot was estimated by the USEPA Toxicity Characteristic Leaching Procedure (TCLP) method 1311 (USEPA, 1992). Briefly, 1 g of soil sample was shaken in 20 mL of unbuffered glacial acetic acid solution (pH 2.88) for 18 h on an orbital shaker at 30 rpm, and then centrifuged at 4000 rpm for 20 min. The supernatant was filtered through quantitative filter paper. The filtrates were analyzed for metals using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 2000, PerkinElmer Co., USA). The plant material was analyzed for metals using a nitric acid digestion (Zarcinas et al., 1987). The samples were mixed and filtered, and analyzed for metals with ICP-OES.

2.4. *Statistical analysis*

Analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine the statistical significance of the biochar treatment effects on soil properties, shoot yield of *S. plumbizincicola*, and solubility and plant uptake of heavy metals using SPSS 17 software (SPSS Inc., USA). Variability in the data was expressed as the standard deviation, and the $p < 0.05$ was considered to be statistically significant.

3. Results and discussion

3.1. *Characteristics of the biochars*

The biochars had high C but low N contents (Table 1). The rice straw biochar had a higher pH value and a higher alkalinity, but lower organic C content and specific surface area than the bamboo biochar (Table 1). The CEC values of bamboo and rice straw biochars were 15 and 45 cmol kg^{-1}, respectively, which were 3 and 9 times higher than the soil, respectively. In the present study, the bamboo biochar had a much larger surface area than the rice straw biochar, indicating that feedstock and pyrolysis temperature can greatly influence biochar surface area. Park et al. (2011) reported that the surface area of chicken manure and green waste biochar produced at 550 °C was 7.27 and 6.87 $m^2\ g^{-1}$, respectively. A biochar with a large surface area and high in acidic functional groups would be expected to be suitable to immobilize cationic heavy metals in soil (Zhang et al., 2013a). The relative P, Si, K, Mg and Ca contents in the rice straw biochar were higher than those in the bamboo biochar (Fig. 1).

3.2. *Influence of biochar on soil EC and pH*

Application of rice straw biochar significantly increased soil electrical conductivity (EC) (Fig. 2A). Compared to the control, the 5% rice straw biochar treatments increased the EC by 350%. The results were consistent with Fellet et al. (2011) who found that mine tailing EC increased significantly with the addition of prune residues-derived biochar. However, there was no significant difference between bamboo biochar treatments and the control. This was expected given the relatively low EC value of the bamboo biochar (Table 1). Although the application of rice straw biochar increased the soil EC by 2–3 folds, the resulting EC was still low and would not lead to saline conditions (Arshad and Coen, 1992). The biochar size fraction had no significant influence on soil EC. The effect of an increase in soil EC on the uptake of heavy metals by plants depends on dominant ionic interactions in soil solution.

Soil pH increased significantly ($p < 0.05$) with biochar application, the highest soil pH corresponding to the 5% fine rice straw biochar treatment (Fig. 2B). The rice straw biochar was more effective than the bamboo biochar in increasing soil pH, as the former had a higher alkalinity than the latter (Table 1). Overall, fine biochars were more effective in increasing soil pH than soil EC, especially at the high rate (5%), which is in agreement with some previous studies (Liang et al., 2006; Uchimiya et al., 2010b). An increase in soil pH would promote heavy metal adsorption and precipitation, thereby reducing their bioavailability (Zhang et al., 2013a). This could have led to the reduction in plant shoot concentrations of Cd, Cu, Pb and Zn, as observed in the current study.

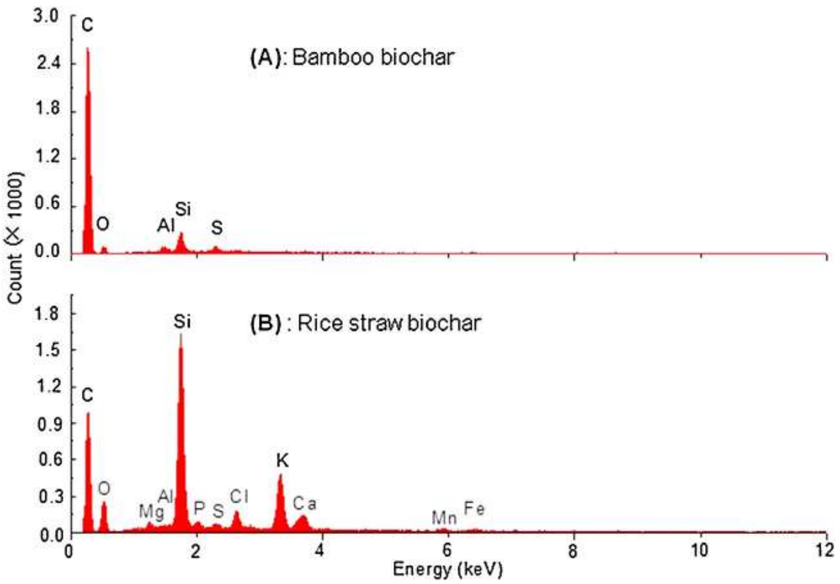

Fig. 1. The energy dispersive X-ray spectra (EDS) collected from the scanning electron microscopy (SEM) regions of bamboo (A) and rice straw (B) biochars.

The increased pH after biochar addition can result in the precipitation of Cd as $CdCO_3$ (Mousavi et al., 2010), Cu as $Cu(OH)_2$ and Pb as $Pb_5(PO_4)_3OH$ (Cao et al., 2011). In addition, metal adsorption to biochar could be one of the mechanisms by which metals are immobilized (Beesley and Marmiroli, 2011).

3.3. Effects of biochar treatments on shoot yield of *S. plumbizincicola*

The shoot dry weight of *S. plumbizincicola* was significantly ($p < 0.05$) increased in all biochar treatments except in the coarse bamboo biochar treatments (Fig. 3). The rice straw biochar treatments produced the highest dry weight of shoot, which was 43% higher than in the control treatment. There was no significant difference in dry weight between different mesh sizes of biochars or loading rates within the rice straw biochar treatments (Fig. 3).

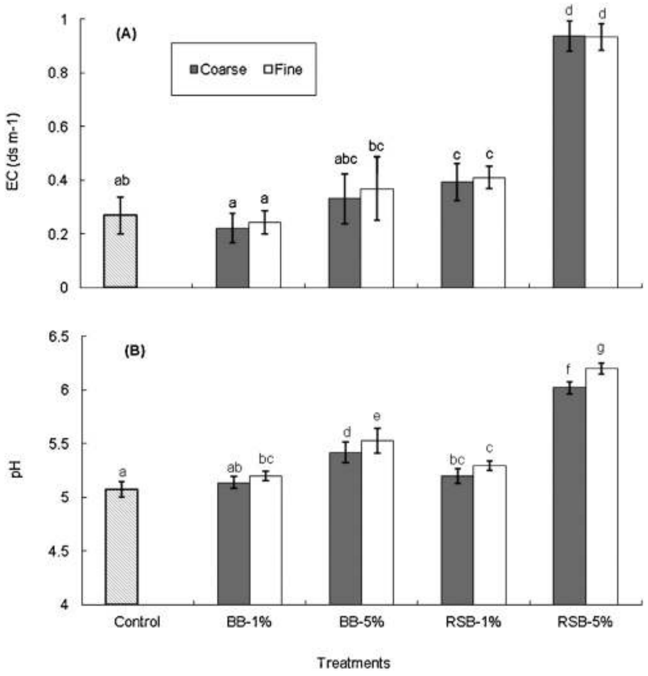

Fig. 2. Effects of biochar treatments on soil electrical conductivity (EC) (A) and pH (B) values. Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

The shoot N concentration in the 5% bamboo biochar treatments (Fig. 4A) and the total shoot N uptake in the 5% fine bamboo biochar treatment (Fig. 4B) were significantly ($p < 0.05$) higher than in the control. All other biochar treatments had no significant effect on N uptake by the *S. plumbizincicola* shoots (Fig. 4). It is unlikely that the higher N uptake in the 5% fine bamboo biochar treatment would be from the additional N supply from the biochar, because N in biochars produced at a temperature higher than 500 °C would not be bioavailable (Wang et al., 2012; Zheng et al., 2013). Enhancement of the shoot N uptake in the 5% fine bamboo biochar treatment may be due to increased efficiency in plant use of soil N in the presence of biochar application (Zheng et al., 2013).

Although the biochar treatments, except the 5% fine bamboo biochar treatment, had no significant effect on the plant shoot P concentration (Fig. 5A), all biochar treatments, except the coarse bamboo biochar treatments, significantly increased the total shoot P uptake (Fig. 5B). Relatively higher P concentration in the rice straw biochar (Fig. 1) may have contributed to the increased shoot P uptake in the rice straw biochar treatments. Regression analysis showed that there was no significant relationship between the *S. plumbizincicola* shoot yield and the N uptake ($R^2 = 0.339$), whereas the shoot yield was significantly ($p < 0.01$) correlated with P uptake by the shoots ($R^2 = 0.719$) (Fig. 5B). This was in agreement with Huang et al. (2012) who found that P fertilizer treatments resulted in greater growth rates and extraction of Zn by *Sedum alfredii*, a hyper-accumulator plant similar to *S. plumbizincicola*. These hyper-accumulating plants may have a higher P demand than other non-accumulating plants. The P applied with the basal fertilizer in the current study might have been insufficient to meet the P requirement for optimal growth of *S. plumbizincicola*. Furthermore, the relatively high concentration of the heavy metals, particularly Zn, in the soil (Table 1) may also have contributed to reduced P availability through precipitation (Loneragan et al., 1979; Bolan et al., 2003b).

Most biochars have been shown to have a liming value when applied to acidic soils (Beesley and Marmiroli, 2011) that would help raise soil pH, as shown in the current study (Fig. 2B).

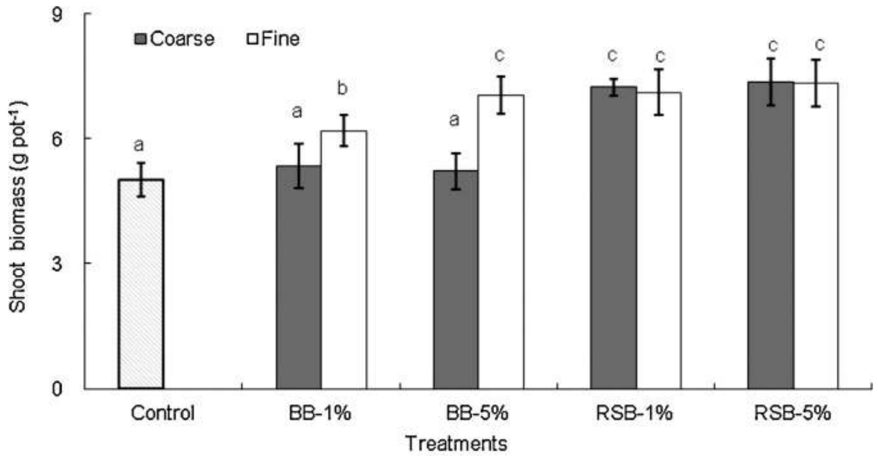

Fig. 3. Effect of biochar application on the shoot dry matter weight of *Sedum plumbizincicola*. Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

The increased soil pH would contribute to an increase in the productivity of crops such as maize, soybean, radish upon biochar addition to an acidic soil (Lehmann et al., 2003; Chan et al., 2008). Recent studies have shown that the addition of biochar to contaminated soils reduces metal toxicity to plants, resulting in decreased metal uptake and increased growth (Park et al., 2011; Zhang et al., 2013b). Previous work reported that biochar derived from forest green waste significantly increased the young quinoa

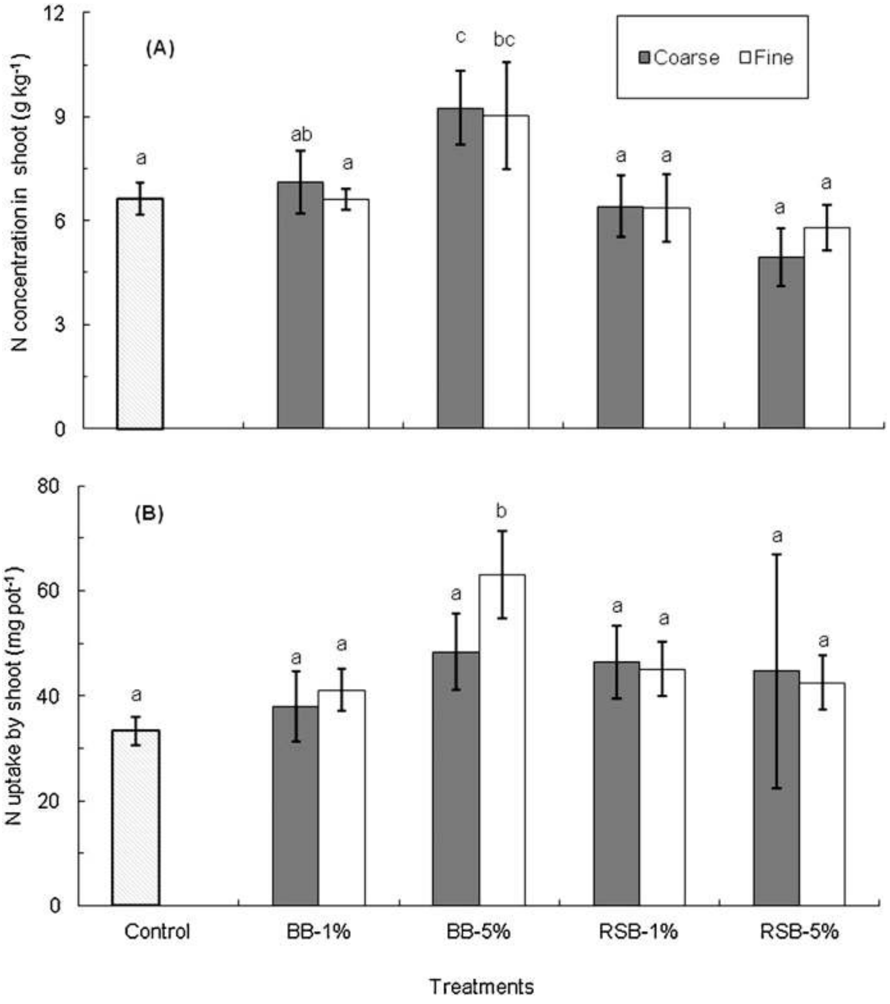

Fig. 4. Effect of biochar application on N concentration (A) and total N uptake (B) in the shoots of *Sedum plumbizincicola*. Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

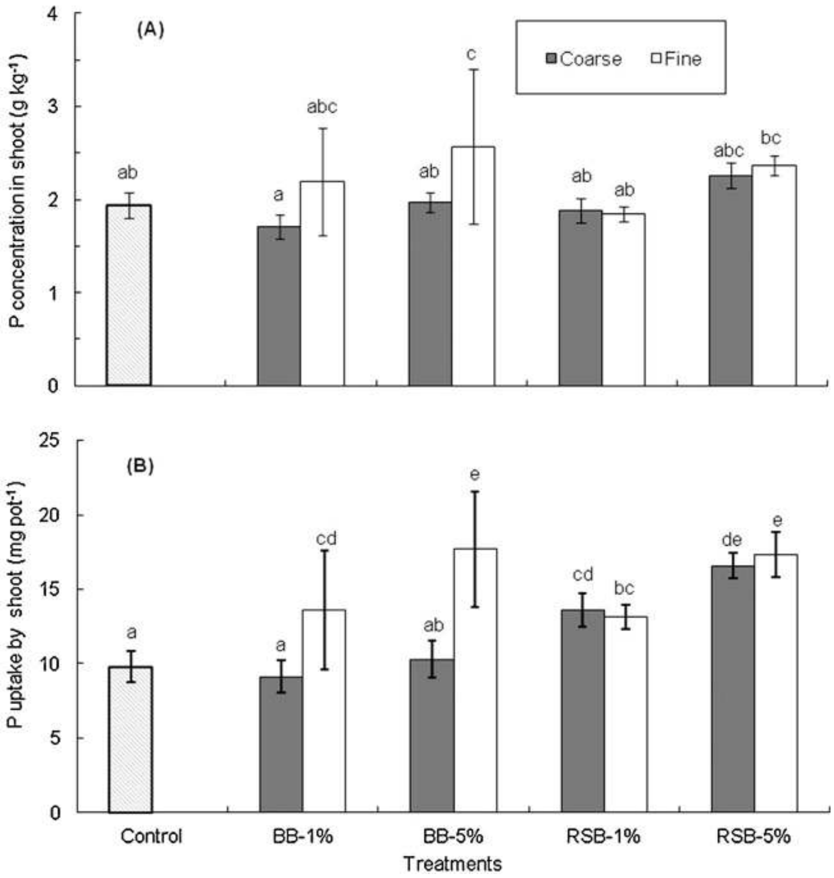

Fig. 5. Effect of biochar application on P concentration (A) and total P uptake (B) in the shoots of *Sedum plumbizincicola*. Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

(*Chenopodium quinoa*) growth in a Cu-contaminated soil (Buss et al., 2012). In addition, oak wood-derived biochar increased lettuce (*Lactuca sativa*) seed germination by 360% and root length by 189% in a Pb contaminated military shooting range soil. Biochar is able to complex metal ions on the surfaces and therefore reduces the metal bioavailability; however, some essential plant nutrients may also be immobilized through this mechanism, thereby reducing plant growth (Beesley et al., 2011). Zhang et al. (2013b) reported that wheat chaff-derived biochar did not improve the growth of emergent wetland species *Juncus subsecundus* in a Cd-contaminated soil. In our study, both the bamboo biochar (fine) and rice straw biochar significantly ($p < 0.05$) increased the shoot dry weight of *S. plumbizincicola* (Fig. 3), which may be attributed to reduced metal toxicity through improvement of soil pH (Fig. 2B) and increased P availability (Fig. 5B).

3.4. Effects of biochar treatments on heavy metal solubility in soil

Concentrations of TCLP-extractable Cd, Cu, Pb and Zn in soil decreased significantly ($p < 0.05$) with increasing rates of biochar application (Fig. 6). The 5% biochar treatment had the greatest decrease in extractable Cd (Fig. 6A) and Cu (Fig. 6B). Application of biochar also significantly ($p < 0.05$) reduced the concentration of extractable Pb (Fig. 6C), and the fine biochar was more effective than the coarse biochars. The concentration of extractable Pb in soils amended with fine and coarse rice straw biochar at a dose of 5% was 4.4 and 6.3 mg kg^{-1}, respectively, whereas those in soils amended with bamboo biochar at the same dose were 8.5 and 11 mg kg^{-1}. Rice straw biochar applications were more effective than those of bamboo biochar in reducing the concentration of soil extractable Pb. The concentration of extractable Zn significantly ($p < 0.05$) decreased when both biochar types were applied at a 5% application rate, with the largest decrease being observed in rice straw biochar treatment. No significant effect was observed at the low dose of biochar application (Fig. 6D).

Méndez et al. (2012) observed that biochar derived from sewage sludge significantly decreased the DTPA- and $CaCl_2$-extractable Cd, Pb and Zn in a Mediterranean agricultural soil. Similarly, Beesley et al. (2010) reported that a hardwood-derived biochar amendment (8.3%, w/w) significantly reduced water-extractable Cd concentration in soil. Fellet et al. (2011) reported that the biochar application at a rate of 10% resulted in a significant decrease in DTPA-extractable Cu bioavailability in the mine tailings. Cao et al. (2011) showed that dairy manure biochar could immobilize Pb in soil via both adsorption and precipitation, thereby leading to the transformation from less stable Pb species to more stable hydroxypyromorphite. This significantly reduced the TCLP-extractable Pb, and the reduction increased with the increasing biochar rates. Previous studies supported this finding, suggesting that the relatively high efficiencies of biochar in immobilizing Pb may be resulted from the precipitation of Pb-hydroxide and Pb-phosphate (Ok et al., 2010; Ahmad et al., 2012). In a recent study, Li et al. (2012) found that the addition of Si (in the form of $Na_2SiO_3{\cdot}9H_2O$) significantly decreased the fraction of exchangeable Pb in a Pb-contaminated soil. This reduced soil Pb availability and the corresponding Pb uptake by banana plants. In our study, rice straw biochar had a higher pH, alkalinity, Si and P concentrations than bamboo biochar (Table 1 and Fig. 1); this may explain the greater reduction in Pb solubility with the application of former biochar (Fig. 6C). The present results indicated that the effect of biochar on metal immobilization

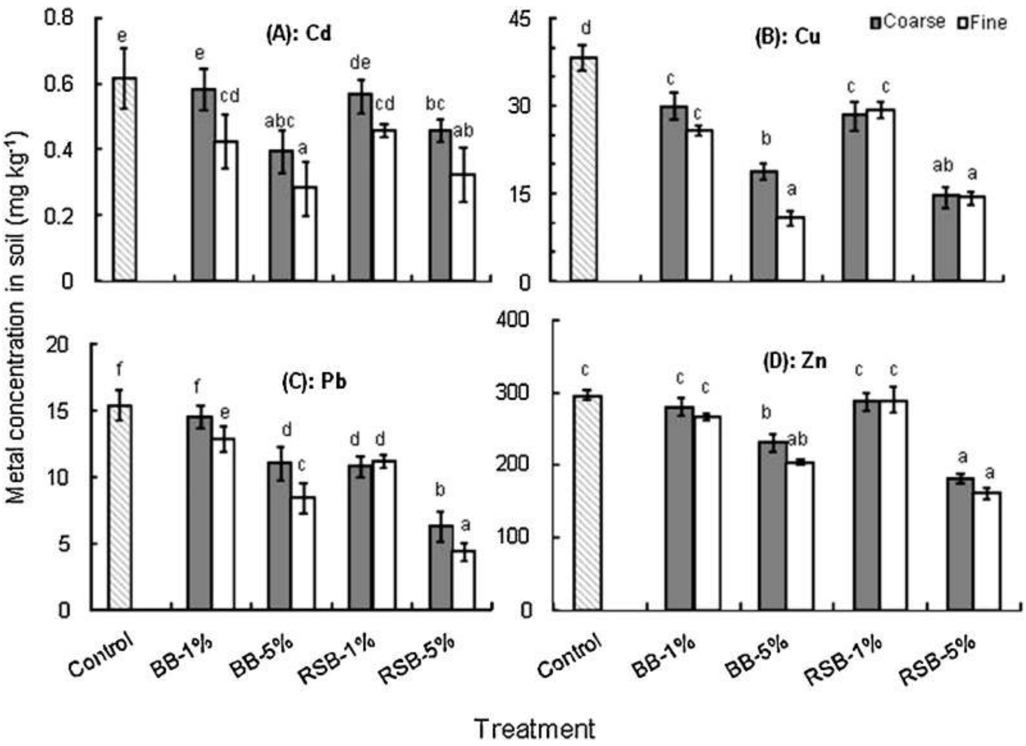

Fig. 6. Effect of bamboo and rice straw biochars on the extractable concentrations of Cd (A), Cu (B), Pb (C) and Zn (D) in soil using the Toxicity Characteristic Leaching Procedure (TCLP). Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

in soil may be influenced by the feedstock materials, pyrolysis conditions, and application rates, whereas the particle size (0.5–1 mm) had a minor effect. Since most biochars have a large surface area, micro-porous structure, high pH and some soluble salts, they can potentially reduce the solubility of heavy metals in soils through adsorption and precipitation (Chan and Xu, 2009; Yuan et al., 2011; Zhang et al., 2013a).

3.5. *Effect of biochar on plant uptake of heavy metals*

The type of biochar source material and grain size had a significant effect on the uptake of Cd, Cu, Pb and Zn by *S. plumbizincicola* (Fig. 7). The concentration of Cd in shoots significantly ($p < 0.05$) decreased with both bamboo and rice straw biochar application (Fig. 7A) by up to 49% and 20%, respectively. However, there was no significant change in Cd concentration with increasing biochar application rates (Fig. 7A). Addition of biochars significantly reduced the plant uptake of Cu (Fig. 7B) and Pb (Fig. 7C) except 1% bamboo biochar treatment. The rice straw biochar additions caused a greater decrease of Cu and Pb concentration in the shoot than that of bamboo biochar. The concentrations of Cu and Pb significantly ($p < 0.05$) decreased with increasing rates of the rice straw biochar. The 5% rice straw biochar treatment significantly ($p < 0.05$) reduced the uptake of Cu and Pb in the shoot from 11.6 to 6.2 mg kg^{-1} and from 61 to 18 mg kg^{-1}, respectively. There was no significant difference in Cu and Pb uptake between 5% bamboo biochar and 1% rice straw biochar treatments. Compared to the control, biochar addition significantly ($p < 0.05$) reduced the uptake of Zn (Fig. 7D).

The particle size of biochar had no significant effect on reducing the concentrations of Cd, Cu and Pb in the plant shoots (Fig. 7), whereas fine biochars were generally more effective on reducing the concentration of Zn in the shoots than the coarse biochars (Fig. 7D). Compared to the control, the coarse and fine biochars reduced the uptake of Zn by 13% and 27%, respectively. Zheng et al. (2012) also reported that fine biochars were generally more effective in reducing Zn concentrations in rice shoots than coarse biochar. This was attributed to a larger specific surface area of the finer biochar (Zheng et al., 2012).

Zhang et al. (2013b) reported that wheat chaff-derived biochar at an application rate of 5% significantly ($p < 0.05$) reduced the Cd concentration of *J. subsecundus* N.A. Wakef. The decrease in Cd concentration in plants in the presence of biochar application may be attributed to both the immobilization of bioavailable metals and ‘dilution effect’ due to increased plant biomass (Park et al., 2011). The bamboo biochar appeared to be more effective than the rice straw biochar in reducing Cd uptake by *S. plumbizincicola* (Fig. 7A), whereas the rice straw biochar was more effective in reducing Cu and Pb uptake by the plant (Fig. 7B, C). The bamboo biochar may have a greater adsorption capacity because it had a much greater surface area than that of the rice straw biochar (Table 1). This suggests that high adsorption of Cd to biochar-amended soil may be one of the reasons for reducing its bioavailability more than that of Cu and Pb. Although Cd adsorbed by the bamboo biochar may have reduced its availability for plant uptake (Fig. 7A), some of the adsorbed Cd seemed to be extractable by the TCLP-solution (Fig. 6A). Although this may be attributed to formation of dissolved organic matter and Cd complexes, the associated mechanism is yet to be explored.

In general, Cu availability in the biochar treatments may be reduced due to sorption, complexation and precipitation (Bolan et al., 2003a; Beesley et al., 2010; Zhang et al., 2013a). Similarly, Zheng et al. (2012) reported that 5% straw biochar additions caused the greatest decrease in Cu and Pb concentrations in rice shoots. Karami et al. (2011) showed that biochar reduced the uptake of Cu and Pb by ryegrass. Park et al. (2011) reported that chicken manure-derived biochar significantly reduced the uptake of Cu and Pb by *Brassica juncea* (L.), however, Cu concentration in the shoots was not significantly influenced by the amount of biochar addition. In the present study, biochar addition also significantly ($p < 0.05$) decreased the uptake of Zn by *S. plumbizincicola*, and the results

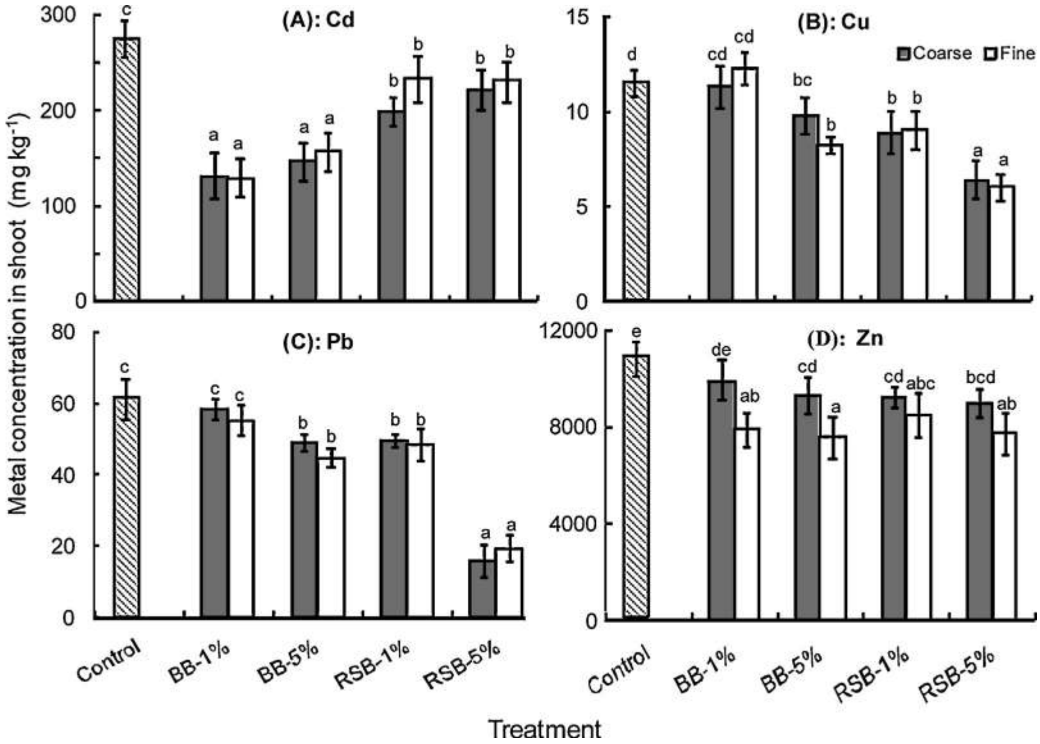

Fig. 7. Effect of bamboo and rice straw biochars on concentrations of Cd (A), Cu (B), Pb (C) and Zn (D) in the shoot of *Sedum plumbizincicola*. Treatments: Control, 1 and 5% bamboo biochar (BB), rice straw biochar (RSB) with two mesh sizes (coarse and fine). Error bars are standard deviation of the means ($n = 4$). Different letters above the columns indicate significant ($p < 0.05$) difference between treatments.

were similar to those reported by Sizmur et al. (2011). The high Si content in the rice straw biochar (Fig. 1) may also play a role in reducing the plant uptake of heavy metals. It was reported that application of Si-rich amendment (e.g., $Na_2SiO_3{\cdot}9H_2O$) can reduce heavy metal concentration in plant shoots due to reduced metal availability in soil (Li et al., 2012), and reduction in the uptake and transport of metals from root to shoot (Gu et al., 2012; Wu et al., 2013). Significant reductions in the concentration of Cd, Cu, Pb and Zn in the shoot with biochar addition in the current study could be attributed to (i) precipitation or co-precipitation of the metals due to increased soil pH and introduction of phosphate and silicate salts (Ahmad et al., 2012), and (ii) adsorption of metals to biochar (Elliott et al., 1986; Namgay et al., 2010). In the rice straw biochar treatments, high Si content may have helped to reduce metal uptake in *S. plumbizincicola* shoot (Wu et al., 2013).

4. Conclusions

Addition of bamboo and rice straw biochars has potential for in situ remediation by immobilizing metals, thereby reducing the uptake of Cd, Cu, Pb and Zn by *S. plumbizincicola* grown in a severely polluted soil. Enhanced soil pH in the biochar treatments may have contributed to the decreasing metal toxicity, thereby increasing *S. plumbizincicola* plant growth. Rice straw biochar was more effective in the reduction of Cu and Pb concentrations in shoots, while bamboo biochar was more effective in the reduction of Cd. Fine biochars were generally more effective in reducing Zn concentrations in shoots than coarse biochars, but not Cd, Cu and Pb concentrations. Biochar application decreased concentrations of TCLP-extractable Cd, Cu, Pb and Zn in soil as well as in the *S. plumbizincicola* shoots. Enhanced precipitation or co-precipitation and adsorption of the heavy metals in the biochar treatments would have contributed to the reduction of the solubility and bioavailability of the metals. The influence of biochar on heavy metal bioavailability varied not only with the feedstock and application rate of biochars, and was metal-dependent. Therefore, biochar should be carefully designed to maximize the reduction of the bioavailability of a given heavy metal in a soil. Furthermore, the effectiveness of a biochar in remediation of contaminated soils should be tested under field conditions.

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