INFLUENCE OF BIOCHAR AMENDMENTS ON SURFACE CHARGE AND BIOAVAILABILITY OF HEAVY METALS IN DEGRADED SOILS

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Abstract

This study investigated the effect of 3 biochar application rates (1%, 5%, and 10%) on the pH, surface charge, and bioavailability of Cu, Pb, Zn on a degraded Acrisols soil and their accumulation in water spinach (*Ipomoea aquatica*). After an incubation period of 28 days, a titration experiment confirmed that increasing the biochar application rates enhanced the negative charge along with an increased pH. In an experiment spiked with metals, the 0.01 M $CaCl_2$-extractability of the metals after incubation significantly decreased with the increasing rate of biochar additions. This is mostly attributed to a rise in the soil pH and an increase in the negative charge as result of the biochar additions. Metal extractability continued to decrease over the next 1,344 h, most probably due to the aging effect. Immobilization speeds exhibited in the order Pb>Cu>Zn, can be partially attributed to the bigger ionic radius of Pb compared to those of Cu and Zn. By the end of incubation period, extractable Cu, Pb and Zn was significantly reduced, irrespective rates of biochar application 1%, 5% or 10%. In a greenhouse experiment, water spinach was unable to grow in the 10%biochar addition because of a high alkaline pH of 9.2. The Cu, Pb, and Zn concentrations and bioaccumulation factor in the grown water spinach decreased along with the increasing biochar application rates in the order 5%>1%>0%, showing a good agreement with the 0.01 M $CaCl_2$-extractable concentrations. The bioaccumulation factors of Pb were far less than those of Cu and Zn, reflecting the immobilization speeds as concluded in the incubation tests. Therefore, biochar amendment into degraded soil for metal immobilization is feasible, provided the appropriate rate for crop growth is applied.

Keywords: **Biochar, surface charge, bioavailability, heavy metal, immobilization, bioaccumulation**

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Introduction

Haplic Acrisol, which is featured by acidity, low nutrients, and low absorption capacity, accounts for 1.8 million ha, or 15%of the total area of Vietnam. Considered as a degraded soil, it is vulnerable to drought in the dry season, soil erosion, and a leaching process due to its light texture. In recent years, rapid land conversion for industrialization in Vietnam poses a threat to the ecosystem, ground water, and agricultural production due to the contamination of soils. The restoration of contaminated soils and the prevention of transferable toxic components to agricultural products, e. g. heavy metals, is thus essential. Conventional remediation techniques (e.g. landfilling, soil washing, and excavation) are often energy intensive, costly on a large scale, and cause considerable disturbance to the environment. Biochar, considered as an *in situ* amendment, can be an alternative technique to reduce the metal mobility and bioavailability of contaminated soils because of its cost-effectiveness, additional benefits to soil fertility, and mitigation of climate change (Sohi, 2012). Although other inorganic minerals and organic materials can be used as ameliorants to reduce the mobility and bioavailability of heavy metals, for example zeolite, red mud (bauxite residue), and chicken manure compost have been reported to adsorb heavy metals, they have rarely been applied in practice because of their unsatisfactory effects or high cost (Jiang *et al*., 2012).

Copper (Cu) is considered as a micronutrient for plants (Thomas *et al*., 1998) but a concentration of 160 μM Cu could show symptoms of heavy metal toxicity (Ouzounidou *et al*., 1998). An excess of Cu in soil leads to plant growth retardation and leaf chlorosis (Lewis *et al*., 2001). Exposure of plants to excess Cu generates oxidative stress and disturbance of cellular ionic homeostasis (Stadtman and Oliver, 1991; Yadav, 2010).

Lead (Pb) is not an essential element for plants but can be easily absorbed and accumulated in different plant parts. Typical toxicity symptoms in plants when exposed to excess Pb are stunted growth, chlorosis, and blackening of the root system. Pb inhibits photosynthesis, upsets mineral nutrition and water balance, changes the hormonal status, and affects membrane structure and permeability. High concentrations of Pb (1 mM) caused 14 to 30 % decreased germination in rice seeds and reduced the growth of seedlings by between 13 to 45 % (Verma and Dubey, 2003). Generally, a Pb content above 10 mg/kg in the soil can inhibit root growth (Breckle, 1991). Rice (*Oryza sativa*) seedlings grown in a sand culture under 500 and 1,000 μM $Pb(NO_3)_2$ in the medium resulted in a 21 to 177 % increase in the level of lipid peroxides, indicating oxidative stress in these plants (Verma and Dubey, 2003).

Zinc is also a nutrient for crops but its high level in soil inhibits its metabolic function, resulting in retarded growth and causing senescence (Yadav, 2010). Generally, when the soil pH decreases, Zn solubility and uptake increases, enhancing toxicity. Toxicology varies in different crops. The toxic level of Zn in soil is 7 ppm for wheat, but 11 ppm for maize (Takkar and Mann, 1978).

Various effects of biochar on heavy metals have been documented. Cu and As are mobilized, whereas Cd and Zn are immobilized in soils amended with biochar as compared to un-amended soil, if hardwood-derived biochar is applied to multi-element (As, Cu, Cd, and Zn) contaminated soil (Beesley *et al*., 2010). The mechanism of metal immobilization has been attributed to the increase in both the soil pH and cation exchange capacity (CEC) and the adsorption of metal complexing dissolved organic carbon (Beesley and Marmiroli 2011; Fellet *et al*., 2011; Karami *et al*., 2011). The incorporation of biochar into the soil is irreversible; therefore, it is of the utmost importance to investigate the effect of biochar on metals' availability to crops before field application. Further, an update of knowledge on the effect of biochar on degraded soil and the metals' availability as well as the uptake to crops are required.

Rice husk biochar is widely available in Vietnam. Annually, the country produces around 45 million tonnes of rice per year creating about 8-9 million tonnes of rice husks (Nuamah *et al.*, 2012). Rice husks are mainly used for cooking, or as a biofilter mixed with dung, or are burnt. A small proportion is being turned into biochar for soil enrichment, water purification, and silicon extraction. The removal of metals by rice husk biochar is mainly due to their complexation with phenonic OH (Xu *et al.*, 2013), or more specifically the chemical adsorption such as complexation (organic groups) and precipitation (inorganic groups) (Nguyen, 2019). Sorption isotherms of rice husk biochar best fit the Freundlich model for Zn^{2+}, As(V), Cr(III), and Cr(VI) (Agrafioti *et al.*, 2014; Nguyen, 2019).

In this study, we hypothesize that biochar amendment into haplic Acrisols significantly increases the soil's pH owing to alkaline substances in the biochar. Though biochar has the potential to remediate soil contaminated with heavy metals, their sorption capacity varies with the feedstock types. Therefore, we hypothesize that biochar made from rice residues could reduce metal extractability (by $CaCl_2$) over time as an immobilization process occurs. A previous study (Houba *et al.*, 1996) indicated that biochar helps reduce the bioavailability of metals in contaminated soil; here in this study, we investigate a similar reduction of metal toxicity and accumulation in water spinach grown on haplic Acrisols - an acidic and loamy soil spiked with metals. The objective of the study is to investigate the effect of 3 biochar application rates (1%, 5%, and 10%) on the pH, surface charge, and bioavailability of Cu, Pb, and Zn on degraded Acrisols soil, and their accumulation in water spinach (*Ipomoea aquatica*).

Materials and Methods

Biochar Properties

Biochar made from rice husks and rice straw (w/w 1:5 corresponding to the proportion of rice residue after harvest) was used in the experiments. The biochar was characterized as alkaline (pHH_2O = 10.6, pH_{KCl} = 10.0 at an extraction ratio 1:10, w/v), with 1% $CaCO_3$, high CEC (80.4 cmolc/kg), and dissolved cations of Ca^{2+}, Mg^{2+}, K^+, and Na^+ that amounted to 16.8, 6.9, 229.8, and 8.5 cmol/kg, respectively (Table 1). The indigenous metals' concentrations of Cu, Pb, and Zn in the biochar were 0.7, 2.1, and 13.9 mg/kg, respectively.

Soil

The soil used in this experiment was taken from a top layer (0-15 cm) of a paddy field in Soc Son district, Hanoi, Vietnam, being classified as haplic Acrisols. The soil is characterized as acidic with pHH_2O = 5.2, pH_{KCl} = 4.2 (extraction ratio 1:2.5, w/v), a low

Table 1. Soil and biochar characteristics used in experiment

Parameter	Unit	Soil	Biochar
pH_{H2O}		5.2	10.6
pH_{KCl}		4.2	10.0
CEC	$cmol_c.kg^{-1}$	9.2	80.4
Ca		2.0	16.8
Mg		0.2	6.9
K		0.2	229.8
Na	$cmol_c.kg^{-1}$	0.1	8.5
Ca-$CaCO_3$		0.004	0.943
OC		1.33	-
N	%	0.13	-
P_2O_5		0.07	-
K_2O		0.22	-
Cu		25.7	0.7
Pb	$mg.kg^{-1}$	13.1	2.1
Zn		74.6	13.9
Water holding capacity	%	36.6	82.2
Surface charge	$mmol_c.kg^{-1}$	-4.15	-20.0

cation exchange capacity (CEC = 9.2 cmolc/kg, extracted by ammonium acetate 1N), and the soluble cations Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} amounted to 2.0, 0.2, 0.2, and 0.1 cmol/kg, respectively (Table 1). The soil texture has 52% sand, 35% silt, and 13% clay, being classified as loamy soil (data not shown).

The indigenous Cu, Pb, and Zn metals' concentrations in the soil were 25.7, 13.1, and 74.6 mg/kg, respectively, being below the maximum permissible levels for cultivable soil of the guidelines by the Vietnamese National Technical Regulation QCVN03:2008/BTNMT.

Incubation Experiment: Evaluation of the Effect of Ph on Surface Charge of Soil Amended with Biochar

The biochar and soil were air-dried, crushed, and sieved to a particle size of <2 mm in diameter. The mixture of soil-biochar was made by adding biochar to the soil in different ratios: 0% (control), 1%, 5%, and 10% (w/w). The experiment included the treatment factor as the biochar rate, and was arranged as a completely randomized design with 3 replicates. Plastic pots, each 1,000 cm^3, were filled with 500 g of the soil-biochar mixture, and covered with a perforated cap to limit water evaporation while ensuring gas exchange. The pots were incubated at 25±1ºC for 28 days in the dark. The moisture content during incubation was kept at 75% water holding capacity by adding water and weighing the pots on a weekly basis. After 28 days of incubation, the soil-biochar mixtures were air-dried before a surface charge analysis. The analysis followed the procedures as described by Nguyen *et al.* (2014). Briefly, 40 mg of the crushed sample was put in a jar before adding 20 ml deionized water. The pH of the slurry was adjusted to the desired values ranging from 2 to 11 by adding HCl or NaOH 0.01N. The slurry was transferred to a teflon (PTFE) container which was connected to a Mütek PCD-05 particle charge detector (BTG Mütek GmbH, Wessling, Germany). PolyDADMAC 0,0002N or PesNa 0,0002N was used for titration depending on whether the charge was positive (cationic) or negative (anionic). The titration was ended when the zeta potential approximately reached zero. Titration was carried out with 3 replicates.

The charge density (q) was represented by 1 millimole of charge in a mass unit and it was calculated from q = V.C/m, where V is the volume of the titration solution (mL), C is the concentration of the titration solution ($mol_{c(+)}$ or $_{(-)}L^{-1}$), and m is the mass of the sample in the solution (g).

Assessing the Immobilization of Heavy Metals (Cu, Pb, Zn) by Biochar Addition to Soil and Its Uptake by Water Spinach 0.01 M $CaCl_2$ Extraction Experiment

The experiment consisted of 4 treatments replicated 3 times, and arranged as a completely randomized design. Each 1,000 cm^3 plastic pot filled with 500 g of soil-biochar mixture was spiked to the levels of 128 mg Cu/kg (Cu^{2+}), 212 mg Pb/kg (Pb^{2+}), and 130 mg/kg (Zn^{2+}) (Table 2). The spiked mixture was incubated in a manner identical to the one described at incubation experiment. After 1, 168, 336, 504, 672, and 1,344 h, 2.5 g of each sample was analyzed using the method proposed by Houben *et al.* (1996). The samples were put into a polypropylene centrifugation tube in which 25 ml of 0.01 M $CaCl_2$ was added and then shaken for 2 h at 25ºC. After shaking, the pH (pH-$CaCl_2$)was measured in the suspension and the supernatant in each centrifuge tube was filtered

Table 2. Natural metal and metal-spiked concentrations in soil-biochar used in plant uptake experiment

Biochar addition %	Cu $mg.kg^{-1}$		Pb $mg.kg^{-1}$		Zn $mg.kg^{-1}$	
	Natural metal	Metal-spiked	Natural metal	Metal-spiked	Natural metal	Metal-spiked
0%	25.7	128	13.1	212	74.6	130
1%	25.7	128	13.1	212	74.6	130
5%	25.7	128	13.1	212	74.6	130
10%	25.7	128	13.1	212	74.6	130

through a membrane filter. The heavy metal concentration in the extract was determined by atomic absorption spectroscopy (AAS) (Solar M6, Thermo Fisher Scientific, Waltham, MA, USA).

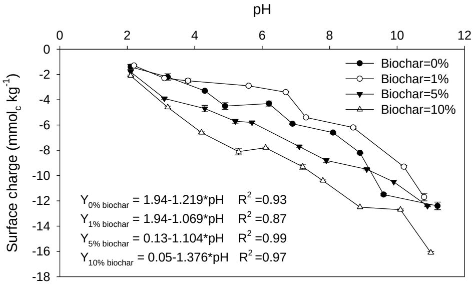

Figure 1. The dependence of the surface charge on the pH of the soil after the biochar amended (n = 3). Bars indicate standards errors

Greenhouse Experiment

Soil or soil-biochar was spiked with 128 mg Cu^{2+} kg^{-1}, 212 mg Pb^{2+} kg^{-1}, and 130 mg Zn^{2+} kg^{-1} (Table 2). Plastic pots (30×25×10 cm) were filled with 3 kg of soil or mixture, and incubated for 28 days at field capacity (75%) in a dark room. Water spinach (*Ipomoea aquatica*) seedlings were then transplanted into the pots with regular watering when needed. Treatments were arranged as a completely randomized design, and replicated 3 times. After 30 days, shoots were harvested by cutting 1 cm above the ground, washed with deionized water, and oven dried at 60°C until a constant weight was reached to measure the percent dry weight. The plant materials were ground through 2 mm sieves and analyzed for metal content in the same way as the soil samples.

Analysis Methods and Data Processing

The soil pH was measured in a slurry of deionized water or KCl 1N (ratio w/v 1:2.5) using a pH meter (S220-K SevenCompact™, Mettler-Toledo (Switzerland), Greifensee, Switzerland). The biochar pH was measured in the same way with a ratio w/v 1:10. The CEC was measured using the pH 7 ammonium acetate 1N method (Sumner and Miller, 1996). The Ca, Mg, K, and Na in the extract were analyzed using AAS (Solar M6, Thermo Fisher Scientific, Waltham MA, USA). The soil and biochar samples were digested by HNO_3 + HCl (ratio 1:3) for heavy metals analysis using AAS.

Data were analyzed using SAS 9.0 with PROC MIXED, considering the biochar rates as the first factor and time as the second factor (SAS Institute, Inc., 2002). Different treatment means were separated by using the LSmeans package ($p<0.05$) as otherwise indicated.

Results and Discussion

The Correlation Between the Surface Charge and pH of the Soil After Biochar Amended

The soil and its mixture with biochar generally had a negative charge and varied with the environment pH. The negative charge increased with the increasing pH, as depicted by the linear relationship (Figure 1). The slopes of the equations increased with the increasing biochar application rates (1.069, 1.104, and 1.376 at 1%, 5%, and 10% biochar addition, respectively) suggesting that the biochar enhanced the negative charge per each unit pH change. The ion adsorption capacity of the soil depends basically on the charge density of the solid phase, and this value is known as the surface charge. On the surface of the solid phase exists 2 types of charges, the permanent charge and the variable charge, in which the variable charge changes depending on the pH of the environment (Nguyen *et al*., 2014).

pH Change Over Time and Heavy Metal Immobilization

The soil pH extracted by 0.01M $CaCl_2$ after 1 h incubation was 5.2, 7.8, and 8.3 at 1%, 5%, and 10% biochar additions, respectively, and were significantly higher than that of the control without biochar (4.5) (Figure 2(a)). After the first incubation period of 168 h, the pH was decreased at all the biochar amended rates (Figure 2(a)), and increased to the starting levels after being incubated for another 168 h, except the pH of the control which reached beyond the starting level (5.1). However, by

504 h, the pH of the control slightly declined again while it was stable in the biochar added treatments. The soil pH was significantly increased by the amendment of biochar at all rates through the incubation experiment ($p<0.01$), in which the liming effect of the biochar addition followed the order 10>5%>1%>control (Figure 2(a)). At the end of the incubation period of 1,344 h, the liming effect is effective only in the 5% and 10% biochar addition treatments. The amendment of 1% biochar did not increase the pH, most probably due to the soil buffering capacity. This is similar to the trend observed by Houben *et al*. (2013).

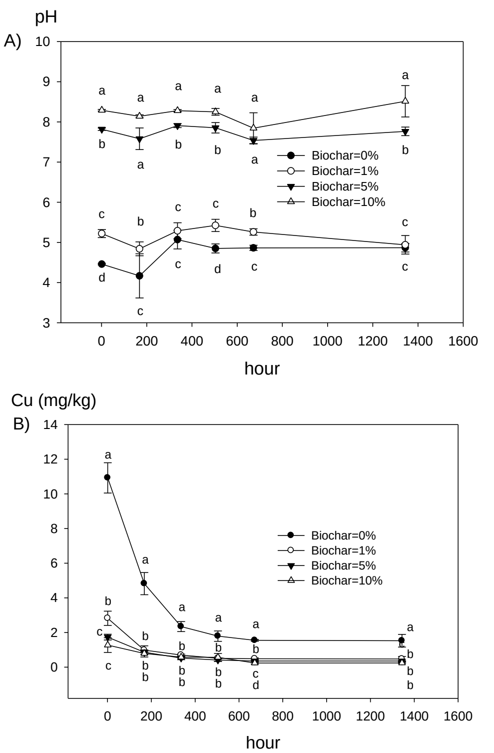

Figure 2. a) change in soil pH and b) change in Cu concentration when the Acrisol was amended with 3 biochar rates compared with the control. Extracted by 0.01 M $CaCl_2$ solution (n = 3). Means followed by the same letter are not significantly different ($p<0.05$) within each sampling time. Bars indicate standards errors.

The soil incubated with the biochar had a neutralized soil acidity owing to substantial alkaline substances in the biochar which were released into the soil, thus increasing the soil pH. The data in Figure 2 suggest that the alkaline substances in the biochar were readily released, thus the soil pH increased once the biochar was incorporated at all experimental rates. The same pattern was found in the other 2 experiments, as depicted in Figures 3(a) and 4(a).

The $CaCl_2$-extractable Cu, Pb, and Zn concentrations were significantly lower ($p<0.05$) in the soil amended biochar compared to the control (Figures 2(b), 3(b), 4(b)). The addition of biochar in increasing rates resulted in a reduction of the extractable metals. The liming effect of the biochar would have contributed to this significant increase in the soil pH, as proved by the relationship between the $CaCl_2$-extractable metal concentrations and the pH. Here, the metals correlated with the pH by an exponential decay equation rather than a linear relationship, as observed by Houben *et al.* (2013). It is likely that our tropical soil has a higher abundance of clay Kaolinite with a lower buffer capacity which induces a quick decrease of metal ions at the beginning of incubation, while soils formed in cooler conditions have an abundance of clay Illite with a higher buffer capacity that gradually absorbs metal ions.

Compared to the situation after 1 h of incubation, the $CaCl_2$-extractable concentrations of Cu, Zn, and Pb at the end of the experiment were lower by factors of 5.3-10.3 for the biochar 1%, 4.9-16.8 for the biochar 5%, and 5.2-1,686 for the biochar 10%, respectively. These decreasing factors were far greater than those observed by Houben *et al*. (2013), which can be explained by the fact that our newly spiked soils had a looser binding of metal cations that were more easily extracted by 0.01M $CaCl_2$.

Metal immobilization was induced by several factors, i.e. the surface charge can absorb metals which depend on hydroxides and increases with the increasing pH (McBride and Blasiak 1979; Bradl 2004). Further, metal

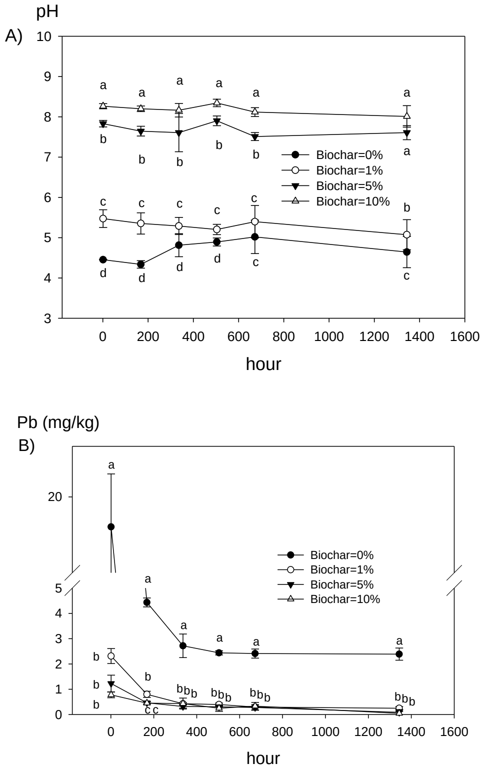

Figure 3. a) change in soil pH and b) change in Pb concentration when the Acrisol was amended with 3 biochar rates compared with the control. Extracted by 0.01 M $CaCl_2$ solution (n = 3). Means followed by the same letter are not significantly different ($p<0.05$) within each sampling time. Bars indicate standards errors

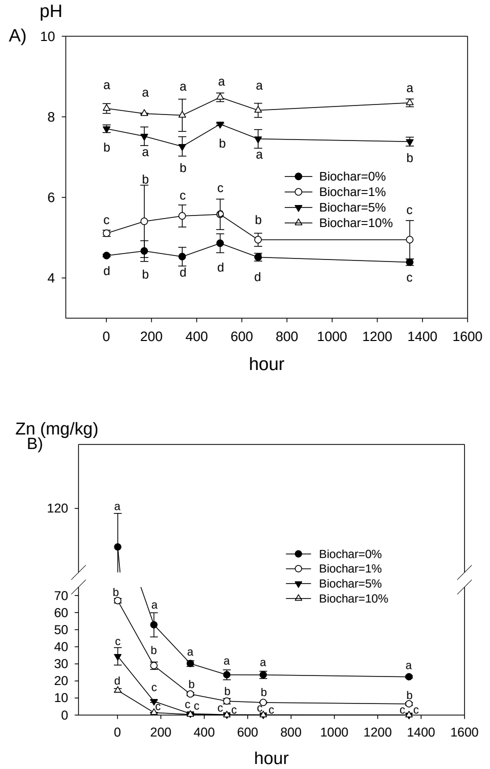

Figure 4. a) change in soil pH and b) change in Zn concentration when the Acrisol was amended with 3 biochar rates compared with the control. Extracted by 0.01 M $CaCl_2$ solution (n = 3). Means followed by the same letter are not significantly different ($p<0.05$) within each sampling time. Bars indicate standards errors

precipitation such as hydroxide (Tabak *et al*., 2003), oxide, carbonate, and phosphate (Lindsay, 1979) are important immobilization processes. This study revealed that the mobility of heavy metals reduced with the decreasing pH and increasing negative surface charge (Figure 1).

Compared to the controls, 0.01 M $CaCl_2$-the extractability after 1 h of the incubation experiments at the 1%, 5%, and 10% biochar additions decreased 74, 84, and 88%for Cu, 88, 94, and 96%for Pb, and 41, 70, and 87%for Zn, respectively. This speed of immobilization followed the order of Pb>Cu>Zn. The pattern is similar to the results reported by Houben *et al.* (2013). Probably a greater affinity of Pb for functional groups (carboxylic and phenolic) situated on the surface of oxidized biochar particles resulted in an increased immobilization speed of Pb. Furthermore, the higher attenuation of Zn and Cu favoring diffusion due to their smaller ionic radius (0.74Å and 0.73Å) compared to that of Pb (1.2Å) would have contributed to the lower absorption of the former ones.

When 5%and 10%of biochar was added, the initial fast metal immobilization was followed by a secondary slow retention, as indicated by the continuous decrease in $CaCl_2$-extractable metals with time. This information

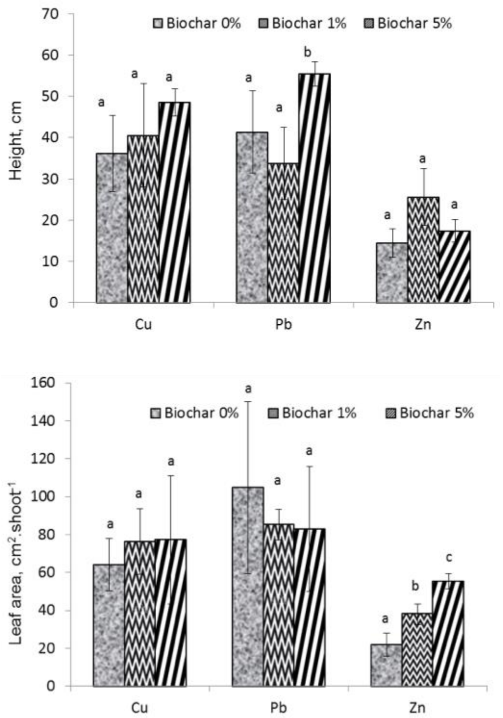

Figure 5. Height and leaf area of water spinach grown in soil and soil amended with biochar 1% and 5% in the metal-spiked experiments. Means followed by the same letter are not significantly different (p<0.05). Bars indicate standards errors

helps to determine the biochar application rate and frequency to improve remediation efficiency (Zhang *et al*., 2013). Increases in sorption with time are usually attributed to the mechanisms with lower reaction rates such as diffusion into micropores of both inorganic and organic soil constituents and surface nucleation-precipitation (Ma *et al*., 2006). However, the mechanism of the aging process requires further understanding, particularly for various pollution agents (Fellet *et al*., 2011).

Plant Growth and Metal Uptake

Water spinach seeds did not grow in the soil with added 10% biochar while they grew well in pots having lower rates of biochar, irrespective of the metal contamination levels. This indicated that the metal levels applied had not impacted the plants' survival rates. The most suitable soil pH ranges were from 5.5 to 7.0 for water spinach (Nguyen 1992); therefore, a pH of 9.2 at 10% biochar amendment (data not shown) was considered as unfavorable for water spinach growth. Further, at 10% biochar, significant amounts of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and HCO_3^- may cause a soil "salinity" condition in which newly germinated shoots would lose water and die. Rillig *et al*. (2010) found that increasing concentrations of hydrothermal carbonization material could be deleterious for plant growth of *Taraxacum*, starting at 10 vol% additions.

Here in our experiment, the 10% biochar application when converted to field application would be 196.5 tons ha^{-1} (bulk density 1.31 g/cm^3, top soil depth for incorporation 15 cm). Such rate was almost double the optimum rate of 100 tons ha^{-1} being recorgnized as having the greatest positive results (Jeffery *et al*., 2011). Matovic (2011) suggested lower application rates of 1-5% to be the optimum for agricultural soils; Park *et al*. (2011) realized that just 1%biochar added would provide the greatest effect on Indian mustard productivity.

Biochar additions had a significant effect on the shoot biomass of the water spinach in the Cu- and Pb-spiked experiments (Figure 5). However, in the Zn-spiked experiment, there were no significant differences in the shoot biomass at the different biochar rates applied.

The results in Table 3 indicated that the Cu, Pb, and Zn concentrations in water spinach decreased with the increasing biochar additions in the following order 5%>1%>0%. The accumulation of the 3 metals in the plants exhibited a pattern of decrease in the concentration and bioaccumulation factor (BF) among the biochar additions (Table 3). The concentrations in the dry shoots ranged from 46.4 to 22.4 mg kg^{-1}, 10.6 to 1.5 mg kg^{-1}, and 125.7 to 80.3 mg kg^{-1} for Cu, Pb, and Zn, respectively. Being 0.01-0.05, the BF of Pb was far lower than those of Cu (0.1-0.3) and Zn (0.4-0.6). This pattern coincides with the $CaCl_2$-extractable metal concentrations in the

Table 3. Cu, Pb, and Zn concentrations in shoots of water spinach grown in soil and soil amended with biochar 1% and 5% in the metal-spiked experiments. Means followed by the same letter in the same column are not significantly different (p<0.05)

Treatment	Metal-spiked 128 mg $Cu.kg^{-1}$		Metal-spiked 212 mg $Pb.kg^{-1}$		Metal-spiked 130 mg $Zn.kg^{-1}$	
	Cu ($mg.kg^{-1}$*)	BF_{Cu}	Pb ($mg.kg^{-1}$)	BF_{Pb}	Zn ($mg.kg^{-1}$)	BF_{Zn}
No biochar (0%)	46.4^a	0.3^a	10.6^a	0.05^a	125.7^a	0.6^a
Biochar 1%	29.1^b	0.2^b	6.5^b	0.03^b	108.4^b	0.5^b
Biochar 5%	22.4^c	0.1^c	1.5^c	0.01^c	80.3^c	0.4^c
CV (%)	*2.6*		*2.0*		*11.5*	

BF: Bioaccumulation Factor is concentration in plant divided by concentration in medium (soil or soil-biochar)

soil (control) in which Pb and Cu were reduced to a greater extent than Zn (Figures 2(b), 3(b), 4(b), and Table 3).

Conclusions

Biochar made from rice residues can help reduce extractability and bioavailability of metals in degraded soil owing to an increase in surface negative charges and the soil pH. The gradual decrease in $CaCl_2$-extractable metals by time, known as the aging effect, cannot be explained by the pH change over time and could be partially attributed to diffusion into the biochar micropores, as indicated by surface negative charges.

The biochar additions of 1% and 5% seem not to enhance water spinach growth and productivity, and is even deleterious at 10%. However, a significant effect of biochar (up to 5%) in reducing metal bioavailability proved that biochar can be used as a remediating medium for contaminated degraded soils.

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