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Article

Effects of Biochar on Soil Quality and Heavy Metal Availability in a Military Shooting Range Soil in Korea

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Heavy metal remediation in shooting range soil is a challenge over the world. The excessive Pb accumulation in the soil can deteriorate soil quality and fertility. The objectives of this research were to evaluate the efficiency of biochar (BC) in improving the physicochemical and biological properties of the soil and to evaluate its effect on Pb availability in a military shooting range soil. Sandy loam soil was collected from shooting range of Gyeonggi Province, South Korea and was incubated for 30 days with different application rates (0-30% w w^{-1}) of BC. The results showed that the addition of BC increased aggregate stability, nitrogen (N) and phosphorus (P) contents, and enzyme activities in soil. Sequential extraction showed that residual and organic bound fractions in the soil amended with BC increased by 33.1 and 16.7%, respectively, and the exchangeable fraction decreased by 93.7% in the soil amended with BC, compared to the unamended soil. We concluded that the application of BC could not only improve physicochemical and biological soil qualities but also stabilize Pb in a shooting range soil.

Key words: Shooting range, Heavy metals, Biochar, Soil quality, Lead

Introduction

Shooting ranges are essential constructions around the world for weapons training and shooting activities. However, shooting activities produce the soil contaminated with heavy metals such as Pb from the used bullets (Dermatas et al., 2006). Nowadays, a huge amount of Pb is being deposited in the shooting range soil worldwide at an annual deposition rate of 200 to 60,000 tons (Craig, 1999; Mellor and McCartney, 1994). Shooting ranges are commonly considered as the second largest source of soil Pb after development of the battery industry (Cao et al., 2008). The contamination of shooting range soil with Pb is well documented (Cao et al., 2008; Dermatas et al., 2006; Grubb et al., 2009; Hashimoto et al., 2009a). Most of the studies indicated that Pb levels in the shooting range soils exceed 1% (Chen and Daroub, 2002; Hashimoto et al., 2010) resulting in degrading soil quality, decreasing soil microbial activities and threating to living organisms (Belyaeva et al., 2005; Lee et al., 2002).

The remediation of shooting range soil has received great interest in the past due to its adverse effects. There are several remediation technologies for remediating heavy metal contaminated soils, such as excavation and landfill, thermal treatment, washing, electro-reclamation, and solidification/stabilization (Aboulroos et al., 2006; Shi and Spence, 2004; Singh and Pant, 2006). However, because of the high cost and low efficiency, these conventional methods are not effective (Aboulroos et al., 2006). The end use of the contaminated soil after remediation is an important factor, which controls the selection of remediation technology (Mulligan et al., 2001). Several soil amendments such as P containing materials and liming materials have been used to remediate the shooting range soil by converting highly mobile and available forms of Pb into less mobile and available forms (Cao et al., 2008; Hashimoto

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et al., 2009a; Li et al., 2009; Moon et al., 2010). However, phosphate-induced immobilization of Pb requires a high amount of available P to stabilize Pb that may result in the leaching of P into ground water and surrounding environment (Dermatas et al., 2008). On the other hand, rise in the soil pH (>8) induced by the lime-based materials for Pb stabilization is not favorable for soil biota.

Biochar (BC) is a charcoal produced from the pyrolysis of biomass at relatively low temperatures (< 700°C) (Lehmann and Joseph, 2009). BC has received great interest during the last few years, due to its beneficial role to mitigate CO_2 emission and to improve soil quality (Major, 2010; Novak et al., 2009). Several studies have shown that BC can improve physicochemical and biological soil properties (Free et al., 2010; Novak et al., 2009; Yeboah et al., 2009). However, in our knowledge, BC has not been widely used so far as a soil amendment for shooting range soils. Additionally, only limited studies have reported on the effect of BC for heavy metal availablity and stabilization in soil.

Recently, Cao et al. (2009) indicated that high content of P in the BC is mainly responsible for Pb stabilization in the aqueous solution due to the formation of stable phosphate minerals. Uchimiya et al. (2010) suggested several possible mechanisms for the stabilization of heavy metals in soil and water by using BC, such as cation exchange, coordination by π electrons of carbon (C) and precipitation. However, most of these studies applied BC to immobilize heavy metals in aqueous solutions or soils but only for a short incubation period (24 h). Therefore, the effectiveness of BC for the stabilization of heavy metals in soils has not been well explored.

In South Korea, there are more than 690 shooting ranges where 267 tons year^{-1} of Pb deposited annually (Ministry of Environment (MOE), 2010). However, little information is available for the soil and water contamination of these sites. Therefore, the objectives of this study are (i) to evaluate the efficiency of BC in improving soil quality related to physicochemical and biological properties, and (ii) to determine its performance on availability and stabilization of heavy metals in a military shooting range soil.

Material and methods

Soil collection A Pb contaminated surface soil was collected from the impact berm (200 m from the firing station) of a military shooting range in Gyeonggi Province, South Korea. Soil samples were air-dried and had all Pb-contained bullets removed passed through a 2-mm sieve, after which subjected to further analysis and the incubation experiment.

Biochar amendment Biochar material (BC250) or BC for short was obtained from University of Bayreuth, Germany, and comprised of 250-kg charcoal mixed with one ton of compost material (50% sewage sludge + 25% freshly chopped lop, grass and leaves + 25% of soil and coarse wood branches). Organic matter (OM) in BC was determined by loss on ignition method (Yerokun et al., 2007). The BC was ground to pass through a 0.5-mm sieve and used for the incubation experiment.

Incubation experiment A soil incubation experiment was conducted using BC at different application rates 0, 1, 3, 5, 10, 20 and 30% (weight basis of soil). Specifically, 100 g of shooting range soil was thoroughly mixed with BC in a high-density polyethylene (HDPE) container. The soil was hydrated to saturation in order to promote the reaction between metal ions and BC, and the hydrated conditions were maintained by periodically adjusting the weights of containers. Then, soil was incubated for 30 d at room temperature without direct sunlight exposure.

Soil analysis The particle size distribution was determined using a hydrometer method as described by Gee and Or (2002). The soil aggregate stability was determined using a wet sieving apparatus (Eijkelkamp, Netherlands). To ensure soil particle distribution, 4 g of 1- to 2-mm air-dried soil aggregate was pre-moistened with distilled water and then was sieved through 0.25 mm into 80 mL of distilled water for 3 min ± 5 s. The water was then evaporated in a dry oven at 110°C to get unstable aggregates. Meanwhile, the remaining soil aggregate was sieved into 80 mL of dispersing solution (2 g L^{-1} sodium hexametaphosphate for the soil with pH >7 or 2 g L^{-1} sodium hydroxide for the soil with pH <7) until only sand particles left on the sieve. Finally, the sample was evaporated and the stable aggregate fraction was calculated.

The soil pH and EC was determined at room temperature by following the 1:5 soil/water extraction methods (NIAST, 2000). Total organic carbon (TOC) content was determined using a Walkley-Black procedure (Nelson and Sommers, 1996), and total C (TC) and total nitrogen (TN) were measured using an elemental analyzer (Flash EA 1112, Thermo-electron Corporation, USA). Dissolved organic carbon (DOC) was measured by a TOC analyzer (TOC 5000A, Shimadzu, Japan). Soil samples for ammonium and nitrate determination were extracted with 2 M KCl. Ammonium-N was measured by an indophenol method as described by Selmer-Olsen (Selmer-Olsen, 1971) and nitrate-N was measured by a spectrophotometer method according to Doane and Horwath (2003), while chlorostannous acid method was adopted to determine available P (Kuo et al., 1996). Total metal contents were determined following the digestion (Mars-X, HP-500 plus, CEM Corporation) according to the USEPA method 3051A (Chirenje et al., 2003). Toxicity characteristics leaching procedure (TCLP) and water extractions were applied to evaluate the leachabillity of Pb and Cu from the amended shooting range soil with BC. The TCLP procedure was performed following the USEPA method 1311 (USEPA, 1992). A sequential extraction procedure was adopted to classify and quantify the Pb fraction of the soil amended with BC according to the procedure of Tessier et al. (1979). The sequential extraction consists of five Pb fractions (exchangeable [using 1 M magnesium chloride], carbonate-associated [using 1 M sodium acetate], Fe/Mn-associated [using 0.04 M hydroxyl amine-hydrochloride in 25% acetic acid], organically associated [using 30% hydrogen peroxide and 0.02 M nitric acid], and residual [using aqua regia]). Water-soluble Cu and DOC were determined using deionized water with a 1:10 soil-solution ratio. The supernatant solution of each extraction was filtered through a 42 Whatman filter paper. Soil Pb and Cu in the digests and TCLP extractions, water-soluble Cu and sequential extraction Pb were measured by atomic absorption spectroscopy (AAS 700, Perkin Elmer, USA).

For soil biological analysis, colony forming units (CFUs) counts were adopted to evaluate the effects of BC amendments on total microbial population (bacteria and fungi) following the description of Taok (2007). Briefly, microorganisms were extracted from soil matrix by making a 100-fold serial dilution using sterile physiological water. The mixture was then shaken vigorously on a vortex for 5 min. Different dilutions were prepared from the supernatant using inoculate petri dishes. Total bacterial counts were performed using nutrient agar medium (Difco). Furthermore, total fungal counts were performed on potato dextrose agar medium (Difco) supplemented by Rose Bengal (1 mg L^{-1}) to inhibit the bacterial growth. Bacterial colonies were counted after 72 h incubation at 30°C and fungi colonies were counted after seven days incubation at 27°C. The activity of five enzymes in the shooting range soil amended with BC was analyzed colorimetrically by a spectrophotometer (Shimadzu-UV 1800). Dehydrogenase activity was measured following the method of Tabatabai (1994). Six grams from a mixture of 20 g of air-dried soil (<2 mm) and 0.2 g of $CaCO_3$ were exposed to 1 mL of 3% aqueous solution of TTC (2, 3, 5-triphenyltetrazolium chloride) for 24 h in the dark at 37°C. The soil was washed and transferred with sufficient amount of methanol, and the concentration of triphenyleformazan in the extracted solution was determined by measuring the intensity of the red color at 485 nm. Urease activity was determined (Tabatabai, 1994). Five grams of <2 mm oven-dried soil was exposed to 5 mL of urea solution (10 mg of urea) for 5 h at 37°C and admixed with 50 mL of 2 M KCl solution by shaking for 1 h. The concentration of NH_4^+ in the extracted solution was determined by measuring the optical density of the color at 690 nm. Acid and alkaline phosphatases were also measured (Tabatabai, 1994). One gram of soil was exposed to 0.2 mL of toluene, 4 mL of buffer solution (adjusting the pH 6.5 for acid phosphatase and pH 11 for alkaline phosphatase), and 1 mL of PNP (p-nitrophenyl phosphate) for 1 h at 37°C. The soil was admixed with 5 mL of solution consisted of 1 mL of 0.5 mol L^{-1} $CaCl_2$ and 4 mL of 0.5 mol L^{-1} NaOH, and the concentration of p-nitrophenol in the extracted solution was determined at a wave length of 410 nm.

Statistics Results were statistically analyzed using the SAS package (ver. 9.1). Means of three replicates for all physicochemical and biological findings were subjected to one way ANOVA. The Tukey's honestly significant difference (HSD) studentised range test was applied for significant differences among means ($p<0.05$). Pearson's correlation coefficient was also calculated among various parameters.

Results

Soil and biochar characterization Table 1 shows selected physicochemical characteristics of the studied shooting range soil and BC. The soil had a sandy loam texture. Soil pH was slightly acidic (6.66) with 0.025 dS m^{-1} EC value. Soil was relatively low in OM (1.04%), and available N (15.01 mg kg^{-1}) and P (8.65 mg kg^{-1}) contents. Total Pb and Cu concentrations in the soil were 4,626 and 225 mg kg^{-1}, respectively. These results indicated that the shooting range soils were severely contaminated by Pb

Table 1. Characteristics of shooting range soil and biochar.

Parameters	Unit	Soil	Biochar
Sand	%	56.6	-
Silt	%	29.4	-
Clay	%	14	-
pH	-	6.66 ± 0.04	6.29 ± 0.02
OM†	%	1.04 ± 0.05	93.04 ± 0.97
Total C	%	0.58 ± 0.02	67.00 ± 1.91
Total N	%	0.045 ± 0.0	2.73 ± 0.10
Available N	mg kg^{-1}	15.01 ± 0.82	300.14 ± 6.61
Available P	mg kg^{-1}	8.65 ± 1.63	290.93 ± 3.64
Total Pb	mg kg^{-1}	4,626 ± 268	BDL‡
Total Cu	mg kg^{-1}	225 ± 82	15.23 ± 4.01

†Organic matter.

‡Below detection level.

Table 2. Changes in soil physicochemical properties as affected by BC application. Means with the same letter within a column are not significantly different at $p<0.05$.

Rates	Aggregate stability	pH	OM†	Total C	Total N	Available N	Available P
%	%		%	%	%	mg kg^{-1}	mg kg^{-1}
0	8.76f	6.10e	1.04ef	0.65f	0.03f	15.00e	7.51c
1	12.55e	6.52d	0.92f	1.11ef	0.04ef	31.09e	8.42c
3	15.00ed	7.21c	1.51ed	2.05ed	0.08ed	66.48d	13.51c
5	16.66d	7.68b	1.76d	2.93d	0.15d	119.28c	17.78c
10	20.07c	7.78b	2.77c	5.15c	0.26c	140.32cb	21.21c
20	24.75b	7.94b	4.12b	10.00b	0.44b	150.14b	40.54b
30	29.41a	8.22a	5.00a	13.43a	0.59a	180.20a	60.35a

†Organic matter.

due to the excessive activity of shooting practices. According to the Ministry of Environment, South Korea (MOE, 2010), the concentration of Pb in shooting ranges is 6.61-folds greater than warning limits of the military shooting range areas (700 mg kg^{-1}) and greatly exceeds the USEPA screening level of 400 mg kg^{-1} (USEPA, 1996).

Biochar was slightly acidic with a pH value of 6.29, and EC value of 0.004 dS m^{-1}. The slightly acidic pH of BC may be induced from the compost material, especially sewage sludge (Singh and Agrawal, 2007). Verheijen et al. (2010) indicated that the pH values of BC produced from a wide variety of feedstocks with a mean of pH 8.1 in a total range of pH 6.2-9.6. The values of TC and TN of BC were 67 and 2.73% by weight, which are in the range of reported values (17.2-90.5% for C and 0.17-7.82% for N) in various studies (Verheijen et al., 2010). Moreover, BC had high concentrations of the available N (300.14 mg kg^{-1}), available P (290.93 mg kg^{-1}) and OM (93.04%). The available P content of BC was similar to other reported values (290.93 mg kg^{-1}) for BC materials (Novak et al., 2009).

Aggregate stability The aggregate stability of unamended and amended soil samples is shown in Table 2. Application of BC significantly increased the soil aggregate stability with higher rates. Maximum aggregate stability, which was 3.36-fold greater than the unamended soil, was observed in the soil amended with 30% BC. The correlation study showed that soil aggregate stability was highly correlated with soil OM ($p<0.001$) (Table 3).

Heavy metals availability Shooting range soil amended with BC caused a pronounced reduction of the TCLP leachable Pb concentration compared to the unamended

Table 3. Linear correlation coefficients between soil properties and the amount of biochar amended for a shooting range soil.

Parameter	Correlation coefficient			
	OM†	TCLP-Pb	TCLP-Cu	pH
Aggregate stability	0.97^{***}	-0.96^{***}	0.81^{**}	0.92^{***}
CFU bacteria	0.94^{***}	-0.96^{***}	0.81^{**}	0.95^{***}
CFU fungi	0.97^{***}	-0.97^{***}	0.79^{**}	0.92^{***}
Alkaline phosphatase	0.99^{***}	-0.84^{**}	0.82^{**}	0.77^{**}
Acid phosphatase	0.94^{***}	-0.81^{**}	0.90^{***}	0.78^{**}
Urease	0.97^{***}	-0.89^{***}	0.82^{**}	0.86^{**}
β-glucosidase	0.99^{***}	-0.88^{***}	0.83^{**}	0.81^{**}
Dehydrogenase	0.97^{***}	-0.77^{**}	0.82^{**}	0.67^{*}

†Organic matter.
$^{*}p<0.05$.
$^{**}p<0.01$.
$^{***}p<0.001$.

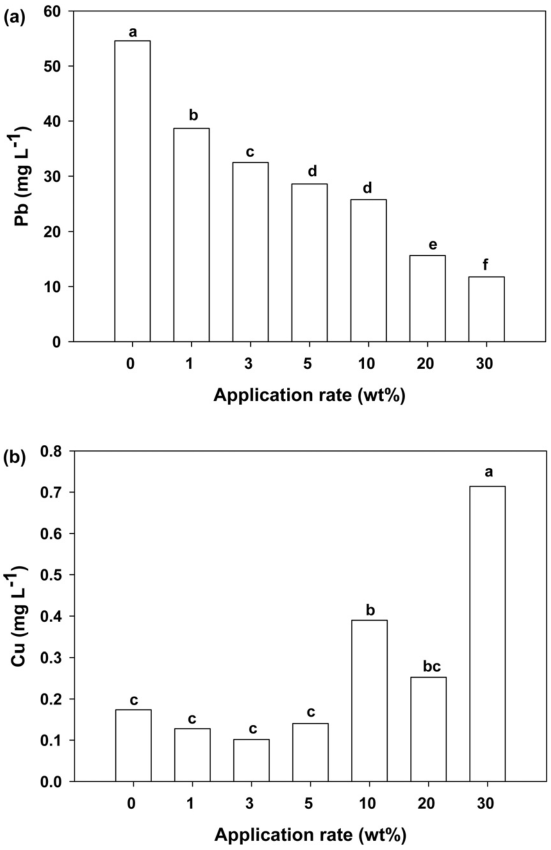

Fig. 1. (a) TCLP-Pb and (b) TCLP-Cu in shooting range soil amended with different application rates of biochar. Bars with same letters are not significantly different.

control (Fig. 1a). The Pb concentrations reduced gradually from 54.57 mg L^{-1} (unamended control) to a minimum of 11.75 mg L^{-1} (30% BC application). Unlike Pb, Cu showed a different trend. Amended shooting range soil with BC caused a pronounced increase in the TCLP-Cu concentration compared to the unamended control (Fig. 1b). The mean Cu concentration increased from 0.17 mg L^{-1} (unamended control) to 0.71 mg L^{-1} (30% BC application). To investigate the effect of BC application on Cu mobilization, water extracted Cu (water-Cu) and DOC were determined. The results indicated a significant increase of DOC by increasing the rate of BC applications. For soils amended with 1-30% BC, the concentrations of DOC ranged from 1.44-12.39 folds greater than the unamended control. The mobilization of Cu was positively correlated with DOC ($r= 0.89$, $p<0.001$).

To investigate the distribution of Pb among different soil pools, sequential extraction analysis was done using 0, 1, 10, 20 and 30% BC amendments. The most abundant fraction of Pb in the unamended sample was the Fe-Mn oxide fraction at 1,554 mg kg^{-1} (30.98%) followed by residual 1,268 mg kg^{-1} (25.27%) and CO_3-bound 977.69 mg kg^{-1} (19.49%) fractions (Fig. 3). Application of BC induced a shift (14.49%) of the exchangeable form of Pb (726.74 mg kg^{-1}) towards less available forms; however, the reduction of exchangeable form of Pb was dependent on the rate of BC application. At 30% BC application, the exchangeable form of Pb was significantly transformed the organic bound and residual fractions at 459.54 and 1,318 mg kg^{-1}, respectively (11.39 and 33.63%).

Soil enzyme activities and microbial populations positively correlated with BC applications (Table 3). A negative correlation among soil enzyme activities, microbial populations, and TCLP-Pb indicated that soil biological properties improved when Pb availability was reduced pursuant to the transformation of Pb into less available

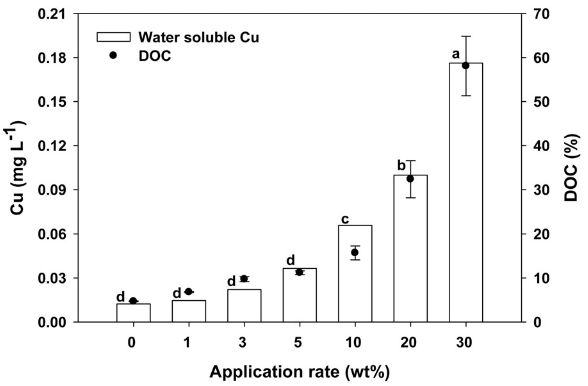

Fig. 2. Water soluble Cu and dissolved organic carbon (DOC) in shooting range soils amended with different application rates of biochar. Bars with same letters are not significantly different. Error bars on circles are standard deviations of four replicates.

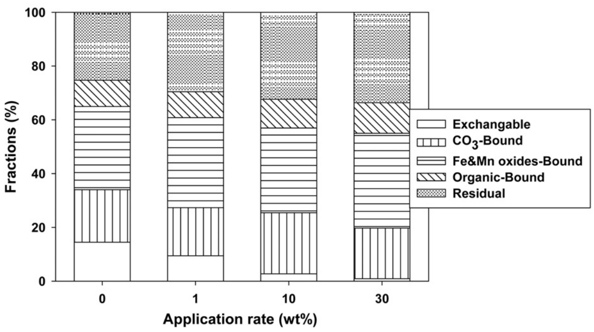

Fig. 3. Fractions ratio of Pb in shooting range soils amended with different application rates of biochar.

forms. A positive correlation was observed between microbial populations and soil pH ($p<0.001$), OM ($p<0.001$), and TCLP-Cu ($p<0.01$) indicating that soil biological properties have been enhanced when Cu availability was increased as a result of Cu mobilization in the shooting range soil amended with BC (Table 3).

Chemical properties Table 2 shows selected chemical properties of the BC amended shooting range soil after 30 d of incubation period. Soil pH was increased from 6.10 in unamended soil to a maximum of 8.22 in soil amended with 30% BC. Similarly, the EC increased up to 1.59 dS m^{-1} in soil amended with 30% BC as compared to the unamended soil (0.03 dS m^{-1}). The application of 30% BC also increased soil OM, TC, and TN, compared to unamended soil (all $p<0.05$). The means of available N and P increased between 31.09-180.20 and 8.42-60.35 mg kg^{-1}, respectively, depending on various application rates of BC.

Biological properties Application of BC enhanced soil biological properties in terms of enzyme activities (Fig. 4) and microbial populations (Fig. 5). Results showed that the acid phosphatase was predominant in the applications of 0, 1 and 3% BC. On the other hand, the alkaline phosphatase was predominant in the applications of 5, 10, 20 and 30% BC. The activities of alkaline phosphatase at rates of 5-30% BC were 1.5-4.3 folds greater than that of acid phosphatase.

Applications of 30% BC soil had the highest enzyme activity and microbial population, which were 7.06-fold (acid phosphatase), 54.52-fold (alkaline phosphatase), 7.81-fold (β-glucosidase), 13.17-fold (urease), and 764.15 -fold (dehydrogenase) greater than the unamended soil ($p<0.05$) (Table 3). The results indicated that bacterial population can be greatly enhanced by BC addition as compared to the fungal one. Similarly, the application of 30% BC had 40.44-fold and 10.55-fold of the colony forming units (CFUs) of bacteria and fungi, respectively, was greater than the unamended control ($p<0.05$) (Fig. 6).

Discussion

Aggregate stability Soil aggregate stability is a relevant indicator of soil erodibility and physical properties of the soil (Table 1). The initial shooting range soil indicated a low aggregate stability (8.76%), mainly due to its low content of fine clay and silt fractions, and OM (1.40%) (Milne and Haynes, 2004; Tisdall and Oades, 1982). However, an increase in the application rate of BC indicated the increasing potential to increase soil aggregate stability (Table 2). Incorporation of OM from BC could be the possible reason of gradual increase in soil aggregate stability (Gregory and Vickers, 2003; Lal, 1998). An increase in OM may increase soil stability (Brodowski et al., 2006; Metzger et al., 1987). Organic matter compounds derived from BC might act as an agent for binding mineral particles together into microaggregates, thereby enhancing soil aggregate stability.

Chemical properties Soil chemical parameters such as pH, OM, and nutrient availability have been used as indicators of soil quality (Chan et al., 2007; Doran and Parkin, 1996; Glaser et al., 2002; Gil-Sotres et al., 2005). With addition of BC, increases in soil OM, soil pH, EC, and available N and P were observed (Table 2). The BC had a higher level of TN (2.73%) while the mineral N was

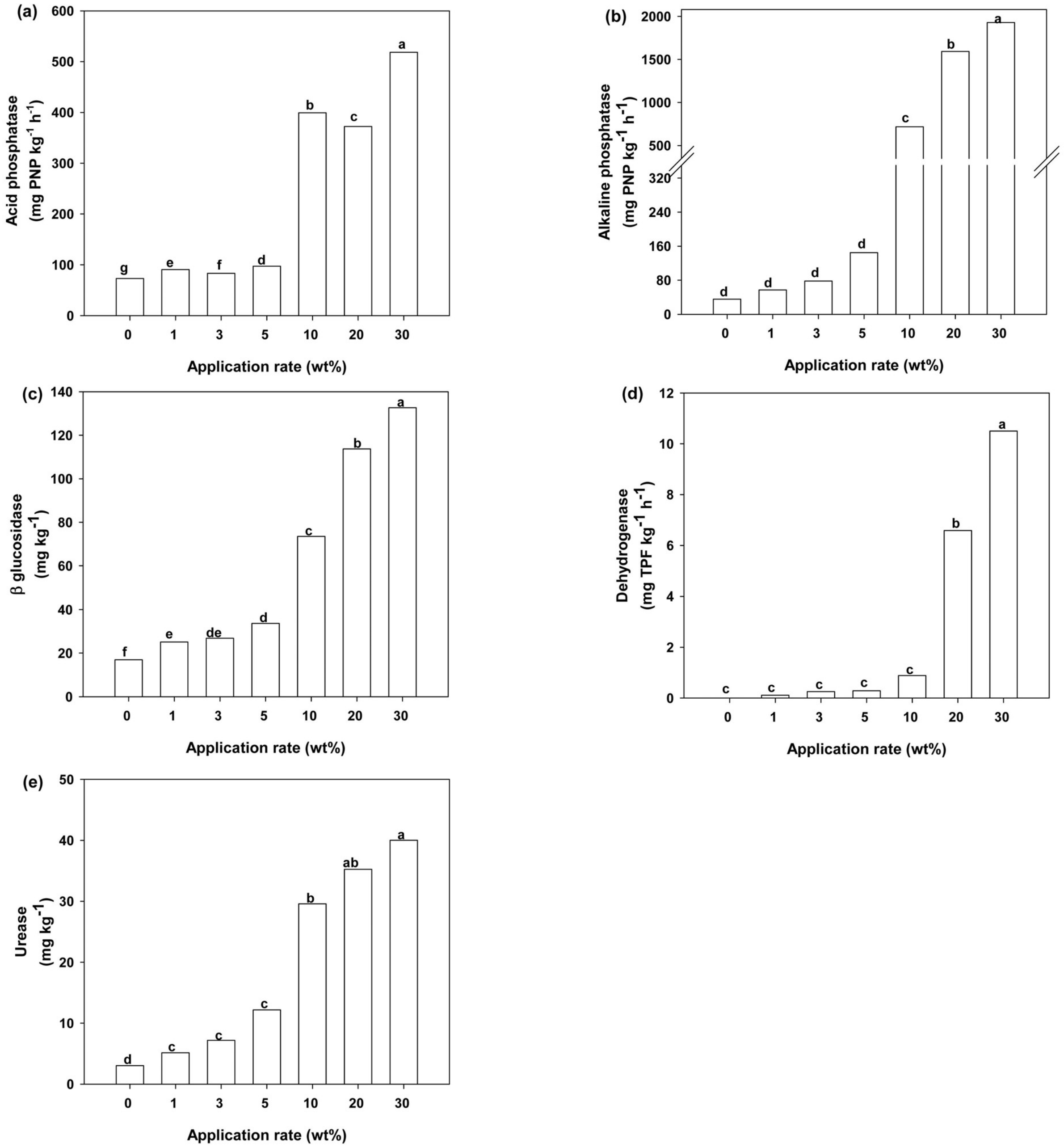

Fig. 4. Enzyme activities in shooting range soils amended with different application rates of biochar. Bars with same letters are not significantly different at 0.05 significant level.

low at 0.3%. Because of the BC priming effect, the mineralization rate and organic N in the soil may be increased (Xu et al., 2006). Significantly, high values of soil pH were found under different rates of BC compared to the unamended control. The addition of 30% BC increased soil pH by 2.1 units. The rise in soil pH could be explained by the ammonification process, as indicated by the increase of soil ammonium concentration by increasing the rate of BC application (data not shown). Specifically, ammonification produces hydroxyl ions that can lead to increases in soil pH (Xu et al., 2006). Another possible explanation is that BC can have a liming effect on the soil pH (vanZwieten et al., 2009); therefore, the application of BC to shooting range soils increases the soil pH. Moreover, the addition of BC raised the soil salinity or EC. The soil salinity increased up to 1.60 dS m^{-1} with increasing application rate of BC. The significant increase in soil salinity was mainly due to the release of the ions during the OM decomposition (Moreno et al., 1999; Usman et al., 2004). The addition of BC to shooting range soil caused a significant increase in available nutrients because application of BC provides additional sources of nutrients through the

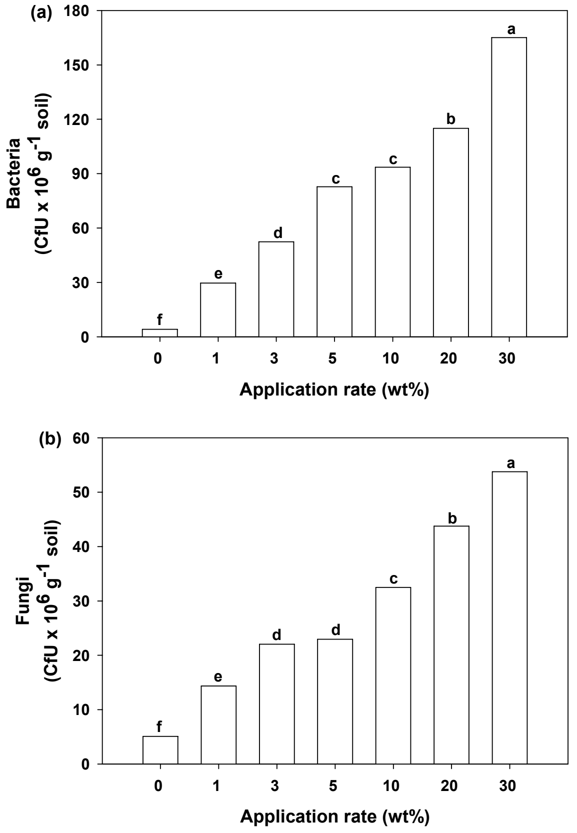

Fig. 5. Populations of (a) bacteria and (b) fungi in shooting range soil amended with different application rates of biochar. Bars with same letters are not significantly different at 0.05 significant level.

decomposition of OM (Moreno et al., 1999). Previous studies have identified that BC applied to soils improved the availability of P to plants (Glaser et al., 2002; Lehman et al., 2003). Pyrolysis of organic biomass from 400 to 700°C results in high concentrations of C and N (Antal and Gronli, 2003). As evidences, our findings show that TC and TN were significantly elevated from 0.65 and 0.03% (unamended control) to 13.43 and 0.59% (30% BC application). Our findings suggest that the potential for increasing soil OC, soil pH, TN, and available N and P due to increasing BC application rate.

Heavy metals availability Addition of organic amendments to contaminated soils has been widely used to reduce toxicity and availability of heavy metals (Gadepalle et al., 2007). In this study, addition of BC to shooting range soil caused a significant decrease in TCLP-Pb up to 78.5% with 30% BC application (Fig. 1). The exchangeable fraction of Pb also reduced up to 93.68% with 30% BC application. The changes of Pb fractions in the shooting range soils after BC application indicated that the readily available form of Pb in BC amended soil was converted into less available form of organic bound fraction (16.67 %) and unavailable form of residual fraction (33.05%) (Fig. 2). Soil pH plays an important role in affecting the solubility and availability of heavy metals in soil (Ok et al., 2008; Ok et al., 2010). A negative correlation was observed between TCLP-Pb and soil pH ($p<0.001$) (Table 3), suggesting that pH controls the availability of Pb in the BC-amended shooting range soil. These findings agree with studies of Cao et al. (2008) and Hashimoto et al. (2009a). They reported that the use of alkaline amendments caused a significant increase in soil pH and a reduction of the TCLP-extracted Pb. These are mainly resulted from the high content of OM in BC. Several studies indicated that OM reduces metal availability and mobility by the metal adsorption on the surface of OM, as well as the formation of stable insoluble organomineral complexes (Shuman, 1999; Walker et al., 2004). For an increase in residual fraction, there are two different possible mechanisms for the transformation of Pb. One is the formation of $Pb(OH)_2$ which is more stable at high pH 8 (Lindsay, 1979). Hashimoto et al. (2009b) suggested that poultry litter ash increased soil pH and stabilized Pb by precipitation and coprecipitation of hydroxides. The other possibility is the formation of stable Pb-pyromorphite by the reaction between available Pb and P in the BC-amended shooting range soil (Hashimoto et al., 2009b). Cao et al. (2009) indicated that high content of P in the BC was mainly responsible for Pb stabilization via formation of stable phosphate minerals.

By contrast, BC addition enhanced the mobilization of Cu in the shooting range soil. The 30% BC application increased the TCLP-Cu 4.11-folds greater than the unamended control (Fig. 2). Similarly, BC increased the water-soluble Cu 14.33-folds greater than the unamended control (Fig. 4). It is evidence that DOC complexes the cationic trace metals and enhance their mobility (Spuller et al., 2007). Consequently, the mobilization of OM as indicated by the elevated DOC concentrations favor the leaching of mobile Cu-DOC complexes. The mobilization of Cu is highly correlated with DOC ($p<0.001$). Similarly, positive correlation between Cu and DOC concentrations was found in soil leachate of a highly contaminated soil (Kalbitz and Wennrich, 1998). However, the mobilization of Cu in the BC-amended shooting range soil was too low to cause any detrimental effect. Furthermore, availability of this amount of Cu to plants might be beneficial as an essential nutrient.

Biological properties Soil microbial populations and enzyme activities are sensitive to soil heavy metal pollution. Typically, soil microbial populations have assumed to play a role in the soil, related to synthesis and decomposition of soil OM and the cycling of nutrients (Wardle and Giller, 1996). Therefore, microbial populations and enzyme activities are very important for the maintenance of soil fertility and they can serve as indicators for soil biological quality. Lee et al. (2002) indicated that most enzyme activities were lower at the shooting range soil due to high Pb concentration. Our results indicated that the addition of BC to shooting range soil enhanced the activity of various soil enzymes and the growth of microbial populations (bacteria and fungi) (Fig. 4, 5). Acid phosphatase was predominant in the 0, 1 and 3% BC applications with pH values of 6.10-7.20 compared to alkaline phosphatase activity. On the other hand, alkaline phosphatase was predominant at 5-30% BC applications along with pH values of 7.68-8.22. These findings are supported by a previous work of Acosta-Martinez and Tabatabai (2004) who reported that acid phosphatase is predominant in acid soils and alkaline phosphatase is predominant in alkaline soils. It is well know that the low soil pH decreased both microbial activities and OM mineralization (Xu et al., 2006). Our results showed that the activity of acid and alkaline phosphatase, urease, β-glucosidase, and dehydrogenase have positive correlations with soil pH ($p<0.01$). The activities of invested enzymes were also positively correlated ($p<0.001$) with soil OM. A negative correlation was observed between enzyme activities and TCLP-Pb. Specifically, urease and β-glucosidase enzymes are sensitive to Pb ($p<0.001$) indicating that soil microbial populations and enzyme activities were enhanced due to reducing Pb availability by immobilization. Application of BC would help mitigate soil acidity and Pb toxicity to soil microorganisms, resulting in improvements in soil biological quality. In addition, both microbial populations and enzyme activity could be potential biological indicators of soil quality changes.

Conclusion

The excessive accumulations of Pb in shooting range soils pose potential environmental problems. Our results clearly indicated that a potential existed for BC to improve soil quality in terms of soil physicochemical and biological properties as well as to stabilize Pb in a military shooting range soil. Application of BC increased aggregate stability, OM, available N and P, microbial populations and enzyme activities of shooting range soil. The BC significantly reduced exchangeable form of Pb to relatively stable forms, including organically bound fraction due to the increase in soil OM, and residual fraction. Our study suggests that at high pH induced by BC, Pb would eventually form relatively insoluble minerals. In addition, high contents of P in the amended shooting range soil might be responsible for the formation of stable Pb-phosphate minerals and therefore, decreasing the mobility of Pb. Our results suggest that the shooting range soils severely contaminated with heavy metals can be restored using BC application. In addition, the economical evaluation for using biochar should be investigated in the future.

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