

Full Length Research Paper

Effect of biochar on soil properties and lead (Pb) availability in a military camp in South West Ethiopia

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Application of biochar to soil can improve numerous physicochemical and biological properties of the soil. The method for lead metal (Pb) remediation in soil is a challenge worldwide. The excessive Pb accumulation in the soil can radically reduce the soil quality and fertility. This study was conducted to find out the efficiency of biochar in improving the physicochemical properties of soil and to evaluate its effect on Pb availability in a military camp soil. Soil sample was collected from military camp of Jimma town, southwestern Ethiopia and was incubated for 90 days with different application rates (0, 2.5, 5, 7.5, 10, 12.5 and 15 t/ha) of biochar. The results showed that the addition of biochar improved, pH, electric conductivity (EC), cation exchange capacity (CEC), organic carbon (OC), organic matter (OM), total nitrogen (TN), exchangeable cations and available phosphorous of the soil and had no significant effect on soil texture. Sequential extraction of Pb showed that at 15 t/ha (4.2 g/kg) application of biochar, the exchangeable form of Pb significantly transformed the carbonate bound, Fe/Mn oxide bound, organic bound and residual fractions to 66.79, 100.5, 112.7 and 112.1 mg/kg, which is reduced by 88.6, 88.9, 88.5 and 88.3%, respectively as compared to the control. It is concluded that the application of biochar could not only improve physicochemical properties of the soil but also stabilize Pb in a military camp soil.

Key words: Lead metal, biochar, soil properties, military camp.

INTRODUCTION

Application of biochar to soil can improve numerous physicochemical and biological properties of the soil such as increased soil pH, cation exchange capacity (CEC) and reducing nitrogen (N) leaching, thereby reducing fertilizer and lime requirements (Van Zwieten et al., 2010), and also enhance soil water holding capacity, soil water permeability, saturated hydraulic conductivity, reduce soil

strength, modify soil bulk density and aggregate stability (Busscher et al., 2010). Cation exchange capacity of biochar has the capacity to exchange cations (such as N in the form of ammonium, NH_4^+) with soil solution, and thus store crop nutrients (Lehmann, 2007). Elevated CECs are due to increases in charge density per unit surface of organic matter which equates with a greater

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degree of oxidation, or increases in surface charge area for cation adsorption, or a combination of both (Atkinson et al., 2010).

Military camps are established in large areas around the world for weapons training and shooting activities. However, shooting activities could lead the soil contamination with heavy metals such as lead (Pb) from the used bullets (Dermatas et al., 2006). Nowadays, a large amount of Pb is being deposited in the military camps soil worldwide within annual deposition rates of 200 and 60,000 tons (Craig, 1999). Military camps are commonly considered as the second largest source of soil Pb after the battery industry (Cao et al., 2008). The contamination of military camp soil with Pb is well documented (Grubb et al., 2009; Hashimoto et al., 2009). Most of the studies indicated that Pb levels in the military camp soils exceed 1%, resulting in degrading soil quality and decreasing soil microbial activities (Belyaeva et al., 2005; Lee et al., 2002).

The remediation of military camp 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 (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 phosphorous (P) containing materials and liming materials have been used to remediate the military camp soil by converting highly mobile and available forms of Pb into less mobile and available forms (Moon et al., 2010). However, phosphate-induced immobilization of Pb requires a high amount of available P to stabilize Pb which may result in the leaching of P into ground water and the surrounding environment (Dermatas et al., 2008). On the other hand, increase in the soil pH (>8) induced by the lime-based materials for Pb stabilization is not favorable for soil biota.

Biochar is a charcoal produced from the pyrolysis of biomass at relatively low temperatures (< 700°C) (Lehmann and Joseph, 2009). Biochar has received great interest during the last few years, due to its beneficial role in improving soil quality (Major, 2010; Novak et al., 2009). However, biochar has not been widely used so far as a soil amendment for military camp soils. Additionally, only limited studies have reported the effect of biochar on heavy metal availability and stabilization in soil. Cao et al. (2009) indicated that high content of P in the biochar is mainly responsible for Pb stabilization in the aqueous solution due to the formation of stable phosphate minerals. Uchimiya et al. (2010) also suggested several possible mechanisms for the stabilization of heavy metals in soil and water by using biochar, such as cation

exchange, coordination by π electrons of carbon (C) and precipitation. However, most of these studies applied biochar to immobilize heavy metals in aqueous solutions or soils but only for a short incubation period (24 h). However, the effectiveness of biochar for the stabilization of heavy metals in soils has not been well studied. Therefore, the objective of this study was to evaluate the effects of biochar on soil physicochemical properties, and its performance on availability and stabilization of Pb in a military camp soil.

MATERIALS AND METHODS

Description of the study area

This study was conducted in an impact area of a military camp in Jimma town, south western Ethiopia. The study area is located at Latitude of 7° 33'N and Longitude of 36° 57'E (Figure 1). The altitude ranges from 1760 to 1920 m above sea level. The mean annual maximum and minimum temperatures are 26.8 and 11.4°C and the relative humidity are 91.4 and 39.92%, respectively. The mean annual rainfall of the study area is 1500 mm (BPEDORS, 2000) and soils are mainly of Nitisols (World Reference Base, 2006).

Preparation of biochar

Biochar of coffee husk was prepared in Jimma University College of Agriculture and Veterinary Medicine (JUCAVM) by using a pyrolysis unit at 500°C temperature and 3 h of residence time. The resulting biochar material was grinded and sieved through a 0.25 mm square-mesh sieve.

Soil sampling and preparation

The soil sample was collected from top soil (0-30 cm) by using auger. The collected soil samples were air-dried, crushed by using mortar and pestle and then passed through a 2 mm square-mesh sieve.

Sampling procedure of physicochemical properties of biochar

Biochar sample was analyzed for physicochemical properties that included surface area, pH, electric conductivity (EC), exchangeable bases (EB) (Ca, Mg, Na and K), cation exchange capacity (CEC), organic carbon (OC), organic matter (OM), total nitrogen (TN) and available phosphorous (Av. P). The surface area was estimated according to Sears (1956) method for silica-based materials. The pH and EC were measured in distilled water at 1:10 biochar to water mass ratio after shaking for 30 min (ASTM, 2009). Biochar OC content was determined by the Walkley-Black method and TN by the Kjeldahl method as sited in Chintala et al. (2013). Av. P was determined by using the Olsen extraction method as sited in Shaheen et al. (2009). Total EB were determined after leaching the biochar with ammonium acetate. Concentrations of Ca and Mg in the leachate were determined by atomic absorption spectrometer. K and Na were determined by flame photometer. CEC was determined at soil pH 7 after displacement by using 1 N ammonium acetate method, and then estimated titrimetrically by distillation of ammonium which was displaced by sodium (Gaskin et al., 2008).

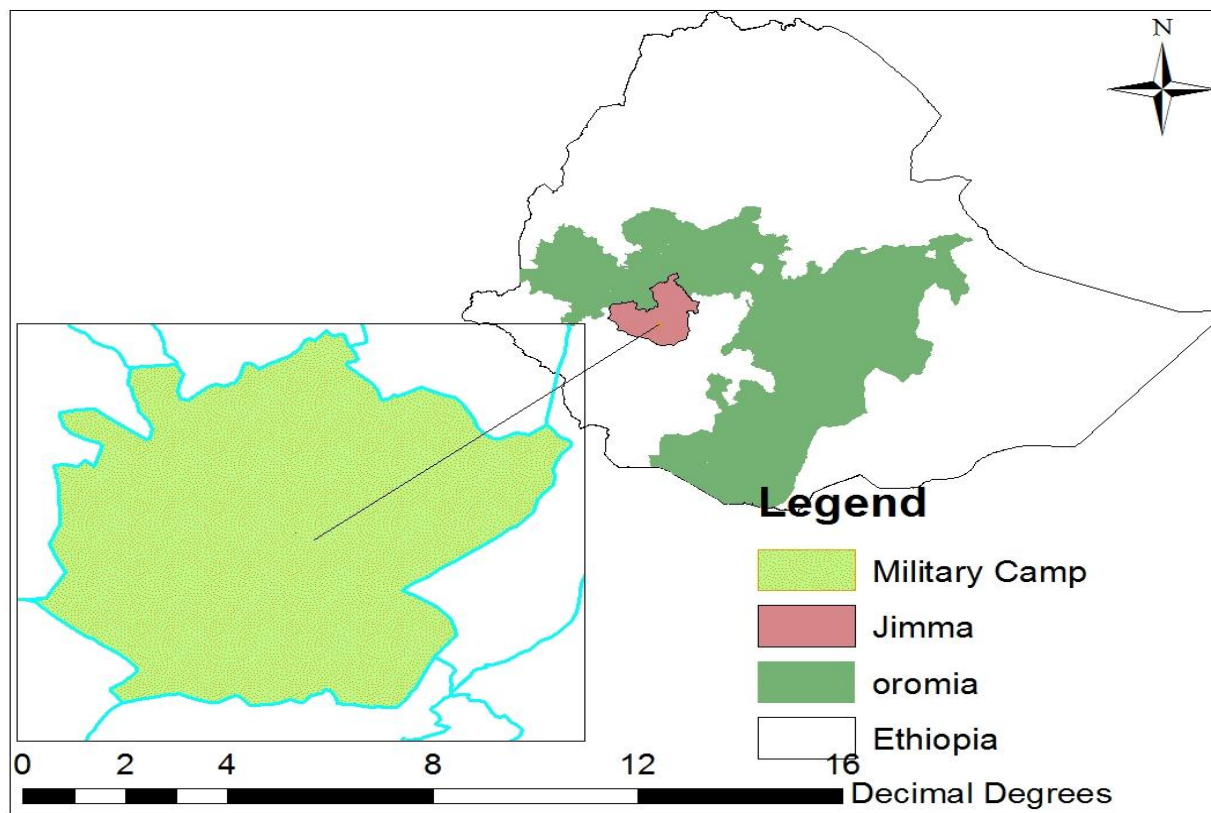


Figure 1. Map of the study area.

Incubation experiment

The effects of different levels of the biochar produced from coffee husk at 500°C temperature on physicochemical properties and availability and stabilization of Pb in a military camp soil were examined by a laboratory incubation experiment. 1 kg of air-dried soil (<2 mm) was weighed in different beakers and biochar was added at rates of 0, 2.5, 5, 7.5, 10, 12.5 and 15 t/ha (equivalent to 0, 0.7, 1.4, 2.1, 2.8, 3.5 and 4.2 g/kg soil) and thoroughly homogenized. The moisture content of the soil-biochar mixture was maintained at field capacity throughout the incubation period, by adding distilled water whenever necessary. Three replicates of each treatment were prepared, randomly placed and incubated in the laboratory at ambient temperature for 90 days. At the end of 90 days, samples were removed from all the treatments and analyzed for pH, OC, OM, TN, Av. p and other parameters were also analyzed as per the standard methods.

Physicochemical properties of soil sample and the soil-biochar mixture

The particle size distribution (texture) of the soil sample and the soil-biochar mixture was determined by the Boycouos hydrometric method (Van Reeuwijk, 1992) after destroying OM using hydrogen peroxide (H_2O_2) and dispersing the soils with sodium hexametaphosphate ($NaPO_3)_6$. Soil bulk density was determined by the undisturbed core sampling method after drying the soil samples in an oven at 105°C to constant weights. The pH of the soil and soil-biochar mixture was determined in water suspension at 1:2.5 soil/soil-biochar: liquid ratio (w/v) potentiometrically using a glass-

calomel combination electrode (Van Reeuwijk, 1992). Electrical EC was measured from a 1:5(w/v) soil to water ratio after a one hour equilibration time as described by ASTM (2009). The Walkley and Black (1934) wet digestion method was used to determine OC content and, percent OM was obtained by multiplying percent soil OC by a factor of 1.724 following the assumptions that OM is composed of 58% carbon. TN was analyzed using the Kjeldahl method by oxidizing the OM in (0.1N H_2SO_4) as described in Black (1965). CEC and EB were determined after extracting the soil samples by 1 N NH_4OAc at pH 7. Exchangeable Ca and Mg in the extracts were analyzed using atomic absorption spectrometer (AAS), while Na and K were analyzed by flame photometer (Rowell, 1994). CEC was then estimated titrimetrically by distillation of ammonium that was displaced by sodium from NaCl solution (Chapman, 1965). Av. P was determined by using 1 M HCl and 1 M NH_4F solutions as an extractant by Bray II method for soils having pH values < 7 (Van Reeuwijk, 1992).

Sequential extraction of Pb

A sequential extraction procedure was adopted to classify and quantify the Pb fraction of the soil amended with biochar according to the procedure of Tessier et al. (1979). The sequential extraction consists of five Pb fractions (exchangeable Pb using 1 M magnesium chloride, carbonate-associated Pb using 1 M sodium acetate, Fe/Mn associated Pb using 0.04 M hydroxyl amine-hydrochloride in 25% acetic acid, organically associated Pb using 30% hydrogen peroxide and 0.02 M nitric acid, and residual Pb using aqua regia). The supernatant solution of each extraction was filtered through a 42 Whatman filter paper. Sequential extraction Pb

Table 1. Analytical results of the soil and biochar for the different physic-chemical properties.

Parameters	Soil	Biochar
Bulk density (gm/cm ³)	1.20	-
Specific surface area (m ² /g)	-	26.20
pH-H ₂ O (1:2.5)	6.12	11.00
EC (dS/m) (1:5)	0.03	6.40
Ca (cmol+)/kg)	8.10	61.50
Mg (cmol+)/kg)	1.20	8.21
K (cmol+)/kg)	0.80	2.80
Na (cmol+)/kg)	0.02	5.15
CEC (me/100g)	24.4	79.20
Organic carbon (%)	4.00	26.40
Organic matter (%)	6.90	46.40
Nitrogen (%)	0.34	2.30
Available P (mg /kg)	4.50	13.90
Total Pb (mg/kg)	3,958	BDL
Sand (%)	29.30	-
Clay (%)	30.70	-
Silt (%)	40.00	-
Texture	CL	

CL = Clay loam, CEC= cation exchange capacity, EC= electrical conductivity, BDL= below detection level.

was measured by atomic absorption spectrometer.

Statistical analysis

The collected data were subjected to different statistical analysis such as analysis of variance (ANOVA) using SAS version 9.2 Software and MS Excel. One-way ANOVA was computed to show significant difference between each treatment for physico-chemical parameters and among each treatment using the general linear model (GLM) procedure of SAS 9.2. Mean separation was done using least significant difference (LSD) after the treatments were found significant at $P < 0.05$.

RESULTS AND DISCUSSIONS

Soil and biochar properties

The selected physicochemical properties and biochar are presented in Table 1 below. The study area soil had a clay loam textural classes. Soil pH was slightly acidic (6.12) with 0.03 dS m⁻¹ EC value. The low value of EC shows that the soil is non-saline which indicates that the total concentration of the major dissolved inorganic solutes like: Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻ and CO₃²⁻ in the soil solution is low (Brady and Weil, 2002). Soil was relatively low in OC (4%), OM (6.9%), and Av. P (4.5 mg kg⁻¹) contents. The total Pb concentration in the soil was 3,958 mg kg⁻¹ suggesting that the military camp soils were severely contaminated by Pb.

The coffee husk biochar produced at 500°C has a 26.2 m²/g surface area which reflects its fine-pore structure generated through a well-controlled activation process. As shown in Table 1, this surface area of biochar produced from coffee husk at 500°C pyrolysis temperatures might be attributable to the removal of -OH, aliphatic C-O, and ester C=O groups from outer surfaces of the feedstock (Chan et al., 2008).

As indicated in Table 1, the coffee husk biochar was more alkaline and has higher base cation concentration. The high pH values of coffee husk biochar may be due to hydrolysis undergone by carbonates and bicarbonates of base cations such as Ca, Mg, Na and K, which were present in the feedstock material (Gaskin et al., 2008). The EC value of coffee husk biochar was found to be higher, indicating the existence of more water soluble salts in coffee husk biochar. The CEC of coffee husk biochar was also found to be higher. This may be due to high negative charge potential of surface functional groups in coffee husk biochar. Av. P, OC and TN were also found to be higher in coffee husk biochar.

Effect of biochar application on soil physico-chemical properties

Texture (particle size distribution)

The particle size distributions of the un-amended and soil-biochar mixtures of the analyzed and the results

Table 2. Effect of biochar application on soil texture (particle size distribution).

Rate (t/ha)	Sand (%)	Clay (%)	Silt (%)	Textural classes
0.0	28.00 ± 2.0	30.67 ± 1.1	41.33 ± 1.1	Clay loam
2.5	27.67 ± 1.5	33.33 ± 1.1	40.00 ± 0.0	Clay loam
5.0	27.67 ± 3.0	34.00 ± 2.0	39.33 ± 4.1	Clay loam
7.5	26.34 ± 1.1	34.33 ± 1.1	39.33 ± 1.1	Clay loam
10.0	26.00 ± 2.0	34.33 ± 1.1	39.67 ± 2.0	Clay loam
12.5	26.00 ± 2.0	35.00 ± 2.0	39.00 ± 2.0	Clay loam
15.0	25.00 ± 2.0	35.33 ± 1.1	38.67 ± 1.1	Clay loam
F-test	ns	ns	ns	
LSD _{0.05}	3.38	4.66	5.62	
CV (%)	7.56	4.78	6.64	

obtained are listed in Table 2 and the sand, clay and silt fractions were not significantly ($P > 0.05$) affected by the application of biochar.

Soil pH

Results of the study of biochar application effect on pH of the soil are given by in Table 3. Statistical analysis of the results revealed a non significant increase in pH as a result of the addition of biochar. However, relatively highest mean pH value was observed in the soil treated with 15 t/ha biochar, while the lowest values were recorded in the control. The lack of significant change in soil pH at the higher biochar rate may be due to the displacement of exchangeable acidity and the high buffering capacity of biochar, thereby retarding a further liming effect (Wang et al., 2014).

OC, OM, TN and Av. P

The application of different rates of biochar on the acidic soil significantly increased the mean soil organic carbon, organic matter and total nitrogen (Table 3) content. The untreated (control) acidic soil had $4.6 \pm 0.4\%$ of OC, $7.93 \pm 0.3\%$ of OM and $0.40 \pm 0.0\%$ TN level, however, due to the addition of biochar, the OC, OM and TN levels increased to a level ranging respectively from 4.6 - 7.1, 7.9 - 12.2 and 0.4 - 0.6% which corresponds to percentage increase of 35.0% OC, 35.1% OM and 34.43% of TN. The highest OC and OM levels and TN were recorded in the soil amended with 4.2 g/kg biochar after three months of incubation period. The high OC, OM and TN content in biochar might have enriched the soil with high organic carbon content and OM. Application of biochar has also resulted in marked changes in the TN content of the soil (Table 3). The TN content of the control soil which was determined to be $0.4 \pm 0.0\%$ was found. Due to application of biochar, the TN level increased to a level ranging from 0.4 ± 0.0 - $0.61 \pm 0.00\%$

TN after two months of incubation period and it increased by 34.43%. The highest increase was recorded in the soil amended with 15 t/ha coffee husk biochar. The observed increase in OC, OM and TN could be due to decomposition which might have occurred when biochar is added to soil (Liang et al., 2006).

The amount of Av. p in soil was also significantly increased by application of biochar (Table 3). The untreated (control) soil had 4.99 ± 0.2 of P after an incubation periods of three months. However, due to the incorporation of biochar, the available P level increased to a level ranging from 4.9-21.4 mg/kg after an incubation period of three months which corresponds to 76.7% increase of the available phosphorus. The highest values of available phosphorus were recorded when biochar was applied at a rate of 15 t/ha after three months of incubation periods. The observed increase in available phosphorus due to application of biochar could be attributed to the improvement in the soil pH which would ultimately reduce the activity of Fe and Al. Van Zwieten et al. (2010) and Chan et al. (2008) also reported the increase in available phosphorus after the application of biochar. The increase in available P with duration of incubation reported in this study is comparable to those reported by Laboski and Lamb (2003), Szychaj-Fabisiak et al. (2005) and Opala et al. (2012).

CEC and exchangeable Ca, Mg and K

The effect of biochar addition on CEC and the contents of exchangeable cations in the soil are presented in Table 3. CEC and exchangeable cations were found to increase upon amendment of the acidic soil with biochar. The untreated acidic soil had 24.95 ± 0.1 me/100 g level before treatment, however, due to the addition of biochar, the CEC level increased to a level ranging from 24.9-34.9 me/100 g after three months of incubation period and it increased by 28.7%. The highest increase in CEC was recorded in the soil amended with biochar at the rate of 15 t/ha (Table 3). The observed increase in CEC due to

Table 3. Effect of biochar application (t/ha) on selected soil chemical properties. Means followed by the same letter within a column are not significantly different from each other at $P < 0.05$.

Rating (t/ha)	pH-H ₂ O	OC (%)	OM (%)	TN (%)	Av.P (mg/kg)	cmol(+)/kg			
						CEC	Ca	Mg	K
0.0	6.2±0.0 ^a	4.6 ± 0.4 ^g	7.93 ± 0.3 ^g	0.40 ± 0.0 ^g	4.99±0.2 ^e	24.95 ± 0.1 ^e	8.57 ± 0.7 ^e	1.3 ± 0.1 ^e	0.85 ± 0.0 ^g
2.5	6.2±0.1 ^a	6.58 ± 0.2 ^f	11.34 ± 0.4 ^f	0.57±0.0 ^f	11.35±0.2 ^{cd}	26.33 ± 0.6 ^d	9.98 ± 0.3 ^d	3.45 ± 0.1 ^d	1.46 ± 0.0 ^{ef}
5.0	6.40±0.4 ^a	6.79 ± 0.2 ^{ef}	11.71 ± 0.5 ^{ef}	0.59 ± 0.0 ^{ef}	11.63±0.1 ^{cd}	28.37 ± 1.1 ^{cd}	16.8 ± 0.8 ^{cd}	3.56 ± 0.1 ^{cd}	1.55 ± 0.0 ^{ed}
7.5	6.5±0.0 ^a	6.86 ± 0.0 ^{d^{ef}}	11.83 ± 0.5 ^{d^e}	0.59 ± 0.0 ^{d^e}	14.41±0.5 ^{bc}	29.27 ± 0.6 ^{bc}	17.5 ± 0.5 ^{bc}	3.63 ± 0.1 ^{bc}	1.99 ± 0.2 ^{bc}
10.0	6.5±0.2 ^a	6.98 ± 0.2 ^{cd}	12.03 ± 0.5 ^{cd}	0.60 ± 0.0 ^{cd}	17.92±2.2 ^{bc}	30.7 ± 0.6 ^{bc}	17.06 ± 0.5 ^{bc}	3.66 ± 0.1 ^{bc}	2.15 ± 0.2 ^{bc}
12.5	6.5±0.2 ^a	6.98 ± 0.2 ^{cd}	12.03 ± 0.5 ^{cd}	0.60 ± 0.0 ^{cd}	19.06±0.9 ^{ab}	32.03 ± 1.1 ^{bc}	17.32 ± 0.8 ^{bc}	3.63 ± 0.1 ^{bc}	2.96 ± 0.0 ^a
15.0	6.6±0.0 ^a	7.08 ± 0.0 ^{cd}	12.21 ± 0.5 ^{cd}	0.61 ± 0.0 ^{cd}	21.41±0.1 ^a	34.99 ± 0.8 ^{ab}	20.84 ± 0.5 ^{ab}	3.83 ± 0.1 ^{ab}	3.01 ± 0.1 ^a
F-test	ns	**	**	**	**	**	**	**	**
LSD	0.38	0.30	0.43	0.025	0.19	2.80	2.18	0.29	0.68
CV	2.31	1.68	1.63	2.03	2.12	2.69	2.69	2.67	11.90

the application of biochar could have resulted from the inherent characteristics of biochar feedstock. Biochar has high surface area, is highly porous, possesses organic materials of variable charge that have the potential to increase soil CEC and base saturation when added to soil (Glaser et al., 2002). Available evidences also suggest that, the intrinsic CEC of biochar is consistently higher than that of whole soil, clays or soil organic matter (Sohi et al., 2009). Therefore, it is quite logical that soil treated with biochar had a highest CEC than the corresponding un-treated soil. Studies by Agusalim et al. (2010) and Chan et al. (2008) have also revealed the increase in soil CEC after the application of biochar. Application of biochar at a rate of 4.2 g/kg on the soil was found to increase the levels of exchangeable Ca and Mg significantly from 8.5 - 20.8 and 1.3 - 3.8 me/100 g, respectively which corresponds to increments by 58.8 and 66.1%, respectively for Ca and Mg. Application of biochar, on the other hand also, increased the values of exchangeable K from 0.85 - 3.0 me/100 g (an

increment by 72.97%). The observed increase in exchangeable cations in the biochar treated soils might be attributed to the ash content of the biochar. The ash content of biochar helps for the immediate release of the occluded mineral nutrients like Ca, Mg and K for crop use (Scheuner et al., 2004; Niemeyer et al., 2005).

Lead (Pb) metal availability

Application of biochar to the soil has brought a linear reduction of the available Pb metal (Figure 2) as compared to the un-amended control. The total Pb pool of the soil reduced gradually from 3953.5 mg/kg (un-amended control) to a minimum of 453.8 mg/kg when the soil is amended with 15 t/ha of biochar after three months of incubation periods. Such a decrease may probably be due to metal retention on the biochar surface.

To investigate the distribution of Pb among different soil pools, sequential extraction analysis was done using 0, 2.5, 5, 7.5, 10, 12.5 and 15 t/ha

biochar amendments. The most abundant fraction of Pb in the un-amended (control) sample was the organic bound fraction at 983 mg/kg followed by residual 963 mg/kg and Fe/Mn oxide bound 874 mg/kg fractions (Figure 2). Application of biochar induced a shift in the exchangeable form of Pb from 545.8 to 61.7 mg/kg which shows a decrease of 89.5% towards the less available form; however, the reduction of exchangeable form of Pb was dependent on the rate of biochar application. At 15 t/ha biochar application, the exchangeable form of Pb significantly transformed the carbonate bound, Fe/Mn oxide bound, organic bound and residual fractions to 66.7, 100.5, 112.7 and 112.1 mg/kg, which corresponds to a reduction by 88.6, 88.9, 88.5 and 88.3%, respectively (Figure 3).

Cui et al. (2011) reported Cd metal reduction (by 40%) as a result of biochar application to a soil high in Cd concentration. Fellet et al. (2014) also reported a reduction of Pb available in soil from 80 to 51 mg/kg, by applying 3% biochar derived from waste orchard. Recently, Puga et al.

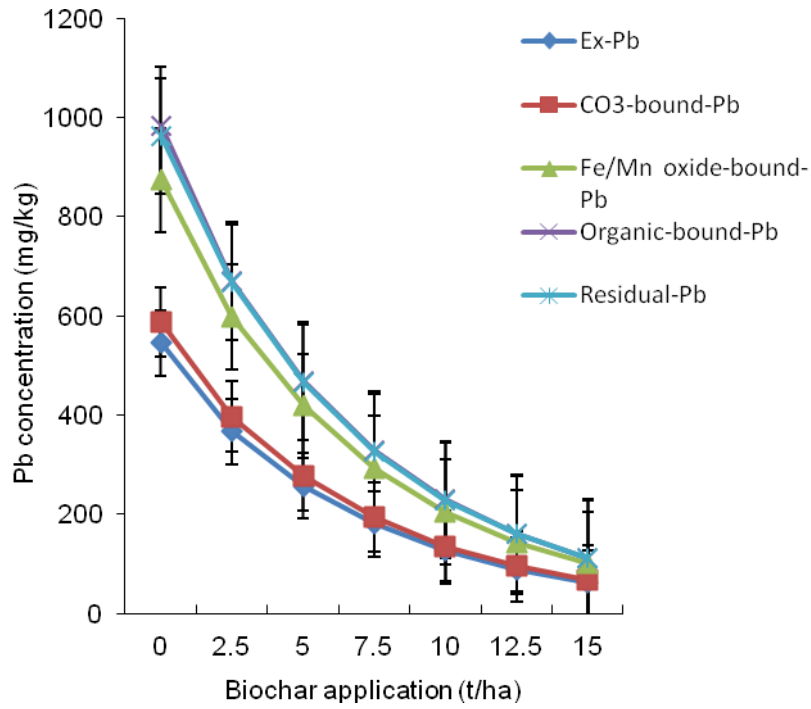


Figure 2. Effect of biochar application on the various Pb pools as determined through a sequential extraction. Vertical bars represent standard errors.

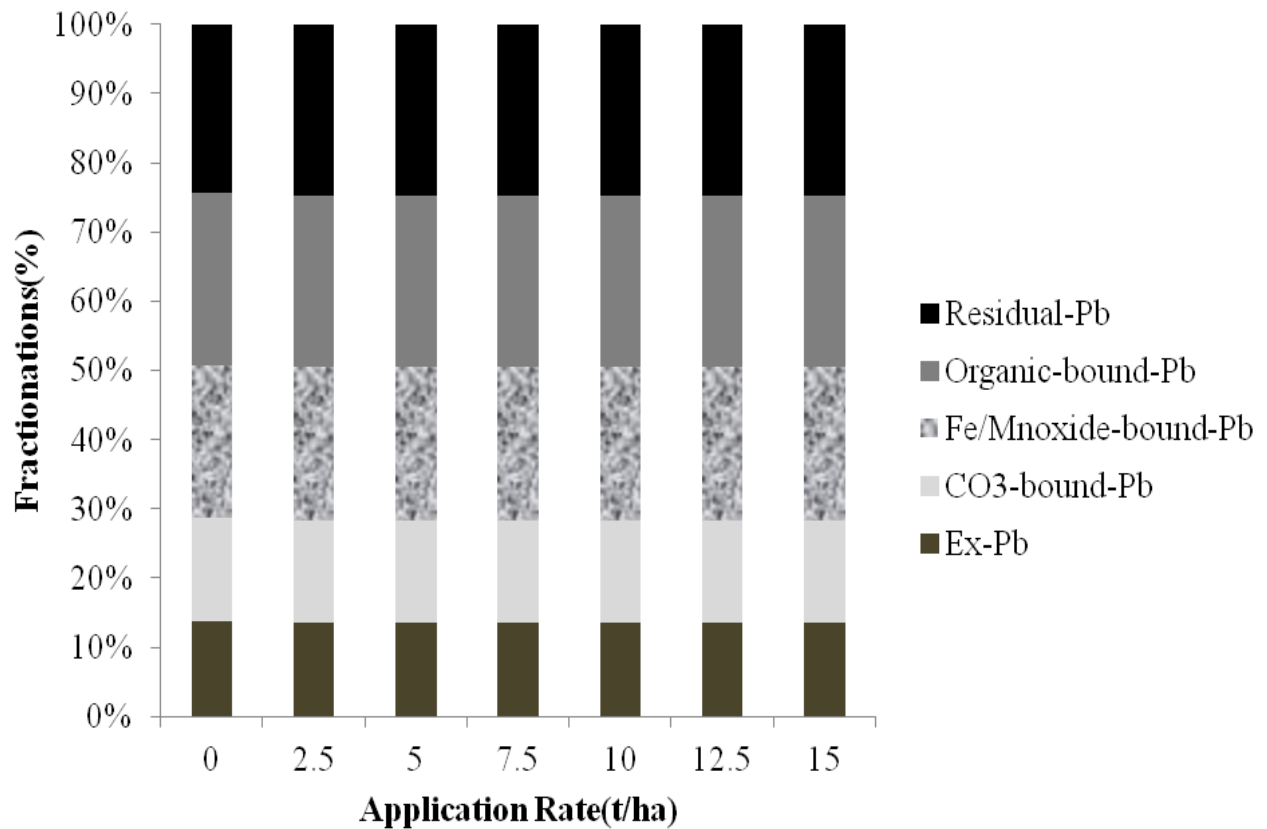


Figure 3. Fractions of Pb in soils amended with different application rates of biochar

(2015) reported a 50% reduction in the available concentration of Pb in Brazil. Therefore, it might be concluded that the results in the present study are consistent with regard to the reduction in the availability of the Pb metal in contaminated soils following biochar application.

Conflict of Interests

The authors have not declared any conflict of interests.

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