



## Original Research Article

### Effects of Biochar on Distribution of Pb and Cd Species in Contaminated Alfisols of Nigerian Northern Guinea Savanna and Sudan Savanna Agro-Ecologies

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#### ABSTRACT

*Heavy metal species' distribution in soils provide information which is used to evaluate the movement and bioavailability of such metals in the soils. The effects of biochar on specie distribution of lead (Pb) and cadmium (Cd) was investigated in contaminated Alfisols of Nigerian Sudan Savanna and Northern Guinea Savanna agro-ecologies. Biochar was derived from wood shavings (plant char (PC)) and bones (bone char (BC)). A sequential extraction procedure was established with six treatments replicated three times in a completely randomized design: B (Barkalau); B+PC (Barkalau + plant char); B+BC (Barkalau + bone char); BG (Bagega); BG+PC (Bagega + plant char); BG+BC (Bagega + bone char). Concentrations of total Pb in the surface soils (0-20 cm) ranged from 1.28-29.31 mgkg<sup>-1</sup> for Barkalau and 1.34-31.25 mgkg<sup>-1</sup> for Bagega while Cd concentration ranged from 0.015-0.085 mgkg<sup>-1</sup> for Barkalau and 0.021-0.092 mgkg<sup>-1</sup> for Bagega. The results indicated that Pb and Cd in Fe-Mn bound fractions dominated in the soils before and after the use of amendments. The average distribution of the fractions in magnitude of the metals obtained from both soils was as follows: Pb in treatments without biochar: bound to oxides > bound to organics > residual > bound to carbonate > exchangeable. Lead in treatments with biochar: bound to oxides > bound to organics > bound to carbonate > residual > exchangeable. Cadmium in treatments was distributed as follows: bound to oxides > bound to carbonates > bound to organics > exchangeable > residual. The addition of biochar modified the partitioning of Pb but showed no effect on Cd distribution in the soils.*

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## 1. INTRODUCTION

Measurement of gross heavy metal content of soils has an important place in characterizing the properties of individual soils and is a measure of their ability to act as “sink” for metal contaminants (Rose, 2004). Soils are the major reservoir for metal contaminants released into the environment by human activities

(Tatiana et al., 2006). The mobility and toxicity of heavy metals are largely predicated by chemical reactions which take place at the hydrous oxide/water interface (Manceau et al. 1996). Heavy metal mobility and bioavailability depend strongly on the chemical and mineralogical forms in which they occur (Baeyens et al., 2003; Abdu et al., 2012). Soil properties such as contents of organic matter, carbonates, oxides as well as soil structure and profile development tend to have a strong influence on heavy metal bioavailability (Kabata-Pendias and Pendias, 2001; Abdu et al., 2012).

Speciation is the study of occurrences of heavy metals in various forms in the soil (Hulanicki, 2000). This study is highly important when dealing with migration and sorption of chemicals in soils (Dube et al., 2001). Metal speciation in soils has been investigated with sequential extraction procedures. In principle, this approach allows the identification and quantification of as many metal forms as there are extraction steps using chemical reagents of different binding strengths and metal-specificity (Tatiana et al., 2006). Depending on the fractionation scheme chosen and extractants used, metal forms are classified into three to seven fractions. Heavy metal speciation influences metal mobility and sorption by soil particles (Yobouet et al., 2010). Transport processes of heavy metals in soil and other media are also known to be related to their speciation (Almas et al. 2006). Unlike many organic contaminants, heavy metals cannot be destroyed by biogeochemical processes, and site restoration relies on their removal (Tatiana et al., 2006). Restoration of lands contaminated by heavy metals depends largely on understanding the chemical forms of the contaminants. Various *in-situ* and *ex-situ* soil cleanup technologies have been employed, of which the most common are incineration, disposal in landfill, flotation, electroremediation, bioleaching, phytoremediation and soil washing with chemicals (Van Benschoten et al., 1997; Peters, 1999; Mulligan et al., 2001; Vandevivere et al., 2001).

Chemical speciation of metals carried out by sequential extraction is essential to the metal mobility and bioavailability (Tessier et al., 1979). The effects associated with the fractions of heavy metals are highly dependent on their chemical species (Yobouet et al., 2010). The exchangeable fraction in the sequential extractions is the amount of metals that are bioavailable for uptake by plants. In this phase, Pb and Cd are easily released into the environment. The associated environmental risks encountered with the presence of heavy metals in soils, plants tissues and water bodies are mainly dependent on the bioavailability and mobility of the heavy metals (Houben et al., 2013). Understanding the behavior, movement, retention, mobilization and simultaneous equilibria of Pb and Cd in a non-uniform environment is insistent to characterizing their bioavailability and mobility (Gomes et al., 2001).

Very few studies such as Hashimoto (2009) and Park et al. (2011) have discussed the influences of biochar on the distribution, speciation and bioavailability of heavy metals in highly contaminated soils. This work seeks to investigate the influence of biochar on distribution of Cd and Pb species in contaminated soils of Barkalau of the Nigerian Northern Guinea and Bagega of the Sudan Savanna agro-ecologies.

## 2. MATERIALS AND METHODS

### 2.1. Experimental Site and Soil Sampling

The alfisols (Bagega and Barkalau) used for the study fall within the Sudan Savannah and Nigerian Northern Guinea agro ecological zones. The Nigerian Northern Guinea Savannah zone has a unimodal rainfall distribution with the average annual temperature and rainfall of 27.3°C and 1051.7 mm respectively (Akintola, 2001). The Nigerian Sudan Savannah agro ecological zone has a low average annual rainfall of 657.3 mm and the prolonged dry season (6-9 months) sustain fewer trees and shorter grasses than the Guinea Savannah (Sowunmi and Akintola, 2016). Contaminated soil from around local mines in Bagega Zamfara State, Nigeria and metal- spiked soil from Barkalau in Kaduna State, Nigeria were used in this study. Composite soil samples (0-15 cm top soil) were collected from a mine site located in Bagega (11.51°N, 6.15°E) in Anka local government area of Zamfara State and a farmland devoid of mining activities in

Barkalau (10.60°N, 7.44°E), Kawo in Igabi local government area of Kaduna State. Random sampling technique was employed in the soil collection processes for both sites. The sampled soils were air dried, crushed and sieved through a 2mm sieve from which subsamples were taken for routine analysis and subsequent greenhouse study. The determined physical and chemical properties of the sampled soils are presented in Table 1 as outlined by Onokebhagbe et al. (2018).

## 2.2. Biochar Preparation

Biochar was prepared from wood dust and cow bones according to the procedure described by Onokebhagbe et al. (2018). The carbonized materials were stored in sealed plastic bags. The two biochars produced were referred to as PC (Plant Char) and BC (Bone Char). The yield, after pyrolysis, was ground to pass through a 2 mm sieve to ensure that all biochar have similar particle size in subsequent experiments. Biochar produced was subjected to chemical analysis as described by Beesley et al. (2010).

## 2.3. Heavy Metal Specie Determination

Lead and Cd speciation in soils was investigated with sequential extraction procedure as developed by Tessier et al. (1979). The layout was a completely randomized design established with six treatments replicated three times in the following order: B (Barkalau); B+PC (Barkalau + Plant char); B+BC (Barkalau + Bone char); BG (Bagega); BG+PC (Bagega + Plant char); BG+BC (Bagega + Bone char). The extraction steps involved the use of chemical reagents of different binding strengths and metal-specificity as described below:

### 2.3.1. Exchangeable fraction

A gram of soil sample was extracted for 1 hr with 8 ml 1 M  $MgCl_2$  at pH 7 under continuous agitation for 1 hour. Lead and Cd concentrations were read off the Atomic Absorption Spectrophotometer (Buck 211VGP AAS).

### 2.3.2. Carbonate fraction

The residue from the exchangeable fraction was leached at room temperature with 8 ml of 1M NaOAc adjusted to pH 5.0 with acetic acid (HOAc) to determine the carbonate fraction. Agitation was carried out for 5 hours to ensure complete dissolution of the carbonates fraction.

### 2.3.3. Fe- Mn oxides fraction

The residue from the carbonate fraction was extracted with 20 ml of 0.3M  $Na_2S_2O_4$ , 0.175M Na-citrate, and 0.0025 M H-citrate as prescribed by Tessier et al. (1979). Cadmium and Pb bound to Fe-Mn species were determined after 6 hours of agitation.

### 2.3.4. Organic fraction

As outlined by Ure et al. (1995), to the residue from the Fe-Mn fraction was added 3 ml of 0.02 M  $HNO_3$  and 5 ml of 30%  $H_2O_2$  adjusted to pH 2 with  $HNO_3$ . The mixture was heated at 85<sup>0</sup> C for 2 hours with occasional agitation. A second 3 ml aliquot of 30% of  $H_2O_2$  (pH 2 with  $HNO_3$ ) was added and heated again at 85 °C for 3 hours, with intermittent agitation. After cooling, 5 ml of 3.2 M  $NH_4OAc$  in 20% (v/v)  $HNO_3$  was added and the sample diluted to 20 ml and agitated for 30 minutes. Determination of Cd and Pb bound to organic matter in solution was carried out using the AAS (Buck 211VGP AAS).

### 2.3.5. Residual fraction

Residue from organic fraction determination was digested with HF-HClO<sub>4</sub> mixture as outlined by Lim and Jackson (1986). The resulting solution was filtered and residual values of Cd and Pb was determined in the AAS (Buck 211VGP AAS). Replicate experiments were carried out with a mixture of soil and various doses of the biochars (PC and BC). The experiment was conducted in triplicates.

## 3. RESULTS AND DISCUSSION

### 3.1. Soil and Biochar Properties

The soils of the two locations have been classified as Typic Haplustalf, order Alfisol in the USDA Soil Taxonomy System (Harpstead, 1973). This soil type is highly weathered, fragile with low activity clay and slightly acidic making its fertility decline under continuous arable cropping (Odunze, 2006; FFD, 2012). The soils are sandy in nature which is attributed to the parent material which is mainly pre-Cambrian basement complex rocks (Malgwi et al. 2000; Voncir et al. 2008; Shehu et al. 2015). The soils have a low level of organic matter, high proportion of sand fractions resulting in low water retention and poor physical stability as shown in Table 1. They are also characterised by low levels of available P, nitrogen and CEC (Table 1). Chemical properties of the biochars used are presented in Table 2. The properties of the biochars vary with the precursor materials as observed by Onokebhagbe et al. (2018).

Table 1: Physical and chemical properties of soils of Bagega and Barkalau

Soil Property	Bagega	Barkalau
Particle size distribution (gkg <sup>-1</sup> )		
Clay	100	120
Silt	200	220
Sand	700	660
Textural class	Sandy loam	Sandy loam
pH <sub>(H2O)</sub>	6.9	7.1
pH <sub>(CaCl2)</sub>	6.6	6.4
EC (dSm <sup>-1</sup> )	0.45	0.9
Organic carbon (g kg <sup>-1</sup> )	5.01	9.5
Organic matter (g kg <sup>-1</sup> )	0.86	1.63
Total nitrogen (g kg <sup>-1</sup> )	0.40	0.70
Available P (mg kg <sup>-1</sup> )	10.95	24.3
Exchangeable bases (cmol kg <sup>-1</sup> )		
Ca	1.22	6.32
Mg	0.48	1.43
K	0.16	0.39
Na	0.50	0.54
CEC (cmol kg <sup>-1</sup> )	2.36	8.68
Extractable heavy metals (mg kg <sup>-1</sup> )		
Extractable Pb	143.98	5.78
Extractable Cd	5.79	2.88

Table 2: Chemical parameters of biochars

Chemical properties	Plant char	Bone char
pH H <sub>2</sub> O	9.4	7.3
pH CaCl <sub>2</sub>	7.9	7.3
Total Nitrogen (g kg <sup>-1</sup> )	7.01	29.8
Total P (g kg <sup>-1</sup> )	1.60	63.2
Exchangeable bases (cmol kg <sup>-1</sup> )		
K	20.51	2.56
Ca	88.00	338.75
Mg	3.08	40.82
Na	5.22	19.67
Micronutrients (mg kg <sup>-1</sup> )		
Cu	27.00	27.00
Mn	57.03	34.28
Co	ND	ND

ND: Not Detected

### 3.2. Effects of Biochar on Pb and Cd Speciation

The data on the effects of biochar on Pb fractions obtained from sequential extraction analysis presented in Table 3 showed that there were significant differences for all fractions obtained from the treatments. The results show that Fe-Mn oxide form of Pb was the most dominant fraction in the values obtained across all treatments. The Pb values of the Fe-Mn oxide fractions obtained from the treatments ranged from  $11.97 \pm 0.99$  to  $31.25 \pm 4.79$  mg kg<sup>-1</sup>. Exchangeable forms of Pb obtained from the treatment ranged from 1.28 to 8.87 mg kg<sup>-1</sup>. In the sequential extractions, increase in values of exchangeable metal concentrations of Pb (8.69 and 9.37 mg kg<sup>-1</sup>; 9.55 and 8.87 mg kg<sup>-1</sup>) in the biochar-amended soils (B + PC and B + BC; BG + PC and BG + BC) were obtained compared to the values (1.28 and 1.34 mg kg<sup>-1</sup>) obtained from the biochar un-amended soils (B and BG, where B denotes soil from Barkalau and BG denotes soil from Bagega) as shown in Table 3. Lead fractions bound to carbonates ranged from 4.89 to 16.13 mg kg<sup>-1</sup>. Higher values of carbonates bound Pb (13.94 and 15.28 mg kg<sup>-1</sup>; 16.13 and 14.21 mg kg<sup>-1</sup>) were obtained from biochar amended soils (B+ PC and B + BC; BG + PC and BG + BC) respectively.

Table 3: Pb fractions in mg kg<sup>-1</sup> of plant char and bone char biochar amended soils (B: Barkalau, B+PC: Barkalau + plant char, B+BC: Barkalau + bone char, BG: Bagega, BG+PC: Bagega + plant char, BG+BC: Bagega + bone char)

Treatments	Exchangeable form	Carbonates form	Fe-MnOxide form	Organic form	Residual form
B	$1.28 \pm 0.363^b$	$4.89 \pm 1.251^b$	$11.97 \pm 0.985^b$	$8.36 \pm 0.680^c$	$6.85 \pm 0.454^c$
B+PC	$8.69 \pm 1.432^a$	$13.94 \pm 1.207^a$	$25.78 \pm 5.500^a$	$14.27 \pm 0.369^b$	$9.86 \pm 0.702^b$
B+BC	$9.37 \pm 1.315^a$	$15.28 \pm 2.900^a$	$29.31 \pm 2.968^a$	$17.34 \pm 2.929^{ab}$	$11.29 \pm 0.646^{ab}$
BG	$1.34 \pm 0.330^b$	$4.94 \pm 1.156^b$	$12.15 \pm 2.226^b$	$8.64 \pm 1.320^c$	$7.13 \pm 0.592^c$
BG+PC	$9.55 \pm 1.790^a$	$16.13 \pm 4.828^a$	$31.25 \pm 4.785^a$	$19.56 \pm 0.726^a$	$13.25 \pm 0.804^a$
BG+BC	$8.87 \pm 2.571^a$	$14.21 \pm 1.399^a$	$27.16 \pm 4.480^a$	$15.34 \pm 1.943^{ab}$	$10.56 \pm 0.804^b$

Means with the same letter(s) are not significantly different at  $p < 0.05$ 

Lower values of carbonates bound Pb (4.89 and 4.94 mg kg<sup>-1</sup>) was obtained from biochar unamended soils (B and BG) respectively as shown in Table 3. Values of Fe-Mn bound Pb obtained were higher in biochar-amended soils (25.78 and 29.31 mg kg<sup>-1</sup> for B + PC and B + BC; 31.25 and 27.16 mg kg<sup>-1</sup> for BG + PC and BG + BC) when compared to biochar-unamended soils with values of 11.97, 12.15 mg kg<sup>-1</sup> for B and BG

respectively. Higher values of the organic fractions were obtained from soils treated with the amendments. Barkalau soil treated with PC and BC amendments gave values of 14.27 and 17.34 mg kg<sup>-1</sup> while Bagega soil treated with amendments gave values of 19.56 and 15.34 mg kg<sup>-1</sup> respectively for PC and BC. Native values of organic fractions obtained for Barkalau and Bagega were 8.36 and 8.64 mg kg<sup>-1</sup> respectively. Table 3 also shows the residual fractions of Pb obtained from after fractionation. The results show that 11.29 and 13.25 mg kg<sup>-1</sup> were obtained as the highest values from treatments B + BC and BG + PC respectively. Native residual fractions of Pb obtained for Barkalau and Bagega were 6.85 and 7.13 mg kg<sup>-1</sup> respectively.

The effects of the biochar amendments on Pb speciation showed contrary results in the distribution of Pb fractions when compared to the native distribution of Pb fractions in soils without biochar amendments as shown in Table 3. This could be due to Pb being held by (exchangeable) electrostatic and specific adsorption when biochar undergoes solubilization (Kabala and Singh, 2001; Kashem et al. 2007; Abdu et al. 2012). Interestingly, each specie was observed to have increased in abundance with the application of the amendments though there was no change in the observed pattern of distribution of the fractions. Concentrations of exchangeable forms of Pb were observed to have increased linearly with the addition of biochar amendments to the soils. This scenario was observed to be the same for other Pb fractions under the influence of biochar amendments. Bone char amendments produced higher values of exchangeable fractions of Pb when compared to the values obtained from treatments under the influence of plant char for the two soils. Values of exchangeable fractions of Pb obtained from Barkalau soil increased in the following order: B + BC > B + PC > B. Similar trend was observed with other fractions for both soils under the influence of biochar amendments. This linear increase in concentration of the various Pb fractions with the addition of biochar amendments could be linked to the extractable properties of the biochars with the formation of complexes and with weak retention of Pb in the soil matrixes (Wong, 2003). The higher fractions obtained with bone char could be attributed to its surface functional groups mostly the hydroxyapatite and amorphous carbonaceous phase (Rojas-Mayorga et al., 2016). Another factor likely responsible for these high values obtained from the use of bone char could be the high pH of the applied bone char. High pH serves to act as an indirect mechanism on the soils' heavy metal speciation, retention or release and heavy metals have been observed to increase with an increase in pH although more research is needed for better explanations (Beesley et al., 2015).

Table 4 shows that Fe-Mn oxide form of Cd was the most dominant fraction in the values obtained across all treatments (unamended Barkalau soil (B), Barkalau amended with plant char (B + PC), Barkalau amended with bone char (B + BC); sole Bagega (BG), Bagega amended with plant char (BG + PC) and Bagega amended with bone char (BG + BC)) as shown in Table 4. The Cd values of the Fe-Mn oxide fractions obtained across the treatments ranged from 0.048 ± 0.018 to 0.92 ± 0.038 mg kg<sup>-1</sup> respectively. There was significant (p<0.05) difference in the values of the exchangeable fractions of Cd as presented in Table 4. Exchangeable forms of Cd obtained from the treatments ranged from 0.019 to 0.067 mg kg<sup>-1</sup>. In the sequential extractions, increase in values of exchangeable metal concentrations of Cd (0.043 and 0.056 mg kg<sup>-1</sup>; 0.067 and 0.049 mg kg<sup>-1</sup>) in the biochar-amended treatments (B + PC and B + BC; BG + PC and BG + BC) were obtained compared to the values (0.019 and 0.025 mg kg<sup>-1</sup>) obtained from the un-amended soils (B and BG) as shown in Table 4. For cadmium fractions bound to carbonates, the results obtained shows that there were significant (p<0.05) differences in the mean values obtained for this fraction. The values ranged from 0.031 to 0.084 mg kg<sup>-1</sup>. Higher values of carbonates bound Cd (0.065 and 0.078 mg kg<sup>-1</sup>; 0.084 and 0.068 mg kg<sup>-1</sup>) were obtained from biochar amended soils respectively. Lower values of carbonates bound Cd (0.031 and 0.047 mg kg<sup>-1</sup>) were obtained from unamended soils (B and BG) respectively.

Values of Fe-Mn bound Cd were higher in biochar-amended soils (0.073 and 0.085 mg kg<sup>-1</sup> for B + PC and B + BC; 0.92 and 0.076 mg kg<sup>-1</sup> for BG + PC and BG + BC) when compared to biochar-unamended soils (0.048 and 0.056 mg kg<sup>-1</sup> for B and BG respectively). There was no significant (p<0.05) difference observed between the effects of the plant char and bone char amendments on the Fe-Mn bound fractions of Cd obtained from Barkalau as the values were at par statistically.

Table 4: Cd fractions in  $\text{mg kg}^{-1}$  of plant char and bone char biochar amended soils (B: Barkalau, B+PC: Barkalau + plant char, B+BC: Barkalau + bone char, BG: Bagega, BG+PC: Bagega + plant char, BG+BC: Bagega + bone char)

Treatments	Exchangeable form	Carbonates form	Fe-Mn Oxide form	Organic form	Residual form
B	$0.019 \pm 0.006$	$0.031 \pm 0.005^{ab}$	$0.048 \pm 0.018^b$	$0.026 \pm 0.004^b$	$0.015 \pm 0.004^d$
B+PC	$0.043 \pm 0.009$	$0.065 \pm 0.003^b$	$0.073 \pm 0.013^b$	$0.051 \pm 0.019^{ab}$	$0.032 \pm 0.001^c$
B+BC	$0.056 \pm 0.013$	$0.078 \pm 0.007^{ab}$	$0.085 \pm 0.044^b$	$0.062 \pm 0.007^a$	$0.042 \pm 0.004^{ab}$
BG	$0.025 \pm 0.006$	$0.047 \pm 0.014^{ab}$	$0.056 \pm 0.021^b$	$0.038 \pm 0.012^{ab}$	$0.021 \pm 0.002^d$
BG+PC	$0.067 \pm 0.025$	$0.084 \pm 0.009^{ab}$	$0.920 \pm 0.038^a$	$0.067 \pm 0.006^a$	$0.049 \pm 0.002^a$
BG+BC	$0.049 \pm 0.026$	$0.068 \pm 0.025^a$	$0.076 \pm 0.004^b$	$0.054 \pm 0.007^{ab}$	$0.036 \pm 0.003^{bc}$
NS					

Means with the same letter(s) are not significantly different at  $p < 0.05$

Higher values of the organic fractions were obtained from soils treated with the amendments. Barkalau soil treated with PC and BC amendments gave values of  $0.051$  and  $0.062 \text{ mg kg}^{-1}$  while Bagega soil treated with amendments gave values of  $0.067$  and  $0.054 \text{ mg kg}^{-1}$  for PC and BC. Endemic values of organic fractions obtained for Barkalau and Bagega were  $0.026$  and  $0.038 \text{ mg kg}^{-1}$  respectively. The residual fractions obtained were the lowest of all fractions of Cd across for the treatments. The results showed that  $0.042$  and  $0.049 \text{ mg kg}^{-1}$  were obtained as the highest values from treatments B + BC and BG + PC respectively. Native residual fractions of Cd obtained for Barkalau and Bagega were  $0.015$  and  $0.021 \text{ mg kg}^{-1}$  respectively.

Cadmium fractions in soils were observed to increase in magnitude under the influence of biochar amendments. Although there was no difference in the pattern of distribution of the cadmium fractions obtained from the treatments, higher values in terms of magnitude of the fractions were obtained from the treatments under the influence of biochar amendments. This could be directly linked to the functional groups of the biochar amendments as observed by Park et al. (2011) who stated the possible mechanism for this increase could be due to electrostatic interactions between  $\text{Cd}^{2+}$  and the functional groups on the biochars.

### 3.3. Percentage Distribution of Pb and Cd Species in Soil under the Influence of Biochar

The percentage distributions of Pb and Cd fractions are presented in Figures 1 and 2. The figures identified the various species of Pb and Cd. They showed that the amount of Pb and Cd extracted from each fraction varied widely. The order of distribution of the metals, considering their magnitude in fractions obtained from both soils was as follows. Lead without any form of amendments in the order: bound to oxides > bound to organics > residual > bound to carbonate > exchangeable. Lead with biochars amendment is in the order: bound to oxides > bound to organics > bound to carbonate > residual > exchangeable. The order of distribution for Cd obtained from the soils with and without biochar amendments followed the order: bound to oxides > bound to carbonates > bound to organics > exchangeable > residual. These were the patterns obtained for both soils as shown in Figures 1 and 2. The fractions were observed to have increased with addition of biochar. Lead and Cd were mostly abundant in the Fe-Mn oxide fractions and other less easily available forms though a small proportion was associated with the exchangeable and residual fractions. This is contrary to the results observed by Beesley et al. (2010) who obtained Pb and Cd as easily available fractions. These fractions are mostly less-labile in soils.

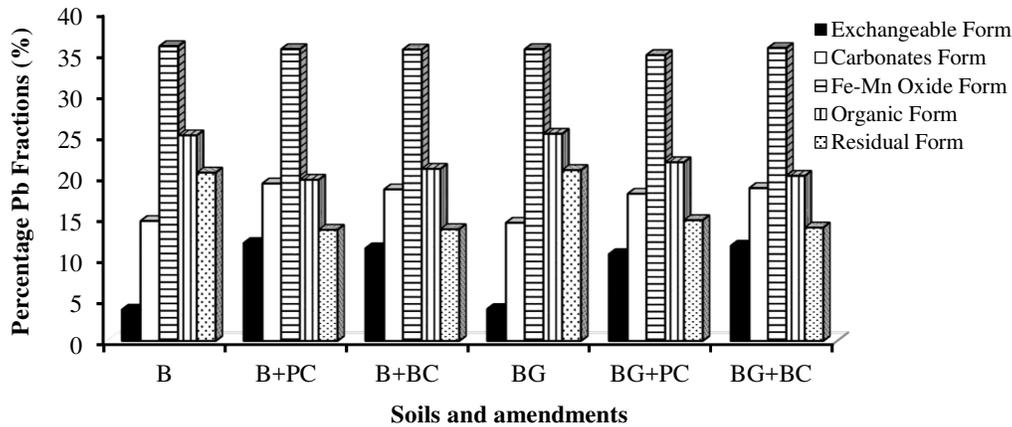


Figure 1: Lead fractions of soils with different amendments (B: Barkalau, B+PC: Barkalau + plant char, B+BC: Barkalau + bone char, BG: Bagega, BG+PC: Bagega + plant char, BG + BC: Bagega + bone char)

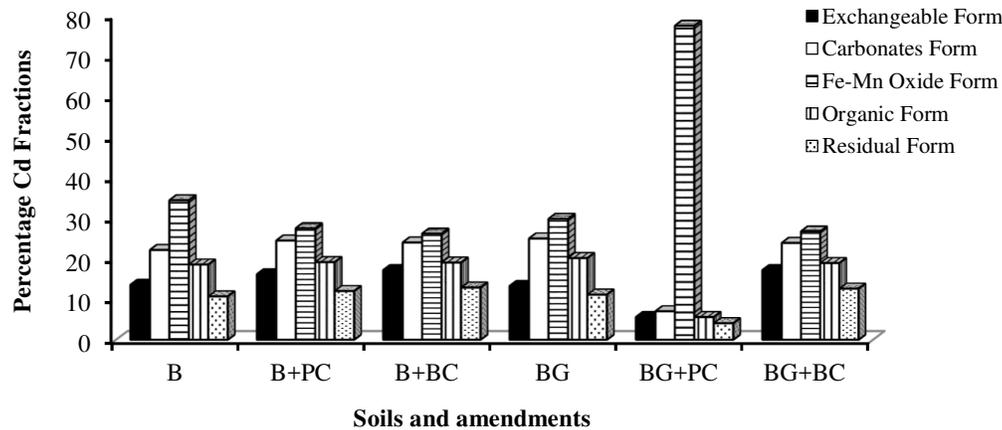


Figure 2: Cadmium fractions of soils with different amendments (B: Barkalau, B+PC: Barkalau + plant char, B+BC: Barkalau + bone char, BG: Bagega, BG+PC: Bagega + plant char, BG + BC: Bagega + bone char)

The large amounts of Fe-Mn oxides and the low organic matter content of the soils could have resulted in greater proportions of Pb and Cd bound to Fe-Mn oxides. Fe-Mn oxides occur in soils as nodules, free gels, crystals and cement between particles (Abdu et al., 2012). These oxides hold heavy metals tightly and can be mobilized under reducing and acidic conditions (Ashraf et al., 2012). This is also an indication of high association and retention capacity of the soil mineral crystal structure. Also, Pb is highly immobile in soil; therefore, its mobility could be highly controlled by change in pH and other unknown factors (Ashraf et al., 2012). Iron-Mn oxides have been found to reduce concentrations of heavy metals in the soil solution by both precipitation and specific adsorption reactions, thereby affecting their bioavailability (Rieuwerts et al., 1998). Metal associations with oxides and organic fractions are not dangerous for the environment because they are less extractable unless when the environment becomes increasingly reducing or oxidizing, can metals be mobilized (Yin et al., 2002; Yobouet et al., 2010).

In summary, Fe-Mn oxides are important components influencing the solubility of Pb and Cd in soils and highly depend on the redox conditions of the soil with dissolution of the oxides occurring in a reducing environment. Addition of biochar to the soil samples caused immobilization of Pb and Cd as noticed with

increase in the immobile fractions with subsequent decrease in the easily exchangeable fractions as observed in Figures 1 and 2. Lead and Cd with high abundance in the phase bound to organics are more available than heavy metals in the residual fraction. Lower fractions of Pb and Cd in the residual form were obtained from the sequential extraction as shown in Figures 1 and 2. This low abundance of the metals in their residual phase compared with its abundance in other geochemical fractions shows higher potential mobility of the metals in the environment, their subsequent release and toxicity. Metals present in the residual fractions are a measure of the degree of how polluted the environment is. The higher the fractions in the residual form, the lower the degree of pollution as this fraction is more of pedogenic and natural origin (Howari and Banat, 2001). The immobile fractions of Pb and Cd obtained were due to their occurrence in low percentages in their residual fractions and high percentages in Fe-Mn fractions as shown in Figures 1 and 2. This shows that the presence of the metals in the soils from the results of sequential extraction were mostly anthropogenic in origin, probably due to mining activities for Bagega soil and artificial spiking for Barkalau soil.

#### 4. CONCLUSION

This study revealed that the chemical fractionation and distribution of Pb in the soil was appreciably affected by the biochar amendments via alteration of soil conditions. The distribution of Pb and Cd fractions in the soil show that their occurrences in surface soils were as a result of human activities. The addition of biochar significantly reduced Pb availability while it had no effect on Cd distribution.

#### 5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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