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Particle Size Effect of Locally Pyrolyzed Biochar on the Remediation of Some Heavy Metals in Crude Oil Contaminated Soils

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Abstract

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Two particle sized biochar from locally pyrolyzed Rhizophora racemose in earthen kiln were assessed on the fate of aluminum (Al), lead (Pb), and zinc (Zn), and the effect on soil organic matter (SOM), organic carbon (SOC) and total nitrogen (TN). Soil samples contaminated with known concentration of crude oil were amended with < 2 mm (B1) and 2-4 mm (B2) biochars incorporated at five different rates (1, 2, 3, 4 and 6 Mg ha^{-1}) in the Teaching and Research Farm, Faculty of Agriculture, Niger Delta University, Bayelsa State. Results obtained shows that exchangeable Pb concentration significantly increased from 0.84-6.09 mg kg^{-1}; with Al from 0.03-0.32 $mgkg^{-1}$ at increasing rate of crude oil and B1 biochar amendment. Conversely, B2 biochar significantly decreased exchangeable Zn concentration from 12.24-3.57 mg kg^{-1}. Using the wet oxidation and van Bemmelen's approach, the incorporation of biochar was observed to significantly influence nutrient availability with SOC, SOM and TN reduced from 2.90-0.87, 5.00-1.50 and 0.13 to 0.4% respectively with B1 incorporation while B2 recorded slight increases on same parameters. Concentration of the heavy metals was found to be associated with pH levels as Pb and Al were strongly adsorbed to colloidal surfaces due to greater surface area of B1 and therefore, were not at hazardous to plants. It is concluded that application of locally pyrolyzed biochar for in situ metal immobilization can be feasible provided surface area of the amendment is increased.

Key words: Biochar, Contamination, Heavy metals, Amendment, Incorporation.

Introduction

Most anthropogenic activities result in the contamination of agricultural soils. This is mostly recorded in either urbano-industrialized areas or sites of exploitation and routes of transportation of natural resources like crude oil and mineral mines. The prevalence of these activities exposes the ecosystem to hazardous substances. Contamination of soils by hydrocarbon and its derivatives has assumed great prominence in many countries, and this has become a global problem (Vidali, 2001). Over the years, several methods have been put in place in the remediation of contaminated soils. The amendment of these contaminated soils is mostly done by stabilizing the contaminants through adsorption and binding process of remediating additives (Burgos, et al., 2008). Of all the methods that have been employed in remediating contaminated soils, the use of

biochar – a carbonaceous material from pyrolysis of biomass – have been greatly utilized (Gomez-Eyles, et al., 2011). The capability of biochar to bind pollutants makes them useful for remediation of urban soils, waste lands and wastewaters (Beesley et al., 2011; Herath et al., 2016; Kookana 2010). Apart from its ability to sequester carbon (Lehmann, 2007a, b), it has also been reported that biochar can adsorb dissolved organic carbon (Pietikainen et al., 2000), improve soil pH and soil macro nutrients content and reduce toxicity of trace metals in leachates (Novak et al., 2009). It can also improve soil fertility, growth of plants and decontamination of various pollutants such as heavy metals and metalloids, hydrocarbons and pesticides (Beesley et al., 2011; Cabrera et al., 2011, Tate et al., 2016).

Plants and animals are known recipients of the adverse effects of crude oil spillage and pollution. Such spillage influences soil and ground water wellness. It is reported that oil spillage has caused constant threat to farmlands, crop plants, forest tree species and other vegetations in oil producing areas in Nigeria and other parts of the world (Agbogidi, 2003; Ogri, 2011).

This study therefore aims at: (1) determining the effect of locally pyrolysed biochar on the amelioration of soils contaminated with crude oil considering cost effectiveness and unavailability of mechanized biochar reactors; (2) assessing the capability of variation in particle size of biochar in reducing bioavailability and concentration of heavy metals in soils contaminated with crude oil.

Materials and Methods

Local pyrolysis

Feedstock of Red Mangrove (Rhizophora racemose) tree was locally sourced and pruned before subjected to slow pyrolysis in a mini pit (Kiln) sunk at the Teaching and Research Farm, Niger Delta University, Wilberforce Island (Amassoma, Bayelsa State; 4°58'52.8"N.6°06'27.2"E). The kiln was properly covered with earthen mud over thin zinc materials to limit oxygen availability. An opening was created at the top for smoke outlet after heat was applied and left for 24 hrs. The pyrolyzed material was collected and allowed to cool for another 24 hrs. The biochar derived was carefully ground using mortar and piston and mechanically screened through 4 and 2 mm sieves to collect two different particle sizes of between 2 – 4 mm and < 2 mm respectively. The two were labelled as B1 and B2 respectively. Quality control measures were taken to prevent cross contamination by thoroughly washing and double rinsing of all equipment and glassware used in the experiment.

Experimental Design

A land measuring 273 m^2 was mapped out for the experiment and six plots designated P0, P1, P2, P3, P4 and P5 measuring 6m x 5m each were delineated in a Randomized Complete Block Design with a 1 m walk between plots. Four out of the six plots were contaminated with Bonny Light Crude Oil (BLCO) of 0.85 kgL^{-1} specific gravity at levels of 10,000, 20,000, 30,000 and 40,000 L/ha. This method was adopted to obtain similar pollution concentrations with on-field pollution. Each plot was split into six sub-plots and amended with 0.0, 1.0, 2.0, 3.0, 4.0, and 6.0 Mg/ha of B1 and B2 amendments. The control plot was contaminated with crude oil without any biochar incorporation to check for effect of the amendment in contaminated soils. All treatments were replicated three times.

Soil physico-chemical Analysis

Soil pH was determined using 10 g of soil samples mixed with 25 mL distilled water, which were stirred and left for 30 min at room temperature (23^o C). Soil pH meter (Elekcity pH-2011, Canada) rod was inserted in the partly settled suspension of each sample after calibration with buffers 4 and 7. Soil organic carbon (SOC) content was determined by the Walkey-Black wet oxidation method whereas organic matter (SOM) was determined by adopting the van Bemmelen's factor of multiplying organic carbon values by 1.724 (Pribyl, 2010). Total nitrogen was determined by Kjeldahl method as described by (Bremner, et al., 1996). Heavy metals concentrations (mg kg^{-1}) were determined using aliquots of soil samples (1

g) digested with 10 mL perchloric acid ($HClO_4$) and another 20 mL general purpose reagent (GPR) grade nitric acid (HNO_3) before adding a drop of sulphuric acid (H_2SO_4). Samples were allowed to stand for 30 min before placed inside a microwave digester for 10 min at 185° C followed by another 10 min at 125° C. Samples were allowed to cool before adding 30 mL distilled water and filtered using the Whatman 42 filter paper. Filtrates were brought to 50 mL mark by adding distilled water and poured into plastic vails and analysed using atomic absorption spectrophotometer (AAS; Perkin-Elmer AA100, MA, USA).

Statistical Analysis

Analysis of Variance (ANOVA) was adopted to analyze concentration of trace metals, SOC, SOM and total nitrogen. This was used to determine the effects of the different particle sizes of biochar on the concentration level of the contaminated soils, whilst Pearson correlation was used to test for relationships between crude oil contamination and biochar amendments. All analyses were carried out using MinitabTM v.17 and graphs plotted using SigmaPlotTM v.10.0 for Windows.

Results and Discussion

Biochar effect on exchangeable heavy metals

Concentration of heavy metals were observed after incorporation and equilibration of biochar amendments. For all treatment levels of crude oil, Pb concentration increased significantly compared to the untreated soil (control) except for the third treatment level (P3) that was similar to the control (Fig. 1C). B1 significantly increased concentration of Pb in P0, P2 and P4 contaminated soils compared to B2. This indicates that in natural soils, < 2 mm biochar can reduce Pb concentration with as little as 1 Mg ha^{-1} of the activated carbon material. Furthermore, at above 6 Mg ha^{-1}, < 2 mm biochar can reduce highly polluted soils when compared to larger particle sizes of the same material. Similar result was obtained when (Tate, et al., 2016) reported a higher effect of < 2 mm particle size biochar in ameliorating soils contaminated with fly ash compared to larger particulate sized biochars. At the various crude oil treatment levels, effect of the amendments on Pb concentration were 20.8% for B1 and 9.2% for B2 in P0 soils; 18.1 and 23.5% in P2 soils while P4 soils had 34.0 and 24.3% respectively. Therefore, the reduction in Pb concentration could be attributed to its retention on the large surface areas of the < 2 mm biochar that have higher negatively charged sites. This also helps in lowering Pb activity in soil solution via complexing by soluble organic ligands or colloidal surfaces (Bell, et al., 1991). Ahmad, et al., (2012) and Beesley, et al., (2010) associated the reduction in Pb concentration with immobilization due to rise in pH thus being adsorbed onto biochar surfaces. Another study by Uchimiya, et al., (2012) associated the immobilization of Pb with low pyrolysis temperature of the ameliorant. They reported that high stability in Pb increases the release of available P, K and Ca from biochars pyrolysed under low temperatures. This further means that the capacity of biochar containing high amount of available P to immobilize Pb can likely be due to the formation of insoluble hydroxyl pyromorphite [$Pb_5(PO_4)_3(OH)$] as reported by (Cao, et al., 2011). On the other hand, Uchimiya, et al., (2011) and Qian, et al., (2016) reported that O-containing functional groups found on biochar surfaces play key roles in binding metals, especially when produced at temperatures not exceeding 350oC. The high O content, as reported, results in high uptake of Cu, Ni, Cd and Pb.

Aluminum (Al) concentration in this study, was found to have been increased but not remarkably at P0, P3 and P4 treatments when compared to the untreated soil (control) for 2 – 4 mm biochar (Fig. 1B). Significant differences were however recorded in P0, P3 and P4 as Al concentration

increased by 25% for B2 when compared to 2.5% for B1 treated soils. At P3, a 25.8% increment was recorded with a 26.7% increment for P4 soils respectively. However, B1 biochar kept Al concentration throughout all crude oil treatments at same level with the untreated soil (control). This explains either, that the large surface area of B1 significantly influenced the retention of Al by strongly binding it to exchange sites (Rieuwerts,

2007) or that the crude oil did not directly influence Al concentration in the soil. There are studies that have associated Al concentration in soil to the pH level of the soil. In a study where, aqueous Al was reacted with different biochar materials in soils with different pH values, (Qian & Chen, 2013) reported that zeta potential of the amendments pyrolysed at different temperatures significantly reduced Al^{3+} concentration with increased pH of 4.5 – 6.0. Conversely, $Al(OH)_4^-$ concentration increased with increased pH of 6.5 – 7.0. They however reported that Al was adsorbed onto the biochar surfaces which influenced its concentration in exchangeable forms. This gives explanation to the level at which Al was reduced in soils of the present study regardless of the particle size of biochar incorporated. In another study, (Qian & Chen, 2014) reported the binding force of Al on the colloidal surface of biochar pyrolyzed at 350oC to be between 100 – 150 eV. This, therefore, is an indicator that biochar possesses great capability of strongly holding unto pollutants and trace metals to its surface to greatly reduce their effects on soil wellness. In this study, however, results show that large particle sized biochar increased Al concentration in P1 and P2 as the electrostatic attraction between positively charged metals and negatively charged biochar surfaces are the prevailing mechanism of immobilization in most contaminated soils.

The incorporation of the two different particle size biochars had distinctive effects on Zn. This was made evident when concentrations of Zn were found to be high in the untreated soil (control) and relatively very low in other soils with increasing crude oil levels. While B1 influenced Zn concentration by 17.7 and 9.9% in P0 and P4, B2 influenced the heavy metal by 32.7 and 10.0% in P0 and P4 respectively. This indicates that both B1 and B2 influenced Zn concentration but at varying degrees. While the incorporation of B1 drastically reduced Zn from 12.2 mg kg-1 in the control to 4.4 mg kg-1 in P0, B2 incorporation reduced Zn to 11.6 mg kg-1 in P0 treatment level (Fig. 1A). This simply translates that, the higher the concentration in soil, the greater the influence of the amendment on crude oil pollution. From P1 however, slight but continuous increase was observed at increasing crude oil levels. It was also observed that slight increase in pH levels influenced Zn concentration in the soil. This corroborates with (Ahmad, et al., 2012) as they associated high pH levels induced by biochar to result in reduced Zn solubility. They further reported that soil pH is considered to greatly influence most trace metals mobility since biochar is alkaline. Since the alkaline nature of the char can induce liming effects, it can as well cause immobilization of metals and subsequently mobilize oxyanions. This biochar-induced increase in soil pH can also influence the sorption of the metals unto colloidal sites.

Biochar effect on soil biochemical properties

As hypothesized, the main effect of different particle sizes of locally pyrolysed biochar on the decomposition process of organic matter is not related to soil organic carbon amounts that may in turn affect the C:N ratio as biochar is known to contain high aromatic carbon that are highly recalcitrant.

Firstly, it was observed that high SOC in the control plot affected amounts of SOM (Table 1). However, it did not translate into low C:N ratio as nitrogen was below 0.5% in the soil. If OM is lost and particulate biochar influences N amount, one would expect a substantial decrease in C:N ratio as reported by (Vandecasteele, et al., 2014). Results from this study, however, indicates that there was significant difference between the control and the B1 incorporated soils for OM content. This could be as a result of either the particle size of the amendment influencing crude oil affinity or reducing OM accumulation by inhibition of hydrocarbon degrading bacteria multiplication. It could also be observed that OC and OM amounts decreased with increasing crude oil levels. Furthermore, there was significant differences between the control and P3 and P4 for OM content while OC was only at P4 (Fig. 2 C and D). However, results showed that there was no significance recorded between B1 and B2 for OC content in the soil at all pollution levels regardless of the high C content in the char material (Table 1) but

significant difference was recorded between B1 and B2 at P4 for OM. Since biochar addition to soil has the capability of affecting soil quality based on inherent soil and biochar properties (Joseph, et al., 2010; Singh & Singh, 2010), the amount of SOC could be attributed to the type of material used, the temperature and or the method of pyrolysis which likely was not suitable for soil application by contributing insignificantly to the nutrient status and further adding recalcitrant C to the soil. Similar result was reported by (Bera, et al., 2016) when soils treated with only biochar could not influence total organic carbon (TOC) due to the temperature of pyrolysis but not the method. Similarly, biochar at both particulate sizes were seen to be ineffective in influencing total nitrogen content in the soil (Fig. 2 B).

Table 1. Properties of biochar used in the experiment

pH	8.9
Ash (%)	4.58
C (%)	72.05
H (%)	3.36
N (%)	1.07
Surface Area (m^2 g^{-1})	24.8

Table 2. Chemical characteristics of soil after contamination with crude oil and amendment with biochar

Sample	p H - H_2O -	SOC %	SOM %	Total N %	C:N	Pb mg/kg	Zn mg/kg	Al mg/kg
P0	4.78	2.90 (0.54) a	5.00 (0.71) a	0.13 (0.36)	22.3	0.84 (0.29) a	12.24 (1.11) a	0.03 (0.05)
P1 B1	4.66	2.06 (0.45)	3.55 (0.60) b	0.09 (0.30)	22.9	3.72 (0.61) b	4.38 (0.66) b	0.03 (0.05) a
P1 B2	4.68	2.61 (0.51)	4.50 (0.67) a	0.11 (0.33)	23.7	0.99 (0.31) a	11.67 (1.08) a	0.30 (0.17) b
P2 B1	5.03	2.64 (0.51)	4.55 (0.67)	0.12 (0.35)	22.0	2.64 (0.51)	2.19 (0.47)	0.03 (0.05)
P2 B2	4.96	2.49 (0.50)	4.30 (0.66)	0.11 (0.33)	22.6	2.52 (0.50)	2.19 (0.47)	0.06 (0.08)
P3 B1	5.12	1.74 (0.42)	3.00 (0.55) b	0.08 (0.28)	21.8	3.24 (0.57)	2.93 (0.54)	0.03 (0.05)
P3 B2	4.84	2.41 (0.49)	4.15 (0.64) a	0.10 (0.32)	24.1	2.52 (0.50)	2.81 (0.53)	0.03 (0.05)
P4 B1	5.14	1.62 (0.40)	2.80 (0.53) b	0.07 (0.26)	23.1	1.38 (0.37)	4.56 (0.68) c	0.03 (0.05) a
P4 B2	5.16	1.91 (0.44)	3.30 (0.57)	0.08 (0.28)	23.9	1.26 (0.35)	3.18 (0.56) d	0.31 (0.18) b
P5 B1	5.22	0.87 (0.29) c	1.50 (0.39) d	0.04 (0.20)	21.8	6.09 (0.78) c	2.88 (0.54)	0.03 (0.05) a
P5 B2	5.09	1.45 (0.38) b	2.50 (0.50) c	0.06 (0.24)	24.2	2.61 (0.51) d	3.57 (0.60)	0.32 (0.18) b

Same alphabets = Not significantly different; Different alphabets = Significantly different ($p < 0.05$); n = 3; ± S.E.
SOC = soil organic carbon; SOM = soil organic matter

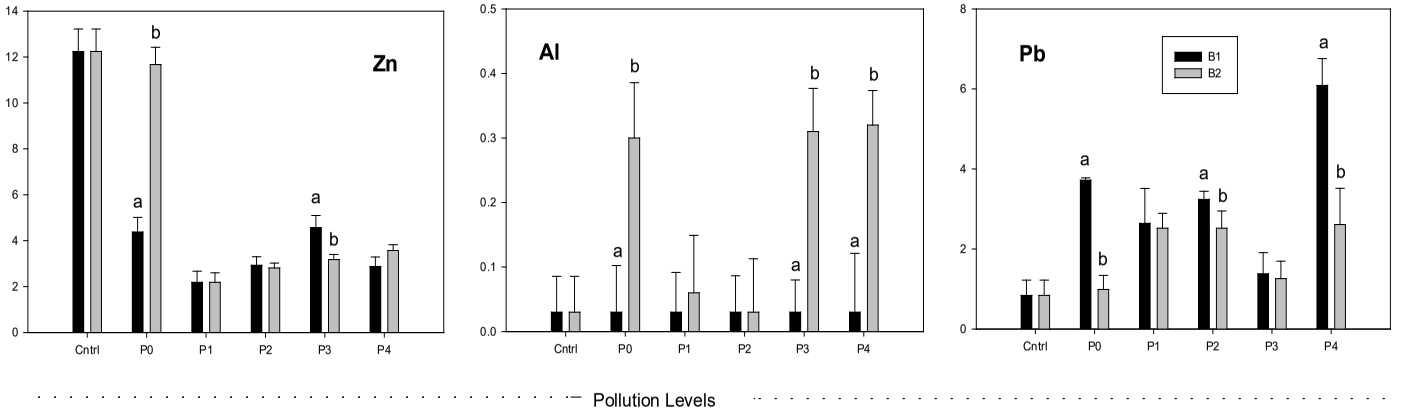

Fig. 1. Concentration of Zn, Al and Pb in soil for each crude oil pollution level and biochar type of < 2 mm (B1) and 2-4 mm (B2). Unintercepting scattered plots indicates significant differences between biochar types in the reduction of heavy metal concentration in soil ($p < 0.05$). Different alphabets = significant difference

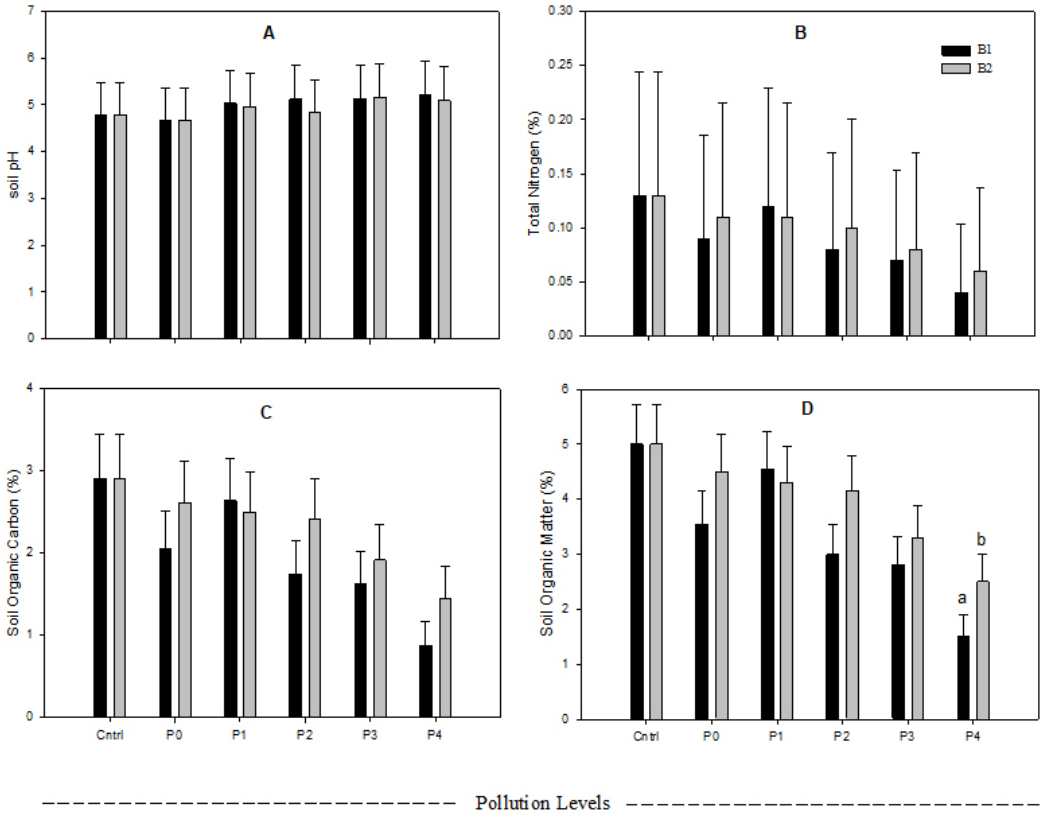

Fig. 2. Concentration of pH (A), Total N (B), SOC (C) and SOM (D) in soil for each crude oil pollution level and biochar type of < 2 mm (B1) and 2-4 mm (B2). Unintercepting scattered plots indicates significant differences between biochar types in the increase of nutrient in soil ($p < 0.05$)

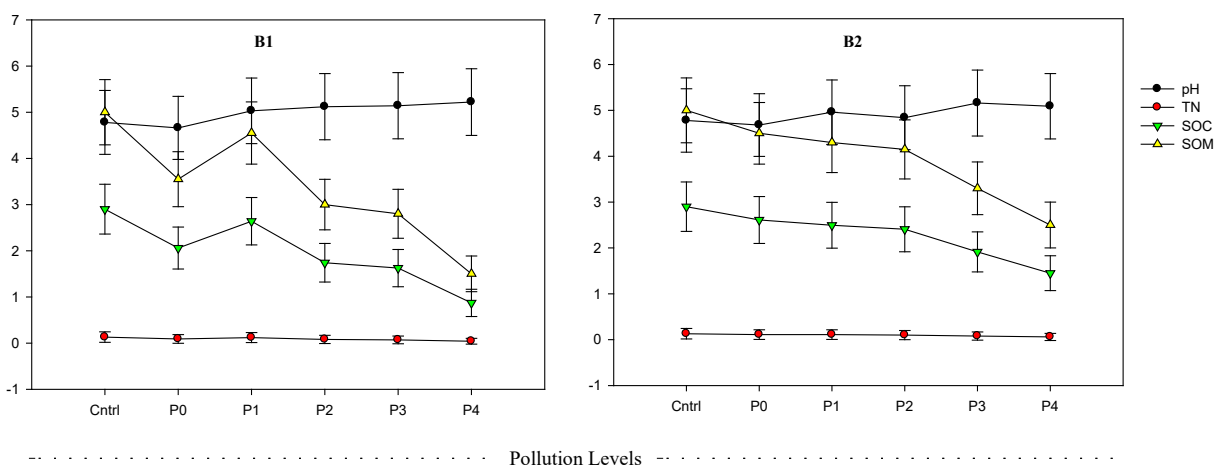

Fig. 3. Comparative effect of biochar types < 2 mm (B1) and 2-4 mm (B2) on soil pH, Total N, SOC and SOM in soil for each crude oil pollution level

Conclusion

The results indicated that application of locally pyrolyzed biochar had considerable influence on soil heavy metal immobilization and some biochemical properties. While Pb concentration was found to be influenced with B1 application compared to B2 as evident from this study, Al concentration can be increased by B2 application than B1. Zinc however showed intertwined influence between B1 and B2 at different application rates on crude oil pollution. Within the period of study, it was also found that soil pH plays significant role in the immobilization of exchangeable metals. While studies have shown that biomass material type and pyrolysis temperature – that are mostly done in mechanized reactors – are leading factors that determine levels of mineralization and or immobilization of metals which the present study did not hypothesized, it is imperative that particle size of the char material should be considered as another important determinant to influencing soil properties. Comparatively, while soil pH increased with increased biochar application regardless of crude oil quantity, OM and OC decreased with increased biochar application in the soil. On the other hand, TN was found not to be influenced by the biochar application (Fig. 3). As evident from our experimental finding, B1 incorporation generally influenced all the biochemical properties more than B2 except for TN (Fig. 3 A and B). Low C:N ratio for both particulate sizes of biochar regardless of its effect on TN over the study period indicated substantial soil ecological functioning with potential for substantial C sequestration through biochar amendment in agricultural soils polluted with crude oil. Therefore, further studies are required to ascertain extents to which different particle sizes of biochar pyrolysed locally by low-earning farmers can improve soil wellness.

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