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## Influence of Locally Pyrolysed Wood and Cattle Dung Biochar on Macronutrients Distribution and Heavy Metal Toxicity in Diesel Contaminated Soils

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#### **Abstract**

A greenhouse study was conducted to assess the influence of locally pyrolysed feedstock in the mineralization of Potassium (K), Phosphorus (P) and Magnesium (Mg) and toxicity of Cadmium (Cd) and Nickel (Ni) heavy metals in soil. Separate amendments of Wood char (WC), Cattle dung (CD) and a combination of both Wood and Cattle dung (WCD) chars weighed at 150 g ( $W_1$ ), 300 g ( $W_2$ ) and 450 g ( $W_3$ ) were assessed for physico-chemical characteristics of incorporated soils contaminated with diesel fuel. Results showed significant influence of the amendments with highest mean concentrations of 7.5  $\pm$  0.36 in WCD ( $W_2$ ), 6.25  $\pm$  0.13 mg kg<sup>-1</sup> in WCD ( $W_3$ ), 12.42  $\pm$  0.28 mg kg<sup>-1</sup> in CD ( $W_2$ ), 122.11  $\pm$  2.71 cmol kg<sup>-1</sup> in CD ( $W_3$ ) and 140.81  $\pm$  34.01 cmol kg<sup>-1</sup> in WCD ( $W_3$ ) soils for pH, organic matter, available P and exchangeable Mg and K respectively. Heavy metals concentration was highest at 0.12  $\pm$  0.01 mg kg<sup>-1</sup> in WCD ( $W_3$ ) and 0.68  $\pm$  0.34 mg kg<sup>-1</sup> in CD ( $W_2$ ) for cadmium and nickel, respectively. These results indicated that CD and WCD were most effective in turning acidic soils basic, influencing carbon sink, increasing organic matter content, mobilizing P, and mineralizing Mg and K while immobilizing Cd and Ni. Correlation analysis showed that locally pyrolysed biochars of CD and WCD possess potential of turning diesel contaminated soils suitable for agricultural use. It was therefore recommended that local farmers can adopt earthen kiln method for pyrolysing feedstock and turn into amendments for contaminated soils.

## Keywords

Local pyrolysis, Amendment, Biochar, Cattle dung char, Wood char

### Introduction

The challenges of agricultural soils being contaminated with crude oil or industrial and domestic wastes are becoming more exacerbating. These contaminants have the capacity to penetrate soils beyond plant root depth of 20-30 cm and contaminate underlying ground water. They are known to play significant roles in agricultural productivity that can result to the loss of fertility, biodiversity and further promote environmental degradation. The widespread problem of an escalating human population growth with diminishing food security and climate change effects (carbon abatement) have been identified as contributing factors in recent times [1]. The exposure of arable lands to hydrocarbon effluents either accidentally or intentionally has further widened the gap in solving such global problems especially at the rural level. Massive industrialization and urbanization have become viable channels through which saturated hydrocarbons like diesel fuels and other substances with similar carcinogenic properties are spilled into soils with little applicable means of control [2]. These substances possess health risk properties that can reach up to 11% of the diesel volume [2,3]; and are mostly found in areas where automobile workshops or filling

stations are situated and operated as well as at flash points of major oil spillage. The resultant effects of these forms of environmental hazards are mostly felt by rural dwellers and farmers as there are inadequacies in response and management of such problems.

Carbon-rich char produced from pyrolytic processes makes materials from biological sources highly recalcitrant [4], thereby possessing great potential for improving agronomic production when applied to soils as an amendment [5]. The application of such "biochar" materials has, however,

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become a widely adopted means of addressing soil infertility problems. It has been established as a viable means of sustainably amending low nutrient-holding soils [6,7].

The incorporation of biochar to soils has been widely reported to possess multiple agricultural benefits of high cation exchange capacity (CEC; 40-80 cmol kg-1), reduced nutrient loss by volatilization and or runoffs as well as the capacity of gradually releasing nutrients (buffering) to growing plants [8]. Furthermore, it has the potential of conditioning soils due to its physico-chemical properties like high surface area (51-900 m<sup>2</sup> g<sup>-1</sup>) that can lead to high percentage base cations, increased water holding capacity, improved electrical conductivity as well as increased soil pH for plant micro- and macronutrients use efficiency [1,6,8-12]. Also, as a result of its affinity and capability to sorb nonpolar organic compounds, biochar can adsorb saturated hydrocarbons, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and benzoinated compounds [13,14] that are composed in diesel contaminated soils. Studies have also shown remarkable influence of biochar in the reduction of phytotoxicity of water-soluble heavy metals by decreasing bioavailability of the metals after contaminated soil was amended with biochar [15-17]. Regardless of the impact of biochar on soil improvement, the availability and access to improved bioreactors by local farmers for massive production is mostly unavailable and cost intensive.

Therefore, this study aims at utilizing locally pyrolysed biochars sourced from wood and cattle dung and a combination of both in the assessment of the availability of

potassium (K), phosphorus (P) and magnesium (Mg) nutrient elements and the reduction in concentration of bioavailable cadmium (Cd) and nickel (Ni) in soils contaminated with diesel

## **Materials and Methods**

## Sample collection and preparation

Soil samples (0-15 cm) were collected from cassava-maizepumpkin arable Experimental Sites (4058'49.7" N: 6006'21.5" E) at the Teaching and Research Farm, Faculty of Agriculture, Niger Delta University, Bayelsa State, Nigeria. Typically, a rotational system of cassava-maize-pumpkin-cucumber experimental cultivation that receives ~ 550 kg N-1 yr-1 in the form of urea and organic manure fertilizers are utilized. Samples were prepared (air-dry) and stored for 2 weeks before gently crushed and sieved (2 mm) to remove debris. Carefully weighed 2 kg of soils were placed into perforated polyethylene bags and spiked with Automotive Gas Oil (AGO) diesel fuel of 0.85 kg L<sup>-1</sup> specific gravity [18,19]. AGO was sourced from a commercial filling station and incorporated with soils at 2:1.7 (w/w) after which, contaminated soils were thoroughly hand-mixed for homogeneity. We selected diesel fuel because our previous studies showed that it has similar long-term effect on soil physico-chemical properties as that of crude oil contaminated fields [20,21].

Feedstock of Red Mangrove (Rhizophora resemosa) from the Permanent Tree crop plantation and Cattle dung from the Animal shed were locally sourced within the Teaching and

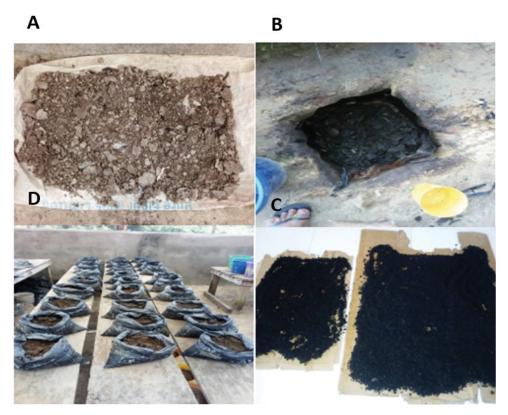


Figure 1: (A) Air dried cattle dung, (B) Pyrolysed biomass in sunk kiln with thin zinc sheets, (C) Sieved biochar (D) Soils incorporated with biochar.

Research Farm and utilized. Feedstock were properly dried and crushed into smaller pieces before subjecting to slow pyrolysis in separate kiln mini pits sunk at  $(75 \times 75 \times 75)$  cm (Figure 1) as described by Tate, et al. [20]. Pyrolyzed materials were collected and allowed to cool before crushed and passed through 2 mm mesh sieves to obtain fine particles. Sieved biochars of wood and cattle dung were weighed using analytical balance at different weights of 150 g (W1), 300 g (W<sub>2</sub>) and 450 g (W<sub>3</sub>) respectively and were further split into three parts of wood char (WC), cattle dung char (CD) and a combination of wood and cattle dung char (WCD). Contaminated soils with no amendment applied served as the control (C) for the study. This method was adopted to compare the effectiveness of the different treatments in the amelioration of the contaminated soils. Contaminated soils were incorporated with the amendments at 10%, 20% and 30% (w/w) respectively and were allowed to equilibrate for 8 weeks. Water was added to soils by sprinkling at field moisture capacity of 25% at 2 days interval throughout the equilibration period.

## **Analytical methods**

Bulk composite soil samples collected from the greenhouse were air-dried, gently crushed, and passed through a 2 mm sieve mesh, bagged, and re-labeled before storage. Chemical properties of soil pH were determined in a soil-salt (0.01 M CaCl<sub>2</sub>) ratio of 1:2 (w/v). Soil samples were collected and allowed to air-dry before a 10 g sample was weighed into beaker and 20 mL of 0.01 M CaCl, added into the beaker at ratio 1:2 (w/v) solution. A glass electrode pH meter was carefully inserted into the suspension and the value taken after 2 minutes as described by Estefan, et al. [22]. Organic carbon was determined through wet oxidation method of Walkey and Black as described by [23]. Organic matter was calculated by adopting the van Bemmelen conversion factor of 1.724 [24]. Exchangeable Bases (K<sup>+</sup> and Mg<sup>2+</sup>) were extracted using NH<sub>2</sub>OAc with Mg<sup>2+</sup> determined using PGI 990 Atomic Absorption Spectrophotometer (PG Instruments Ltd., UK), while K⁺ was determined by ATS 200S Flame Photometer (ATS-Technology, Cyprus). Available phosphorus (P) was determined by extraction with Bray P-1 method of Bray and Kurtz [25]. Heavy metals (Cd and Ni) were extracted using 1N HNO<sub>3</sub>-HClO<sub>4</sub> (Di-Acid) 2:1 mixture and analyzed with Atomic Absorption Spectrophotometer as described by [26].

Differences of means and standard deviation were compared (p < 0.05) and post hoc analysis using a Turkey's pair wise comparison to compare significant difference between treatments was used to know which was most effective in

mineralizing plant nutrient elements and immobilizing heavy

#### **Results and Discussion**

Results of physical and chemical characterization on collected soil and pyrolyzed feedstock analyzed in the laboratory for the study are presented in Table 1.

## Effect of different biochar types on soil reaction

The results indicated that pH levels of the different amended soils ranged from medium acidic to slightly alkaline (Table 2). In CD, WC and WCD, pH (CaCl<sub>2</sub>) ranged from 6.2-7.5 with the control soils having lower pH ranges of 5.4 - 5.8. This means that the amendments at all levels significantly increased soil pH. The distribution pattern for W<sub>1</sub>, W<sub>2</sub> and W<sub>3</sub> in CD, WC and WCD varied one from another; however, the control soil had similar mean values regardless of the amount of the amendment incorporated. This implies that pH of CD, WC and WCD amended soils were increased from slightly acidic (6.3  $\pm$  0.40) to slightly alkaline (7.5  $\pm$  0.25) with increasing biochar quantities, mostly with WCD amendment. The control was found to be moderately acidic (5.6  $\pm$  0.21) after contamination. However, there was remarkable increase in the pH of control contaminated soil from 4.3 as shown in Table 1. This can be associated with the induction of potential drought at the surface layers of polluted soils due to the hydrophobic nature of diesel oil, could potentially aggravate salinization, thus raise pH level [27]. It can also be inferred that these changes in soil pH of treated soils is due to the organic anions and inorganic carbonate inherent in the biochar as an organic material. Previous literatures have reported biochar pH values between pH 4.0 and pH 12.0, with typical values ranging slightly above pH 7.0 [28]. Zhao, et al. [29] found pH levels of biochar amended soils between 8.8 and 10.8, stating that, such outcomes are dependent on the biomass feedstock type which the result of this study can as well be attributed to.

# Effect of different biochar types on organic carbon, organic matter and available phosphorus

Most of the reported mean values of Organic carbon content in CD, WC and WCD treated soils exceeded that of the C soil with the lowest mean value of  $1.31 \pm 0.04 ~\rm g ~kg^{-1}$  found in the C. This indicates that the soil was initially low in Organic C. For CD incorporated soil,  $W_2$  weighted biochar remarkably increased organic C content, which is an indicator that biochar from cattle droppings, when incorporated at such amounts, can influence carbon abatement. WC however had

Table 1: Physical and chemical characterization of wood char, cattle dung and soil.

PH Ash Total C Total N Surface area

	рH	Ash	Total C	Total N	Surface area	<b>Bulk Density</b>
		(wt%)	(%)		(m <sup>2</sup> g <sup>-1</sup> )	(gm <sup>-3</sup> )
Wood char	8.9	4.58	72.05	1.07	24.8	1.13
Cattle char	9.3	3.41	73.20	5.87	32.4	1.26
Soil	4.3	ns	1.50	0.03	19.1	1.03

ns: not supplied

**Table 2:** Physico-chemical characteristics of diesel contaminated soils amended with different sources of biochar.

Amendment	pH (CaCl <sub>2</sub> )	acl <sub>2</sub> )	Organic Carbon (g kg <sup>-1</sup> )	arbon (g	Organic Ma	Matter (g kg <sup>-1</sup> ) Available P (mg kg <sup>-1</sup> )	Available P (	mg kg <sup>1</sup> )	Exchangeable Mg (cmol kg <sup>-1</sup> )	Mg (cmol kg⁻¹)	Exchangeable K (cmol kg <sup>.1</sup> )	( (cmol kg <sup>.1</sup> )
	Range	e Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Меап
C	5.4-5.8	.8 5.6 ± 0.21	1.26-1.38	1.31 ± 0.04 2.17-2.37		2.26 ± 0.10	5.98-6.09	6.03 ± 0.06	50.22-50.42	50.22 ± 0.08	4.65-4.83	4.71 ± 0.08
8	W1 6.5-6.8	.8 6.6±0.15a	3.07-3.67	3.43 ± 0.32	5.30-6.33	5.81±0.51a	9.53-10.32	9.83 ± 0.43a	81.04-83.72	82.16 ± 1.37a	71.80-102.70	91.48 ± 17.07a
	W2 7.0-7.	7.0-7.4 7.2 ± 0.21b		3.46-3.67 3.55 ± 0.11	6.05-6.33	6.19 ± 0.14b 12.20-12.73	12.20-12.73	12.42 ± 0.28b	44.71-130.12	122.11 ± 2.61b	106.50-174.44	140.81 ± 34.01b
	W3 7.1-7	W3 7.1-7.6 7.3 ± 0.25c 3.35-3.71 3.50 ± 0.19	3.35-3.71		5.92-6.40	6.15 ± 0.24b 9.17-10.99	9.17-10.99	10.28 ± 0.97a	119.03-124.01	10.28 ± 0.97a 119.03-124.01 122.11 ± 2.71b 59.24-211.33	59.24-211.33	140.10 ± 76.50b
WC	W1 5.9-6.	5.9-6.7 6.3 ± 0.40a	3.36-3.43	3.39 ± 0.03	5.85-5.92	5.88 ± 0.03	8.73-9.41	8.98 ± 0.34	40.50-46.01	44.09 ± 3.14	7.41-8.71	8.10 ± 0.64a
	W2 6.9-7.3	.3 7.1 ± 0.21b		3.10-3.37 $3.21 \pm 0.14$	5.50-5.81	$5.65 \pm 0.15$	7.22-9.73	$9.10 \pm 2.22$	42.14-54.74	$47.61 \pm 6.44$	10.93-15.22	12.49 ± 2.35b
	W3 7.0-7	7.0-7.6 7.3 ± 0.30c	3.02-3.35	$3.15\pm0.18$	5.30-5.78	$5.53 \pm 0.24$	9.10-10.71	9.81 ± 0.82	46.20-53.11	48.59 ± 3.91	14.71-17.41	16.20 ± 1.39c
WCD	W1 6.8-7	6.8-7.0 6.9 ± 0.10a	3.28-3.59	3.28-3.59 3.39 ± 0.17 5.71-6.1	5.71-6.19	5.95 ± 0.24a	8.80-9.53	9.07 ± 0.38a	60.20-68.83	64.72 ± 4.34a	41.41-49.92	45.32 ± 4.25a
	W2 7.1-7	W2 7.1-7.8 7.5 ± 0.36b	3.51-3.65	3.51-3.65 3.57 ± 0.07 6.05-6.29		$6.17 \pm 0.12b$ 9.72-13.40	9.72-13.40	11.91 ± 1.92b	11.91 ± 1.92b 82.03-101.60	$90.81 \pm 9.93b$	92.32-96.53	94.41 ± 2.06b
	W3 7.3-7	W3 7.3-7.8 7.5 $\pm$ 0.25b 3.52-3.71 3.59 $\pm$ 0.10 6.12-6.40	3.52-3.71	$3.59\pm0.10$			10.92-13.37	$6.25 \pm 0.13b$ $10.92-13.37$ $12.25 \pm 1.23b$ $95.40-112.04$	95.40-112.04	$106.19 \pm 9.33c$	127.41-131.40 130.01 ± 2.27c	130.01 ± 2.27c
C: Control Soil, CD: Cattle Dung Char; WC: Wood Char; WCD: Wood + Cattle	; CD: Cattle I	Dung Char; WC	: Wood Cha	;; WCD: Woo		ung Char; W <sub>1</sub> :	150 g; W <sub>2</sub> : 300	) g; W₃: 450 g; №	1ean ± Standard	Deviation; n = 3;	Means with diff	Dung Char; $W_1$ : 150 g; $W_2$ : 300 g; $W_3$ : 450 g; Mean $\pm$ Standard Deviation; n = 3; Means with different letter = significantly

its greatest influence at  $W_1$  incorporation. Although, studies have shown that biochar from plant sources possess higher organic C abatement potential due to their cellulosic composition. It however still depends, to a large extent, the plant type and method of pyrolysis, i.e., specific plant sourced biochars have higher potentials of increasing soil C content than others depending on the pyrolytic method. In WCD amended soils,  $W_3$  was found to greatly influence soil C content. This shows that when both sources of biochar are combined and incorporated into diesel contaminated soils, there is higher potency of such soil having significant amount of C, thereby turning the soil into a good C sink.

Organic matter content of all the soils showed similar trends as with differences observed for organic C. Although, the lowest mean value of Organic M in the control soil was found to be above 1.50 g kg<sup>-1</sup>; the mean value trend for other amendments were observed as WCD > CD > WC with W<sub>3</sub>, W<sub>1</sub> and W<sub>2</sub> accordingly. It was also observed that all soils had over 2.50 g kg<sup>-1</sup> Organic M content after contamination and incorporation with WC having lowest amounts. The results therefore suggest high organic M content with a carbon turnover likely influenced by the biomass of hydrocarbon utilizing microorganisms [30].

Results obtained for mean values of available phosphorus across all treatments indicated that the amount found within soils were critical due to the high level of contamination according to (Bray P-1) critical range of 10.9 - 21.4 mg kg-1 and critical value of 15 mg kg<sup>-1</sup> for plant utilization [31]. CD, WC and WCD chars had slight influence on available P for W<sub>1</sub>, W<sub>2</sub> and W<sub>3</sub> when compared to the control (Table 2). At  $W_1$ , there was an 11.28%, 8.76% and 9.03% increase while W<sub>2</sub> had 18.92%, 9.12% and 17.41% increment respectively. On the other hand, W, had a 12.39%, 11.01% and 18.21% for CD, WC and WCD treatments respectively. These values obtained inferred that contaminated soils incorporated with the least 500 kg ha<sup>-1</sup> of cattle dung or combined cattle dung and wood chars can have an above 10% influence on available P content in such soil. Soils contaminated with high levels of crude oil derived fuels will however require phosphorus fertilizer application to raise P level considering the Bray P-1 critical value earlier stated. Although available P could be said to be moderate, the results however, also suggests that soil pH influenced P fixation.

# Effect of different biochar types on exchangeable bases (Mg<sup>2+</sup> and K<sup>+</sup>)

Exchangeable Mg<sup>2+</sup> was found to be significantly high in CD treated soils comparatively to C, WC and WCD. While mean values of Mg<sup>2+</sup> ranged above 80.0 cmol kg<sup>-1</sup> for CD; WCD was moderate, and WC could be said to be low (< 50 cmol kg<sup>-1</sup>). Such results however

indicate that animal droppings contain high quantities of the base element compared to plant biomass. The values of Mg<sup>2+</sup> further showed that there was an increase when soil was amended with CD at W<sub>2</sub> and W<sub>3</sub> as compared to W<sub>1</sub>. But was no remarkable difference between W<sub>2</sub> and W<sub>3</sub> incorporation. Similar results of no differences between the various weights were obtained in soils amended with WC whereas WCD soils showed remarkable differences between W<sub>1</sub>, W<sub>2</sub> and W<sub>3</sub> respectively. This suggests that Mg2+ concentration increases in soils with increased biochar application considering the source of the biochar as reported by [32]. Exchangeable K<sup>+</sup> values indicated that CD amended soils were influenced when incorporated with W<sub>2</sub> and W<sub>3</sub> with corresponding increment in the amount of char added when compared to W<sub>1</sub>. Similarly, WC and WCD soils showed remarkable increases in K<sup>+</sup> content at all weighted levels of the amendment. This corroborates with [33] findings that stated that significant increases in the concentration of K<sup>+</sup> were found when biochar from plant and animal residues were applied at > 50 t ha<sup>-1</sup> with no fertilizer.

## Effect of different biochar types on heavy metal immobilization in the soil

The effect of different biochars on the toxicity levels of heavy metals was assessed by analyzing the Di-Acid extractable metal concentrations released into soil solution by the soil-biochar mixtures at incorporation periods. This provides insight on the heavy metal pools which can be regarded as a solubility, bioavailability, and mobility indicator in soils. This procedure was adopted by [26].

Mean Cadmium concentration indicated that CD increased levels of the heavy metal within the soil. The implication is that it makes the metal mobile and more bioavailable for plant root systems accumulation. This, on the other hand, is

disadvantageous as the bioaccumulated metal is transferred through food chain pathways by livestock and humans at consumption (Table 3). This further reveals that CD was able to extract the metal from surface sites into soil solution. On another hand, this could be said to be advantageous as it portends the capacity of the amendment to make the metal readily leachable. In comparison with C, WC and WCD, all weights of  $W_1$ ,  $W_2$  and  $W_3$  were found to be effective on the toxicity of Cd considering the critical limit of 0.20 mg kg<sup>-1</sup> for Cd as reported by de Vries, et al. [34].

Nickel concentration was observed to be lowest in CD compared to other amendments. Although least concentration was observed in soils incorporated with W<sub>2</sub>. WC proved to be more effective in increasing the mean concentration of the metal across all weighted amendments. This indicates that WC influenced mobility and bioavailability of Ni than C, CD and WCD. This however does corroborate with findings by [35] who related the bioavailability of Ni to high organic matter content of soils as organic matter was found to be relatively high in the present study. Following available results, it could be inferred that specific heavy metals can be made mobile, soluble, or bioavailable by biochar from specific sources.

Correlation coefficients of the variables with the different biochar amendments are shown in Table 4. This was used to measure the strength of relationship between the variables and the amendments on a scale of -1 (perfect inverse relation), 0 (no relation) to +1 (perfect relation).

For the nutrient element P, all amendments were found to strongly correlate except for WCW<sub>1</sub>. This is an indication that WC (W<sub>1</sub>) had less influence on the mineralization of available P. Furthermore, it is an indication that biochar amendments possess high capabilities of turning immobile P readily available for crop utilization regardless of such soils

		Total H	eavy metals (mgkg <sup>-1</sup> )		
Amendment		Cd		Ni <sup>2+</sup>	
		Range	Mean	Range	Mean
С		0.12-0.15	0.12 ± 0.01	4.00-4.15	4.06 ± 0.08
CD	W1	0.15-0.23	0.19 ± 0.04	1.10-4.48	2.79 ± 1.69
	W2	0.14-0.17	0.15 ± 0.02	0.34-1.02	0.68 ± 0.34
	W3	0.11-0.32	0.22 ± 0.10	0.53-7.34	3.94 ± 3.41
WC	W1	0.16-0.33	0.24 ± 0.08	7.01-9.06	8.04 ± 1.03
	W2	0.13-0.26	0.19 ± 0.06	7.05-9.66	8.36 ± 1.31
	W3	0.17-0.18	0.18 ± 0.01	7.98-8.35	8.16 ± 0.19
WCD	W1	0.08-0.15	0.12 ± 0.04	1.57-1.68	1.62 ± 0.05
	W2	0.07-0.24	0.16 ± 0.08	0.09-7.66	5.12 ± 4.36
	W3	0.12-0.18	0.12 ± 0.01	0.74-1.34	0.97 ± 0.33

Table 3: Extractable heavy metal concentration of diesel contaminated soils.

C: Control Soil; CD: Cattle Dung Char; WC: Wood Char; WCD: Wood + Cattle Dung Char;  $W_1 = 150 \text{ g}$ ;  $W_2 = 300 \text{ g}$ ;  $W_3 = 450 \text{ g}$ ; Mean  $\pm$  Standard Deviation; n = 3; Means with different letter = significantly different at p < 0.05

Amendment	ОМ	P	Mg	K	Cd	Ni
CDW1	0.951	-0.956	0.784	-0.989	-0.974	-1.000
CDW2	0.732	0.971	-0.433	0.680	0.998*	-1.000
CDW3	0.741	0.931	0.959	0.965	0.922	1.000
WCW1	0.564	0.803	-0.774	0.674	0.882	1.000
WCW2	0.639	0.976	0.920	0.919	-0.976	1.000
WCW3	0.781	0.980	0.124	-0.163	0.883	-1.000
WCDW1	0.809	0.902	-0.999*	0.952	0.996*	-0.998*
WCDW2	0.971	0.947	-0.656	-0.942	0.644	0.869
WCDW3	0.794	-0.988	1.000*	-0.168	-0.046	-0.930

Table 4: Correlation coefficient calculated for the effect of amendments on soil properties

are polluted with diesel fuel or not. This falls in agreement with [33] who established significant increase in available P concentration with biochar application rates of > 50 t ha<sup>-1</sup>. CD (W<sub>3</sub>) increased concentrations of Mg and K as there was a strong positive correlation between the nutrients and the amendment (r = 0.959, 0.965; p < 0.05). A significantly strong relationship was observed for Mg in WCD ( $W_3$ ) (r = 1.000\*; p < 0.05) whereas, WCD ( $W_1$ ) had a significantly strong but negative relationship with the element ( $r = -0.999^*$ ; p < 0.05). This is to say that reduced quantity of the amendment also reduced concentration of Mg.

Nickel positively correlated with CD (W<sub>3</sub>), WC (W<sub>1</sub>) and WC ( $W_2$ ) (r = 1.000; p < 0.05) while negatively correlate with CD  $(W_1)$ , CD  $(W_2)$ , WC  $(W_3)$ , WCD  $(W_4)$  and WCD  $(W_3)$  (r =-1.000;  $-0.998^*$ ; -0.930; p < 0.05) respectively. This implies that cattle dung and the combination of cattle dung and wood char amendments strongly influenced Ni concentration with an increased amount. It further shows that only WCD (W<sub>1</sub>) significantly influenced concentration of the heavy metal in the soil. Cadmium had positive and significant relationship with amendments of CD  $(W_2)$ , CD  $(W_3)$  and WCD  $(W_1)$  (r = $0.998^*$ , 0.922 and  $0.996^*$ ; p < 0.05) respectively. On the other hand, there was a relatively similar inverse relationship in soils amended with CD ( $W_1$ ) and WC ( $W_2$ ) (r = -0.974, -0.976; p < 0.05) which implies that the amendments reduced concentration of the metal in soil solution at such quantities.

### Conclusion

Results from the study generally revealed high concentration of organic matter, available phosphorus, and the exchangeable bases as influenced mostly by biochar from cattle dung feedstock and the combined cattle dung and wood sourced biochar. It also revealed that concentration of cadmium and nickel at colloidal exchange sites can be reduced by the attraction of cation bases from the large surface area of the biochar, displacing heavy metals and thereby increasing mobility and bioavailability within soil solution. This end result can be said to be advantageous in sandy or loamy soils as it potent for easy leaching of such heavy metals from the soil. However, this may depend on the pH of the soil as it has been revealed that mobility of the heavy metals largely depends on pH levels of the soil. Conversely, in clayey soils, this outcome may be disadvantageous as such soils are not easily leachable.

The study further reveals that locally pyrolysed biochar have similar capacity of increasing soil nutrients and reducing heavy metal concentration as those pyrolysed in bioreactors with well-regulated temperature and time that produces more bulky and crystalline chars with large surface areas for specific soil related problems. This study, therefore, can bridge the existing knowledge gap for local farmers who find it difficult in adopting biochar incorporation as an amendment for polluted soils due to the cost associated with laboratory pyrolysis. Also, further research is required to assess the potency of this method for amending all heavy metals associated with crude oil contamination of agricultural soils.

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<sup>\*</sup>Correlation is significant at p < 0.05; \*\*Correlation is significant at p < 0.01

## **Conflict of Interest**

The authors declared that no conflict of interest exist in the publication of this work.

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