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RESEARCH ARTICLE

RESIDUAL EFFECTS OF INORGANIC FERTILIZER AND BIOCHAR ON LEAD AND CADMIUM UPTAKE BY *Amaranthus cruentus L. ON* CONTAMINATED SOIL OF BAGEGA, NIGERIA

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ABSTRACT

The need to remediate contaminated mine soils has led to the adoption of biochar technology. Soils obtained from gold mining sites are heavily contaminated soils due to the presence of heavy metal occlusions in the gold ores. Therefore, a two-trial study was conducted to assess heavy metal uptake by *Amaranthus cruentus* from biochar amended contaminated mine soils. The experiment was factorial and laid out in a completely randomized design with biochar at seven levels (control; woodchar and bonechar at three rates each) and mineral fertilizer (15-15-15 NPK) at three rates to give rise to twenty-one biochar and fertilizer treatment combinations with three replications. Harvested plant tissues were subjected to wet digestion to determine the concentrations of Pb and Cd. Determined Pb concentrations (0.82-1.04 and 0.74-1.15 mg kg^{-1}) in plant tissues were under the critical limit of 2.0 mg kg^{-1} set by WHO. Cadmium concentrations (0.38-0.49 and 0.32-0.50 mg kg^{-1}) in plant tissues obtained from both trials were above the critical limit of 0.02 mg kg^{-1} set by WHO. Values of Pb uptake by plants ranged from 1.99-12.64 mg kg^{-1} and 0.05-0.71 mg kg^{-1} in both cropping trials, while Cd uptake ranged from 0.09-0.37 and 0.002- 0.016 mg kg^{-1}. Uptake values of Pb and Cd obtained from the first trial were comparatively higher than values obtained from the second trial. A combination of 30 t ha^{-1}bonechar and 80 kg 15-15-15 NPK enhanced Pb and Cd uptake in both trials while 30 t ha^{-1} woodchar suppressed heavy metal uptake. Biochar made from plant sources is more suitable for remediating heavy metal contaminated soils.

KEYWORDS

Remediation, Uptake, Woodchar, Bonechar, Heavy metals, *Amaranthus cruentus*

1. INTRODUCTION

Human activities have been known to cause excessive pollution in soils with consequential effects on agricultural activities and human health. Anthropogenic activities such mining are commonly responsible for the production of materials and waste that are hazardous to the environment and human health. In several locations of Northern Nigeria, reports have indicated contamination of agricultural soils due to gold mining activities in the areas (Uzoekwe and Mbamalu, 2020; Darma et al., 2022). Previous studies have revealed high concentrations of heavy metals in soils from gold mine sites of Bagega, Zamfara state of Nigeria (Tijjani et al., 2019; Yahaya et al., 2021). The presence of these abnormal concentrations of Pb and Cd in the soil can lead to their enhanced uptake by crops (Oyinlola and Onokebhagbe, 2008). These metals, when excessive in the food chain can be toxic; cause acute and chronic diseases (Jarup, 2003; Jaishankar et al., 2014). These heavy metal contamination and uptake by food crops have been linked to the deaths of children and adults in Bagega town of Anka local government area of Zamfara State of the northern part of Nigeria (Abdu and Yusuf, 2013; Waziri and Andrews, 2013).

Lead and cadmium occur as occlusions in gold ores and are usually released into the environment through human activities with subsequent uptake by crops when such soils are used for farming activities. These crops act as major pathways for heavy metal uptake. Many crops such as *Amaranthus cruentus* have been found to be hyper accumulators of these heavy metals from the soil (Tangahu et al., 2011). *Amaranthus cruentus* take up heavy metals in large quantities especially when grown on heavy contaminated soils. Its uptake of heavy metal increases when grown in contaminated soils hence their use as phytoextractors (Cho-Ruk et al., 2006).

The need to remediate heavy metal contaminated soils has led to the adoption of biochar as a potential material for cleaning up of heavy metal contaminated soils and water (Onmonya et al., 2022). Biochar is a carbonized product of slow thermal pyrolysis of organic materials (Shih-Hao and Chieng-Sheng, 2013). These organic sources which include organic wastes, such as livestock manures, bones, sewage sludge, crop residues, woodchips, rice husk, cereal stubbles and composts which when pyrolyzed, are used as soil amendments (Jien and Wang, 2013). Depending on the precursor material, biochar has been shown to immobilize some

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heavy metals in the soil thereby exhibiting a potential contaminant removal property (Onokebhagbe, 2020). Therefore, this study was carried out to evaluate the residual influence of biochar on the concentrations and uptake of Pb and Cd by *Amaranthus cruentus* on contaminated mine soil of Bagega in Zamfara state of Nigeria.

2. Materials and Methods

2.1 Soil Sampling and Biochar Production

Contaminated soil for this study was sampled from an active gold mine using random system of sampling. Composite soil samples (0-15 cm topsoil) were collected from a mine site located in Bagega (11.51^{0}N, 6.15^{0}E) in Anka local government area of Zamfara State. Source of pollution in Bagega was due to gold mining activities leading to the release of high levels of heavy metals into the immediate environment (MSF, 2012). Biochar used for this experiment was produced from two sources viz bones and sawdust. Source of heat for the pyrolysis was external. The products of the pyrolysis were labelled BC and PC denoting bonechar and woodchar respectively.

2.2 Screen House Experiment

Screen house experiment involved incubating 5 kg soils per pot with the biochar for a period of one month. *Amaranthus cruentus* grains were sown in the pots and harvested after a period of six weeks. Replanting was carried out after two weeks for another period of six weeks to determine the residual effects of the biochar on Pb and Cd uptake. This second cropping was devoid of fresh fertilizer and biochar input. Each experiment was terminated at the end of six weeks. Harvested amaranths were rinsed, oven dried, weighed (dry matter yield) and ground for subsequent heavy metal analysis.

2.3 Laboratory Analysis

Dried plant samples were ground and subjected to wet-digestion procedures as outlined (Lim and Jackson, 1986). Lead and cadmium concentrations in the digested tissues were determined using the atomic absorption spectrophotometer (Buck 211VGP AAS). Uptake of Pb and Cd by plant samples was estimated by multiplying the dry matter yields (Table 3) of the plants with the concentrations of Pb and Cd obtained. Soil and biochar samples were subjected to routine analysis following standardized processes as outlined (Sarkar and Haldar, 2005). Soil mechanical analysis was determined using the Bouyoucous-hydrometer method (Bouyoucous, 1962). The textural class was obtained from the determined values of the mechanical analysis with the aid of USDA textural triangle. The pH of the soil and biochar samples were determined in water and in 0.01M KCl solution, using a 1: 2 soil: water ratio and soil: KCl ratio on a two-way equilibration with buffer solution at pH 4.0 and 7.0.

Soil organic carbon (OC) in the sample soil and biochar was determined by the wet oxidation method of Walkley and Black as described (Nelson and Sommers, 1986). Micro-Kjeldahl digestion procedure outlined by Bremmer was employed in the determination of Total nitrogen in the soil and biochar samples (Bremmer, 1996). Extraction of exchangeable bases (Ca, Mg, K and Na) in the soil and biochar samples was determined with 1M ammonium acetate (1M NH_4OAc) solution buffered at pH 7.0 as described (Anderson and Ingram, 1993). Calcium and Mg in the extracts were determined using an atomic absorption spectrophotometer (Buck 211VGP AAS) while K and Na were determined on flame photometer. Exchangeable acidity in the soil sample was determined by the method outlined (Udo et al., 2009). Electrical conductivity of the saturated paste extract of 1:2 soils to water ratio was determined using a conductivity meter at 25^{0}C (Bower and Wilcox, 1965).

Available Phosphorus in the soil and biochar samples was determined using the Bray 1 and Olsen procedures (Udo et al., 2009). Phosphorus in the extract was determined colometrically by the molybdate-phosphoric-blue method using ascorbic acids as a reducing agent (Reeuwijk, 1993). Cation exchange capacity of the soil was determined with 1M ammonium acetate (NH_4OAc) solution buffered at pH 7.0 (Chapman, 1965). Total concentrations of Pb and Cd in the soil and plant samples were determined by wet digestion procedures outlined (Lim and Jackson, 1986). Total Cd and Pb concentration in the digest were read off the atomic absorption spectrophotometer (AAS) (Buck 211VGP AAS).

2.4 Treatments and Design

The experimental layout was a completely randomized design. It was a factorial experiment with two factors; biochar at seven levels (control; woodchar and bonechar at three rates each) and mineral fertilizer (15-15-15 NPK) at three rates which gave rise to twenty-one biochar and fertilizer treatment combinations. These were replicated three times giving rise to sixty-three experimental units. The treatments were:

Factor (a): Biochar [Woodchar (PC) and Bonechar (BC)], with each biochar consisting of three rates at 10, 20 and 30 t ha^{-1} as well as control pot with zero biochar.

Factor (b): Mineral fertilizer at three rates consisting of: No NPK (15-15-15) ie 0 g NPK per pot (F0); 40 kg NPK (15-15-15) per ha at 0.2 g NPK per pot (F1) and 80 kg NPK (15-15-15) per ha at 0.4 g NPK per pot (F2).

2.5 Data Analysis

The recorded data was subjected to descriptive statistics, a two-way analysis of variance and DMRT at 5% level of significance using Proc GLM of SAS computer software package (version 9.1).

3. Results

3.1 Properties of Soil and Biochar

The properties of the soil used for this study are presented in Table 1. The soil is classified as sandy loam. The pH is slightly acidic while the values of organic carbon, organic matter, Total Nitrogen, Available P and bases are low as against established threshold values of properties of soils of Sudan savannah agro ecology of the northern part of Nigeria (Esu, 1991). The soil was observed to have very high Pb and Cd contents.

Table 1: Properties of Bagega Soil

Soil Property	Bagega
Particle Size Distribution (g kg^{-1})	
Silt	100
Clay	200
Sand	700
Textural Class	Sandy loam
pH in H_2O	6.9
pH in KCl	6.6
EC (dS m^{-1})	0.45
Organic Carbon (g kg^{-1})	5.01
Organic Matter (g kg^{-1})	8.61
Total Nitrogen (g kg^{-1})	0.4
Available P (mg kg^{-1})	10.95
Exchangeable Bases (cmol kg^{-1})	
Ca	1.22
Mg	0.48
K	0.16
Na	0.5
CEC (cmol kg^{-1})	3.2
Total heavy metal content (mg kg^{-1})	
Pb	346.98
Cd	65.79

Table 2 shows the properties of the biochar used for the study. The pH of the biochar is alkaline. Notably, these biochars showed contrasting properties in their contents. Contents of Total Nitrogen, Available P and base cations obtained from the bonechar were higher when compared to the contents obtained from woodchar used for the study.

3.2 Effects of Fertilizer and Biochar Application on Pb Concentrations and Uptake in Plant Tissues

Data in Table 3 shows the effects of fertilizer and biochar application on Pb concentrations and uptake in plant tissues. The data shows that there were no significant ($p<0.05$) differences among the treatment means of Pb concentrations in plants under the influence of fertilizer on Bagega soil in the first trial. Lead concentrations ranged from 0.82 to1.04 and 0.74 to 1.15 mg kg^{-1}. Minimum concentrations of Pb (0.82 and 0.74 mg kg^{-1}) were obtained from treatments with 30 t ha^{-1} PC doses in both cropping seasons while 30 t ha^{-1} BC produced the highest Pb concentrations of 1.04 and 1.15 mg kg^{-1} in both seasons.

Differences in uptake values of Pb obtained under the influence of NPK fertilizer were significant ($p<0.05$). Uptake values under the influence of fertilizer ranged from 3.59 to 8.74 mg kg^{-1} in the first cropping season. The highest uptake value of 8.74 mg kg^{-1} was obtained from treatments under the influence of 80 kg NPK ha^{-1}. Residual effects of fertilizer on Pb concentrations and uptake in the plant tissues obtained from the second cropping are also shown in Table 3. The table revealed that there were no significant ($p<0.05$) differences in Pb concentrations obtained from treatments under residual influence (second cropping) of fertilizer. Uptake values of Pb were significantly ($p<0.05$) different under the residual influence of fertilizer. These values ranged from 0.15 to 0.36 mg kg^{-1} (pot treatment under the residual influence of 80 kg NPK ha^{-1}).

Table 2: Characteristics of Biochar Used in the Study.

Chemical properties	Woodchar	Bonechar
pH in H_2O	9.4	7.3
pH in KCl	7.9	7.3
Total Nitrogen (%)	0.7	2.98
Carbon (%)	68.03	8
Total P (%)	0.16	6.32
Basic cations (%)		
K	0.8	0.1
Ca	1.76	6.78
Na	0.12	0.45
Mg	0.04	0.49
Micronutrients (mg kg^{-1})		
Cu	27	27
Mn	57.03	34.28

Table 3: Effects of Combined Fertilizer and Biochar Application on Pb Concentration and Uptake

Treatments	First Croping		Second Cropping	
	Concentration (mg kg^{-1})	Uptake (mg kg^{-1})	Concentration (mg kg^{-1})	Uptake (mg kg^{-1})
Fertilizer				
F0	0.92	3.59^{b}	1.08	0.15^{b}
F1	0.91	3.91^{b}	1.07	0.18^{b}
F2	0.90	8.74^{a}	0.95	0.36^{a}
SE±	NS	1.497	NS	0.059
Biochar				
B0	0.82	1.99^{c}	1.17^{a}	0.08^{d}
PC1	0.97	2.42^{c}	1.02^{ab}	0.07^{d}
PC2	0.94	3.46^{c}	1.03^{ab}	0.05^{d}
PC3	0.85	10.88^{ab}	0.74^{b}	0.09^{d}
BC1	0.91	5.64^{bc}	0.10^{ab}	0.46^{b}
BC2	0.93	3.74^{c}	1.02^{ab}	0.28^{c}
BC3	1.04	12.64^{a}	1.15^{a}	0.71^{a}
SE±	NS	2.402	0.091	0.065
Interaction				
Fertilizer*Biochar	NS	*	*	*

*Denotes significancy at $p<0.05$. Means with the same letter(s) are not significantly different at $p< 0.05$. NS: Not significant at $p<0.05$.PC= woodchar, B0= Zero biochar; PC1= 10 t ha^{-1}woodchar; PC2= 20 t ha^{-1}woodchar; PC3= 30 t ha^{-1}woodchar; BC1 = 10 t ha^{-1}bonechar; BC2 = 20 t ha^{-1}bonechar; BC3 = 30 t ha^{-1}bonechar; F0= Zero fertilizer, F1=40 kg NPK ha^{-1}, F2= 80 kg NPK ha^{-1}.

Plate 1: *Amaranthus cruentus* growing under the influence of biochar in contaminated soil in the screen house.

Under the influence of biochar, Pb uptake values by *Amaranthus cruentus* ranged from 1.99 to 12.64 mg kg^{-1}. Differences among uptake means under the influence of biochar were significant ($p<0.05$). The highest Pb uptake (12.64 mg kg^{-1}) was obtained from pot treatment under the influence of 30 t ha^{-1}BC in the first cropping season. In the second cropping season, differences in the Pb concentration and uptake values were significant ($p<0.05$) under the residual influence of biochar. Lead concentrations in the plant tissues ranged from 0.74 to 1.17 mg kg^{-1} while uptake values ranged from 0.05 to 0.71 mg kg^{-1}. Pot treatment of 30 t ha^{-1}BC resulted in the highest uptake value of 0.71 mg kg^{-1}. However, on average, higher concentrations of Pb were obtained in the second cropping compared to Pb concentrations in the first cropping while lower Pb uptake was obtained in the second cropping under the residual influence of inorganic fertilizer and biochar when compared to the first cropping season.

3.3 Interaction Effects of Biochar with NPK Fertilizer Application on Pb Concentrations and Uptake by *Amaranthus Cruentus* L.

The interaction of biochar (30 t ha^{-1} bonechar) with 80 kg NPK ha^{-1} resulted in highest Pb uptake (28 mg kg^{-1}) in the first cropping season (Table 4). This was not significantly ($p<0.05$) different from Pb uptake of 27.60 mg kg^{-1} obtained from biochar (30 t ha^{-1} woodchar) interaction with 80 kg NPK ha^{-1}. Moreover, interaction of other rates of biochar with NPK fertilizer gave uptake values of Pb that were not significantly ($p<0.05$) different from each other.

In the second cropping season, concentrations of Pb in the plant tissues under the residual interaction of biochar with inorganic fertilizer were significantly ($p<0.05$) different as shown in Table 4. Maximum Pb concentrations of 1.48 mg kg^{-1} were obtained from treatments under the control and sole influence of NPK fertilizer. The lowest concentration of 0.69 mg kg^{-1} was obtained from treatment combination of 30 t ha^{-1} woodchar and 80 kg NPK ha^{-1}. Considering Pb uptake under the residual influence of the treatment factors, values obtained were lower than previous uptake values of Pb obtained from the first cropping season as shown in Table 4. Furthermore, a combination of 30 t ha^{-1} bonechar with 80 kg NPK ha^{-1} resulted in the highest Pb uptake of 1.32 mg kg^{-1} while the lowest uptake of 0.01 mg kg^{-1} was obtained from control and sole 40 kg NPK ha^{-1}. The data also shows that apart from uptake values of 0.71 and 1.32 mg kg^{-1}, other values under the various combinations were not significantly ($p<0.05$) different from each other statistically.

Table 4: Interaction Effects of Biochar with Fertilizer on Pb Concentrations and Uptake by *Amaranthus cruentus*

		Concentration (mg kg^{-1})				Uptake (mg kg^{-1})			
		Fertilizer				Fertilizer			
Cropping	Biochar	F0	F1	F2	SE±	F0	F1	F2	SE±
	B0					0.77^{b}	ND	2.20^{b}	
	PC1					3.87^{b}	1.00^{b}	2.40^{b}	
First	PC2					4.90^{b}	4.23^{b}	1.20^{b}	
	PC3		NS		NS	1.00^{b}	4.03^{b}	27.60^{a}	1.748
	BC1					10.67^{b}	5.67^{b}	0.60^{b}	
	BC2					3.17^{b}	6.67^{b}	1.40^{b}	
	BC3					0.73^{b}	9.20^{b}	28.00^{a}	
	B0	1.48^{a}	1.48^{a}	0.85^{b}		0.01^{d}	0.01^{d}	0.02^{d}	
	PC1	0.97^{ab}	1.01^{ab}	1.09^{ab}		0.09^{cd}	0.04^{d}	0.07^{cd}	
Second	PC2	1.06^{ab}	1.20^{ab}	0.83^{b}		0.07^{cd}	0.05^{d}	0.05^{d}	
	PC3	0.80^{b}	0.73^{b}	0.69^{b}	0.160	0.07^{cd}	0.12^{cd}	0.07^{cd}	0.043
	BC1	1.10^{ab}	0.98^{ab}	0.91^{ab}		0.26^{cd}	0.18^{cd}	0.71^{b}	
	BC2	1.02^{ab}	1.02^{ab}	1.02^{ab}		0.19^{cd}	0.37^{c}	0.14^{cd}	
	BC3	1.18^{ab}	1.11^{ab}	1.17^{ab}		0.25^{cd}	0.30^{cd}	1.32^{a}	

Means with the same letter(s) are not significantly different at $p< 0.05$. NS: Not significant at $p<0.05$.PC= woodchar, B0= Zero biochar; PC1= 10 t ha^{-1}woodchar; PC2= 20 t ha^{-1}woodchar; PC3= 30 t ha^{-1}woodchar; BC1 = 10 t ha^{-1}bonechar; BC2 = 20 t ha^{-1}bonechar; BC3 = 30 t ha^{-1}bonechar; F0= Zero fertilizer, F1=40 kg NPK ha^{-1}, F2= 80 kg NPK ha^{-1}. ND= Not detected.

3.4 Effects of Fertilizer and Biochar Application on Cd Concentration and Uptake in Plant Tissues

Cadmium concentrations in plant tissues of *Amaranthus cruentus* under the influence of inorganic fertilizer varied from 0.43 mg kg^{-1} (80 kg NPK ha^{-1}) to 0.46 mg kg^{-1} (control) as shown in Table 5 in the first cropping season. The data revealed that there were no significant ($p<0.05$) differences among the treatment means of cadmium concentrations in the plants grown on the contaminated mine soil of Bagega. With respect to Cd uptake, a similar scenario played out. Uptake values under the influence of fertilizer obtained in the first cropping season were not significantly ($p<0.05$) different statistically though the values ranged from 0.13 to 0.28 mg kg^{-1}.

The residual effects of fertilizer (second cropping) on concentration of Cd in plant tissues are depicted in Table 5. The Cd concentrations ranged from 0.45 to 0.49 mg kg^{-1} in the plant tissues of *Amaranthus cruentus*. The concentration values obtained from Bagega soil were not significantly ($p<0.05$) different from each other statistically. Contrarily, there were significant ($p<0.05$) differences among the treatment means of the Cd uptake values obtained under the residual influence of fertilizer. Values of Cd uptake ranged from 0.005 to 0.009 mg kg^{-1}. Overall, uptake values obtained from the second cropping were generally lower than values obtained from the first cropping. Cadmium concentrations recorded under the influence of biochar in the first cropping were not significantly ($p<0.05$) different as presented in Table 5. In contrast, uptake values under the same influence were significantly ($p<0.05$) different statistically. Uptake values ranged from 0.09 to 0.37 mg kg^{-1}. The highest uptake (0.37 mg kg^{-1}) was recorded under the influence of 30 t ha^{-1} woodchar while the lowest uptake (0.09 mg kg^{-1}) was obtained from 20 t ha^{-1} bonechar.

Residual effects of the incorporated biochar revealed significant ($p<0.05$) differences among Cd concentrations in the plant tissues obtained from the second cropping as obtained from Table 5. Cadmium concentrations in the plant tissues ranged from 0.32 to 0.56 mg kg^{-1}. Statistically, concentration values of 0.43, 0.45, 0.48 and 0.50 mg kg^{-1} obtained from other biochar treatments were at par with the average highest concentration (0.56 mg kg^{-1}) obtained from pots with no biochar treatment. Uptake values under the residual (second cropping) influence of biochar revealed significant ($p<0.05$) differences among treatment means. Uptake values ranged from 0.003 to 0.016 mg kg^{-1}as shown in Table 5. A comparison of these values also revealed that Cd uptake was lower in the second cropping when compared to its uptake in the first cropping. Also, there was no linear increment or decrease with increase in biochar rates in the values of the concentrations of Cd in the plant tissues obtained from this experiment.

3.5 Interaction Effects of Biochar With NPK Fertilizer Application on Cd Concentration and Uptake by *Amaranthus Cruentus* L.

In the first cropping, effects of combined fertilizer and biochar application on Cd uptake in plant tissues obtained from contaminated mine soil of Bagega showed significant ($p<0.05$) differences as presented in Table 6. Highest cadmium uptake (0.91 mg kg^{-1}) was enhanced by the combined application of 30 t ha^{-1}woodchar and 80 kg NPK ha^{-1}. This was at par statistically with 0.57 mg kg^{-1} which was obtained from a combined treatment of 30 t ha^{-1} bonechar and 80 kg NPK ha^{-1}.

Interaction of biochar with fertilizer in the second cropping resulted in significant ($p<0.05$) differences in concentration and uptake values of Cd. Cadmium concentrations in the plant tissues ranged from 0.29 to 0.71 mg kg^{-1} as shown in Table 6. However, the highest Cd concentration (0.71 mg kg^{-1}) was influenced by the sole fertilizer application of 40 kg NPK ha^{-1}. Cadmium uptake values obtained from the second cropping ranged from

0.01 to 0.04 mg kg^{-1} (Table 6). There was low variability among the means of the treatments as about 90 % of uptake values obtained from the treatment combinations were statistically at par. The highest Cd uptake of 0.04 mg kg^{-1} was obtained from treatment with 30 t ha^{-1} BC enhanced with 80 kg NPK ha^{-1}. This was followed by treatment with 10 t ha^{-1} BC enhanced with 80 kg NPK ha^{-1} which gave an uptake value of 0.02 mg kg^{-1}. There was no linear increment in uptake values of Cd with increase in the biochar rates.

Table 5: Effects of Combined Fertilizer and Biochar Application on Cd Concentration and Uptake

Treatments	First Cropping		Second Cropping	
	Concentration (mg kg^{-1})	Uptake (mg kg^{-1})	Concentration (mg kg^{-1})	Uptake (mg kg^{-1})
Fertilizer				
F0	0.46	0.23	0.49	0.006^{ab}
F1	0.44	0.13	0.46	0.005^{b}
F2	0.43	0.28	0.45	0.009^{a}
SE±	NS	NS	NS	0.002
Biochar				
B0	0.38	0.15^{ab}	0.56^{a}	0.005^{c}
PC1	0.48	0.25^{ab}	0.50^{a}	0.006^{bc}
PC2	0.45	0.22^{ab}	0.48^{ab}	0.003^{c}
PC3	0.38	0.37^{a}	0.32^{b}	0.003^{c}
BC1	0.49	0.17^{ab}	0.43^{ab}	0.012^{ab}
BC2	0.48	0.09^{b}	0.45^{ab}	0.006^{bc}
BC3	0.48	0.26^{ab}	0.50^{a}	0.016^{a}
SE±	NS	0.081	0.045	0.0019
Interaction				
Fertilizer*Biochar	NS	*	*	*

*Denotes significance at $p<0.05$. Means with the same letter(s) are not significantly different at $p< 0.05$. NS: Not significant at $p<0.05$.PC= woodchar, B0= Zero biochar; PC1= 10 t ha^{-1}woodchar; PC2= 20 t ha^{-1}woodchar; PC3= 30 t ha^{-1}woodchar; BC1 = 10 t ha^{-1}bonechar; BC2 = 20 t ha^{-1}bonechar; BC3 = 30 t ha^{-1}bonechar; F0= Zero fertilizer, F1=40 kg NPK ha^{-1}, F2= 80 kg NPK ha^{-1}.

Table 6: Interaction Effects of Biochar with Fertilizer on Cd Concentrations and Uptake by *Amaranthus cruentus*

		Concentration (mg kg^{-1})				Uptake (mg kg^{-1})			
		Fertilizer				Fertilizer			
Cropping	Biochar	F0	F1	F2	SE±	F0	F1	F2	SE±
	B0					0.32^{bc}	ND	0.27^{bc}	
	P1					0.48^{abc}	0.07^{bc}	0.19^{bc}	
First	P2					0.37^{bc}	0.22^{bc}	0.06^{c}	
	P3		NS			0.04^{c}	0.17^{bc}	0.91^{a}	0.078
	B1					0.32^{bc}	0.17^{bc}	0.02^{c}	
	B2					0.08^{bc}	0.18^{bc}	0.03^{c}	
	B3					0.02^{c}	0.19^{bc}	0.57^{ab}	
	B0	0.62^{ab}	0.71^{a}	0.40^{abc}		0.01^{bc}	0.01^{bc}	0.01^{bc}	
	P1	0.47^{abc}	0.49^{abc}	0.56^{abc}		0.01^{bc}	0.01^{bc}	0.01^{bc}	
Second	P2	0.54^{abc}	0.47^{abc}	0.43^{abc}		0.01^{bc}	0.01^{bc}	0.01^{bc}	
	P3	0.38^{bc}	0.29^{c}	0.31^{bc}	0.081	0.01^{bc}	0.01^{bc}	0.01^{bc}	0.002
	B1	0.58^{abc}	0.36^{bc}	0.36^{bc}		0.01^{bc}	0.01^{bc}	0.02^{b}	
	B2	0.42^{abc}	0.49^{abc}	0.43^{abc}		0.01^{bc}	0.01^{bc}	0.01_{bc}	
	B3	0.51^{abc}	0.42^{abc}	0.59^{abc}		0.01^{bc}	0.01^{bc}	0.04^{a}	

Means with the same letter(s) are not significantly different at $p< 0.05$. NS: Not significant at $p<0.05$.PC= woodchar, B0= Zero biochar; PC1= 10 t ha^{-1}woodchar; PC2= 20 t ha^{-1}woodchar; PC3= 30 t ha^{-1}woodchar; BC1 = 10 t ha^{-1}bonechar; BC2 = 20 t ha^{-1}bonechar; BC3 = 30 t ha^{-1}bonechar; F0= Zero fertilizer, F1=40 kg NPK ha^{-1}, F2= 80 kg NPK ha^{-1}. ND= Not detected.

4. Discussion

4.1 Plant Tissue Concentrations of Pb and Cd Under The Influence of Biochar and Fertilizer

This study showed that the sampled soils used for the experiment contained high levels of Pb and Cd concentrations. Lead was absorbed less by the plants from the study soil in both trials when compared to contents of Cd in the plant tissues. The Pb concentrations obtained from both trials were lower than the WHO permissible limits of 2.0 mg kg^{-1} for Pb in plant tissues while Cd concentrations obtained from the plant tissues obtained from the two cropping seasons were higher than 0.02 mg kg^{-1} WHO established threshold for Cd (WHO, 1996). The low concentrations of Pb in the plant tissues was occasioned by low bioavailability to plants due to the modifying effects of the high pH of the biochar on Pb bioavailability. This resulted in the formation of immobile Pb hydroxides commonly formed in soils under high pH conditions (Jung, 2008). A group researcher also reported low Pb absorption in plants despite its high levels in the soil due to its immobilization by biochar (Moreira et al., 2013). This result also contrasts the results obtained by which identified and reported an increase in Pb concentration in plants tissues with increase in biochar doses from sewage (Singh and Agrawal, 2010).

The relative high values of Pb concentrations obtained from the second cropping under the residual effects of inorganic fertilizer and biochar could also be due to the plants' increased unselective effort in accessing nutrients from the soil through the extensive development of their roots and uptake by mass flow. Furthermore, increase in incubation period of biochar could have led to increase in the content of surface functional groups released from the root exudates and biochar as observed by FT-IR analysis of the experimental biochar thereby enhancing Pb solubility and absorption by plant roots (Onokebhagbe, 2020). Previous studies have recognized the role played by these functional groups on bioavailability of Pb (Prasad and Freitas, 2003; Li et al*.,* 2016). These functional groups on biochar surfaces, through complex formations with Pb, play an important role in Pb speciation in soil and hence enhance its bioavailability to plants (Ashworth and Alloway, 2008).

Interaction of fertilizer with biochar revealed that absorption of Pb was higher in plants under the sole influences of fertilizer. This can be directly linked to the influence of the inorganic fertilizers on the pH of the soil samples. Fertilizers are known to increase soil acidity thereby increasing solubility of heavy metals as well as enhancing their mobility (Sintorini et al., 2021). Previous studies confirmed the increase of Pb concentrations in plant tissues with increase in soil acidity (Lasat, 2002; Adewole et al., 2009). The concentrations of Cd obtained from the first experiment were relatively similar to the values obtained from the second experiment. The values obtained under the residual effects of fertilizers and biochar were high. The high concentrations of Cd in the plant tissues could be directly linked to its high content in the soils used for the experiment as shown in Table 1. This conclusion is in line with the report of that obtained similar results with the use of spinach and lettuce grown on soil enriched with Cd (Fytianos et al., 2001).

Interaction of the inorganic fertilizers with biochar enhanced Cd concentrations (second cropping) and its uptake by plants. The high content of Cd in plant tissues under the sole influence of inorganic fertilizers could be due the modification of the soil pH by the fertilizer, increasing the soil acidity thereby increasing its mobility (Adewole et al., 2009). Cadmium is known to have high mobility in the soil and it is easily absorbed by plant roots and transported to the shoots (Sekara et al., 2005). The influence of surface functional groups from the biochars on Cd uptake cannot also be ruled out. Uptake mechanisms could as well be influenced by these surface functional groups thereby enhancing Cd absorption and uptake by plant roots considering its high values in plant tissues obtained from the second cropping (Table 5). This could have resulted from the increase in mobility of Cd ions enhanced by the presence of these surface functional groups in the soil solution due to lengthy incubation of the biochars in the soil. These surface functional groups contain compounds that possess a high affinity for Cd and other heavy metals leading to its possible enhanced solubility and bioavailability (Sposito et al., 1982). Another possible factor responsible for the relative high values obtained from the second cropping could be due to the plants' increased unselective effort of accessing nutrients from the soil likewise observed for Pb. Under the combined influence of inorganic fertilizer and biochar, the test crop "*Amaranthus cruentus"* did not accumulate Pb and Cd as the concentrations obtained were not consistent with values reported by which had confirmed the crop as a heavy metal hyper accumulator (Mattina et al., 2003; Abdu et al., 2011).

4.2 Uptake of Pb and Cd Under the Influence of Biochar and Fertilizer

Lead uptake obtained from the second trial, under the residual effects of fertilizer and biochar was a lot lower than the values obtained from the initial trial. This is due to the fact that uptake of Pb from the soils is as a result of two dynamic processes, the absorption of Pb by the *Amaranthus cruentus* and the accumulation of dry matter expression of the growth of the plant (Park et al., 2011). Lower dry matter yields obtained from the second trial directly affected Pb uptake by the plants. The poor growth of the plants was influenced by the low nutrient status of the soil samples as shown in Table 1. The high uptakes of Pb were enhanced under the sole influence of fertilizer and well as combined maximum rate of fertilizer and biochar. Lower Pb uptake by the plants was observed under the sole influence of maximum rate of PC which could be directly linked to the low dry matter yield and high sorption capacity of woodchar for Pb ions (Onokebhagbe, 2020). This as earlier explained is due to the fact that Pb tends to bind to functional groups on the surface of the woodchar in the sample soils, thus limiting its uptake by *Amaranthus cruentus* L. (Wang et al., 2004).

The Cd uptake values obtained from the first experiment were relatively higher than the values obtained from the second experiment. Reasons for this are similar to that obtained for Pb as earlier discussed. The relative low uptake values obtained from second cropping as shown in Table 5 could be due to the plants' decreased dry matter yield observed during the second trial. Uptake values in both cropping season were relatively low when compared to the results reported by Onokebhagbe et al., (2017) which revealed high Pb and Cd uptake by amaranths grown in soils contaminated with textile effluents. This can be attributed to the poor nutrient status of the soil which was already exhausted after the first cropping season as there was no replenishing of the soil with mineral fertilizers during the second trial. High sorption of Cd in the soil by biochar could have played a role in its low bioavailability. This was established in the results by when the biochar was subjected to Cd-sorption (Onokebhagbe, 2020).

5. Conclusion

Conclusively, results obtained from this study revealed that biochar minimized Pb and Cd uptake by *Amaranthus cruentus* L. Effects of biochar use on the concentrations of Pb and Cd in plant tissues were pronounced for Pb on the soil sample on the first trial. Lower values of Pb concentrations were obtained in this trial while there was no remarkable change in concentrations of Cd in the plant tissues for both trials. Concentrations of Pb and Cd in the plant tissues were enhanced by sole use of fertilizer in the cropping seasons. Uptake of Pb and Cd was lower in the second cropping under the residual influence of inorganic fertilizer and biochar. The use of biochar showed a significant performance in minimizing uptake of Pb and Cd by the plant. Application of woodchar has been determined to be more suitable as soil amendment for reducing Pb and Cd uptake in contaminated soils.

Ethical Compliance

The authors have followed ethical standards in conducting the research and preparing the manuscript.

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