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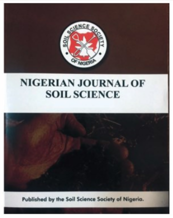

# Biochar and composted poultry manure causes on immobilization and migration of heavy metals in maize plants beside a mining site.

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## ABSTRACT

Mining sites in Amagu-Enyigba Ebonyi state Nigeria have deposits of heavy metals especially lead and zinc. Most crops grown in such sites are always hyper-accumulators of these metals. It is against this backdrop that the present study was conducted. The study aimed to ascertain the effect of biochar and composted poultry manure in immobilizing metals in the soil and subsequent reduction in maize uptake. The study was a pot experiment conducted in a screen house with 10 kg of soil sampled from farms adjacent to mining sites and control samples collected about 5 km away from the mining sites. The applied treatments consisted of different sources of biochar applied at a uniform rate of 10 tons/ha, equivalent to 22.2 g/10kg. Biochar applied showed significant variations in the concentration of heavy metals after the planting period of 6 weeks. It also observed that heavy metals accumulated more in the plant root than the shoot, except in a few cases. Based on my findings, I recommend 10 t/ha of empty oil palm bunch biochar (EOPBB) and composted poultry manure (CPM) in combined application to farmlands in this beside mining sites; meanwhile, further studies on increased rates of empty oil palm bunch biochar be encouraged in such environment.

## 1.0. Introduction

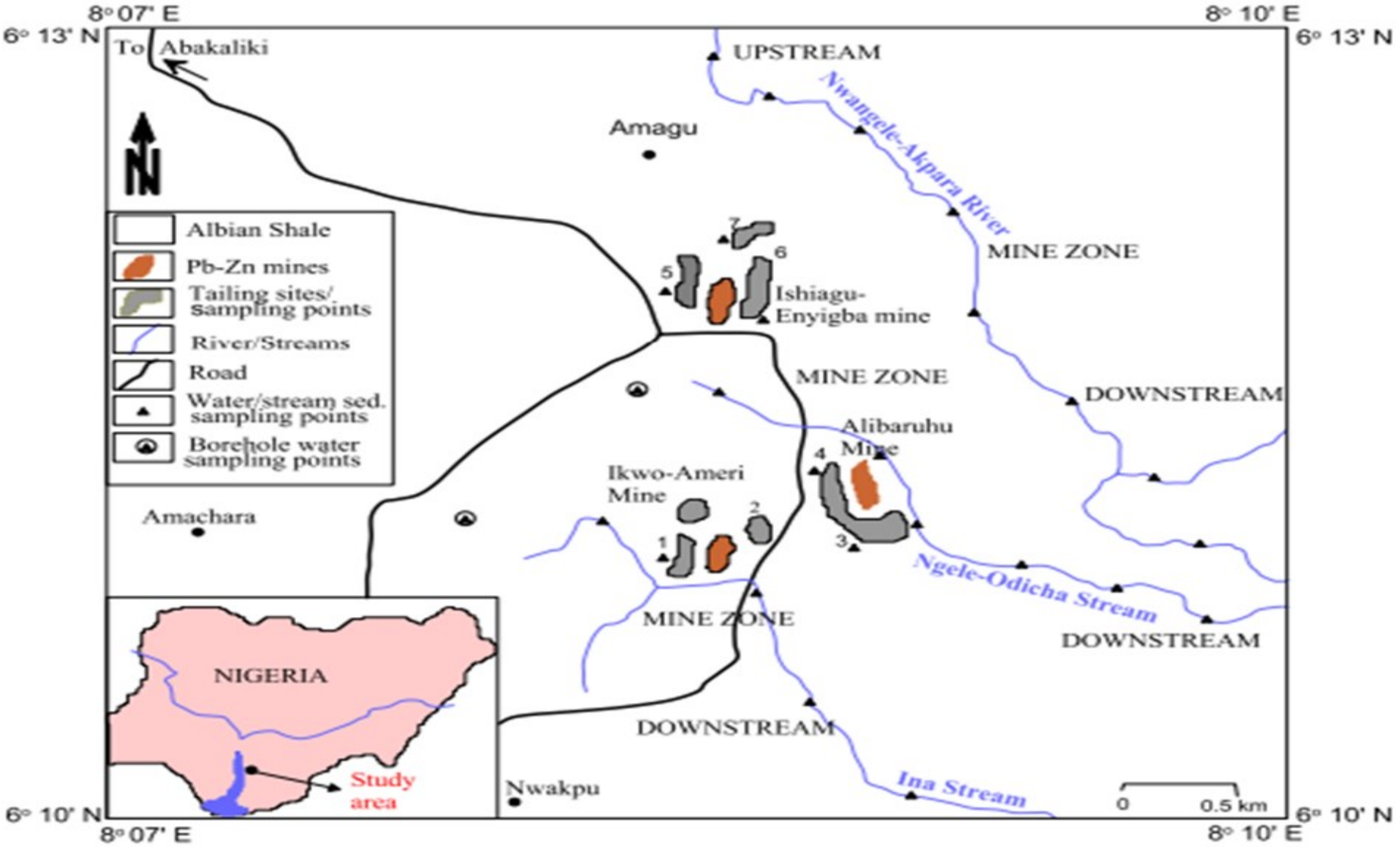
Soil pollution by heavy metals (HMs) potentially poses a significant threat to the environment and human health through multiple absorption pathways. This is due to toxic waste emissions from industrial processing, mining activities, waste (i.e., biosolids and manures) application, wastewater irrigation, and ineffective pesticide and chemical management in agricultural production (Bolan *et al.*, 2004; He *et al.*, 2005; Mench *et al.*, 2010). Soil contamination by heavy metals derives from both the soil parent material (lithogenic source) and various anthropogenic sources. The impact of the exploitation of mineral resources is usually detrimental to the environment, some of which include vegetation damage, destruction of prime arable lands, soil pollution, ecological disturbance, biodiversity loss, loss of fauna and flora and water pollution (Adekoya, 2003; Adegboye, 2012); retard growth of plants or soil microorganisms, may be transferred into the plant tissue and via food chain may endanger the human health (Kleckerová *et al.*, 2013). The issue becomes compounded when a natural deposit of ores of these elements is embedded in the soil, which is involved in soil formation processes. Heavy metals can persist in the environment for many decades or even indefinitely. HMs belong to the group of non-biodegradable, persistent, inorganic chemicals with high atomic mass (>20) and density (>5 g $cm^{-3}$) that have cytotoxic, genotoxic, and mutagenic effects on humans and animals. Heavy metal adsorption is influenced by soil pH, ion exchange capability, redox potential, and the proportion of silicate clays, organic matter, and Fe and Mn oxides.

The addition of organic amendments to polluted soils can affect a wide range of processes, resulting in changes in physiochemical soil properties and fertility status and changing the heavy metal distribution in the soil (Bernal *et al*., 2007). As a result, high-quality composted manure that is abundant in biologically stable and humified organic matter, non-phytotoxic, and has low heavy metal concentrations should be generally embraced in the amelioration of such farmlands (Kidd *et al*., 2009). Organic amendments, according to Guo *et al*. (2006) and Tejada *et al*. (2011), are heavy metal immobilizers. Heavy metals such as Cu, Cd, Pb, Zn, Fe, and others have been immobilized by organic amendments such as poultry manure, cattle manure, pig manure, crop residues, rice hulls, straw, sawdust, and so on. According to Adesodun *et al*. (2010), poultry manure improved microbial processes and bioremediation rates in polluted sites. Biochar is a potent by-product of the pyrolysis of agricultural and forestry waste biomass residues (Liu *et al*., 2011; Xu *et al*., 2013). Application of biochar to soil has been considered as having great potential to enhance long-term carbon sequestration because most carbon in biochar has an aromatic structure and is very recalcitrant in the environment (Lehmann 2007). Biochar typically has a high pH value and cation exchange capacity, enabling it to improve soil productivity (Jeffery *et al*., 2011; Kookana *et al*., 2011) and adsorb pollutants in soils (Beesley *et al*., 2011; Yuan and Xu 2011). Biochar can help stabilize heavy metals in polluted soils, improve the consistency of the soil (Ippolito *et al*., 2012), and minimize heavy metal uptake by crops (Komárek *et al*., 2013). Therefore, the objective of this study was to observe the influence of different biochar sources on the migration of heavy metals in maize plants. A combination of composted poultry manure and biochar may potentially provide a new alternative for natural and heavy metal-contaminated soil remediation.

## 2.0.Materials and methods

### *2.1. Description of location for sample collection:*

Soil samples were collected from cultivated arable farmlands beside a mining area in Amagu, Enyigba in Abakaliki local government area of Ebonyi State (Fig. 1). The study area is located between latitude 06$^0$ 12' N and longitude 08$^0$ 08' E in the derived savanna vegetation of the Southeast ecological zone of Nigeria. The area had about 60m as its highest elevation 30m as its lowest elevation above sea level, and was characterized by an average rainfall of 1750-2000 mm per annum. The highlands are characterized by drought-resistant grasses, along with flowing streams and rivers. (Nnabo, 2015). The plains are underlain by shale and some mudstones. The screen house study was conducted in the screen house at Michael Okpara University of Agriculture Umudike (latitude 05º2' North and longitude 07º33' East). NRCRI, (2020).



Figure

**Soil sample collection:** The soil samples used for the analysis were randomly collected between the depth of 0 – 20cm using a soil auger and spade. Soil samples were collected from cassava cultivated farmlands about 20 m away from the mining site, while control samples were also collected about 5 km away from the mining site. In each location (mining site and control site), random soil samples were collected at different points and bulked together, air-dried at room temperature (27 $^0$C) and sieved with a 2 mm and 4 mm sieve for laboratory analysis and greenhouse experiment, respectively.

**Biochar production and collection of research materials:**

Empty oil palm bunch feedstock was pyrolyzed at 320 $^0$C in a double-barrel metallic drum (height 67 inches × diameter 22.5 inches). The pyrolysis process was carried out in 45 minutes, while the temperature was determined using an infra-red meter. The biochar was allowed to cool, finely ground using an automated grinding machine and passed through a 0.25 mm mesh sieve size. Maize seed (*Oba super 6*) was sourced from the Research and Training Unit of Michael Okpara University of Agriculture, Umudike.

**Experimental procedures and test crop**: Ten kilograms (10 kg) of collected soil samples were placed in a 12-litre container. Different biochar sources were applied at a uniform rate of 10 tons/ha, replicated three times (n=3) in a completely randomized design and allowed for two weeks before planting. In each pot, three seeds were planted and then thinned to two seedlings after 14 days of germination. Hand-picking of weeds was done at their slightest emergence during the experiments.

**Laboratory analysis**: Soil Physico-chemical analysis conducted included: Particle size analysis, using Bouyoucos hydrometer method as described by Kettler *et al.* (2001). Soil pH was determined in a 1:2.5 soil to water ratio using an electrode pH meter (Mclean, 1965). Organic carbon was determined according to the Wet dichromate oxidation method described by Walkey and Black (1934) and modified by Nelson and Sommers (1996). Available phosphorus was determined using the Bray 2 method of Bray and Kurtz (1945) described by Kuo (1996). Total nitrogen was determined using the micro Kjeldahl method described by Bremner (1996). Exchangeable acidity was determined by extracting 5g of soil with 1N KCL and titrating with 0.5N NaOH using phenolphthalein indicator as described by Mclean (1965). Heavy metals in the soil were determined using the Aqua Regia method (3:1 ratio of HCl: $HNO_3$), a method described by Ehi-Eromosele et al.. (2012), while nitric acid was used in extraction in the plant samples. Plant biomass was harvested, washed with flowing tap water and oven-dried at 60 $^0$C for 72 hours in a hot air oven.

**Bioconcentration Factor (BCF): T**he Bioconcentration factor for each plant/soil pair was calculated to obtain valuable data using equation (1). BAF is the ratio of the heavy metals in the root and the shoot to the heavy metals in the soil.

$$\text{BCF} = \frac{C_{root} + C_{shoot}}{Csoil} \quad \ldots \quad (1)$$

*C root* = Dry weight of heavy metals concentration in the root (mg/kg).

*C shoot*= Dry weight of heavy metal concentration in the shoot (mg/kg).

*C soil* = Dry weight of heavy metals concentration in the soil (mg/kg).

**Statistical Analysis:** Data collected were subjected to analysis of variance using the Genstat package. Treatment means for each parameter measured was compared at p ≤ 0.05 using the Least Significant Difference.

## 3.0. Results and discussion

### *3.1. Some selected physicochemical properties of soil samples were used in the study.*

The physicochemical and microbial properties of the soil samples used for the experiment are presented in Table 1. Particle size distribution shows percentage sand of 710 in the farmland about 3km away from the mining area (control) was higher than the farmlands beside the mining site with 670. T-test indicates a significant difference (P≤0.05) in the percentage sand of the two farmlands. The percentage silt also showed a significant difference between the two farmlands, with the mining site having 240 % as against that in the control site with a percentage silt of 200. There was no significant difference in percentage clay between the two farmlands (Table 1). Based on the results, the soil was observed to belong to the textural class of Sandy clay loam (SCL). The low Soil pH values have been attributed to the intensely leached unconsolidated sedimentary parent materials and sesquioxide's dominance in the exchange complex (Lekwa and Whiteside, 1986). But soils from the mining area of the study area were more acidic than those of the control. This could be attributed to the intensity of anthropogenic activities occurring in the area. Amagu-Enyigba had high soil acidity values as a result of shale parent materials having insertions of limestone (FDALR, 1985). Total organic carbon content was higher at the farmlands in the control site than farmlands beside the mining site with the value of 1.04 and 0.98 %, respectively and showed a significant difference (P≤0.05) between the two sites. The soil organic matter content of Amagu was classified as been low when compared with the soil fertility ratings of the Federal Department of Agricultural Land Resources (FDALR) 2004. A similar finding was observed by Ano *et al.* (2007), who reported that mining activity reduced the SOM content of soil of mining areas. The low organic matter content of Amagu soils could also be attributed to the areas' scanty vegetation, which is an indication of highly mineralized soil with poor fertility status. Total nitrogen content was slightly higher in the control site (0.05%) than in the mining site (0.04 %). The low nitrogen values gotten from the study were similar to the findings reported by Ogbodo (2006), who conducted similar experiments on soils of Abakaliki. The C: N ratio was higher at the mining site (25:1) than the control with the ratio of 21:1.

### 3.2. *The physical and chemical composition of organic*

Table 1: Physicochemical properties of soil samples used in the study.

| Soil parameters | Mining site | Control site | T-test value |
|---|---|---|---|
| % sand (g/Kg) | 670 | 710 | 0.008 |
| %silt (g/Kg) | 240 | 200 | 0.008 |
| % Clay (g/Kg) | 90 | 90 | n.s |
| pH | 4.83 | 4.94 | n.s |
| Exchangeable acidity cmol/kg | 2.8 | 2.1 | n.s |
| Organic carbon (%) | 0.98 | 1.04 | 0.035 |
| Total nitrogen (%) | 0.04 | 0.05 | 0.035 |
| C:N ratio | 24.5:1 | 20.8:1 | |
| Lead (Pb) mg/kg | 7342.0 | 1933 | |
| Zinc (Zn) mg/kg | 1709.0 | 474 | |
| Copper (Cu) mg/kg | 17.7 | 16 | |

*amendments used for the study.*

The selected physical and chemical properties of the different sources of biochar produced at about 320 $^0$C are shown in Table 5. The pH of the biochar showed variance across the different sources. Empty oil palm bunch biochar (EOPBB) and Empty maize cob biochar (EMCB) recorded a pH of 8.5 and 8.11, respectively; which indicates alkalinity; while wood shavings biochar (WSB) had the least pH value of 6.45, this could be attributed to the feedstock used in pyrolysis. The total organic carbon was also highest as WSB with the value of 56.3 %, while EMCB and EOPBB had a total organic carbon content of 40.12 and 52.2 %, respectively. Three heavy metals were analyzed to ascertain their influence in the experiment. The highest concentration of lead (Pb) was found in EMCB with the value of 0.66 mg/kg > EOPBB (0.54) > WSB (0.45) > CPM (0.03). Zinc concentration was observed to range between 0.10 to 1.23mg/kg across the different organic materials. Zinc was highest (1.23 mg/kg) in EOPBB, while WSB had the least (0.10 mg/kg) concentration. Copper concentration was highest in EOPBB (0.28 mg/kg), while EMCB had the least concentration (0.04 mg/kg).

Table 2: Selected chemical composition organic amendments used for study.

| PROPERTIES | EMCB | EOPBB | WSB | CPM |
|---|---|---|---|---|
| pH | 8.11 | 8.50 | 6.45 | 8.01 |
| Available phosphorus (ppm) | 0.15 | 0.34 | 0.21 | 0.99 |
| Total organic carbon (%) | 40.1 | 52.2 | 56.3 | 3.87 |
| Lead (pb) (mg/kg) | 0.66 | 0.54 | 0.45 | 0.03 |
| Zinc (Zn) (mg/kg) | 0.92 | 1.23 | 0.10 | 0.13 |
| Copper (Cu) (mg/kg) | 0.04 | 0.28 | 0.14 | 0.06 |

### *3.3. The effect of biochar and CPM on heavy metal concentration.*

The level of Lead (Pb) in the soil, root and shoot of the cultivated maize crop is presented in Table 3. The concentrations of lead (Pb) in the soil were observed to be extremely above the permissible limit for agricultural soils, according to FAO, WHO. The different biochar application significantly ($P \leq 0.05$) increased, the concentration of lead (Pb) in the soil and varied in an increasing order of; CONTROL (2964 mg/kg) < EMCB (3791 mg/kg) < WSB (4283 mg/kg) < EOPBB (4890 mg/kg). Lead concentration increased highest (39.4 %) with soil amended with EOPBB. According to the table, there was a 35.4 % increase in the Pb concentration of the soil after the application of composted poultry manure (CPM). These findings were contrary to the findings of Ahmad *et al.* (2012), who observed a reduction using mussel shell, cow bone, and biochar to reduce Pb toxicity in the highly contaminated military shooting range soil in Korea.

The mean levels of copper (Cu) in the soil, as shown in Table 3, were also recorded to exceed the permissible limit (100 mg/kg) for agricultural soils according to Food and Agricultural Organization (FAO). The different biochar applied had fluctuating but significant ($P \leq 0.05$) reductions between 714 – 297 mg/kg. Biochar sourced from oil palm bunch was observed to increase the concentration of copper by 33.2 % after application, while biochar sourced from empty maize cob and wood shavings was reduced by 30.8 and 35.3 %, respectively. This could be attributed to the mineral components such as phosphates and carbonates in biochar which could have contributed significantly to the stabilization of heavy metals in soils because these salts can precipitate with heavy metals and reduce their bioavailability (Cao *et al.* 2009). The result further indicated a significant interaction between biochar applied and CPM in the concentration of copper in the soil.

The mean concentration of zinc (Zn) in the soil was observed to be generally above the permissible limit (300 mg/kg) for agricultural soils as described by FAO, except for treatment applied with EMCB. According to the table, different biochar sources significantly reduced Zn concentration in the rhizosphere. The highest reduction was recorded with EMCB, while WSB recorded the least reduction capacity. This reduction could be attributed to the fact that most biochars are alkaline material and have a liming propensity, which could have also contributed to reducing the mobility of the heavy metals in contaminated soils (Sheng *et al.*, 2005). The alkalinity of biochar may have also promoted heavy metal precipitation in soils. However, the adsorption ability of the same type of biochar varies with different types of heavy metals. A similar trend of reduction (55.1 %) in zinc concentration was also observed at 10 tons/ha of CPM. A significant interaction was recorded between biochar applied and CPM in the reduction of bioavailability of zinc in the soil, probably due to its mobility.

The increase in selected heavy metal concentration after the application of organic materials could be attributed to the fact that biochar had high surface area and pore volumes, which possess a greater affinity for metals because metallic ions can be physically adsorbed onto the char surface and retained within the pores (Kumar *et al.*, 2011). Moreover, it has been observed by different authors that numerous biochars surfaces have negatively charged sites and can sorb metals positively charged through electrostatic attractions and ligands. The increasing affinity for metal cations as observed could be attributed to the increase in soil pH caused by the alkaline nature of the biochar used, and this dissociates $H^+$ from functional groups such as carboxyl, phenolic, hydroxyl, and carbonyl functional groups (Bolan *et al.*, 2003). Apart from mobilization mediated by acids, metal accumulation in rhizosphere soil has also been observed and partly attributed to immobilization by root mucilage (Tamas and Martinoia, 2006). Carboxylic acids remain the most investigated component of root exudates due to their potential effect on metal bioavailability via complexation processes. Amongst the range of carboxylates exuded into the rhizosphere, malate, citrate, and oxalate seem to have the most pronounced effects on metal complexation (Hinsinger, 2020).

The concentration of Lead (Pb) in the plant root is presented in Table 3. According to the table, lead was observed to reduce significantly across the different biochar applied. Its reduction followed a sequence of 13.9, 16.7 and 24.1 %

at EMCB, WSB and EOPBB, respectively. This general reduction in lead in the root could be attributed to immobilization of insoluble Pb salts as precipitates in intercellular spaces, fixation in the cell wall by negatively charged pectins, and accumulation in the vacuoles of cortical and rhizodermal cells and the plasma membranes of cells (Shahid *et al*., 2015); similar results were also recorded by Kushwaha *et al*., (2018). Significant interaction existed between biochar applied and CPM in the reduction of lead in the roots of maize plants. The mean concentration of copper (Cu) in the root is also presented in Table 3. According to the table, copper was observed to reduce significantly by 54.8 % across the different rates of CPM applied. Biochar sourced from empty maize cobs was observed to record the highest increase in zinc concentration in the root of a maize plant by 46.1 %. There was a significant interaction between biochar applied and CPM in the increase in the concentration of zinc in the roots of maize plants; this could be traced to the mobility of zinc in the plant tissues.

The mean concentrations of lead (Pb) in the plant shoot of maize were highest in soil samples amended with biochar. According to the table, lead concentration recorded the highest (8.91 mg/kg) concentration at WSB by 57.3 % and the least increment by 41 % at EMCB (14.8 mg/kg) compared with control. A significant increase in lead concentration in the shoot after the introduction of CPM was also observed. The mean concentration of copper (Cu) in maize shoots showed significant fluctuations in value. Biochar sourced from empty maize cob was observed to record the only significant reduction in copper concentration, while other biochar sources increased its bioaccumulation in the shoot. A similar trend of reduction in copper concentration was also observed at 10 tons/ha after the application of CPM. The mean concentration of zinc (Zn) in maize shoots showed a significant reduction in values. EOPBB was observed to record the highest reduction by 33.7 % in zinc bioavailability also in the shoot. A similar trend of reduction (76.3 %) in copper concentration was also observed at 10 tons/ha after the application of CPM. The stunted and poorly developed root system (fibrous), as observed in the green-house experiment, could be attributed to the toxicity of copper on the maize root, which is related to a severe reduction in the elongation growth of the longest root as well as root plasma membrane permeability of the seedlings was reported (McBride, 2001). Significant inhibition of root length of all crop seedlings at higher Pb is also reported (Hasnian et al., 1993). The root growth inhibition by Pb toxicity most probably results from non-selective suppressive of both cell division and cell elongation of the seedlings (Ivanov *et al*., 1988). The toxic effects of Cu often affected mitotic activity and cell division of roots with a subsequent increase in the root number of seedlings (Hall & Williams, 2003). Significant interaction existed between biochar applied and CPM in the bioavailability of zinc in the shoot. While the extractable concentrations of metals in the rhizosphere give a momentary picture of metal availability to plants, the cumulative uptake of metals over the entire growth period is better reflected by the metal concentration in the plants. This uptake is distributed between roots and shoots, and as is commonly found, roots retain a larger proportion of absorbed metals and translocate limited amounts to shoots. Low translocation ratios may partly stem from root surface adsorption of metals, contributing to an extension of the extraradical immobilization observed in rhizosphere soil (Hinsinger *et al*., 2006).

Table 3: Effect of composted poultry manure and biochar heavy metal (mg/kg) accumulation in soil and maize plant after harvest.

| | | **Concentration in soil** | | | **Concentration in root** | | | **Concentration in shoot** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Treatments | | Lead | Copper | Zinc | Lead | Copper | Zinc | Lead | Copper | Zinc |
| | Control | 2964 | 46.1 | 714 | 251.2 | 8.17 | 32.2 | 6.32 | 4.2 | 43.8 |
| Biochar | EMCB | 3791 | 31.9 | 297 | 216.1 | 12.7 | 59.7 | 8.91 | 3.5 | 36.6 |
| | EOPBB | 4890 | 69.1 | 488 | 190.6 | 13.3 | 58.7 | 11.4 | 4.3 | 29.1 |
| | WSB | 4283 | 29.8 | 621 | 209.3 | 11.3 | 48.5 | 14.8 | 5.4 | 37.5 |
| CPM | 0t/ha | 3142 | 37.5 | 718 | 215.4 | 15.7 | 54.0 | 8.3 | 19.8 | 33.1 |
| | 10t/ha | 4867 | 50.9 | 322 | 218.2 | 7.1 | 45.5 | 12.4 | 4.7 | 36.8 |
| Biochar LSD$_{0.05}$ | | $1181^{*}$ | $26.6^{*}$ | $1.30^{*}$ | $29.2^{**}$ | n.s | $19.5^{*}$ | $0.01^{***}$ | $12.9^{***}$ | $9.9^{*}$ |
| CPM LSD$_{0.05}$ | | $835^{***}$ | n.s | $0.92^{***}$ | n.s | $3.77^{***}$ | n.s | $0.02^{***}$ | $9.16^{**}$ | $7.1^{*}$ |
| Biochar × CPM LSD$_{0.05}$ | | n.s | $37.6^{*}$ | $1.83^{**}$ | $41.3^{*}$ | n.s | $26.9^{**}$ | n.s | $18.32^{*}$ | $14.0^{***}$ |

Note: EMCB = Empty maize cob biochar; EOPBB= Empty oil palm bunch biochar; WSB= Wood shavings biochar; CPM= Composted poultry manure; FAO= Food and Agricultural Organization
* = $p \leq 0.05$;
** = $p \leq 0.01$;
*** = $p \leq 0.001$

### *3.4. The bio-concentration (BCF) factor of maize during the study.*

The bioconcentration factor (BCF) represents a ratio of metal content in plant and soil content (Waterlot *et al*., 2013). This index allows evaluating plant ability to transfer heavy metals from soil to tissues. The different sources of biochar (Figure 2) resulted in an increase in the bioconcentration factor when compared to the control. Copper was also recorded to possess the highest bioconcentration factor across each source of biochar applied, while zinc recorded the least. A similar trend was observed after the application of CPM (Figure 3).

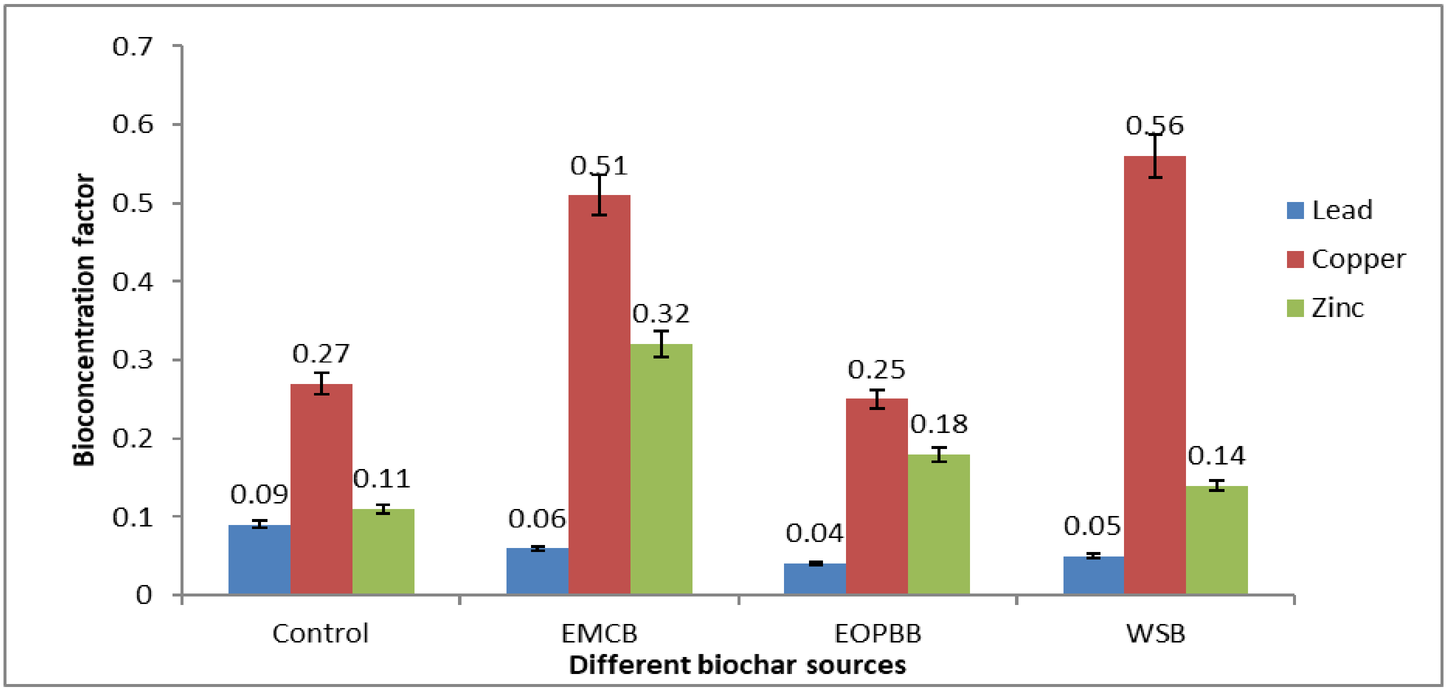


Fig 2: Bioconcentration factor (BCF) of heavy metals in maize crop with different biochar.

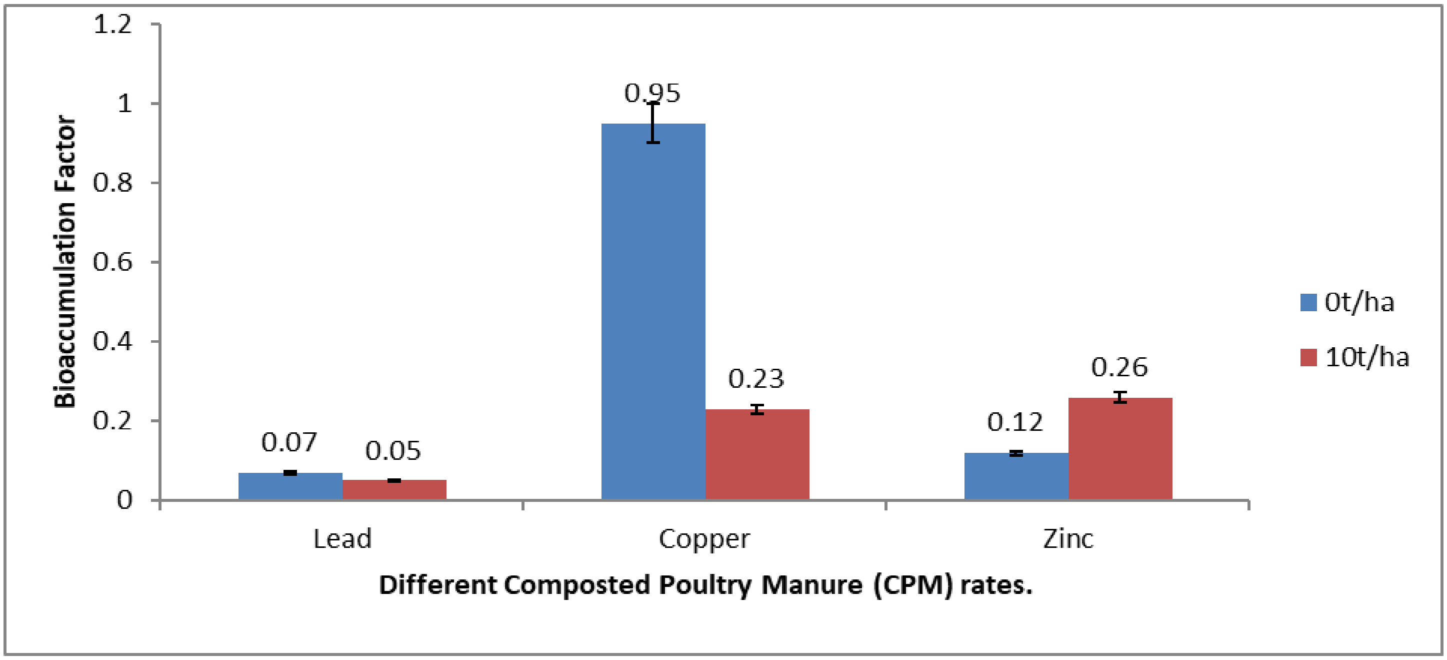


Fig 3: Bioconcentration factor (BCF) of heavy metals in maize crop with Composted Poultry Manure.

## 4.0. **Conclusion and Recommendation**

The results from this research showed that soils collected from farmlands beside the mining area had high concentrations of lead, copper and zinc due to the human activities on the natural deposits of its ores. The application of biochar was observed to have a varying effect on individual heavy metals analyzed. In general, biochar and poultry manure were able to increase its bioavailability in the soil due to immobilization and chemical reactions due to the root exudates. Zinc was also recorded also in the shoot of the maize plant due to its mobility. Heavy metal uptake by plants was significantly reduced but had a higher concentration at the root region. Finally, owing to the natural deposits of heavy metals, it would be of research relevance to increase the rates of biochar to be applied in further experiments.

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