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# FRACTIONATION OF LEAD-ACID BATTERY SOIL AMENDED WITH BIOCHAR

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***ABSTRACT***

***Mobile (bio)available metal concentration in contaminated soils can be minimized through biological immobilization and stabilization methods using a range of organic compounds, such as "biochar." Biochar has a high surface area, highly porous, variable – charge organic material that has the potential to increase soil water holding capacity, surface sorption and base saturation when added to soil. The soil was characterized before and after amending by standard method. The parent soil used for this study was collected from lead–acid battery chargers' workshop. The physico-chemical properties of the soil are: pH=5.0, 0.24% organic carbon, 32.5 cmol.kg$^{-1}$ CEC, 1.02, 23.0, 17.36, 10.05, 7.25 and 9.74 mg.kg$^{-1}$, for N, Na, P, Zn, Cu and Pb respectively. The pH, organic carbon and CEC of the biochar were 8.59, 78.70% and 82.27cmol.kg$^{-1}$ respectively, while the concentration of heavy metals in the biochar ranged; 0.10 –1.20mg.kg$^{-1}$. There is a gradual decrease in the concentration of the heavy metals as the concentration of biochar increases from 5 – 20%. Fractionation result shows that the heavy metals (Zn,Cr,Cd,Cu and Pb) were mainly associated with the residual fraction, the mobility factor for the heavy metals was calculated and found to be higher for all metals in the parent soil than the Biochar amended soil. Contamination levels were moderate for Cd and Cr, considerably for Pb, Cu and Zn. The results indicated that long term discharge of these battery chargers' wastes into the environment will cause accumulation of some toxic metals in soils which may lead to elevated levels of these metals in plants.***

***Keywords: Biochar, Lead–acid Battery, Fractionation and Heavy metals.***

## INTRODUCTION

The evaluation of heavy metals contamination of soils as a means of monitoring the status of the environment for the good of the ecosystem is crucial. With increased exploitation of natural resources, industrialization and urbanization, most areas of the Niger Delta region of Nigeria are facing an increasing ecological problems arising from the release of pollutants into both the aquatic and terrestrial environments. Heavy metals constitute significant group of these pollutants (Udosen, *et al.,* 2006). While many heavy metals are essential elements at low levels of concentration, they can exert toxic effects at concentrations higher than permitted in the environment. Mobile (bio) available metal concentration in contaminated soils can be minimized through biological immobilization and stabilization methods using a range of organic compounds, such as "biochar", which is a form of environmental black carbon produced using the pyrolysis of C-based biomass (Verheijen *et al.*, 2010). Biochar is produced as a soil amender for agricultural and environmental gain, which distinguishes it from other carbonaceous products such as activated carbon (AC) and charcoal. Application of biochar to soil can help improve soil properties and enhance soil quality by retaining higher moisture, nutrients and microbial activity, therefore increasing crop production (Warnock *et al.*, 2007; Major *et al.*, 2007). Recent attention has been given to biochar as a soil amender because of its potential soil conditioning properties and benefits to physico-chemical characteristics. Organic carbon contents of biochar have been reported to be as high as 90%, depending on the source material which encourages experimental application to soils to sequester carbon (Lehmann, 2007a and b). Further potential benefits of adding biochar to soil have also been reported; these include the adsorption of dissolved organic carbon (Pietikainen *et al.*, 2000), increases in soil pH and key soil macro-elements and reductions in trace metals in leachates (Novak *et al.,* 2009). Unlike other soil amendments, biochar's longevity in soil reduces the possibility of heavy metal accumulation associated with repeated applications of other amendments (Joseph *et al.,* 2009), such as sewage sludge. Application of biochar into contaminated or polluted soils can also reduce the bioavailability of heavy metals to plants (Abeh *et al.*, 2007). Therefore, the objectives of this study are: to determine chemical speciation of heavy metals in the soil and to prepare and apply biochar from palm kernel, to lead-acid battery soil.

## MATEERIALS AND METHOD

### Soil Sampling, Biochar Preparation

Topsoil (0 – 15cm) samples were collected from lead–acid battery workshops in Benin City. The soil samples were air – dried, pooled and sieve to less than 2mm. The palm kernel shells used in the preparation of the biochar were obtained from a Palm Oil Mill in Uselu, Benin City. The palm kernel shells were pyrolysed at 500$^0$C for 8hrs (Lehmann, 2007a). The char produced was ground and sieved to less than 2mm.

The biochar was applied to the soil at four different concentration (5%, 10%, 15% and 20%), in triplicates, mixed thoroughly and turned over frequently for seven weeks.

**pH:** Twenty grams of the soil sample was weighed into a 50mL beaker and 20mL of distilled water was added. The soil/water mixture (ratio 1:1) was allowed to stand for 30 minutes and stirred occasionally with a glass rod. The ele pH meter was calibrated using buffer 4 and 7. The electrodes were rinsed and subsequently immersed into the soil/water mixture. The pH was recorded. (Black, 1965)**.**

**Cation Exchange Capacity:** Five grams of soil sample was weighed into a 250mL polypropylene bottle and 100mL of 1M $NH_4OAc$ solution was added and stoppered. The mixture was shaken for 30mins in a mechanical shaker (Heldoph) at 200rpm for 30mins. The supernatant was filtered through Whatman No.1 filter paper.

The concentration of $K^+$ and $Na^+$ in the extract were determined by Flame photometer while $Mg^{2+}$ and $Ca^{2+}$ were determined using Atomic Absorption Spectrophotometer (Buck Scientific VGP 210 model). The equipments were calibrated using various concentrations of the metals ranging from 2-20ppm prepared from analytical grade reagents (Sigma, BDH and Buck Scientific). The summation of the various cations was reported as action exchange capacity (Black, 1965).

**Phosphorus:** Five grams of the soil was weighed into a polypropylene bottle and 40mL of the extracting solution was added and stoppered. The mixture was shaken manually for one minute and filtered with Whatman filter paper No. 1. The clear supernatant was kept for phosphorus determination, (Bray and Kurtz, 1947).

**Nitrogen**: Finely ground soil (0.2g) was weighed into a 100mL Kjedahl digestion flask. One tablet of selenium catalyst and 4mL of concentrated $H_2SO_4$ were added to the flask and heated on the digester until the mixture became clear. The mixture was cooled until just warm to touch and 10mL distilled water was added and the mixture filtered through a Whatman No.1 filter paper into a 100mL volumetric flask. The flask was further rinsed with distilled water and the filtrate made up to mark. The concentration of nitrogen in the filtrate was determined by colorimetric method (Vogel's, 2008).

**Calculation:**

$$N(ppm) = \frac{IR \times SR \times CV \times extract\,volume \times 10^{-6} \times 100 \times cf}{Weight\,of\,sample \times Aliquot\,taken}$$

Where

IR = Instrument reading

SR = Reciprocal of slope obtained from plot of standards

CV = Color volume

cf = Correction factor

Soil particle size was determine using the hydrometer method **(**Bouyoucos 1962). Soil organic carbon was determine using the Walkley and Black method (1934), while chemical fractionation and total heavy metals determination was carried out according to Tessier *et al.,* (1979). This involves the separation of metal into five operationally defined fractions: exchangeable (F1), bound to carbonate (F2), bound to Fe-Mn oxide (F3), bound to organic matter (F4) and residual fraction (F5). All glasswares used were soaked and washed with chromic acid. Bulk scientific standard solution was used to calibrate the Atomic Absorption Spectrometer (Pg A500 model). Procedural blank samples were subjected to similar extraction method using the same amount of reagents.

## RESULTS AND DISCUSSION

The results obtained from the physico-chemical analysis of the biochar, parent soil and soil-amended with biochar are shown in Table 1. Soil pH is the most widely accepted parameter which exerts a controlling influence on the availability of micro-nutrients and heavy metals in the soil to plants (Sanders, 1982; Igwe *et al.*, 2005). Banjoko and Sobulo, (1994) reported that some Nigerian soils especially in the forest and savannah regions are within a pH range of 5.70 – 6.50. This was taken as the normal pH range for ordinary soils that favour plant and microorganisms. The pH of the soil from the lead-acid battery charger workshop (0%) was found to be in the range of acidic region (5.18- 5.22) and acidity controls availability, mobility and toxicity of heavy metal ions in the soils.

**Table1. Physico-Chemical Properties of Biochar, Soil and the Amended Soil**

| | **Biochar** | **0%** | **5%** | **10%** | **15%** | **20%** |
|---|---|---|---|---|---|---|
| | | **Control** | **Amendment** | **Amendment** | **Amendment** | **Amendment** |
| Clay (%) | - | 11.90 | - | - | - | - |
| Silt (%) | - | 5.80 | - | - | - | - |
| Sand (%) | - | 82.30 | - | - | - | - |
| Soil pH | 8.59 | 5.20 | 5.51 | 5.92 | 6.78 | 7.84 |
| C (%) | 78.70 | 0.24 | 3.96 | 7.97 | 11.73 | 15.95 |
| N (%) | 0.17 | 1.02 | 1.03 | 1.05 | 1.07 | 1.08 |
| Na (mg/kg) | 1200.01 | 23.00 | 58.67 | 134.67 | 230.37 | 255.00 |
| K (mg/kg) | 8860 | 117.00 | 728.67 | 1348.67 | 1967.67 | 2578.00 |
| Ca (mg/kg) | 5400 | 4300.00 | 4539.67 | 4800.33 | 5104.33 | 5368.33 |
| Mg (mg/kg) | 5200 | 1272.00 | 1432.00 | 1630.67 | 1826.67 | 2025.33 |
| CEC (cmol/kg) | 82.27 | 32.50 | 36.72 | 41.64 | 46.77 | 51.44 |
| P (mg/kg) | 5200.96 | 17.36 | 268.20 | 535.90 | 772.30 | 1065.90 |

There is a gradual increase in soil pH as biochar application rate increases from 5% (5.51) to 20% (7.84) as shown in Table 1. This increase in soil pH is as a result of the alkaline reaction of biochar used i.e the liming effect of biochar is attributed to ash accreation as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, small amount of heavy metals, phosphates, organic and inorganic nitrogen. In agreement with this, Arocena and Opio (2003), also reported the capacity of ashes to neutralize acidic soil. Another reason for the increase in soil pH due to application of biochar could be because of high surface area and porous nature of biochar that increases the cation exchange capacity (CEC) of the soil. These favors nutrient availability and crop productivity (Yamato *et al.,* 2006). Application of biochar on soil from lead-acid battery charger workshops significantly increased the mean values of soil organic carbon and total nitrogen (Table 1). The highest values of organic carbon and total nitrogen were observed in soils amended with 20% palm kernel shell biochar (Table 1). The increase in organic carbon and total nitrogen due to addition of biochar could result from the presence of high amount of carbon and nitrogen in the palm kernel shell. The highest values of organic carbon at biochar treated soils indicate the recalcitrance of organic-carbon in biochar. High organic carbon in soils treated with biochar has also been reported by Solomon *et al., (*2007) and Liang *et al., (*2006). They also reported higher organic carbon and total nitrogen at the ancient *terra preta* compared with adjacent soils. The amount of available phosphorous in the parent sample soil was also significantly increased by application of biochar. The observed increase in available phosphorus could be due to the presence of high phosphorous in the palm kernel shell. The increase in soil pH and CEC, that reduce the activity of iron and aluminium, could also contribute to the highest values of available phosphorus. As soil pH increases the available phosphorous increases in soils treated with biochar with 20% having the highest available P. The CEC of the soil sample is low (32.50). CEC is known as a good indicator for evaluating soil fertility, more especially for nutrient retention and thus it prevents cations from leaching into the groundwater. The clay and soil organic matter in the parent soil(0%) are quite low, this accounts for the low amount of various metal cation such as $Ca^{2+}$.$Na^{+}$,$K^{+}$ and $Mg^{2+}$ in the parent soil sample. These metals are usually retained in the clay or soil organic matter (SOM) by complexation, adsorption and ion-exchange. The application of biochar and stabilization for seven weeks gave a higher CEC values compare with that of the parent soil (Table 1), and the CEC values increases gradually with increase in biochar application rates, 20% having the highest CEC value of (51.44). This could be attributed to the inherent characteristic of biochar. Biochar has high surface area, highly porous, variable charge organic matter that has the potential to increase soil CEC and surface sorption capacity when added to soil and thus increase the exchangeable base (Glaser *et al,* 2002; Lehman *et al*., 2003). The higher cation adsorption capacity of biochar may be attributed to the high surface negative charge resulting from oxidation of functional groups, mainly carboxylic and phenolic on the outer surface area of the biochar (Liang *et al*., 2006), Cheng *et al.,* 2006 and 2008), showed that CEC values increase with time of incubation or stabilization as the biochar ages in the presence of $O_2$ and $H_2O$ and possibly lead to the formation of stable biochar-trace element complexes in soil. The sand fraction forms the predominant fraction in terms of particle size Distribution for the parent soil sample (0%), with a value of (82.3%), with low clay (11.90%), low Silt (5.80%) total carbon (0.24), so they tend to be permeable and suggesting low accumulation of plant material and high level of automobile waste.

The metals (Pb, Cu, Zn, Cr and Cd) gradually decrease in concentration as the biochar increases 5%>10%>15%>20% (Fig 1). These metals seem to be adsorbed to biochar particle by surface complexation reaction leading to reduce concentration (Liang *et al.,* 2006). All the heavy metals were within the permissible limit of Canada and India except for Cr which exceeded the permissible limit of India standards (Awashti, 2000).

Conversion of exchangeable form of heavy metals to less-available organic-bound metals via complexation reactions has been attributed as the reason for the significant reduction in extractable heavy metals in biochar amended soil (Brown *et al.,* 2005; Farfel *et al.,* 2005; Pichtel and Bradway 2008), thus binding of

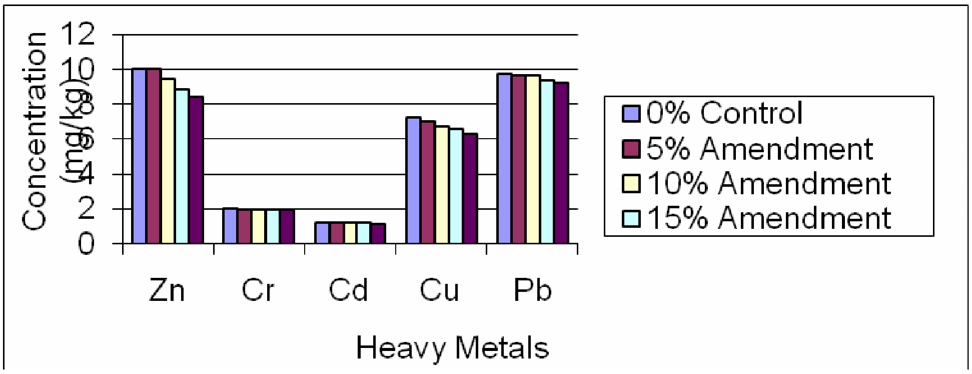

**Figure 1: Levels of Heavy Metals in Parent and Amended Soils**

heavy metal in these fractions may reduce Pb, Cu, Zn, Cr and Cd in the exchangeable fraction resulting in decrease in its bioavailability and mobility. In this study the Fractionation results indicate that soil amended with biochar show lower exchangeable and carbonate fraction for Pb,Cu,Zn,Cr and Cd, as the biochar application rate increases with 20% having the lowest concentration.

The highest concentration of the metal bound to exchangeable and carbonate phase was observed for Pb (1.79 mgkg$^{-1}$) and Zn (1.70 mgkg$^{-1}$) at 0% soil without biochar. Accumulation of Zn and Pb could be as a result of waste from battery charger dumpsites.

The results in Fig 2 show that Lead in the battery charger workshop soil are concentrated in the last three fractions. The majority of Lead in the soil and soil amended with biochar was associated with the residual fraction, having the range from (0%) 2.11 to (20%) 2.42. The residual fraction is considered the most stable, less reactive and less bioavailable since it is occluded within the crystal lattice layer of silicates and well crystallized oxide minerals (Segarra *et al.,* 2008).

The organic and Fe-Mn Oxide fraction could be considered relatively stable, slowly mobile and poorly available but could change with variations in redox conditions (Horsfall and Spiff, 2005). The carbonate have been implicated as immobilizing most heavy metals by providing an adsorbing or nucleating surface and by buffering the soil pH, They are only stable in soils with high pH, thus 20% (1.42) biochar application is more stable and lower in concentration than 0% (2.11) which is the higher and more liable.

The exchangeable fraction which is the mobile and bioavailable fraction for plants uptakes gave the result of 1.32(20%) and 1.79(0%). This fraction represents heavy metals soluble in water as well as those held by electrostatic adsorption. The amount of metal in this phase indicated the environmental conditions of the soil. The high concentration of lead in this fraction suggests a greater contamination risk for lead (Wangboje *et al.,* 2014). Copper content was observed to be greater in residual fraction followed by organic bound fraction, Fe – Mn oxide fraction, carbonate fraction and exchangeable (Fig 3). The exchangeable fraction of copper shows a much higher concentration at 0% than 20%. The high concentration of Copper in this fraction also suggests a greater contamination risk for copper (Wangboje *et al.,* 2014).

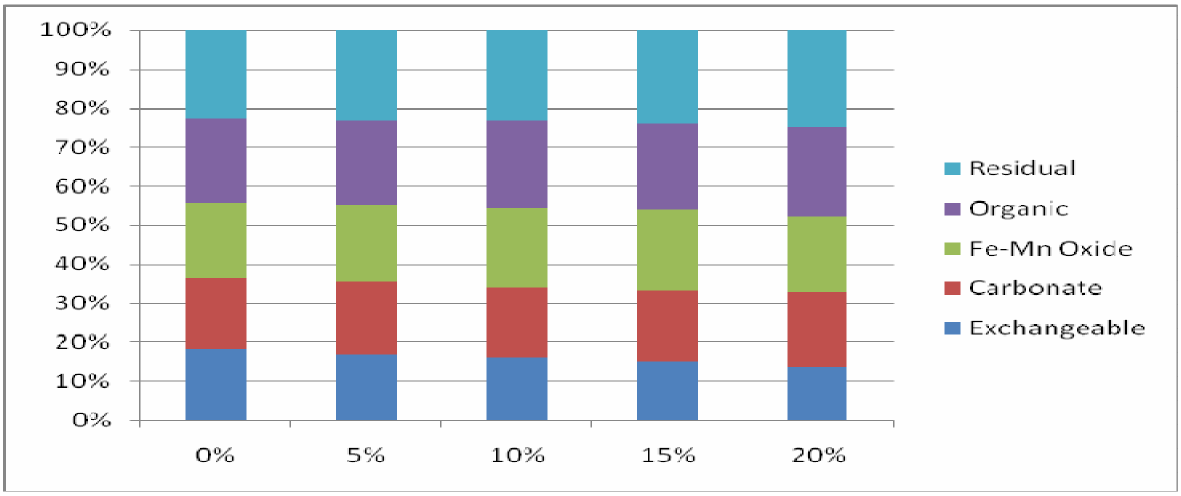

**Figure 2: Percentage of Pb in the Various Geochemical Phases as a Function of Pb Content of Parent and Amended Soils**

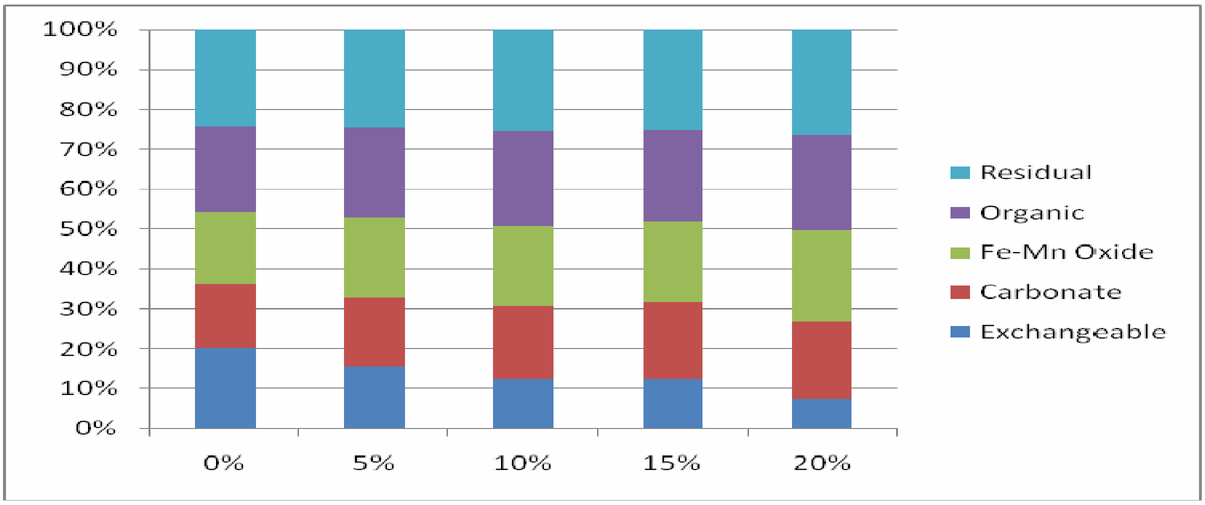

**Figure 3: Percentage of Cu in the Various Geochemical Phases as a Function of Cu Content of Parent and Amended Soils**

The largest portion of zinc which were found in the residual fraction (2.33-2.66%), metals bound to exchangeable, carbonate, Fe-Mn oxide and organic fraction were in the range of 0.62-1.70, 1.06-1.69, 1.11-1.72, 2.25-2.66% respectively. The exchangeable fraction of zinc shows a much higher concentration at 0% than 20% (Fig 4). The high concentration of zinc in this fraction pose serious environmental problem to the underground water (Wangboje *et al.,* 2014).

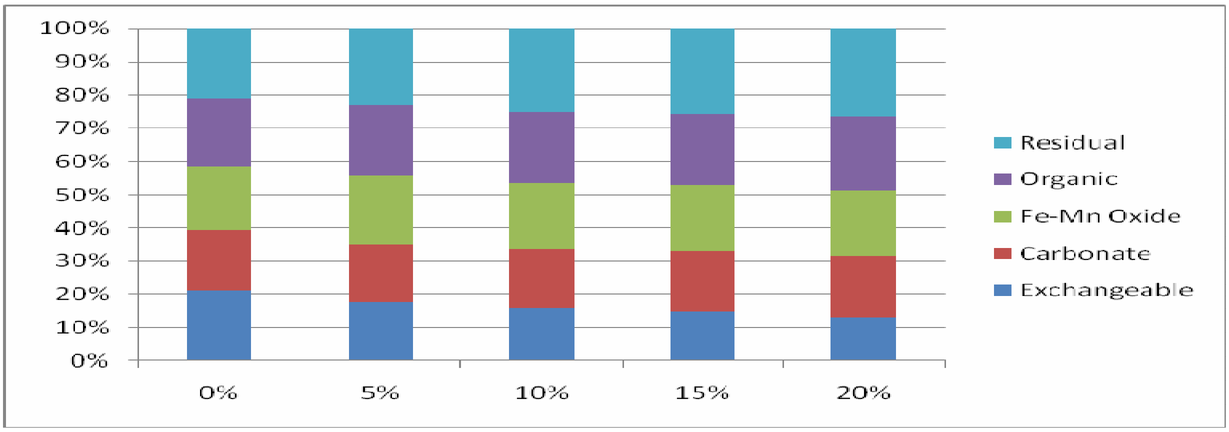

**Figure 4: Percentage of Zn in the Various Geochemical Phases as a Function of Zn Content of Parent and Amended Soils**

Although the concentration of cadmium in this study is low, accumulation of it could be hazardous. The association was seen to be in the order residual>organic>Fe-Mn Oxide> carbonate>exchangeable (Fig. 5).

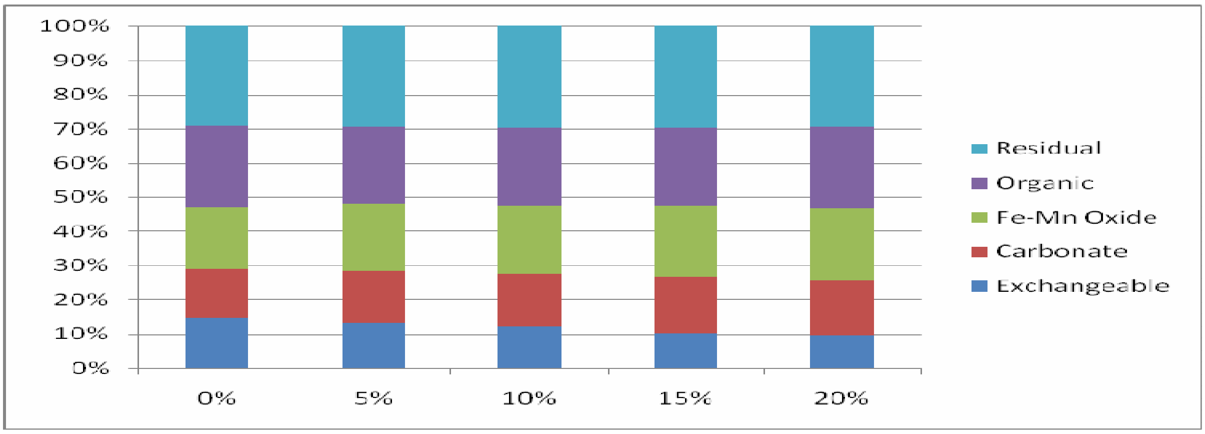

**Figure 5: Percentage of Cd in the Various Geochemical Phases as a Function of Cd Content of Parent and Amended Soils**

Chromium in the soil was mainly found in the residual fraction, (0.49-0.60). About 0.27-0.33, 0.45-0.48 and 0.33-0.39% was bound to carbonate, Fe-Mn oxide, and organic respectively. While a low range of 0.20-0.26% was bound to exchangeable.

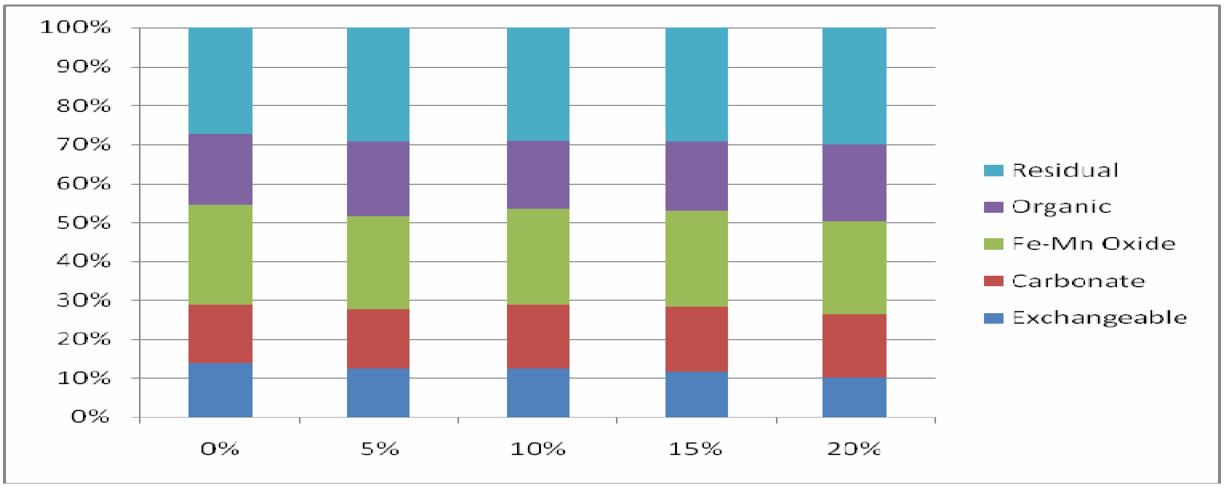

**Figure 6: Percentage of Cr in the Various Geochemical Phases as a Function of Cr Content of Parent and Amended Soils**.

The relative index of metal mobility was calculated as a mobility factor (MF) on the basis of the following equation.

$$MF = \frac{F1 + F2\ X\ 100}{F1+F2+F3+F4+F5} \quad \text{- - - - - - - - - - - - - - - (1)}$$

A high Mobility Factor value for heavy metals in soil has been interpreted as evidence of relatively high lability and biological availability (Ma and Rao 1997; Kabala and Singh 2001). In general the mobility factor was higher for all metals in the parent soil than the biochar amended soil (Table 2). This indicates a greater bioavailability and mobility and also shows formation of stable biochar-trace element complexes in soil.

**Table 2: Mobility Factor for Metals in Parent and Amended soils**

| Levels of Biochar amendment | Zn | Cr | Cd | Cu | Pb |
|---|---|---|---|---|---|
| **0%** | **36** | **29** | **29** | **37** | **37** |
| **5%** | **27** | **28** | **29** | **33** | **35** |
| **10%** | **27** | **29** | **28** | **31** | **34** |
| **15%** | **26** | **29** | **27** | **32** | **33** |
| **20%** | **21** | **28** | **26** | **27** | **32** |

The Environmental risk factor (ERF) was use to determine environmental risk in order to establish potential threat of heavy metals (Saenz, *et al.,* 2003). The ERF was calculated using the formula;

ERF=CSQV – Ci/CSQV -------------------------(2)

Where CSQV= Concentration of sediment quality value (heavy metal concentration in residual fraction of sediment which is equivalent to the background/pre-industrial concentration).

Ci = heavy metal concentration in the first four fractions of sediment.

From the result (Table 3) the heavy metals in the parent soil pose a potential threat to the environment (ERF < 0).

The contamination factor (CF) was calculated as:

CF = Metal concentration in sediment/Background concentration of metal in sediment (Lin *et al.,* 2009). - -- - - - - - - - - - - - - -- - -- - - - - - -- - (3)

Since the contamination factor (CF) values exceeded unity (Table 3), the parent soil is clearly contaminated with these metals.

**Table 3: Contamination Factor (CF) and Environmental Risk Factor (ERF) for Heavy Metals in the Parent soil**

| Heavy metals | Contamination factor (CF) | Environmental risk factor (ERF) |
|---|---|---|
| Pb | 3.53 | -1.42 |
| Cu | 3.08 | -1.38 |
| Zn | 3.08 | -0.75 |
| Cd | 2.44 | -2.12 |
| Cr | 2.69 | -2.20 |

**Key: 1<CF<3 = Moderate contamination (Cd, Cr)**
**3<CF<6 = Considerable contamination (Pb, Cu, Pb)**

## CONCLUSION

The results obtained in this study revealed that the soil from lead-acid battery workshop is moderately contaminated with Cd and Cr, considerably contaminated with Pb, Cu and Zn. Addition of biochar increases soil pH, organic carbon, total nitrogen, available phosphorus and CEC of the soil from lead-acid battery workshop. The presence of plant nutrients and ash in the biochar and also high surface area, porous nature and the capacity of biochar to act as a medium for microorganism are identified as the main reasons for the increase in soil properties. The palm kernel shell biochar show a high sorption capacity of the heavy metals studied and it increases at the highest level of biochar treatment (20%). There was an increase in the fractionation studies in reducible, oxidisable and residual fraction in all the metals. This trend indicates that the distribution of the metals in biochar amended soil is gradually shifting from the more labile fractions to the more stable fraction. Therefore application of biochar can be used to remediate soil and improve soil fertility from a contaminated or highly polluted soil.

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