

COMPARATIVE STUDIES ON THE USE OF FLY ASH AND SLUDGE IN THE REMEDIATION OF HEAVY METAL-POLLUTED SOIL

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Abstract

Often the remedial measures required to clean-up sites contaminated with heavy metals are so complex that their implementation becomes economically unsustainable. In this work, an investigation has been carried out to assess the potential use of fly ash from coal – fired power stations and sludge from oil palm in immobilizing heavy metals contained in soils from a severely contaminated battery dumpsite in Benin metropolis. Parallel experiments were carried out with soil amended with flyash and sludge at different levels. The amended soil was left for a stabilization period of eight weeks. The parent and the amended soils were analyzed for physicochemical properties using standard methods. The results of the physicochemical properties for parent soil showed the pH, organic carbon and CEC to be 3.0, 4.6% and 9.36meq/100g respectively. The pH, organic carbon and CEC for the fly ash and sludge were respectively 10.5, 0.8%, 4.27meq/100g and 5.2, 45.47%, 15.15 meq/100g. The pseudo metal concentration for the parent soil was 515mg/kg for Fe, 220.3 mg/kg for Zn, 130.15mg/kg for Cu, 48.19 mg/kg for Mn and 52.43 mg/kg for Ni. After amendment, the exchangeable fraction (bioavailable) was reduced to the non-available form. The parent soil was highly contaminated with Fe, Zn, Cu and Ni but was moderately contaminated with Mn. On amendment, fly ash and sludge reduced the level of contamination of metals. From the environmental risk factor, Fe, Zn and Mn posed no potential threat to living organism.

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1.0 INTRODUCTION

The evaluation of heavy metals in contaminated soils as a means of monitoring the status of the environment for the good of the ecosystem is crucial because with increased exploitation of natural resources, industrialization and urbanization, most area of the Niger Delta region of Nigeria are facing increasing ecological problems arising from the release of pollutant into both the aquatic and terrestrial environments. Heavy metals constitute a significant group of these pollutants [1]. While many heavy metals are essential elements at low levels of concentration, they can exert toxic effects at concentration higher than permitted in the environment [2]. 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 fly ash and sludge. Sludge also known as biosolids, is one of the major solid organic

waste produced by waste water treatment plants in cities around the globe. The application of sludge on agricultural land is a common practice around the world. Land application of sludge and municipal solid waste has been shown to benefit crop production and improve soil quality [3, 4, 5, 6]. However to realize this benefit, application of sludge must be conducted in an environmentally sustainable manner [8, 9]. Unlike fly ash, sludge characteristically contains high levels of the major plant nutrients, N and P, and is enriched in organic matter. Benefits of sludge application on soils however, have to be weighed against the potential hazards associated with certain sludge borne constituents (e.g. heavy metals and organic contaminants). Historically, the use of fly ash in agriculture has been based on its neutralizing potential and supply of essential elements such as Ca, S and Mo [11, 12]. . However, the use of fly ash as an agricultural amendment can be enhanced by blending

it with potentially acid forming organic by-products such as sewage sludge. The latter contains significant amount of N and P [14]. Consequently, fly ash may serve as a composting ingredient along with sewage sludge. Its basic properties permit the neutralization of the acidic sewage sludge thereby minimizing the bioavailability of heavy metals and the attendant consequences to plants. Therefore, the objectives of this study are to: (i) determine the level of metal pollution in the lead acid battery dumpsite, (ii) determine metal content in fly ash and sludge before application, (iii) compare the separate effects of fly ash and sludge in the immobilization of heavy metals and (iv) determine the contamination factor and the environmental risk factor of these metals in the soil.

2.0 MATERIALS AND METHODS

2.1 Soil Sampling, Sludge, Fly ash Preparation and Experimental Design

Soil samples were collected from lead-acid battery dumpsite located in Uwelu market, in Benin Metropolis. The site is geographically situated as follow: Latitude 6° 23'00" N and Longitude 5° 35' 00"E. Topsoil (0-15 cm) samples were collected from the dumpsite using the grid method. The soil sample was air – dried, pooled and sieved to less than 2 mm. The sludge and fly ash were collected from oil palm boiler feeder at Okomu oils located at Okomu in Ovia South West of Edo state. The sludge and fly ash were air dried for a period of six weeks, sieved with a 2 mm sieve. They were separately applied to the soil at four different concentrations (5, 10, 15 and 20 %), mixed thoroughly and turned over frequently for eight weeks for stabilization. About 20 g was taken

from each amendment and control to determine the concentration of metals in various geochemical forms in the soils.

2.2 Determination of Physico-Chemical Properties of Soil

The pH and the CEC were determined by the method employed by Black (1965). The hydrometer method described by Day (1965), Bouyoucos (1936), Anegebe and Okuo (2013) were used in evaluating the particle size. The methods of Nelson and Sommer (1982), Black (1965), Walkley and Black (1934) were used to determine the organic carbon content. The concentration of phosphorus was obtained by Bray and Kurtz (1974)'s method. The nitrogen content was determined by colorimetric method [21]. The exchange acidity was determined as reported by Spark *et al* (1996) while chemical fractionation and total heavy metals determination was carried out according to [23]. 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 and rinsed with distilled water. 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. All reagents used were of analytical grade and obtained from Sigma, BDH and Bulk Scientific. They were used without further processing.

3.0 Results and Discussion

Table 1. Physicochemical Parameters of the Parent Soil, Sludge and Fly ash.

S/N	PARAMETERS/UNITS	SOIL	SLUDGE	FLYASH
1.	pH	3.0	5.2	10.5
2.	EC ($\mu\text{s}/\text{cm}$)	3999	3666	2349
3.	PO_4^{3-} (mg/kg)	11.0	596.0	399.6
4.	SO_4^{2-} (mg/kg)	152.8	640.2	569.4
5.	Cl^- (mg/kg)	446.71	382	411.3
6.	Ca (meq/100g)	6.57	9.14	0.64
7.	Mg (meq/100g)	0.83	2.10	0.16
8.	Na (meq/100g)	1.32	2.99	2.04
9.	K (meq/100g)	0.65	1.32	1.43
10.	CEC (meq/100g)	9.36	15.55	4.27
11.	Exch. Acidity (meq/100g)	1.0	-	-
12.	Nitrogen (%)	0.39	0.50	0.06
13.	Organic Carbon (%)	4.6	5.47	0.08
14.	Organic matters (%)	7.95	9.46	1.38
15.	Clay (%)	6.39	-	-
16.	Silt (%)	5.19	-	-
17.	Sand (%)	88.42	-	-
18.	Fe (mg/Kg)	-	670	935
19.	Zn (mg/Kg)	-	126.2	180.5
20.	Cu (mg/Kg)	-	111.0	97.00
21.	Cr (mg/Kg)	-	7.40	18.2
22.	Ni (mg/Kg)	-	0.14	23.0
23.	Mn (mg/Kg)	-	0.036	340.5

From the textural analysis, the parent soil had a clay content of 6.39% which is very low, silt 5.19% and sand 88.42% which makes the soil to be classified as loamy sand. The soil texture plays an important role in mobility of metals in soil. Texture reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy metals in soils. The clay soil retains high amount of metals when compared to sandy soil. The result from the physiochemical parameters of the parent soil showed that the soil is acidic with a pH of 3.0 which is a threat to plant growth. pH is the most widely acceptable parameter which controls the influence of the availability of micronutrients and heavy metals in the soil to plant [24, 25].

Soil acidity controls availability, mobility and toxicity of heavy metal ions in the soils. Most metals tend to be less mobile in soil with high pH as they tend to form insoluble complexes. Anegebe and Okuo (2013) as well as Banjoko and Sobulo (1994) reported that some Nigerian soils especially in the Savannah and forest regions are within a pH range of 5.7-6.50. This is assumed to be the normal pH range for ordinary soils that favour plant and microorganisms. The fly ash was alkaline with a pH of 10.5 and the sludge had an acidic pH of 5.2 (Table 1). The organic matter (OM) content was quite low for fly ash due to the low value of CEC while that of sludge was high (Table 1). Organic matter is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability. However because of the complexation of metals by soluble OM, the addition of OM can result in release of metals from solids to the soil solution. According Hazelton and Murphy (2007), the cation exchange capacity (CEC) of 6-12 is low and the CEC obtained from the analysis of the soil and fly ash were 9.36 and 4.27 meq/100g respectively, which is within the range; while that of the sludge was high with a CEC value of 15.55. The soil CEC is a measure of the negative site of the soil colloid in which the positive charge cation act on. Soil CEC is also known as a good indicator for evaluating soil fertility. The relatively low level of CEC suggests that leach ability and permeability of metals in the soil may be high [28]. The PO_4^{3-} and SO_4^{2-} were found to be lower in the fly ash compared to the sludge which was higher due to the high EC. The electrical conductivity (EC) of the parent soil, fly ash and sludge were high with values of 3999, 2349 and 3666 $\mu\text{s}/\text{cm}$ respectively. Soil electrical conductivity (EC) is a measure of the amount of salts in soil (salinity of soil). It is an important indicator of soil health. It affects crop yields, crop suitability, plant nutrient availability, and activity of soil microorganisms which influence

key soil processes including the emission of greenhouse gases such as nitrogen oxides, methane, and carbon dioxide. Excess salts hinder plant growth by affecting the soil-water balance. For certain non-saline soils, determining EC can be a convenient and economical way to estimate the amount of nitrogen (N) available for plant growth [27]. In general the pseudo metal concentration in parent soil was higher than that of sludge and fly ash amended soil, except for Cu amended with sludge and Mn amended with 20% fly ash. This may be due to the high amount of Cu and Mn in sludge and fly ash respectively. The pseudo metal content (Fe, Zn, Cr, Ni and Mn) of the fly ash was higher than that of sludge except for Cu which had a higher concentration in sludge (Table 1). Distribution of heavy metals between soil and solute is the key for evaluating the environmental impact of the metals. For Cu, in particular, OM (both solid and dissolved solids) can affect its mobility substantially [29]. The level of pseudo metals for the parent soil was higher for Fe with a value of 515.8 mg/kg (fig 1) and Mn had the least value of 48.19 mg/kg (fig 5).

Conversion of exchangeable form of heavy metals to less-available forms of the metals via complexation reactions may be the reason for the significant reduction in extractable heavy metals in amended soil, thus binding of heavy metals in these fractions may reduce Ni, Zn, Mn and Fe in the exchangeable fraction resulting in decrease in its bioavailability and mobility. In this study, the fractionation results indicate that soil amended with sludge and fly ash show lower exchangeable fraction for Ni, Zn, Mn and Fe (Figs. 1-4 and 7-10), when compared to the parent soil.

The high concentration of Fe in exchangeable fraction suggests a greater contamination risk for Fe. Accumulation of Fe could be as a result of waste from battery charger dumpsites. The exchangeable fraction is the mobile and bioavailable fraction for plants uptake. This fraction represents 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. This fraction of Fe reduces in concentration as application of fly ash and sludge increased (Figs. 1 and 2), it was observed that the majority of the Fe in the amended soil with fly ash and sludge was associated with the Fe-Mn oxide fraction. To the fraction bound to carbonate, the concentration increases on the application of sludge and fly ash. 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 [39]. This fraction increases on application of amendment. The organic and Fe-Mn Oxide fraction could

beconsideredrelatively stable, slowly mobile and poorly available but could change with variations in redox conditions [30]

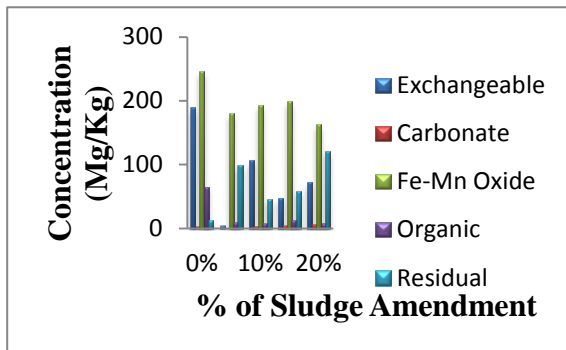


Fig. 1 Concentration of Fe in Parent and Amended Soil with Sludge

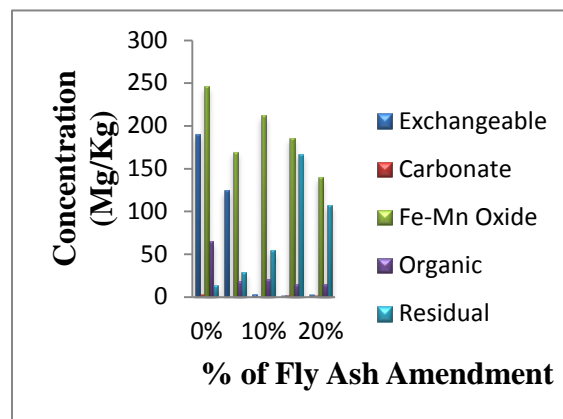


Fig. 2 Concentration of Fe in Parent and Amended Soil with Fly Ash

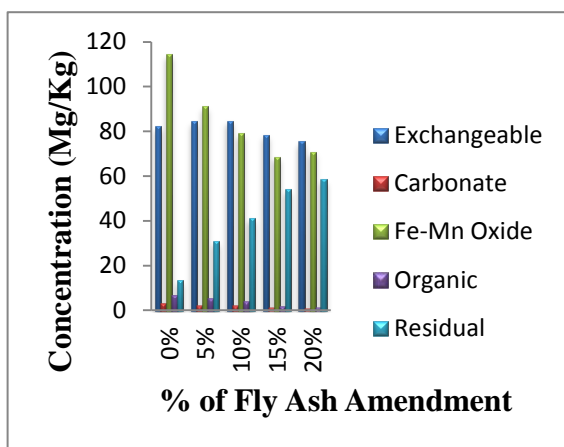


Fig. 3 Concentration of Zn in Parent and Amended Soil with Sludge

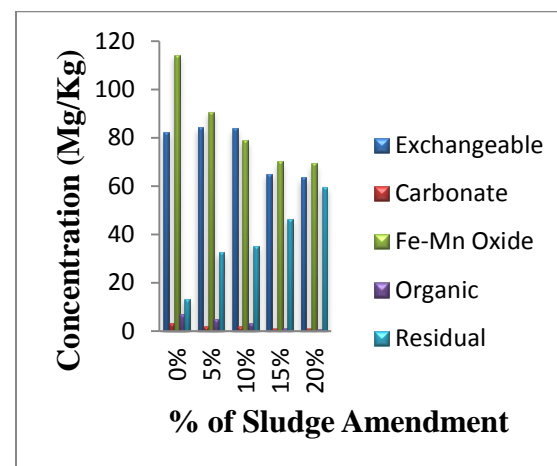


Fig. 4 Concentration of Zn in Parent and Amended Soil with Fly

The exchangeable fraction of zinc in the amended soil show is high concentration for sludge compared to that amended with fly ash which suggests that the flyash is more effective in reducing contamination risk in the soil. A range of 35.7-42.3% and 33.6-42.6% of Zn are present in the Fe-Mn oxide fraction in the sludge and fly ash amended soil respectively. Mn was mainly in the residual fraction. It was observed (Figs. 3 and 4) that there was a decrease in the first four fraction of Zn as the concentration of sludge and fly ash in the amendment increase, except for 20% amendment using fly ash, while Mn did not follow a particular pattern. (Figs. 5 and 6). The residual fraction for both Zn and Mn were observed to increase as the % amendment increased with both sludge and fly ash, thus reducing the mobility and bioavailability of these metals. Large portion of Ni was associated with the organic bound fraction with 0 % having the highest concentration (32.48 mg/kg) and the least concentration was found in 20% soil amended with both sludge and fly ash

(Figs. 7 and 8). The carbonate has been implicated as immobilizing most heavy metals by providing an adsorbing or nucleating surface and by buffering the soil pH [31]. The carbonate bound fraction has the highest concentration with 10 % and the least in 5% soil amended with sludge, and a range of 0.08-0.28 in 10 % and 15 % soil amended with fly ash. There was no observable trend in the first four fractions as the application of sludge and fly ash increases; however there was an increase in the residual fraction on amendment with fly ash, thus making this metal less available for plant uptake.

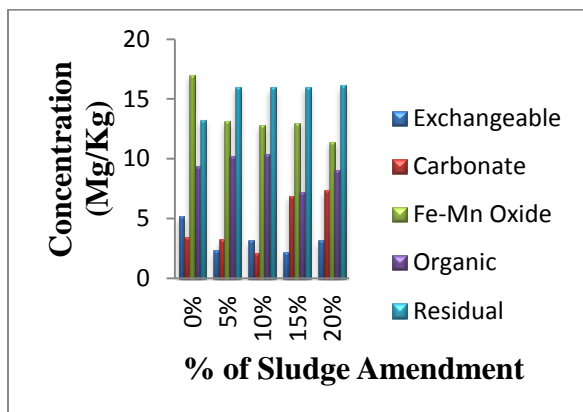


Fig. 5 Concentration of Mn in Parent and Amended Soil with Sludge Ash

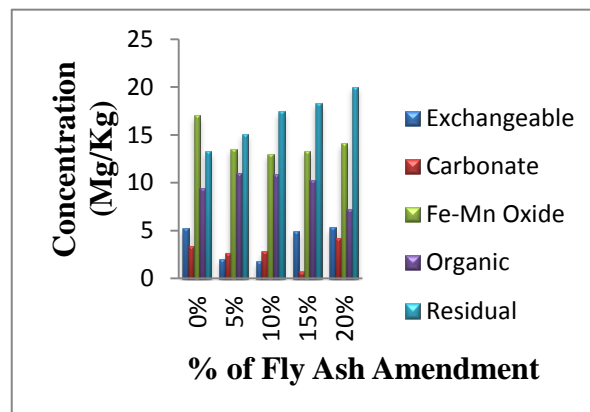


Fig. 6 Concentration of Mn in Parent and Amended Soil with Fly Ash

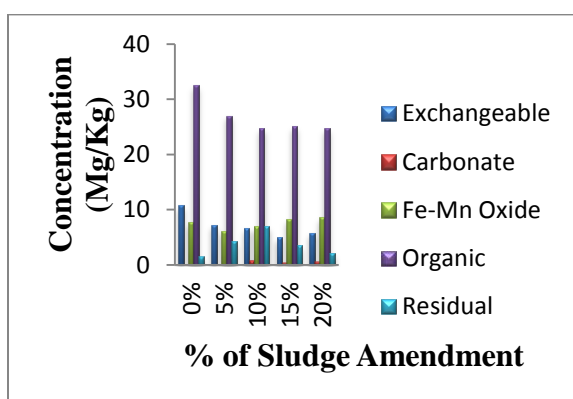


Fig. 7 Concentration of Ni in Parent and Amended Soil with Sludge Ash

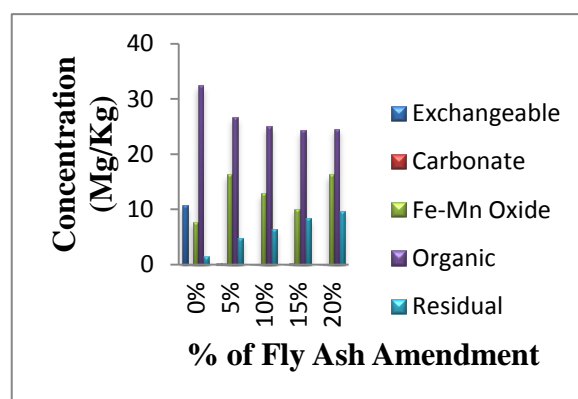


Fig. 8 Concentration of Ni in Parent and Amended Soil with Fly Ash

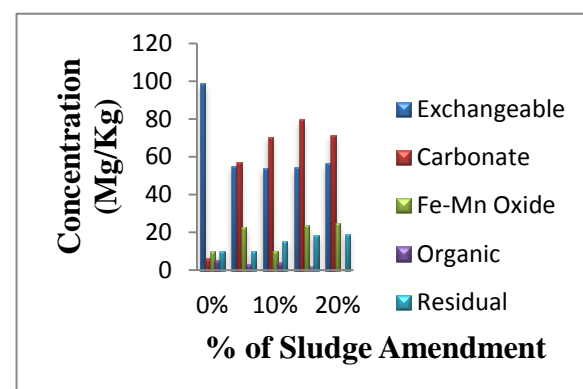


Fig. 9 Concentration of Cu in Parent and Amended Soil with Sludge Ash

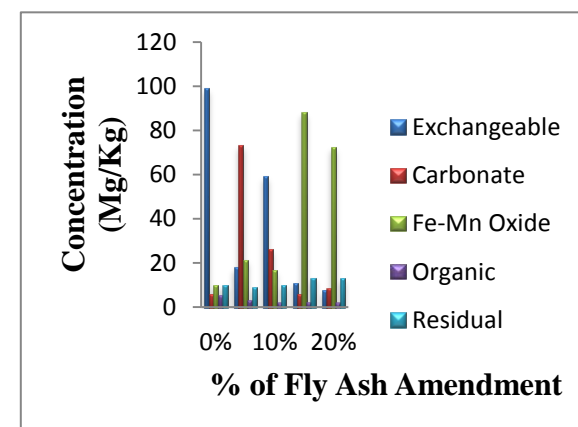


Fig. 10 Concentration of Cu in Parent and Amended Soil with Fly Ash

Application of sludge increases the pseudo metal concentration of Cu as the amendment increases (fig. 9), this is due to high amount of Cu inherent in the sludge. However there is conversion of exchangeable form of Cu to less-available forms of the metal (Figs. 9 and 10), thus making it less available for plant uptake.

3.1 Mobility Factor

The operationally defined extraction sequence fractionates the heavy metals in the soil in the order of decreasing solubility. As a result, the exchangeable and carbonate (F1 + F2) fractions which are the early fractions, capture the most reactive and presumably the most mobile and bioavailable fractions [32]. The relative index of metal mobility was calculated as a

mobility factor (MF) [32, 33] on the basis of the following equation.

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

Where;

F1 = Exchangeable metal content fraction

F2 = Metal content bound to carbonate fractions

F3 = Metal content bound to Fe-Mn Oxide fraction

F4 = Metal content bound to organic matter fraction

F5 = Residual metal content fraction.

Table 2. Mobility Factor for Metals in Parent and Amended soils with Sludge

Levels of Sludge amendment	Fe	Zn	Mn	Cu	Ni
0%	37.2	38.8	17.7	80.5	20.7
5%	1.8	40.3	12.4	75.7	16.3
10%	31.0	42.2	12.0	80.0	16.3
15%	15.9	36.0	20.1	75.3	12.6
20%	21.2	33.2	22.4	74.3	15.2

Table 3. Mobility Factor for Metals in Parent and Amended soils with Fly Ash

Levels of Fly Ash amendment	Fe	Zn	Mn	Cu	Ni
0%	37.2	38.8	17.7	80.5	20.7
5%	36.6	40.6	10.5	73.2	1.0
10%	1.4	41.2	10.1	75.9	0.3
15%	0.9	38.9	11.8	14.2	0.8
20%	1.4	36.9	18.8	15.5	0.3

A high mobility factor value for heavy metal in soil has been interpreted as evidence of relatively high liability and biological availability [16, 33, 34, 35]. There is a reduction in mobility factor for Fe, Cu and Ni on application of amendment with sludge and fly, this shows the

potential of sludge and fly ash in reducing bioavailable metal concentration. Conversely there was no significant change in the mobility factor for Zn and Mn on both fly ash and sludge amended soil (Table 2 and 3).

3.2 Environmental Risk Factor (ERF) for Fe, Zn, Cu, Mn and Ni in parent soil, soil amended with flyash and sludge.

Potential threat of heavy metals on living organisms of the parent soil and the amended soil was evaluated in terms of Environmental Risk factor (ERF). Saenz *et al.* (2003) established that; $ERF = CSQV - C_i / CSQV$, ----- (2)

Where;

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

C_i =heavy metal concentration in the first four fractions (exchangeable, carbonate bound, bound to Fe-Mn oxide and organic bound) of soil.

When $ERF < 0$, there is potential threat to living organisms.

When $ERF > 0$, there is no threat to living organism.

Table 4. Environmental Risk Factor (ERF) for Fe, Zn, Cu, Mn and Ni in parent soil and soil amended with sludge.

Levels of Sludge amendment	Fe	Zn	Mn	Cu	Ni
0%	46.7	7.1	11.2	-6.2	-20.7
5%	96.6	26.8	14.2	-3.8	-5.4
10%	38.1	30.4	14.1	6.8	1.4
15%	54.1	43.4	14.2	9.5	-7.6
20%	117.9	57.2	14.2	11.1	-16.2

Table 5. Environmental Risk Factor (ERF) for Fe, Zn, Cu, Mn and Ni in parent soil and soil amended with Fly Ash.

Levels of Fly Ash amendment	Fe	Zn	Mn	Cu	Ni
0%	46.6	7.1	11.2	-6.2	-20.7
5%	17.2	24.9	13.2	-4.4	-4.25
10%	49.4	37.0	15.8	-0.2	0.3
15%	165.4	51.1	16.7	5.3	4.3
20%	105.3	55.8	18.5	6.2	5.5

From the results, it was observed that Fe, Zn Cu and Mn for both parent and amended soil pose no environmental threat to living organism, at 20% amendment. While Ni for both parent and amended soil poses potential threat to living organism (Table 4 and 5).

3.2 Contamination factor

In this study, contamination factor (CF) was calculated based on the equation described by Lin, (2009).

CF = metal concentration in soil (exchangeable, carbonate, organic, Fe – Mn oxide bound) / background concentration of metals in soil (residual). (3)

If CF >1 the soil is contaminated, if CF <1 the soil is not contaminated, when 1 < CF < 3 the soil is moderately contaminated, 3 < CF < 6 the soil is considerably contaminated and when CF > 6 it is highly contaminated.

Table 6: Contamination Factor for Fe, Zn, Cu, Mn and Ni in Uwelu market soil and soil amended with sludge.

Levels of Sludge amendment	Fe	Zn	Mn	Cu	Ni
0%	6.0	11.2	2.6	14.1	22.7
5%	2.0	5.6	1.8	13.8	9.6
10%	6.9	4.8	1.8	9.1	5.6
15%	4.5	3.0	1.8	8.8	11.1
20%	2.1	2.3	1.9	8.0	18.3

Table 7. Contamination Factor for Fe, Zn, Cu, Mn and Ni in parent soil and soil amended with Fly Ash.

Levels of Sludge amendment	Fe	Zn	Mn	Cu	Ni
0%	6.0	11.2	2.3	14.1	22.7
5%	11.2	6.1	1.9	13.2	9.1
10%	4.4	4.1	1.6	10.3	6.0
15%	1.2	2.8	1.6	8.1	4.1
20%	1.5	2.5	1.5	6.9	4.2

The result shows that the parent soil were highly contaminated with Fe, Zn, Cu and Ni concentration and moderately contaminated by Mn. On amendment, the level of contamination was significantly reduced for most metals.

4.0 Conclusion

The results obtained in this study revealed that the soil from lead-acid battery workshop is highly contaminated with Fe, Zn, Cu and Ni concentration and moderately contaminated by Mn. Application of fly ash and sludge reduces the contamination. From

the results of the contamination factor and mobility factor, it was observed that application of fly ash is more effective than sludge in reducing the level of contamination and bioavailability.

References

- [1] Udosen, E. D., Benson, N. U., Essien, J. P and Ebong, G. A. (2006). Relation between Aquaregia. Extractable Heavy Metals in Soils and *Manihot Utilissima* within Municipal Dumpsite. *International Journal of Soil Sciences* 1(1): pp 27 – 32.

- [2] Dean-Ross, D. and Mills, A. I. (1989). Bacterial Community Structure and Function Along a Heavy Metal Gradient. Applied and Environmental Microbiology, 2002 – 2009. American Society of Microbiology.
- [3] McCalla, T.M., Peterson, J.R. and Lue-Hing, C. (1977). Properties of Agricultural and Municipal Wastes, In; Elliot, L.F. and Stevenson, F.J. eds., Soils for Management of Organic Wastes and Wastewaters, American Society of Agronomy, Madison, WI: pp.9 – 43.
- [4] Page, A.L. and Chang, A.C. (1994). Overview of the Past 25 years: Technical Perspective, In; Clapp, C.E., Larson, W.E. and Dowdy, R.H. ed., Sewage Sludge; Land Utilization and the Environment. SSSA Misc. Publ. ASA, CSSA and SSSA, Madison, Wisconsin, pp. 3 – 6.
- [5] NRC – National Research Council, (1996). Use of Reclaimed Water and Sludge in Food Crop Production, National Academy Press, Washington, D.C.
- [6] Basta, N.T., (1995). Land Application of Biosolids: A Review of Research Containing Benefits Environmental Impacts and Regulation of Applying Treated Biosolids, Oklahoma Agric. Exp. Station Tech. Bull. B – 808.
- [7] Basta, N.T. (2000). Examples and Case Studies of Beneficial Reuse of Municipal By-Products, In: J. F. Power and W. A. Dick, eds., Land Application of Agricultural, Industrial and Municipal By-Products, Soil Science Society of America, Madison, WI, pp.481 – 504.
- [8] (Council for Agricultural Science Technology) (1976), Application of Sewage Sludge to Croplands; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals, Rept. 83, Council for Agricultural Science and Technology, Ames: IA pp 77 .
- [9] Chaney, R.L., Hornik, S. B. and Simon, P. W. (1977), Heavy Metal Relationship during Land Utilization of Sewage Sludge in the Northeast, In: Land as a Waste Management Alternative Proceedings of the 1976 Cornell Agricultural Waste Management Conference, R. C. Loehr, ed, Ann Arbor Science Publisher, Ann Arbor, MI.
- [10] Martens, D.C. (1971). Availability of Plant Nutrients in flyash, *Compost Sci*: 12: pp15 – 19.
- [11] Page, A.L., Elsewi, A. A. and Stranghan, I. R. (1979). Physical and Chemical Properties of Fly Ash from Coal-fired Plants with Reference to Environmental Impacts. *Residue Rev*: 71: pp 83 – 120.
- [12] Adriano, D. C., Page, A. L., Elsewi, A. A., Chang, A. C., and Stranghan, I. R. (1980). Utilization and Disposal of Fly Ash and other Coal Residue in Terrestrial Ecosystems; a Review, *J. Environ. Qual*: 9: pp 333 – 334.
- [13] Day, P.R. (1965): Particle Fractionation and Particle Size Analysis. pp 454-467.
- [14] Bouyoucos, G.J. (1936): Direction for making mechanical analysis of soils by the hydrometer method. *Soil Science*, 3: 42
- [15] Anegebe, B. and Okuo, J.M. (2013): The Impacts of Quarry Factory on the Physico-Chemical properties of Soil and their Potential Health effects on the Surrounding Ecosystem. *Nigeria Journal of Applied Science* **31**: pp126-135.
- [16] Nelson, D.W. and Sommers, L.E. (1982). Total Carbon, Organic Carbon and Organic Matter. In: Page, A.L., Miller, R.H. and Keeney, D.R. (Eds) Methods of Soil Analysis. Part 2; American Society of Agronomy, Madison, Wisconsin: pp 539 – 579.
- [17] Black, G.R. (1965). Particle Density. Methods of Soil Analysis, Part 1. In: C.A. Black (ed) American Society of Agronomy Monograph, No. 9.
- [18] Walkley, A. and Black, I.A. (1934). An Examination of the Detjare Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid titration. *Soil Sci*. 37: pp 29 -36.
- [19] Bray, R.M. and Kurtz, L.T. (1947). Determination of Total Organic and Available Forms of Phosphorus in Soil. *Soil Sci*. 56: pp 39 – 45.
- [20] Vogel's, (2008): text book of quantitative chemical analysis. 6th Edition, Prentice Hall, England, pp 277.
- [21] Sparks, D.L., Page, A.L. and Helmke, P.A. (1996). Methods of Soil Analysis: Chemical Methods. Part 3. American Society of agronomy, Madison, Wisconsin, USA.
- [22] Tessier, A. Campbell, P.G.C. and Blsson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*. 52(1): pp 45-53.
- [23] Sanders, J.E. (1982). The Effect of pH Upon the Cu and Cupric ion Concentrations in Soil Solution. *J. Soil Sci*. 33: pp 679 – 689.
- [24] Igwe, J.C., Nnorom, I.C. and Gbaruko, B.C. (2005). Kinetics of Radionuclides and Heavy Metals Behavior in Soils: Implications for Plant Growth. *African J. of Biotechnology*, 4(13): pp 1541 – 1547.
- [25] Banjoko, A. and Sobulo, R. A. (1994). Particle Size in Distribution of Fe, Mn, Zn, Cu and B in some Nigerian Soils. *Nig Journal of Sci*. **34**: pp 60 - 163.
- [26] Hazelton, P. A and Murphy, B.W. (2007). Interpreting Soil Test Results: What do all the Numbers Mean? CSIRO Publishing, Collingwood.
- [27] Okiemen, F.E., Emwanta, D.O. and Odilayo, O.O. (2012). Stabilization of heavy Metals in CCA Contaminated Soil. *International Journal of Applied Environmental Sciences*. 7(2): pp 215-232.
- [28] Temminghoff, E.J.M., Van Der Zee, S.E.A.T.M. and De Haan, F.A.M. (1998). Effects of

Dissolved Organic Matter on Mobility of Cu in a Contaminated Sandy Soil. *European. J. Soil Sci.* 49 (4):617-628.

[30] Horsfall, M. (Jnr.), and Spiff, A. (2005): Speciation and bioavailability of heavy metals in sediment of Diobu River, Port Harcourt, Nigeria. *European Journal of Science Reserve.* 6(3):pp 20-26.

[31] Anegebe, B., Okuo, J.M., Ewekay, E.O and Ogbeifun, D.E. (2014). Fractionation of Lead-Acid Battery Soil amended with Biochar. *Bayero Journal of Pure and Applied Sciences.* 7(2): pp 36-43,

[32] Salbu, B., Kreling, T. and Oughton, D.H. (1998). Characterization of Radioactive Particles in the Environ. *Anal.* 123: pp 843 – 849.

[33] Kabala, C. and Singh, B. R. (2001). Fractionation and Mobility of Copper, Lead and Zinc in Soil Profile in the vicinity of a Copper Smelter, *J. Environ. Qual.* 30: pp 485 – 495.

[34] Ma, L.Q. and Rao, G.N. (1997). Effects of phosphate rock on sequential Chemical extraction of lead in contaminated soils. *J. Environ. Qual.* 26 (3):788-791.

[35] Ahumada, I. Mendoza, J. and Ascar, L. (1998). Sequential Extraction in Soils Irrigated with Waste Water. *Commun. Soil Sci. Plant Anal.* 30: pp 1057-1519.

[36] Lin, W. J. (2009). Ecological Degeneration and Heavy Metals Pollution in Zinc Smelting Areas. *Ecol. Environ. Sci.* 18: pp149-153.

[37] Maslin, P. and Maier, R. M. (2000) "Rhamnolipid-Enhanced Mineralization of Phenanthrene in Organic-Metal Co-Contaminated Soils," *Bioremediation Journal.* 4(4): pp 295–308.

[38] Saenz, M., Blasco, J. and Gomez-Parra, A. (2003): Speciation of heavy metals in sediments of three coastal ecosystems in the Gulf of Cadiz, southwest Iberian peninsula. *Environmental Toxicology and Chemistry.* 22(12): pp 33-39.

[39] Segarra, M.J.B., Prego, R., Wilson, M.J. Bacon, J. and Santos-Echeandia, J. S. (2008): Metal speciation in surface sediments of the Vigo Ria (N.W. Iberian Peninsula) *Science Marjor.* 72(1): pp119-12

