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ORIGINAL ARTICLE

THE ROLE OF SEWAGE SLUDGE APPLICATION ON THE HEAVY METALS CONCENTRATIONS OF SOIL OF AUTOMOBILES DUMPSITE

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ABSTRACT

Background: The physicochemical and levels of heavy metals of locations on automobile dumpsite located in Akure, Ondo State, Nigeria were investigated prior to the application of sewage sludge. **Objectives:** The effect of application of sewage sludge on the physicochemical parameters and heavy metals concentration was investigated to determine the suitability of the sewage sludge as amendment in contaminated soil reclamation. **Materials and Methods:** Physicochemical parameters such as pH, Organic Matter Content and Cation Exchange Capacity (CEC) were determined prior to application of amendment to soil, after which the distribution of heavy metals in various soil fragments were carried out on the amended and non-amended soil. **Results:** The mean values of pH, organic matter content and cation exchange capacity of soil of the two locations were 6.85, 12.45% and 16.65 Meq/100g respectively; the pH, organic matter and CEC increased with addition of sewage sludge to 7.4, 16.4% and 20.6 Meq/100g respectively. The mean concentrations (in mg/kg) of soil samples (1a and 2a) were 185, 170, 8.5, 127.5, 133.5, 75 and 1675 for Co, Cr, Pb, Zn, Cu, Ni and Fe respectively. The corresponding concentrations of heavy metals (in mg/kg) after the addition of amendment (1b and 2b) were 185.6, 171.5, 9.2, 128, 135.7, 78.25 and 1766.5 respectively. The concentration of water extractable heavy metals before and after amendment (top soils) ranged from (21.8 to 38.6); (16.1 to 15.1); (1.6 to 1.6); (26.2 to29.1); 36.4 to 38.4); (11.2 to 12.2); 48.2 to 48.9) for Co, Cr, Pb, Zn, Cu, Ni and Fe, and (22.0 to 38.2); (18.2 to 17.8); (1.8 to 1.7); (28.1 to 28.9); (36.2 to 38.4); (11.4 to 12.4) and (48.6 to 50.1) for bottom soil respectively. The heavy metals considered in this study were found in all extractive phases, with highest concentrations as bound to organic matter. **Conclusion:** The distribution of the heavy metals considered in this study at non-exchangeable phase of soil after application of amendment revealed that most of them may not be bio-available to plant and as a result a probable option for soil reclamation However, this strategy should be considered for field applications.

***Keywords**: Akure, physicochemical properties, heavy metals, sequential extraction, water extractable metal, soil contamination.*

1. INTRODUCTION

Like many cities among developing countries, Akure is a fast growing urban centre in Ondo state, Nigeria faced with environmental challenges such as improper disposal of refuse near residential areas and other public places within the town. In this specific location, it is very common to find large amounts of refuse dumpsite within the residential areas and along some minor and major road network. Most dumpsites are located on abandon plots of land, the cultivation of crop on this dumpsite may lead to physical and chemical interaction between the crop and the deposited waste materials which may due to degree of exposure [1, 2]. The presence of microorganisms and biochemical activities, liberates lots of enzymes in the soil, hence make soil a dynamic system. The use of fertilizers for agricultural purposes has deposited bio-solids on the soil, since the applications of fertilizers act as a source of nutrients for crop production owing to their high content of organic matter [3]. In the soil profile, the content is gradually decreasing by leaching. Some factors affect the behaviour of the elements in the soil, such as their sorption [4], soil pH which influences metal solubility [5]. According to soil parameters, heavy metals may enter the food chain in significantly elevated amounts [6, 7, 8, 9].

In the surroundings, heavy metals in high esteem are toxic and dangerous to most organisms and even to the society as a whole. Anthropogenic activities such as mining have continuously increased the levels of these metals in the environment such as soils, waters, sediments [10, 11]. In our entire atmosphere today, heavy metals are tremendously persistent, non-biodegradable and readily accumulate to toxic levels [12, 13, 14, 15]. Heavy metals at low concentrations are deadly because there is no good mechanism for their elimination from the body [16]. Heavy metals can accumulate to phytotoxic levels, especially in low pH soils, which reduces plant growth and enter the food chain when plants are consumed by animals [17]. In the environment, soil is the compartment which receives heavy metals coming from different sources and controls their movement to other compartments [10, 18, 19, 20].

Auto-mechanic workshop offer several repair services varying from simple and fast oil change to complex engine rebuilding. Organic chemicals such as, petrol, grease, solvent, diesel, lubricating oil, gas and bio-diesel can be discharged into the environment, such products can be highly toxic and hazardous to farm animal, man and soil [21]. Metals are essential components of the ecosystem, whose bioavailability depend mainly on geological and biological processes [22]. The total content of elements depends on chemical and physical properties of both the soil and the elements. Micronutrients such as Fe, Cu, Zn and Mn are essential metals for yield and plant growth. Plants may accumulates heavy metals existing in the soil, such as Ni, Cr, Cd and Pb which are not essential for plant growth but can cause serious problems to the environment. Lead is classified in the list of priority pollutants by the United States Environmental Protection Agency (USEPA) [23] with a carcinogenicity B (probable human carcinogen). Increase or decrease mobility in soils may be as a result of natural substances which may bind or sorbed with a particular heavy metals [24]. Pollution occurs if toxic heavy metals are taken up by plants or transported in drainage waters to associated water supplies; such water then enters human food chain through consumption or intake of such contaminated water or plant.

Recently, the application of biochar as soil amendment gained attention because of its potential soil conditioning properties and benefits to physico-chemical characteristics. Other benefits of biochar include: high organic matter content which encourages its ability to sequester heavy metals. As a result of these, it is important to identify other organic materials that could be applied as amendment in the immobilization of heavy metals on historically contaminated sites.

This study investigates the simple pot trials for the application of sewage sludge as an effective amendment in immobilization of heavy metals, with a view for the future application of the technique in soil reclamation studies.

2. MATERIALS AND METHODS

2.1 Study area and Soil sampling: Soil samples (contaminated sample) for this present study were collected from On yearugbulem automobile dumpsite along Owo / Ilesha express way, Akure South Local Government Area, Ondo state, Nigeria. The surface soil samples, after removing the overlying wastes, were collected randomly from the dump site in duplicate from two auto-mobile workshops dumpsites at 0-15 cm depth. Control sample was collected from uncultivated soil at the same depth and 100 m away from dump site. Sewage sludge was also collected from Ekiti State Water Corporation, Ado Ekiti, Ekiti state, Nigeria which was allowed to settle and the water was decanted. The sludge samples (amended sample) including other samples were air dried for about two weeks. After which they were sieved with 2 mm diameter sieve. The sieved samples were mixed in 4:1 ratio (i.e., 4 kg of contaminated sample and 1kg of amended sample). After the addition of amendment, the potted samples were watered with distilled water to approximate field capacity and were allowed to incubate for four months. The pots were placed in individual trays to prevent loss of water, amendments and other soil components. Composite samples were made out of them in a polyethylene bag as representative sample and taken to the laboratory for the analysis. The method described by Morera et al. (2005) was employed in the study [25].

2.2 Analyses of some physicochemical parameters of soil samples:

a) Soil pH: The pH meter was standardized using potassium hydrogen phthalate and ammonia buffer soil solution. 2 g of the soil sample was weighed into a 50mL beaker and 20mL of distilled water was added. The beaker was allowed to stand for 30 mins, during which it was stirred with a glass rod occasionally. The electrode of the pH meter was inserted and the pH value was recorded.

b) Organic matter content: The mass of empty clean and dried porcelain dish was determined after which 2 g of air dried soil was placed into the porcelain dish and mass of soil and dish recorded. The dish and the content were placed on a muffle furnace and the temperature was increased gradually up to about 400^o C and the sample was left in the furnace overnight. It was carefully removed with tongs and the organic matter content was determined by difference.

c) Cation Exchange Capacity: The cation exchange capacity (CEC) was determined by extracting the cations with 1 M ammonium acetate buffer at pH 7.0. 30 mL of 1M CH_3COONH_4 was added to 5 grams of soil. The suspension was shaken for 2 hours and then centrifuged (15 minutes, 6000 rpm). After centrifugation and filtration, the filtrate was transferred into a 100 mL volumentric flask and two other volumes of 30 mL ammonium acetate were added successfully after 30 minutes of agitation and centrifugation. The final filtrates were made-up to 100 mL with ammonium acetate solution.

d) Sequential Extraction: Sequential extraction procedure according to Tessier et al. (1979) was used to evaluate the fractionation of soil metals [26]. Sequential extractions were carried out in duplicate, using 1 g air-dried soil. Soil samples were placed in 50 mL polycarbonate centrifuge tubes, mixed in a stepwise fashion with various reagents, and the suspensions were equilibrated as described in Table 1. Following equilibration, the solution and solid phases were separated by centrifugation at 1225 g for 10 min. between all successive extractions; the solid residues were suspended in 5 ml of 0.1M NaCl, shaken by hand, and centrifuged to displace the extraction solution remaining from the previous step. The supernatant was added to the former extractant. This step was intended to reduce sample dispersion and to minimize the re-adsorption of the metal. The supernatants were filtered through a 0.45 µm membrane, and the solid residues were preserved for the subsequent extractions. The concentrations of Co, Cr, Pb, Zn, Cu, Ni and Fe in the various extracts were determined by Atomic Absorption Spectrophotometer (AAS, Perkin Elmer Model 306).

e) Determination of water Extractable fraction: Each sample was extracted with 50 cm^3 of distilled/deionized water. The mixture was shaken for 5 hours at 23° C and left to stand overnight. It was later filtered and the filtrate was analyzed with Atomic Absorption Spectrophotometer (AAS, Perkin Elmer Model 306).

f) Sample preparation and analysis of heavy metals: The digestion method recommended by Nwajei and Gagophein (2000) was used for the digestion of the raw soil sample and the cultured soil sample prior to instrumental analysis of the availability, compositions and concentrations of the heavy metals in them [27].
1 g of dried and homogenized soil was weighed into 150 mL conical flask, a mixture of HNO_3: $HClO_4$: HF in the ratio 3:1:3 was added. The mixture was placed on hot plate for 3 hours at 80° C. The digest was filtered into 100 mL standard flask and made to mark with distilled water. The procedure is repeated for all other soil samples. Metal concentrations in solution were determined by ASS (ASS, Perkin Elmer model 306).

Table 1: Table presents the sequential extraction procedure.

Fraction	Solution	Equilibrium conditions
Exchangeable	8 ml 1M $MgCl_2$ (pH 7)	1 h, room temperature
Carbonates	8 ml 1M NaOAc (pH 5)	5 h, room temperature
Fe and Mn oxides	20 ml 0.04M NH_2OH/HCl in 25% (v/v) HOAc	6 h, 96°C
Organic matter	3 ml 0.02M HNO_3 + 5 ml 30% H_2O_2 (pH 2)	3 h, 85°C
	5 ml 3.2M NH_4OAC in 20% (v/v HNO_3 + 7 ml water)	20 min, room temperature
Residual	HNO_3-HCl digestion	

3. RESULTS

3.1 Physicochemical parameters

Table 2 shows the results of physiochemical parameters such as pH, organic matter (%), and exchangeable cations (meq/100g), of soil samples collected from an automobile dumpsite before and after application of amendments.

Table 2: The table presents the results of physicochemical analysis of soil sample collected from automobile dumpsite

Sample	pH	Organic Matter (%)	CEC (meq/100g)
Top	6.8±0.02	12.1±0.01	16.5±0.03
Bottom	6.9±0.02	12.8±0.02	16.8±0.02
After amendments	7.4± 0.03	16.4±0.02	20.6±0.02
Mean for top and bottom	6.85	12.45	16.65

The pH of the soil samples analyzed increases from 6.85 to 7.4 and due to the application of amendment. The sub-soils are basically slightly acidic. Alkaline soils have a high saturation of base cations (K^+, Ca^{2+}, Mg^{2+} and Na^+). The organic matter of the top and bottom soil sample was almost the same. However, the organic matter increased after the addition of amendments from 12.1 - 16.4. Based on total soils examined, the cation exchange capacity (CEC) varied from 16.5 - 20.6 after sewage sludge was applied across all studied soils with decreasing order down the profiles at each sample location since the CEC is dependent upon the pH of the soil.

3.2 Heavy metals concentration

The results of heavy metals concentration in the soil sample before and after addition of amendments to soil of the automobile dumpsite is depicted in Table 3.

Table 3: The table presents the results of heavy metal concentrations in the soil sample before and after addition of amendments to soil of the automobile dumpsite

Location/Amendment	Co	Cr	Pb	Zn	Cu	Ni	Fe
1a	190.0	200.0	11.0	136.0	164.0	60.0	1380.0
2a	180.0	140.0	6.0	119.0	103.0	90.0	1970.0
1b	190.2	201.0	12.2	136.8	168.2	63.3	1487.0
2b	181.0	142.0	6.2	119.2	103.2	93.2	2046.2
C	0.1	0.4	0.2	2.5	0.2	40.0	71.0
Mean (x) (1a & 2a)	185.0	170.0	8.5	127.5	133.5	75.0	1675.0
Mean (y) (1b & 2b)	185.6	171.5	9.2	128.0	135.7	78.25	1766.5

a: is the top soil; **b**: is the bottom soil.

From the results of heavy metals in Table 3, the mean cobalt (Co) concentrations in the soil sample (185 mg/kg) analyzed increased after the addition of amendment (185.5 mg/kg) which could lead to iron deficiency in plant. The mean concentration of chromium (Cr) in the soil sample analyzed was observed to be 170 mg/kg and increased after the addition of amendment to the soil sample (171.5 mg/kg). The concentration of lead observed in the soil sample was (8.5 mg/kg) and after amendments, the concentration increased to 9.2 mg/kg. The concentration of zinc (Zn) in the soil samples increased from (127.5 to 128 mg/kg) after the addition of amendments whereas (2.5 mg/kg) at the control site. The concentrations of Zn observed in this study including the control (2.5 mg/kg) fell within the lower limit of (20 - 200 mg/kg). The concentration of copper (Cu) in the soil sample analyzed increased from (133.3 to 135.5 mg/kg after amendments. The concentrations of Cu recorded in this study including the control (0.2 mg/kg) fell within the lower limit of 10-40 mg/kg. The concentration of nickel (Ni) in the soil samples analyzed increased from (75.0 to 78.25 mg/kg) after amendment. The concentration of iron (Fe) concentration in the soil sample increased from (1675.0 to 1766.5 mg/kg) after amendment. The concentrations of Fe observed in this study including the control (71.0 mg/kg) fell below the lower limit of (10000-50000 mg/kg).

3.3 Geo-accumulation index

The results of geo-accumulation index of the soil sample before and after amendment were depicted in Table 4.

Table 4: The table presents the geo-accumulation index of the soil sample before and after amendment.

Sample	Co	Cr	Pb	Zn	Cu	Ni	Fe
1a	1	0	0	0	0	0	-
2a	1	0	0	0	0	0	-
1b	1	0	0	0	0	0	-
2b	1	0	0	0	0	0	-

The following classifications have been observed in various farm land, Igeo>5 = class 6 (very strong contamination intensity), Igeo> 4 - 5 = class 5 (strong to very strong contamination intensity), Igeo > 3 - 4 = class 4 (strong intensity), Igeo > 2 - 3 = class 3 (moderate to strong contamination intensity), Igeo > 1 - 2 = class 2 (moderate contamination intensity), Igeo > 0 -1 = class 1 (uncontaminated to moderate intensity) and Igeo < 0 = class 0 (practically uncontaminated). The geochemical index obtained for all the heavy metals recorded in the soil sample before and after addition of amendment were all the same.

3.4 Water Extractable heavy metals in soils

The concentration of water extractable heavy metals in the soil samples collected on locations at automobile dumpsite was depicted in Table 5.

Table 5: The table presents the concentration of water extractable heavy metals in the soil samples collected on locations at automobile dumpsite.

Sample/Heavy metals(mg/kg)	Co	Cr	Pb	Zn	Cu	Ni	Fe
1a	21.8	16.1	1.6	26.2	36.4	11.2	48.2
2a	38.6	15.1	1.6	29.1	38.4	12.2	48.9
1b	22.0	18.2	1.8	28.1	36.2	11.4	48.6
2b	38.2	17.8	1.7	28.9	38.4	12.4	50.1

Table 5 shows the concentration of water extractable heavy metals in the soil samples analyzed before and after addition of amendment. From the results, the cobalt concentration of the top soil increased from (21.8 to 38.6 mg/kg) and bottom sample increased from (22.0 to 38.2 mg/kg), cobalt is very beneficial to plant and the sewage sludge increased the bio-available cobalt concentration. From the results, cobalt concentration of the top soil increased from

(21.8 to 38.6 mg/kg) and bottom sample increased from (22.0 to 38.2 mg/kg) respectively. Cobalt is very beneficial to plant and the sewage sludge increased the bio-available cobalt concentration. However, reverse is the case with chromium, because the amendment applied decreased the concentration of chromium in the top soil (16.1 to 15.1 mg/kg) and bottom (18.2 to 17.8 mg/kg) respectively. The iron concentration of the soil sample increased from (48.2 to 48.9 mg/kg) for the top soil, after the addition of amendment a noticeable increment was also observed in the bottom soil sample after the addition of amendment.

3.5 Distribution of heavy metals in contaminated soil

The results of sequential extraction of heavy metals from soil collected from the contaminated site are depicted in Table 6.

Table 6: The table presents the results of sequential extraction of heavy metals in amended soil sample

Sample/Heavy metals (mg/kg)	Co	Cr	Pb	Zn	Cu	Ni	Fe
Exchangeable	23.0	20.2	1.8	28.2	35.6	12.8	46.7
Bound to carbonate	56.2	72.8	4.2	42.7	48.7	15.6	50.62
Bound to Fe and Mn oxide	11.6	9.8	0.8	2.1	2.8	0.8	56.8
Bound to organic matter	65.8	86.6	5.6	58.2	52.1	22.1	687.8
Residual	28.2	16.2	1.2	12.5	17.2	1.8	382.6

The results revealed from the results that all the heavy metals considered in this study were found in appreciable levels in all extractive phases of soil. The concentrations of heavy metals (mg/kg) in exchangeable phase of soil are as follows: Co (23.0), Cr (20.2), Pb (1.8), Zn (28.2), Cu (35.6) and Ni (12.8), all in mg/kg. These results were observed to be closer to the results of water extractable heavy metals (Table 5).

4. DISCUSSION

Soil pH naturally affects plant nutrients availability by controlling the chemical forms of the nutrients [28]. However, most plant thrives in pH range of 5.5 and 7.0. Nevertheless, many plants have adapted to flourish at pH values outside this range [29]. Also according to [30] Nyle and Ray (2005), it was established that micronutrient cations in close proximity to neutral pH generally results to be soluble enough to satisfy plant needs without becoming soluble enough to be toxic. Both micronutrients and macronutrient are necessitating by plants, however there accessibility are affected by soil pH [31].

Soil organic matter exerts numerous positives effects on soil physical and chemical properties, as well as the soil's competence to provide authoritarian ecosystem services [32] meanwhile, Brady and Weil (1999) summarizes that the presence of soil organic matters (SOM) as being crucial for soil function and good soil quality [33]. Soil organic matter increases soil fertility by providing cation exchange sites and acting as reserve for plant nutrients especially in the case of nitrogen (N), phosphorous (P), and sulphur (S), along with micronutrients which are slowly released upon soil organic matter content and its fertility.

However, organic matter in soil increases through an increase in available negative charges. As a result of this, organic matters build up positively impacts in order to increase soil fertility. Furthermore, it was observed that the organic matters in the sewage sludge were responsible for the change in pH and CEC respectively [34]. According to Casado-Vela *et al*. (2007) and Chang *et al.* (1981), sewage sludge from treatment of municipal waste water (MWW) is branded by elevated contents of organic matter, N, P, K, Ca and Mg and other toxic compounds [3-35]. All these factors are responsible for the change in the pH, organic matter content and cation exchange capacity (CEC) of the soil sample analyzed in this study area.

According to Boisson *et al*. (1999), the most common heavy metals found at contaminated sites in order of abundance are Pb, Cr, As, Zn, Cd, Cu and Hg [36]. These metals are essential since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnifications in the food chain [37]. Whenever these toxic heavy metals were found in the soil, they are wrapped up by initial fast reactions within some minutes or a couple of an hours, followed by slow absorption reactions which usually takes some days or a year and are therefore redistributed into different chemical forms with vary bioavailability, mobility and toxicity [38].

Cobalt can produce its own toxicity symptoms which includes loss of leaves from a plant and pale colour. The high values of Cr observed could be as a result of the continuous burning or incineration of municipal solid waste of various compositions such as household batteries, electric lighting or bulbs, fluorescent lamps, pigments and paints residues, thermometers and other medical wastes from hospitals or health centres and film pack batteries [39]. Bishnoi *et al*. (1993) reported that chromium affects seed germination, plant growth, photosynthesis and the uptake of a variety of nutrients [40].

The trace Pb content of the soils at the these locations might probably be due to automobile emissions (the dumpsite was located close to a busy road) coupled with the complex nature of the municipal solid waste which contains Pb containing materials such as dry and wet cells [41]. High levels of Pb have been found to cause brain tumour, liver and kidney damage in children and nerve damage in adults and also decrease life expectancy by reducing average age by about 9-10 years [42, 43]. Ionic lead, Pb^{2+}, lead oxides and hydroxides as well as lead-metal oxy-anion complexes are the general forms of lead that are found in the soil, ground water, and surface water. Holmgren et al. (1997) also reported that high lead concentration is most likely found in leafy vegetables (e.g. carrot) [44]. Generally, at concentration less than (30 mg/kg), the farm produce is considered safe meanwhile; any level above this range there will be risk of lead poisoning through the food chain.

Through water percolation zinc can dissolved and sink to contaminate groundwater. Plants often have a zinc uptake that their system cannot handle, due to accumulation of zinc in soils which could later interrupt the properties of soil negatively and influence the activities of microorganism and earthworms thus retarding the breakdown of organic matter.

Copper and Zinc are two important essential element for plants microorganism, animals and humans. The high amount of Cu in soil samples could be due to materials such as waste from demolished buildings and construction (which contains cement), tire treads and lubricating oil [45, 46]. Solubility of Cu increased at pH 5.5, which is rather close to the ideal farmland pH of 6.0 - 6.5.

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. At high concentration, nickel usually affect soil microorganism but develop resistance after a while. Reddy *et al.* (2004) reported that nickel is not known to accumulate in plant or animals and has not been found to biomagnifies up the food chain [47].
It was observed in the study that Fe is the most predominant factor in all the sample analysed in the soil. The role of iron in plants is to help plant produce chlorophyll. Iron is also responsible for the green pigment formed by plants. It also helps plant to get oxygen [48].

The assessment of geo-accumulation index presented in Table 4 will assist in determining the degree of pollution accumulated in the soil (refuse dump site) by heavy metals [49, 50, 51]. From Table 4, cobalt geochemical index is 1for all the samples and it might be concluded that cobalt concentration in the soil sample was as a result of human activities. However, Cr, Pb, Zn, Cu and Ni geo-accumulation were observed to be 0. The value indicates that all the heavy metals presence in the soil sample (i.e. Cr, Pb, Zn, Cu and Ni) is not as a result of human activities.

However, bioavailability of iron is essential from plant growth meaning that the addition of sewage sludge is beneficial for plant since it enhances the bio-available iron in the soil. According to Schuser (2008), iron deficiency in plant leads to leaves turning yellow, fruit quality and quantity yield of fruit [52]. However, the value obtained for exchangeable iron in Table 6 is higher than that of Table 5. Copper and iron were more bio-available both in Table 5 and Table 6, however the values obtained from Table 6 for copper (35.6 mg/kg) and iron (46.7 mg/kg) are lower than that of Table 5 with concentration range of (48.2 to 50.1 mg/kg) and (36.2 to 38.4 mg/kg) for copper. Lead and nickel concentration of the soil sample before and after addition of amendment did not change with greater variation. However, lead availability in the soil sample is very ranging from (1.6 to 1.8mg/kg) and that of nickel range from (11.2 to 12.4mg/kg). These two heavy metals were the least available both in Table 5 and 6. Zinc is an essential metals and the zinc concentration of sample soil increased with the addition of amendment with values ranging from (26.2mg/kg to 29.1mg/kg).

Apparently, the essential nutrients for plant in the soil sample were enhanced with the addition of sewage sludge while those of Pb and Cr were reduced to some extent.
Heavy metals are more soluble in exchangeable phase of soil when compared to other phases of soil *viz* a *viz;* carbonate bound, Fe and Mn bound, organic matter bound. Infact, metals in residual fraction of soil are less soluble and hence low bioavailability. Reports have indicated that mobility and bioavailability of heavy metals depends on how soluble these metals are in soil fractions [11, 53].

In all, iron was found to be the highest in all phases of soil, with concentration of 687.8 mg/kg as bound to organic matter. The concentration of heavy metals in these phases of soil vary from bound to organic matter > residual > bound to Fe and Mn > bound to carbonates > exchangeable. Iron has been reported in abundance in Nigerian soil [54, 55]; though iron is an essential metal, its availability in high dosage can impart negatively on the food chain [56]. The distribution of these metals in various phases of soil can best be explained considering the scheme below:

a) **bio-available Species:-**This is the name corresponding to exchangeable and bond to carbonates species, as they reveal a mobility relative to the environment and are potentially available for plants.

Results show that the amounts of Co, Cr, Zn, Cu, Ni and Fe, in bio-available form are very high, namely above 20 % in soil. All the samples are in bio-available form (ranges from 4 and 73%), and are mainly bound to carbonates.

b) **species bound to Fe-Mn oxides:-** Rationally, Fe and Mn occur mainly in the oxide fraction. In the soil Fe (60 %) and Mn (40%) are main contributors. The fraction of Co, Cr, Pb, Zn, Cu and Ni associated with oxides is very less in the soil especially in the case of Pb, Ni, Zn and Cu.

c) **species bound to organic matter:-** High amounts of Fe (up to 75 %) and also Cr, Co, Zn and Cu are bound to the organic matter.

d) **species in residual fraction:-** The proportion of Fe (above 50 %) in the residual form of is much higher than the other elements. The order of element follows Fe>Co>Cu> Cr>Zn. The weight of Pb and Ni in this fraction is relatively low. In summary, for all elements, an increase of the fraction bound to Fe/Mn oxides occurs with an increase of Fe and Mn content in soil. However, the exchangeable concentration of iron was still the highest with (46.17 mg/kg), the exchangeable concentration of cobalt (23.0 mg/kg) and chromium (20.2 mg/kg) were very close, however chromium was bounded to more organic matter (86.8 mg/kg) compared to cobalt (65.8 mg/kg), to carbonate (72.8 mg/kg) compared to cobalt (56.2 mg/kg), to residual (16.2 mg/kg) compared to cobalt (28.2 mg/kg), however, the concentration of cobalt bounded to Fe and Mn oxide was higher than that of chromium with values of (11.6 and 9.8 mg/kg) respectively. This result revealed that cobalt will be readily available for exchange with the plant than chromium. Also, from Table 6, high concentration of copper was bound to Fe and Mn oxide and organic matter with concentrations (52.1 and 48.4mg/kg) respectively, thereby, reducing the bio-available copper in the soil.

Walter et al. (1996) reported that the organic matter in soil affect copper chemistry in the soil leading to complexation of more than 97% of the copper in the soil. Indeed, complexing is of great consequence in maintaining enough Cu in solution for plant utilization [57, 58]. Although, low concentration of copper in soil can also leads to stunted growth in plant, small grains and corn leaves appear olive or yellowish green in colour and often the leaves fail to unroll as they emerge. Consequently from Table 6, the bio-available zinc was very high, however, high concentration of zinc was bounded to carbonate (42.7 mg/kg), organic matter (58.2 mg/kg). Zinc is an important tool for proper plant growth, though this study has shown that zinc uptakes declines as pH increases and high level of phosphorous intensify zinc deficiency in a number of crops.

Also, Ni was recorded to be bio-available with concentration of 12.8 mg/kg since nickel concentration in the soil sample was only higher than that of Pb (1.8mg/kg). The overall lead concentration was very low. However, this is very beneficial, since Pb has environmental implications on human health and physical activities. In the study, it was found that all the heavy metals analysed in the soil sample after amendment revealed that they are mostly bounded to organic matter.

5. CONCLUSION AND RECOMMENDATIONS

Soil in the dumpsite was found to be higher in the level of heavy metals than the background samples. The investigation revealed that nearby farmland are at less risk of pollution of their farm products with accumulation of these metals. A significant proportion of the heavy metals are present in residual phase of soil. These findings also reinforce the need for increased adoption of standardized sequential extraction procedures. Also, environmental impact assessment of this site is therefore necessary regularly in order to prevent the people living around the vicinity and general public at large from being exposed to unnecessary hazards through environmental pollution. The government of the state should embark on the utilization of this waste dumpsite for bio-fuel production. Consequently, a periodical evaluation of the soil status is also necessary in this area.

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