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Fractions of heavy metals in soils of selected dumpsites from Osun State, Nigeria.

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Abstract

Research has shown that the fractions in which heavy metals exist in the soil are the prime determinant of their availability and uptake in plants. Though comprehensive studies have been conducted on heavy metal fractions in soils, there is a dearth of information on the fractions of heavy metals of study locations. Therefore, this research investigated the concentrations of Pb, Cd, Cr and Ni in selected dumpsites soils located at Osogbo, Ife, Ilesha and Ido-Osun towns of Osun State and the fractions in which the metals exist in the soils. Each dumpsite was sampled in a completely randomized block design with 3 replicates and soil samples collected at a depth of 0-30cm. The soils were subjected to routine analysis and analyzed for total Pb, Cd, Cr and Ni concentrations. The soils heavy metal fractions were also analyzed by sequential extraction procedure (SEP), and their concentrations were read using atomic absorption spectrometer (AAS). The results revealed that the soil pH ranged from 6.73-8.23, Organic Carbon ranged from 22.99-43.05 (g/kg), the soils are sandy loam in texture except for Ife dumpsite that is sandy clay loam. The heavy metal concentrations (mg/kg) of the dumpsite soils ranged from 95.5-177.34 for Pb, 1.18-15.16 for Cd, 24.17-55.14 for Cr and 37.10-42.39 for Ni. There were significant differences ($p<0.05$) in concentrations of Pb, Cd and Cr among the dumpsites except for N. Pb and Cd concentrations in the soil were above the FAO/WHO permissible levels. However, Cr and Ni were below the levels. Most considerable proportions of the heavy metals were found in the residual fractions of the soil followed by the reducible fraction while exchangeable fractions had the least concentrations of the metals. The order of concentrations of most of the heavy metals in the soil fractions was: residual > reducible > oxidizable > exchangeable fraction.

Keywords: Heavy metals, Fractions, Dumpsites, Osun State.

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1.0 Introduction

Influence of heavy metals on the physiological functions of plants and animals has gained broad research across different disciplines. The joint section of the world health organization and the food and agricultural organization has reviewed what is now known as the permissible levels of heavy metals in soils, plants water and animals. However, there is still widespread of ongoing research aimed at investigating the concentrations of heavy metals in both agronomic and non-agronomic materials and mediums as these will serve as the basis for policymakers to formulate policies that will protect the general populace from the harmful effects of heavy metals.

Heavy metals are metals with a high specific gravity of 5 g/cm^3 or more. Notable metals of agronomic importance within this range include; copper, mercury, lead, cadmium, chromium, nickel etc. The pollution of soils with heavy metal is of global concern as a result of its potential impact on the environment and to human health (Emurotu and Onianwa, 2017). Soils can biodegrade almost all organic compounds found in waste, converting them into harmless substances. However, since inorganic products such as heavy metals are non-biodegradable, they persist and accumulate in the soil (Nkop et al., 2016).

Dumpsite also known as landfill is a disposal site where solid waste, such as paper, glass and metal is buried between layers of dirt and other materials in such a way as to reduce contamination of the surrounding land. Classical unlined sanitary landfills and open dumps are well known to release large amounts of hazardous and otherwise deleterious chemicals to nearby groundwater, surface water and soil also to the air, via leachate and landfill gas (Adebara *et al.,* 2016). Dumpsites usually contain paper, food waste, metal scraps, glass, ceramics, and ashes. The oxidation processes release the heavy metals contained in them to the soil of the waste dumpsite, thereby contaminating the soil (Ukpong *et al.,* 2013).

Once the soil is contaminated, it will not only affect the rapid growth of crops and quality yield of agricultural products but also pose a threat to human health via the food chain (Emurotu and Onianwa, 2017).

Exposure to heavy metals through the soil-crop pathway and other sources can cause blood, bone disorders, kidney damage, decreased mental capacity and neurological damage (Nkop et al., 2016).

However, the mobility and bioavailability of heavy metal depend absolutely on their speciation or chemical forms. These forms are determined by sequential extraction technique which gives vivid information about a metal affinity to the soil components together with the strength to which they are bound to the soil matrix (Thomas, 2015). The theory behind SEP is that most mobile metals are removed in the first fraction and continue in order of decreasing mobility. All SEPs facilitate fractionation. Tessier et al. (1979) named these fractions exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound, and residual. These are often referred to in the literature as exchangeable, reducible, oxidizable and residual fractions of heavy metals, respectively Zimmerman and Weindorf, 2010).

According to Nkop et al., (2016), investigation of heavy metals is essential since slight changes in their concentration above the acceptable levels, whether due to natural or anthropogenic factors, can result in severe environmental and subsequent health problems. It has been observed that some dumpsites in Osun state are used as the preferred location for crop production, mostly fruits and vegetables. This study investigated the concentrations of Pb, Cd, Cr and Ni in the dumpsite soils and also the fractions in which the metals exist in the soils.

2.0. Materials and Methods

2.1. Description of Study Locations

The research was conducted at Osun State, Nigeria and located within the coordinates of $7^0$30'N $4^0$30'E. It comprises of about 3,416,959 people according to 2006 national census. Major semi cities in terms of pollution density, industry and commerce within the state include Osogbo, Ilesha, Ife and Ede. The study locations were strategically selected to cover these four towns as the dumpsites selected were the primary dumping site for the towns. Hence the study was carried out in four dumpsites located in Osun State with the following coordinates; Osogbo: Lat. 7° 47′ 38.32″ N, Long. 4° 29′ 25.42″ E, Ile-Ife: Lat. 7° 29′ 50.30″ N Long. N4° 36′ 11.74″ E, Ilesha: Lat. 7° 37′ 0.15″ N and Long. 4° 44′ 59.616″ E, and Ido-Osun: Lat 7°46′ 27.15″ N and long. 4° 26′ 32.31″ E.

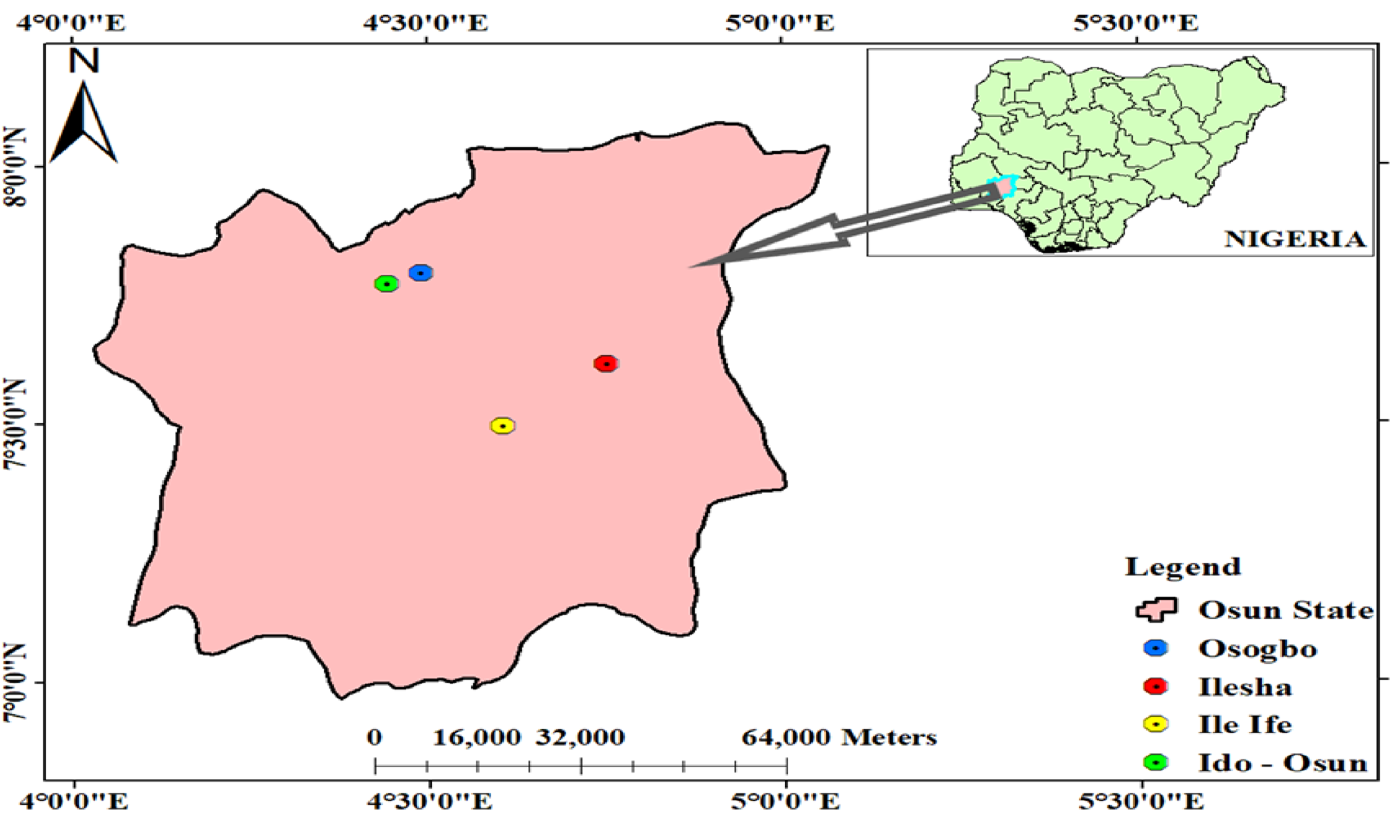

Figure 2.1: Map of Osun State Showing the Study Locations (Google Earth, 2019).

2.2. Site Sampling and Sample Collection

A sampling area which gave good coverage of each of the dumpsites sampled was used for sample collection. The field sampled in each dumpsite was demarcated into three equal partitions (Khan *et al*., 2008). Three (3) soil samples were randomly collected at a depth of 0-30cm within each plot and bulked to give a composite sample. Hence, one bulked sample was obtained from each plot, giving a total of three (3) soil samples from each dumpsite and 12 soil samples from the 4 dumpsites used. Soil samples were collected with a clean auger and shovel, bagged using a nylon bag and labelled appropriately. The same procedure was also used to obtain a control soil sample from a few kilometres from the dumpsites and in a location with no sign or history of refuse dumps. The samples were immediately taken to the laboratory for further preparations and analysis. This was as described by (Khan *et al*., 2008).

2.3 Sample Handling and Preparation

The soil samples were air-dried in a clean environment, all metallic and bottle particles were removed, and the soil samples were crushed and sieved with 2 mm mesh and stored in a labelled polythene bags for future use.

2.4. Routine Analysis of Soil Sample

The pH of soil samples was measured at a 1:2 soil-water ratio using pH electrode conductivity meters as described by Eze and Ekanem, (2014). The soil organic carbon was determined by Walkley and Black oxidation method (Walkley and Black, 1934). The total nitrogen content of the soil was determined by modified Kjeldahl digestion and distillation method using FAO (2008) soil bulletin guidelines. The available soil phosphorus was also determined by Bray P method following FAO (2008) guidelines. Exchangeable K, Na, Mg and Ca where determined by the batch method as described by Amacher *et al.* (2003) while the soil particle sizes were analyzed by hydrometer method also as described by FAO (2008).

2.5. Digestion of soil sample and heavy metal analysis

2.0g of prepared soil sample was digested with 15.0 ml nitric acid, 20.0 ml perchloric acid and 15.0 ml hydrofluoric acid. The mixture was heated on a hot plate for 3hours and allowed to cool. The digest was then filtered using Whatman filter paper into a 100.0 ml volumetric flask and made up to mark with distilled water. This method was as described by Nkop *et al*. (2016). The digested samples were determined for Pb, Cd, Cr and Ni concentrations using atomic absorption spectrometer.

2.6. Sequential Extraction of Heavy Metals in the Soil

The BCR 4 step procedure was followed for the sequential extraction of heavy metals from the soil samples as described below;

i. *Exchangeable fraction*. Pb, Cd, Cr and Ni in about 2.0g of each sample were extracted at room temperature with 8 mL of 1M magnesium chloride with continuous agitation for 1 hour at pH 7.0.
ii. *Reducible fraction:* Residue from (i) was extracted with 10 mL of 0.1 M hydroxylamine hydrochloride (NH2OH.HCl) in 25 % (v/v)) HOAc agitated for 1h (bound to Fe-Mn Oxide, C)
iii. *Oxidizable:* To the residue from (ii) were added 3 mL of 0.02 M nitric acid (HNO3) and 5 mL at pH 2, heated at 85 ºC for 1 h with continuous agitation for 5 h. and centrifuged.
iv. *Residual fraction:* Residue from (iii) was digested with 8 mL of aqua regia (HCl and HNO3, 3:1 v/v) and heated to dryness respectively. About 30 mL of distilled water was added to the residue, warmed and allowed to cool and filtered with ashless Whatman 40 filter paper. The resulting solutions were analyzed with flame atomic absorption spectrophotometry, Buck 304 u/c with air acetylene flame for determination of Pb and Cd, Cr and Ni. This method is as described by Omotunde *et al.* (2011)

3.0. Results

3.1. Physical and Chemical Properties of Soils of the Four Dumpsites in Osun State Studied.

Table 4.1 shows the chemical and physical properties of dumpsite soils in Osun state studied. The pH of the four dumpsite soils varied from slightly acidic to slightly alkaline and ranged from 6.7 at the Ido-Osun dumpsite to 8.2 for Ife dumpsite. The organic carbon content of the soils was high and ranged from 30.71 g/kg found at Osogbo dumpsite to 43.05 g/kg found for Ife dumpsite. The CEC of the study location soils ranged from 39.26 cmol/kg at Ido-Osun dumpsite to 77.87 cmol/kg for Ife dumpsite. The soil texture showed that soils of Osogbo, Ilesha and Ido-Osun dumpsite are sandy loam textured while the soil of Ife dumpsite is sandy clay loam. The total nitrogen of the dumpsite soils studied as shown in Table 4.1 ranged from 1.20% at Ilesha dumpsite to 7.68% at Osogbo dumpsite while Ife and Ido-Osun dumpsites had a total nitrogen concentration of 1.34% and 3.14% respectively. The calcium (Ca), Magnesium (Mg) and potassium (K) concentration of the dumpsite soils, as shown in the tables were also relatively high.

3.2. Mean Value of Total Heavy Metals (Pb, Cd, Cr and Ni) from the Four Dumpsites and Control Sites in Osun State.

The total concentration of lead (Pb), Chromium (Cr), Cadmium (Cd) and Nickel (Ni) in the soils of the four dumpsites studied and also the control sites are as shown in table 4.2. The mean concentration of lead in the dumpsites ranged from 177.30mg/kg at Ilesha dumpsite to 95.90mg/kg at Ido-Osun dumpsite. The total concentration of cadmium ranged from 15.20mg/kg found at Ife dumpsite to 1.20mg/kg at Ido-Osun dumpsite. The mean concentration of chromium in the dumpsites soils ranged from 55.10mg/kg at Ilesha dumpsite to 23.10mg/kg at Ife dumpsite, while the total concentration of nickel in the dumpsites ranged from 42.40mg/kg at Ilesha dumpsite to

Table 3.1: Physical and Chemical Properties of Soils of the Four Dumpsites in Osun State.

	Locations			
Soil Properties	**OSOGBO**	**ILESHA**	**IDO-OSUN**	**IFE**
pH (H_2O)	7.87	7.67	6.73	8.23
CEC (cmol/kg)	41.47	56.46	39.26	77.87
OC (g/kg)	30.71	32.06	22.99	43.05
N (g/kg)	17.68	0.21	0.14	0.34
Ca (cmol/kg)	35.60	44.84	28.32	70.24
Mg (cmol/kg)	3.48	5.13	15.56	5.74
K (cmol/kg)	5.71	5.03	1.74	1.98
Available P (mg/kg)	178.50	168.98	188.95	172.63
Particle Size Distribution (g/kg)				
Sand	675	663	652	613
Clay	117	121	141	285
Silt	208	216	207	102
TC	SL	SL	SL	SCL

OC = Organic Carbon, TC = Textural Class, SL = Sandy Loam, SCL = Sandy Clay Loam

Table 3.2: Mean Value of Total Heavy Metals (Pb, Cd, Cr and Ni) Concentrations from the Four Dumpsites and Control Sites in Osun State Studied

	Concentrations (mg/kg)			
Locations	**Pb**	**Cd**	**Cr**	**Ni**
Osogbo	121.90	7.60	41.80	37.10
OC	3.65	1.61	0.67	5.63
Ilesha	177.30	6.90	55.10	42.40
ILC	3.98	0.84	0.55	0.56
Ife	149.10	15.20	23.10	39.80
IFC	7.34	8.79	0.39	2.38
Ido-Osun	95.90	1.20	24.20	38.90
IC	4.62	0.47	0.62	1.59

Pb = Lead, Cd = Cadmium, Cr = Chromium, Ni = Nickel; OC = Osogbo control site, ILC= Ilesha control site, IFC = Ife control site, IC = Ido-Osun control site.

Table 3.3: Concentration of Pb, Cd, Cr and Ni in Exchangeable and Oxidizable Fractions of the Dumpsites Soils.

Locations	**Heavy metal concentrations (mg/kg) Exchangeable fractions**			
	Pb	Cd	Cr	Ni
OSOGBO	1.67	0.98	1.33	3.22
IFE	0.33	0.23	2.67	3.79
EGBEDORE	2.77	0.92	0.88	12.34
ILESHA	2.33	1.17	2.97	2.61
CONTROL	0.67	0.03	0.03	ND
	Oxidizable fractions			
OSOGBO	33.55	0.34	12.67	15.33
IFE	53.69	2.97	16.39	18.97
EGBEDORE	ND	0.02	ND	0.65
ILESHA	16.89	1.95	21.67	12.33
CONTROL	0.01	0.04	ND	0.07

ND = Not detected, Pb = Lead, Cd = Cadmium, Cr = Chromium, Ni = Nickel

Table 3.4: Concentration of Pb, Cd, Cr and Ni in Reducible and Residual Fractions of the Dumpsites Soils Studied

Locations	**Concentrations (mg/kg) Reducible fractions**			
	Pb	Cd	Cr	Ni
OSOGBO	3.67	0.88	9.33	7.13
IFE	7.22	0.77	3.65	3.44
IDO-OSUN	2.33	0.31	0.33	17.22
ILESHA	13.87	2.77	12.33	12.58
CONTROL	0.12	0.12	ND	0.05
	Residual fractions			
	Pb	Cd	Cr	Ni
OSOGBO	61.72	3.27	12.94	19.45
IFE	56.7	3.98	13.33	15.72
IDO-OSUN	36.58	0.67	2.43	14.62
ILESHA	66.76	3.25	13.71	10.34
CONTROL	0.27	0.08	ND	ND

ND = Not detected, Pb = Lead, Cd = Cadmium, Cr = Chromium, Ni = Nickel

Table 3.5: Percentage of the Total Heavy Metals in Exchangeable, Oxidizable, Reducible and Residual Fractions of the Dumpsite

	Exchangeable Fraction (%)				Reducible fraction (%)			
Locations	**Pb**	**Cd**	**Cr**	**Ni**	**Pb**	**Cd**	**Cr**	**Ni**
OSOGBO	1.37	12.86	3.18	8.67	3.03	11.54	22.33	19.21
IFE	0.22	1.52	11.57	9.51	4.84	5.07	15.82	8.63
IDO-OSUN	2.81	1.69	3.64	31.73	2.43	26.27	1.37	44.23
ILESHA	1.32	17.03	5.37	6.15	7.82	40.20	22.36	29.67
	Oxidizable fraction (%)				Residual fraction (%)			
Locations	Pb	Cd	Cr	Ni	Pb	Cd	Cr	Ni
OSOGBO	12.03	4.46	30.32	14.37	50.92	42.91	30.97	52.40
IFE	23.02	19.59	27.69	47.62	38.02	26.25	57.78	39.45
IDO-OSUN	13.31	34.4	ND	14.14	38.12	56.77	10.05	37.60
ILESHA	9.52	28.3	39.29	29.08	37.65	47.16	24.86	25.95

37.10mg/kg at Osogbo dumpsite. The concentration of the heavy metals in most of the four dumpsites studied is in the order: Pb > Cr > Ni > Cd.

3.3. Concentration of Pb, Cd, Cr and Ni in Exchangeable, Oxidizable, Reducible and Residual Fractions of the Dumpsites Soils in Osun state.

Table 3.3 shows the concentration of lead (Pb), cadmium (Cd) Chromium (Cr) and Nickel (Ni) in the exchangeable and oxidizable fractions of the dumpsites soils located in Osogbo, Ife, Ilesha and Ido-Osun towns in Osun state Nigeria.

In the exchangeable fractions, the mean concentration of Pb ranged from 0.33mg/kg in Ife dumpsite to 2.77mg/kg in Ido-Osun dumpsite soil. The mean concentrations of cadmium in the dumpsites studied ranged from 0.23mg/kg in Ife dumpsite to 1.17mg/kg in Ilesha dump sites. Chromium mean concentrations ranged from 0.88mg/kg in Ido-Osun dumpsite to 2.97mg/kg in Ilesha dumpsite while the concentration of nickel in the exchangeable fractions of the dumpsites soils ranged from 12.34mg/kg in Ido-Osun dumpsite to 2.61mg/kg in Ilesha dumpsite.

In the oxidizable fraction of the dumpsite soils, the mean concentration of Pb, Cd, Cr and Ni as found in Osogbo, Ife, Ilesha and Ido-Osun dumpsites studied were as shown in table 4.10. The concentration of Pb ranged from 53.69mg/kg in Ife dumpsite to 0.00mg/kg in Ido-Osun dumpsite, where no value was detected in the oxidizable fraction. Cd concentration in this fraction ranged from 2.97mg/kg in Ife dumpsite to 0.02mg/kg found in Ido-Osun dumpsite. Chromium concentration in the oxidizable fraction of the soil ranged from 2.43mg/kg in Ido-Osun to 13.71mg/kg in Ilesha dumpsite, while Nickel concentration in this fraction ranged from 19.45mg/kg to 10.34mg/kg in Ilesha dumpsite.

The concentrations of Pb, Cd, Cr and Ni in the reducible and residual fractions of the soils in Osogbo, Ife, Ido-Osun and Ilesha dumpsites studied were as shown in table 3.4. Lead (Pb) concentrations in the reducible fraction ranged from 2.33mg/kg in Ido-Osun dumpsite to 13.87mg/kg in Ilesha dumpsite. In the residual fraction, Pb concentration ranged from 36.58mg/kg in Ido-Osun dumpsite to 66.76mg/kg in Ilesha dumpsite soil. For cadmium, the range in a reducible fraction of the soil was 0.31mg/kg in Ido-Osun to 2.77mg/kg in Ilesha, and the range in the residual fraction is 0.67mg/kg in Ido-Osun to 3.98mg/kg in Osogbo dumpsite soil. Chromium concentration in the reducible fraction of the soil ranged from 0.33mg/kg in Ido-Osun dumpsite to 12.33mg/kg in Ilesha dumpsites while the concentration of the metal in the residual fraction of the soil ranged from 2.43mg/kg in Ido-Osun to 13.71mg/kg in Ilesha dumpsites. For nickel, the highest concentration in the reducible fraction of all the dumpsites studied was 17.22mg/kg in Ido-Osun dumpsite while the least concentration was 3.44mg/kg in Ife dumpsite soil. However, relatively low concentration of nickel ranging from 10.34mg/kg to 19.45mg/kg was found in Ilesha and Osogbo dumpsites, respectively.

3.4. Percentage of The Total Heavy Metals in Exchangeable, Oxidizable, Reducible and Residual Fractions of the Dumpsite Soils Studied.

The percentage of the total lead (Pb), cadmium (Cd), Chromium (Cr) and nickel (Ni) in the exchangeable, oxidizable, reducible and residual fractions of the soil are as shown in table 3.5.

The percentage concentration of lead for all the fractions ranged from 37-50.92%, 9.52-23.02%, 2.43-7.82% and 0.22-2.81% is the percentage of the total soil Pb contributed by the residual, oxidizable, reducible and exchangeable fractions of the soils respectively. While, Percentages of cadmium contained in the four fractions are within the range of 26.25-56.77%, 5.07-40.20%, 4.46-34.4%, and 1.52-17.03% in the residual, reducible, oxidizable and exchangeable fractions of the dumpsite soils respectively.

The range of percentage concentrations of chromium in the fractions were 10.05-57.78%, 0.00-39.29%, 1.37-22.36% and 3.18-11.57% for residual, reducible, oxidizable and exchangeable fractions of the dumpsite soils respectively. However, percentage of the soil Ni in these fractions ranged from 25.95-52.40%, 8.63-44.23%, 14.14-29.08% and 6.15-31.73% in the residual, reducible, oxidizable and exchangeable fractions of the dumpsite soils respectively.

Hence, the largest proportions of the heavy metals were found in the residual fractions of the soil while the least concentrations of the metals were in the exchangeable fractions.

4.0. Discussions

The chemical and physical properties of the four dumpsite soils in Osogbo, Ife, Ilesha and Ido-Osun towns in Osun state, Nigeria studied as shown in table 3.1 reveals that the pH of the four dumpsite soils varied from slightly acidic to alkaline. The lowest pH of 6.73, which is slightly acidic, was found at the Ido-Osun dumpsite soil while the highest pH of 8.23, which is alkaline was found at the Ife dumpsite soil. However, Osogbo and Ilesha dumpsite soils were slightly alkaline at a pH of 7.87 and 7.67, respectively. The results of this study correspond with the findings of Thomas., (2015), who reported that the pH of dumpsite soils in Ibadan Nigeria ranged from slightly alkaline to slightly acidic. However, the findings of Obasi *et al.* (2012) differ slightly with a report of neutral to alkaline soil pH in their study of dumpsite soils along Enugu/Port-Harcourt road. An alkaline soil may not favour metal mobility due to high sorption of these metals in them while low pH condition may enhance metal solubility (Thomas., 2015).

Most tropical soils are usually characterized by low pH due to poor CEC of the soils, especially the soils of regions with high rainfall like Southern Nigeria and Osun state in particular. However, the dumpsite soils analyzed varied from slightly acidic to alkaline. The slightly alkaline and alkaline status of the soils may be due to the observed incidence of continuous burning of the dumpsite refuse and also the high organic matter content of the soils. The organic matter is a direct product of soil organic carbon can increase the CEC of a soil which in return has a direct positive effect on soil pH due to increased ability to retain more cation (Khan et al., 2015).

The cation exchange capacity of soil is another factor that plays a vital role in heavy soil metals. The high CEC values of the soils may be due to the high organic carbon content of the soils. It is known that organic matter can increase the cation exchange capacity of a soil. This is because decomposed organic matter (humus) has a high CEC [which it also impacts on the soil. The soil texture also influences the CEC of soil with clay soil having higher CEC than silt and sandy soils. This may be partly the reason Ife dumpsite, which is sandy clay loam (SCL) had a higher CEC value compared to the other 3 dumpsites, which are sandy loam (SL) in texture.

The total concentration of lead (Pb), Chromium (Cr), Cadmium (Cd) and Nickel (Ni) in the four dumpsites located in the towns of Osogbo, Ilesha, Ife and Ido-Osun in Osun state Nigeria studied as well as the total heavy metal concentration of their respective control sites corresponded with the findings of Olufunmilayo et al., (2014) who reported Pb, Cd and Ni concentrations within this range in dumpsites soils located at Iree town of Osun state. Also, Obasi *et al.,* (2012) reported lead and Nickel concentrations of dumpsite soils along Enugu/Port-Harcourt road within this range but reported higher cadmium concentration in the dumpsite soils they studied. Nkop *et al.* (2016) however reported lower Pb concentrations within the range of 2.18 mg/kg to 13.14 mg/kg in dumpsite soils located within the premises of University of Uyo, while Onyedikachi and Okon, (2014) reported low to high Pb concentrations within the range of 3-144 mg/kg in dumpsite soils located in Gombe state Nigeria.

There was no significant difference ($t = 1.09$, $t = 2.143$; $p < 0.05$) in lead concentration between Ilesha and Ife and Ilesha and Osogbo dumpsite soils. There was also no significant difference ($t = 1.05$, $t = 2.05$, $t = 1.03$; $p < 0.05$) in lead concentration of Osogbo, Ife and Ido-Osun dumpsites soils. However, there was a significant difference (($t = 3.15$; $p < 0.05$) in lead concentration between Ilesha and Ido-Osun dumpsite soils. Cadmium has l.s.d of 9.03. There was no significant difference ($t = 2.04$, $t = 2.24$, $t = 0.20$, $t = 1.74$, $t = 1.54$; $p < 0.05$) of this metal between Ife and Osogbo, Ife and Ilesha, Osogbo and Ilesha, Osogbo and Ido-Osun and Ilesha and Ido-Osun dumpsite soils studied except between the soils of Ife and Ido-Osun dumpsite where the significant difference ($t = 3.79$; $p < 0.05$) in cadmium concentration was observed. Chromium has l.s.d of 14.87. There was a significant difference ($t = 5.09$, $t = 5.27$, $t = 2.89$, $t = 3.07$; $p < 0.05$) in chromium concentration between Ilesha and Ido-Osun, Ilesha and Ife, Osogbo and Ido-Osun, and Osogbo and Ife dumpsite soils. However, there was no significant difference ($t = 2.19$, $t = 0.18$; $p < 0.05$) in Chromium concentration in the soils of Ilesha and Osogbo dumpsites and also soils of Ido-Osun and Ife dumpsites. Ni has l.s.d of 37.83. There was no significant difference ($p < 0.05$) in Ni concentration among all the dumpsites.

The high variations of concentration of these heavy metals in the soils of the different dumpsites studied may be attributed to many factors such as; differences in materials disposed of in the dumpsites, the duration in which the pollutants have remained in the soil as well as other anthropogenic activities such as burning of the wastes. Hence, no single dumpsite can be used to conclude on the concentration of heavy metals in another dumpsite since heavy metal concentration among dumpsites differs under prevailing circumstances within the site.

The concentration of lead discovered in the soil of Osogbo, Ilesha and Ife dumpsites exceeded the permissible level recommended by FAO/WHO (2001). However, the concentration of lead in the soil of Ido-Osun dumpsite was below the FAO/WHO permissible level. Lead toxicity in the soil may pollute both crops and underground water. The concentration of cadmium in all the dumpsites studied exceeded the FAO/WHO permissible level of cadmium concentration in soils. Cadmium toxicity is of great concern. Khan et al. (2015) reported that even at low concentration, cadmium toxicity could lead to various physiological anomalies.

On the contrary, chromium and Nickel concentration in all the dumpsites, soils studied where below the FAO/WHO permissible levels of the metals in soils. The results obtained are in agreement with the findings of many researchers which have reported Pb, Cd, Cr and Ni concentrations in dumpsite soils above the FAO/WHO (2001) recommended levels (Emurotu and Onianwa, 2017; Olufunmilayo et al., 2014; Thomas, 2015). The high concentration of these heavy metals in the dumpsites soils may be due to the indiscriminate disposal of electronics, chemicals and other heavy metal-containing materials in the dumpsites. All of the dumpsites studied showed significant higher concentration Pb, Cd, Cr, and Ni compared to their control sites. Since the control sites are located within few meters from the dumpsites, it shows that the high concentration of Pb, Cr, Cd and Ni in the dumpsite is as a result of anthropogenic activities rather than pedogenic characteristics of the parent materials.

The concentration of lead (Pb), cadmium (Cd) Chromium (Cr) and Nickel (Ni) in the exchangeable and oxidizable fractions of the dumpsites soils located in Osogbo, Ife, Ilesha and Ido-Osun towns in Osun state Nigeria revealed that In Osogbo dumpsite, the order of heavy metal concentration in the exchangeable fraction of the soil is: Ni > Pb > Cr > Cd. The order in Ife dumpsite is Ni > Cr > Pb > Cd, the range in Ido-Osun dumpsite is Ni > Pb > Cr > Cd, While the order in Ilesha dumpsite is Ni > Pb > Cr > Cd.

The order of concentration of the metals in the oxidizable fraction for the different dumpsites studied was; Osogbo dumpsite: Pb > Ni > Cr > Cd. Ife dumpsite: Pb > Ni > Cr > Cd. Ido-Osun dumpsite: Ni > Pb > Cr > Cd and the order in Ilesha dumpsite was Pb > Cr > Ni > Cd. Hence in the oxidizable fraction of the dumpsite soils, Pb was the most concentrated heavy metal in this fraction followed by Ni while Cd was the least concentrated heavy metal. The high lead concentration may be as a result of indiscriminate disposal of batteries and other high lead-containing wastes which releases excess lead to the soil. Hence, Pb dominated the oxidizable fraction of the soils of the most dumpsites studied. This may suggest hope that organic matter can actively bound lead in the soil. It was also observed that most of the metals studied were more concentrated in the oxidizable fraction compared to the exchangeable fraction of the soils except in Ido-Osun dumpsite where the concentration of the metals in the oxidizable fraction was found to be relatively lower. The low concentration of the metals in the oxidizable fraction in Ido-Osun dumpsite could be as a result of the lower organic carbon content of the soil to other dumpsites studied. The oxidizable fractions are those heavy metals bound to the organic fraction of the soil. Therefore, it is expected that the higher the organic content of the soil, the higher the concentration of metals in the organic fraction (oxidizable fraction).

This is in support of findings of Jimoh and Sabo (2013) who reported a lower concentration of lead in the exchangeable fraction compared to other metals. In general, the lower concentrations of the heavy metals in the exchangeable fraction may be responsible for the much lower uptake of the metals in the plants since the exchangeable fraction of heavy metals is also known as the available fraction of the metals. However, in the oxidizable fraction of the dumpsite soils studied, Pb was the most concentrated heavy metal while the results also showed that Cd was the least concentrated metal in both the exchangeable and oxidizable fractions of all four dumpsite soils studied.

From the result, it was observed that the highest concentrations of all the metals studied (Pb, Cd, Cr and Ni) were in the residual fraction of the soil. The results obtained agree with the findings of Jimoh and Sabo, (2013) that reported highest concentrations of Pb, Cd, Cr and Ni in the residual fractions of the soil compared to other fractions. However, this study revealed a relatively low concentration of nickel in the two fractions. The high concentration of the heavy metals in reducible and residual fractions of the soil will help to reduce the availability and uptake of the metals by plants since heavy metals in these fractions of the soils are usually not available for plant uptake.

The percentage of the total metal concentration found in the different fractions of the soils were as shown in table 4.12. it was observed that the largest percentage of the heavy metals were in the reducible and residual fractions of the soil. The results obtained support the findings of Osakwe *et al*. (2012) who reported low percentage of Pb, Cd, Cr and Ni in the Exchangeable and oxidizable fractions of the dumpsite soils but a higher concentration of the metal in the reducible and residual fraction of dumpsite soils located in Asaba, Delta State, Nigeria.

The order of percentage of total lead concentration in the different fractions of the soil is residual > oxidizable > reducible > exchangeable. The order of concentrations for the soil cadmium is residual > reducible > oxidizable > exchangeable fraction—chromium and cadmium were found to share a similar trend in their concentrations within the soil fractions. A similar trend also existed for nickel. Hence, the most considerable proportions of the heavy metals were found in the residual fractions of the soil followed by the reducible fraction while the least concentrations of the metals were in the exchangeable fractions.

The results obtained agree with the findings of Jumoh *et al.,* (2013) who reported the same order in Pb and Cd concentrations within the four fractions of dumpsite soils located within Kano metropolis, Nigeria. However, the order for Cr and Ni concentrations within the soil fractions differs with the finding of Jumoh *et al.,* (2013) who reported higher concentrations of Cr and NI in the oxidizable fractions of the soil than the reducible fractions. The differences may be as a result of variations in the organic matter content, variation in regional rainfall and also variations in the soil type of the dumpsites. Khan *et al.*, (2015) reported that the higher the organic matter content of a soil, the lower the uptake of heavy metals by plants which also suggests more bonding of the heavy metals in the oxidizable fraction of the soils. However, he also pointed out that the nature of the organic matter in the soil will determine the extent of bounding. The high rainfall in Southern Nigeria may promote the formation of organic acids within dumpsite, which may also limit the ability of organic matter to form a complex with heavy metals in the soil.

5.0. Summary and Conclusion

Dumpsites located at Osogbo, Ife, Ido-Osun and Ilesha towns in Osun State Nigeria were studied for Pb, Cd, Cr and Ni concentrations and also the fractions of the heavy metals in the dumpsite soils.

The soils of the Dumpsites studied were contaminated by Pb, Cd, Cr and Ni at varying concentrations. There were also variations in the level of contamination of the dumpsite soils by these heavy metals from one dumpsite to another except for nickel with no significant difference in its concentration in all the dumpsite soils.

The concentrations of lead (Pb) and cadmium (Cd) in soils of all the dumpsites studied were above the FAO/WHO (2001) permissible levels of 100mg/kg and 0.3mg/kg for these metals in soils respectively. However, Nickel (Ni) and Chromium (Cr) were below 50 mg/kg and 100mg/kg respective permissible levels.

The order of Dumpsite pollution by the sum of the mean of total heavy metals (Pb, Cd, Cr and Ni) studied was Ilesha dumpsite > Ife dumpsite >Osogbo dumpsite >Egbedore dumpsite.

The residual fraction of the dumpsite soils had the highest percentage of the heavy metal concentration while the exchangeable fraction had the least concentration of Pb, Cd, Cr, and Ni studied. The trend from highest to lowest was, residual > oxidizable> reduceable> exchangeable.

Therefore, in conclusion; There is Pb, Cd, Cr and Ni pollution of dumpsite soils located within Osogbo, Ife, Ido-Osun and Ilesha towns in Osun state Nigeria. Lead (Pb) is the most abundant heavy metal in the dumpsites. However, only Pb and Cd concentrations in the soils of the four dumpsites studied exceeded the FAO/WHO permissible levels of the metals in the soil while Cr and Ni concentrations in the dumpsite were below the permissible levels.

In the four dumpsites studied, the residual fraction of the soil had the highest percentage of heavy metal concentration. The trend from highest to lowest was residual > oxidizable > reducible > exchangeable.

6.0. Recommendations

The concentration and bioaccumulation of Pb, Cr, Cd and

Ni in the soils of sites studied are high enough to cause physiological anomalies in plants growing in the polluted soil and animals that feed on the plants. This is because heavy metals are known to be highly non-biodegradable and can bioaccumulate in living organisms. Therefore, the dumpsite soils are not suitable for agronomic practices. Also, the plants growing in the dumpsites should not be consumed by humans or fed to domestic animals.

Heavy metals are known to exist in dynamic phases and can change from one phase to another in the soil. Hence, there is the possibility of more release of heavy metals from a residual, reducible or oxidizable fraction of the soil to exchangeable sites in nearest future. Therefore, the dumpsite soils should not be used for agricultural purposes without proper remediation. Also, increasing the pH and organic matter status of soil may help to alleviate heavy metal toxicity. There is a need to carry out more studies to determine the best on-field approach that can be used for phytoremediation of the heavy metal polluted soils.

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