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Distribution and Risk of Metals in Soils of Refuse Dumpsites in Some Urban Towns in Delta State, Nigeria

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ABSTRACT: Refuse dumpsites often contain materials capable of polluting surrounding soils. In this study, the spatial distribution of metals in soils of refuse dumpsites in three urban towns (Ughelli, Sapele, Orhuwhorun) in Delta State, Nigeria were examined. Soil samples were collected from three dumpsites in the aforementioned towns at depths 0-15 cm, 15-30 cm and 30-45 cm, respectively. Some physicochemical properties of the soil profiles such as pH, Electrical Conductivity (EC) and Total Organic Carbon (TOC) were determined using standard methods, while metals concentration were determined using atomic absorption spectrometry after digestion with *aqua regia*. The results for all sites and depths ranged as follows: pH: 4.64 to 7.85; EC (μ∫ cm^{-1}): 60.8 to 451; and TOC (%): 0.06 to 1.49 %. Metals concentration (mg kg^{-1}) ranged as follows: 0.05 to 4.5 for Cd, 9.0 to 149 for Pb, 4.20 to 15.4 for Cr, 1.0 to 14.5 for Ni, 1.0 to 124 for Cu, 20 to 510 for Zn, and 1650 to 11865 for Fe. The potential ecological risk of the metals is in the order of Cd > Pb > Cu > Zn > Cr > Ni. The study indicates that the metals studied except Cd do not pose environmental risk considering their relatively low concentrations.

Keywords: Dumpsite, Metals, Delta State, Risk, Soil

Introduction

Nigeria's population has increased greatly over the years and this has resulted in increased waste generation. Even though solid waste is an asset when managed appropriately, it can be a threat to human life. It can pollute soil, water and air (Bishop, 2000). The Nigerian Government at all tiers via their respective agencies has invested much in the enforcement of sanitation laws and waste management but much has not been achieved. Moreover, the unpredictable growth of housing units in the urban cities has made monitoring and managing of waste complicated (Ogbemudia and Mbong, 2013). These have led to haphazard dumping of waste at every nook and cranny of major towns and cities in Nigeria. Urbanization gives rise to a lot of industrial, commercial and agricultural activities. Wastes emanating from these activities are deposited on every available space indiscriminately. A typical refuse dump comprised of organic, inorganic, electrical and electronic wastes and sundry wastes (Nduka *et al*., 2010).

There is no doubt that these dumps contribute significant amounts of metals migrating to the soil. Surface runoff from such refuse dumpsites also end up in the groundwater or in the surface water, thereby increasing the metal burden of the aquatic ecosystem (Osakwe, 2012). Some metals have bio-importance as trace elements but, the biotoxic effects of many of them in human biochemistry are of great concern. They enter the body system through food, air, and water and bioaccumulate over a period causing adverse health effects (Athalye *et al*.,

2001). For instance, cadmium is associated with kidney disease and linked to hypertension. There is also some evidence that cadmium can replace zinc in zinc-containing enzymes, which causes itai-itai disease with lethal consequences and binds calcium out of bones to cause osteoporosis (European Commission, 2002). Besides, it has cancinogenic, mutagenic and teratogenic effects (Vukojevic *et al*., 2006). Lead influences the nervous system, slowing down nervous response (ATSDR, 2006). Lead toxicity has also been linked with reduced intelligence and lowered school achievement scores, as well as, juvenile delinquency and violent behaviour (European Commission, 2002). The most common symptom of copper toxicity is injury to red blood cells and lungs as well as damage to the liver and pancreatic functions (Ontario Online, 2006). Long-term exposure to copper causes the irritation of the nose, mouth, and eyes as well as headaches, stomach aches, dizziness, vomiting and diarrhoea (Lenntech, 2008). Nickel toxicity includes cancer of the lungs, chronic bronchitis, reduced lung function and dermatitis (Abbas *et al*., 2014), while inhaling or ingesting Cr overtime can cause nose bleeding, ulcers, convulsion, kidney and liver damage, cancer, gene mutation and teratogenicity (Abbas *et al*., 2014).

Soils contaminated with metals are not only a problem to plant nutrition and food chain; they may constitute a direct health hazard as well. Since the protection of both terrestrial and aquatic ecosystem from contamination is a global concern, monitoring the concentration of metals in the environment is therefore necessary. Some studies (Amos-Tautua *et al*., 2013; Ogbemudia and Mbong, 2013; Ogundele *et al*., 2013; Ogbeibu *et al*., 2013; Adelekan and Alawode, 2011; Osakwe, 2010; Nduka *et al*., 2010; Nwajei *et al*., 2007; Amusan *et al*., 2005) have been carried out to determine the concentrations of metals in soil samples around dumpsites in different parts of Nigeria. However, information regarding the sources and ecological risks of metals in soils from refuse dumpsites in the Niger Delta is still scanty. Thus, the objectives of the present study are to determine the concentrations, sources and ecological risk of metals in soils of refuse dumpsites in major towns in the Niger Delta of Nigeria.

Materials and Methods

Description of the study area: The study area (Figure 1) comprised of three major towns of Ughelli (UGH), Sapele (SAP) and Orhuwhorun (UDU). Ughelli lies within Longitude 5.30º N and Latitude 5.59 º E. The town was originally an agricultural centre but several industries have now developed there. It hosts the Beta Glass factory and Shell petroleum Development Company. Sapele lies within Longitude 5.54 º N and Latitude 5.54 º E. The town has one of Nigeria's major seaports. It hosts the African Timber and Plywood Company. Orhuwhorun is a suburb of Warri. It lies within Longitude 5.45 º N and Latitude 5.43 º E. The study area experiences moderate rainfall and moderate humidity for the most part of the year. The climate is equatorial and is marked by two distinct seasons: the dry season and the rainy season. The dry season lasts from about November to April and is significantly marked by the cool "harmarttan" dusty haze from the north-east winds. The rainy season spans May to October with a brief dry spell in August, but it frequently rains even in the dry season. The area is characterised by a tropical equatorial climate with a mean annual temperature of 32.8 ℃ and annual rainfall amount of 2673.8 mm (Iwegbue *et al*., 2018).

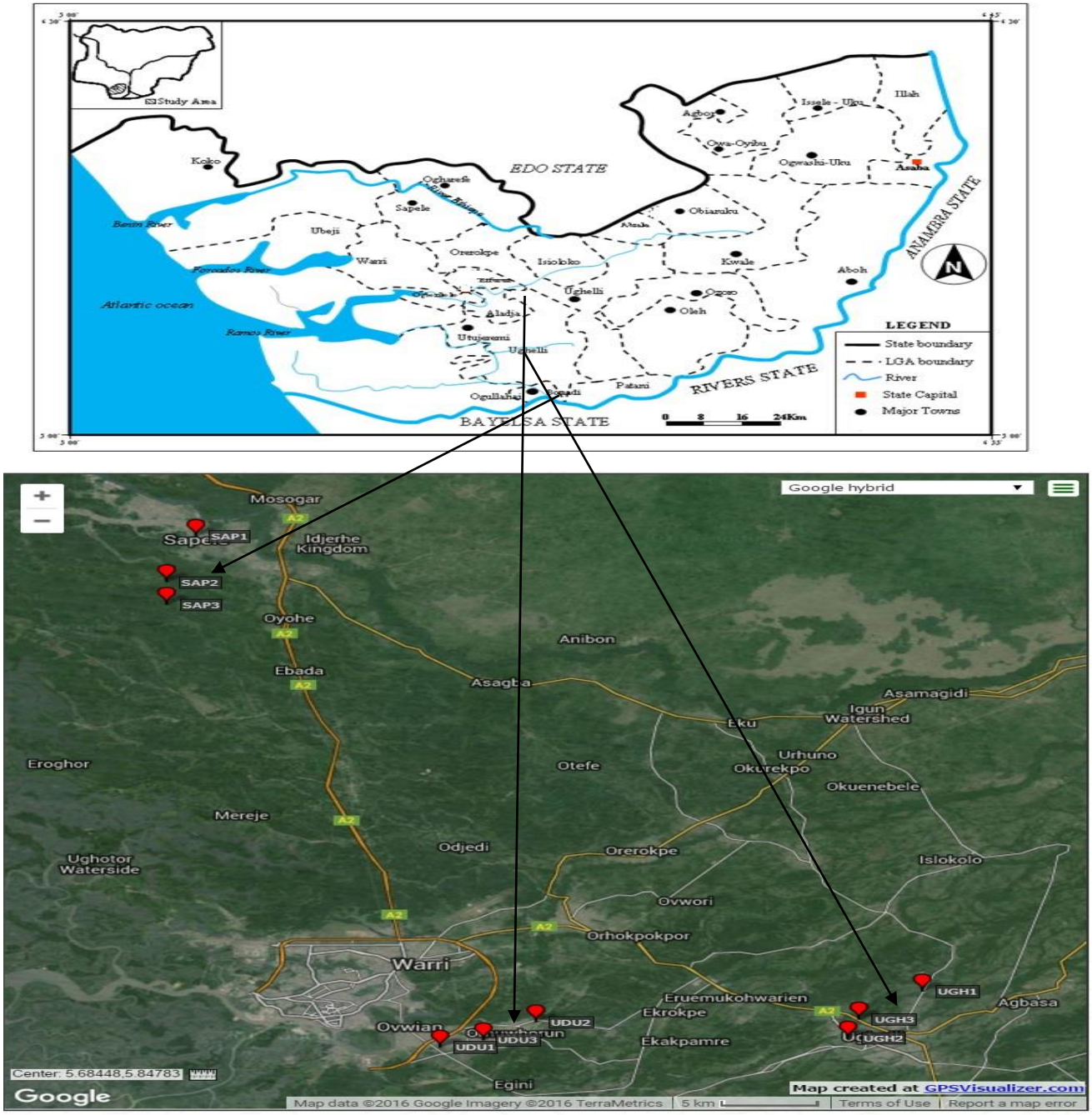

Figure 1: Map of study area

*Sample collection***:** Soil samples were collected from nine (9) dumpsites. That is, three (3) dumpsites each from Sapele (SAP), Orhuwhorun (UDU) and Ughelli (UGH) at depth 0-15 cm and 15-30 cm and 30-45 cm depths. Soil samples were collected with a stainless soil corer after removal of the uppermost debris from the soil layer. Samples were kept in black polythene bags, stored and immediately transferred to the laboratory. In the laboratory, the soil samples were air-dried, twigs and stones removed and sieved over stainless steel sieves (< 2 mm). Thereafter, they were stored at 4^{o}C before analysis.

Determination of some soil physicochemical properties: The soil pH was determined in soil suspension (1:2 soil to water ratio) using a glass electrode pH meter. The soil electrical conductivity (EC) was determined in soil suspension (1:2 soil to water ratio) using a conductivity meter. The total organic carbon of the soil was determined by the wet oxidation digestion method of Walkley and Black (1934) as described by Radojevic and Bashkin (1999).

Metals determination in the soil samples: About 0.5 g of the soil sample was placed in digestion tube followed by addition of 15 mL of aqua regia (3:1 HCl : HNO_3) and was swirled to wet the sample and allowed to stand overnight. The next day, the tube was heated in a heating block of 50^{o}C for 30 min and raised to a temperature

of 120 ^{o}C for 2 h. The digest was cooled and filtered through a Whatman No. 1 filter paper and made up to 25 mL with 0.25 mol/L HNO_3 (Radojevic and Bashkin, 1999). The samples solution was subsequently analysed for Cd, Pb, Zn, Ni, Cu, Fe and Cr using air-acetylene atomic adsorption spectrophotometry (Perkin Elmer Analyst 200).

Quality assurance programme: Sterilized and disposable rubber gloves were worn during analysis. All the bottles for metal analysis were washed with metal-free detergent and sterilized by soaking with 10 % HNO_3 analar grade overnight and then rinsed several times with distilled water. For every five samples, a procedural blank was used for monitoring interferences and cross contaminations, all results were blank-corrected. All analysis was done in replicate and the results were expressed as mean of the replicate analysis.

Statistical analysis: Analysis of variance (ANOVA) was used to determine whether the concentrations of metals varied significantly among sampling locations and depths with a p-value less than 0.05 ($p<0.05$) consider statistically significant. Pearson's correlation coefficient was used to determine the relationship between physicochemical properties and heavy metals. The statistical analysis was performed using SPSS version 19.

Data Treatment

Contamination/pollution index: The contamination/pollution index (CPI) was obtained by using the CPI equation given by Lacatusu (2002).

$$\text{CPI} = \frac{\textit{Concentration of metal in soil}}{\textit{Reference value}} \qquad (1)$$

The reference value of metals used in this study is the Department of Petroleum Resources (DPR) of Nigeria target value of heavy metals in soil (DPR, 2002). CPI value greater > 1 define a pollution range and < 1 define the contamination range. The significance of the CPI has been documented by Iwegbue *et al.* (2018).

Index of geoaccumulation (Igeo): The Igeo enables the assessment of contamination by comparing current and pre-concentration and was originally used with bottom sediments (Muller, 1969). The Igeo equation used in this study is given as follows (Muller, 1969):

$$\text{Igeo} = \text{Log}_2 \frac{C_n}{1.5 \times B_n} \qquad (2)$$

where C_n is the measured concentration of the element in the soil and B_n is the geochemical background concentration. The crustal abundance values for the respective metals (Turiekian and Wedepohl, 1961) were used as geochemical background concentrations. The value 1.5 in the equation allow for natural fluctuations in the concentration of a given metal in the soil and very small anthropogenic influences. The Igeo classification given by Muller (1961) can be found in Iwegbue *et al.* (2018).

*Enrichment Factor (EF)***:** The Enrichment factor of metals in the soil was calculated following the equation of Reimann and De Caritat (2000).

$$\text{EF} = \frac{(\textit{Concentration of test metal})}{(\textit{Concentration of reference metal})} \div \frac{(\textit{Background concentration of test metal})}{(\textit{Background concentration ofreference metal})} \qquad (3)$$

In this case, Fe was chosen as the reference metal because it is the most abundant metal in the earth crust among those studied. The crustal abundance values for the respective metals (Turiekian and Wedepohl, 1961) were used as background concentrations for the estimation of the EF. Five enrichment categories are recognized based on the enrichment factor (Sutherland, 2000; Loska and Wiechula, 2003).

Ecological risk assessment of metals in soils: The method of determining ecological risks of metals was originally introduced by Hakanson (1980). Hakanson (1980) gave the equation for ecological risk as:

$$\text{RI} = \Sigma \text{Er} \qquad (3)$$

where

$$\text{Er} = \text{Tr} \times \text{CF} \qquad (4)$$

$$\text{CF} = \frac{C_s}{C_n} \qquad (5)$$

where: Tr is the biological toxic factor of a single metal. Hekanson (1980) demonstrated Tr value for Cd, Cu, Pb, Cr, Zn and Ni to be 30, 5, 5, 2, 1, and 5, respectively.
CF is the contamination factor
C_s and C_n are metal concentrations for samples and background respectively.

Also, the background concentrations used are the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961). These are; 0.3, 45, 20, 90, 95 and 68 for Cd, Cu, Pb, Cr, Zn and Ni, respectively. Er is the ecological risk of each metal and RI shows the ecological risk of multiple metals. The Er and RI have been classified into five and four categories depending on their values respectively. Er value <40 denotes low

potential ecological risk; ≥40<80 moderate potential ecological risk; ≥80<100 strong potential ecological risk; ≥100<320 very strong potential ecological risk and ≥320 extremely strong potential ecological risk. RI value <150 indicates low ecological risk; ≥150<300 moderate ecological risk; ≥300<600 strong ecological risk and ≥600 very strong ecological risk.

Results

The individual results obtained for each physicochemical property and metal concentrations are shown in Table 1. Table 2 and Table 3 show the result of the ecological risk of metals and correlation analysis of metals in soils of the sampled dumpsites, respectively. The principal component analysis (PCA) is shown in Table 4. The computed CPI, Igeo and EF of metals in the soils of the studied dumpsites are displayed in Figures 2, 3 and 4, respectively.

Table 1: Physicochemical properties and metal concentrations (mg kg^{-1}) of soils in sampled dumpsites

DEPTH	SITES	pH	EC (µ∫/cm)	TOC (%)	Cd	Pb	Cr	Ni	Cu	Zn	Fe
0-15 cm	SAP1	7.57	188	0.54	1.50	16.5	10.2	2.50	4.00	408	3900
	SAP2	7.60	212	0.85	ND	35.5	7.20	6.00	68.5	300	5535
	SAP3	7.85	214	0.37	1.50	10.0	7.60	1.00	ND	53.5	3360
	UDU1	7.10	173	1.49	ND	45.0	6.50	1.00	66.0	29.5	3437
	UDU2	7.60	145	0.26	ND	12.0	7.90	1.50	1.00	165	2790
	UDU3	7.13	411	0.06	ND	54.0	4.60	1.00	2.00	71.0	4430
	UGH1	7.46	170	0.61	2.00	70.0	10.1	3.00	25.0	285	2810
	UGH2	7.11	245	0.92	3.00	112	14.9	14.5	66.5	505	11865
	UGH3	6.25	84.9	0.21	1.00	149	8.50	7.50	40.0	338	5260
15-30 cm	SAP1	7.50	126	1.25	ND	15.0	6.85	1.00	3.00	39.5	5055
	SAP2	7.73	192	0.14	1.00	22.0	5.70	3.00	11.0	64.5	3990
	SAP3	7.70	189	0.73	ND	12.0	4.40	1.50	ND	35.5	4210
	UDU1	7.10	139	0.35	ND	21.0	13.4	1.50	1.00	33.0	5110
	UDU2	6.45	67.3	0.23	0.50	16.0	9.70	2.00	ND	50.0	3370
	UDU3	6.64	451	0.11	1.50	15.0	15.4	3.00	ND	55.5	6820
	UGH1	5.33	90.6	0.49	2.50	131	9.90	6.00	124	330	10050
	UGH2	6.90	173	0.46	0.50	17.5	7.10	1.50	1.00	29.0	4580
	UGH3	4.95	64.1	0.16	3.00	131	10.0	9.50	19.0	273	4160
30-45 cm	SAP1	7.53	134	0.21	ND	10.0	8.60	3.00	4.50	23.5	4860
	SAP2	7.56	164	0.06	ND	18.5	4.20	1.00	2.50	18.5	2850
	SAP3	7.70	211	0.45	ND	9.00	7.40	ND	ND	27.5	1650
	UDU1	6.15	125	0.28	1.00	31.5	14.2	5.00	2.50	133	8750
	UDU2	6.00	70.6	0.61	ND	16.5	10.6	1.50	ND	36.0	3030
	UDU3	6.93	417	0.37	2.50	17.0	10.8	1.50	ND	21.0	4640
	UGH1	5.14	60.8	0.23	3.00	60.5	14.2	7.50	74.0	375	9660
	UGH2	6.82	162	0.38	ND	21.0	11.5	7.00	9.50	20.0	5790
	UGH3	4.64	61.8	0.45	4.50	134	8.20	4.00	12.5	510	3340

SAP = Sapele; UDU =Orhuwhorun; UGH = Ughelli; ND = Not detected

Table 2: Ecological risk of metals in sampled dumpsite soils

DEPTH	SITES	Cd	Pb	Cr	Ni	Cu	Zn	RI
0-15 cm	SAP1	150	4.1	0.2	0.2	0.4	4.3	159
	SAP2	0	8.9	0.2	0.4	7.6	3.2	20
	SAP3	150	2.5	0.2	0.1	0.0	0.6	153
	UDU1	0	11.3	0.1	0.1	7.3	0.3	19
	UDU2	0	3.0	0.2	0.1	0.1	1.7	5
	UDU3	0	13.5	0.1	0.1	0.2	0.7	15
	UGH1	200	17.5	0.2	0.2	2.8	3.0	224
	UGH2	300	28.0	0.3	1.1	7.4	5.3	342
	UGH3	100	37.1	0.2	0.6	4.4	3.6	146
15-30 cm	SAP1	0	3.8	0.2	0.1	0.3	0.4	5
	SAP2	100	5.5	0.1	0.2	1.2	0.7	108
	SAP3	0	3.0	0.1	0.1	0.0	0.4	4
	UDU1	0	5.3	0.3	0.1	0.1	0.3	6
	UDU2	50	4.0	0.2	0.1	0.0	0.5	55
	UDU3	150	3.8	0.3	0.2	0.0	0.6	155
	UGH1	250	32.8	0.2	0.4	13.8	3.5	301
	UGH2	50	4.4	0.2	0.1	0.1	0.3	55
	UGH3	300	32.8	0.2	0.7	2.1	2.9	339
30-45 cm	SAP1	0	2.5	0.2	0.2	0.5	0.2	4
	SAP2	0	4.6	0.1	0.1	0.3	0.2	5
	SAP3	0	2.3	0.2	0.0	0.0	0.3	3
	UDU1	100	7.9	0.3	0.4	0.3	1.4	110
	UDU2	0	4.1	0.2	0.1	0.0	0.4	5
	UDU3	250	4.3	0.2	0.1	0.0	0.2	255
	UGH1	300	15.1	0.3	0.6	8.2	3.9	328
	UGH2	0	5.3	0.3	0.5	1.1	0.2	7
	UGH3	450	33.5	0.2	0.3	1.4	5.4	491

Table 3: Correlation analysis of metals in sampled dumpsite soils

	EC (µ∫/cm)	TOC (%)	Cd	Pb	Cr	Ni	Cu	Zn	Fe
0-15 cm depth									
EC (µ∫/cm)	1.000	-0.186	-0.101	-0.195	-0.260	-0.100	-0.197	-0.250	0.194
TOC (%)		1.000	0.063	-0.023	0.230	0.193	0.766*	0.041	0.230
Cd			1.000	0.388	0.887*	0.617**	0.085	0.654**	0.569**
Pb				1.000	0.394	0.702*	0.471	0.487	0.561**
Cr					1.000	0.779*	0.298	0.830*	0.701*
Ni						1.000	0.616**	0.796*	0.936*
Cu							1.000	0.324	0.563**
Zn								1.000	0.656**
Fe									1.000
15-30 cm depth									
EC (µ∫/cm)	1.000	-0.231	-0.080	-0.435	0.401	-0.271	-0.292	-0.382	0.174
TOC (%)		1.000	-0.478	-0.198	-0.477	-0.415	0.005	-0.190	0.057
Cd			1.000	0.890*	0.296	0.950*	0.607**	0.895*	0.463
Pb				1.000	0.134	0.921*	0.757*	0.987*	0.507**
Cr					1.000	0.195	0.056	0.134	0.375
Ni						1.000	0.499	0.888*	0.270
Cu							1.000	0.832*	0.844*
Zn								1.000	0.596**
Fe									1.000
30-45 cm depth									
EC (µ∫/cm)	1.000	-0.045	-0.061	-0.447	-0.123	-0.424	-0.397	-0.519	-0.217
TOC (%)		1.000	0.093	0.138	0.203	-0.160	-0.246	0.065	-0.335
Cd			1.000	0.862*	0.251	0.329	0.470	0.872*	0.268
Pb				1.000	0.063	0.367	0.366	0.951*	0.114
Cr					1.000	0.704*	0.480	0.232	0.843*
Ni						1.000	0.673**	0.477	0.825
Cu							1.000	0.604**	0.658
Zn								1.000	0.314
Fe									1.000

*Pearson correlation is significant at 0.01 level of significance (1 tailed)
**Pearson correlation is significant at 0.05 level of significance (1 tailed)

Table 4: PCA factor loadings after varimax with Kaiser Normalization Rotation for metals and some physicochemical properties of dumpsite soils

	0-15 cm depth				**15-30 cm depth**			**30-45 cm depth**		
	Component				**Component**			**Component**		
	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**
pH		-.971			-.910			-.855	-.388	
EC				.959	-.415		.786	-.505		
TOC			.949		-.485	.380	-.642			.963
Cd	.908				.913			.857		
Pb	.368	.902			.917	.357		.980		
Cr	.964						.829		.928	.329
Ni	.786	.468	.310		.967			.339	.839	
Cu		.373	.892		.523	.791		.481	.634	-.329
Zn	.860				.883	.452		.973		
Fe	.727	.357	.343	.421		.939			.943	
% Variance	**48.95**	**17.09**	**15.37**	**11.66**	**57.30**	**18.79**	**13.79**	**51.05**	**21.25**	**12.04**

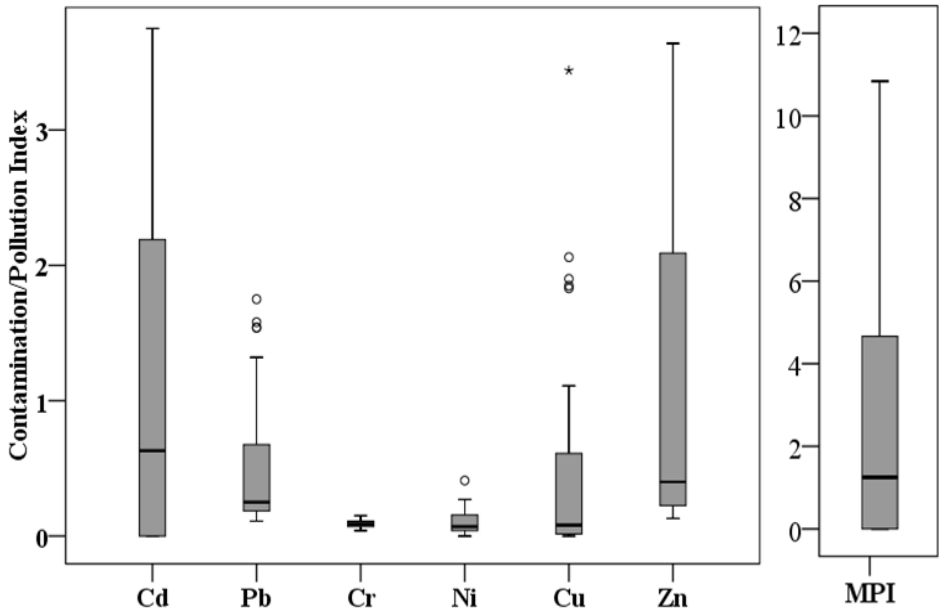

Figure 2: Box Whisker plot of contamination/pollution index of metals in dumpsite soil

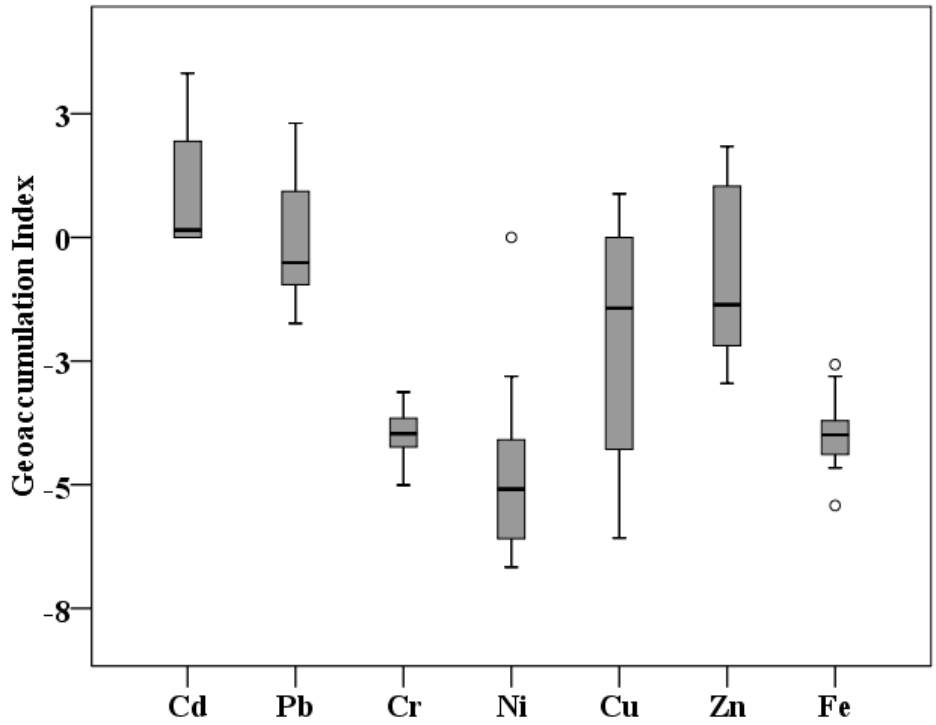

Figure 3: Box Whisker plot of Geoaccumulation index of metals in dumpsite soil

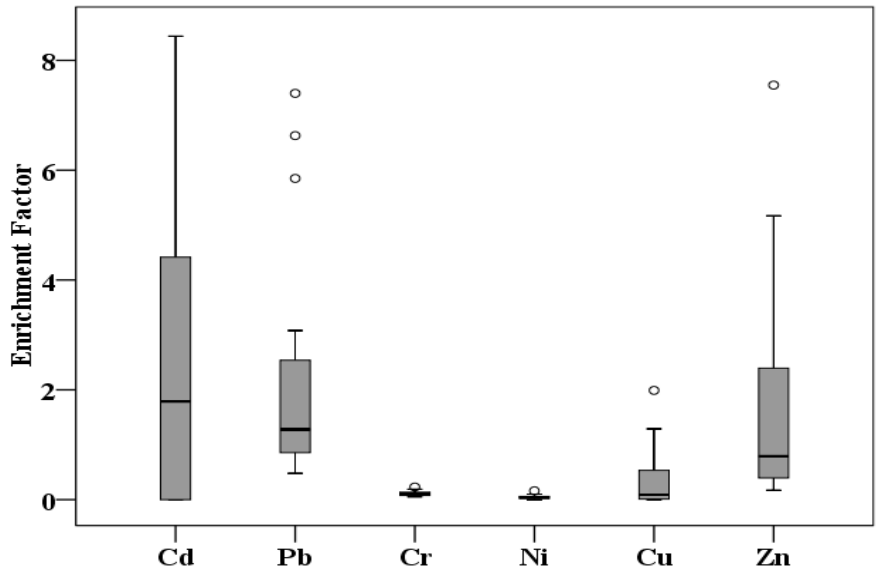

Figure 4: Box Whisker plot of Enrichment factors of metals in dumpsite soil

Discussion

Physicochemical properties of dumpsite soils: Soil pH is a major factor influencing the availability of element in soil (Igwe *et al*., 2005). It is well known that metal concentrations in soil solution and consequently leaching can be much enhanced in soils with low pH and/or redox potential (Adie and Osibanjo, 2009). Most metals in the pH range of 6.0 – 9.0 are not always in the free form (Adie and Osibanjo, 2009). The pH of the soils in this study ranged between 4.64 and 7.85 for all sites and depth. The highest and lowest pH values were obtained at sites SAP3 (0-15 cm depth) and UGH3 (30-45 cm depth). The pH of the soils decreased with depth in all sites. The pH of the soil samples in this study is slightly acidic to neutral. This near neutrality to slight acidic is common to anaerobic soils in the Niger Delta (Odu *et al*., 1985; Osakwe, 2010). The soil pH values obtained in this study were similar to the range of 5.9-6.2 reported in soils of municipal waste dumpsites at Obafemi Awolowo University, Ile-Ife (Amusan *et al*., 2005), 5.5-6.4 reported in soils of dumpsites in PortHarcourt municipality and environs (Ogbonna *et al*., 2009), 4.21-7.26 for soils of refuse dumpsites in Akure (Oviasogie *et al*., 2009), 4.9-7.4 for soils around automobile dumpsites in Agbor and Environs (Osakwe, 2010), 4.17-7.4 for Aladimma dumpsite soils (Amadi, 2011) and 5.9-6.7 for soils of dumpsites in Njoku market, Imo State, Nigeria (Ubuoh *et al*., 2012).

The electrical conductivity of the dumpsite soils in this study ranged from 60.8 to 451 µs cm^{-1} for all sites and depth. The highest and lowest EC was observed at sites UDU3 (15-30 cm depth) and UGH1 (30-45 cm depth), respectively. Electrical conductivity decreased with depth in all sites except at site UDU3. Higher EC was obtained at site UDU3 relative to other sites. These values were comparable to those reported by Akpoveta *et al*. (2010), Osakwe (2010) and Amadi (2011) for dumpsites soils. For example, Akpoveta *et al*. (2010) reported EC values in the range of 165-201 µs cm^{-1}, Osakwe (2010) reported EC values in the range of 202-478 µs cm^{-1} while Amadi reported EC values in the range of 38.0-198 µs cm^{-1}. The high conductivity values obtained in this study might be due to the presence of scraps in these dumpsites. These high values of EC imply that there is a significant presence of trace metal ions or ionisable materials in the soil (Arias *et al*., 2005).

The total organic carbon (TOC) of these soil profiles ranged from 0.06 to 1.49 %. The highest TOC value was obtained at site UDU1. There was no regular trend in the values of TOC in these soil profiles. The values of TOC obtained in this study were lower than 0.08-3.41 %, 0.85-6.04 % and 29.6-77.8 % reported by Ogbonna *et al.* (2009), Ubuoh *et al*. (2012) and Osakwe (2014). While soil organic carbon is not a requirement for plant growth, the levels of organic matter in soils influence many chemical and physical processes and it is an important indicator of the soil as a rooting environment (Okalebo *et al*., 1993).

Metal concentrations in dumpsite soils: The individual results obtained for the metals are shown in Table 2. Analysis of variance showed that the concentration of metals varied significantly with depth and among the locations ($p < 0.05$).

Cadmium was detected in 56% of these soil samples at concentrations ranging from 0.5 to 4.5 mg kg^{-1}. The highest concentration of Cd was found at site UGH 3 (30 – 45cm depth). Cd was found majorly in the soil samples of UGH 1, UGH2 and UGH3. The concentrations of Cd obtained in majority of the soil samples in this study were higher than the DPR target value of 0.8 mg kg^{-1} stipulated for Nigerian soils but were lower than the DPR intervention value of 17 mg kg^{-1}. Various concentration of Cd in dumpsites soils have been reported in literature. The concentrations of Cd obtained in this study were comparable to some reported in the literature (Odukoya *et al*., 2011; Ogbemudia, and Mbong, 2013). The concentrations of Cd in these soil profiles were higher than concentrations reported by Nwajei *et al*. (2007) in soil around refuse dumpsites in Onitsha, Oviasogie *et al*. (2009) for dumpsites in Akure and Akpoveta *et al*. (2010) for the soil around scrap dumpsites. However, higher concentrations of Cd have been reported in the literature. For instance, Amusan *et al*. (2005) reported Cd concentrations ranging from 17. 0 to 47.06 mg kg^{-1} in refuse dumpsites soils in the Obafemi Awolowo University, Ile-Ife. Also, Ogbonna *et al*. (2009) reported Cd concentrations of 1. 28 to 21.31 mg kg^{-1} dumpsite soils in Port-Harcourt municipality.

In this study, Pb was detected in all sites and depth. The concentrations of Pb in these soil profiles ranged from 9.0 to 149 mg kg^{-1}. The highest and lowest concentrations of Pb were observed at sites UGH3 (0 – 15 cm depth) and SAP3 (30 – 45 cm depth), respectively. The concentrations of Pb decreased with depth at all sites except site UDU2. The DPR target value for Pb is 85 mg kg^{-1}. The concentration of Pb obtained in site UGH3 (0-15cm, 15-30 cm and 30-45 cm) and UGH2 (0-15 cm) were higher than the DPR target value. The concentrations of Pb obtained in this study were below the DPR intervention value of 530 mg kg^{-1} for Pb. The concentration of Pb obtained in this study were higher than those reported by Nwajei *et al*. (2007), Ogbonna *et al*. (2009), Oviasogie *et al*., (2009), Amadi (2011), Osakwe (2011) and Ogbemudia and Mbong (2013). However, the concentrations of Pb in this study were lower than others reported in the literature (Amusan *et al*., 2005; Adefemi and Awokumi, 2009; Adelekan and Alawode, 2011; Odukoya *et al*., 2011).

The concentration of chromium in these soil samples ranged from 4.20 mg kg^{-1} (at 30 – 45 cm depth of site SAP2) to 15.4 mg kg^{-1} (at 15 – 30 cm depth of site UDU3) in all sites and depth. The concentrations of Cr decreased with depth except at sites UDU1, UDU2, UDU3 and UGH1. The concentrations of Cr obtained in this study were lower than the DPR target and intervention values of 100 mg kg^{-1} and 380 mg kg^{-1} respectively **(**DPR, 2002) and also comparable to values reported by Adefemi and Awokunmi (2009). Lower concentrations of Cr in dumpsites soils have been reported in the literature. For instance, Amadi (2011) reported Cr concentrations ranging from 1.56 to 5.28 mg kg^{-1} in Aladima dumpsite soils. Furthermore, Nwajei *et al*. (2007) and Oviasogie *et al*. (2009) reported Cr concentrations in the range of ND – 0.96 and ND – 9.0 mg kg^{-1} respectively in dumpsites soil in Onitsha and Akure, respectively.

Nickel was detected at concentrations ranging from 1.0 – 14.5 mg kg^{-1} in these soil profiles. The highest concentration of Ni was found at 0 – 15 cm depth of the site UGH2. Ni was not detected at site SAP3 (30-45cm depth). In these soil profiles, the concentrations of Ni increased with depth except at sites SAP1, UDU3, UGH2 and UGH3. The concentrations of Ni in these dumpsites soils were lower than the DPR target and intervention values of 35 mg kg^{-1} and 210 mg kg^{-1} in soils, respectively (DPR, 2002). The concentrations of Ni obtained in this study were lower than those reported in the literature (Adelekun and Alawode, 2011; Chengo *et al*., 2013). The concentrations of Ni in this study were, however, higher than those reported by some other researchers (Adefemi and Awokunmi, 2009; Oviasogie *et al*., 2009; Akpoveta *et al*., 2010).

In this study, Cu was detected at concentrations ranging from 1.0 to 124 mg kg^{-1}. The highest concentration of Cu was found at site UGH1 (15–30 cm depth). Copper was not detected at site SAP3 while it was detected only at the surface soil (0 – 15 cm depth) of sites UDU2 and UDU3. The DPR target value for Cu in soil is 36 mg kg^{-1}. Copper concentrations in 19% of these soil samples were higher than the DPR target value. The concentration of Cu in these soils was, however, lower than the DPR intervention value of 190 mg kg^{-1}. The concentrations of Cu in these soil profiles were comparable to Cu concentrations reported in dumpsite soils in the literature (Amusan *et al*., 2005; Adefemi and Awokunmi, 2009; Ogboma *et al*., 2009, Akpoveta *et al*., 2009; Iwegbue *et al*., 2010; Amadi *et al*., 2011).

The concentrations of Zn in these soil profiles ranged from 20 to 510 mg kg^{-1}. The highest and lowest concentrations of Zn were observed at the 30 – 45 cm depth of sites UGH2 and UGH3 respectively. The concentrations of Zn in these soil profiles decreased with depth except at site UDU1 and UGH1 and UGH3. The concentrations of Zn in 41% of these soil samples were higher than the 140 mg kg^{-1} DPR target value for Zn in soils but Zn concentrations

in all samples were lower than the DPR intervention value of 720 $mgkg^{-1}$. A wide range of Zn concentrations have been reported in the literature for dumpsite soil (Amusan *et al*., 2005; Akpoveta *et al*., 2010; Iwegbue *et al*., 2010; Amadi, 2011; Ogbemudia and Mbong, 2013). Amusan *et al*. (2005) reported a concentration of Zn ranging from 63.2 to 102.11 mg kg^{-1} in soils of dumpsites in Ile-Ife, Nigeria while Amadi (2011) reported Zn concentration ranging from 68.3 to 290 $mgkg^{-1}$ in soil Aladinma dumpsite. Also, Adefemi and Awokunmi (2009) reported a Zn concentration of 72.47 to 201.6 mg kg^{-1} in dumpsites of Ado-Ekiti.

The concentrations of Fe in these soils ranged from 1650 to 11865 mg kg^{-1} in all sites and depth. The highest and lowest concentrations of Fe were observed at sites UGH2 (0 – 15 cm depth) and SAP3 (30 – 45 cm depth), respectively. The concentrations of Fe decreased with depth at sites SAP2, SAP3 UGH2 and UGH4. There is no DPR target value for Fe in Nigeria. However, the values of Fe obtained in this study were lower than 47000 mg kg^{-1} crustal abundance value of Fe (Tunekien and Wedepohl, 1960). The concentrations of Fe obtained in this study were higher than those reported in the literature (Amusan *et al*., 2005; Adefemi and Awokunmi, 2009; Ogbonna *et al*., 2009; Akpoveta *et al*. 2009; Amadi, 2011; Osakwe, 2010; Ogbemudia and Mbong, 2013) but comparable to those reported by Iwegbue *et al*. (2010).

Contamination/pollution Index (CPI): The CPI and multiple pollution index (MPI) of the soil samples in this study are displayed in Figure 2. The CPI of the metals for all sites and depth ranged from 0.63 to 5.63 for Cd, 0.12 to 1.75 for Pb, 0.04 to 0.15 for Cu and 0.14 to 3.64 for Zn. For Cd, 7% of the samples fall within the severe contamination range, 22% each falls within slight pollution and moderate pollution while only one sample falls within the severe pollution range. For Pb, 19% of the samples fall within the slight pollution range while others fall within the contamination range. The CPI of Cr and Ni falls within the contamination range. For Zn, 22% of samples fall into the contamination range while 37% of samples fall into the pollution range. The MPI for all sites and depth ranged from 1.18 to 10.84.

Geoaccumulaton Index (Igeo): The Igeo of these soil profiles from the dumpsites are displayed in Figure 3. The Igeo of Cd ranged from 0.15 to 3.32. Based on the Muller (1969) classification, 7% of the samples fall into unpolluted to moderately polluted (class 2), 22% falls into moderately polluted (class 3), 22% falls into moderately polluted to strongly polluted (class 4) and 4% falls into strongly polluted (class 5). For Pb, only 41% of the samples have a different degree of pollution. For instance, 15%, 11% and 4% of the samples fall into class 2, class 3 and class 4, respectively. Cr, Ni and Fe have Igeo values < 0. Thus, they fall into unpolluted class (class 1). For Cu, 11% fall into class 1 i.e the unpolluted to moderately polluted while for Zn, 11% and 26% fall into class 1 and class 2 respectively.

Enrichment Factor (EF): The EF values of metals in the soils of the dumpsites in this study are shown in Figure 4. The EF values ranged from 1.71 to 21.11, 0.52 to 7.40, 0.05 to 0.23, 0.01 to 0.01, 0.02 to 2.01 and 0.22 to 7.5 for Cd, Pb, Cr, Ni, Cu and Zn respectively. According to Suntherland (2000) and Loska and Wiechula (2003) classification, 48%, 26%, 22% and 4% of the samples falls into the deficiency to minimal enrichment, moderate enrichment, significant enrichment and very high enrichment respectively for Cd. For Pb, 70%, 4% and 4% of the samples falls into the deficiency to minimal enrichment, moderate enrichment and significant enrichment respectively while for Zn, 70%, 19% and 3% of the samples fall into the deficiency to minimal enrichment, moderate enrichment and significant enrichment respectively. Chromium, Ni and Cu have enrichment factors that fall into deficiency to minimal enrichment category for all samples.

Ecological Risk of metals: The potential ecological risk of metals is shown in Table 2. The potential ecological risk of the metals is in the order of Cd > Pb > Cu > Zn > Cr > Ni. The potential ecological risk of the metals except Cd was in the low potential ecological risk category (i. e. < 80). However, Cd has a strong potential ecological risk (> 80) in 48% of the samples. The RI values of these soil profiles ranged from 3.0 to 491. The highest and lowest values were observed at the 30 – 45 cm depth of sites UGH3 and SAP3, respectively. Low ecological risk of metals (RI value < 150), moderate ecological risk of metals (RI values $\geq$ 150 < 300) and strong ecological risk of metal (RI value $\geq$ 300 < 600), were associated with 63%, 19% and 19% of these soils samples respectively with significant contribution from Cd pollution.

Correlation analysis: Pearson correlation coefficients of metals in the dumpsites soils are summarized in Table 3. At the 0 – 15 cm depth in Table 4, significant positive correlation (r^2> 0.50) at 0.01 and 0.05 level of significance were observed between Cr/Cd, Ni/Cd, Pb and Cr, Cu/TOC, Cu/Ni, Zn/Cd, Cr, and Ni, Fe/Cd, Pb, Cr, Ni, Cu and Zn which may suggest a common origin. At the 15 – 30 cm depth, Pb correlated with Cd, Ni correlated with Cd and Pb, Cu correlated with Cd and Pb, while Zn correlated with Cd, Pb, Ni and Cu. Meanwhile, Fe correlated with Pb, Cu and Zn. Similarly, at 30 – 45 cm depth, EC correlated with pH, Pb correlated with Cd, Ni correlated with Cr, Cu correlated with Ni, Zn correlated with Cd, Pb and Cu while Fe correlated with Cr, Ni and Cu. With the exception of

Cu at the 0-15 cm depth, there was no correlation between the metals and TOC. This indicates that TOC has no influence on the metals in these soil profiles.

*Principal Component Analysis (PCA)**:*** PCA was applied to assist in the identification of sources of the metals. The result of the PCA analysis is shown in Table 4. At the 0-15 cm depth, four factors were obtained accounting for 93.07% of the total variance. Factor 1 is dominated by Cd, Cr, Ni, Zn and Fe, accounting for 48.95% of the total variance. This suggests that Cd, Cr, Ni and Zn may be present in the same speciation form in these soils. Factor 2 accounts for 17.09% of the total variance and was dominated by Pb. In this factor, there is moderate loading of Ni. Factor 3 accounts for 15.37% of the total variance and was dominated by TOC and Cu while factor which accounts for 11.66% of the total variance have high loading of electrical conductivity (EC) and moderate loading of Fe. At the 15–30 cm depth, three-component factors accounting for 87.88% of the total variance were observed. Factor 1 which account for 57.30% of the total variance was dominated by Cd, Pb, Ni Cu and Zn. Factors 2 which accounts for 18.79% of total variance high loading of Cu and Fe and a moderate loading of Zn. Factor 3 accounting for 13.79% of the total variance was dominated by EC and Cr. At the 30 – 45 cm depth, three factors were obtained accounting for 84.34% of the total and variance. Factor 1 which accounts for 51.03% of the total variance was characterised by high loadings of Cd, Pb and Zn. Factor 2 which accounts for 21.25% of the total variance was loaded with Cr, Ni, Cu and Fe while factor 3 which accounts for 12.04% of the total variance was dominated by TOC.

Conclusion

The distributions and risk of metals in soils around refuse dumpsites in three urban towns in Delta State were determined in this study. The results of the study showed that the pH and EC of the soils decreased with depth. The pH values indicate that the soils were slightly acidic to neutral while the EC values suggest that there is a significant presence of metal ions or ionisable materials in the soils. There was no regular trend in the TOC values and TOC has no influence on the metals in these soil profiles. The metal contaminations followed the order; Fe > Zn > Pb > Cu > Cr > Ni > Cd. The study indicates that the metals studied except Cd do not pose environmental risk considering their relatively low concentrations.

References

Abbas SH, Ismail IM, Mostafa TM, Sulaymon AH: Biosorption of heavy metals: A review. J Chem Sci Technol 3(4): 74-102. 2014.

Adefemi SO, Awokunmi EE: The impact of municipal solid waste disposal in Ado-Ekiti metropolis, Ekiti State, Nigeria. Afri J Environ Sci Technol 3(8): 186-189. 2009.

Adelekan BA, Alawode AO: Contributions of municipal refuse dumps to heavy metals concentrations in soil profile and groundwater in Ibadan Nigeria. J Appl Biosci 40: 2727 – 2737. 2011.

Adie GU, Osibanjo OO: Assessment of soil pollution by slag from an automobile battery manufacturing plant in Nigeria. Afri J Environ Sci Technol 3(9): 239 – 250. 2009.

Akpoveta OV, Osakwe SA, Okoh BE, Otuya BO: Physicochemical characteristics and levels of some heavy metals in soils around metal scrap dumps in some parts of Delta State, Nigeria. J Appl Sci Environ Manage 14(4): 57– 60. 2010

Amadi AN: Assessing the effects of Aladimma dumpsite on soil and groundwater using water quality index and factor analysis. Aust J Basic Appl Sci 5(11): 763-770. 2011.

Amos-Tautua BMW, Onigbinde AO, Ere D: Assessment of some heavy metals and physicochemical properties in surface soils of municipal open waste dumpsite in Yenagoa, Nigeria. Afri J Environ Sci Technol 8(1): 41-47. 2013.

Amusan AA, Ige DV, Olawale R: Characteristics of soil and crop uptake of metals in municipal waste dumpsites in Nigeria. J Human Ecol 1(2): 167-171. 2005.

Arias ME, Gonzalez-Perez JA, Gonzalez-villa FJ, Ball AS: Soil health: A new challenge for microbiologists and chemists. Int Microbiol 8: 13-21. 2005.

Athalye RP, Mishra V, Quadios G, Ullal V, Gokhale KS: Heavy metals in the abiotic and biotic components of Thane Creek, Indian Pollut Res 18(3): 329 - 333. 2001.

ATSDR: TOXFAQs for copper. Retrieved from http://www.atsdr.cdc.gov/tfacts/ 32.html on December 12th 2019. 2006

Bishop PL: Pollution prevention: Fundamentals and practice. McGraw-Hill Companies Inc., U.S.A., pp. 67-89. 2000

Chengo K, Murungi J, Mbuvi H: Speciation of chromium and nickel in open-air automobile mechanic workshop soils in Ngara, Nairobi, Kenya. World Environ 3(5): 143-154. 2013.

DPR (Department of Petroleum Resources): Environmental guidelines and standards for the petroleum industry in Nigeria (revised edition). Department of Petroleum Resources, Ministry of Petroleum and Natural Resources, Abuja, Nigeria. 2002

European Commission: Heavy metals in waste. Project Env. E. 3/ETU.2000/0058. Final Report. 2002.

Hakanson L: An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res, 14: 975–1001. 1980.

Igwe JC, Nnorom IC, Gbaruko BC: Kinetics of radionuclides and heavy metals behaviour in soils: Implications for Plant growth. Afr J Biotechnol 4(13): 1541-1547. 2005.

Iwegbue CMA, Beecroft OV, Ogala JE, Egobueze FE, Tesi GO, Nwajei GE, Martincigh BS: Concentrations and ecological risks of metals in surface sediments of some coastal creeks in the Niger Delta, Nigeria. Afr J Aquatic Sci 43(3): 241-253. 2018.

Iwegbue CMA, Nwajei GE, Ogala JE, Overah LC: Determination of trace metal concentrations in soil profiles of municipal dumps in Nigeria. Environ Geochem Health, 32: 415-430. 2010.

Lacatusu R: Appraising levels of soil contamination and pollution with heavy metals. In: Land information system for planning the sustainable use of land resources. HJ Heinike, W Eckrelman, AJ Thomasson, RJA Jones, L Montanarella and B Buckley (eds). European Soil Bureau Research Report No 4, Office for Official Publication of the European Communities, Luxembourg, pp. 393 – 402. 2000.

Lenntech: Toxicological effects of copper. Retrieved from http://www.lenntech.con/ periodic-chart-elements/Cu-en.htm 2008

Loska K, Wiechula D: Application of principle components analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere 51: 723-733. 2003.

Muller G: Index of geoaccumulation in sediment of the Rhine River. Geol J 2: 108-118. 1969.

Nduka JK, Anyakora C, Obi E, Obumselu FO, Ezenwa TE, Ngozi-Olehi LC: Polyaromatic hydrocarbons (PAHs) and inorganic chemical contaminants at refuse dumpsites in Awka, South Eastern Nigeria: A public health implication. J Sci Res Reports 2(1): 173-189. 2010.

Nwajei GE, Iwegbue CMA, Okafor MI: Heavy metals in surface soils under waste dumps from Onitsha, Nigeria. J Biol Sci 7(2): 405-408. 2007.

Odu CTI, Esurosu OF, Nwaboshi IC, Ogunwale JA: Environmental study (soil and vegetation) of Nigeria Agip oil company operation area. A report submitted to Nigeria Agip Oil Company Limited, Lagos, Nigeria. pp 102-107. 1985.

Odukoya AM, Abimbola AF, Lawal O: Potential soil contamination with toxic metals in the vicinity of active and abandoned dumpsites. Agric Biol J North Am 2(5): 785 – 790. 2011.

Ogbeibu AE, Chukwurah NA, Oboh IP: Effects of open waste dump-site on its surrounding surface water quality in Ekurede-Urhobo, Warri, Delta State, Nigeria. Nat Environ 1: 1-16. 2013.

Ogbemudia FO, Mbong EO : Soil reaction (pH) and heavy metal index of dumpsites within Uyo municipality. Merit Res J Environ Sci Toxicol 1(4): 082-085. 2013.

Ogbonna DN, Kii BL, Youdeowei PO: Some physicochemical and heavy metal levels in soils of waste dumpsites in Port-Harcourt Municipality and crunons. J Appl Sci Environ Manage 13(4): 65-70. 2009.

Ogundele, DT, Bodunde VT, Bale AT: Assessment of heavy metal pollution of waste dump sites in Kwara State using *Carica Papaya, Musa Spp* and *Cocorhrous Olitorous* as indicators. IOSR J Environ Sci Toxicol Food Technol 6(2): 01-04. 2013.

Okalebo JR, Gathma KW, Woomer PL: Laboratory methods of soil and plant analysis: A working manual tropical soil biology and fertility program. TSBF Institute, Nairobi, Kenya. 1993.

Ontario Online: Copper in the environment. Retrieved from http://www.ene.Gov.on.ca/ cons/4141e.htm. 2006

Osakwe SA: Distribution of heavy metals in soils around automobile dumpsites in Agbor and environs, Delta State. J Chem Soc Ethiopia *35*(1): 53-60

Osakwe SA: Chemical partitioning of iron, cadmium, nickel and chromium in contaminated soils of South-Eastern Nigeria. Res J Chem Sci *2*(5): 1-9. 2012

Osakwe SA: Heavy metal contamination and physicochemical characteristics of soils from automobile workshops in Abraka, Delta State, Nigeria. Int J Nat Sci Res *2*(4): 48-58. 2014

Oviasogie PO, Omoruyi O, Okoro D, Ndiokwere CL: Evaluation of physicochemical properties and distribution of Pb, Cd, Cr and Ni in soils and growing plants around refuse dumpsites in Akure, Nigeria. Afr J Biotechnol *8*(12): 2757-2762. 2009.

Radojevic M, Bashkin VN: Practical environmental analysis. Royal Society of Chemistry, Cambridge, UK. 1999.

Reimann C, De Caritat P: Intrinsic flaws of element enrichment factor (EF's) in environmental geochemistry. Environ Sci Technol 34: 5084-5091. 2000.

Sutherland RA: Bed sediment associated trace element in urban stream Oahu, Hawaii, Environ Geol 39: 361-627. 2000.

Turekian KK, Wedepohl KH: Distribution of the elements in some major units of earth crust. Bull Geol Soc Am, 72: 175-192. 1961.

Ubuoh EA, Akande SOC, Akhionbare SMO: Assessment of wood waste dumpsite on dynamics of soil physiochemical characteristics in Njoku timber market, Imo State, Nigeria. Int J Multidiscip Sci Engineer 3(2): 1-4. 2012.

Vukojevic V, Sabovljevic M, Sabovljevic A, Mihajlovic N, Dragzic G, Vucinic Z: Determination of heavy metal deposition in the county of Obrenovac (Serbia) using mosses as bio-indicators II: Cadmium (Cd), Cobalt (Co), and Chromium (Cr). Arch Biol Sci 58(2): 95 – 104. 2006