https://dx.doi.org/10.4314/ijs.v22i3.10

GEOCHEMICAL ASSESSMENT OF HEAVY METAL IMPACT ON SOIL AROUND EWU-ELEPE DUMPSITE, LAGOS STATE, NIGERIA

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(Received: 27th August, 2020; Accepted: 24th April, 2020)

ABSTRACT

The concentrations of certain heavy metals in the top soils around the Ewu-Elepe dumpsite and its environs were determined with a view to ascertaining the level of metal pollution in the soils of the dumpsite vicinity. Thirty-two (32) soil samples were randomly collected within the dumpsite vicinity and one control sample was collected from a distance of about 9.0 km from the dumpsite. The samples were prepared according to standard procedures and analyzed for some heavy metals (Ni, Mn, Co, Cd, Cu, Pb, and Zn) using the Atomic Absorption Spectrophotometer at the Geochemistry Laboratory of the Department of Geology, Obafemi Awolowo University, Ile-Ife. The geochemical data was subjected to both univariate and multivariate statistical treatments and comparisons were made with various world standards. The results obtained showed that the mean concentrations of Ni (12.00 ppm), Mn (525.60 ppm), Co (5.64 ppm), Cu (44.59 ppm), and Zn (105.28 ppm) were within the acceptable limits for agricultural soils while those of Cd (1.40 ppm) and Pb (33.74 ppm) exceeded the limits. Geo-accumulation index and contamination factor revealed that the soils around the dumpsite were moderately contaminated with Cd and slightly contaminated with Pb. The overall decreasing order of heavy metal concentration in the dumpsite soil is: Cd > Pb > Zn > Cu > Mn > Co > Ni. The study concluded that the soils around the Ewu-Elepe dumpsite was contaminated with Cd and Pb and as such should be discouraged in its usage for agricultural related purposes as these highly toxic trace elements can be absorbed by plants. A well-engineered landfill that takes into consideration the local geology and the topography of the area should be designed so as to prevent infiltration of leachates into the soil and shallow groundwater systems.

Keywords - Heavy metals, Soil, Ewu-Elepe, Nigeria, Dumpsite, Contamination.

INTRODUCTION

Solid waste collection and disposal have always being a universal problem. However, developed countries have found a way around their solid waste management problems while developing countries are still battling with theirs (Arneth *et al.,* 1989; Adewole, 2009; Ogunseiju, 2014). Waste is most of the time contained in landfills with impermeable bottom liner and leachate collection centers to prevent environmental pollution in the developed countries, while open dumps are the most common methods of waste disposal in developing countries of the world. The reason why the open dump systems of waste management are being operated in developing countries is due to technical, financial, complex and the expensive engineering system involved in setting up a sanitary landfill (Ogunseyiju, 2014). Large population and obsolete techniques used in waste management complicate the problem in developing country.

Waste disposal in landfills is an integral part of waste management strategy around the world. The production of by-products of organic and inorganic decomposition known as leachates in landfills pose a serious threat if released to the environment (Arneth *et al.,* 1989; Kjeldsen, 1993). Physical, chemical and microbial processes are usually involved in the release of pollutants from the wastes into the environment (Kimmel and Braids, 1974). Leachates when released into the underlying groundwater forms a contaminant plume that can alter the physical, chemical and microbial properties of groundwater (Baedecker and Back; 1979; Ogunseiju, 2014). The result of mass transfer processes of contaminants into the leaching water percolating through the waste layer is described as leachate pollutant.

Solid waste and sewage generation and their poor disposal mechanism in urban areas of most developing countries have become an inherent threat to the environment. Open dumps are usually sited in reserved areas such as outskirts of towns far from residential areas, but with the upsurge in cities population as a result of rural-urban migration, these reserved areas are being occupied by people thereby increasing the possibility of cities pollution and its attendant impacts on the populace. Most open dumpsites in the developing countries operate without appropriate impermeable bottom liner; effective leachate collection centre and subsequent treatment system, which combine to worsen the leachate problem. This is typical of Ewu-Elepe dumpsite in Ginti Estate, Ikorodu, Lagos State, Nigeria.

Solid wastes are materials which are discarded after it has served its purpose or are no longer useful, while industrial wastes are usually by-product or end-product of materials from large scale production factories and industries (Awomeso *et al.,* 2010). Numerous biochemical reactions occur within waste bodies leading to production of landfill gas and leachates, which contribute to the pollution of air, water, and soil.

Several studies have shown that municipal and industrial wastes in open dumps may increase the heavy metal concentrations in soils and groundwater (Carlson and Ole*,* 1976; Okoronkwo *et al.,* 2005) which may have effects on the host soils, crops, and human health (Smith *et al.,* 1996). According to literatures, there exists transfer of heavy metals from contaminated soils to plants and from plants to animals with subsequent transfer through the food chain up to man (Oskarson et al., 1972); Ojo, 2013; Adesiyan, 2018). Thus, the environmental impacts of leachates emanating from dumpsites are greatly complicated by their heavy metal contents. Although, heavy metals are naturally present in the soil, geologic and anthropogenic activities increase the concentration of these elements. Ademoroti (1990) established that there is a positive linear correlation between heavy metals (Cd, Pb, and Ni) in the soil and the crops grown on it.

The Ewu-Elepe dumpsite is situated within a residential estate in which subsistence farming is largely practised. Heavy metals are of grave negative effects to plants, animals and humans when it is above acceptable limits. Non biodegradable materials deposited in the dumpsite cause these metals to accumulate thereby posing major health risks to humans. This study undertaken at the Ewu-Elepe dumpsite was to evaluate the pollution status of the area around the dumpsite with respect to its soil heavy metal contents and thereby determine whether the dumpsite environment was polluted to the point that was inimical to the biological species inhabiting the dumpsite environment.

MATERIALS AND METHODS

Geology, Description of the Study Area and Sampling

The study area, Ewu-Elepe dumpsite is situated in Ginti Estate, Ewu-Elepe off Ijede road, Ikorodu Local Government Area of Lagos State, Nigeria. It lies between Latitudes 06° 35' and 06° 36' North of the equator and Longitude 003° 34^1 and 003°35^1 East of the Greenwich (Fig. 1a). It is about eight (8) hectares and has been in operation since November 2008 till date.

The study area is located within the Eastern Dahomey Basin. The Dahomey Basin extends from southeastern Ghana in the West, through Southern Togo and Southern Benin Republic (formerly Dahomey) to Southwest Nigeria. The geologic succession in Lagos spans through the cretaceous Abeokuta Formation, which unconformably overlies the rocks of the basement complex to the Quaternary Deltaic Plain Sands (Obiora and Onwuka, 2005). Ikorodu is directly underlain by the Benin Formation (Fig. 1b), which consists predominantly of sands, sandstone with thin lenses of clays and shales. The study area consists predominantly of coastal sands and river alluvium. The Benin Formation consists of yellow and white, sometimes cross-bedded sand, pebbly beds and clays with some sandy clay lenses. The thickness is unknown except in the Niger Delta, where it is about 2,000 meters thick (Merki, 1972). It also contains plant remains in addition to planktonic foraminifera, which have been recovered from its lower part offshore; and these indicate a Miocene age. Its upper part is believed to be Pliocene to Recent.

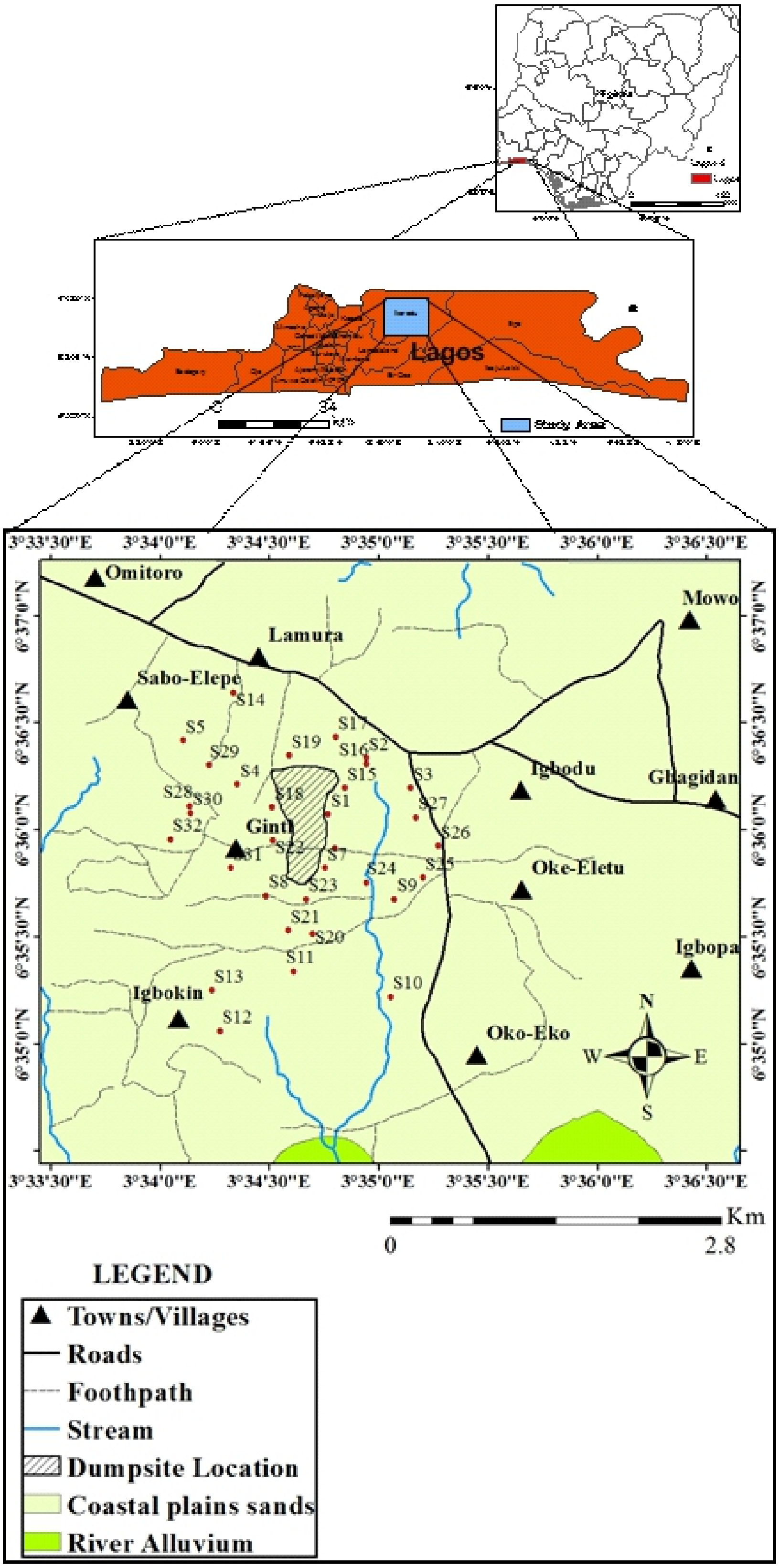


Figure 1: Map of Nigeria and the Administrative Map of Lagos State showing Ikorodu, The study Area (a) and the Geological Map of Ikorodu Area showing the Ewu-Elepe Dumpsite and Sampling Points (b)

Sample Collection, Treatments and Instrumental Analysis

A total of thirty-three (33) surface soil samples were collected; thirty-two (32) of which were from within the vicinity of the dumpsite, while one (1) control sample was collected at a distance of about 9.0 km from the dumpsite (Fig. 1b). The materials used during the sampling exercise include topographic map, Global Positioning System (GPS), sample bags, plastic scoop, rubber gloves, permanent marker, paper tape, hand auger, hammer, and safety boots. The soil samples were collected by means of a 20 cm steel pipe (auger). The auger was driven into the earth by applying pressure using a hammer. The soil sample was then scooped out using a plastic scoop and placed in a sample bag made of buff material, which was appropriately labeled and the GPS coordinates duly taken. The auger was cleaned after each sample collection, while the labeled soil sample bags were sealed and transported to the laboratory for analyses.

Sample Preparation and Analysis

The soil samples in the sealed buff sample bags were first left in the laboratory to dry under room temperature for 21 days. The dried samples were then disaggregated using mortar and pestle and then sieved using a 177µm pore size sieve. The sieved samples were put in prescription sachets and labeled accordingly. The mesh was thoroughly cleaned after each sample was sieved to prevent cross-contamination. Using a metlar digital weighing balance, 1.0 g each of the sieved samples was weighed into a clean conical flask and partial digestion of the sample using aqua regia (a combination of HCl and HNO_3 in a ratio of 3:1) was carried out as follows. The sample in the conical flask was moistened with 2 drops of distilled water and 10 mls of aqua regia was added to each inside the fume cupboard. The conical flask containing the mixture was then placed on a hotplate in the fume cupboard and heated to volatilize until about 2 mls of the mixture was left in the flask. After this, the conical flask was removed from the hotplate and left to cool down inside the fume cupboard. The thus digested sample was then filtered into a 50ml volumetric flask and distilled water was added to the filtrate in the flask to make up to the mark. The final solution was then poured into the sample bottle and labeled. The resulting extractants were later analyzed for Co, Cu, Cd, Zn, Pb, Mn and Ni using the Atomic Absorption Spectrophotometer (AAS) (Varian Spectra AA 55B) at the Geochemistry Laboratory of Geology Department, Obafemi Awolowo University, Ile-Ife. Standard solutions used to produce working calibration curve were prepared for each element from their stock solutions.

RESULTS AND DISCUSSION

The results of the geochemical analysis are presented in Table 1. Table 2 shows the summary of statistical parameters of heavy metal concentrations (ppm) in the soil samples. Generally, the results obtained from the study shows that soil samples from the vicinity of Ewu-Elepe dumpsite have higher metal concentrations when compared with the control sample (Table 1). The mean concentrations of the heavy metals in ppm are as follows: Ni = 12.00, Mn = 525.60, Co = 5.64, Cd = 1.40, Cu = 44.59, Pb = 33.74 and Zn = 105.28 (Table 2). The mean concentrations of Cu, Zn, Pb and Cd in the study area revealed their enhanced concentrations when compared with US average and world average while Ni and Mn were lower. There were no stipulated values for Co concentrations to be compared with.

The results also showed variations in the distribution of the elements and this are revealed in the frequency plots (Figures 3a & 3b). The distribution of all the elements in the soil samples had obvious breaks except for manganese and the breaks implied that there were absences of elements in some concentrations and this in turn indicated that the metals were not evenly distributed in the soils. The plot of manganese data without breaks implied that Mn was present in all the samples and was thus evenly distributed. All the heavy metals except Zn and Ni were positively skewed with respect to the mode. Positive skewness implies that the values are asymmetrical to the frequency distribution while negative skewness implies that the values are distorted.

There was a strong positive correlation between Zn and Pb (0.752), Pb and Cu (0.719) and between Cu and Cd (0.914). A fairly positive correlation exists between Cu and Mn (0.684), Pb and Mn (0.630), Cd and Ni (0.574), Cd and Mn (0.582), Cu and Ni (0.580), Pb and Cd (0.572), Zn and Mn (0.581), Zn and Cu (0.568) and between Zn and Cd (0.476) (Table 3). This indicates that the heavy metals were likely to be closely associated or from similar sources.

Table 1: Heavy Metal Concentrations (ppm) of Soil Samples from the Ewu-Elepe Dumpsite

Location	**Ni**	**Mn**	**Co**	**Cd**	**Cu**	**Pb**	**Zn**
1	BDL	437.70	7.50	1.20	0.05	29.65	137.74
2	9.06	63.57	0.50	0.35	7.50	16.94	30.97
3	19.50	118.33	BDL	0.60	14.20	23.62	42.92
4	12.70	134.15	BDL	0.80	11.30	20.58	40.36
5	12.96	494.65	2.50	1.05	43.40	35.26	140.99
6	12.60	207.69	1.05	0.75	23.60	20.36	135.85
7	13.10	138.59	0.60	0.40	2.40	19.37	48.54
8	8.52	198.20	BDL	0.30	13.25	2.88	39.31
9	8.10	247.37	0.55	0.35	12.75	15.68	27.34
10	6.57	752.10	0.70	0.60	13.10	16.11	37.11
11	6.11	515.31	0.75	0.35	11.50	13.98	30.65
12	11.18	243.42	BDL	0.40	13.05	16.89	32.25
13	15.22	233.84	0.50	0.50	17.90	18.46	38.10
14	19.67	224.39	0.45	0.40	16.15	21.49	41.09
15	16.07	1084.75	4.00	2.20	119.3	63.48	143.41
16	10.87	476.97	3.60	0.95	50.45	49.61	147.90
17	13.28	985.23	5.35	1.65	56.70	50.83	151.79
18	8.55	599.59	2.45	0.95	50.00	50.77	144.94
19	16.19	729.45	2.75	1.25	71.45	63.71	142.04
20	10.44	669.78	3.65	0.70	54.15	32.99	137.01
21	11.17	1207.08	4.00	1.55	54.10	48.64	140.58
22	5.59	409.70	4.05	1.30	70.20	35.16	146.25
23	15.24	1208.46	5.35	1.40	40.70	31.68	139.76
24	12.77	532.99	2.90	2.10	26.95	25.93	143.11
25	4.05	486.24	3.05	0.50	22.80	20.41	82.42
26	16.58	510.08	3.95	1.10	38.35	33.77	146.27
27	9.84	284.68	2.15	1.05	27.20	29.71	146.96
28	13.35	924.40	4.10	5.45	147.50	31.90	143.78
29	10.34	388.78	1.45	1.90	50.60	46.33	144.96
30	11.12	437.07	4.55	2.80	65.85	57.20	144.39
31	11.25	666.72	110.10	1.80	64.20	65.64	149.32
32	32.44	1207.18	7.40	8.40	216.45	71.01	150.29
33 (Control)	4.87	295.57	0.95	0.45	8.65	17.30	61.12

BDL – Below Detection Limits

Table 2: Statistical Summary of Heavy Metal Concentrations (ppm) in Soil Samples (N = 32) of Ewu-Elepe Dumpsite vicinity compared with U.S Average, World Average and Excessive level of Heavy Metals in Soils; after Adriano (1992) and Limit Values of Heavy Metal Concentrations for East Germany Soils; after Machelett *et al* (1993)

Elements	Min	Max	Standard Deviation	Threshold	Mean (This Study)	USA	WA	EL	LV
Ni (ppm)	0.00	32.44	5.72	23.44	12.00	20	40	100	50
Mn (ppm)	63.57	1208.46	338.50	1202.60	525.60	560	850	1500	--
Co (ppm)	0.00	110.10	19.25	44.14	5.64	--	--	--	--
Cd (ppm)	0.30	8.40	1.62	4.64	1.40	0.5	0.03	5	3
Cu (ppm)	0.05	216.45	45.33	135.25	44.59	25	20	100	100
Pb (ppm)	2.88	71.01	17.80	69.34	33.74	20	10	200	100
Zn (ppm)	27.34	151.79	51.43	156.71	105.28	54	50	250	300

USA: US Average of Heavy Metals in Soils
WA: World Average of Heavy Metals in Soils
EL: Excessive Level of Heavy Metals in Soils
LV: Limit Values of Heavy Metal Concentrations for East Germany Soils.

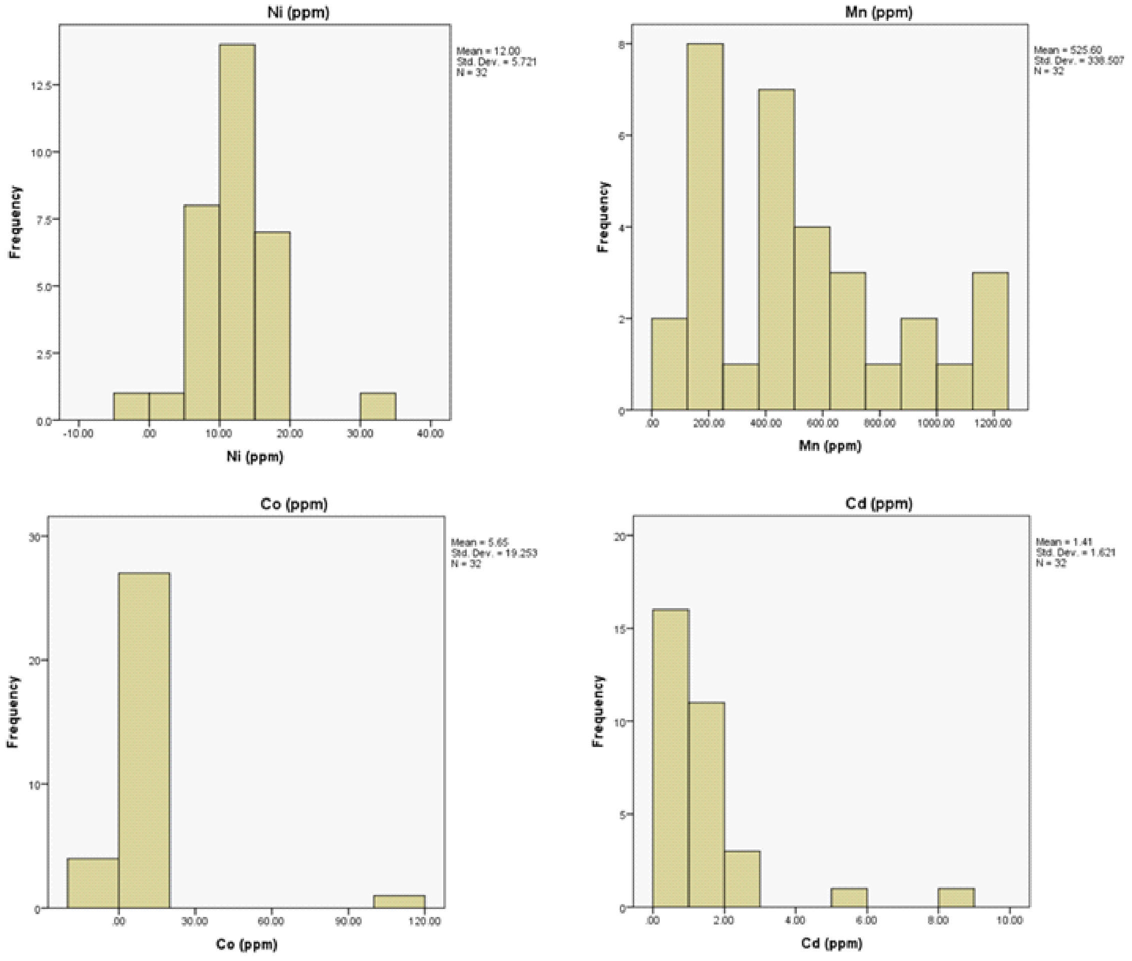


Figure 3a: Frequency Distribution of Ni, Mn, Co and Cd in Soil Samples from the Study Area

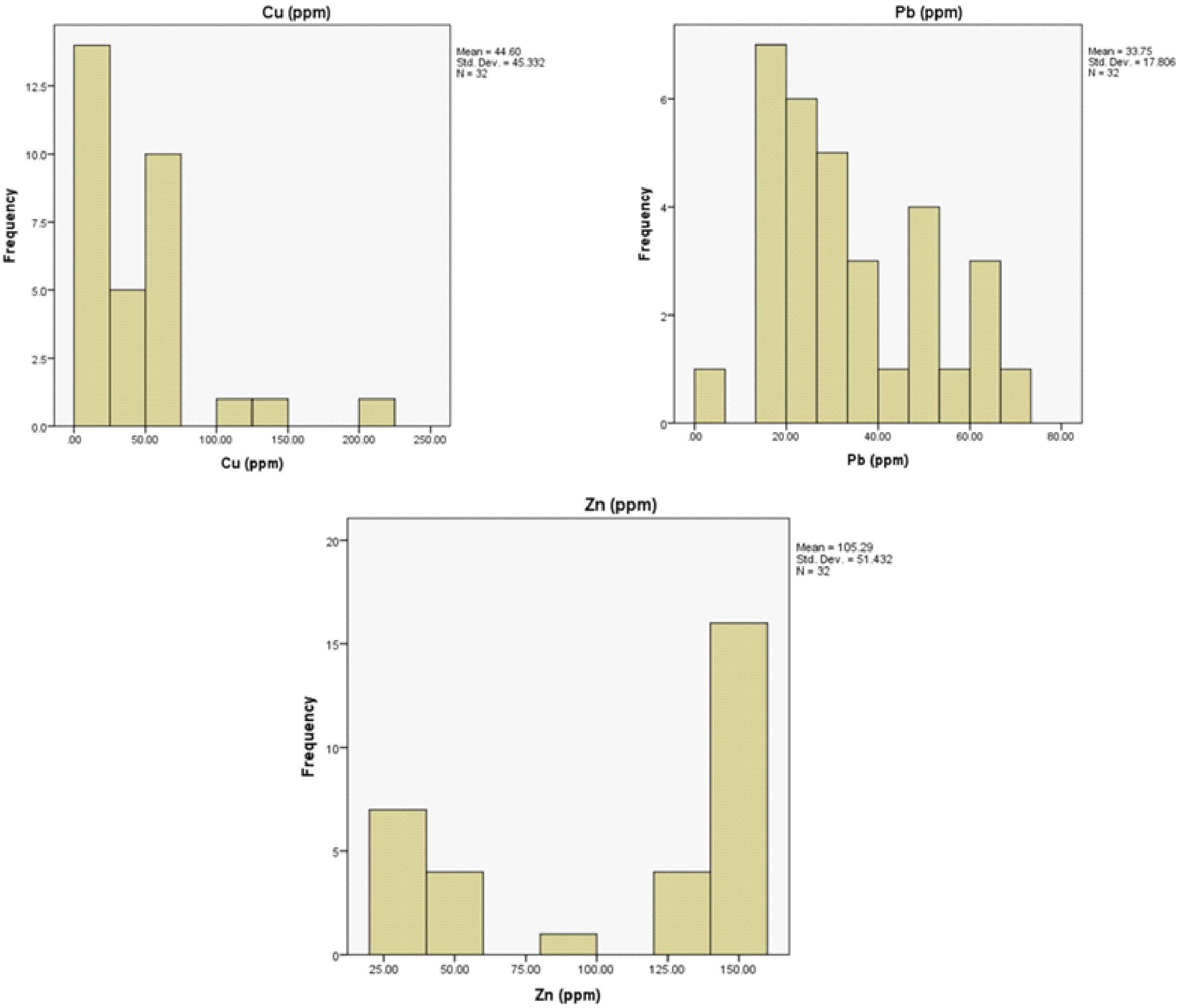


Figure 3b: Frequency Distribution of Cu, Pb and Zn in Soil Samples from the Study Area.

Table 3: Correlation Matrix for Geochemical Data of Soil Samples from the Study Area

	Ni	Mn	Co	Cd	Cu	Pb	Zn
Ni	1						
Mn	0.291	1					
Co	-0.024	0.170	1				
Cd	0.574*	0.582*	0.119	1			
Cu	0.580*	0.684*	0.155	0.914**	1		
Pb	0.382	0.630*	0.404	0.572*	0.719**	1	
Zn	0.109	0.581*	0.257	0.476*	0.568*	0.752**	1

****** Strong positive correlation
* Fairly positive correlation

Contamination Factor (CF) and Geo-accumulation Index (I_{geo})

Contamination Factor (CF) and Geo-accumulation Index (I_{geo}) are used to assess the level of soil contamination and /or pollution. The CF is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani *et al.,* 2004). It is expressed as:

$CF = C_{metal} / C_{background}$

Where:

CF is contamination factor;

C_{metal} is the mean concentration of metal in soil and

$C_{background}$ is the background concentration (value) of metal either taken from the literature (average crustal abundance) or directly determined from a geologically similar material.

In this study, the average crustal abundance of elements in an uncontaminated soil used as the background concentration value is from Dineley *et al.* (1976). The contamination factor is classified into four descriptive classes (Table 4a). Table 4b shows the contamination factor of the soil samples within and around the dumpsite.

Geo-accumulation Index (I_{geo}) is a common criterion used to evaluate the heavy metal pollution in soils and sediments. It was proposed by Muller (1979) to determine metal contamination in sediments, by comparing current concentrations with pre-industrial levels. It is expressed as:

$$I_{geo} = \ln [C_{metal} / 1.5 * C_{background}]$$

Where:

I_{geo} is geo-accumulation index;

C_{metal} is the mean concentration of metal in soil and

$C_{background}$ is the background concentration (value) of metal either taken from the literature (average crustal abundance) or directly determined from a geologically similar material.

Table 4a: Descriptive Classes of the Contamination Factor

CF	**Description**
CF<1	Low degree of contamination
1<CF<3	Moderate degree of contamination
3<CF<6	Considerable degree of contamination
CF>6	Very high degree of contamination

Source: Hakanson (1980)

Table 4b: Contamination Factor of Metals in Soils from the Dumpsite

Elements	**C_{metal}**	**$C_{background}$**	**CF**	**Description**
Ni	12.00	80	0.15	Low degree of contamination
Mn	525.60	1000	0.53	Low degree of contamination
Co	5.64	23	0.25	Low degree of contamination
Cd	1.40	0.15	9.33	Very high degree of contamination
Cu	44.59	70	0.64	Low degree of contamination
Pb	33.74	I6	2.1	Moderate degree of contamination
Zn	105.28	132	0.79	Low degree of contamination

The factor 1.5 (a constant) is incorporated in the relationship to account or possible variation in background data due to lithogenic effect. The geo-accumulation index (I_{geo}) scale consists of seven grades ranging from unpolluted to highly polluted (Table 5a). Table 5b shows the geo-accumulation index in soils within and around the dumpsite. The summary of metal contamination and geo-accumulation indexes of the study area is presented in Table 6.

Table 5a: Muller's Classification for the Geo-accumulation Index (I_{geo})

I_{geo} Value	Sediment Quality
≤ 0	Unpolluted
0-1	From unpolluted to moderately polluted
1-2	Moderately polluted
2-3	From moderately polluted to strongly polluted
3-4	Strongly polluted
4-5	From strongly to extremely
>6	Extremely polluted

Source: Loska *et al* (2003)

Table 5b: Geo-accumulation Index (I_{geo}) in Soils from Ewu-Elepe Dumpsite

Elements	C_{metal}	$C_{background}$	I_{geo}	Description
Ni	12.00	80	-2.30	Unpolluted
Mn	525.60	1000	-1.05	Unpolluted
Co	5.64	23	-1.81	Unpolluted
Cd	1.40	0.15	1.83	Moderately polluted
Cu	44.59	70	-0.86	Unpolluted
Pb	33.74	I6	0.3	From unpolluted to moderately polluted
Zn	105.28	132	-0.63	Unpolluted

Table 6: Metal Contamination Factor and Geo-accumulation Index of Metals in Soil from Ewu-Elepe Dumpsite

Parameters	C_m	B_m	CF	I_{geo}	Summary of Contamination
Ni	12.00	80	0.15	-2.30	Uncontaminated
Mn	525.60	1000	0.53	-1.05	Uncontaminated
Co	5.64	23	0.25	-1.81	Uncontaminated
Cd	1.40	0.15	9.33	1.83	Moderately contaminated
Cu	44.59	70	0.64	-0.86	Uncontaminated
Pb	33.74	16	2.1	0.3	Slightly contaminated
Zn	105.28	132	0.79	-0.63	Uncontaminated

Using the Hakanson, (1980) classification table of Contamination Factor (Table 4a), it can be seen as presented in Table 4b that Ni, Mn, Co, Cu and Zn has low degree of contamination in the surface soils of the study area, while Pb has a moderate degree of contamination and Cd has very high degree of contamination. On the other, hand using Muller's (1979) classification for the geo-accumulation index (I_{geo})(Table 5a), it can be seen as presented in Table 5b that the same Ni, Mn, Co, Cu and Zn falls into unpolluted class in the soils, while Pb belongs to the unpolluted to moderately polluted class and Cd belongs to the moderately polluted class.

Distribution of Metals in the Soils of the Study Area

Table 7 shows the average abundance of selected heavy metals in the earth crust for various rocks (Levinson, 1974), compared with the mean values of the heavy metals in this study.

Nickel

Nickel is a siderophile metallic element with chalcophilic and lithophilic affinities (Kabata-Pendias and Pendias, 2001).

In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicate minerals, detrital primary Fe oxides, hydrous Fe and Mn oxides, and clay minerals. It is concentrated in shale (up to 90 ppm) relative to greywacke (*ca.* 40 ppm), quartzitic sandstone (*ca.* 20 ppm) and limestone (<5 mg ppm). Mielke (1979) cites levels of Ni in shale, sandstone and carbonate rocks as 68, 2 ppm, and 20 ppm, respectively.

Anthropogenic sources of Ni include fertilizers, steel works, metal plating and coinage, fuel combustion and detergents (Reimann and de Caritat 1998). In the presence of some organic complexing agents, Ni is capable of forming neutral or negatively charged complexes, making the metal highly mobile in relation to other trace elements. Consequently, Ni concentrations may be high in soil contaminated by sewage and leachate from waste pits. Nickel is highly mobile under acidic, oxidizing conditions (Kabata-Pendias and Pendias, 2001).

Nickel has been shown to be essential for microorganisms and has been implicated as having an essential role in human metabolism (McGrath, 1995). The World Health Organisation recommends a daily intake of 10 μg day^{-1} for humans (WHO, 1996). Nickel deficiency retards growth and impairs iron uptake. Most Ni^{2+} compounds are relatively non-toxic, but some compounds are highly toxic, and extreme excesses of Ni are both toxic, causing dermatitis and gastric irritation, and carcinogenic illnesses (WHO, 1996).

Table 7: Average Abundance of Selected Heavy Metals in the Earth Crust for various Rocks (Levinson, 1974)

Heavy Metals	Earth crust	Ultramafic	Basalt	Granodiorite	Granite	Shale	Limestone	Soil	This Study
Ni (ppm)	75	2000	150	20	0.5	70	12	5-500	12.00
Mn (ppm)	950	1300	2200	1200	500	850	1100	850	525.60
Co (ppm)	25	150	50	10	1	20	4	1-40	5.64
Cd (ppm)	0.2	--	0.2	0.2	0.2	0.2	1	--	1.40
Cu (ppm)	55	10	100	30	10	50	15	2-100	44.59
Pb (ppm)	12.5	0.1	5	15	20	20	8	2-200	33.74
Zn (ppm)	70	50	100	60	40	100	25	10-300	105.28

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.

In the present study, Ni was detected in all the 33 samples with concentration values ranging from BDL to 32.44 ppm and a mean value of 12.00 ppm. The background values vary from 0.00 to 23.44 ppm. An anomalous value of 32.44 ppm was recorded in sample 32. Figure 4a show the distribution of Ni within and around the dumpsite. The concentration values of Ni in samples from the dumpsite when compared to Adriano's U.S and World averages and Machelett's limits (Table 2) showed that the mean value of Nickel is lower than Adriano's excessive levels. However, the concentration of Ni in sample 32 is above Adriano's U.S average. Comparing the mean value of Ni with the average abundance present in shale and soils (Table 7), the concentrations of Nickel in surface soils of the study area were significantly low and thus pose no health risk to the inhabitants of the area.

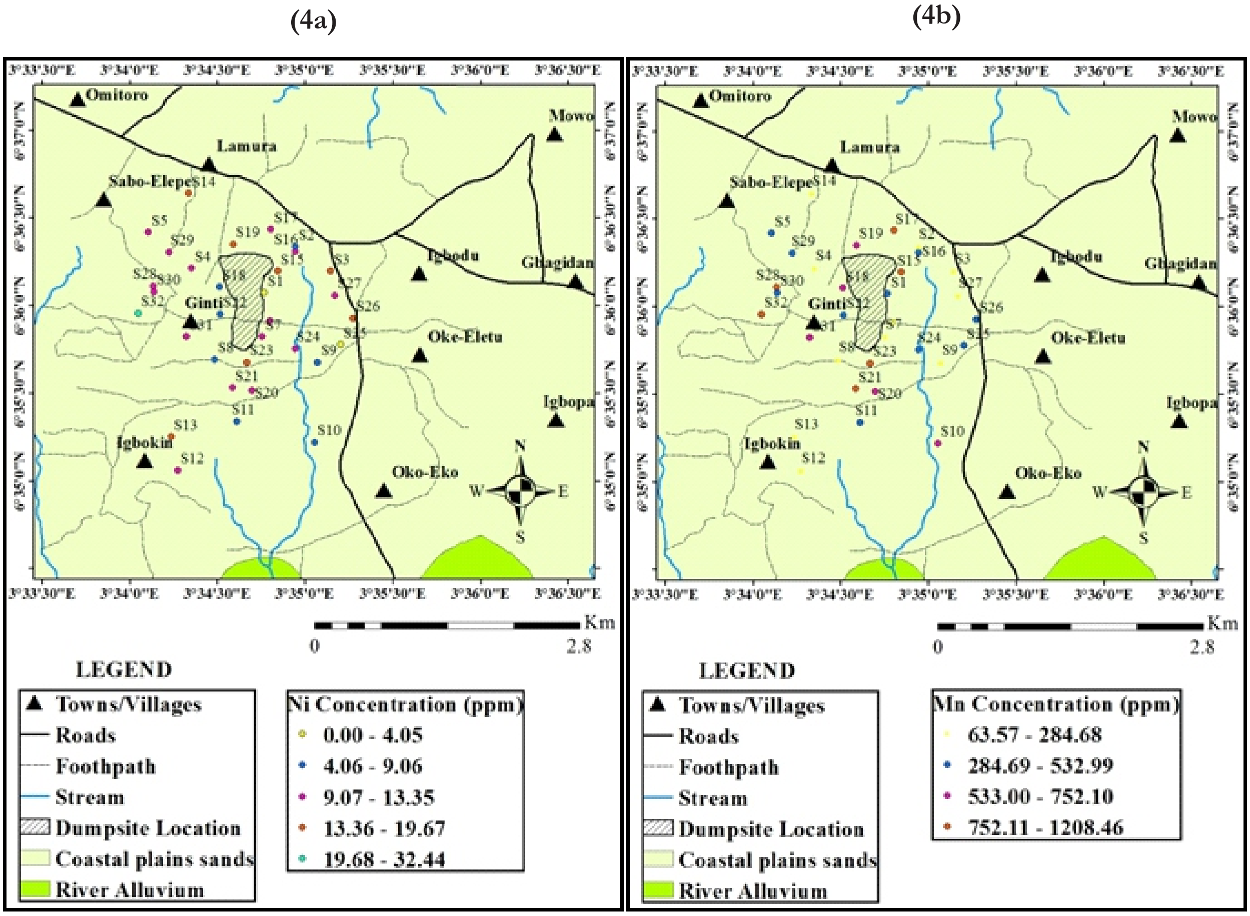
Manganese

Manganese (Mn) is relatively abundant in the Earth's crust with an average upper crustal abundance of 600 ppm and a bulk continental crust average of 1400 ppm (McLennan and Taylor, 1999). It is a common lithophile element. The Mn content of sedimentary rocks is controlled by the geochemistry of the source rock and the redox conditions of the depositional environment (Wedepohl, 1978).

Manganese may occur in detrital phases such as mafic silicates, magnetite and ilmenite, but the largest proportion is typically held in secondary Mn^{4+} oxides that form either discrete concretions or surface coatings on primary minerals and lithic fragments. Shale and greywacke generally have higher levels of Mn (*ca.* 700 ppm) relative to coarser quartzitic sandstone and grits (*ca.* 170 ppm). Carbonate rocks, particularly dolomite, may also contain high concentrations of Mn, on average *ca.* 550 ppm (Wedepohl, 1978).

Anthropogenic sources of manganese include mining and smelting, engineering, traffic and agriculture. It is also used in the manufacture of steel, glass, dry batteries and chemicals. Permanganate is a powerful oxidizing agent and is used in quantitative analysis and medicine.

Manganese was detected in all 33 samples, ranging in concentration values from 63.47 ppm to 1208.46 ppm, with a mean value of 525.60 ppm. The background values vary from 63.47ppm to 1202.60ppm. A few anomalous values of 1207.08 ppm, 1208.45 ppm, and 1207.18 ppm were recorded in samples 21, 23 and 32 respectively. Figure 4b show the distribution of Mn within and around the dumpsite. The concentration values of Mn in samples from the dumpsite when compared to Adriano's U.S and World averages and Machelett's limits (Table 2) indicated that the mean value of Mn is lower than Adriano's excessive levels. However, the concentrations of Mn in samples 21, 23, and 32 are above Adriano's U.S and world averages. Comparing the mean value of Mn with the average abundance present in shale and soils (Table 7), it is indicated that the concentration of Mn is low and the anomalies are insignificant. The concentration values are also below the excessive level of heavy metals in soils (1500 ppm). This implies that the abundance of Mn in the soil of the study area is within the safe limit and thus poses no health risk to the inhabitants of the area.


(4a)

(4b)

Figure 4a & 4b: Point symbol Map showing the Concentration of Ni and Mn in the Study Area

Cobalt

Cobalt is a member of the first row transition series of elements, which displays chalcophile and siderophile properties. Minerals such as quartz, feldspar and pure calcium carbonate generally contain very little Co (<2 ppm); also pure sandstone and limestone are very low in Co. In sedimentary rocks, Co tends to vary with the Fe and Mn content and is concentrated in the fine-grained fractions. Arkose and greywacke are more enriched; their Co concentrations usually reflecting the abundance of mafic minerals (Ure and Berrow, 1982).

Cobalt is a biologically essential element and is found in vitamin B12. It can be toxic to humans at doses of 25 mg per day or more. However, problems related to deficiencies are more likely than excess dose toxicity. Co has metabolic links with iron and copper, which can be depressed at high levels of cobalt intake, leading to anaemia (Mertz, 1987).

Anthropogenic sources of cobalt include coal combustion, special steels, fertilisers and lead batteries (Reimann and de Caritat, 1998). Environmental pollution problems from Co are generally less significant than those associated with some other heavy metals (Cole and Carson, 1981).

Cobalt was detected in all the 33 samples analysed, ranging in concentration values from BDL to 110.10 ppm, with a mean value of 5.64 ppm. The background values ranges from BDL to 44.14ppm and there is a single anomaly of 110.10 ppm in sample 31. Cobalt was unevenly distributed in the soil samples. Figure 5a shows the distribution of Co within and around the dumpsite. The concentration values of Co in samples from the dumpsite when compared with the average abundance present in shale and soils (Table 7) indicates that the concentration of Co in the area was low, with the anomaly insignificant and probably due to human activities resulting from the closeness of sample 31 location to Ginti town.

The concentration values were below the average crustal abundance in an uncontaminated soil. Thus, the occurrence of Co in Ewu-Elepe soils may largely be as a result of the presence of the element in trace quantities within some minerals that make up the underlying rocks. This does not pose any health risk to the inhabitants of the study area.

Cadmium

Cadmium is a low-abundance, chalcophile element that most commonly occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals (Reimann and de Caritat, 1998).

The average crustal abundance of Cd is rather low, between 0.1 and 0.2 ppm (Smith, 1999b). Generally lower levels occur in sandstone and limestone, but higher levels are found in shale (0.8 ppm), especially organic-rich sediments, and in marine manganese nodules and phosphorite (Fergusson, 1990). In the surface environment, Cd is most mobile under oxidising conditions at pH levels below 8 (Brookins, 1988).

In industrialised and semi-industrialised areas, there is a grave concern over anthropogenic accumulations of Cd in the environment. Cd is classified as a very toxic element with respect to soil biological activity, plant metabolism and the health of humans and animals (Kabata-Pendias and Pendias, 2001).

Percentage levels of Cd loadings in sewage sludge are a concern for disposal and limit or prevent sludges being applied to land as fertilisers. Cadmium is used extensively in industrial processes including electroplating and battery, paint, ink and plastic manufacturing. Leaching of waste from these processes may have an impact on surface water chemistry. The increasing use of Zn in fertilisers may lead to Cd contamination as Cd is almost always associated with Zn extraction processes.

Phosphate fertilizers contain between 5 and 100 ppm Cd and up to 300 ppm Cd may be present in sewage sludge. According to EU recommendations, soil treated with sewage sludge should not contain more than 3 ppm Cd. Cadmium has no essential biological function, but it tends to accumulate in plants and aquatic biota, with consequent problems of toxicity.

Cadmium is toxic to humans through the inhalation of dust, causing lung damage, and may cause cancer from long-term exposure (WHO, 1996). It is also teratogenic and embryocidal (Smith, 1999b). The maximum tolerable intake of Cd is regarded as 7 ìg kg^{-1} of body weight (WHO, 1996). Uptake by some invertebrates may show a complicated relationship with pH, showing a maximum in bioaccumulation at pH 5.5 (Vesely, 1994).

Cadmium was detected in all the 33 samples, ranging in concentration values from 0.30– 8.40 ppm with a mean value of 1.40 ppm (Fig. 6). The background value ranges from 0.30– 4.64 ppm. Cadmium was not evenly distributed in the soil samples as anomalous values of 5.45 and 8.4 ppm were recorded in samples 28 and 32, respectively. Figure 5b shows the distribution of Cd within and around the dumpsite. In comparison with Adriano's U.S and World averages (Table 2), the mean value of Cd was lower than Machelett's limits while the maximum value was higher than Adriano's excessive levels. The concentration values of Cd in samples from the dumpsite when compared with the average abundance present in shale and soils (Table 7) indicated that the concentration of Cd was significantly high in surface soils of the study area. The mean values of 1.40 ppm obtained in this study were higher than the average abundance of 0.15 ppm (Dineley *et al.,* 1976) in an uncontaminated soil.

The calculated geo-accumulation index (Igeo) of 1.83 for Cd in this study indicates that the soils around the dumpsite are moderately polluted (Table 5b). Cadmium metal is used as an anticorrosive by being electroplated on steel. Cadmium sulphide and selenide are commonly used as pigments in plastics, batteries and in various electronic components. When these products are no more serviceable, they are thrown into the dump as waste and during decomposition; the Cd component is leached into the surrounding soil and over time gets accumulated in the soil.

Cd is extremely toxic and the use of soil high in the metal for cultivation of vegetables and other food crops could cause adverse health effect to consumers, such as renal disease and cancer (Che *and Lin.,* 2003). Moreover, when ingested by humans, Cd accumulates in the intestine, liver and kidney and chronic exposure to the element causes proximal tubular disease and osteomalacia (Pascual *et al.,* 2004). The high concentration of Cd obtained in the soils of the study area may pose a great danger for the health of the inhabitants of the study area, as Cd is very soluble at lower pH values and may be remobilized from surface soils to water bodies where it may be taken up by plants, animals and ultimately man.

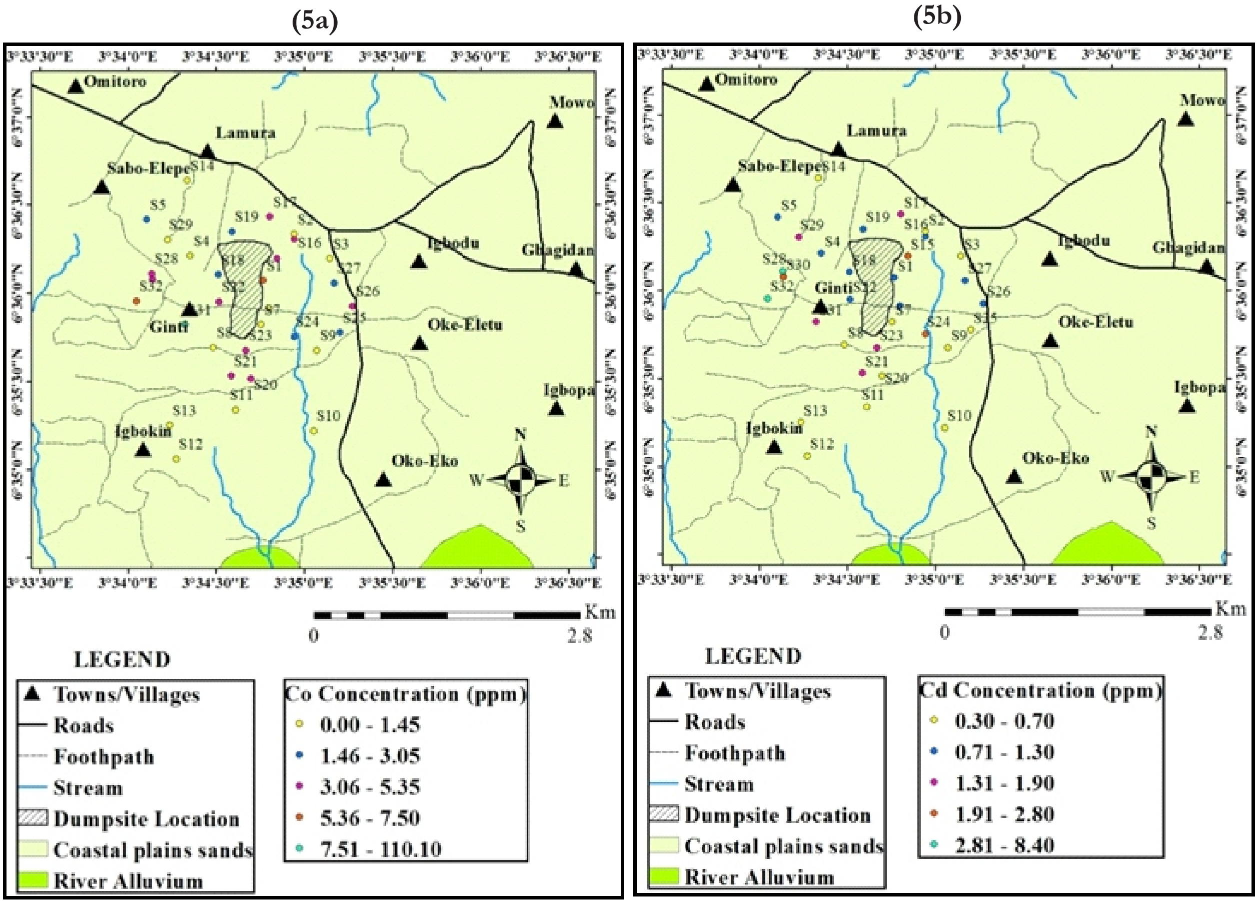


Figure 5a & 5b: Point symbol Map showing the Concentration of Co and Cd in the Study Area

Copper

Copper is a member of the first row transition elements with relatively elevated enrichment in, fine-grained clastic rocks, particularly black shale - (*ca.* 50 ppm) relative to quartzo-feldspathic and carbonate sediments (5–15 ppm). Copper is mobile under oxidising, acidic conditions, especially at pH values in the range 5.0 to 6.0. Average Cu levels in soil vary from 13 to 24 ppm (Kabata-Pendias and Pendias, 2001), while compounds of the element are widely used in agriculture and are a possible source of drainage anomalies. Anthropogenic sources of copper may include waste products from copper mining and smelting, the electrical industry, agriculture, sewage sludge and steel works.

Copper is an essential trace element for all organisms, and humans can tolerate levels up to 12 mg per day (WHO, 1996), although the element can be toxic at extremely high levels. For example, Reimann and de Caritat (1998) reported examples of kidney failure in small children resulting from drinking water from new copper pipes in low pH environments containing high concentrations of Cu up to about 1ppm.

However, Cu was detected in all the 33 samples, ranging in concentration values from 0.05 to 216.45 ppm with a mean value of 44.59 ppm. The background values ranges from 0.05 to 135 ppm. Anomalous values of 147.5 and 216.45 ppm were found in samples 28 and 32, respectively. Figure 6a shows the distribution of Cu within and around the dumpsite. The mean value of Copper concentrations in the soils of the study area is higher than Adriano's U.S and World averages and lower than Machelett's limits and excessive levels (Table 2), while the maximum value is higher than Adriano's U.S and World average, Machelett's limits and excessive levels. The concentration values of Copper in samples from the dumpsite when compared with the average abundance present in shale and soils (Table 7); indicates that the concentration of copper is low and the anomaly is not significant. Copper concentration values are below the average crustal abundance in an uncontaminated soil. The calculated (Igeo) value indicates that the soil is uncontaminated with copper and as such poses no health challenge to the inhabitants of the area.

Lead

Lead, a chalcophile metallic element is the most abundant of the transition elements (Greenwood and Earnshaw 1984). In sedimentary rocks, the distribution of Pb is controlled by the presence of primary detrital minerals, such as feldspar, mica and sulphides, clay minerals (Heinrichs, 1974; Heinrichs, *et al.,* 1980) and organic matter. Pure limestone (5 ppm) and quartzitic sandstone (*ca.*10 ppm) are typically depleted in Pb relative to shale and greywacke (*ca.* 23 ppm). The sedimentary rocks with the highest concentrations are black shale, reflecting the affinity of Pb for organic matter.

Lead from vehicle exhausts, in the form of tetraethyl Pb, was, until recently, a significant source of contamination. In urban environments, road dusts can contain very high levels of Pb (Archer and Barret, 1976). In addition, Pb-bearing glass and pottery glazes, batteries, old lead-based paints, solder, alloys, cable sheathing, pigments, ammunition, plastic stabilizers and the corrosion of lead pipes in areas of soft water and sewage sludge are all potential sources of Pb.

Lead was detected in all the 33 samples ranging in concentration values from 2.88 to 71.01 ppm with a mean value of 33.74 ppm. The background values ranges from 2.88 to 69.34 ppm with an anomalous value of 71.005 ppm as obtained from sample 32. Figure 6b show the distribution of Pb within and around the dumpsite. The mean value is higher than Adriano's U.S and World averages and lower than Machelett's limits and excessive levels (Table 2), while the maximum value of lead is higher than Adriano's U.S and World average, and lower than Machelett's limits and excessive levels. The concentration values of lead in samples from the dumpsite when compared to the average abundance of the element present in shale and soils (Table 7) indicated that the concentration of lead was low. The mean values of lead obtained in this study were higher than the average crustal abundance of 16 ppm (Dineley *et al.,* 1976) in an uncontaminated soil. The calculated geo-accumulation index (Igeo) for lead indicates that the soils around the dumpsite falls into unpolluted to moderately polluted category (Table 5b) and may as such be a source of health problems to the inhabitants of the area.

Lead has no known biological role (not essential) in plants or animals and is highly toxic to mammals and aquatic life. It can cause mental impairment in young children, neuropathy and hypertension in adults and may be lethal at high levels, *e.g.,* over 25μg kg^{-1} of body weight (WHO, 1996). It is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. In addition, Pb reduces sperm count, damages kidney, liver, blood vessels, nervous system and other tissues in human.

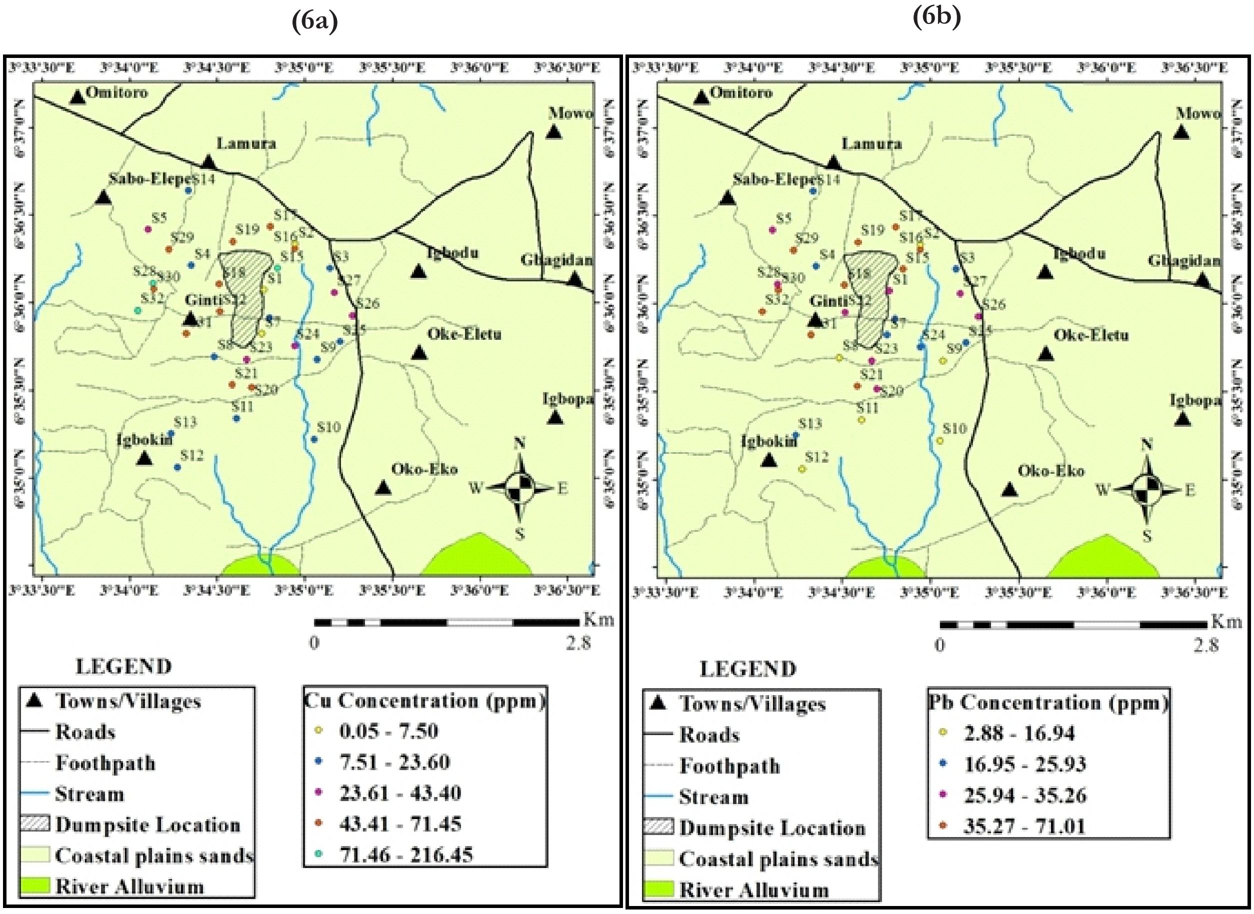


Figure 6a & 6b: Point symbol Map showing the Concentration of Cu and Pb in the Study Area Zinc

Zinc

Zinc is the heaviest member of the first row transition series of elements, and it is also a chalcophile metallic element. The Zn content in soil depends on the nature of parent rocks, texture, organic matter and pH, and ranges from 10 to 300 ppm (Mihaljevic, 1999b) with an estimated global average of 64 ppm (Kabata-Pendias and Pendias, 2001). The different forms of Zn in soil may include: water soluble; exchangeable and extractable from soil surfaces; occluded by soil hydrous oxides; precipitates; immobilised in living organisms and biological residues, and constituents in the lattice of primary and secondary minerals (Mihaljevic, 1999b). Since, Zn is easily adsorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons (Kabata-Pendias and Mukherjee, 2001). Anthropogenic sources of zinc are significant, arising mainly from human activities such as mining, waste combustion, and steel processing. A major use of Zn is as an anti-corrosion coating. It is also used as a constituent of brass, as a white pigment (ZnO) in paint and rubber products, and in the manufacture of dry batteries (Mihaljevic, 1999b).

In the study area, Zn was detected in all the 33 samples ranging in concentration values from 27.34 ppm to 156.71 ppm, with a mean value of 105.28 ppm. Figure 7 show the distribution of Zn within and around the dumpsite. In comparison with Adriano's U.S and World averages (Table 2), the mean and maximum values of Zinc is higher than Adriano's U.S and World Averages but lower than excessive limits and Machelett's limits. The concentration values of Zn in samples from the dumpsite when compared with the average abundance present in shale and soils (Table 7) indicated that the concentrations of Zn in the surface soils of the study area were low. Also, the Zinc levels were below the average abundance in an uncontaminated soil. Therefore, it can be inferred that there is Zn deficiency in the surface soils of the study area. Zinc is an essential element for plants and animals but can be toxic at elevated concentration.

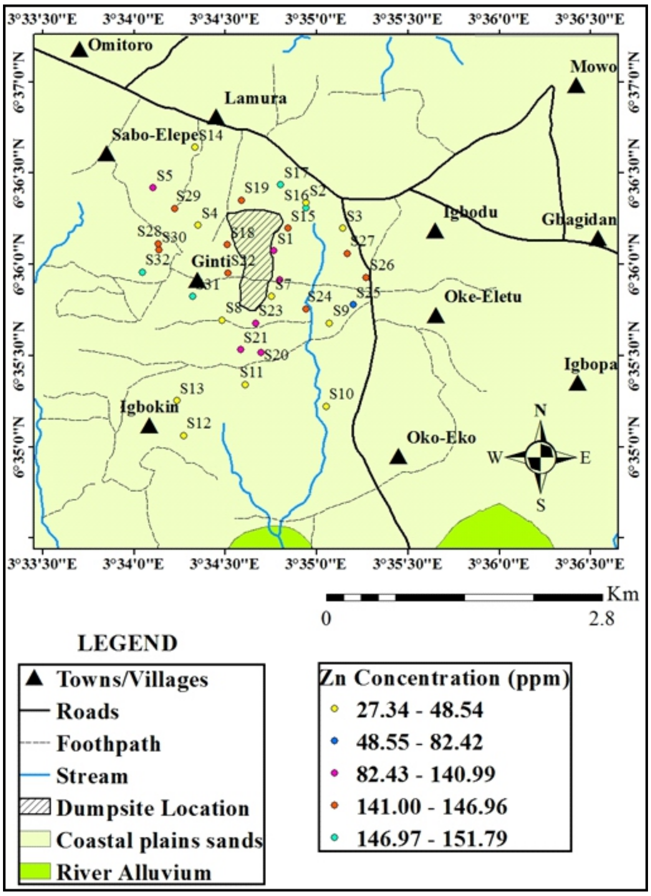


Figure 7: Point symbol Map showing the Concentration of Zn in the Study Area

CONCLUSION

The geochemical analytical data of the soil samples revealed that the Ewu-Elepe dumpsite and its environs had higher heavy metal concentrations when compared with the control sample that is about 9.0 km away from the site. This may be connected with the dumping of inorganic waste materials in the dumpsite. The result also revealed the following trend in their order of geo-accumulation in the soil: Cd > Pb > Zn > Cu> Mn > Co > Ni. Contamination factor (CF) and geo-accumulation (I_{geo}) index further confirmed that the soil from the dumpsite was moderately contaminated with Cd, slightly contaminated with Pb and presently uncontaminated with Co, Zn, Cu, Mn, and Ni.

Above all, a well-engineered landfill that incorporates the local geology and the topography of the area should be designed so as to prevent infiltration of leachates into the soil and shallow groundwater system. Although, no severe pollution may have occurred at present apart from that of Cd and to some extent Pb, but continuous dumping of waste at the dumpsite may lead to the enrichment of the soil with other metals that are presently at uncontaminated levels. Therefore, separation and recycling of wastes as well as the use of sanitary landfills and incinerators should be encouraged. Due to the toxicity of heavy metals, cultivation around the dumpsite and the use of manure from the dumpsite for agricultural purposes should be discouraged as vegetables and other food plants can easily absorbed these toxic metals from soil.

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