

HEAVY METALS, PROFIE OF THE PROPOSED DUMP-SITE AT NTA-K-INYANG ITAM, AKWA IBOM STATE, NIGERIA.

ABSTRACT

Levels of trace metals (Cr, Cd, Mn, Fe, Cu, Co, Ni, V, Zn and Pb) in soil from Ntak-Inyang Itam, Itu Local Government Area were determined using standard analytical procedures involving the use of atomic absorption spectrophotometry. Results of the analysis shows that at the debt of 0-15cm at five locations distributed in the area, Cr at sample sites B and E had a mean value of $5.00 \pm 0.55 \mu\text{g}/\text{kg}$ which is lower when compared to sample sites A, C and D. Also Cr in the study area had a coefficient of variation (C.V) of 3.14% which signifies stability. Cd in the four sampling points (A, B, C and E) seems to maintain a constant mean value of $0.14 \pm 0.01 \mu\text{g}/\text{g}$ except for point D (Esuk in Ntak-Inyang) which has a mean concentration of $0.19 \pm 0.02 \mu\text{g}/\text{g}$. Mn exhibited different mean value at different (five) sampling points and a C.V of 1.99% which was the least and the most stable in the area among the ten metals analysed. Fe exhibited the highest concentration in all the sampling points, with a C.V of 4.99%. The result of analysis of copper (Cu) shows a total mean concentration of $8.29 \pm 0.67 \mu\text{g}/\text{g}$ while Cobalt (Co) in the four sampling points had the same mean value of $0.11 \pm 0.1 \mu\text{g}/\text{g}$ except in sample point A (sloping area of AKRUBEL) which increases to a value of $0.22 \pm 0.6 \mu\text{g}/\text{g}$. Nickel (Ni) in sampling point C and D exhibited the same mean value of $0.83 \pm 0.9 \mu\text{g}/\text{g}$ while other sampling points (A, B, D and E) the mean varies. Vanadium (V) in the samples were generally low, sample point A and D had a mean concentration of $0.10 \pm 0.01 \mu\text{g}/\text{g}$. Sample point C, D and E had $0.05 \pm 0.01 \mu\text{g}/\text{g}$ each. Zinc (Zn) had a mean concentration of $2.72 \pm 0.60 \mu\text{g}/\text{g}$ and a C.V of 10.4% while Lead (Pb) stood at a C.V of 3.2%. The results were compared with various National and International standards, on the whole the area was not found to be polluted by these metals. Hence the area is suitable for sitting the dump-site, with intermittent monitoring.

Keywords: Akwa Ibom state, Profiling, Heavy metals, Dump site, points

Introduction

There is need for an overall profiling of the proposed major Dumpsite at Ntak Inyang, Itam, Itu L.G.A of Akwa Ibom State. This will establish the background data of the area, for proper pollution monitoring. Environment according to Ikpe (2019) is known as the sum of human surroundings consisting of the atmosphere, hydrosphere, lithosphere and biota. As

such human daily activities and means of survival are dependent on the environment in which they live; hence there is need for best environmental management practices. The proposed siting of a major dumpsite in Ntak-Inyang Itam, Itu Local Government area of Akwa Ibom State, will pose a serious deleterious effect on biota as well as human, If serious environmental monitoring is not carried-out. Substances whose function to the environment and man are hazardous, thereby upsetting the natural cycle of the ecosystem are known as pollutants (Ikpe *et al.*, 2016).

Pollutants could be primary or secondary. Primary pollutants are those substances or materials that come from point sources and can contaminate the environment directly. They include domestic wastes (mainly effluents containing organic and inorganic compounds or materials). Other includes certain gases such as SO₂, SO₃, NH₃, H₂S, CO, etc. Secondary pollutants on the other hand are substances which become harmful only when they react with other substances. A typical example is Nitric Oxide (NO) which becomes harmful only when it reacts with ozone in the atmosphere (Ogbeifun *et al.*, 2019)

Also, various activities of man in recent years have increased the quantity and distribution of Heavy Metals in the atmosphere, land and water bodies (Ikpe, 2019). However, Okuo and Okolo, 2006 describe Heavy Metals to be of great ecological significance today due to their toxic and accumulative nature. Mining, dumping of old damage vehicles are some of the sources of land heavy metal pollution. Pollution of streams, rivers flowing through agricultural areas where fungicides and pesticides may have been used and even pollutants from industrial effluent contributes most of these heavy metals at the reception sites (Okuo and Okolo, 2006). This study is at providing background data of the proposed major dumpsites at Ntak-Inyang, Itam, Itu Local Government Area of Akwa Ibom State, Nigeria, which will provide a monitoring base for pollution of the area, for a cleaner and healthier environment.

MATERIALS AND METHOD

2.1. Physiography of the Study Area

This research was carried out in Ntak-Inyang Itam, Itu Local Government Area of Akwa Ibom state. The area is located within latitude $04^{\circ} 42' N$ and $05^{\circ} 23' E$ and Longitude $08^{\circ} 42' N$ and $07^{\circ} 41' E$ North of the equator. It is situated in the western part of Itu Local Government Area, which is the South-South zone of Nigeria. Moreso, it is bounded in the Northern part of the state by Odiok-Itam, in the west by Ikot-Obong Itam, in the East by Atai Idung, in the South by Ikot Obio Atai Itam all in Itu Local Government Area, covers a landmass of approximately 25,175 square kilometers with a population of 983,209 according to 1999 Nigeria population census.

Mbak Atai Itam is the Headquarters of the local government Area, the area is generally undulating and the major occupation of the people are mostly farming and petty trading.

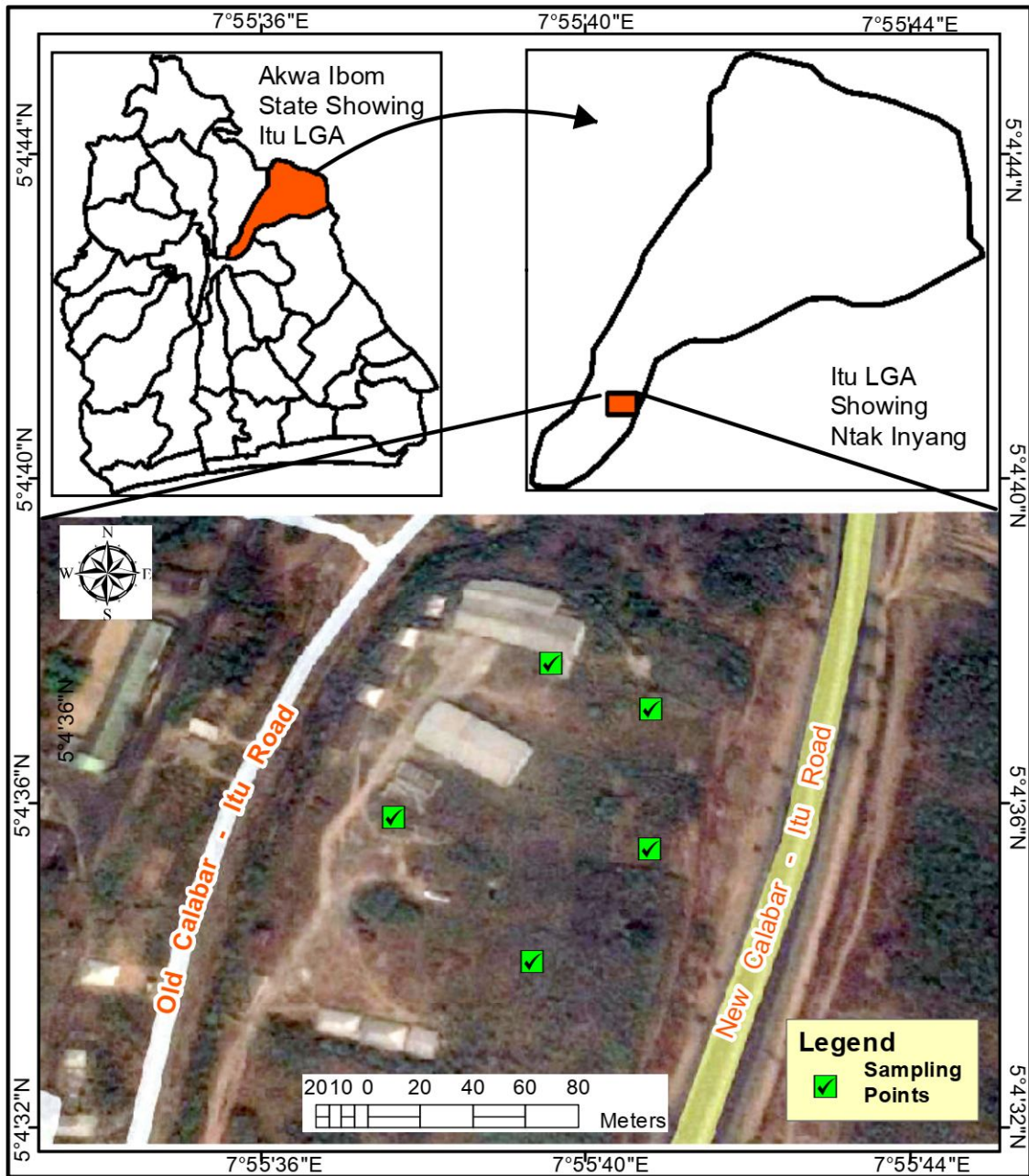


Figure 1: Location of sampling points in Ntak-Inyang Itam community.

2.2. Sampling

One hundred Soil samples were collected during dry season(November,2020 to January,2021) for three months using soil auger, ensuring equal depth of 0-15cm; along triangular grid transected 50cm apart at five different locations making up the area under study (Ikpe, 2020). As shown in Table 1

Table 1. Site Description of the study area

Site Code	Site Description	Co-ordinates		
		Latitude	Longitude	Elevation
Sample point A	Sloping area of Akwa rubber estate, Ntak Inyang Itam.	5°4'35.64''N	7°55'39.19''E	40m
Sample point B	West of Ntak-Inyang by AKBC studio	5°4'37.59''N	7°55'36.69''E	37m
Sample point C	East of Ntak-Inyang by former JCC company and to the slaughter	5°4'35.55''N	7°55'40.87''E	39m
Sample point D	Esuk Itam in Ntak-Inyang	5°4'34.06''N	7°55'39.35''E	41m
Sample point E	Hilly side of Akwa Rubber Estate Limited (AKRUBEL)	5°4'35.86''N	7°55'37.70''E	40m

Samples were collected around the grid points and homogenized before sample preparation and analysis, according to AOAC, 2000.

2.2.1. Sample Treatment

The samples were carefully spread on a wooden cardboard devoid of dust to prevent contamination. It was air-dried under room temperature for forty-eight hours in order to enhance proper sieving of the soil samples using 20 mm mesh size. The samples were spread at reasonable distance from each other to avoid cross-contamination of one into another especially when they are dried. The dried samples were then transferred into entirely new calico bags preparatory to grinding (A.O.A.C., 2000). The grinding was done using porcelain mortar in order to increase the surface area of the sample which will enhance effective digestion of the samples in order to obtain good representative samples of the area under consideration through homogenous mixture of the consolidated loose soil samples.

2.2.2. Digestion

One (1g) of the dried sieved samples were weighed into a 100 ml clamp digestion flask, it was followed by adding Ten (10 ml) ml of concentrated nitric acid (HNO_3) and five (5ml) ml of perchloric acid (HClO_4) in the ratio of 2:1 respectively. This was covered with a watch glass and allowed to stand for one hour (1hr). The mixture was placed on a regulated hotplate under fume cupboard and heated gradually to near dryness with colour changing to white (clear). The samples were removed from the hot plate and allowed to cool before leaching; the residue was dissolved in 5 ml of 20% HNO_3 . The dissolved mixture was filtered to the volume of 100 ml of standard volumetric flask with deionized water. Moreso, a blank/control solution was prepared following the same procedures, but without using the

ground soil sample. The filtrate were collected in small sample bottles ready for heavy metals analysis using atomic absorption spectrophotometer, the Unicam 919 solar system model.

2.3. Preparation of Standard for the Unicam 919 Solar System Atomic Absorption Spectrophotometer (AAS)

Ten (10) standards were prepared for use by Unicam 919 AAS following instructions in the manufacturer's manual. These standards were prepared from $\text{Pb}(\text{NO}_3)_2$, MnCl_2 , CdSO_4 , FeCO_3 , CoCl_2 , $\text{Zn}(\text{NO}_3)_2$, CuSO_4 , $\text{K}_2(\text{Cr})_4$, $\text{Ni}(\text{Co})_4$, VCl_3 .

2.3.1: Preparation of Pb Standard from $\text{Pb}(\text{NO}_3)_2$

To prepare lead standard, the relative molecular mass (RMM) of the compound has to be known. The Relative Molecular Mass of a compound is the sum of the relative atomic masses of all the atoms in one molecule of the substance.

In this case, the relative molecular mass of $\text{Pb}(\text{NO}_3)_2 = 331.2\text{g}$.

From calculation,

$$\text{Relative atomic mass of Pb} = 207.2$$

$$\text{Relative atomic mass of N} = 14 \times 2 = 28$$

$$\text{Relative atomic mass of O} = 16 \times 3 \times 2 = 96$$

$$\text{Therefore; Relative molecular mass of } \text{Pb}(\text{NO}_3)_2, \text{RMM} = 207.2 + 28 + 96 = 331.2\text{g}$$

However, if 207.2g of lead contains in 331.2g of $\text{Pb}(\text{NO}_3)_2$,

$$\text{Then 1g of lead (Pb) will contain } \frac{1 \times 331.2}{207.2 \times 331.2}$$

$$= 0.00483\text{g } \text{Pb}(\text{NO}_3)_2$$

Therefore 0.00483g $\text{Pb}(\text{NO}_3)_2$ was accurately weighed and dissolved in 1dm^3 of solution i.e. the 0.00483g $\text{Pb}(\text{NO}_3)_2$ was dissolved in 500 ml of solution in a 1dm^3 volumetric flask and made up to 1dm^3 with deionized water. This solution now contains 1000 mg of Pb in 1 litre i.e. 1000 ppm stock.

From the stock; 2, 4, 6,8,10 part per million (ppm) could be prepared (ie working standard)

To prepare 2 ppm stock, apply dilution principle;

$$C_1V_1 = C_2V_2$$

$$1000 \times V_1 = 2 \times 100 \text{ ml}$$

$$\therefore V_1 = \frac{2 \times 100}{1000} = 0.2 \text{ ml}$$

Therefore 0.2 ml of stock was diluted to 100 ml with deionized water to give 2 ppm solution. Other standards were prepared using the same procedure. Each of the standards was aspirated into AAS flame and the absorbance recorded. The sample concentration was determined by the formula given in equation (2):

$$C_{m(s)} M_g/K_g = \frac{C_{m(AAS)} mg/L \times V_{ml} \times 1l \times 10^3 g}{M_{s(g)} \times 1K_g \times 10^3 ml}$$

Where; C_m - Concentration of metal

V - Volume of the digest (ml)

1L - One litre

M_s - Metal sample used for digestion

1kg - One Kilogram

Alternatively,

The sample concentration can be determined by another formula given in equation (3)

$$i. e. \frac{\text{Absorbance of sample} - \text{Absorbance of blank} \times \text{Conc. of standard}}{\text{Absorbance of standard} - \text{Absorbance of blank}} \quad (3)$$

$$\text{Total conc.} = \frac{A_{\text{sample}}}{A_{\text{standard}}} \times \frac{\text{Standard conc}}{1}$$

Where A is the Absorbance

From here the concentration of each element at the same depth was known. The result expressed in $\mu\text{g/g}$. (Ikpe *et al.*, 2020)

3.0. Results and Discussion

The Table 2 below contains the concentration of the Heavy metals of the soil samples taken from various sampling points at Ntak-Inyang Itam in Itu Local Government area of Akwa Ibom State Nigeria.

3.1. Chromium (Cr)

The concentration of Chromium is lower at sample point B (west of Ntak-Inyang) and sample point E (Hilly side of Akwa Rubber Estate) with a mean of $5.00 \pm 0.55 \mu\text{g/g}$ at the depth of 0-15 cm. Also, sample point D (Esuk in Ntak-Inyang) recorded the highest mean of $10.00 \pm 0.53 \mu\text{g/g}$, probably it is the settling point of the slopping area. Consequently, comparing the result with standard (Hayes, 1973) of 5.00-300 ppm and chemical society of Britain Standard of 0-25 ppm. They appear to be in agreement since the result fell within these approved standards. Therefore the soil could not be said to have been polluted by Chromium (Cr). On the other hand, since chromium is essential for plant growth at micro concentration, the low level of chromium could enhance plant growth. Moreover chromium is much less toxic to plants than other heavy metals. Nevertheless since the metal has been found to be implicated in adverse health effect on human beings, care should be taken not to introduce excess chromium into the soil. This is very important since the metal seems to be highly stable in the soil (C.V = 3.14%).

1.2 Cadmium (Cd)

Cadmium in the four sampling points seems to maintain a constant mean value of $0.14 \pm 0.01 \mu\text{g/g}$, in all the sampling points except point D (Esuk Itam in Ntak Inyang) which has a mean concentration of $0.19 \pm 0.02 \mu\text{g/g}$, . the increment may have resulted from the topography of the site which aided the running water and caused erosion during wet season. A critical observation of the results indicated that the concentration of Cadmium follows a particular pattern of increase with the topography of the area. The mean concentration of

cadmium ($0.15 \pm 0.01 \mu\text{g/g}$) at the depth of 0-15cm in this soil fell within Hayes (1973) standard of 0.10-0.70ppm, these implies that the soil was not polluted by cadmium (Cd). Similarly a coefficient of variation (C.V) of 3.77% indicates stability of the metal in the soil.

3.3 Manganese (Mn)

The mean concentration of manganese has been found from the analysis to be $24.930 \pm 0.97 \mu\text{g/g}$ at a depth of 0-15 cm. When comparing this result with the Haye (1973) standards of 100.00-4000.00 ppm, the soil is said to be deficient in Mn. The deficiency is suspected to be caused by the presence of much calcium which could interfere with other micro nutrients thus leading to the deficiency of Mn (Ikpe *et al.*, 2019) the level of Mn is in fair agreement with Ude (1980) in the soil of similar percent material.

Sample point A and B showed a high concentration of 31.67 ± 0.55 and $31.25 \pm 0.65 \mu\text{g/g}$ respectively which could be attributed to leaching. Manganese has the least coefficient of variation (C.V) of 1.99% and this signifies stability of the metal in the soil.

3.4 Iron (Fe)

According to Ademoroti (1996) and Aluko *et al.* (2013) natural soils contain significant concentration of iron. Eddy *et al.* (2006) added that pollution of the environment by iron cannot be overwhelmingly linked to waste material alone but other ordinary sources of iron must be taken into consideration. Besides iron had earlier been reported to be abundant element in Nigeria soil (Amusen and Olawafe, 2005), of all the heavy metal analyzed for, Fe exhibited the highest concentration level in all sampling points. These high levels may have been attributed to dumping of scraps of vehicles as well as by industrial activities of defunct J. C. C. Construction Company, Akrubel and Pime Water Company.

However the total mean of iron (Fe) from the result of analysis is $24.92 \pm 0.97 \mu\text{g/g}$ at the depth of 0-15cm and this falls below Hayes (1973) standard of 7000.00-500,000 ppm and chemical society of Britain accepted standards (1975) of 3,000-500,000 ppm. Compared with

other metal analyzed in the environment Fe could be said to be unstable in the soil (C. V = 4.99%).

3.5 Copper (Cu)

Various ways in which copper could be introduced into the environment was enumerated by Ikpe (2019) to include: using copper in treating algae blooming as fungicide, discharge of effluent from pulp, paint and dyes, cleaning and duplicating from printing press house and textile, leach ate and garbage from municipal solid. The result of copper analysis in all the sampling points shows a total mean concentration of $8.29 \pm 0.67 \mu\text{g/g}$ which compares with Hayes (1973) standard of 2.00-100.00 ppm confirmed that it fell within the standard. Moreso, it does not show any pattern of distribution at the depth of 0-15cm. meanwhile, the coefficient of variation of Cu was 3.74% which is relatively low and hence signifies stability.

3.6 Cobalt (Co)

The concentration of cobalt in four sampling points had the same mean value of $0.11 \pm 0.01 \mu\text{g/g}$, except in sample point A (sloping areas of AKRUBEL) which increases to a value of $0.22 \pm 0.6 \mu\text{g/g}$. This is suspected to have been as a result of leaching.

Furthermore, the total mean of cobalt in the study area was $0.11 \pm 0.62 \mu\text{g/g}$, this shows that cobalt level fell below Hayes (1973) standard of 1.00-40.00 ppm. It has the highest percentage of C. V of 11.35 %, thereby signifying instability of the metal in the soil. Going by the standard given by chemical society of Britain (1975) cobalt level fell within its standard in the area under study, except in sample point E (hilly-side of AKRUBEL) where the concentration level was below detection limit (BDL).

3.7 Nickel (Ni)

According to Spiff and Horsfall (1998) waste water containing nickel originates primarily from metal industries, particularly plating operations, printing and air craft

industries. Nickel influences the amount of iron our bodies absorb from food and its high concentration in the body could result to irritation of the respiratory tract, cancer, pulmonary and gastrointestinal toxicity due to exposure to nickel carbonyl compound (Abdullahi, 2013; Ubong *et al.*, 2021). Long term contact can cause reduced body weight, heart and liver damages and skin irritation. The symptoms of exposure to some toxic nickel compounds include nausea, vomiting, headache and insomnia. Nickel in the study is in agreement with the accepted standard of 0-100 ppm of the chemical society of Britain (1975) and fell below the Hayes (1973) standard of 1.00 ppm . The coefficient of variation showed 11.15 % of Nickel. This proved its instability in the soil samples.

3.8 Vanadium (V)

The mean values of vanadium in the samples were generally low. Generally two sets of concentration of V. were observed. While sample A and B had mean value of 0.10 ± 0.01 $\mu\text{g}/\text{g}$ sample C D and E had mean concentration of 0.05 ± 0.01 $\mu\text{g}/\text{g}$ each. Thus vanadium fell below the approved standard and as such was deficient in the study area. Also with a C. V of 5.7% the metal could be said to be instable with respect to other heavy metals.

3.9 Zinc (Zn)

Industries dumping (discharging) waste which carry significant quantities of zinc include, steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, silver and stainless steel, yarn and fibre production, newspaper production and ground wood pulp production (Spiff and Horsefall, 1998; Nsi *et al.*, 2022; Ikpe *et al.*, 2022) zinc in excess causes anaemia while deficient in the body causes dermatitis. It is worthy of note that zinc is an important element for plant because it plays an important role in protein synthesis, nucleic acid metabolism and cell growth. Also an excess zinc can be detrimental, it

causes vomiting abdominal pains, cramps, renal damage, hemorrhagic pancreation and death (Nazanim *et al.*, 2013; Ubong *et al.*,2022) from the foregoing it has become very necessary to implement existing policies to check unwarranted dumping of refuse into our environment to advert possible health hazards.

Following the led down standards by (Hayes 1975) and chemical society of Britain (10-300 ppm) a mean concentration of 2.72 ± 0.60 $0.60 \mu\text{g}$ /g of zinc from the study site could be said to be quite low and hence below the standards. Meanwhile the C.V shows a high variability of 10.49% thus signifying instability of Zn.

3.10: Lead (Pb)

The trend in Pb concentration in all the samples shows high lead level compared with metals such as Cd, Ni, V and Zn (Hayes 1973). The concentrations fell within the approved standard. The source of Pb in these samples could be attributed to discharge as smoke from the automobile of the AKRUBEL and defunct JCC Construction Company and dumping of scraps by individual. This is so because these waste disintegrated and washed down by rain into the soil while the lead oxide sent into atmosphere could later fall with rain and get diffused into the soil thereby polluting the soil. The general result of lead concentration shows that the area had a high content range of 5.56 ± 0.64 - $13.33 \pm 0.46 \mu\text{g}/\text{g}$

When compared with Hayes (1973) and chemical society of Britain (1973) standards it confirms that the area is polluted with lead. The coefficient of variation exhibited a percentage of 3.32% indicating its stability.

Consequently, the presence of Pb in the body may lead to anaemic and other serious medical conditions including reduced intelligent (Prasad, 2004). Also Bioaccumulation of Pb in human body counteract with the performance of Mitochondria thereby impairing respiration and causes constipation paralyses and eventual death (Ezeokonkwo, 2014;Ikpe

,2019 and Ubong *et al.*,2020). Hence there is need for routine environmental evaluation and remediation to avoid serious adverse implication.

UNDER PEER REVIEW

Table 2: Levels of Heavy Metals in soil samples ($\mu\text{g/g}$)

Location: (Samples point)	Depth (cm)	Cr	Cd	Mn	Fe	Cu	Co	Ni	V	Zn	Pb
A	0- 15	8.75 ± 0.42	0.14 ± 0.01	31.67 ± 0.55	577.67 ± 99.08	9.14 ± 0.51	0.22 ± 0.06	3.33 ± 0.69	0.10 ± 0.01	2.56 ± 0.39	5.56 ± 0.64
B	0-15	5.10 ± 0.55	0.14 ± 0.01	31.25 ± 0.65	584.19 ± 82.97	6.00 ± 0.67	0.11 ± 0.01	1.67 ± 0.36	0.10 ± 0.01	2.24 ± 0.39	8.89 ± 0.56
C	0-15	7.50 ± 0.49	0.14 ± 0.01	22.50 ± 1.80	588.37 ± 14.35	10.00 ± 1.01	0.11 ± 0.01	0.83 ± 0.09	0.05 0.01	2.88 0.79	6.67 0.95
D	0-15	10.00 ± 0.53	0.19 ± 0.02	27.08 ± 1.99	572.56 ± 39.01	10.86 ± 0.01	0.11 ± 0.01	0.83 ± 0.09	0.05 ± 0.01	3.20 ± 0.88	13.33 ± 0.46
E	0-15	5.00 ± 0.55	0.14 ± 0.01	12.08 ± 0.60	551.16 ± 45.83	5.43 ± 0.57	0.00 ± 0.00	0.42 ± 0.04	0.05 ± 0.01	2.72 ± 0.55	12.22 ± 0.64
C.V(%)		3.14	3.77	1.99	4.99	3.74	11.35	11.15	5.71	10.41	5.21

CV= Coefficient of Variation.

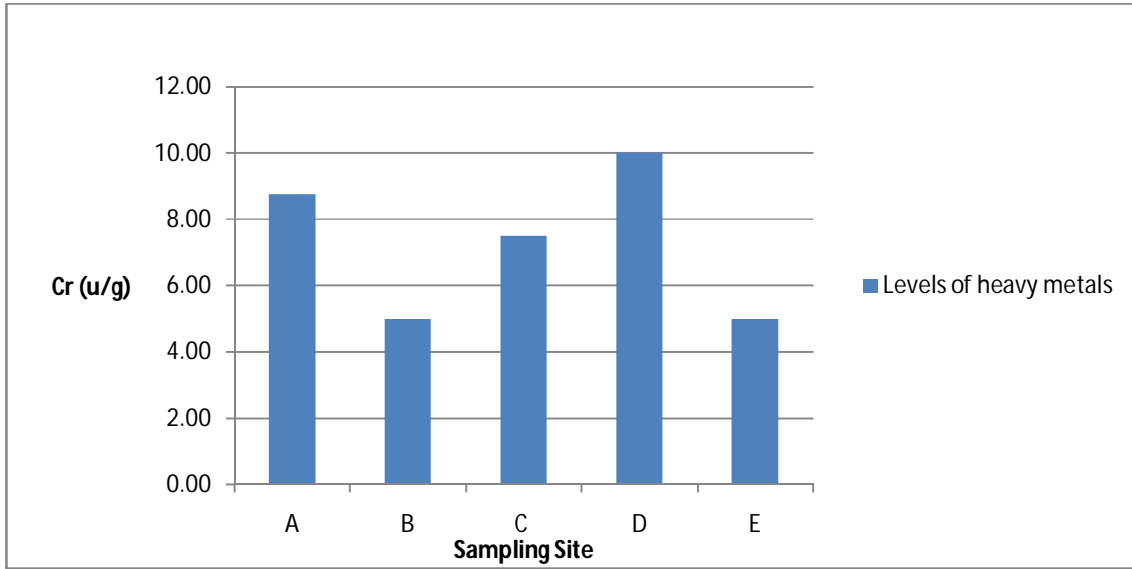


Fig 2: Graphical representation of Chromium Concentration in the samples

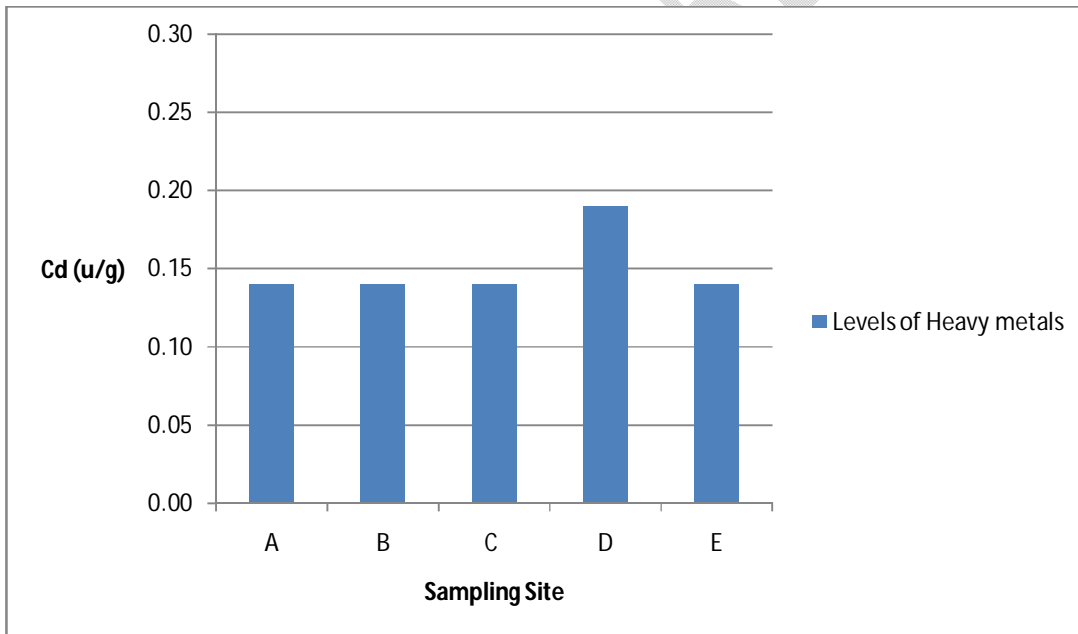


Fig 3: Graphical representation of Cadmium Concentration in the samples

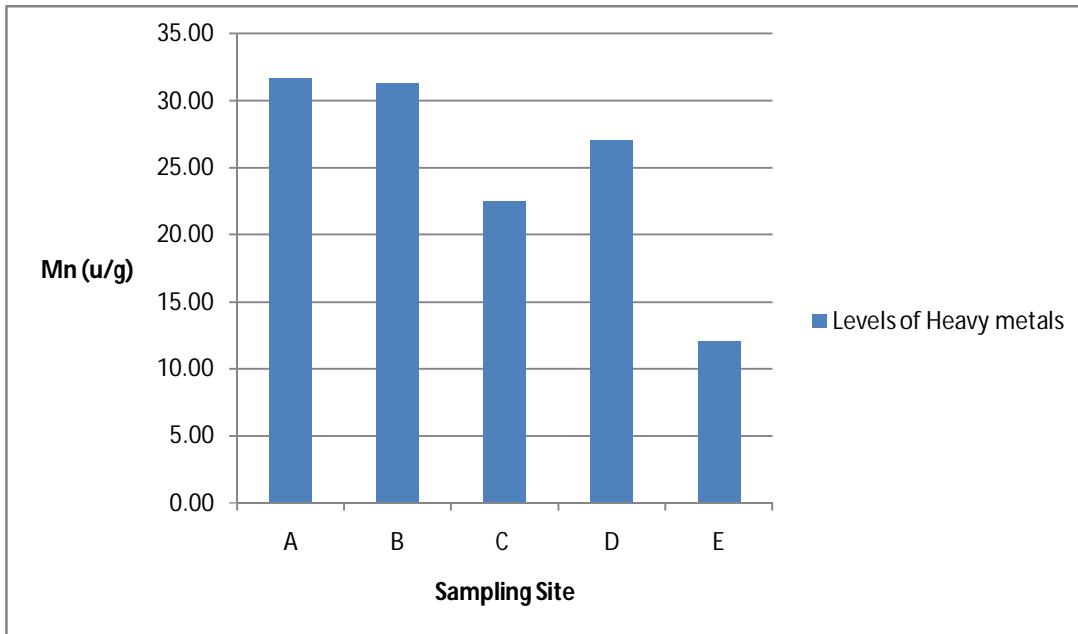


Fig 4: Graphical representation of Manganese Concentration in the samples

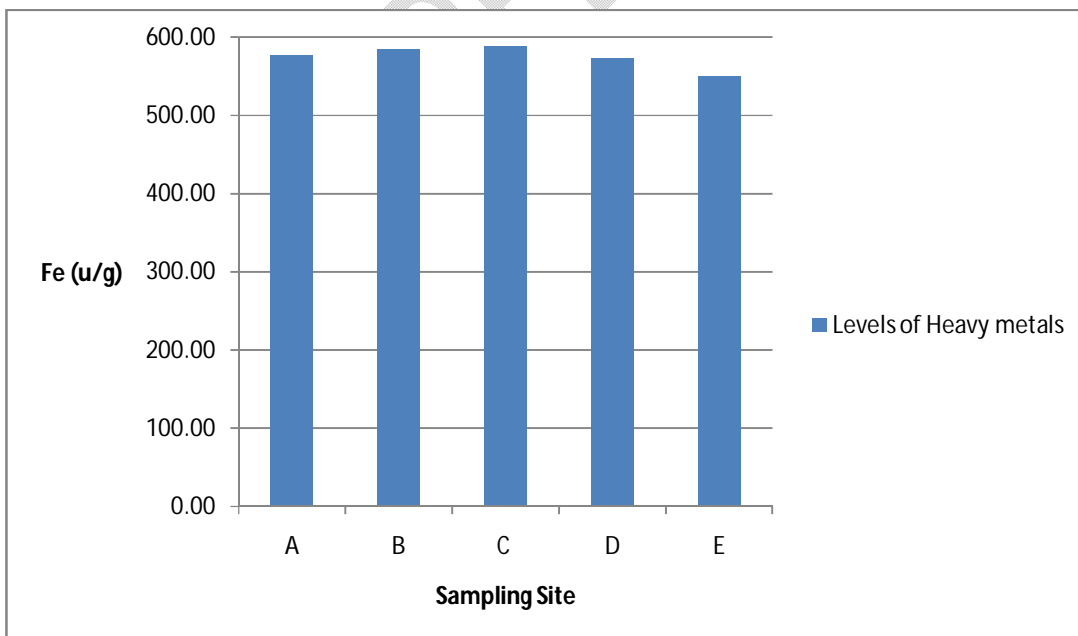


Fig 5: Graphical representation of Iron Concentration in the samples

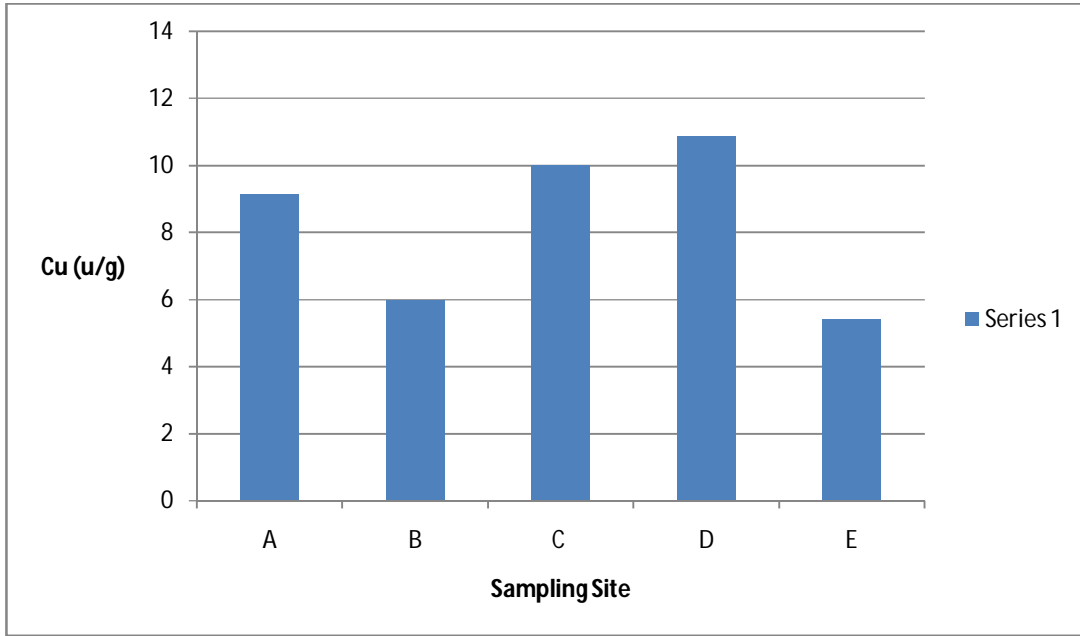


Fig. 6: Graphical representation of Copper Concentration in the samples

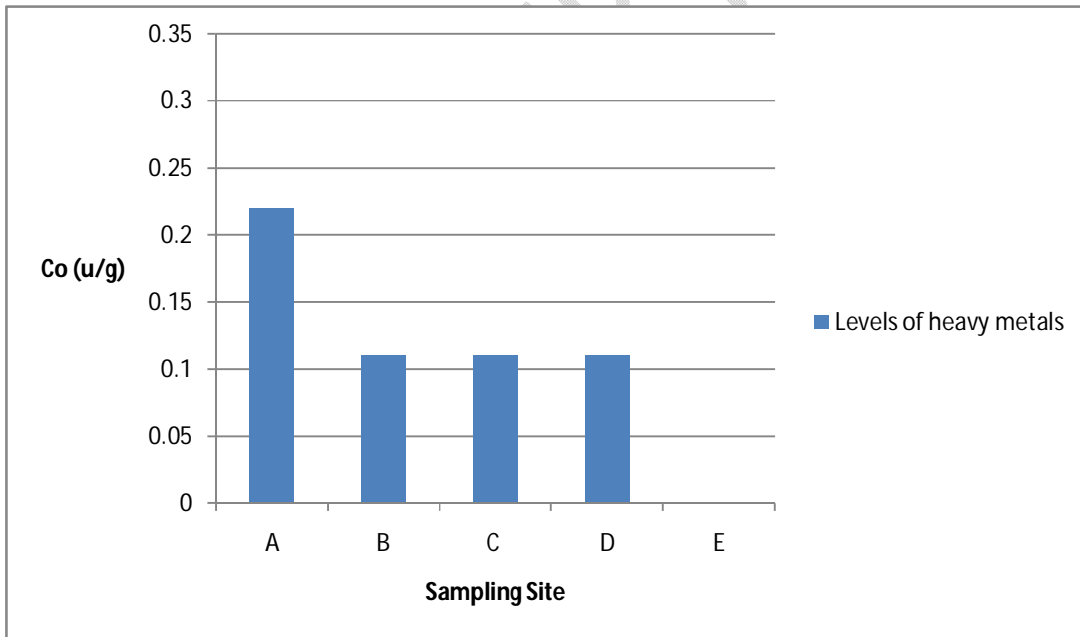


Fig. 7: Graphical representation of Cobalt Concentration in the samples

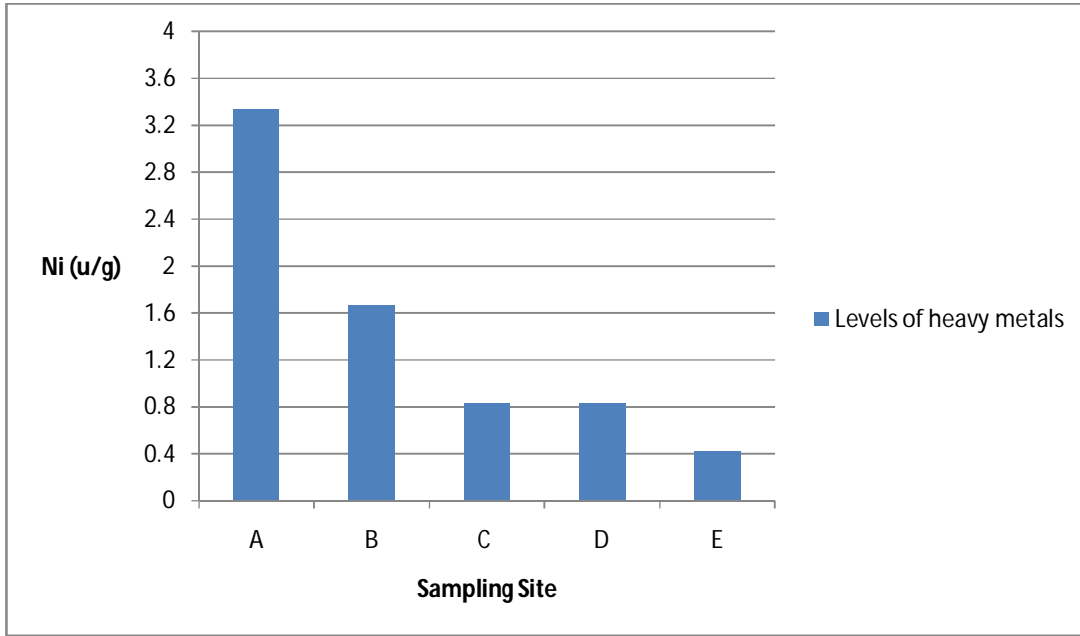


Fig .8: Graphical representation of Nickel Concentration in the samples

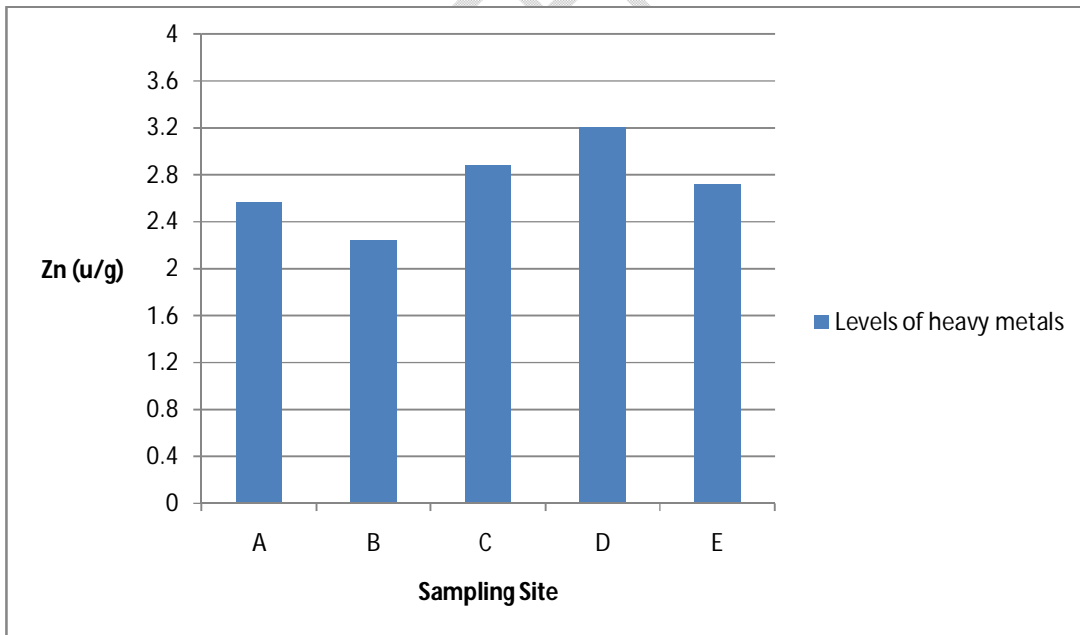


Fig. 9: Graphical representation of Zinc Concentration in the samples

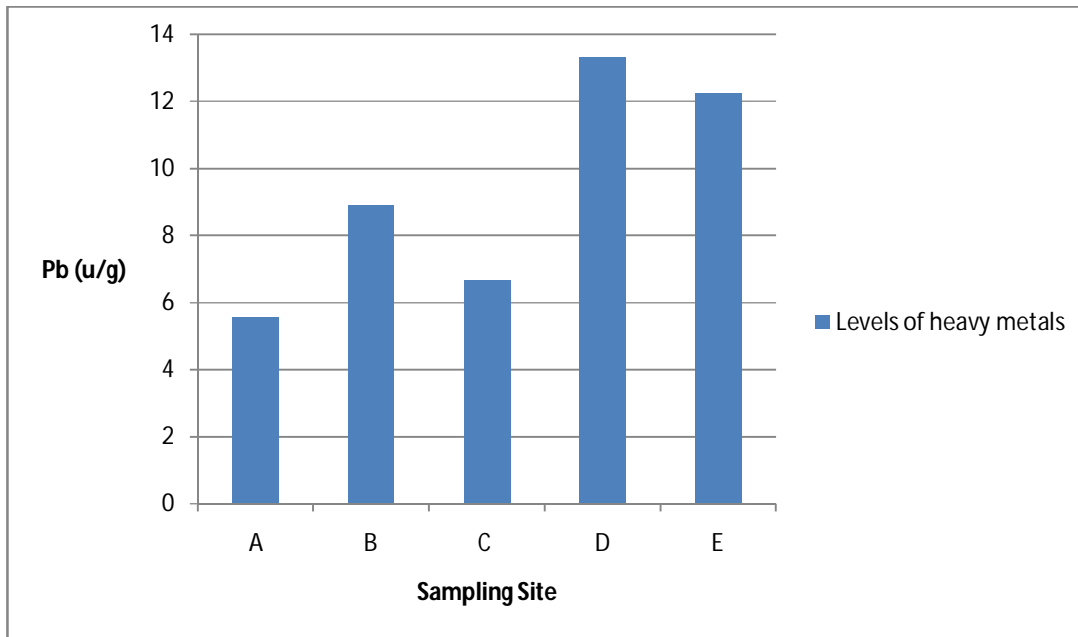


Fig. 10: Graphical representation of Lead Concentration in the samples

CONCLUSION

The experimental findings showed that the area is not polluted with any of these metals under investigation, when compared with the available national and international standards. Hence is recommended for sitting of the dumpsite. While an intermittent monitoring should be undertaken for a cleaner and safer environment.

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