

Pollution Status of Dumpsites within Uyo Metropolis, Akwa Ibom State, Nigeria

ABSTRACT

The study evaluates the heavy metals, geo-accumulation index and contamination factor in soil around dumpsites in Uyo, Akwa Ibom State, Nigeria. Soil samples were collected, during rainy season, at depth of 0-15cm and 15-30cm from two study sites (A, B) and a control site (C). Soil samples were all analyzed for heavy metals (Pb, Ni, Cd and Cu) using Atomic Absorption Spectroscopy (AAS). The concentration of Lead at site A for depth 0-15 cm ranged from 13.71 -14.90 mg/kg with a mean value of 14.38 ± 0.61 mg/kg; Nickel varied from 2.35 – 3.22 mg/kg (2.74 ± 0.44 mg/kg); Cadmium ranged from 3.78 – 4.13 mg/kg (3.93 ± 1.18 mg/kg); Copper ranged from 27.84 – 28.34 mg/kg (28.14 ± 0.27 mg/kg). The heavy metals concentration in soil at sites A and B followed the sequence, $Cu > Pb > Cd > Ni$ while at the control site; $Cu > Cd > Ni > Pb$. The calculated geo-accumulation index (I_{geo}) showed that the soil samples from sites A and B for Pb, Ni and Cu belong to class 2, which implies that the soil was moderately contaminated. The I_{geo} values for Cd at sites A and B were classified as 4, indicating a strongly contaminated soil. However, I_{geo} of Cd at the control site is class 3, implying moderately to strongly contaminated soil. Calculated contamination factor (CF) showed that Pb, Ni and Cu for sites A, B and control at depths 0-15cm were in class 1 (low contamination), while Cd contamination was class 4 except at control site (15 - 30cm) which showed CF of class 3. The contamination degrees (CD) for the sampling sites A and B showed considerable contamination and their pollution load index (PLI) indicated a progressive deterioration of the sites; however, the control site recorded very minimal state of pollution. Generally, the results found that the top soil (0 – 15 cm) was more contaminated than the sub soil (15 – 30 cm) of all sample sites studied. The results of this study imply that the inhabitants around Sites A and B are exposed to Cadmium pollution and the soil is not suitable for agricultural practice, since plants can take up these toxic metals and bio-accumulate them in their tissues. Cadmium, at high concentration in plants, can cause serious clinical and physiological effects on humans when consumed as food.

Keywords: Heavy metal, Dumpsites, Contamination Factor, Geo-accumulation Index, Pollution Load Index

1. INTRODUCTION

“Dumpsite is the most common and oldest form of waste disposal; however, in most developing countries, there is a lack of basic engineering technicality to mitigate soil and groundwater contamination associated open dumpsites” [1]. Poor management of dumpsites could create a number of adverse environmental impacts, which include wind-blown litter, offensive odour, repulsive sight, attraction of mice and pollutants, generation of

methane and other greenhouse gases. Dumpsites are provided for solid wastes, which comprises of both organic and inorganic wastes; tons of toxic solid wastes from a variety of sources annually find their way into dumpsites. The upsurge in population density, and the resultant increase in urbanization and industrialization, has led to an increase in the amount of waste generated, which is a cause for concern. "Due to disposal issues, most cities in Nigeria establish centers where wastes can be easily disposed and assessed for final evacuation at government approved dumpsites. However at certain times, delay in evacuating the waste to dumpsites come into play and wastes are allowed standing without removal to approved dumpsites. The decaying organic components mix with inorganic components and water in the dump, then flow as leachate through the soil surface/strata and contribute to the contamination of the ecosystem" [2].

"Heavy metal contamination of urban topsoil is usually deduced from man-made sources such as emissions from automobile exhaust, waste incineration, land disposal of wastes, use of agricultural inputs, emissions from industrial processes and wet or dry atmospheric deposits" [3]. "The presence of heavy metals in an environment alters the structure and functions of the ecosystem due to the fact that their presence has effect on the nature of the physical and chemical properties of the soil. As human population increases, the intensity of anthropogenic threat exerted on the environment increases as a result of industrialization and agricultural activities" [4]. "Apart from soil environment and aquatic ecosystem, atmospheric inorganic contaminants of natural origin or anthropogenic sources of heavy metals could led to serious ecological consequences and pose human health risks" [5]. "Heavy metals are potentially hazardous to humans and various ecological receptors because of their toxicity, persistence, bioaccumulative and non-biodegradable nature" [6].

Several studies have indicated that heavy metals are responsible for most health and ecological issues in Nigeria; however, there is a gap in knowledge on the contributions of open dumpsites to these ecological issues. Accordingly, the aim of this study is to evaluate the pollution status of dumpsites within Uyo metropolis, using some ecological risk assessment parameters.

2. MATERIAL AND METHODS

2.1 Description of the Study Area

The sampling was carried out at three (3) sites in Uyo LGA, Akwa Ibom State, Nigeria; Site A was a dumpsite at Uyo village road, Site B was at Ukana Ufot road dumpsite while Control Site C was at the University of Uyo, Soil Science field. The study area occupies the east Central portion of Akwa Ibom State, situated at 5.03° N 7.93° E and 196 meters' elevation above the sea level. The average annual temperature in Uyo is 26.4°C. Uyo serves as the administrative and political headquarters of the Akwa Ibom State and the prime occupation of the settlers is business.

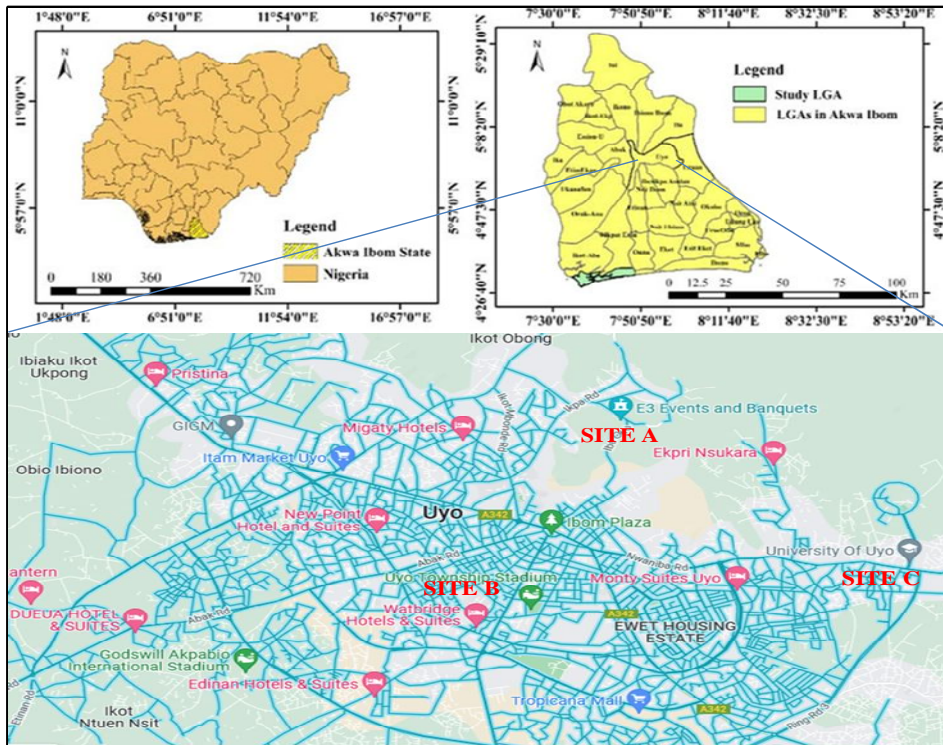


Fig. 1: Map showing the study area

Table 1: Geographical location of the sampling site

Sampling station	Latitude °N	Longitude °E	Description of anthropogenic activities
Uyo Village road (site A)	5.061484	7.942644	Human activities like hawking, pedestrian movement, vehicular traffic and dumpsite.
Ukana Offot road (site B)	5.0238	7.9173	Human activities like hawking, pedestrian movement, food and drinks vendors, vehicular traffic and dumpsite.
University of Uyo, Soil science field (site C)	5.0427	7.9183	Human activities like pedestrian movement, food and drinks vendors, light vehicular passage.

2.1 Sample Collection, Preparation and analysis

The sample was collected from the sampling location using soil auger. The soil sample was collected, during the rainy season, at 0-15 cm and 15-30 cm depth around the sampling area. It was thoroughly mixed and transferred into clean and labeled polythene bag for onward analysis in the laboratory.



Plate 1: Picture of one the dumpsites in the study

The soil sample was air-dried to constant weight for 6 hours. The air-dried samples were crushed and sieved through 2.00 mm mesh to obtain a representative sample and reduced into laboratory size by coning and quartering. Thereafter, 1.0 g of each sample was weighed out for digestion using reagent grade chemicals. Sample digestions were carried out by adopting method USEPA 3050B sample digestion protocol [7]. 10 mL nitric acid (HNO_3) was added to beakers containing 1g soil sample, then covered with watch glass and heated for 15 minutes without boiling. Samples were cooled, 5 mL HNO_3 was added and heated for 30 minutes until no brown fumes were given off. Solution was allowed to evaporate to less than 5 mL and allowed to cool. 2 mL water and 3 ml 30% hydrogen peroxide (H_2O_2) was added and heated for 2 hours until effervescence ceased. Solution was reduced to 5 mL via evaporation. 10 mL hydrochloric acid (HCl) was added and heated for 15 minutes without boiling. After cooling, the digested samples were filtered using a Whatman filter paper (grade 41, pore size 20 μm) into 100 mL volumetric flask. The filtrate was diluted to the mark with deionized water at 25°C and ready for analysis. Each sample was digested in triplicates for the purpose of reproducibility. The blank determination was also carried out in similar manner. The presence of heavy metals was determined using Atomic Absorption Spectrophotometer (Unicam 969 thermo elemental) [8].

2.2 Ecological Risk Assessment

2.2.1 Index of geo-accumulation (I_{geo})

Geo-accumulation index was introduced by Barbieri [9]. This index is used to assess anthropogenic impact of pollutants on the environment and is calculated using the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (2.1)$$

Where C_n is the measure of the metal concentration in the sediment, B_n is the background concentration of the element (average shale concentration has been given by Turekian & Wedepohl [10], which are $Pb=20\text{mg/kg}$, $Cd=0.3\text{mg/kg}$, $Ni=68\text{mg/kg}$ and $Cu=45\text{mg/kg}$ and 1.5 is the factor compensating background data [11])

The I_{geo} factor is not comparable to other indices of metal enrichment due to the nature of the I_{geo} calculation; it involves a log function and background multiplication of 1.5. It is composed of seven grades (0-6) indicating various degrees of metal enrichment above the average shale value ranging from unpolluted to very high polluted sediment quality. Class 0 (uncontaminated): $I_{geo} \leq 0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated sediment): $1 < I_{geo} < 2$; Class 3 (moderately to strongly contaminated): $2 < I_{geo} < 3$; Class 4 (strongly contaminated): $3 < I_{geo} < 4$; Class 5 (strongly to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $5 < I_{geo}$. Class 6 is an open class and comprises all values of the index higher than class 5.

2.2.2 Metal contamination factor (CF)

Contamination factor was calculated by comparing the mean trace metal concentration with average shale concentration given by Turekian & Wedepohl [10], which is used as global standard reference for unpolluted sediment. CF for each metal was determined by the following equation:

$$\text{Contamination factor (CF)} = \frac{\text{Mean metal concentration at contaminated site}}{\text{metal average shale concentration}} \quad (2.2)$$

Hakanson [12] classified CF values into four grades as follows; $CF < 1$ in class 1 with low CF; $1 \leq CF < 3$ in class 2 with moderate CF; $3 \leq CF < 6$ under class 3 with considerable CF; and $CF \geq 6$ is class 4 with very high CF.

2.2.3 Contamination degree (CD)

CD is the sum of all CF values of a particular sampling site. Ahdy & Khaled [13] classified CD in terms of four grade ratings of sediments, i.e. $CD < 6$ follows the class 1 which shows low CD, $6 \leq CD < 12$ follows the class 2 it shows moderate CD, $12 \leq CD < 24$ follows the class 3 it shows considerable CD and $CD \geq 24$ follows the class 4 with very high CD.

2.2.4 Pollution Load Index (PLI)

Pollution load index defines the estimated metal contamination status and the necessary action that is required to be taken in alleviating undesirable condition. Pollution load index for each site was determined by the method proposed by Tomlinson *et al.* [14]. The PLI for a

single site is the nth root of n number multiplying the factors (CF values) together. PLI for each site was determined by the following equation:

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \dots \times CFn)} \quad (2.3)$$

where CF is the contamination factor and n is the number of parameters.

According to Mohiuddin *et al.* [15], PLI = 0 indicates a perfect state of pollution; PLI = 1 points indicate only baseline levels of pollutants present and PLI > 1 would indicate progressive deterioration of sites.

3. RESULTS AND DISCUSSION

3.1 Heavy metals in soil

Table 2: Descriptive statistics of heavy metals in soil of some dumpsite in Uyo metropolis in dry weight (mg/kg)

Metals	Soil depth	Control site (mg/kg)	Site A (mg/kg)	Site B (mg/kg)	WHO (mg/kg)
Pb	0 – 15 cm	0.47 – 0.56 (0.51±0.05)	13.71 – 14.90 (14.8±0.61)	16.07 – 16.38 (16.22±0.16)	85
	15 – 30 cm	0.41 – 0.43 (0.42±0.01)	12.77 – 14.13 (13.63±0.75)	14.32 – 14.53 (14.45±0.12)	
Ni	0 – 15 cm	1.36 – 1.70 (1.56±0.18)	2.35 – 3.22 (2.74±0.44)	2.59 – 2.98 (2.76±0.20)	35
	15 – 30 cm	0.98 – 1.35 (1.16±1.19)	2.35 – 2.44 (2.38±0.05)	2.18 – 3.33 (2.27±0.08)	
Cd	0 – 15 cm	2.54 – 2.66 (2.59±0.06)	3.78 – 4.13 (3.93±1.18)	4.06 – 4.27 (4.15±0.11)	0.8
	15 – 30 cm	1.52 – 1.57 (1.55±0.03)	3.78 – 4.10 (3.99±0.18)	2.92 – 3.32 (3.07±0.22)	
Cu	0 – 15 cm	24.89 – 25.20 (25.09±0.17)	27.84 – 28.34 (28.14±0.27)	25.68 – 26.01 (25.87±0.17)	36
	15 – 30 cm	22.74 – 24.00 (23.26±0.66)	25.68 – 25.92 (26.48±1.18)	30.30 – 31.65 (30.76±0.77)	

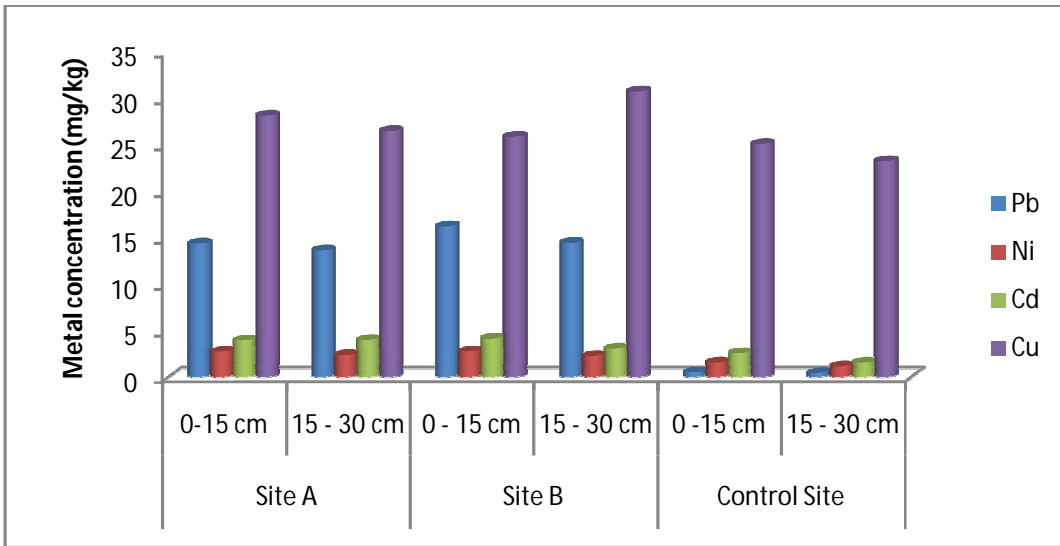


Figure 2: Comparative study of the levels of heavy metals at the sampling sites

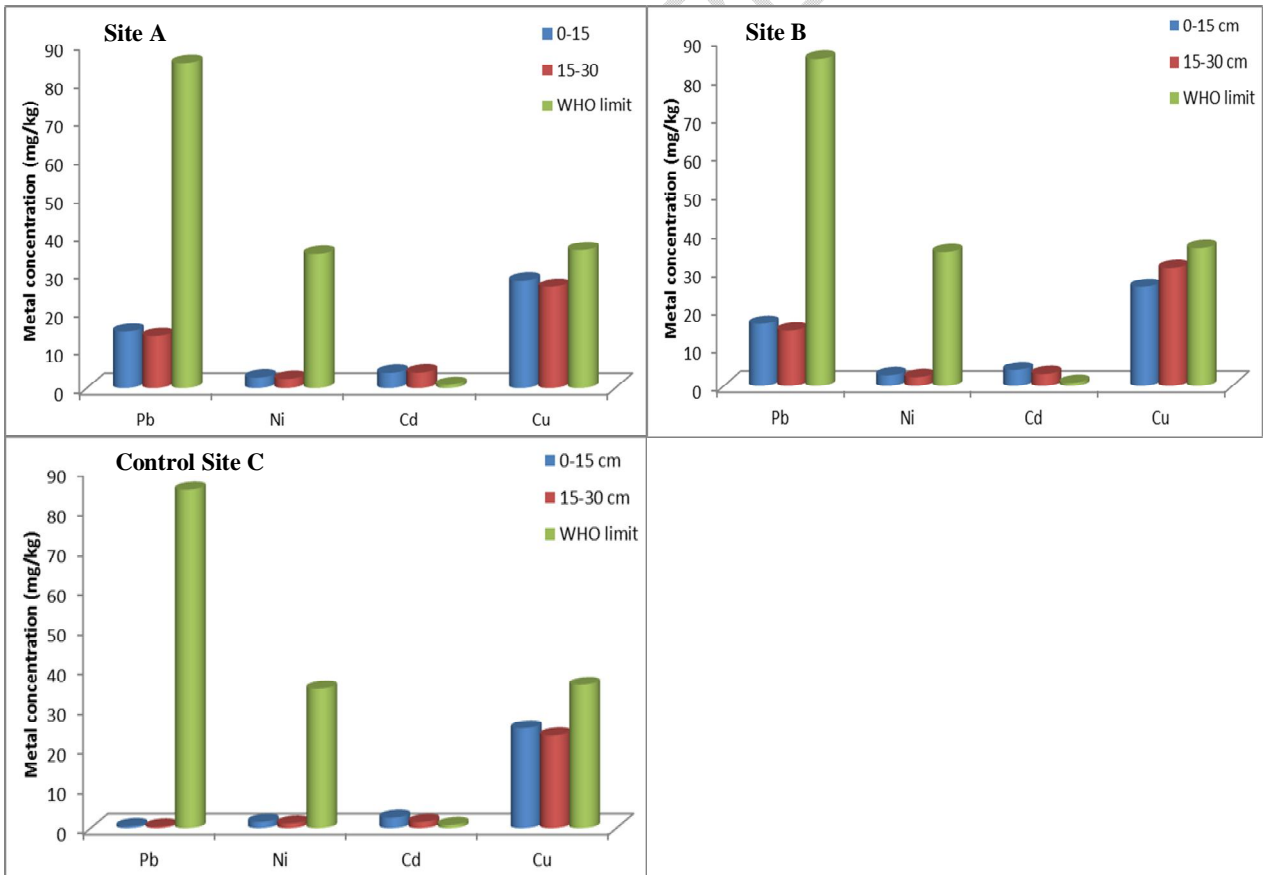


Figure 3 : Comparison of heavy metals concentration in different soil depths at sampling sites with WHO recommended limits

Site A

The descriptive statistics of heavy metals in soil dumpsite obtained from Uyo metropolis for sampling sites are presented in Table 2. Figure 2 gives the comparative study of the levels of heavy metals at all the sampling sites. Comparison of the levels of heavy metals at Site A with WHO permissible limit is given on Figure 3. The concentration of lead (Pb) at Site A (0-15 cm) ranged from 13.71 -14.90 mg/kg (14.38 ± 0.61 mg/kg) which were below the WHO permissible limit of 85.0 mg/kg [16]. Nickel concentration range of 2.35 – 3.22 mg/kg (2.74 ± 0.44 mg/kg) was less than the WHO permissible limit of 35.0 mg/kg. The value for Cadmium ranged from 3.78 – 4.13 mg/kg (3.93 ± 1.18 mg/kg), above the WHO permissible limit of 0.8 mg/kg while copper concentration (28.14 ± 0.27 mg/kg) was below the permissible limit of 36.0 mg/kg. The heavy metals concentration in soil at site A (0-15 cm) followed the sequence; Cu > Pb > Cd > Ni. According to studies [17, 18], heavy metals like cadmium (Cd), lead (Pb), and nickel (Ni), indirectly distributed in the environment as a result of human activities, could be very toxic even at low concentrations. Cd has similar chemical properties like Zn, which may account in part for its toxicity in biological system. Zn being an essential trace element in plants and animals can be substituted with Cd and may cause the malfunctioning of metabolic processes [19]. Cd is very toxic to human, and specifically targets the bones and kidneys.

The levels of lead at site A (15-30 cm) ranged from 12.77 -14.13 mg/kg (13.63 ± 0.75 mg/kg); Nickel ranged from 2.35 – 2.44 mg/kg (2.38 ± 0.05 mg/kg); Cadmium ranged from 3.78 – 4.10 mg/kg (3.99 ± 0.18 mg/kg). With the exception of cadmium, the heavy metals were below WHO permissible limit. From Figure 3, copper was next to the most prominent peak (lead), ranging from 25.68 – 25.92 mg/kg (26.48 ± 1.18 mg/kg) and was less than WHO permissible limit of 36.0 mg/kg. Cu is a micro element which is essential in plant growth and occurs naturally in soil and sediments. It is an important component of enzymes and is necessary for normal growth and development. However, anthropogenic activities may raise the level of Cu in soil above their natural background levels; this may lead to hair and skin decolourations, dermatitis, respiratory tract disease in humans [20].

Site B

The concentration of lead in soil at Site B (0-15 cm) ranged from 16.07 – 16.38 mg/kg (16.22 ± 0.16 mg/kg) and below the WHO permissible limit of 85.0 mg/kg. It has been stated that high Pb concentration in environmental compartments indicates pollution from oil spill and other industrial activities [21]. Lead is a well-known neurotoxin which causes the impairment of the neurodevelopment in children. According to ATSDR [22], lead accumulates in the skeleton and its mobilization from bones during pregnancy and lactation causes exposure to fetuses and breastfed infants. Nickel in Site B ranged from 2.59 – 2.98 mg/kg (2.76 ± 0.2 mg/kg), lower than the WHO permissible limit of 35.0 mg/kg [16]. Cadmium values varied ranged from 4.06 – 4.29 mg/kg (4.15 ± 0.11 mg/kg), which exceeds the WHO permissible limit of 0.8 mg/kg. Copper range of 25.68 – 26.01 mg/kg (25.87 ± 0.17 mg/kg) was lower than the permissible limit of 36.0 mg/kg, hence poses no health hazard. Generally, the heavy metals concentration in soil at site B (0-15 cm) follow the order; Cu > Pb > Cd > Ni.

The concentration of lead in soil at Site B (15-30 cm) ranged from 14.32 -14.53 mg/kg (14.45 ± 0.12 mg/kg) were below the WHO permissible limit of 85.0 mg/kg. The value of Nickel ranged from 2.18 - 3.33 mg/kg (2.27 ± 0.08 mg/kg), below the WHO permissible limit of 35.0 mg/kg. The mean value of cadmium (3.07 ± 0.22 mg/kg) was above the WHO permissible limit of 0.8 mg/kg. Furthermore, copper (30.76 ± 0.77) was below the WHO permissible limit of 36.0 mg/kg. The heavy metals concentration in soil at Site B (0-15 cm) follow the sequence; Cu > Pb > Cd > Ni.

Site C

Site C was the control site with no dumpsite and relatively fewer commercial activities. The concentration of lead at soil depth of 0-15 cm ranged from 0.47 - 0.56 mg/kg (0.51 ± 0.05 mg/kg); nickel (1.56 ± 0.18 mg/kg); cadmium (2.59 ± 0.06 mg/kg) and copper (25.09 ± 0.17). With the exception of cadmium, concentration of heavy metals analysed in Site C were below the WHO permissible limit (Figure 3). The metals were slightly lower at the subsoil (15 – 30 cm) of the control site, compared to the top soil (0 – 15 cm). Generally, the heavy metal rank profile in Site C was $Cu > Cd > Ni > Pb$. This is at variance with Sites A and B where the heavy metal sequence was $Cu > Pb > Cd > Ni$. Comparatively, Site C had the least amount of heavy metals in the soil, which can be attributed to the minimal commercial activity and absence of an open dump at the site.

3.2 Ecological Risk Assessment

The ecological risk assessment parameters utilized in this study are geo-accumulation index, contamination factor and pollution load index, as shown on tables 3 and 4

Table 3: I_{geo} values for heavy metal concentration in soil dumpsites obtained from Uyo metropolis

Site	Soil depth	Pb	Ni	Cd	Cu
A	0 - 15 cm	0.1438	0.0081	2.6287	0.1255
	15 – 30 cm	0.1363	0.0070	2.6689	0.1181
B	0 – 15 cm	0.1622	0.0081	2.7759	0.1154
	15 – 30 cm	0.1445	0.0067	2.0535	0.1372
Control	0 – 15 cm	0.0051	0.0046	1.7324	0.1119
	15 – 30 cm	0.0042	0.0034	1.0368	0.1037

Table 4: CF values for heavy metal concentration in soil dumpsites obtained from Uyo metropolis

Site	Soil depth	Pb	Ni	Cd	Cu	CD	PLI
A	0 – 15 cm	0.7190	0.0403	13.1000	0.6253	14.4846	1.9
	15 – 30 cm	0.6815	0.0350	13.3000	0.5884	14.6049	1.7
B	0 – 15 cm	0.8110	0.0406	13.8333	0.5749	15.2598	2.0
	15 – 30 cm	0.7225	0.0334	10.2333	0.6836	11.6728	1.6
Control	0 – 15 cm	0.0255	0.0229	8.6333	0.5576	9.2393	0.2
	15 – 30 cm	0.0210	0.0171	5.1666	0.5169	5.7216	0.1

The I_{geo} value for lead, nickel and copper at Site A (0-15cm) were 0.1438, 0.0081 and 0.1255 respectively, which belong to class 2 and indicates moderate contamination (Table 3). The I_{geo} value of cadmium (2.6287) belongs to class 4, indicating strong contamination. CF for lead, nickel and copper was 0.7190, 0.0403 and 0.6253 respectively, falling under the low CF class, while Cd belongs to the high CF class 4. The CD for this sampling site had the value of 14.4846 (class 3), which shows considerable CD. The pollution load index which estimate the metal contamination status at this site was observed to be 1.9, indicating progressive deterioration of the site

The I_{geo} values for Pb, Ni, and Cu at Site A (15-30 cm) were 0.1363, 0.0070 and 0.1181 respectively. These values are categorized under I_{geo} class 2, which implies moderately contamination. However, Cd I_{geo} of 2.6689 (class 4) reveals a strong contamination of the sample sites. Lead, nickel and copper which had low CF of 0.6815, 0.0350 and 0.5884 respectively, while a high CF value of 13.3000 was recorded for Cd. The CD value of 14.6049 for this sampling site belongs to class 3, which implies a considerable contamination of the site. The pollution load index status at this Site A (15-30cm) was observed to be 1.7, indicating progressive deterioration of the site.

The I_{geo} value for heavy metals concentration in soil dumpsite at Site B (0-15cm) were as follows; Pb (0.1622), Ni (0.0081) and Cu (0.1154), implying moderate contamination. Cadmium I_{geo} value of 2.7759 was found for the site, which indicates a strong contamination. CF for lead, nickel and copper was 0.8110, 0.0406 and 0.5749 respectively, which were quite low (class 1); however, cadmium had a high CF of 13.8333 (class 4). The observed CD value of 15.2598 for this sampling site belongs to class 3 and reveals a considerable degree of contamination. The pollution load index status at this Site B (0- 15 cm) was 2.0, indicating progressive deterioration of the site. CF for lead, nickel and copper at Site B (15 – 30 cm) was low, with values of 0.7225, 0.0334 and 0.6836 respectively, while the value for Cadmium (10.2333) is class 4. The observed value of 11.6728 for CD of this sampling site belongs to class 2, which implies a moderate contamination of the site. Ultimately, the pollution load index status at this Site B (15-30cm) was observed to be 1.6, indicating progressive deterioration of the site.

The I_{geo} for Pb, Ni and Cu in Site C (0-15 cm) were 0.0051, 0.0046 and 0.1119 respectively. These values belong to class 2 which implies that they are moderately contaminated; however, it is contaminated with cadmium (Class 3). CF of site C were 0.0255, 0.0229 and 0.5576 for lead, nickel and copper respectively, while CF for Cd was 8.6333 (class 4). The CD for this sampling site had the value of 9.2393 and the pollution load index status was 0.2, indicating a very minimal pollution state.

The I_{geo} values at Control site (15-30 cm) were Pb (0.0042), Ni (0.0034), Cd (1.0368) and Cu (0.1037). These values imply that the site was moderately contaminated with Pb, Ni and Cu; but was strongly contaminated with Cd. CF values of Pb, Ni and Cu were 0.0210, 0.0171 and 0.5169 respectively, and belong to class 1 (low CF), while Cd with value of 5.1666, belongs to class 3 with considerable CF. The pollution load index status of Site C (15 -30 cm) was observed to be 0.1, indicating a perfect state of pollution.

4. CONCLUSION

This study examined the pollution status of heavy metals in soil at Uyo dumpsites in Akwa Ibom State, Nigeria, using indicators such as I_{geo} , CD, CF and PLI. The results of this study have shown that the two dumpsites are moderately contaminated with Pb, Ni and Cu; while contamination with Cd is significant. The PLI of the two dumpsites ranged from 1.6 – 2.0, indicating a progressive deterioration of the sites. Generally, it was found that the top soil (0 – 15 cm) was more contaminated with the heavy metals than the subsoil (15 – 30 cm). This may imply an anthropogenic source of contamination, rather than natural. Comparison of the dumpsites with a control site has confirmed that the dumpsites are more contaminated with the heavy metals under investigation. However, the concentrations of Pb, Ni and Cu for all study sites were below the WHO permissible limit, while Cd was above the permissible limit. The heavy metals concentration in soil at sites A and B followed the sequence; Cu > Pb > Cd > Ni while at the Control site, C: Cu > Cd > Ni > Pb. The calculated I_{geo} revealed that the soil samples were moderately contaminated with Pb, Ni and Cu but strongly contaminated with Cd. The CD for the sampling sites of A (0-15 cm), A (15 -30 cm), B (0 -15 cm) showed considerable CD; the PLI for these sites indicates a progressive deterioration of the sites while the Control sites and Site B (15 -30 cm) showed a perfect state of pollution. These results imply that the inhabitants around the sampling sites are liable to cadmium pollution and the soil around the dumpsites is not suitable for agricultural practice, since plants have the ability to take up toxic metals and bio-accumulate them in their tissues. At high levels in plants, Cd can cause serious clinical and physiological effects on humans when such plants are continuously consumed. Thus, there is need for frequent monitoring of the levels of these toxic metals in soils of urban area and adopt measures to mitigate their harmful effect on the exposed populace and ecosystem.

REFERENCES

1. Jiya MJ, Bala JD, Mustapha HI, Kuti IA, Musa ET, Yerima YI, Daniel ES, Akos MP. Heavy metals concentration in the dumpsite soils using geo-accumulation index and ecological risk assessment. Agric Eng Int: The CIGR e-journal. 2019;21(3):7-17
2. Kumari P, Kaur A, Gupta NC. Extent of Groundwater Contamination Due to Leachate Migration Adjacent to Unlined Landfill Site of Delhi. Environmental Claims Journal. 2018; DOI: 10.1080/10406026.2018.1543825

3. Onianwa P. Monitoring atmospheric metal pollution: a review of the use of mosses as indicators. *Environ Monit and Assess.* 2001;71(1):13-50.
4. Ubong U, Ekwere I, Ikpe E. Risk and Toxicity Assessments of Heavy Metals in *Typanotonus fuscatus* and Sediments from Iko River, Akwa Ibom State, Nigeria. *Inter Journ of Environ and Climate Change.* 2020;10(3):38 - 47.
5. Ite AE, Ubong UU, Etesin UM, Nsi EW, Ukpong EJ, Ekanem AN, Ufot UF, Udo AI. Heavy metals in epiphytic lichens and Mosses of Oil-Producing Commities of Eket and Ibeno, Akwa Ibom State-Nigeria. *Amer Journ of Environ Protec.* 2016;4(2):38-47.
6. Ekwere IO, Horsfall M, Otaigbe JOE. A study on the Photocatalytic Reduction of Some Metals ions in Aqueous Solution using UV – Titanium dioxide System. *Inter Res Journ of Pure & Appl. Chem.* 2019;18(2):1 –7.
7. USEPA. Method 3050B acid digestion of sediments, sludges, and soils 1.0 scope and application. Washington, DC, USA. 1996.
8. Peters J, Combs S, Hoskins B, Jarman J, Kovar J, Watson M, Wolf A, Wolf N. Recommended methods of manure analysis (A3769). University of Wisconsin, Madison, WI, USA. 2003.
9. Barbieri M. The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. *J Geol Geophys,* 2016;5(1):1-4.
10. Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. *Geol Soc of Amer Bull.* 1961;72(2):175-192.
11. Taylor, S. Abundance of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta.* 1964;28(8):1273-1285.
12. Hakanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Wat Res.* 1980;14(8):975-1001.
13. Ahdy HH, Khaled A. Heavy metals contamination in sediments of the western part of Egyptian Mediterranean Sea. *Austral Journ of Basic and Appl Sc.* 2009;3(4): 3330-3336.
14. Tomlinson D, Wilson J, Harris C, Jeffrey D. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer meeresuntersuchungen.* 1980;33(1):566-575.
15. Mohiuddin K, Zakir H, Otomo K, Sharmin S, Shikazono N. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. *Intern Journ of Environ Sc & Tech.* 2010;7(1):17-28.
16. WHO. Permissible limits of heavy metals in soil and plants. Geneva, Switzerland. 1996.
17. Ubong UU, Ekwere IO, Akpan AD. Assessment of Heavy Metals in Chicken Feeds obtained from Uyo, Akwa Ibom State, Nigeria. *Journ of Chem Soc of Nig.* 2022;47(4).
18. Ubong UU, Ekwere IO. Distribution and Human Health Risk Assessment of Heavy Metals in Tissues of *Callinectes sapidus* from Iko River, Akwa Ibom State, Nigeria. *Asian Journ of Environ & Ecol.* 2022;19(3):1-8. <https://doi.org/10.9734/ajee/2022/v19i3408>

19. Tang L, Qui R, Tang Y, Wang S. Cadmium-zinc exchange and their binary relationship in the structure of Zn-related proteins: A mini review. *Metallomics*. 2014;6(8) DOI: [10.1039/c4mt00080c](https://doi.org/10.1039/c4mt00080c)
20. Khan SA, Khan L, Hussain I, Marwat KB, Akhtar N. Profile of heavy metals in selected medicinal plants. *Pakistan Journ of Weed Sc Res*. 2008;14(1-2):101-110.
21. Osuji LC, Onojake,CM. Trace heavy metals associated with crude oil: A case study of Ebocha-8 Oil-spill-polluted site in Niger Delta, Nigeria. *Chem & Biodivers*. 2004;1(11): 1708-1715.
22. ATSDR. Toxicological profile for benzene. US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA. 2007.

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