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Concentration of Heavy Metals in Soils at the Municipal Dumpsite in Calabar Metropolis

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Authors' contributions

This work was carried out in collaboration between both authors. Author VFE wrote the protocol, managed the analyses of the study, the literature searches and wrote the first draft of the manuscript.

Author SBAU designed the study and performed the statistical analysis. Both authors read and approved the final manuscript.

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ABSTRACT

This research was carried out to investigate the levels of heavy metals in soils at the municipal dumpsite in Calabar, Cross River State, Nigeria. Composite soil samples were collected from five different landscape positions along a toposequence (crest, upper slope, middle slope, lower slope and valley/swamp) at the dumpsite in Calabar. The control sample was taken from an adjacent plot. The control soil was slightly acidic (5.6) while soils from the dumpsite were slightly acidic (6.7 -7.4) to slightly alkaline in reaction. In all the dumpsite locations the levels of Mercury (0.4-1.0 mg/kg), Chromium (0.66 - 200 mg/kg), Nickel (26 - 748.6 mg/kg), Lead (118 - 4548 mg/kg), and Zinc (1248 -2864 mg/kg) were above the permissible limits in soil whereas iron and copper concentrations were within soil limits. Generally the values of Mercury (Hg), Cadmium (Cd), Chromium (Cr), iron (Fe), Nickel (Ni), Lead (Pb), Zinc (Zn) and Copper (Cu) observed for the dumpsite were higher than the control soil. The metal contamination/pollution index assessment revealed that the soils in the dumpsite were excessively polluted with impending negative effect on plants animal, humans and the environment at large. It is expedient that necessary actions be put in place to sort at source, recycle and reuse wastes materials to minimize the quantity of these toxic metals in the environment.

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1. INTRODUCTION

Municipal waste composition is a heterogeneous collection of different materials including organic material plastic, metal, textiles etc. Municipal waste remains a serious problem all over the world because it contaminates soil, water bodies and endangers human health and the environment at large [1]. Levels of urbanization and modernization of a place have profound effect on the production and composition of municipal waste; however, some general trends portray high content of organic matter (50-90 percent) [2,3]. According to Obeng and Wright [4] very large quantities of solid wastes are generated in urban areas. Some of the waste materials generated across various cities consist of food waste, paper cardboard, faeces, screens, plastics, broken bottles, batteries, metals, textiles, bones, glass, ceramics expired drugs, cosmetics and other hazardous waste. The volume and composition may however be subject to large seasonal variations. Easily degradable fractions of municipal waste are put at between 40 and 87 percent in weight [3,4,5,6].

The composition of waste is not different in Calabar, a city that has witnessed population upsurge and industrial evolution in the last decade. Presently, Calabar is faced with the challenge of daily collection and disposal of large volumes of municipal waste. A ravine at Ikot Effanga Mkpa was designated for the disposal of these wastes. Currently, the ravine is full and overflows its bounds. The location and management of this very active dumpsite in Calabar, now located within the city due to population influx and expansion is of great concern. Improper classification and treatment of waste can lead to soil pollution and toxic leachate/runoff into nearby water bodies. The process of burning these wastes concentrates heavy metals in the bottom ash. This research aims to assess the Metal Contamination/Pollution Index (MPI) of the soils at the municipal dumpsite in Calabar. This index value represents the ratio between the heavy metal content effectively measured in soil by chemical analysis and reference value obtained from the control soil.

2. STUDY LOCATION

2.1 Location, Climate and Vegetation of the Area

This experiment was carried out at the municipal dumpsite located in Ikot Effanga Mkpa, Calabar (Fig. 1). Calabar lies between latitude 04°57" and 05°05" N and longitude 08°19" and 08°25" E. Calabar is the Capital of Cross River State and has often been described as the tourism hub of Nigeria. Administratively the city is divided into Calabar municipality and Calabar South. It has a land area of 406 sq Km and a population of 371,022 as at 2006 [7]. The area is characterized by tropical climate with a mean rainfall of 2360mm (range 2290-2680 mm) with distinct dry season of 3-4 months and wet seasons of 8- 9 months and two peaks exhibited in June to July and September to October. Ambient temperature and relative humidity is high throughout the year. The mean daily minimum temperature varies from 21 to 24°C and the mean maximum is from 27 to 30°C. The mean relative humidity varies from 82 - 87% with tropical maritime winds of 60-70% [8]. Calabar is within the lowland rainforest ecological zone with large area of undisturbed vegetation in some areas [8]. It is a semi-industrial and residential area.

2.2 Sampling Locations

The sampling site is an undulating landscape used by Calabar Urban development Authority and Environmental Sanitation Authority for solid waste disposal. Wastes dumped at the site were mainly plant trimmings, domestic-household waste, hospital waste, industrial waste, faecal waste etc. The waste dump has an area of 2,355 sq m. Sampling points were established along the waste dump toposequence. Global positioning system (GPS) (model= SporTrak Map^(R)) was used to determine the latitude, longitude and elevation of each slope position. Samples taken from the control plot which was the highest points near to the dump site served as control or non-dump site. The coordinates of the sampling points are presented below (Table 1).

Table 1. Coordinates and elevation of the sampling locations

Coordinates	Control	Crest	Upper slope	Middle slope	Lower slope	Valley/Swamp
Latitude	05°02'09N	05°02'03N	05°02'05N	05°02'08N	05°02'02N	05°02'01N
Longitude	008°21'51E	008° 21'54E	008°21'52E	008°21'50E	008°21'50E	008°21'50E
Altitude	27 m	25 m	23 m	22 m	22 m	14 m

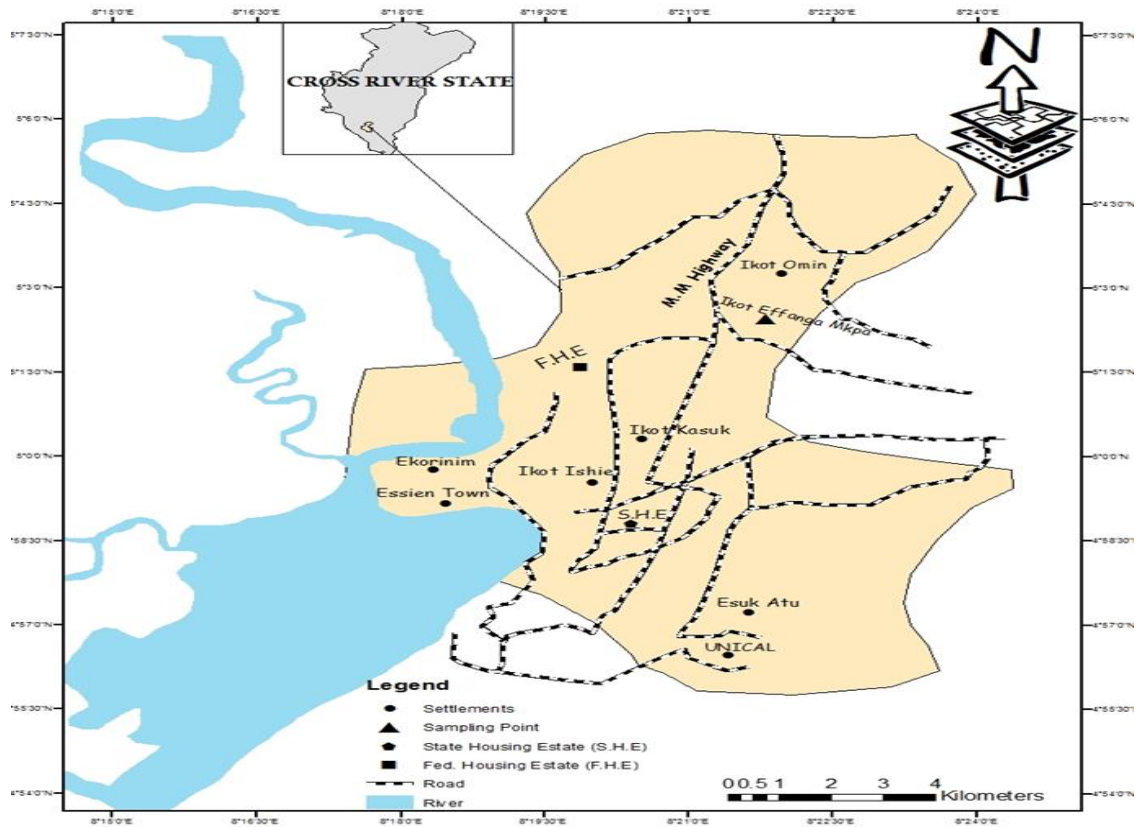


Fig. 1. Map of Calabar showing the study area

3. MATERIALS AND METHODS

3.1 Sampling Procedure

An area measuring 20 m x 20 m was marked out at each sampling location along the toposequence. Soil samples were collected with the aid of an auger from five points of the marked area at a depth of 0–30 cm. The five soil samples

were bulked to form a composite sample for each sampling location [9]. Five (5) representative composite soil samples were collected from the crest, upper slope, middle slope, lower slope and valley/swamp for the dumpsite and one from the control plot. A total of six (6) composite samples were collected in all. The samples collected were placed in sampling bags, labeled and transported to the laboratory for heavy metal analyses.

Table 2. Interval of contamination/pollution index of heavy metals in soil and its significance

MPI	Significance	Remarks
< 0.1	Very slight contamination	No negative effect on soil, plant and environment
0.10 – 0.25	Slight contamination	“
0.26 – 0.5	Moderate contamination	“
0.51 – 0.75	Severe contamination	“
0.76 – 1.00	Very severe contamination	“
1.1 – 2.0	Slight pollution	Will pose negative effect on soil, plant and environment
2.1 – 4.0	Moderate pollution	“
4.1 – 8.0	Severe pollution	“
8.1 – 16.0	Very severe pollution	“
> 16.0	Excessive pollution	“

Adapted from [11]

Table 3. Maximum permissible limits for heavy metals in soil

Heavy metals mg/kg	EU STD mg/kg	UK STD mg/kg	US STD mg/kg	WHO (mg/kg)	Ranges for uncontaminated soil (mg/kg) (Nangia, 2001)
Fe	-	-	-	-	7000- 55000
Zn	300	200	200-300	12- 60	10-300
Hg	-	-	-	0.001-0.04	0.01-0.3
Cu	140	63	80-200	1-12	2-100
Cd	3.0	1.4	400	0.002-0.5	0.01-0.7
Cr	180	6.4	400	0.002-0.2	5-3000
Pb	300	70	300	0.3-10	2-200
Ni	-	-	-	0.1-5	10-1000

*EU = Europe, *UK= United Kingdom, *US = United States, *WHO = World Health Organization,
*STD = Standard
Source: [12,13,14]

3.2 Determination of the Heavy Metal Contents of the Soil at the Dump Site

The soil samples were air dried and passed through a 2mm sieve. Soil portions (2.5 g each), were acid-digested in microwave assisted Kjeldahl digester by adding 5 ml of concentrated nitric acid, 2 ml hydrochloride acid and 1 ml of hydrofluoric acid. The vessels were capped and heated in a microwave unit at 800 W to a temperature of 210°C for 20 minutes with pressure of 40 bar. The digested samples were analyzed for heavy metals (Pb, Ni, Cd, Cu and Zn) by Atomic Absorption Spectrophotometer (AAS) of UNICAM 919 model [10].

3.3 Quantification of Soil Heavy Metal Contamination/Pollution Index (MPI)

The quantification of MPI was derived using the equation given by Lacatusu [11].

$$\text{MPI} = \frac{\text{Concentration of metals in soil}}{\text{Reference soil (control)}} \quad (1)$$

The maximum permissible limits of heavy metals in soils as established by standard regulatory bodies in Europe (EU), United Kingdom (UK) and United State of America (USA) as presented in Table 3 above in total form.

4. RESULTS AND DISCUSSION

The distribution of heavy metals: Mercury (Hg) Cadmium (Cd), Chromium (Cr), iron (Fe), Nickel (Ni), Lead (Pb), Zinc (Zn) and Copper (Cu) as analyzed for Calabar municipal dumpsite and Control sites are presented on Table 4.

The pH of the soils around the Municipal dump site in Calabar were 5.6, 7.0, 6.7, 7.4, 5.9, 7.4 for the control plot, crest, upper slope, middle slope, lower slope and valley/swamp respectively. The results indicated that the control plot and the lower slope had slightly acid pH while, the crest, upper slope, middle slope and valley/swamp had neutral to slightly alkaline pH.

Soil is a major sink for heavy metals released into the environment by industrial and human activities. Nonetheless, heavy metals above certain limits exhibit adverse ecological effects and are toxic to plants, animals and humans at large [15,16,17]. An assessment of the soils at the dump site in Calabar metropolis revealed an enrichment and wide spread of heavy metals (Figs. 2-9).

Mercury was observed at the dump sites with values ranging between 0.4 and 1.00 mg/kg while the control plot recorded a mean values 0.1 mg/kg (Table 4 and Fig. 2). The values recorded for the crest, upper slope, middle slope lower slope and the valley/swamp at the dumpsite were within the 0.01- 0.3 mg/kg range for uncontaminated soil as outlined by Nangia [14], but exceeded the 0.001- 0.04 mg/kg range accepted by WHO. Comparing the data obtained at the dump sites with the control to determine the heavy metal contamination/pollution index (MPI) as outlined by Lacatusu [11], the soils of the dumpsite were found to be moderately to very severely polluted with mercury.

The determined concentration of Cd in soil at the dumpsite showed a range of 0.66-1.6 mg/kg, while the control site had a mean value of 0.66 mg/kg (Table 4). The Cd concentration recorded for the control plot and dump sites were within

the uncontaminated soil range (0.01-0.7 mg/kg) except for the crest and Valley which exceeded the level [14]. The values for Cd across the sampling points exceeded the 0.002-0.5 mg/kg in soil range set by WHO but were below the maximum permissible concentration of 3.0, 1.4 and 3.0 mg/kg set out by EU, UK and USA Standards respectively for Cd in soil. Despite the low concentration of Cd observed at the dumpsite the pollution index classified the soils of the dump site in Calabar as being in a state of very severe to excessive pollution (Table 5 and Fig. 3) [11].

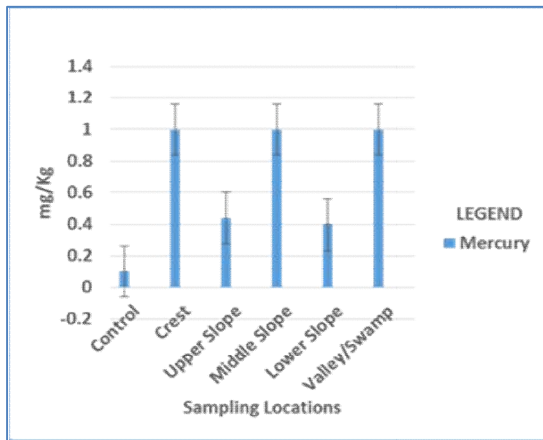


Fig. 2. Concentration of Mercury in the municipal dump site in Calabar

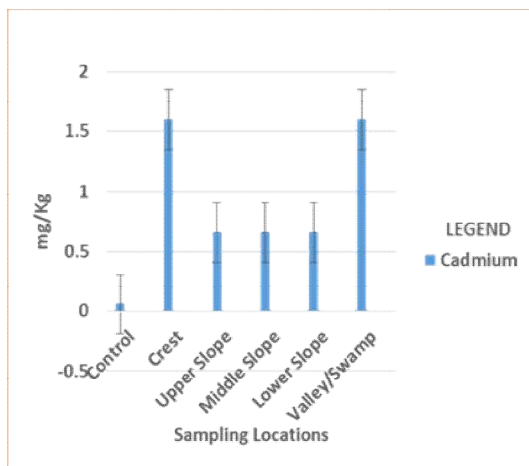


Fig. 3. Concentration of Cadmium in the municipal dump site in Calabar

Chromium (Cr) detected at the dump site had a range of 0.66 - 200.00 mg/kg while the control had a mean of 0.66 mg/kg. The concentrations of Cd observed at the crest, upper slope and middle

slope of the dumpsite were way higher than the concentration recorded at the control site revealing that the impact of Cr pollution in these locations is not due to anthropogenic source. The observed high concentration of Cr in these soils could be attributed to wastes containing high levels of chromium. The values observed for Cr at the dumpsite were much higher than the WHO limits (0.002-0.2 mg/kg) and the 6.4 mg/kg UK standard but within the uncontaminated soil range (5-3000 mg/kg) of Nangia [14] and the 400 mg/kg USA standard. The Lacatusu [11] classification view this soil as being very severe to excessively polluted (Table 5 and Fig. 4).

Iron (Fe) was observed to be the most abundant metal at the study site with values ranging between 768-11.928 mg/kg while the control was observed to contain quantities 280.0mg/kg (Fig. 5). The highest concentration of iron (11,928.0 mg/kg) was obtained at the crest followed by the middle slope and upper slope with values of 7336 mg/kg and 8226 mg/kg respectively. The values observed for Fe at the dumpsite were within the normal uncontaminated soil range (7000 – 55000 mg/kg) recommended by Nangia [14]. The values obtained for Fe could be attributed to the abundant Fe containing waste at the dumpsites which are eventually leached into the underlying soils. The levels of Fe recorded for the dump site soils when compared to the control places the soils in the very severe pollution to excessive pollution class (Tables 4 and 5) with negative effects of Fe on soil and plants expected.

The concentration values obtained for Nickel (Ni) at the dumpsite (Fig. 6), revealed a range of 26.0-748.6 mg/kg for the dump site while a mean of 28.0 mg/kg was recorded for the control (Table 4). These values exceeded the WHO acceptable limits in soil but fitted into the range of 10-1000mg/kg for uncontaminated soils as outlined by Nangia [14]. The contamination/pollution index revealed that the soils at the valley/swamp had very severe contamination while the upper and middle slopes had moderate and excessive pollution respectively with consequences of posing negative effects to soil and particularly plants raised on these soils.

Lead (Pb) was the third most abundant metal at the investigated dumpsite (Fig. 7), with values ranging between 118.0 mg/kg - 4548.0 mg/kg for the dumpsite concomitantly (Table 4). The mean value of Pb concentration recorded at the upper slope of the dump site (4548.0 mg/kg) was

higher than the mean (+1262.60) value indicating the high impact of Pb pollution in the dump site soils. The levels of Pb in soils of the crest, upper slope and middle slope were observed to be higher than the WHO (0.3- 10 mg/kg) acceptable levels, (2-200.0 mg/kg) noted for uncontaminated soil by Nangia [14], and also above the standard limits of 300 mg/kg by EU, and USA, and 70 mg/kg by UK (Table 3). These high levels of Lead observed at the study site is of great concern as Pb has been documented to have harmful health effects even at middle (0.01 mg/kg) levels [13]. The high quantities of dumped scraped lead proof pipes, batteries and paint materials in the dump site could be responsible for the observed high levels of Pb. The class MPI following the Lacatusu [11] index classified the soils under excessive pollution at the upper and upper slope to moderate pollution at the middle slope and very severe pollution at the valley/swamp (Table 5).

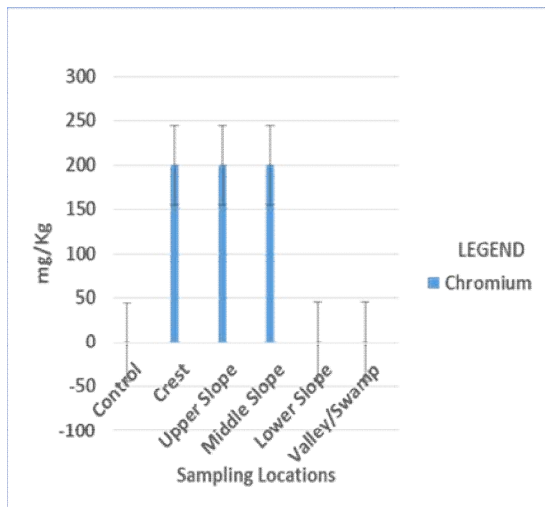


Fig. 4. Concentrations of Chromium in the municipal dump site in Calabar

Zinc was the second most abundant element at the dumpsite (Fig. 8), with a mean values of 9.90 mg/kg and 1248.0-2864.0 mg/kg for the control and dumpsite. The highest value of 2864.0 mg/kg was recorded at the upper slope, closely followed by values of 2245.0 mg/kg and 2248.0 mg/kg from middle slope and crest respectively. These values indicated great variation (88.60 %) in the level of Zinc between the dump site soils and the control soil. The variation in concentration level of Zinc in these soils portrays the impact of pollution from dumping activities. The quantity of Zn observed along the

Toposequence of the dumpsite in Calabar greatly exceeded the range of 12- 60 mg/kg recommended by WHO, 10-300 mg/kg for uncontaminated soil as noted by Nangia [14] and the permissible standard of 300 and 200 mg/kg set out by EU and UK as standard in soils, indicating the extent of Zn pollution in this soil. The contamination/pollution index classified the soils of the dumpsite as excessively polluted with Zn across the sampling points (Table 5).

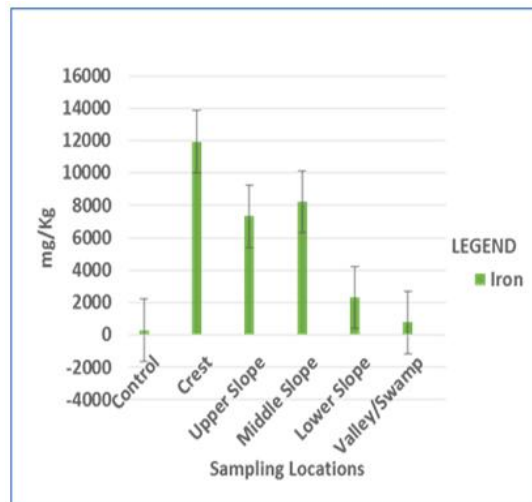


Fig. 5. Concentration of Iron in the municipal dump site in Calabar

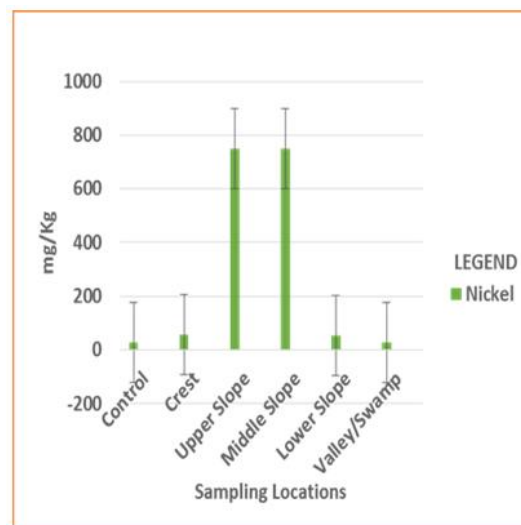


Fig. 6. Concentration of Nickel in the municipal dump site in Calabar

Table 4. Mean concentrations of heavy metals in the municipal dumpsite in Calabar

Heavy metal	Mercury (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Iron (mg/kg)	Nickel (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Copper (mg/kg)	pH (mg/kg)
Control (Mean)	0.1	0.06	0.06	280.0	28.0	129.0	9.90	10.3	5.6
Crest	1.00	1.60	200.00	11928.00	58.30	4548.00	2248.00	28.06	7.00
Upper slope	0.44	0.66	200.00	7336.00	748.60	2196.00	2864.00	28.06	6.70
Middle slope	1.00	0.66	200.00	8226.00	748.50	384.50	2245.00	32.30	7.40
Lower slope	0.40	0.66	0.66	2321.00	52.00	200.11	2011.00	21.00	6.90
Valley/swamp	1.00	1.60	0.76	768.00	26.80	118.00	1248.00	21.00	7.40
Range	0.4-1.00	0.66-1.6	0.66-200	768 -11928	26 -748.6	118-4548	1248-2864	21.0-32.36	6.7-7.4
Mean (Dumpsite)	0.77	1.04	120.28	6115.80	326.84	1489.32	2123.20	26.08	7.10
Mean	0.47	0.67	75.30	3927.26	214.78	979.20	1330.70	20.16	6.52
SD	0.42	0.64	103.34	4576.03	329.68	1607.07	1179.08	8.99	0.80
CV	89.36	95.52	137.23	116.51	153.49	164.12	88.60	44.59	12.26

Table 5. Contamination/pollution index (MPI) of heavy metals in soils of the municipal dump site in Calabar

Heavy metals (mg/kg)	Depth (cm)	Concentration (mg/kg)	Control site	MPI	Class interval Lacatusu (2000)	Significance	Remarks
Crest							
Mercury	0-30	1.00	0.10	10	0.76-1.00	Very severe pollution	Will pose negative effect on soil, plant and environment
Cadmium	"	1.60	0.06	26.6	>16.0	Excessive pollution	
Chromium	"	200.0	0.06	3,333	>16.0	Excessive pollution	
Iron	"	11928.0	280.0	42.6	>16.0	Excessive pollution	
Nickel	"	58.3	28.0	2.08	2.1-4.0	Moderate pollution	
Lead	"	4548.0	129.0	35.25	>16.0	Excessive pollution	
Zinc	"	2248.0	9.90	229.0	>16.0	Excessive pollution	
Copper	"	28.0	10.3	2.71	2.1-4.0	Moderate pollution	
Upper slope							
Mercury	0-30	0.44	0.10	4.4	4.1-8.0	Severe pollution	Will pose negative effect on soil, plant and environment
Cadmium	"	0.66	0.06	11	8.1-16.0	Very severe pollution	
Chromium	"	200.0	0.06	3333.3	>16	Excessive pollution	
Iron	"	7336.0	280.0	26.2	>16	Excessive pollution	
Nickel	"	748.6	28.0	26.7	>16	Excessive pollution	

Heavy metals (mg/kg)	Depth (cm)	Concentration (mg/kg)	Control site	MPI	Class interval Lacatusu (2000)	Significance	Remarks
Lead	"	2196.0	129.0	17.0	>16	Excessive pollution	"
Zinc	"	2864.0	9.90	289.29	>16	Excessive pollution	"
Copper	"	32.36.0	10.3	3.14	2.1-4.0	Moderate pollution	"
Middle slope							
Mercury	0-30	1.00	0.10	10	8.1-16.0	Very severe pollution	Will pose negative effect on soil, plant and environment
Cadmium	"	0.66	0.06	11	8.1-16.0	Very severe pollution	
Chromium	"	200.0	0.06	3333.3	>16	Excessive pollution	
Iron	"	8226.0	280.0	29.37	>16	Excessive pollution	"
Nickel	"	748.5	28.0	26.73	>16	Excessive pollution	"
Lead	"	384.5	129.0	2.98	2.1-4.0	Moderate pollution	"
Zinc	"	2245.0	9.90	226.76	>16	Excessive pollution	"
Copper	"	32.30	10.3	3.13	2.1-4.0	Moderate pollution	"
Lower slope							
Mercury	0-30	0.40	0.10	4	2.1-4.0	Moderate pollution	Will pose negative effect on soil, plant and environment
Cadmium	"	0.66	0.06	11	8.1-16.0	Very severe pollution	
Chromium	"	0.66	0.06	11	8.1-16.0	Very severe pollution	
Iron	"	2321.0	280.0	8.29	8.1-16.0	Very severe pollution	"
Nickel	"	52.0	28.0	1.86	1.1 – 2.0	Slight pollution	"
Lead	"	200.11	129.0	1.55	1.1 – 2.0	Slight pollution	"
Zinc	"	2011.0	9.90	203.1	>16	Excessive pollution	"
Copper	"	21.0	10.3	2.0	1.1 – 2.0	Slight pollution	"
Valley/Swamp							
Mercury	0-30	1.00	0.10	10	8.1-16	Very severe pollution	Will pose negative effect on soil, plant and environment
Cadmium	"	1.60	0.06	26.6	>16	Excessive pollution	
Chromium	"	0.76	0.06	12.66	8.1-16	Very severe pollution	
Iron	"	768.0	280.0	2.74	>16	Excessive pollution	"
Zinc	"	1248.0	9.90	126.06	>16	Excessive pollution	"
Copper	"	21.0	10.3	2.03	1.1-2.0	Slight pollution	"
Nickel	"	26.80	28.0	0.95	0.76-1.00	Very severe contamination	No negative effect effect on soil, plant
Lead	"	118.0	129.0	0.91	0.76-1.00	Very severe contamination	

Copper (Cu) is considered as a micronutrient for plants however, it may be toxic in excess quantities [18]. Evaluation of Cu in soils of Calabar Municipal dump site (Fig. 9) showed that the dumpsite had values ranging from 21.0-32.36 mg/kg while the soils control recorded a mean of 10.30 mg/kg. Values for Cu obtained at the dump site were within the uncontaminated soil range of 2-100 mg/kg as outlined by Nangia [14] and 140 mg/kg, 63 mg/kg and 80-200 mg/kg standards in soil as set out by the EU,UK, and US but exceeded the 1-12 mg/kg acceptable soil range by WHO. According to the contamination/pollution index the soils of the dumpsite are slightly - moderately polluted with Cu (Table 5).

documented by previous researchers [13,19,20] for different locations.

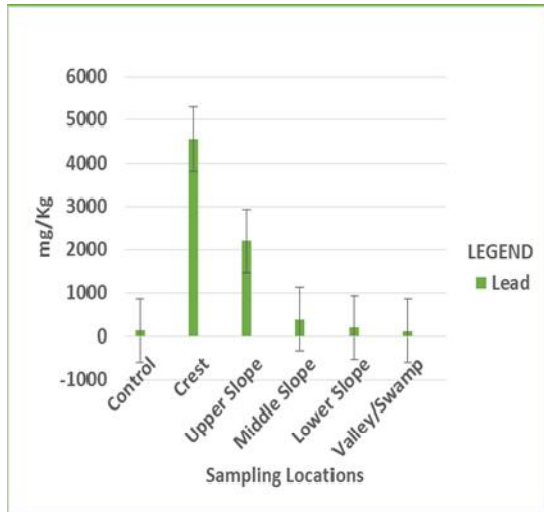


Fig. 7. Concentration of Lead in the municipal dump site in Calabar

From the results above, it is obvious that the crest accumulated the highest amount of heavy metals, followed by the upper slope > middle slope > lower slope > valley/swamp. The heavy metals contents in the dump site Mercury, Cadmium, Chromium, Iron, Nickel, Lead Zinc and Copper increased more than values obtained from the control site (Figs. 2 - 8). The Contamination/pollution Index (MPI) of heavy metals in soil at the crest, upper slope, middle slope, lower slope and valley/swamp indicates that the soils at the dump site were Very severely contaminated to Excessively polluted with Cd, Cr, Fe, Pd and Zn which could pose negative effect on soil, Plant and the environment at large (Table 5). Similar trend of higher levels of heavy metals (Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in dumpsites above the control soils have been

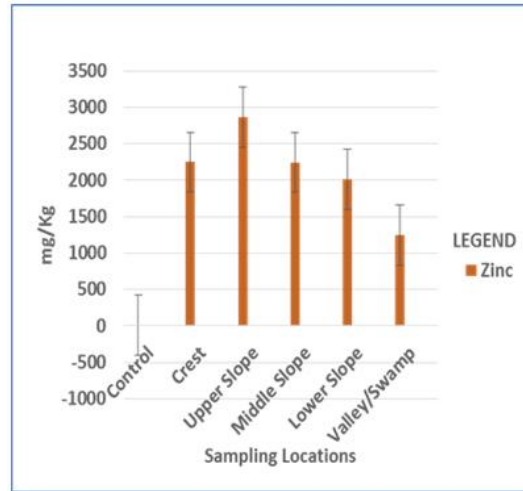


Fig. 8. Concentration of Zinc in the municipal dump site in Calabar

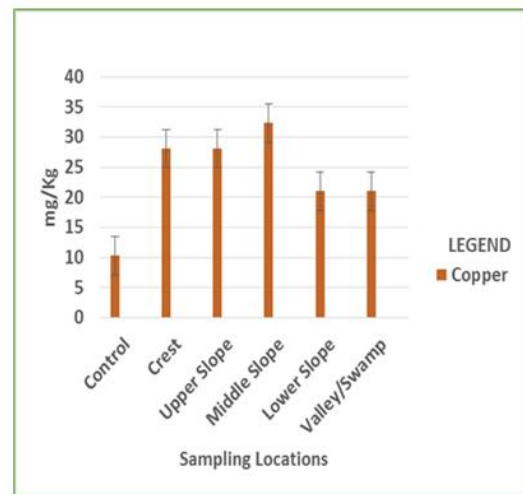


Fig. 9. Concentration of Copper in the municipal dump site in Calabar

5. CONCLUSION

The heavy metal contamination levels of soils at the municipal dumpsite in Calabar were analyzed and determined. Results obtained indicated that the soils of the dumpsite contained considerable high levels of heavy metals (Fe, Zn, Cr, Cu, Cd, Hg Ni and Pb). The great variation between means of the control and that of the dumpsite as observed from the coefficient of variation values suggest that waste dumping has contributed significantly to the levels of toxic metals in these

soils. The metal contamination/pollution index assessment revealed that the soils in the area belong to the excessive pollution category with impending negative effect on plants, animal, humans and the environment at large. It is expedient that necessary measures be put in place to sort waste at source for ease of recycling and reuse of waste materials. The reuse of metallic waste materials will minimize the quantity of metals at the dumpsites. This will aid in reducing the impact of these metals which by virtue of their variable valences can exhibit multifarious effects on soil properties depending on their concentration levels and the length of exposure of the soil to such contaminants.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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