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Comparative Analysis of Seasonalchangesin Soil Contaminations from Heavy Metals at Solid Waste Dumpsites in Portharcourt, Nigeria.

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Abstracts
Background*: This study investigated the soil contamination levels from four Heavy metals (Mercury (Hg), Arsenic (As), Lead (Pb), Cadmium (Cd) in rainy and dry seasons at solid waste dumpsites in Port Harcourt, Rivers State Nigeria. located around markets and insemi-industrial and residential areas. The study will also investigate the seasonalatmospheric changes in temperature on the solid waste and the resultant effect on concentrations and contamination levels of these heavy metals*
Materials and Methods*: Thirty soil samples were collected in each season and analyzed at the Rivers State University, Institute of Pollution Studies Research Laboratory using Atomic Absorption Spectrophotometer (AAS). Results for each season were subjected to further analysis such as graphical, statistical, Hierarchical cluster analysis (HCA) and Principal Component analysis (PCA).*
Results*: High mercury concentration values above the DPR permissible limit of 0.3mg/kg was recorded for soil in all dumpsites during in both seasons with highest values of 4.52mg/Kg at semi-industrial dumpsites during rainy season and 1.96mg/Kg at residential dumpsites during Dry season. As, Pb and Cd values are below permissible limit The NIPI values also confirm these four metals ''Heavily Polluted '' the soil at residential and semi- industrial dumpsites during rainy season while market and residential dumpsites are ''Heavily Polluted' during Dry season. Soil pollution indices (PLI) showed 0.024, 0.033, 0,032 for Rainy season and 0.42, 0.76 and 0.38 for Dry season for Markets, Residential and Semi- industrial respectively. The Hierarchical cluster analysis (HCA) for both rainy and Dry seasons shows highest similarity in heavy metal distribution at both Market and residential dumpsites. Principal component analysis (PCA) for rainy season confirms Mercury to be highest pollutant in semi- industrial dumpsites, while for dry season indicates Mercury to be prominent pollutant in Residential areas.*
Conclusion:*The toxicity level of Mercury at all dumpsites on soil is high and this could pose some health risks on the humans residing around these dumpsites. This underscores the need for proper waste management and the need to develop technology for in-situ disposal of mercury containing disused solid wastes. An engineering process system for mercury extraction from disused products should be put in place to reduce the level of soil contamination and health risk to humans.*

Keywords: ***Heavy metals,soil contamination, wastes, dumpsites.***

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I. Iintroduction

Household and municipal solid waste often containing toxic heavy metals such as Lead, Cadmium, Mercury, Chromium and Arsenic are dumped in dumpsites often very close to areas of human activities. The implication is that the soil environments aroundsuch dumpsites are likely to be impacted by the toxic properties of these heavy metalsthereby posing some health risk for human beings. It is based on this assumption that major receptacle dumpsites within residential (Housing), Semi – industrial (Small scale engineering industry) and markets(commercial foodstuff marketing) are selected for this study. Monitoring of heavy metal content at these dumpsites can facilitate recommendation of suitable preventive measures.

Heavy metals constitute an ill-defined group of inorganic chemical hazards. Okiemie [13] stated that those most commonly found at contaminated sites are Lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, nickel, and **selenium** are some of the metals called 'heavy' because of their high relative atomic mass which persists in nature and can cause damage or death in animals, humans, and plants even at very

low concentrations (1 or 2 micrograms in some cases).Heavy metals are also known to have impacts in soil ecosystem.

Table 1: Permissible level of heavy metals in soils

Heavy metals mg/kg	EU STD mg/kg	UK STD mg/kg	US STD mg/kg	WHO (mg/kg)	DPR, Nigeria. 1991 mg/kg) (
Iron (Fe)					7000 - 550,000
Zinc (Zn)	300	200	200 - 300	12 to 60	10 -- 300
Mercury (Hg)				0.001-0.04	0.3
Copper (Cu)	140	63	80 - 200	1 to 12	2 -- 100
Cadmium (Cd)	3	1.4	400	0.002-0.5	0.7
Chromium (Cr)	180	6.4	400	0.002-0.2	1-- 1000
Lead (Pb)	300	70	300	0.3-10	85
Nickel (Ni)				0.1-5	5-500
Arsenic (As)					29

*EU = Europe, *UK= United Kingdom, *US = United States, *WHO = World Health Organization, *STD = Standard*
Source:[6], [2], [9]

Ideriah [7] studied the levels of some heavy metals in soils around designated municipal solid waste dumpsites and a control site within Port Harcourt and its environs. The concentrations of the metals in soils in both seasons were: As (0.50 - 20.5)ug/g; Cd (0.20 -13.0)ug/g; Cr (0.50 - 100.0) ug/g; Cu (2.50 - 910.0) ug/g; Ni (0.50 - 34.0) ug/g; and Pb (1.0 - 127.5)ug/g. The mean concentrations of Cd and Cu in the soils from the waste dumpsite are sufficiently high to cause environmental concern as their concentrations exceeded tolerable limits.

Anjanapriya [1] conducted a research on Preliminary Assessment of Heavy Metals in three Municipal Solid Waste Open dumpsites andeight heavy metals were detected. These are Mercury, Arsenic, Cadmium, Nickel, Lead, Copper, Chromium and Zinc. This paper discusses that the heavy metals concentration was high in solid waste than leachate in all dump site. The metals of Mercury, Arsenic and Cadmium were high in solid waste at Melur dumping site but Nickel,Lead, Chromium and Cadmium were high in Thirumangalam dumping site, Furthermore, In the work of[4]. the paper discusses the trace metal contents in fine fraction of municipal solid waste (MSW) collected from different soil depth levels of Perungudi dumping ground (PDG), near Chennai. Heavy metal concentrations of these samples were compared with the water extracts prepared from the MSW fine fraction. The concentrations of As, Hg, Cr, Cd, Cu, Pb, Ni and Zn were estimated and found to be in mg/kg level inMSW In certain cases, metal contents are beyond the limits prescribed for compost by Central Pollution Control Board (CPCB). However, all values are within the acceptable limits of United States Environmental Protection Agency (USEPA) standards.

The resent work done by [11],[12], on soil and groundwater contamination at Iwofe, Allu and Iguruta solid waste dumpsites in Port Harcourt reveals that apart from Cadmium which exceeds DRP (1991) recommended limits, all other elements are within these limits. In Aluu dumpsite, the soil is slightly contaminated with Co, moderately contaminated with Pb, severely contaminated with Ni, Cr, and Cu, very severely contaminated with Zn and Mn and slightly polluted with Cd. In Iwofe, the soils are slightly contaminated with Pb and Co, moderately contaminated with Ni and Mn, severely contaminated with Cu, very severely contaminated with Zn and slightly polluted with Cd. Results of PLI shows that all the soils are in good condition. Result of enrichment factor (EF) shows no enrichment for all the analyzed metals except Cd, which shows minor enrichment in all three dumpsites. The dumpsites in Iguruta, Iwofe and Choba in Port-Harcourt are associated with little negative effects on the soils and groundwater in the surroundings. This study also revealed that all the analyzed geochemical parameters including cations, anions and heavy metals in groundwater sources in the vicinity of three major dumpsite situated in Aluu, Igwuruta and Iwofe are low and within WHO (2011) and NIS (2007) recommended limits for potable drinking water.

II. Material and Methods

This study was carried out in Port Harcourt, the capital and largest city of Rivers State, Nigeria. It lies along the Bonny River and is located in the Niger Delta.The area is bounded geographically by latitudes 4°46'N to 5°00'N and longitudes 6°55' E to 7°03' E. Open dump sites are the most common waste disposal methods in Port Harcourt and many cities in Nigeria. They are located on low-value lands around residential, Markets and

semi – industrial locations around the city and include Rukpokwu village, Rumuokoro, Rumuomasi, Diobu, Marine Base, and Borokiri dumpsites. The dumpsites within the study area and the locations of all the sampling points were recorded with the aid of a garmin Global Positioning System (GPS). include; Residential, Markets & Industrial as stated below. Figure 1 is a map of the Study area while the locations and coordinates of the study sites are shown in Table 2.

Table 2: Locations and Coordinates of Sampling Points

S/no		Location Name	Codes	GPS
1		Okija Market	MA01	N 04^o 47’ 50.5’’ E 006^o 59’ 54.6’’
2		Creek Road Market	MA02	N 04^o 45’ 31.5’’ E 007^o 01’ 33.0’’
3	Market Areas (MA)	Rumokuta (Market area)	MA03	N 04^o 51’’ 58.2’’ E 007^o 00’ 02.8’’
4		Water side (Creek road)	MA04	N 04^o 45’ 31.2’’ E 007^o 01’ 27.4’’
5		Mile 1 Market	MA05	N 04^o 47’ 37.2’’ E 006^o 59’ 43.8’’
6		Trans Amadi	SIA01	N 04^o 49’ 22.7’’ E 007^o 02’ 22.1’’
7		Stadium road	SIA02	N 04^o 49’ 30.9’’ E 007^o 01’ 29.2’’
8	Semi Industrial area. (SIA)	Odili Road	SIA03	N 04^o 48’ 14.2’’ E 007^o 02’ 57.7’’
9		Elekohia	SIA04	N 04^o 49’ 07.8’’ E 007^o 01’ 35.0’’
10		D/Line	SIA05	N 04^o 48’ 10.1’’ E 007^o 00’ 00.8’’
11		Borokiri	RA01	N 04^o 44’ 47.4’’ E 007^o 02’ 29.5’’
12		Marine base	RA02	N 04^o 46’ 17.4’’ E 007^o 01’ 29.0’’
13	Residential Areas (RA)	Elekohia Residence	RA03	N 04^o 49’ 06.2’’ E 007^o 01’ 49.4’’
14		Diobu residential	RA04	N 04^o 47’ 33.6’’ E 007^o 00’ 03.0’’
15		Rukpokwu village	RA05	N 04^o 54’ 11.7’’ E 006^o 59’ 19.0’’

This study will comparatively evaluate the extent of soil contamination by heavy metals generated from household solid waste being dumped at the waste dumpsites around the market areas, semi- indusrial areas and residendial areas, distintly show dumpsites location with the highest heavy metal contarmination level and therefore suggest a conceptual engineering management system reduce or eliminate the contermination

Field work: Soil samples were collected at about 1-15cm depth using hand auger into sealed polythene bags. Sampling tools were washed with water and dried before the next sample was collected. 1 kg of soil sample and another 1kg of control samples were collected at each sampling sites (Table 2). A total of thirty (30) soil samples were collected. Samples were labeled properly to reflect date of collection, location and code number of soil samples.

Laboratory work: The collected soil was placed on clean plastic sheet, oven dried for three hours and then sieved through a 0.2 mm mesh size to remove stones, plant roots in order to have uniform soil particle size. 500 mg of the soil sample is transferred to digestion vessels with 7.5 ml of HCl and 2.5 ml of concentrated HNO3(3:1 HCl: HNO3). The vessels were carefully shaked and placed in a fume hood for about 20 min for pre-digestion for clear solution before being placed on the turntable of the microwave system. The pre-digested samples in the digestion vessels were closed and heated on microwave oven up to 80^{o}cand thereafter allowed to cool. The resulting transparent solution was filtered and diluted to 50ml using deionized water. (Allen et al., 1986). Then it was analyzed for concentration of Mercury, Cadmium, Lead and Arsenic using an atomic absorption spectrometer (Modal – ELICO, SL 173) as described in ASTM D3651. This involved direct aspiration of the sample into an air/acetylene or nitrous oxide/acetylene flame generated by a hollow cathode

lamp at a specific wavelength peculiar only to the metal programmed for analysis. For every metal t investigated, standards and blanks will be prepared and used for calibration before samples will be aspirated. Concentrations at specific absorbance displayed on the data system monitor for printing.

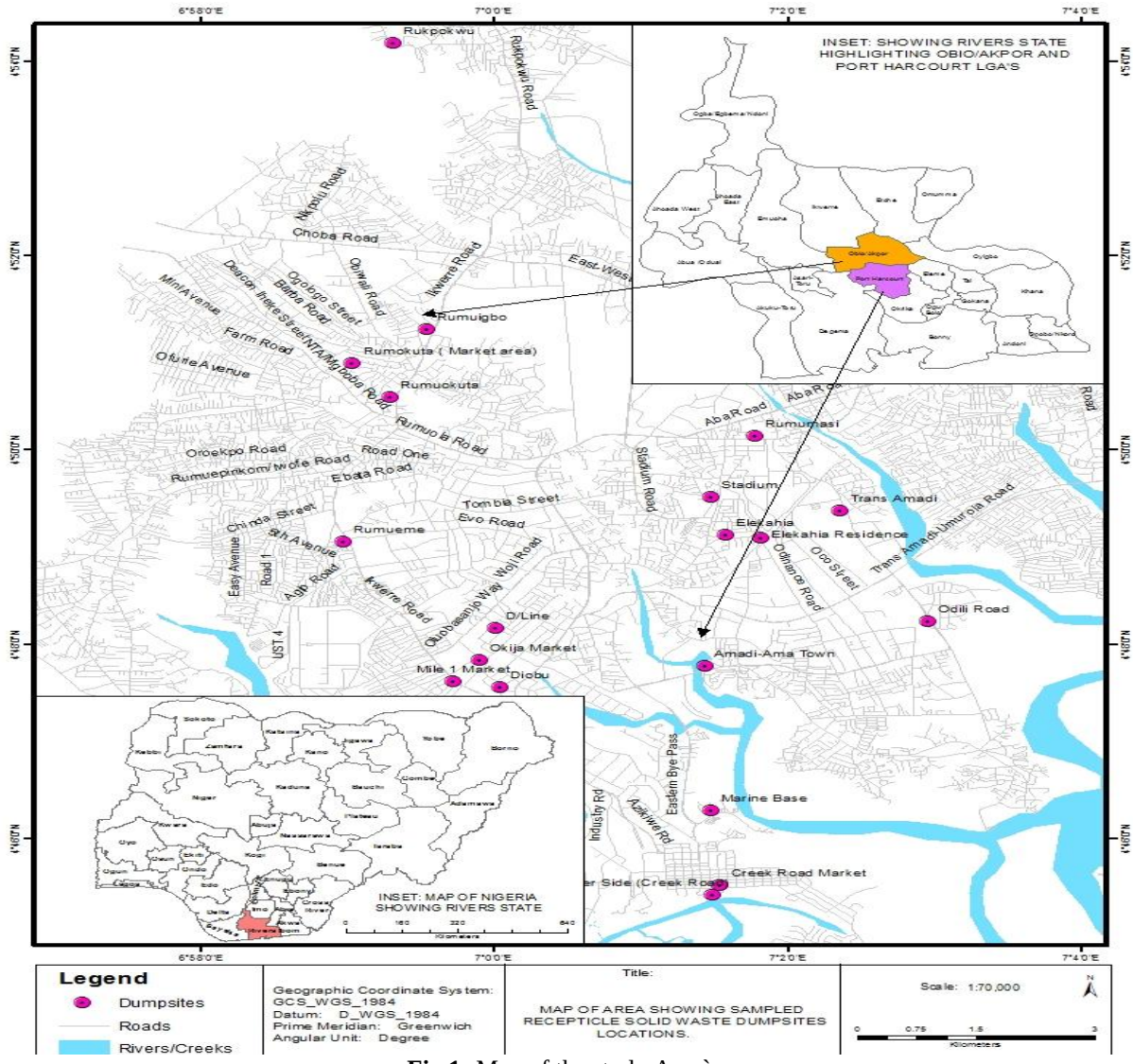

Fig 1: Map of the study Area`

Data analysis

Soil pollution indices

Pollution assessment models are indicators used to assess the presence and intensity of anthropogenic contaminant deposition on soils. In this study, the following pollution assessment models were employed: Contamination Index (CI), Pollution Load Index (PLI), Modified Contamination Degree (mCD), Geo-accumulation Index (Igeo),

Contamination index (CI):The contamination factors were derived by using the CI equation as defined by[8]

$$CF = \frac{Cn}{Bn} \quad (1)$$

Where Cn = measured metal concentration and Bn = background concentration from control site. The CI classification scheme is presented in Table3

Pollution load index (PLI): The PLI gives a generalized assessment on the level of soil contamination. ThePLI is obtained using [14] approach as follows:

$$PLI = [CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n]^{1/n} \quad (2)$$

where, CF= contamination factor; and n = number of metals.The PLI classification scheme is presented in Table 3.

Modified contamination degree (mCD):The mCD is an empirical assessment of the overall degree ofcontamination by pollutants in an area. The mCD was calculated as defined by [5] as follows:

$$mCD = \frac{\sum_{i=1}^{n} Cf_i}{n} \quad (4)$$

where Cf = contamination factor, n = number of analyzed metals, and is the metal.
Where Imean=average concentration of all pollution indices considered, and Imax= maximum pollution index. The NIPI classification scheme is presented in Table 3

Nemerow integrated pollution index (NIPI): The NIPI was also employed to assess the overall pollutionintegrity of the area. NIPI was calculated as defined by [10]as:

$$NIPI = [0.5 \times (I_{mean}^2 + I_{max}^2)]^{1/2} \quad (5)$$

Where Imean=average concentration of all pollution indices considered, and Imax= maximum pollution index. The NIPI classification scheme is presented in Table 3.

Table 3: Soil pollution models classification schemes utilized in this study.(copied from [11])

Contamination Index [8]		Modified Contamination Degree [5]		Pollution Load Index [14]		Nemerow Integrated Pollution index[10]	
Value	Interpretations	Value	Interpretation	Value	Interpretation	Value	Interpretation
< 0.1	Very slight contamination	<1.5	Very low degree of contamination	0	Background concentration	≤0.7	safe
0.1 -0.25	Slight contamination	≤1.5 mCD<2	Low degree of contamination	>0 PLI ≤1	Unpolluted to Moderately polluted	>0.7 NIPI≤ 1	precaution
0.26 -0.5	Moderate contamination	≤2 mCD<4	Moderate degree of contamination	>1 PLI ≤2	Moderately polluted	>1 NIPI ≤2	Slight Polluted
0.51 - 0.75	Severe contamination	≤4 mCD<8	High degree of contamination	>2 PLI ≤3	Moderately to High Polluted	>2 NIPI≤ 3	Moderately polluted
0.76 - 1.0	Very severe contamination	≤8 mCD<16	Very high degree of contamination	>3 PLI ≤4	High Polluted	>3	heavily Polluted
1.1 - 2.0	Slight Pollution	≤16 mCD< 32	Extremely high degree of contamination	≥5	Very high Polluted		
2.1 - 4.0	Moderate Pollution	≥32	Ultrahigh degree of contamination				
4.1 - 8.0	Severe Pollution						
8.1 - 16	Very severe pollution						
>16	Excessive pollution						

III. Results

Table 4: RAINY Season Soil Results for Heavy Metals (mg/kg)

			Market Area						Semi - Industrial						Residential						
			Okija Market	Creek Road Market	Rumokuta (Market area)	Water side (Creek road)	Mile 1 Market		Trans Amadi	Stadium Road	Odili Road	Elekohia	D/Line		Borokiri	Marine Base	Elekohia	Diobu	Rukpokwu village		
			N 04o 47' 50.5" E 006o 59' 54.6"	N 04o 45' 31.5" E 007o 01' 33.0"	N 04o 51" 58.2" E 007o 02.8"	N 04o 45' 31.2" E 007o 00' 27.4"	N 04o 47' 37.2" E 006o 01' 59' 43.8"		N 04o 49' 22.7" E 007o 02' 22.1"	N 04o 49' 30.9" E 007o 01' 29.2"	N 04o 48' 14.2" E 007o 02' 57.7"	N 04o 49' 07.8" E 007o 01' 35.0"	N 04o 48' 10.1" E 007o 00' 00.8"		N 04o 44' 47.4" E 007o 02' 29.5"	N 04o 46' 17.4" E 007o 01' 29.0"	N 04o 49' 06.2" E 007o 01' 49.4"	N 04o 47' 33.6" E 007o 00' 03.0"	N 04o 54' 11.7" E 006o 59' 19.0"		
S/no	Heavy metal name	mg/kg	MA001	MA002	MA003	MA004	MA005	Average	SIA001	SIA002	SIA003	SIA004	SIA005	Average	RA001	RA002	RA003	RA004	RA005	Average	DPR Limit
1	Mercury	Hg	1.612	0.825	1.081	0.718	0.563	0.960	8.714	5.035	3.432	1.382	4.067	4.526	2.797	1.546	0.603	2.035	0.213	1.4388	0.3
2	Arsenic	As	1.490	0.883	1.533	2.230	1.400	1.507	2.361	2.047	1.868	1.543	3.036	2.171	3.678	5.049	1.869	1.400	5.025	3.4042	29
3	Lead	Pb	0.066	0.069	0.068	0.087	0.074	0.073	0.035	0.036	0.049	0.030	0.058	0.042	0.058	0.086	0.057	0.066	0.126	0.0786	85
4	Cadmium	Cd	0.001	0.003	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.0022	0.7

Table 5: RAINY Season Range, Mean and Standard Deviation in Market, Semi-Industrial and Residential

PAHs	Market			Semi - Industrial			Residential			Control		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Mercury	0.563-1.612	0.96	0.411	1.382-8.714	4.526	2.697	0.021-2.797	1.438	1.05	0.000-0.002	0.001	0.001
Arsenic	0.883-2.230	1.507	0.481	1.543-3.056	2.171	0.567	1.400-5.049	3.404	1.716	0.001-0.002	0.001	0.001
Lead	0.066-0.087	0.073	0.008	0.030-0.058	0.042	0.012	0.057-0.126	0.078	0.029	0.02-0.08	0.05	0.022
Cadmium	0.001-0.003	0.002	0.001	0.001-0.002	0.002	0.001	0.002-0.003	0.003	0.001	0.000-0.002	0.001	0.001

Table 6: DRY Season Soil Results for Heavy Metals (mg/kg)

			Market Area						Semi - Industrial						Residential						
			Okija Market	Creek Road Market	Rumokuta (Market area)	Water side (Creek road)	Mile 1 Market		Trans Amadi	Stadium Road	Odili Road	Elekohia	D/Line		Borokiri	Marine Base	Elekohia	Diobu	Rukpokwu village		
			N 04o 47' 50.5" E 006o 59' 54.6"	N 04o 45' 31.5" E 007o 01' 33.0"	N 04o 51" 58.2" E 007o 00' 02.8"	N 04o 45' 31.2" E 007o 01' 27.4"	N 04o 47' 37.2" E 006o 59' 43.8"		N 04o 49' 22.7" E 007o 02' 22.1"	N 04o 49' 30.9" E 007o 01' 29.2"	N 04o 48' 14.2" E 007o 02' 57.7"	N 04o 49' 07.8" E 007o 01' 35.0"	N 04o 48' 10.1" E 007o 00' 00.8"		N 04o 44' 47.4" E 007o 02'	N 04o 46' 17.4" E 007o 01' 29.0"	N 04o 49' 06.2" E 007o 01' 49.4"	N 04o 47' 33.6" E 007o 00' 03.0"	N 04o 54' 11.7" E 006o 59' 19.0"		
S/no	Heavy metal name	Mg/kg	MA001	MA002	MA003	MA004	MA005	Average	SIA001	SIA002	SIA003	SIA004	SIA005	Average	RA001	RA002	RA003	RA004	RA005	Average	DPR Limit
1	Mercury	Hg	1.006	0.851	1.069	0.768	0.715	0.882	0.694	0.613	0.586	0.616	0.610	0.624	3.641	1.712	1.998	1.165	1.302	1.9636	0.3
2	Arsenic	As	3.650	4.404	3.829	3.645	4.319	3.969	4.072	3.683	3.528	3.273	3.194	3.550	3.142	3.548	4.156	3.476	3.981	3.6606	29
3	Lead	Pb	0.900	0.000	2.500	3.100	0.000	1.300	0.000	0.000	7.800	0.000	0.000	1.560	0.000	14.760	19.660	1.800	12.600	9.764	85
4	Cadmium	Cd	2.100	2.200	6.700	2.700	2.000	3.140	1.900	2.700	3.100	2.400	4.100	2.840	1.100	4.400	4.400	2.200	2.500	2.9200	0.7

Table 7: DRY Season Range, Mean and Standard Deviation in Market, Semi-Industrial and Residential

PAHs	Market			Semi - Industrial			Residential			Control		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Mercury	0.715-1.069	0.88	0.152	0.586-0.694	0.62	0.041	1.302-3.641	1.96	0.994	0.04-0.08	0.74	0.2
Arsenic	3.645-4.319	3.97	0.367	3.194-4.072	3.55	0.351	3.142-4.156	3.66	0.407	0.2-0.3	0.251	0.054
Lead	0.000- 2.500	1.3	10.808	0.000-7.800	1.56	3.488	0.00-19.600	9.76	8.493	0.00-0.002	0.001	0.001
Cadmium	2.000-6.700	3.14	2.008	1.900-4.100	2.84	0.829	1.00-4.400	2.92	1.448	0	0	0

Seasonal Variations of Heavy Metal levels in soil.

Table 8: RAINY and DRY Season Heavy Metal Average Concentrations at the Dumpsites (mg/kg)

		Market		Residential		Semi- Industrials		Control	
		Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
Mercury	Hg	0.9600	0.8820	1.4388	1.9636	4.5260	0.6240	0.001	0.74
Arsenic	As	1.5070	3.9690	3.4042	3.6606	2.1710	3.5500	0.001	0.251
Lead	Pb	0.0730	1.3000	0.0780	9.7640	0.0420	1.5600	0.05	0.01
Cadmium	Cd	0.0020	3.1400	0.0020	2.9200	0.0020	2.8400	0.001	0

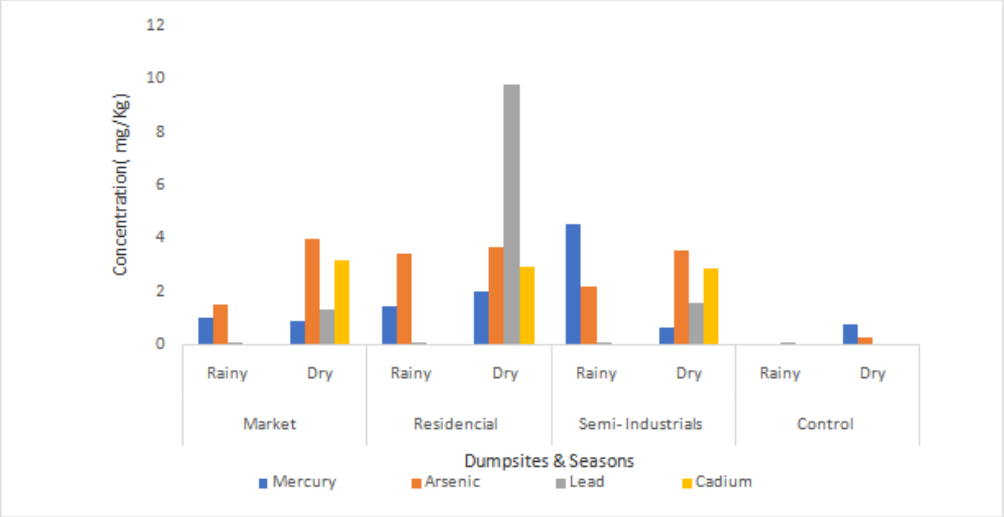

Fig. 2: Seasonal Variations of Heavy Metal concentrations at the dumpsites**.**

Mercury : Rainy season indicated that Mercury (Hg) ranged from 0.563 to 1.612mg/kg (∑0.96mg/kg), 1.382 to 8.714mg/kg (∑4.526mg/kg), and 0.021 to 2.797mg/kg (∑1.438mg/kg) for Markets, Semi-industrial and residencial dumpsites respectively. The Dry season mercury concentration ranged from 0.715 to 1.069mg/kg (∑0.88mg/kg) for Markets dumpsites, 0.586 to 0.694mg/kg (∑0.62mg/kg) for Semi- industrial dumpsites and 1.302 to 3.641mg/kg (∑1.96mg/kg) for Residencial dumpsites. The DPR maximum soil permissible limit is 0.3mg/kg while WHO limits range 0.001 – 0.04mg/kg. The control value is 0.001mg/kg for rainy season and 0.74mg/kg for dry season.

Arsenic: The concentration of Arsenic (As) for Rainy season ranged from 0.883 to 2.230mg/kg (∑1.507mg/kg), 1.543 to 3.056mg/kg (∑2.171mg/kg), and 1.400 to 5.049mg/kg (∑3.404mg/kg) for Markets, Semi-industrial and residencial dumpsites respectively. The Dry season concentrations ranged from 3.645 to 4.319mg/kg (∑3.97mg/kg) for Markets dumpsites, 3.194 to 4.072mg/kg (∑3.55mg/kg) for Semi- industrial dumpsites and 3.142 to 4.156mg/kg (∑3.66mg/kg) for Residencial dumpsites. The DPR maximum soil permissible limit is 29mg/kg. The control value is 0.001mg/kg for rainy season and 0.251mg/kg for dry season.

Lead: The concentration of Lead(Pb) for Rainy season ranged from 0.066 to 0.087mg/kg (∑0.073mg/kg), 0.030 to 0.058mg/kg (∑0.042mg/kg), and 0.057 to 0.126mg/kg (∑0.078mg/kg) for Markets, Semi-industrial and residencial dumpsites respectively. The Dry season concentrations ranged from 0.00 to 2.500mg/kg (∑1.30mg/kg) for Markets dumpsites, 0.00 to 7.800mg/kg (∑1.56mg/kg) for Semi- industrial dumpsites and 0.00 to 19.600mg/kg (∑9.76 mg/kg) for Residencial dumpsites. The DPR maximum soil permissible limit is 85mg/kg while WHO limits range 0.3 – 10.0mg/kg. The control value is 0.05mg/kg for rainy season and 0.001mg/kg for dry season.

Cadmium: The concentration of Cadmium (Cd) for Rainy season ranged from 0.001 to 0.003mg/kg (∑0.002mg/kg), 0.001 to 0.002mg/kg (∑0.002mg/kg), and 0.002 to 0.003mg/kg (∑0.003mg/kg) for Markets, Semi-industrial and residencial dumpsites respectively. The Dry season concentrations ranged from 2.000 to 6.700mg/kg (∑3.14mg/kg) for Markets dumpsites, 1.900 to 4.100mg/kg (∑2.84mg/kg) for Semi- industrial dumpsites and 1.00 to 4.400mg/kg (∑2.92mg/kg) for Residencial dumpsites. The DPR maximum soil permissible limit is 0.7mg/kg while WHO limits range 0.002 – 0.5mg/kg. The control value is 0.001mg/kg for rainy season and 0.000mg/kg for dry season.

Analysis of Seasonal Variation of Integrated Soil Pollution Index

Table 9: Seasonal Variation Soil Pollution Indexes.

Dumpsites	Cd		mCd		PLI		NIPI	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
Markets	3.25	7.03	0.81 VLDC)	1.75 VLDC)	0.024 (UP)	0.42 (UP)	2.33 (MP)	3.033 (HP)
Residential	4.87	10.43	1.21 (VLDC	2.61 VLDC)	0.033 (UP)	0.76 (UP)	3.472 (HP)	4.979 (HP)
Semi- Industrials	15.07	5.77	3.76 (MDC)	1.44 (MDC)	0.032 (UP)	0.38 (UP)	10.934 (HP)	2.708 (MP)

Cd – Degree of contamination. mCd – Degree of Contamination. PLI – Pollution Load Index.NIPI – Nemerow integrated pollution index. VLDC – Very Low degree of contamination. MDC- Moderate degree of Contamination. UP – Unpolluted. MP- Moderately Polluted. HP – Heavily Polluted.

Table 10: Overall Seasonal Variation Soil area Pollution Status(NIPI)

	Rainy	Dry
Market	2.33	3.03
Residential	3.47	4.97
Semi- Industrial	10.93	2.7

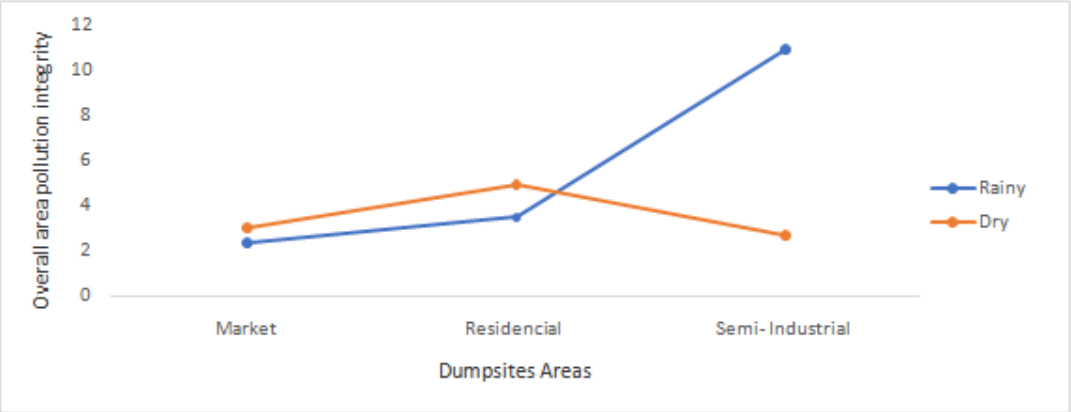

Fig 3: Graphical Representation of Seasonal Variation Soil Pollution Integrity

Table 8 and 9 show the comparative rainy and dry season variations on the soil pollution indexes. The highest NIPI value is 10.934 for soils in Semi- industrial dumpsites during rainy season. The market and semi- industrial dumpsites in dry season are 3.033 and 4.979 respectively. The soil can therefore be classified as 'Highly Polluted'.

Statistical Multivariate Analysis

A 2-sample t-test was carried out in Minitab 18, to compare the level of significance between impacted dump sites and control for all locations using 95% confidence level at p = 0.05. The results are presented on Table 10 and 11 for rainy season and 12 and 13 for dry season In Rainy season, the P- values between the controls sites and all the dumpsites show no significance while in dry season all the P-values were significant

Table 11: RAINY season Range, Mean and Standard Deviation in Market, Semi-Industrial and Residential

PAHs	Market			Semi - Industrial			Residential			Control		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Mercury	0.563-1.612	0.96	0.411	1.382-8.714	4.526	2.697	0.021-2.797	1.438	1.05	0.000-0.002	0.001	0.001
Arsenic	0.883-2.230	1.507	0.481	1.543-3.056	2.171	0.567	1.400-5.049	3.404	1.716	0.001-0.002	0.001	0.001
Lead	0.066-0.087	0.073	0.008	0.030-0.058	0.042	0.012	0.057-0.126	0.078	0.029	0.02-0.08	0.05	0.022
Cadmium	0.001-0.003	0.002	0.001	0.001-0.002	0.002	0.001	0.002-0.003	0.003	0.001	0.000-0.002	0.001	0.001

Table 12: Summary of Paired T-test Result for Heavy Metals Showing the Three Locations in Rainy season

Comparison	T-value	P-value	Remark
Market vs Control	-1.520	0.266	Not significant
Semi-Industrial vs Control	-1.550	0.219	Not significant
Residential vs Control	-1.680	0.191	Not significant

Table 13: Dry season Range, Mean and Standard Deviation in Market, Semi-Industrial and Residential for Heavy Metals

PAHs	Market			Semi - Industrial			Residential			Control		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Mercury	0.715-1.069	0.88	0.152	0.586-0.694	0.62	0.041	1.302-3.641	1.96	0.994	0.04-0.08	0.74	0.2

Arsenic	3.645-4.319	3.97	0.367	3.194-4.072	3.55	0.351	3.142-4.156	3.66	0.407	0.2-0.3	0.251	0.054
Lead	0.000-2.500	1.3	10.808	0.000-7.800	1.56	3.488	0.00-19.600	9.76	8.493	0.00-0.002	0.001	0.001
Cadmium	2.000-6.700	3.14	2.008	1.900-4.100	2.84	0.829	1.00-4.400	2.92	1.448	0	0	0

Table 14: Summary of Paired T-test Result for Heavy Metals Sampling DuringDry Season

Comparison	T-value	P-value	Remark
Market vs Control Site	-2.74	0.071	Significant
Semi-Industrial vs Control Site	-2.47	0.090	Significant
Residential vs Control Site	-2.32	0.103	Significant

Hierarchical Cluster Analysis (HCA)and Principal Component Analysis

Hierarchical Cluster Analysis and Principal Component Analysis were applied on the measured data to determine the sources of contamination as well as the level of pollution by comparing with the control site. Figures 4and 5 show the Hierarchical Cluster Analysis for rainy and dry seasons respectively. The similarity between the level of pollution in the control site and all other dumpsites is Low; 24.18 for rainy season and 8.73 for dry season. However, market and residential shows high similarities between eachother; 98 for rainy season and 88 for dry season.

Hierarchical Cluster Analysis (HCA)

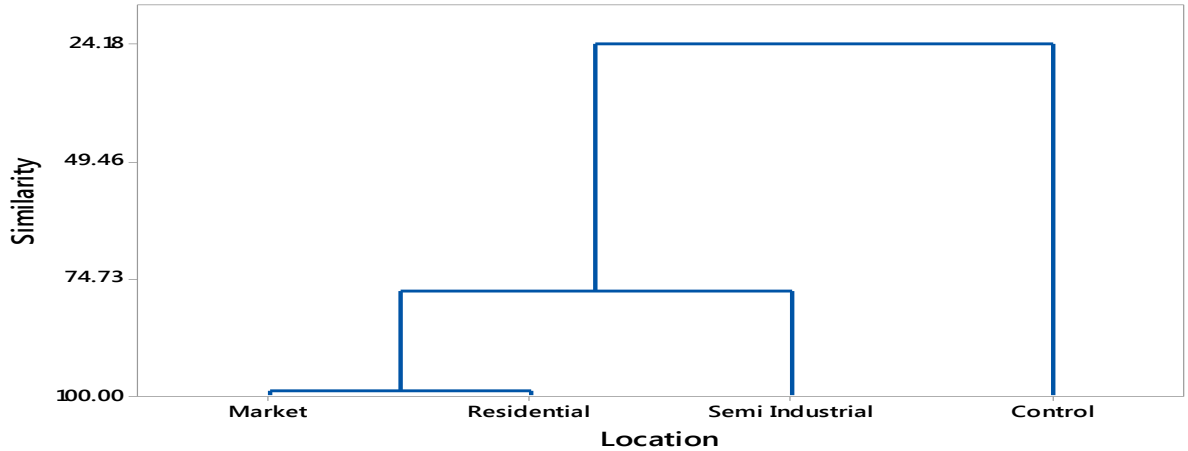

Figure 4: Dendrogram for Heavy Metal Distribution at Various Locations using Complete Linkage Method in Rainy Season

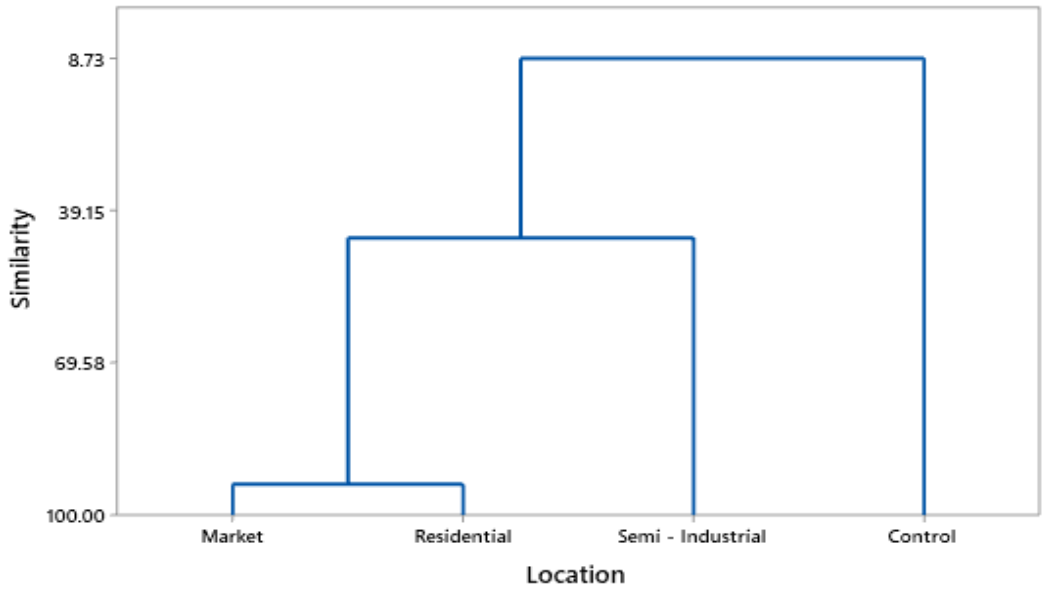

Fig. 5: Dendrogram for Heavy Metal Distribution at Various Locations using Complete Linkage Method in Dry Season

Principal Component Analysis (PCA)
Principal Component Analysis was applied on the measured data to determine the sources of contamination

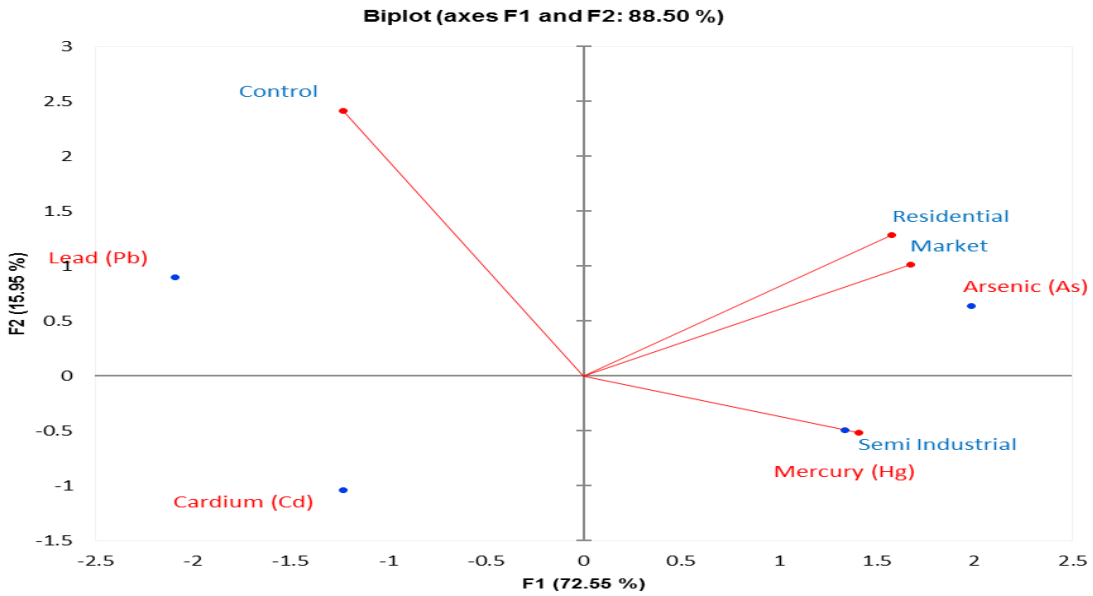

Fig 6: Biplot of PCA of Heavy Metal Distribution for Rainy Season

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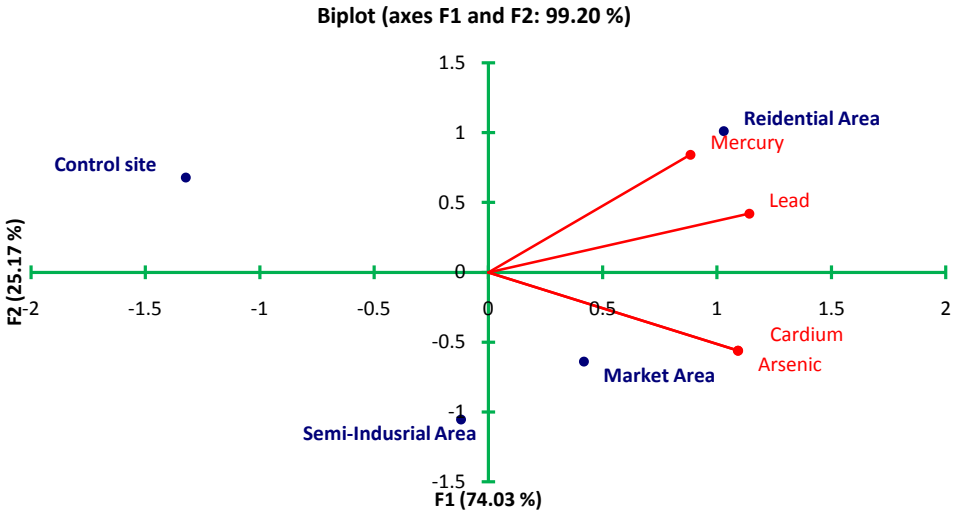

Fig. 7: Biplot of heavy metals and sampling locations in Dry Season

IV. Discussion

The results of the heavy metals are presented on Table 4 and 5 for rainy season while Table 6 and7 represent the dry season metal data in soil. Table 8 below showed the seasonal variation of heavy metal concentrations in soil at the different dumpsites. The total concentrations of the four heavy metals are higher in dry season than in the rainy season. Mercury concentrations ranged 0.92mg/kg to 4.52mg/kg across all the sites in rainy season while in dry season it ranges 0.62mg/kg to 1.96mg/kg.The lower range in dry season is due to evaporation of mercury due to high atmospheric temperature in dry season. However, these values are observed to higher above the DPR limits of 0.3mg/kg at all season. Arsenic concentrations ranged 1.5mg/kg to 2.17mg/kg across all the sites in rainy season while in dry season, it ranges 3.55mg/kg to 3.96mg/kg. The values in dry season is higher due to the fact that the organic components of the solid waste generated more Arsenic compound due to high atmospheric temperature during dry season. Lead concentrations ranged 0.04mg/kg to 0.07mg/kg across all the sites in rainy while in dry season, it ranges 1.3mg/kg to 9.7mg/kg in dry seasons.The lower values in rainy season is due to rain rapid percolation of the Lead to the underground water during rainfall. Cadmium concentrations ranged within0.002mg/kg during rainy season while 2.84mg/kg to 3.14mg/kg

across all the sites in dry seasons. Generally, the total concentrations of the four metals are observed to have higher values mostly in dry season than rainy season. Fig. 2 is the graphical representation

The computed contamination factor [8], in Table 9for rainy season and Dry season showed values for Mercury in Rainy season as 3.2, 4.76 and 15.0 for Markets, Residential and Semi-industrial dumpsites respectively. The Market dumpsites value falls on range 2.1 to 4.0 and classified as 'Moderate Pollution, the residential dumpsites value falls on ranges 4.1 to 8.0 and classified as 'Severe Pollution', and the Semi-industrial dumpsites value ranges 8.8 to 16 and classified as 'Very Severe Pollution. The Dry season values showed 2.94, 6.54, 2.08 for Markets, Residential and Semi-industrial dumpsites respectively. The Market dumpsites value falls on range 2.1 to 4.0 and classified as 'Moderate Pollution, the residential dumpsites value falls on ranges 4.1 to 8.0 and classified as 'Severe Pollution', and the Semi-industrial dumpsites value ranges 1.1 to 2.0 and classified as 'Slight Pollution'. These Rainy season values for Arsenic, Lead and Cadmium for rainy season are all below <0.1 and therefore classified as 'Very Slight Contamination' classification however in Dry season, Cadmium values indicated considerable pollution.

Soil pollution indexes (PLI)[14], gives a generalized assessment on the level of soil contamination. The values showed 0.024, 0.033, 0,032 for Rainy season and 0.42, 0.76 and 0.38 for Dry season for Markets, Residential and Semi- industrial respectively. These values as per [14], falls within the range of >0 to ≤1 and these categorized the soil at each of these dumpsites as 'Unpolluted'. This is also computed on Table 9 for rainy and dry seasons.

The Nemerow integrated pollution index (NIPI) [10], values in Table 10 (Fig 3) that assess the overall soil pollutionintegrity of the area. In rainy season, the values are 2.33, 3.47 and 10.94 for Markets, Residential and Semi- industrial dumpsites respectively.The Market dumpsites value falls on ranges >2 to ≤ 3 and classified as 'Moderate Polluted, the residential dumpsites value falls on ranges >3 and classified as 'Heavily Polluted', and the Semi-industrial dumpsites value ranges also >3 and classified as 'Heavily Polluted.The Dry season values showed 3.033, 4.979, 2.708 for Markets, Residential and Semi-industrial dumpsites respectively. The Market and Residential dumpsites value falls on range >3 and classified as 'Heavily Polluted', while the Semi-industrial dumpsites value ranges >2 to ≤ 3 and classified as 'Moderate Polluted' These findings clearly show that high soil pollution integrity in residential dumpsites in both rainy and dry seasons. These 'heavy pollution' soil integrity statues of the soil in all the affected dumpsites is due to the presence of Mercury as the main contaminant.

The statistical multivariate analysis(T-test) with control sites for rainy season(Table 12) showed P-values as 0.266,0.219 and 0.191 for Market, Semi-industrial and Residential respectively. Since the P>0.05, this indicated statistically that there ''no significant difference'' between the mean test variables at each of the dumpsites and the control sites. This further signified that the occurrence of metal at the respective dumpsites and the control sites is by chance. Hence, we accept the null hypothesis. However, for Dry season as shown in table 14, P-values are 0.071,0.090 and 0.103 for Markets, Semi- industrial and Residential dumpsites respectively. The P>0.05 and this indicates statistically that there is observed ''significant difference'' in the test variables between the control sites and each of the dumpsites. This agrees with the findings of [7]

The Hierarchical cluster analysis (HCA) Fig.4 for rainy and Fig.5 Dry seasons shows highest similarity in heavy metal distribution at both Market and residential dumpsites. While the Principal component analysis (PCA) (Fig 6) for rainy season confirms Mercury to be highest pollutant in semi- industrial dumpsites, the PCA (Fig.7) for dry season indicates Mercury to be prominent pollutant in Residential areas.

Conclusively the findings shows high level of soil contermination by mercury at all municipal soli waste dumpsites both during the rainy and Dry seasons are all above the DPR (1991) Permissible limits (0.3mg/kg) of heavy metals in soil, this signifies that toxicity level of Mercury at all dumpsites on soil is high and this has health risk effect on the humans around these dumpsites.. This therefore confirmed the need for waste management in-situ disposal of mercury containing disused solid waste to be developed. Also, an engineering process system for extraction of Mercury from disused products should be put in place to reduce the level of soil contamination and health risk to humans.

V. Conclusion

This research has shown that dumpsites receive wastes containing heavy metals. Mercury contamination stands out in this regard as soils from all the dumpsites show significant amount of mercury. Mercury occurs most in dumpsite located in semi-industrial areas.

To reduce the presence of mercury in dumpsites, it is recommended that mercury containing solid wastes be segregated at the point of generation in residential and semi- industrial areas. An engineering process system can also be developed to remove mercury especially from waste/ disused fluorescent bulbs and tubes.

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