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ASSESSMENT OF HEAVY METAL POLLUTION IN SOIL AT A REFUSE DUMPSITE IN UNIVERSITY OF CROSS RIVER STATE (UNICROSS), CALABAR, SOUTH-SOUTH, NIGERIA

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ABSTRACT
Total concentration and pollution indices of mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), and cobalt (Co) in dumpsite soil located in University of Cross River State, Calabar were evaluated in this work. Soil samples were collected at 0 - 15cm depth from two sampling stations at the dumpsite once in the months of April, August and December, 2021 and analyzed to the closest mg/kg using Atomic Absorption Spectrophotometer (AAS). The concentrations of the heavy metals showed that Cd>Pb>Ni>Cr>As>Co. All the concentrations of the heavy metals examined when compared with those of average value of heavy metals in shale showed that all the metals were lower than their corresponding world average value except Cd. Geoaccumulation index indicated unpolluted to moderately polluted for all metals studied except Cd which indicated strong to very strongly polluted. Contamination factor for Cd indicated very high contamination. Contamination degree for site 1 and 2 indicated considerable degree of contamination and moderate degree of contamination respectively. Pollution load index values investigated were within the baseline level for all the stations. The heavy metal pollution is attributable to the waste deposited at the dumpsite located in the institution. It is recommended that the dumpsite be relocated to another location that is far away from the residential area and from drinking water sources like boreholes.

Keywords: Heavy metal, Geoaccumulation Index, Contamination factor, UNICROSS, Calabar

INTRODUCTION
Open garbage dumps are much established in urban areas and are the most well-known approaches of discarding waste. The act of landfill as a strategy for garbage removal in many emerging nations is a long way from standard plan (Adewole, 2009). The contamination of soil through the indiscriminate dumping of waste usually alters the soil quality in terms of soil nutrient as soil is very important to human existence and creates a potentially negative impact in the environment for years even after the dumpsite is closed or relocated (Iravanian and Ravari, 2020; Lar *et al*., 2014). Solid and liquid wastes age and their unfortunate removal system in the metropolitan areas of most emerging nations have turned into a danger to the climate (Udofia *et al.,* 2016). Dumpsites in urban areas in Nigeria contains homegrown trash, wood, horticulture squander, modern waste, emergency clinic waste, polythene sacks, plastics, broken glasses, deserted vehicles, debris, dust, discarded clothes and shoes, human waste, domestic emissions, and weathering of building and pavement surfaces (Adeoye *et al*., 2018).

The development of heavy metals in soil from anthropogenic sources has been accounted for to be unsafe to crops and human wellbeing (Okori and Barde, 2022; UNEP, 2007). Human activities in most cases have introduced these potentially hazardous metals to the environment. This is as a result of the development and expansions of urban areas promoting a major threat to ecology (Mahmood and Malik 2014; Jeyol and Vincent, 2022). High concentration of non-essential heavy metals/metalloids in soils and irrigation water represent a threat to the environment, food safety and human and animal health (Henao and Ghneim-Herrera, 2021). Dumping of refuse indiscriminately and the untimely evacuation of this refuse at the dumpsite in University of Cross River State in Calabar, creates a potentially negative impact on the environment. When it rains, the plastic waste get littered on the streets of the campus and some flow within the drainage channel that passes through the university into the nearby River (Great Kwa River) polluting the water body with plastics ranging from; bottle caps, sachets, cups, plates, beverage bottles, straws, food wrappers, cigarette butts, baby diapers and sanitary pads. These dumpsites usually discharge their effluent into nearby gardens cultivated by the peasant farmers living near the University. Plants take up heavy metals by absorbing them from deposits on the part of the plants exposed to air, from polluted environment as well as from contaminated soils. Uzoma *et al.* (2013) reported that excessive concentration of heavy metals in plants can cause oxidative stress, stomatal resistance, affect photosynthesis and chlorophyll florescence process. Vegetable plants growing on heavy metal contaminated soil can accumulate high concentrations of trace elements to cause serious health risk to consumers (Maslin and Maier, 2010).

While several previous studies have documented heavy metal contamination of soil in dumpsites in Calabar metropolis (Emori et al., 2015; Okori and Barde, 2022) there is rarity of studies focused on the quality of environmental media. In this study, Geoaccumulation Index (Igeo), Contamination Factor (CF), Contamination Degree (CD) and Pollution Load Index (PLI) were used to determine the heavy metal potentials to contaminate the environment and their degree of contamination.

MATERIALS AND METHODS

Description of the Study Area

The assessment was carried out at a dumpsite located in the University of Cross River State, in Calabar Metropolis (Fig. 1). This dumpsite gets a great deal of waste from the inhabitants and guests of the University, especially merchants who trade at a mini-market located at the major entrance into the institution. The two main climate conditions in the study area are dry season (October – March) and wet season (April – September). The area is characterized by high annual rainfall in the range of 350-400mm. The mean annual temperature is in the range of 24^0C to 28^0C (Emori *et al*., 2015).

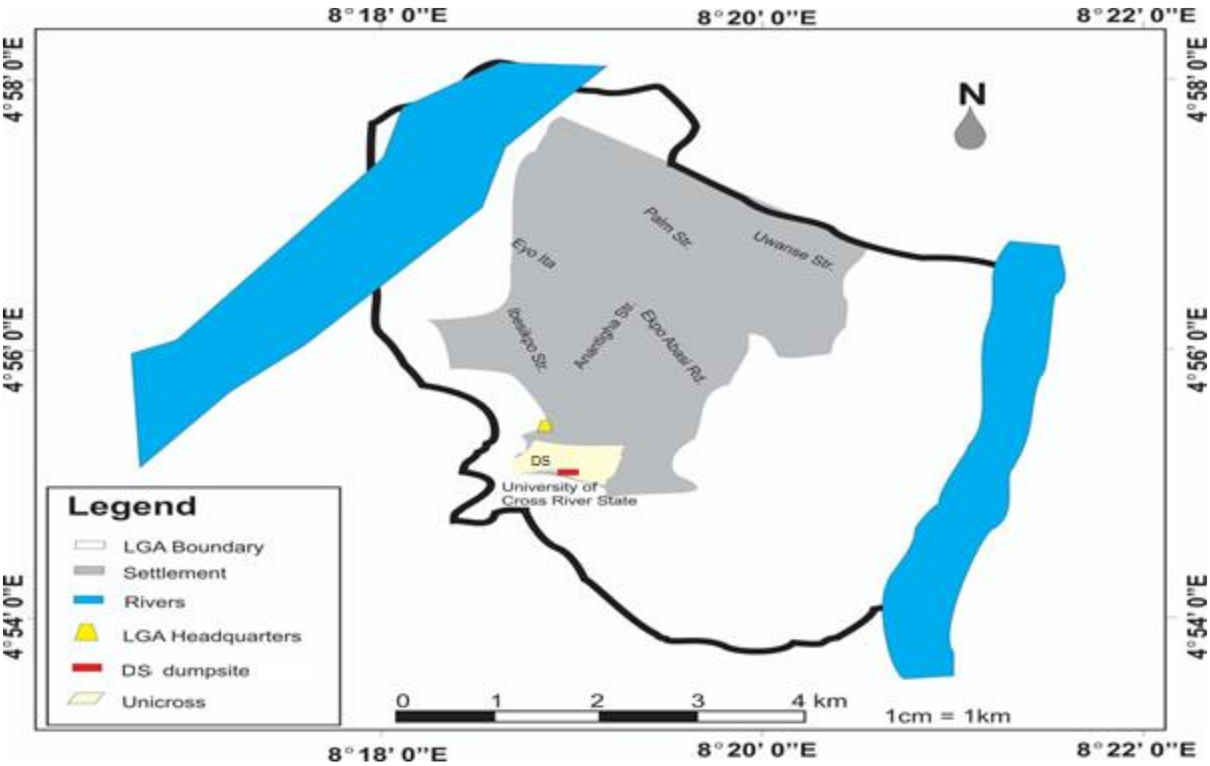

Figure 1: Map of the study area showing sampling station

Soil sample collection and analysis

Surface soil samples (0-15cm depth) were gathered from the dumpsite of the review region from the months of April, August and December, 2021, utilizing clean polythene sacks with plastic clasps. The sacks were marked appropriately on the field and afterward taken to the research facility for pre-treatment. In the research facility about 10g of air-dried soil was weighed into plastic bottles and 100 ml DTPA extractant was added. The solution was shaken for 2 hrs and filtered with Whatman filter paper. The resulting extract amount (filtrate) was used to analyze the concentrations of Hg, Pb, Cr, Cd, As, Ni and Co using AAS (Atomic Absorption Spectrometer) applying appropriate standards as described by James (1995).

Determination of Geo-accumulation Index

Geo-accumulation index (Igeo) indicates the degree of pollution of soil with regards to the chemical background concentration of the heavy metals. The Igeo values were calculated according to Lar *et al.* (2014) as expressed mathematically below.

$$Igeo = log2\; C_n/1.5B_n \qquad (1)$$

Where C_n = concentration of the examined element in the sample, and B_n = geochemical background value of the element in reference environment.

The geo-accumulation index, consist of seven grades (0 to 6) based on the increasing numerical value of the index and ranges from unpolluted to extremely polluted (Loska *et al*., 2003):

Igeo Value	Grade	Classification
≤0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly polluted to extremely polluted
>6	6	Extremely polluted

Contamination Factor (CF)

Contamination Factor is an indicator of soil and sediment heavy metals contamination ratio and can be calculated from the formula adopted from the work of Kieri *et al.* (2020) as:

$$CF = \frac{C_{sample}}{C_{background}} \qquad (2)$$

Where CF is the concentration factor, C_{sample} is the concentration of metal measured in the soil and $C_{background}$ is the concentration of the element in global shale. The background values were obtained from the work of Turekian and Wedpohl, 1961, being the average crustal value of each metal in shale. Hakanson (1980) classified CF values according to the four classes depicted as follows: CF < 1 = low; 1<CF<3 = moderate; 3<CF<6 = considerable; CF>6 = very high

Contamination Degree

Contamination degree is the sum of all CF values of a particular sampling site. Degree of contamination is classified into four categories (Singh *et al*., 2017) as follows: CD < 6 – low degree of contamination; 6 ≤ CD < 12 – moderate degree of contamination; 12 ≤ CD < 24 – considerable degree of contamination; CD > 24 – very high degree of contamination.

Pollution Load Index

The pollution load index (PLI) of a specific site or zone is assessed according to the index described by Tomlinson *et al*. (1980). This tool is used to assess the heavy metal pollution and is calculated based on the formula shown below:

$$PLI \text{ for a station} = (CFn \times CFn \times CFn \times CFn \times CFn)^{1/n} \quad (3)$$

Where n is the number of heavy metals, CF is the contamination factor of each metal in the sample (Perumal, 2021). According to Mohiuddin *et al.* (2010), PLI = 0 indicates a perfect state of pollution; PLI = 1 point indicate only baseline levels of pollutants present and PLI > 1 would indicate progressive deterioration of sites.

Statistical Analysis

All data obtained from this study were analyzed using a one-way analysis of variance (ANOVA) with SPSS version 20 software. Descriptive statistics provided the means and standard deviations of the data obtained.

RESULTS AND DISCUSSION

Heavy metals concentration in dumpsite soil

The results obtained from the determination of total heavy metal concentration in dumpsite soil at University of Cross River State in Calabar Metropolis are shown in Table 1. The concentrations of the heavy metals showed that Cd>Pb>Ni>Cr>As>Co. The mean concentration of heavy metals in the dumpsite soil were BDL (Hg), 2.228 ± 0.147 mg/kg (Pb), 0.916 ± 0.050 mg/kg (Cr), 3.564 ± 0.208 mg/kg (Cd), 0.500 ± 0.034 mg/kg (As), 1.493 ± 0.075 mg/kg (Ni), and 0.026 ± 0.004 mg/kg (Co). All the concentrations of the heavy metals examined when compared with those of average value of heavy metals in shale showed that all the metals were lower than their corresponding world average value except Cd. Usually, the heavy metal pollutants in soils often derived from two major sources, including natural (soil parent materials) and various anthropogenic sources (transportation, industrial activities, and agricultural activities) (Su *et al*., 2022). The presence of Cd above recommended levels could be as a result of their presence in refuse being deposited in the dumpsite. In a survey of groundwater surrounding waste sites in the United States, Cd concentrations up to 6000 μg/L were found (ATSDR, 2012). Leachates from municipal solid waste landfills in the European Union can reach Cd concentrations up to 2700 μg/L (EU, 2007).

Cadmium is generally more bioavailable in soil. Plants accumulate cadmium from soil (Daniel *et al*., 2016). The United States Environmental Protection Agency (US-EPA) maximum permissible limits (MPL) and the European Union allowable permissible threshold for cadmium in soil is 3mg/kg (Environment Agency, 2014a). The mean Cadmium concentration in soils around the dumpsite was higher than 3mg/kg. There was a significant difference in cadmium concentration between soils from dumpsite and the control. Emori *et al*. (2015) reported higher concentration of Cadmium in dumpsites in Calabar metropolis when compared to mechanic workshops. Cadmium levels observed were higher than the observations of Ayodele *et al*. (2014) who reported cadmium levels below detectable limits for soils around granite quarries at Ikole-Ekiti, Nigeria, and a lower range of 0.06-0.07 was also observed for Durumi quarry site Mpape Abuja, Nigeria by Ojo *et al.* (2018).

Table 1: Mean Heavy Metals Concentration in Soil from a Dump Site in UNICROSS, Calabar

Heavy metals (mg/kg)	Average Shale Values (ASV) (Control)	Heavy Metals Concentrations in Dumpsite soil		
		Sampling point 1	**Sampling point 2**	**Mean**
Hg	0.4	BDL	BDL	BDL
Pb	20	2.453 ± 0.003 (2.450 – 2.456)	2.663 ± 0.146 (2.518 – 2.811)	2.558 ± 0.146 (2.450 – 2.811)
Cr	90	0.923 ± 0.005 (0.918 – 0.928)	0.909 ± 0.078 (0.819 – 0.996)	0.916 ± 0.050 (0.819 – 0.966)
Cd	0.3	3.672 ± 0.002 (3.670 – 3.674)	3.457 ± 0.272 (3.213 – 3.751)	3.564 ± 0.208 (3.213 – 3.751)
As	13	0.514 ± 0.004 (0.510 – 0.518)	0.486 ± 0.048 (0.432 – 0.526)	0.500 ± 0.034 (0.432 – 0.526)
Ni	68	1.522 ± 0.001 (1.510 – 1.513)	1.476 ± 0.114 (1.402 – 1.607)	1.493 ± 0.075 (1.402 – 1.608)
Co	19	0.025 ± 0.001 (0.014 – 0.026)	0.027 ± 0.006 (0.021 – 0.033)	0.026 ± 0.004 (0.021 – 0.033)

Values are in Mean ± Standard deviation, Ranges are in parenthesis ( )

Geo-accumulation index of dumpsite soil

The summary of the geo-accumulation index of the soil from a dumpsite in UNICROSS is shown in Table 2. The geo-accumulation index values of the dumpsite soil were 0.0256, 0.00204, 4.767, 0.0125, 0.0044, and 0.00027 for Pb, Cr, Cd, As, Ni, and Co respectively. The geo-accumulation index of Pb, Cr, As, Ni, and Co fell within the pollution class 1, while Cd fell within the pollution class 5 of the geo-accumulation index interpretation scale (Table 2).

Table 2: Geo-accumulation Index of Heavy Metals in Soil from a Dumpsite in UNICROSS, Calabar

Heavy metals	Geo-accumulation index	Pollution class	Inference
Pb	0.0256	1	Unpolluted to moderately polluted
Cr	0.00204	1	Unpolluted to moderately polluted
Cd	4.767	5	Strong to very strongly polluted
As	0.0125	1	Unpolluted to moderately polluted
Ni	0.0044	1	Unpolluted to moderately polluted
Co	0.00027	1	Unpolluted to moderately polluted

Based on the values of I_{geo}, the soil around the dumpsite indicated unpolluted to very strongly polluted possibly due to the anthropogenic inputs such as deposit of refuse in the dumpsite. The mean I_{geo} of the metals increased in the order of Cd>Pb>As>Ni>Cr>Co. Odat (2015) found Cd to have the highest average I_{geo} in the soil along Irbid/zarga high way in Jordan. The distribution of metal concentration in the study area was attributed to anthropogenic influences such as vehicular emission. Cadmium is a pervasive environmental pollutant of increasing global concern. It is thought to be of greater alarm to rapidly industrializing developing countries because of the increasing pace of industrial activities in these countries with increasing consumption and discharge into the environment (Anetor, 2012). Long-term exposure to cadmium through air, water, soil, and food leads to cancer and organ system toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems (Rahimzadeh *et al*., 2017).

Contamination Indices

The contamination factor (CF), contamination degree (CD) and pollution load index (PLI) values for the heavy metals in the soil are shown in Table 3. The average CF values for Pb (0.1280), Cr (0.0102), As (0.0385), Ni (0.0221) and Co (0.0014) were <1, thus the soil samples had a low level of contamination. The average CF value of Cd (11.8817) indicated that the soil had very high contamination. In this study, the average CF values of heavy metals were ranked based on the following order: Cd>Pb>As>Ni>Cr>Co. Contamination degree for site 1 (12.4362) indicated considerable degree of contamination while site 2 (11.7271) indicated moderate degree of contamination.

Table 3: Contamination Indices of the Study Sites

Heavy metals (mg/kg)	Sampling Point 1	Sampling Point 2	Mean
Contamination Factor of Heavy Metals			
Pb	0.1227	0.1332	0.1280
Cr	0.0103	0.0101	0.0102
Cd	12.2400	11.5233	11.8817
As	0.0395	0.0374	0.0385
Ni	0.0224	0.0217	0.0221
Co	0.0013	0.0014	0.0014
Contamination Degree of Heavy Metals			
CD	12.4362	11.7271	12.0819
Pollution Load Index of Heavy Metals			
PLI	0.0511	0.0510	0.0511

The average PLIs of the heavy metal value is 0.0511. These result indicates that the soil in the study area has low pollution load index. PLI values were less than 1 for all the heavy metals in all the sampling sites, thus indicating that the levels of the heavy metals investigated in this study were within the baseline level for all the stations. The contamination factor value of Cd was however higher possibly due to the effect of anthropogenic contaminants arising possibly from discharge of refuse in the dumpsite.

CONCLUSION

Soil pollution in the present study was successfully assessed using Geoaccumulation Index (Igeo), Contamination Factor (CF), Contamination Degree (CD) and Pollution Load Index (PLI) approaches. Cadmium has been found to be a major contaminant in the soil necessitating further frequent monitoring. The PLI values indicated that the soil in the study area has low pollution load index. Despite this, prolong dumping of waste on the dumpsite may constitute some health dangers. It is recommended that the dumpsite be relocated to a distant area far away from residential areas.

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