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HEAVY METALS CONCENTRATION IN SOME SELECTED DUMPSITES AND GROUNDWATER IN CALABAR, CROSS RIVER STATE, NIGERIA

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ABSTRACT: *Heavy metals concentration in soil from dumpsites and borehole water in Calabar, Nigeria was analysed. Four dumpsites: Lemna (008°21'55.912"E and 05°2'08.725"N), Nassarawa (008°21'35.168"E and 05°4'51.544"N), University of Calabar female hostel (008°20'57.937"E and 04°56'16.612"N) and Goldie market (008°20'29.34"E and 04°56'29.198"N) were selected as sampling locations while a plot of land (008°21'43.9"E and 04^0'58.04 227"N) was selected as a control which were labeled S1, S2, S3, S4 and PC respectively. Soil and water samples were collected for a period of twelve months following a standard procedure and analysed for heavy metals using atomic absorption spectrophotometer (AAS) while physicochemical properties of water were analysed using their respective meters. The results obtained showed that in dumpsites soil: Cadmium was the highest occurring metal with a mean concentration of 1.457±0.493 mg/kg in S4 while As in S1 was the lowest occurring metal with a concentration of 0.001 ± 0.000 mg/kg and Hg was below detection limit in all sampling locations. In water: Chromium was the highest occurring metal with a concentration of 0.006 ± 0.001 mg/l and the lowest was Cobalt and Lead with concentrations of 0.001 ± 0.000 in about all the sampling locations while Arsenic and Mercury were below detection limit in all the sampling locations. Cd, Pb and Cr in S4 soil, Cd and Cr in S4 water and TDS, electrical conductivity and hardness of water from all dumpsites were above the WHO limit while strong positive correlation was found between some heavy metals concentration in soil and water.*

KEYWORDS: Heavy metals; Dumpsites; Groundwater; Boreholes; Calabar; Physicochemical properties; Correlation analysis

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INTRODUCTION

Municipal solid waste commonly known as garbage or refuse is wastes consisting of everyday items that are discarded by the public with variation from country to country and from city to city (Afon and Okewole, 2007; Ogwueleka, 2009). This waste changes significantly with time and may include durable goods, non-durable goods, containers and packaged food waste, yard trimmings and miscellaneous inorganic waste (Babayemi and Dauda, 2009). Adewumi *et al*., (2005) opined that the generation and indiscriminate disposal of urban solid waste in Nigeria is on the increase due to the increase in rural-urban migration, industrialization, poverty, decreasing standard of living, poor governance, population growth and low level of environmental awareness. Solid wastes consist of biodegradable parts which decompose with time and emit bad odour while the non biodegradable parts made up of metals, chemicals, explosives or radioactive substances are highly reactive and toxic, posing a severe danger to human, plants or animal life (Gobo and Ubong, 2001).

Groundwater is water located beneath the earth's surface in soil pore spaces and in the fractures of rock formations (Benett, 2011) which is made available through digging of wells or boreholes or natural discharge as springs and seeps (Okhuebor and Izevbuwa, 2020). According to Carrard *et al.* (2019), 66% of households in urban areas and 60% of households in rural areas rely on groundwater for drinking which accounts for about 20% usage while agriculture and industrial uses account for about 80% groundwater withdrawal worldwide. Groundwater is facing a serious threat of heavy metals and chemical contamination as a result of human activities including agriculture, industrial activities and indiscriminate household wastes disposal which is a great challenge to human population (Li *et al.*, 2021). Uncontrolled waste disposal was reported to generate serious heavy metals pollution in the soil, water and plants (Ferronato and Torreta, 2019; Jessica *et al.*, 2020) through leaching, absorption and bioaccumulation which poses harm to the entire ecosystem. This research was carried out to assess the influence of refuse dumping on heavy metals concentration in soil and groundwater in Calabar, Cross River state, Nigeria.

MATERIALS AND METHODS

The Study Area

The study was carried out in Calabar Metropolis of Cross River State, Nigeria which is located between longitude 8^{o} 14' 11.34" E and 8^{o} 24' 13.30" E and latitude 4^{o} 51' 55.78" N and 5^{o} 06' 19.504^{0}'58.04 227''N with an elevation of 4-51m above sea level (Eze and Effiong, 2010). Four dumpsites: Lemna (008°21'55.912''E and 05°2'08.725''N), Nassarawa (008°21'35.168''E and 05°4'51.544''N), University of Calabar female hostel (008°20'57.937''E and 04°56'16.612''N) and Goldie market (008°20'29.34''E and 04°56'29.198''N) were selected as sampling locations for this study while a plot of land (008°21'43.9''E and 04^{0}'58.04 227''N) was selected as a control. These sampling locations and the control were labeled S1, S2, S3, S4 and PC respectively.

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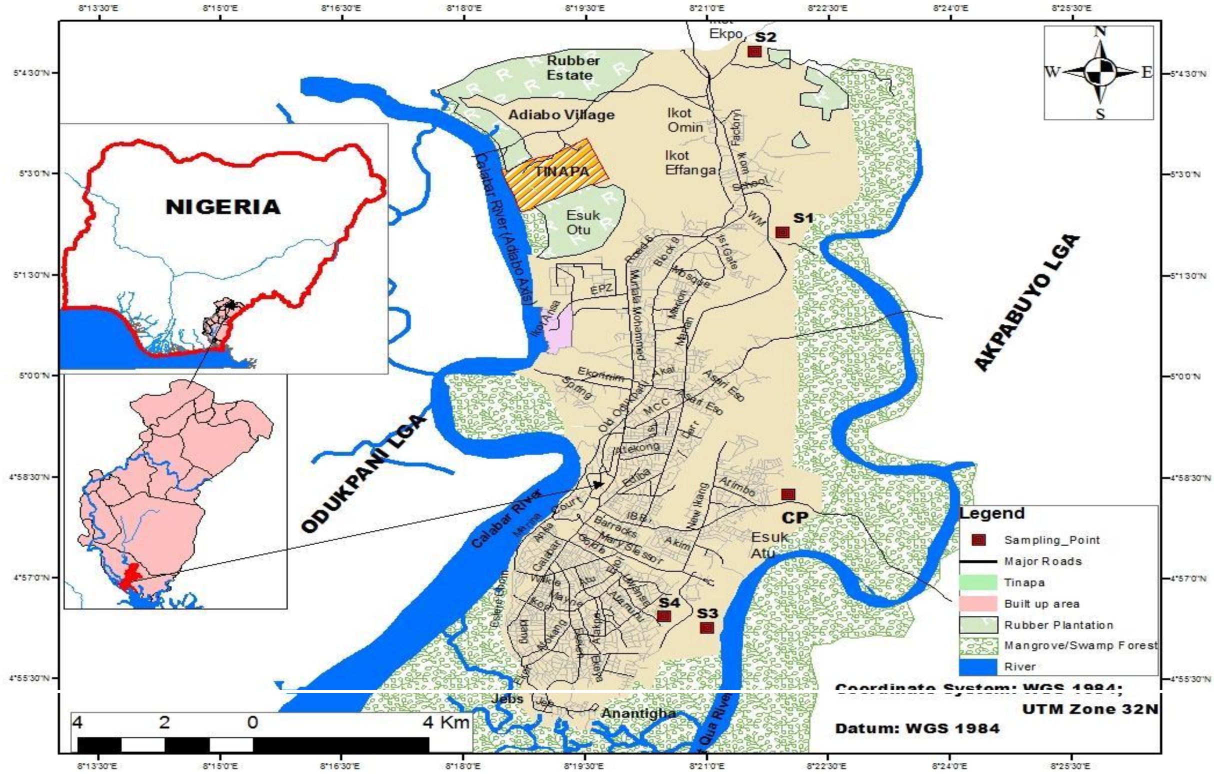

Sample Collection

Soil samples from each of the dumpsites were collected at a depth of 0–10 cm using a soil auger and transported to the laboratory in labeled polythene bags for analysis. One liter of borehole water from each sampling location was collected in a plastic container that was previously washed with water and detergent, soaked in 10% nitric acid and rinsed with deionised water according to Bate and George (2021) and the collected samples were properly labeled and stored in an ice packed container for transportation to the laboratory.

Analysis of Samples

All glasswares used in the analysis of samples were washed using liquid soap, rinsed with distilled water and soaked overnight in 10% nitric acid according to Asuquo and Bate (2020) and High pure (Anal R grade) chemicals and double distilled water were used for preparing solutions for analysis.

Soil samples were air dried, crushed and sieved through 2mm mesh and 1 gramme was weighed into 250 ml beaker and 20 ml nitric acid, hydrofluoric acid, and perchloric acid mixture in the ratio 3:1:1 was added to it. The samples were then diluted to 50ml with distilled deionized water according to Bate and Sam-Uket (2019) and the analysis for heavy metals: Cd, Pb, Cr, Ni, Co, As and Hg was done using atomic absorption spectrophotometer (AAS).

50 ml of each borehole water sample was acidified to methyl orange with concentrated nitric acid and evaporated to 10 ml. It was transferred into 125 ml conical flask, 5 ml concentrated nitric acid and 10 ml perchloric acid were added and the mixture heated gently until white dense fumes of $HCLO_4$ appeared. The digest was cooled at room temperature, filtered through

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Whatmann 41 filter paper and the volume made up to 100 ml with distilled water which was used for heavy metals analysis in atomic absorption spectrophotometer according to Srikanth *et al*. (2013).

Borehole water samples' physicochemical properties: Temperature, dissolved oxygen (DO), pH and electrical conductivity (EC) were determined in–situ using HANNA digital thermometer (Model 280), DO meter (Model DO–5509), Pocket pH meter (pH–1 Model) and METTLER TOLEDO conductivity meter respectively while BOD_5 was determined by incubating the water for five days after which DO readings were taken again and BOD_5 = the first day DO minus the fifth day DO (DO_1–DO_5). Other physicochemical parameters: Turbidity, total dissolved solids and total hardness were measured using their respective meters in the laboratory.

Statistical Analysis

Analysis of variance (ANOVA) was used to determine the differences in heavy metals concentration and physicochemical properties across sampling while Pearson's correlation analysis was used to evaluate the relationship between mean heavy metals concentration in soil from dumpsites and water.

RESULTS

Heavy Metals Concentration in Dumpsite Soil

In the dumpsite soil, Cadmium was the highest occurring metal with a mean concentration of 1.457±0.493 mg/kg in S4 while As in S1 was the lowest occurring metal with a concentration of 0.001 ± 0.000 mg/kg and in all sampling locations, Hg was below detection limit. Heavy metals concentration in soil from the control location were all below WHO maximum permissible limits for soil and most of the metals concentration in soil from dumpsites were above the WHO limit with a significant difference ($P < 0.05$) among sampling locations and the control. Mean heavy metals concentrations in dumpsites soil from Calabar during this study are presented in table 1.

Water Physicochemical Parameters

Temperature was highest (29.877 ± 0.835^{0}C) in S1 and lowest (28.837 ± 0.901^{0}C) in PC with no significant difference among sampling locations, highest and lowest pH were 6.730 ± 0.188 in S4 and 6.585 ± 0.167 in S2 respectively while turbidity was highest (0.263 ±0.056 NTU) in S3 and lowest (0.156 ± 0.020 NTU) in PC. Electrical conductivity was highest (1047.500 ± 9.746 µs/cm) in S2 and lowest (1000.750 ± 10.242 µs/cm) in PC, total dissolved solids was highest (672.575 ± 35.983 mg/l) in S1 and lowest (567.350 ± 20.211 mg/l) in PC while highest and lowest total hardness were 260.675 ± 20.345 mg/l in S3 and 217.325 ± 6.562 mg/l in PC respectively. Temperature, pH, turbidity and DO/BOD in all sampling locations were within the WHO limits while total hardness, TDS and conductivity were above the WHO limit in all sampling locations except PC. Physicochemical parameters of borehole water around selected dumpsites in Calabar during this study are presented in table 2.

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Heavy Metals Concentration in Water

The highest occurring heavy metal in borehole water was Chromium with a concentration of 0.006 ± 0.001 mg/l and the lowest was Cobalt and Lead with concentrations of 0.001 ± 0.000 in about all the sampling locations while Arsenic and Mercury were below detection limit in all the sampling locations. Only Cadmium and Chromium differed significantly ($P < 0.05$) across sampling locations and the duo plus Nickel and Cobalt in S2 were above the WHO limits for heavy metals in drinking water. Heavy metals concentration in borehole water around selected dumpsites in Calabar during this study is shown in table 3.

Relationship between Heavy Metals Concentration in Dumpsite Soil and Water

The highest positive relationship between mean metal concentrations in dumpsite soil and water was 0.81 between Ni and Cr and the lowest 0.61 between Cd and Pb. Negative relationship was highest (-0.74) in Ni/Pb and lowest (-0.14) in Co/Pb. Table 4 shows the correlation matrix of the relationship between mean metals concentration in dumpsite soil and borehole water in Calabar during the study.

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Table 1: Heavy Metals Concentration in Dumpsites Soil in Calabar during the Study

Heavy metals (mg/kg)	PC	S1	S2	S3	S4	P–value	Inference	WHO limit
Cd	0.248±0.106	0.605 ±0.316	0.485 ± 0.054	0.611±0.068	1.457±0.493	P>0.05	Sig. diff.	1.0
Pb	0.002±0.001	0.082 ± 0.070	0.057 ± 0.054	0.270 ±0.116	1.198±0.470	P>0.05	Sig. diff.	0.05
Cr	0.012±0.005	0.208 ± 0.098	0.447 ± 0.039	0.293±0.123	1.866±0.156	P>0.05	Sig. diff.	0.10
Ni	BDL	0.124 ± 0.016	0.328 ± 0.418	0.152± 0.087	0.226± 0.057b	P<0.05	Not. Sig.	0.05
Co	0.017±0.034	0.034 ± 0.030	0.065 ± 0.128	0.032±0.045	0.343±0.126	P>0.05	Sig. diff.	
As	BDL	0.001 ± 0.000	0.003 ± 0.001	0.017±0.005	0.019±0.008	P<0.05	Not. Sig.	0.001
Hg	BDL	BDL	BDL	BDL	BDL	-	-	0.001

Values are in mean ± standard deviation, BDL = Below detection limit

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Table 2: Physicochemical Parameters of Borehole Water around Dumpsites in Calabar during the Study

Parameters	PC	S1	S2	S3	S4	P–value	Inference	WHO Limit
pH	6.677 ± 0.038	6.625 ±0.170	6.585 ± 0.167	6.652 ± 0.170	6.730 ± 0.188	P<0.05	Not. Sig.	6.5 – 8.5
Turbidity (N.T.U)	0.156 ± 0.020	0.262 ± 0.057	0.262 ± 0.060	0.263 ±0.056	0.176 ± 0.022	P<0.05	Not. Sig.	5.0
Conductivity (µs/cm)	1000.750 ± 10.24	1044.250 ± 6.130	1047.500 ± 9.746	1029.000 ± 15.811	1039.750 ± 7.410	P>0.05	Sig. diff.	1000
DO (mg/L)	6.71± 3.11	5.93 ± 2.89	6.01 ± 2.82	5.58 ± 3.40	6.51 ± 4.01	P>0.05	Not. Sig.	5.0
BOD (mg/L)	4.585 ± 0.193	4.632 ± 0.199	4.602 ± 0.244	4.670± 0.187	4.617± 0.234	P<0.05	Not. Sig.	≤5.0
TDS (mg/L)	567.350 ± 20.21	672.575 ± 35.983	661.125 ± 30.652	671.150 ± 24.444	658.925± 27.950	P>0.05	Sig. diff.	600
Hardness (mg/L)	217.325 ± 6.562	255.391 ± 31.564	254.400 ± 20.168	260.675 ± 20.345	255.175 ±20.939			250
Temperature (°C)	28.837 ± 0.901	29.877 ± 0.835	29.762 ± 0.944	29.580 ± 0.486	29.565 ±0.502	P<0.05	Not. Sig.	<40

Values are in mean ± standard deviation

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Table 3: Heavy Metals Concentration in Borehole Water around Dumpsites in Calabar during the Study

Heavy metals (mg/l)	PC	S1	S2	S3	S4	P–value	Inference	WHO Limit
Cd	0.002 ± 0.001	0.004 ±0.001	0.003 ± 0.002	0.004 ± 0.001	0.005 ± 0.002	P>0.05	Sig. diff.	0.003
Pb	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000	0.001 ±0.000	0.001 ± 0.000	P<0.05	Not. Sig.	0.01
Cr	0.003 ± 0.001	0.004± 0.001	0.005 ± 0.0001	0.004 ± 0.002	0.006 ± 0.001	P>0.05	Sig. diff.	0.01
Ni	BDL	0.003 ± 0.001	0.002 ± 0.001	0.003 ± 0.001	0.002 ± 0.001	P<0.05	Not. Sig.	0.01
Co	0.001 ± 0.000	0.001 ± 0.000	0.002 ± 0.001	0.001 ± 0.000	0.001 ±0.001	P<0.05	Not. Sig.	0.001
As	BDL	BDL	BDL	BDL	BDL	-	-	-
Hg	BDL	BDL	BDL	BDL	BDL	-	-	-

Values are in mean ± standard deviation, BDL = Below detection limit

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Table 4: R–values of Correlation between Mean Heavy Metals Concentration in Dumpsite Soil and Water in Calabar

	Cd(S)	**Pb(S)**	**Cr(S)**	**Ni(S)**	**Co(S)**	**As(S)**	**Hg(S)**
Cd(W)	1						
Pb(W)	0.61	1					
Cr(W)	0.79	0.73	1				
Ni(W)	0.67	-0.74	0.81	1			
Co(W)	-0.47	-0.14	-0.45	-0.3	1		
As(W)	0.00	0.00	0.00	0.00	0.00	0	
Hg(W)	0.00	0.00	0.00	0.00	0.00	0.00	0

(S) = Heavy metals in soil, (W) = Heavy metals in water

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DISCUSSION

The higher concentration of heavy metals in dumpsites soil could be attributed to the solid waste disposed in the dumpsite which over time dissociate and add their metallic content to the soil (Oni *et al*., 2011). The current trend in the municipal waste disposal and management practices increases the heavy metals burden of the soil and underground water (Albores *et al*., 2000; Okoronko, *et al*., 2006; Elaigwu *et al*., 2007). Leachates from refuse or waste dumpsites constitute a source of heavy metal pollution to both soil and aquatic environment (Odukoya *et al*., 2007). S4 dumpsite had higher concentration of cadmium, lead, chromium, nickel and arsenic compared to the soil samples from other dumpsites which could be attributed to disposal habits, age of the dumpsite and the content of waste (Luter *et al*., 2011). The mean concentration of cadmium in S4, lead, chromium, nickel and arsenic in S2, S3, and S4 dumpsites were above the WHO acceptable limit. This is a serious health threat to the people living around as Chromium causes nose irritation, nose ulcer, kidney and skin irritation, Arsenic causes skin, lung, bladder and kidney disorder, Lead causes neuro-developmental effects, hypertension, impaired fertility and anemia while Cadmium and nickel cause kidney disorders (Balali-Mood *et al*., 2021).

Physicochemical parameters of water are closely related to its pollution status as they provide current information about the concentration of various solutes at a given time and form a basis for judging the suitability of water for its designated uses and to improve existing conditions (Ftsum *et al.*, 2015). TDS, electrical conductivity and hardness of borehole water from all sampling locations except the control were above the WHO limit which is an indication of dissolution of substances form these dumpsites into the groundwater (Taiwo *et al.*, 2020). Water with high levels of TDS and hardness is unpalatable for drinking, requires much detergent in laundry work and may cause scale deposition in the treatment works and distribution system hence elevated levels of TDS and hardness require specific analysis for each contaminant to determine potential health effects (Manoj and Avinash, 2012).

The concentration of heavy metals in boreholes around each studied dumpsite were higher than that of the control borehole which denotes that the levels of heavy metals in boreholes around the studied dumpsites were raised by the infiltration of contaminants and leachates of the dumpsites. Cobb *et al*. (2000) reported that dumpsites can transfer significant levels of toxic and persistent metals into the soil environment which infiltrate into the borehole water. The borehole around S4 dumpsite had higher concentration of cadmium and chromium above the WHO limit which could be attributed to disposal habits and the content of waste in the area (Udosen *et al*., 2006). Water from boreholes around the studied dumpsites pose a moderate to high health risk considering its physicochemical properties and heavy metals concentration (Bate and George, 2021) which may increase if indiscriminate waste disposal in these areas continue. A strong positive correlation was found between some heavy metals concentration in dumpsite soil and borehole water which implies that these metals may be from the same source (Boateng *et al*., 2019).

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CONCLUSION

This study explored levels of heavy metals in soil samples from dumpsites and the nearby boreholes together with a control in Calabar, Nigeria. Heavy metal levels in soil and borehole water were higher in all dumpsites than in the control while Cd, Pb and Cr in S4 soil, Cd and Cr in S4 water and TDS, electrical conductivity and hardness of water from all dumpsites were above the WHO limit. Strong positive correlation was also found between some of the heavy metals concentration in soil and water. It is therefore suggested that indiscriminate waste dumping should be discouraged, the wastes should be segregated and non-biodegradable and toxic ones should be treated specially.

Author Contribution: Sam-Uket Nwuyi Okori carried out the field work and laboratory analysis while Bate Garba Barde conducted the statistical analyses and arranged the manuscript for publication.

Declaration of interest: The authors declare that there is no conflict of interest.

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