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Characteristics of Phsysicochemical Parameters, Heavy Metals and Influence of Distance to Land Fill on Possible Ground Water Contamination in Calabar Municipality

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ABSTRACT: This study investigates the vulnerability of groundwater contamination from	Corresponding Author:
dumpsites in Calabar Municipality, Cross River State, Nigeria. Groundwater contamination,	Emmanuel Efobe Ndoma
particularly due to leachate. The research aimed to determine the physicochemical properties of	
leachate, assess groundwater quality against national and international standards, explore the effect	
of proximity to dumpsites on contamination levels, and, laboratory analysis, and statistical	
techniques were employed. Nine Groundwater sample were gotten from three sample location and	
five leachate samples were collected from Lemna Dumpsite, which is the only Government	
Approved Dumpsite in Calabar and key physicochemical parameters-including Biological	
Oxygen Demand (BOD), Chemical Oxygen Demand (COD), heavy metals, and Total Dissolved	
Solids (TDS) were measured. This indicates that leachate from the dumpsites is a primary source	
of contamination in the groundwater. Factor analysis identified a single dominant factor responsible	
for over 99% of the variation in contamination, suggesting that leachate percolation is the main	
driver of contamination. The Water Quality Index (WQI) calculated for the groundwater samples	
from Ikot Efanga, Ikot Ene Obong, and Ikot Ansa indicated that all the sampled sites fell within the	
poor to very poor water quality categories, underlining the health risks associated with groundwater	KEYWORDS:
consumption. The study concludes that improved waste management practices are essential to	contamination, dumpsites,
mitigate groundwater contamination in Calabar Municipality. Recommendation were made: on the	leachate, groundwater,
implementation of effective waste management practices.	Physicochemical

1.1 INTRODUCTION

Solid waste is a significant environmental problem affecting countries worldwide much of which comes from industrial processes, packaging, and consumer goods (Abubakar et al., 2022). As noted by Wondimu (2020), solid waste includes the unwanted or useless solid materials produced from residential, industrial and commercial activities in a specific area. In its entirety, solid waste is usually classified according to its origin (domestic, industrial, commercial, institutional and construction), according to its potential hazard (toxic, non-toxic, radioactive, flammable, infectious, among others), as well as according to solid waste contents (organic material, glass, metal, plastic paper, among others) (Awasthi, Chataut and Khatri, 2023).

Leachate is a major concern associated with solid waste management, particularly in landfill sites where it forms as rainwater percolates through the waste, picking up dissolved and suspended contaminants along the way (Lindamulla et al., 2022). According to Envieq (2018), the word "leachate" is commonly used in its ecological context, meaning the water or liquid that percolates through a landfill and carries the high concentration the dissolved or suspended matter of the industrial wastes or putrescible. It drains from the soil or the dumped wastes and severely harms the environment. Leachate is a by-product derived from municipal solid wastes due to their physical, chemical, and biological changes and was formed in landfills, incineration plants, composting plants, and transfer stations, with high strength and toxicity (Youcai, 2018). Leachate is produced due to percolation of water through processed waste, after which the compaction and covering of waste resulting in generation of this phenomenon (Sholichin, 2012). Pollution control for leachate is a world-wide concern and still a big challenge in source reduction and pollutant removals. Leachate

must be treated properly before it is discharged into the water receivers or recycling using integrated leachate treatment processes (Youcai, 2018). In its wide meaning, leachate is any liquid that has passed through any matter and extracted its components.

Groundwater is water that exists beneath the Earth's surface in the pore spaces and fractures in rocks and sediments. It has its origin from rainfall or snow, and then moves through the soil profile into the groundwater system, where it eventually makes its way back to surface streams, lakes, or oceans.

Groundwater contamination by leachate is a significant environmental concern associated with improper solid waste management practices (Parvin and Tareq 2021). Leachate from Municipal Solid Waste (MSW) disposal sites presents the greatest threat for pollution of groundwater that serves as domestic water supply. Leachate from some MSW landfills contain sufficient concentrations of lead to cause leachate contaminated groundwater to contain levels of lead that Impair the use of the groundwater for domestic water supply.

Calabar Municipality has inadequate solid waste management (SWM) as a major environmental problem. The contributing factors range from technical problems to financial and institutional constraints. There is an absence of properly designed solid waste management and disposal facilities in the state, therefore posing contamination risk to water sources. Groundwater has been reported to be the major source of water supply in Calabar (Ekwok et al., 2020), and its contamination is a major environmental and health concern. Despite the inherent impact on the environment, many cities and areas in Nigeria including Calabar still rely on sanitary landfills for the disposal of household wastes (Eteng, Offiong and Offiong, 2013). The implication is the continuous contamination of available water sources with inherent effects on human health. Solid waste disposal by landfill poses a threat to groundwater and surface water quality through the formation of polluting leachate. Leachate can percolate through the base of the landfill and enter the groundwater system (Mohd et al., 2011). Therefore, this study is set to investigate the level of Groundwater vulnerability of leachate contamination from Landfill and dumpsite across Calabar Municipality. However, the researchers did not analyzed for the impact of leachate from these dumpsites on groundwater in the area.

All the previous works reviewed were carried out outside Calabar Municipality and those done in Calabar such as Ekwok et al. (2020) and Agbaji and Ejemot-Nwadiaro, (2019) were concerned with waste management. The only work that assessed the impact of leachate on groundwater was that of Udofia et al., (2016). However, the work did not analyze the composition of the landfill leachate in the study nor consider the effect of distance from the landfill and groundwater pollution by the leachate.

1.2 THE STUDY AREA

Calabar Metropolis consists of Calabar Municipality. It is located between Latitudes 04° 46' 00" and 05° 06' 00"North of the Equator and Longitudes 08° 14' 00"and 08° 26' 00" East of the Greenwich Meridian (Figure 1). Calabar Municipal shares boundaries with Odukpani Local Government Area, in the north, Akpabuyo Local Government Area in the east and Calabar River in the west. The city is about 48km from the estuary where Cross-and Calabar Rivers meet before joining the Atlantic Ocean

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Figure 1: Map of Calabar Municipality Showing LEMNA Dumpsite and Various Leachate Sample Point Source: Adapted from the Administrative Map of Calabar Municipal LGA

2. MATERIALS AND METHODS

This study discusses the data requirement and the sources and methods that were used in acquiring them. Similarly, how all the data were processed and analyzed are equally explained to achieve the set objectives. Field survey was employed for this study; the coordinates of all the dumpsites across the study area were captured for the spatial mapping to get distribution of dumpsites, water samples were taken at specific distance away from the dumpsite and leachate samples were taken from the dumpsites. Laboratory test was used in determining the composition of leachate and the levels of physicochemical parameters of groundwater in assessing the levels of leachate contamination of groundwater in the study area.

3 RESULT AND DISCUSSION

The section covers results of laboratory analysis of physicochemical characteristics and heavy metal concentration of leachates around Lemna wastes dump site, the quality of underground water sampled in Calabar municipality, and the effect of distance on

borehole water quality. The results are presented in tables, graphs while inferential statistics of Pearson's correlation and factor analysis were used to analyze the data

3.1 Physicochemical characteristics of leachate generated across the Dumpsite in the study area

Table 1 is the physicochemical characteristic of leachate samples collected from various distances within (0-5m, 6-10m, 11-15m, 16-20m, and 21-25; henceforth {L1}, {L2}, {L3}, {L4}, and {L5} respectively in Lemna dumpsite in Calabar Municipality (Plate 1). The table indicates that the minimum values for Lead across the five sampled sites are 6.00 while the maximum value is 6.80. The table further indicates that the mean and standard deviation of Lead is 6.4780 and 0.291. Temperature values in degree centigrade (⁰C) vary from one sampled location to another. However, the minimum, maximum, mean and standard deviations are 28, 29, 28.34 and 0.32 respectively. Table 1 also shows that Dissolved oxygen demand (NTU) has minimum values of 210, maximum values of 250 while the mean and standard deviation are 230.00 and 15.81. Furthermore, table 1 indicates that biological oxygen demand has minimum and maximum values of 20 and 190 while the mean and standard deviations are 142.00 and 71.20. More so, the table revealed that the total dissolved solid has minimum value of 477.0, maximum value of 9200.0 with mean of 4525.0 and standard deviation of 3940.05.

S /	Parameters	Uni	1	2	3	4	5	Min	Max	Mean	SD
Ν		t									
1	Ph	-	6.55	6.88	6.59	6.52	6.5	6.0	6.80	6.47	0.29
2	Temperature	^{0}C	27.9	28.1	28.5	28.6	28.6	28	29	28.34	0.32
3	Dissolved oxygen	NT	240	220	250	210	230	210	250	220.00	15 01
	demand	U						210	230	230.00	13.81
4	Biological oxygen demand	Mg/ l	190	170	140	20	190	20.0	190.0	142.00	71.20
5	Total dissolve solid	Mg/ l	7872	4080	996	477	9200	477.0	9200	4525.00	3940.0 5
6	Electrical conductivity	μs/c m	3.88	4.36	1.973	0.945	10.3	0.95	10.26	4.28	3.61
7	Chemical oxygen demand	Mg/ l	900	2100	2100	1500	1230 0	900.0	2100	1566.00	531.77
8	Chloride content	Mg/ l	949.8	519. 8	240.0	499.8	1289. 6	240.0	1289. 6	699.80	416.58
9	Total hardness (as	Mg/	1414	3838	1414	1414	4848.	1414.0	4848.	2595 76	1643.7
	CACO ₃)	1		.4			4	1414.0	4	2383.70	5
10	Sulphate (SO ² 4)	Mg/ l	9500	1350	7000	9000	1850 0	7000.0	18500	11500.0	4568.9 1
11	Nitrate NO ₃	Mg/ l	56	63	70	50	270	50.00	270.0	101.80	94.32

Table 1: Descriptive statistics of physicochemical parameters in leachates around waste dumpsites in Calabar Municipality

Source: Laboratory analysis and summary statistics by the author (2024)

The laboratory result of electrical conductivity shows that the minimum and maximum values across the five sampled locations are 0.95 and 10.26 while the mean and standard deviations are 4.28 and 3.61 respectively. The table also indicates that chemical oxygen demand has minimum values of 900.00 and maximum values of 2100.00 while the mean and standard deviations are 1566.0 and 531.77 respectively. Chloride content has minimum and maximum values of 240.00 and 1289.60 while the mean and standard deviations are 699.80 and 416.58.



Plate 1: Collection of Leachate sample at Lemma dumpsite by the author with assistant from the field assistant.

Total hardness has minimum values of 1414.00 while the maximum value is 4848.40. The mean and standard deviation of total hardness is 2585.76 and 1643.75 respectively. Table 1 further revealed that sulphate have minimum and maximum values of 7000.00 and 18500.0 while the mean and standard deviations are 11500.00 and 4568.91. The distribution of nitrates in Table 1 indicates that the minimum and maximum values of 50.00 and 270.00 with mean and standard deviations of 101.80 and 94.32 were recorded.

Table 2. Heavy metal concentration in sampled leachates											
	Parameters	Unit	1	2	3	4	5	Min	Max	Mean	SD
1	Iron (Fe)		25.85	26.8 5	8.88	1.58	22.8	1.58	26.85	17.19	11.31
2	Nickel (Ni)	Mg/l	0.46	0.38	0.09	0.27	0.4	0.09	0.46	0.31	0.14
3	Magnesium (Mg)	Mg/l	7.10	7.13	6.52	5.48	7.16	5.48	7.16	6.67	0.72
4	Zinc (Zn)	Mg/l	1.15	1.62	0.02	0.01	2.78	0.01	2.78	1.11	1.16
5	Manganese (Mn)	Mg/l	2.03	2.21	0.90	0.67	1.46	0.67	2.21	1.45	0.67
6	Lead (Pb.)	Mg/l	0.28	0.48	0.41	0.59	1.27	0.28	1.27	0.60	0.38
7	Chromium (Cr.)	Mg/l	4.06	3.47	0.06	0.10	0.71	0.06	4.06	1.68	1.93

Table 2: Heavy metal concentration in sampled leachates

Source: Laboratory analysis and summary statistics by the author (2024)

The values of heavy metals as presented in Table 2 varied across the sampled locations in the study area. Iron recorded minimum and maximum values of 1.58 and 26.85 with mean and standard deviations of 17.19 and 11.31 respectively. More so, Nickel has

minimum and maximum values of 0.09 and 0.46 with mean and standard deviations of 0.31 and 0.14 while Magnesium had minimum and maximum values of 5.48 and 7.16 with mean and standard deviations of 6.67 and 0.72. Zinc recorded minimum and maximum values of 0.01 and 2.78 with mean and standard deviations of 1.11 and 1.16. The table also shows that Manganese have minimum and maximum values of 0.67 and 2.21 with mean and standard deviations of 0.67. The minimum and maximum values for Lead in the table are 0.28 and 1.27 while the mean and standard deviation is 0.60 and 0.38. Chromium has minimum and maximum values of 0.06 and 4.06 with mean and standard deviations of 1.68 and 1.93.

Table 2 is the organic strength of the sampled leachates. The result indicates that at location L1, the effluent has an organic strength of 0.21, in location L2, the organic strength is 0.08 while in locations L3, L4 and L5, the values of organic strength are 0.06, 0.01 and 0.07 respectively.

Table 3: Organic strength of waste water (BOD and COD ratio)

	(2)		2 1				
Biological oxygen demand	Mg/l	190	170	140	20	190	142.00
Chemical oxygen demand	Mg/l	900	2100	2100	1500	12300	1566.00
Organic strength		0.21	0.08	0.06	0.01	0.01	0.074

Source: Calculation by the author (2024) derived by dividing the values of BOD by COD (i.e. BOD and COD ratio).

The characteristics of leachates are often influenced by many factors such as biochemical changes, physicochemical processes including dissolution, adsorption, dilution, precipitation and volatilization (Apiah et al., 2021). The result indicates that Lead values were above 6 in all the five sampled locations. The high values for sample point closed to waste dumpsite showed that there was a decrease in the concentration of free volatile acids due to anaerobic decomposition (Kanmani & Gandhimathi, 2013). More so, the high Lead may be attributed to the fact that the Lemna dumpsite is older than five years. According to Bhalla et al. (2014), when a dumpsite is about five years old or younger,Lead values of leachates are often less than 6.5. In such a case, the decomposition of organic material released carbon dioxide which combines with the water to form carbonic acid resulting in lower Lead in the leachate samples (Amono et al., 2021).

Temperature is basically important for its effect on other properties of leachates. The temperature of the leachate sampled is high across the nine sampled locations, as a mean value of temperature of 28.34 °C is recorded in the study area. The high temperature in the leachate sampled is an indication that some reactions could be speeded up by the discharge of this leachates into stream. It will also reduce the solubility of oxygen and amplified odour due to anaerobic reaction (Olarewaju et al., 2012). Conductivity of leachate is a useful indicator of its salinity or total salt content. Electrical conductivity showed variety across the sampled points. Overall, a mean value of 4.28 µs/cm is recorded (Table 3). The low levels of electrical conductivity in the study area could therefore be attributed to the low content of potassium and chloride (Balali-Mood et al., 2021). More so, the values of electrical conductivity revealed that the leachates contain high proportion of pollutants, the significance is that considerable amount of dissolved organic materials are present in the dumpsites; such materials can provide adsorptive sites for certain chemicals and biological agents. This process may eventually foster pollution of surrounding soils, vegetation and underground water within the area of the dumpsite. Such similar trend was observed previously (Aluko et al., 2002).

The values of heavy metals in the sampled leachates varied across the study locations. Table 3 indicates that the selected heavy metals analyzed for are high. Iron Mg/L across the nine sampled points ranged from 1.58 to 26.85. The high concentration of Fe in the leachate indicates that Fe scraps are likely dumped in the dumpsite. Elevated levels of lead in leachate had also been observed by Moturi et al. (2004) and this may be attributed largely to the disposal of batteries, lead-based paints and lead pipes found at the site. Nickel Mg/L ranged from 0.09 to 0.46 and Magnesium Mg/L ranged from 5.48 to 7.10. The higher concentration of these heavy metals in dumpsites could be attributed to the solid waste disposed in the dumpsite which over time dissociate and add their metallic content to the soli (Saana et al., 2016). Leachates from refuse or waste dumpsites constitute a source of heavy metal pollution to both soil and aquatic environment (Odukoya et al., 2007).

The presence of lead in the dumpsite, leachate can be attributed to the sub-surface geology of the site which consists of clay. These metals have the affinity to be absorbed by clay soil (Igboama et al., 2022). 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).

The results of chemical parameters in the sampled boreholes may pose a moderate to high health risk considering its physicochemical properties and heavy metals concentration (Badmus et al, 2022) 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). In addition Pearson's correlation coefficient matrix between physiochemical parameters of concentrations in the sampled underground water at 5 % significant was carried to

check for inter-relationship between the parameters' concentrations. The correlation coefficient simply tells us whether the association between the parameters is strong or weak indicating if the source of contamination is from same source or not. In Ikot Effanga, Lead, Dissolved oxygen, biological oxygen demand, electrical conductivity, chemical oxygen demand, hardness, nitrate and iron accounted for 82.997 % of the total variance in the data matrix with eigenvalue of 9.960. Implying the sources of these parameters are more likely to originate from leachates in the waste dump sites. Similarly, in Ikot Ene Obong pH, Temperature, Dissolved oxygen, biological oxygen demand, chemical oxygen demand, chloride, hardness, sulphate and iron explained 81.968 % of the total variance in the data matrix with eigenvalue of 9.836. This means the sources of these parameters are more likely to originate from leachates while in Ikot Ansa Temperature, total dissolved solid, electrical conductivity, chemical oxygen demand, and chloride accounted for 76.803 % of the total variance in the data matrix with eigenvalue of 9.216. The result of the factor analysis confirmed the fact there is a significant relations between waste dumpsites and contamination of underground water in the study area.

The physical parameters pH, temperature, total dissolved solid, electrical conductivity, and hardness of water sampled indicated higher concentrations in borehole water closer to dump sites. The result of this study corroborates extant study by Bukunmi (2021) where it was indicated that there is a strong positive correlation between waste dump site distance and water physical parameters especially lead, total dissolved solid and hardness. It has also been ascertained that the concentrations of contaminants varies inversely with the distance hence samples with high contaminant concentrations were found to be close to the dumpsite (Nagarajan et al. (2012). Therefore, groundwater contamination drops as one move away from the dump sites.

On the chemical properties of borehole water, the study shows that distance also affects the concentration of the parameters. For instance, the concentration of the biological demand at Ikot Effanga (8.43 mg/l) which is closest sampled location to a waste dump site was higher compared to the two locations (Ikot Ene Obong and Ikot Ansa). Other parameters like chloride, sulphate, nitrate, iron, magnesium, manganese and lead also showed reduction in concentration with distance from the waste dump sites. As one moves away, the percolation of leachate becomes gentler. This has been accounted for by the natural attenuation, mainly controlled by factors like dilution, sorption, ion exchange and degradation processes (Banu and Berrin 2015). The high concentration of this parameter at certain distance from the waste dump site can also be attributed to the fact that there are located at dry dump site implying less inorganic dissolved solids like nitrate, sulphate and phosphate anions or cations like sodium, magnesium and iron (Bukunmi, 2021).

The concentration of heavy metals also varies with distance. Heavy metals are generally required for the effective functioning of biological organism, but when it concentration exceed the body requirement, it becomes toxic to man and other biological organisms.

SUMMARY OF FINDINGS

This study analyzed the physicochemical characteristics and heavy metal concentration of leachates around Lemna wastes dump site, the quality of underground water sampled in Calabar municipality, and the effect of distance on borehole water quality.

The findings revealed that the physicochemical characteristics of leachate generated across the designated dump sites varied from one sampled location to the other. The minimum values for lead across the five sampled sites are 6.00 while the maximum value was 6.80. The temperature minimum, maximum, mean and standard deviations are 28, 29, 28.34 and 0.32 respectively, while dissolved oxygen demand has minimum values of 210 and maximum values of 250. Similarly, the values of heavy metals varied across the sampled locations in the study area. Iron recorded minimum and maximum values of 1.58 and 26.85 with mean and standard deviations of 17.19 and 11.31 respectively.

CONCLUSION

This study analyzed the physicochemical characteristics and heavy metal concentration of leachates around Lemna wastes dump site in Calabar municipality and found that the values of heavy metals varied across the sampled locations in the study area. the study revealed that the concentration of heavy metals such as nickel, magnesium, Zinc, manganese, lead and chromium in boreholes around most of the studied dumpsite were higher than that of the WHO limit in some sampled locations 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.

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