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Authors' contributions

This work was carried out in collaboration between both authors. Author EOA wrote the first draft of the manuscript under the supervision of author BCA. Author BCA designed and proof read the entire manuscript. Both authors went to field, collected and collated data for the study. Both authors read and approved the final manuscript.

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ABSTRACT

Leachates from selected open dumpsites in Port Harcourt region were analysed for radiometrics and for heavy metal parameters. For radiometrics, gamma ray spectroscope was used while Heavy metal parameters used spectrophotometer. These parameters were compared among the selected dumpsites of different study areas and established international standard FEPA and WHO/INIS were used. Dumpsites leachates show mean of potassium ⁴⁰K(71.715± 0.3 Bq kgl⁻), Uranium ²³⁸U (11.129± 0.021 Bqkgl⁻), Thorium ²³²Th (1.813± 0.073 Bqkgl⁻) and Heavy metals show iron (20.966mgl⁻), Copper (25.787 mgl⁻), cadmium (3.592mgl⁻), nickel (1.557mgl⁻), zinc (129.855 mgl⁻), Magnesium (1.062mgl⁻), lead (1.269 mgl⁻) Chromium (1.966 mgl⁻). These recorded mean are above limits recommendation of World Health Organization (WHO). The radiometric and Heavy metals analyses revealed that the physical environment, the surface water and underground water quality are at risk. If the leachate containing the element of heavy metals and radioactive elements are not



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managed well by the concerned authorities, human and its environment would be subjected to danger. It is important that local, state, federal government and other stakeholders pay attention to dumpsite leachates to provide safe facilities to control the waste water and embark on daily orientation on the dangers associated with leachates. This will help minimize the spread of diseases through water and air within the dumpsite locations.

Keywords: Dumpsite; leachate; radioactive; heavy metal parameters.

1. INTRODUCTION

As man strives to survive in his environment, he tends to create wastes. These wastes are dangerous to human health and the entire environment. The solid waste when interact with liquid produces leachates. Leachate is a chemical cocktail that flows out of dumpsites. It is a mixture of different contents both organic and inorganic materials. Some of the leachates are hazardous due to its composition.

Hazards posed by such waste dumpsites are not only in terms of odour and presence of disease causing micro–organism, but can arise from the radiation emanating from such dumpsites [1], which occur as a result of accumulation and reaction of different radioactive materials in the waste products indiscriminately dumped on open waste site. At waste dumpsites, there are possibilities for radiation to be emitted due to the presence of radioactive wastes (gamma- γ , Beta- β , Alpha- α , Ca-14, Uranium -U, and Thorium -Th) in the dumpsites as well as naturally occurring radionuclides in the soil.

According to Dusing et al. [2], rivers impacted upon by leachate are usually yellow in appearance and support severe overgrowth of sewage fungus. It is pertinent to note that toxic metals and organics when available in leachates can cause chronic toxin accumulation in Local and far populations. Observation has shown that diseases may sprout through water pollution, mostly groundwater contamination which may spread beyond human reasoning due to its complex flow patterns.

Leachates are generated when water is absorbed into solid waste disposal site that contains bacterial, chemical pollutants, organic pollutants and non-organic, heavy metals, dissolved and colloidal solids and a variety of pathogens that potentially contaminate groundwater and surface water [3]. Leachate quality is different and this difference is caused by several factors such as: composition and depth of solid waste, availability of moisture and

oxygen content, design and operation of the dumpsite and life expectancy of the solid waste. Leachates resulting from the decomposition of solid waste contain concentrations of COD, BOD, ammonia nitrogen and heavy metals such as: Zinc, Copper, Cadmium, Lead, Nickel, Chromium and Mercury [4].

Leachate would penetrate into the ground if poorly managed and treated, especially dumpsites that have a layer of permeable soil or landfill without sheeting layer or failure of the sheeting layer. Groundwater pollution is a major problem that exists in a sanitary dumpsite and is identified as a major problem in many countries in the world. Nasir et al. [5], reported that 71.4% of local authorities are facing serious ground water pollution, while 57.2% are dealing with the problem of leachate management [5].

Leachate from dumpsite frequently exceeds standard for drinking and surface water, often for several decades. The leachate has frequently significant potential to pollute groundwater and surface water. The most common pathway for leachate to the environment is from the bottom of the dumpsite through the unsaturated soil layers to the ground water, then by groundwater through hydraulic connections to surface water. However, pollution potential from leachate is the concentration and flux of the leachate. The dumpsite setting such as the hydro geological setting and the degree of protection provided and the basic quality, volume, sensitivity of the receiving groundwater and surface water must be considered [6].

The primary components in leachate from dumpsite that constitute a significant pollution potential are dissolved organic matter and inorganic salts. Trace elements in leachates are limited and generally do not constitute groundwater pollution problem due to strong attention. Where groundwater is used (as drinking water or for irrigation) downstream from dumpsite, leachate has great potential to pollute the environment. Where groundwater is not used or is not usable downstream, the leachates pollution potential (if not diluted to ambient concentration) is transferred to where the groundwater is hydraulically connected to the receiving surface water [7].

Dumpsite leachates are important potential contamination source of ground and surface waters. When the water is not properly collected, treated and safely disposed, it causes extensive contamination of streams, creeks and water wells [8]. The effluents are difficult to deal with and biological processes are totally inefficient for the toxic nature of stabilized leachates.

The aim and objectives of this study is to compare the radiometric and heavy metal parameters of leachates in open dumpsites of Eliozu, Egbelu and Aluu to ascertain the leachate impact on surface and underground water quality and find a way to solve the problems.

2. LITERATURE REVIEW

Leachate production starts at the early stages of the landfill or the dumpsite and continue several decades even after closure of dumpsite. It is generated mainly by the unfiltered water, which passes through the solid waste fill or dumps and facilitates transfer of contaminants from soil phase. Due to the inhomogeneous nature of the waste and because of the differing compaction densities, water percolates through and appears as leachate at the base of the site. Depending on the geographical and geological nature of a leachates may seep dumpsite. into the ground and possibly enter ground water sources. Thus, it can be a major cause of ground water pollution [9].

Avwiri and Olatubosu, [10], reported their studies on 'Environmental Radioactivity in selected dumpsites in Port Harcourt' using Radalert Nuclear Radiation monitor and a Geographical Position System (GPS). The study showed that the activity of the soil samples obtained through Gammar Spectrometry showed higher doze rate on the soil. It also showed that the radionuclide concentration for the locations was at permissible threshold of 1.0m Sv/ur for soil. Again, Iyama et al. [11], carrying out a work on 'physical Quality of Leachates at Rumuolumeni Dumpsites in Port Harcourt', showed that there was no significant difference in temporal dimension (seasonally) but high level spatial variation (stations) in most parameters. The research revealed that dumpsites remain pollutant entrants to the environment. Abdulraham et al. [12] also carried out a study on 'Physical and Chemical Parameters on Solid Waste Dumpsite in Oko-Olowo in Ilorin Metropolis' The study revealed that there was a higher concentration of Lead obtained from leachate (Pb 3.2%) and Manganese (Mn 48.6%) at the University of Ilorin and Oko-Olowo. This also suggested that the neighbourhood of the two dumpsites are exposed to high environmental risks.

This work however, considered 'Radiometric and Heavy Metal Analysis of Leachates in Selected Open Dumpsites in Port Harcourt Region'. Radiometric methods rely on radioactive betadecay, a fundamental process in nature, during which a neutron spontaneously transforms into a proton and an electron, and an energetic, but weakly interacting neutrino. Individual neutron decays are unpredictable, but the average rate of decay of a large population of neutrons follow a simple exponential decay, the rate of which depends on the mass of the particle into which a neutron is bound. The radioactive decay rate of any Isotope may therefore be represented by a single number, its characteristic "half-life", t1/2, the average time it would take for a population of radioactive particles to decline by one-half, or its inverse, the decay constant λ . Also, Heavy metal in the other hand tend to be leachate out of fresh landfill or dumpsites, they later become largely associated with massive solid waste derived from dissolved organic matter which plays an important role in heavy metal speciation and migration [13,14,7].

3. MATERIALS AND METHODS

In the preparation of reagents, chemicals of analysis: grade purity and distilled water was used. All glass ware were washed with detergent and rinsed with distilled water before drying in the oven at 105°c. All weighing used Toledo ABS₄ analytical weighing balance.

Leachate drain of about 2fts equivalent to the depth of 60cm was constructed to collect the waste mass into a pond by gravity during the period from (December 2021–January, 2022). For this study, dumpsites were identified within Port Harcourt metropolis, Rivers State, Nigeria. The five (5) identified dumpsites include: Chindah (active), Egbelu (active), Aluu Air Port road (active), mile 3 Diobu (active) and Timothy lane Rumuola (active).

However, only three (3) out of these dumpsites were taken with five (5) sampling points across

each of the three (3) dumpsites and then the control standard.

Leachate samples were collected in plastic container previously cleaned by washing in nonionic detergent, rinsed with tap water and later soaked in 10%HNO₃ for 24hrs and finally rinsed with de-ionized water prior to usage. During sampling, bottles were rinsed with sample leachates three times and filled to the brim.

For precision and accuracy, the heavy metals characteristics in leachate samples of the study area were based on the WHO standard value as seen in 'Table 2' and 'Appendix 1'. For radiometric parameters in leachates, in samples of the study area, results of analysis were based on the 'International Nuclear Information System [15].

3.1 Sample Treatment

The sample container (high density poly ethylene-HDPE bottles) were used for heavy metal analysis, and washed with metal free detergent rinsed with tap water.

They were soaked in 1m HNO_3 for 2hrs and later rinsed with demineralize water and kept in airtight container till sample period. All samples that were collected were in ice chest to maintain the temperature below 4°C during transportation from the field to the laboratory.

3.2 Determination of Radiometric of Leachates Sample

All the field meters and equipment to be used were checked and calibrated according to manufacturer's specifications. Total concentration of major cations and heavy metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) per U.S.E.P.A method 6010B or portable radiometric nuclear radiation monitoring spectrometer meter (model BGO-Super-SPEC Rs230) and concentration of major anions are determined by ion chromatography using E.P.A. method 9060,300,325.2, 353.1, 353.2, 375.2, 4500D and 4500E (DOE 2008, 2014, 2015) etc.

The samples were transferred into smaller sample bottle and 5ml of hydrochloric acid (HCL) was added to stabilize the sample. The samples were .kept incubated in the dark room for 28 days. The concentration of radionuclide (40 K,

 238 U, 232 Th) in the samples after the incubation period, were determined by gamma ray spectroscopy using a 7.62cmx 7.62cm Nal (TI) detector surrounded with adequate lead shielding that reduces the background by a factor approximately 95%. Using a counting time of 25, 200S, the activities of various radionuclide were determined in Bqk-1 from the count spectra obtained from each of the samples using the gamma ray photo peak corresponding to energy of 1120.3 Kev (214 Bi), 911.21Kev(228AC) and 1460.82Kev(40 K) for 238 U, 232 Th and 40 K respectively.

3.3 Heavy Metal Analysis

The heavy metal present in the samples were usina atomic absorption analvzed spectrophotometer. Two (2) grams of the respective sample was transferred into a Kjeldahl; 20 ml of concentrated nitric acid (HNO₃) was added and the sample pre-digestion by heating gently for 20mins. More acid was thereafter added and digestion continued. Digestion was stopped when a clear digest was obtained. The flask was cooled and the content transferred into 50ml volumetric flask and made to the mark with distilled water. The digested samples were analyzed for heavy metals (Pb, Cr, Cu, Ni, Fe and Ca) by Atomic Absorption Spectrophotometer (AAS) of UNICAM 919 model. The equipment absorbed the digested sample and gives the concentration of the metals present in the sample [16].

4. RESULTS AND DISCUSSION

The comparison of radiometric and heavy metal analysis of leachate samples are presented in Table 1 (radioactive) and Table 2 (heavy metals).

4.1 Radiometric Parameters

Potassium (⁴⁰**K):** The potassium (⁴⁰K) shows the ratings of 58.772 ± 0.4 mg⁻¹, 77.892 ± 0.45 Bqkg⁻¹, 78.542 ± 0.05 Bqkg⁻¹ and 71.735 ± 0.3 Bqkg⁻¹(mg/l). And the standard value for the observed parameter rated 4.08+1.84Bqkg⁻¹. These are above limits recommendation of World Health Organisation (WHO). This agrees with Jeevarenuka et al. [17] that shows K⁴⁰ has a higher mean level when determined with gamma-ray spectrometer with rating dose of 199.1Bqkg⁻¹.



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Fig. 1. Map of the study area showing sample points Source: Rivers State Ministry of Land and Housing

Uranium (²³⁸U): The results revealed that rating dose of ²³⁸U were 11.019 \pm 0.02Bqkg⁻¹, 14.439 \pm 0.028Bqkg⁻¹, 7.930 \pm 0.015Bqkg⁻¹ and the mean of 11.129 \pm 0.021Bqkg⁻¹. And the standard value for the parameter rated 6.4 \pm 2.01Bqkg⁻¹. This is below the permission limits recommendation of World Health Organisation at <50Bqkg⁻¹ (^{55Gynh-1}). This result agrees with Abdelaal and Rove [18] that worked on the characteristics of low-level leachates in North America, reported that Uranium (U²³⁸) was dominant radionuclides with low concentration in leachates.

Thorium (²³⁸**Th):** The results revealed that the rating dose value of leachates of ²³⁸Th are 2.106 \pm 0.18Bqkg⁻¹, 1.416 \pm 0.021Bqkg⁻¹, 1.918 \pm 0.017Bqkg⁻¹ and the mean of 1.813 \pm 0.073. And the standard value for the observed parameter is 1.01 \pm 0.3.

This is below the recommended rating dose of <50(55Gynh-1) and at the permissible level of World Health Organisation (WHO). This result also agrees with Saffanah et al. [19] which reported that the radioactivity levels of thorium was below limiting index of below 50Bgkg^{-1(55Gynh-1)}.

4.2 Heavy Metals

Iron (Fe): The result revealed the mean of 17.232, 33.343, 12.322 mgl-. The variable levels of Fe determined in different site shows Fe to be above the World Health Organisation permissible limit (7.500). There was a high concentration of Fe in the study area which agrees with Edokpayi, Odiyo, Msagati and Popoola [20] who reported higher concentration of Fe in waste water in Limpopo province of South Africa.

Copper (Cu): Copper values obtained from the result ranges from 7.476, 23.897, 45.987 mgl.. This is above the (WHO) World Health Organisation permissible limit of < 2,000mgl-1. It is also above the standard value. Copper has density $8.96g/cm^3$ and atomic weight $63.5g.cm^3$. The average concentration in crystal forms are 8.1×103 khm⁻³ and 55mgkg⁻¹ respectively. This indicates negative since it's above its permissible range.

Table 1. Radiometric p	parameters in leachates in s	mples of the stud	ly area and WHO	standard value
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		^{₄₀} K(Bq	/kg) Potasssium	²³⁸ L	J (Bq/kg) Uranium	²³² T	h (Bq/kg) Thorium	
Site I	l(Egbelu)	58.772	± 0.4	11.	019 <u>+</u> 0.02	2.106	6 ± 0.18	
Site I	ll(Aluu)	77.892	± 0.45	14.4	439 <u>+</u> 0.028	1.416	6 ± 0.021	
Site I	III(Eliozu)	78.542	± 0.05	7.9	30 ± 0.015	1.918	3 ± 0.017	
	Counting Time 25,280 seconds							
S/N	Parameters	Units	Site I (Egbelu)	Site II (Aluu)	Site III (Eliozu)	Mean \overline{x}	Standard Value	WHO Average
1	Potassium (⁴⁰ K)	Bq/kg	58.772 <u>+</u> 0.4	77.892 <u>+</u> 0.45	78.542 <u>+</u> 0.05	71.735 <u>+</u> 0.3	4.08 <u>+</u> 1.84	<50/55 Gynh-1
2	Uranium (²³⁸ U)	Bq/kg	11.019±0.02	14.439 <u>+</u> 0.028	7.930 <u>+</u> 0.015	11.129±0.021	6.4 <u>+</u> 2.02	<50/55 Gynh-1
3	Thorium (²³² Th)	Bq/kg	2.106±0.18	1.416 <u>+</u> 0.021	1.918 <u>+</u> 0.017	1.813±0.073	1.01±0.3	<500/55 Gynh-1

Source: Researchers' Field Work, 2022

Table 2. Presentation of heavy metals characteristics in leachate samples of the study and standard values

Parameters	Site I (Egbelu)	Site II (Aluu)	Site III (Eliozu)	Mean (<i>x</i>)	(FEPA)Standard Values	WHO Standard
Iron Fe (mg/l)	17.232	33.343	12.322	20.966	7.500	1.000
Copper Cu (mg/l)	7.476	23.897	45.987	25.787	3.020	2.000
Cadmium Cd (mg/l)	3.345	4.543	2.889	3.592	0.151	0.005
Nickel Ni (mg/l)	0.878	2.696	1.098	1.557	0.010	<10.00
Zinc Zn (mg/l)	123.455	98.564	167.546	129.855	57.510	5.000
Magnesium Mn (mg/l)	1.145	0.587	1.453	1.062	0.050	0.050
Lead Pb (mg/l)	1.334	0.687	1.785	1.269	0.057	0.01
Chromium Cr (mg/l)	0.089	3.476	2.333	1.966	0.500	0.05

Source: Researchers' Field Work, 2022

Cadmium (Cd): The results revealed a range of 3.345, 4.543, 2.889. In comparison with the mean (3.592 mg/l) both site I and site III were below the mean level. While site II (4.543) was above the mean. The three metals were above the permissible level of World Health Organisation (WHO) 1997 at 0.151.

Zinc (Zn): The Zn concentration ranges from 123.455, 98.564, 167.546 mgl- respectively. The values were higher than the World Health Organisation (WHO) at 5.000mgl-. This result agrees with Al-Yagout & Hamoda [21] who recorded high levels of zinc in a landfill.

Magnesium (Mn): The Mn concentration ranges from 1.145, 0.587, 1.453 mgl-, the values except site II, others were above the mean value of 1.062. The result revealed that the heavy metal was higher than the WHO limits of 0.050 mgl.

Lead (Pb): The Pb concentration ranges from 1.334, 0.687, and 1.785 respectively. All the concentrations were above the permissible limits of WHO (0.01 mg/l). Lead is a metal belonging to period 6 of the periodic table with atomic number 82, atomic mass 207.2, Pb according to WHO is 0.01 mgl-. Therefore the Pb study sampling was recorded higher than the acceptable limit. This argues with Mahdi et al. [22] that high concentration of Pb in the environment can be detrimental to human health [23-25].

Chromium (Cr): The results obtained shows 0.089, 3.476, 2.333 respectively. The values were higher than W.H.O standard of 0.05 mgl-. This is very dangerous to the environment. This negative trend agrees with Mahdi [22] that the high concentration of Cr in the environment can cause anaemia to humans [26,27].

5. CONCLUSION

In Port Harcourt region, solid waste management has been a serious problem, especially the inability of the citizens to separate the contents based on the composition. While waste generation is a problem for developing societies like Africa, advanced countries use it to make more money and create new recycled materials or products to boost the economy. The study has compared the radiometric and heavy metal parameters of leachates in open dumpsites of Eliozu, Egbelu and Aluu and found that the heavy metals are above the permissible level of World Health Organisation (WHO) and as such can be detrimental to human health. In other words, the leachate has a negative impact in the environment especially on the surface and underground water quality.

6. RECOMMENDATIONS

The following recommendations are therefore vital:

- 1. Dumpsites should be located very far away from residential areas.
- 2. Proper remediation should be carried out especially in abandoned dumpsites.
- 3. Appropriate infrastructure in line with international best practices should be put in place in dumpsites to ensure proper channelization and recycling of leachates.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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	Parameters	Control sites	FEPA Limits	WHO Standard				
	A Radiometrics							
1	⁴⁰ K (Bqkg ⁻¹)	33.420 <u>+</u> 0.21	NA	55Gynh ^{-(INIS)}				
2	238 U (Bqkg ⁻¹)	8.721±0.32	NA	55Gynh ^{-(INIS)}				
3	²³² Th (Bqkg ⁻¹)	1.515±0.031	NA	55Gynh ^{-(INIS)}				
	B Physical							
4	Ph	7.8	7.5	7.00				
5	Temperature (°C)	25.93	26.5 (°C)	Ambient				
6	Alkalinity (mg/l)	2128	450.57(mg/l)	<150				
7	Turbidity (NTU)	72.30	20.551(mg/l)	<50				
8	Conductivity (us/cm)	9200	680.30 (NTÚ)	<5000				
9	TDS (mg/l)	4200	2000(mg/l)	<2000				
10	DO (mg/l)	1.32	5.90(mg/l)	<5				
		C Chemic	al					
11	No ₃ (mg/l)	372	18.01(mg/l)	1.00				
12	Po ₄ (mg/l)	746.37	3.00(mg/l)	NA				
13	So ₄ (mg/l)	730.12	420.50(mg/l)	<500				
14	CI (mg/l)	1120.8	510.00(mg/l)	<600				
15	NH_3 (mg/l)	1.12	0.10(mg/l)	NA				
	D Heavy Metal							
16	Fe (mg/l)	9.131	7.500(mg/l)	0.3				
17	Cu (mg/l)	8.621	3.020(mg/l)	2.0				
18	Cd (mg/l)	3.102	0.151(mg/l)	0.003				
19	Ni (mg/l)	1.010	0.010(mg/l)	0.05				
20	Zn (mg/l)	95.132	57.510(mg/l)	5.00				
21	Mn (mg/l)	0.621	0.050(mg/l)	0.1				
22	Pb (mg/l)	1.342	0.057(mg/l)	0.05				
23	Cr (mg/l)	0.098	0.500(mg/l)	0.05				

APPENDIX-I

Control Sites, FEPA and WHO standard

World Health Organisation WHO (1997), International Nuclear Information System INIS (2004) on radiometric $({}^{40}K, U^{238} \text{ and } {}^{232}\text{Th})$

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