

# Original Research Article

## **Radiometric and Heavy Metal Analysis of Leachates in Selected Open Dumpsites in Port Harcourt Region**

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### **ABSTRACT**

Leachates from selected open dumpsites in Port Harcourt region were analysed for radiometric using gamma ray spectroscope and 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  $^{40}\text{K}$ (71.715± 0.3 Bqkg<sup>l</sup>), Uranium  $^{238}\text{U}$  (11.129± 0.021 Bqkg<sup>l</sup>), Thorium  $^{232}\text{Th}$  (1.813± 0.073 Bqkg<sup>l</sup>) and Heavy metals show iron (20.966mg<sup>l</sup>), Copper (25.787 mg<sup>l</sup>), cadmium (3.592mg<sup>l</sup>), nickel (1.557mg<sup>l</sup>), zinc (129.855 mg<sup>l</sup>), Magnesium (1.062mg<sup>l</sup>), lead (1.269 mg<sup>l</sup>) Chromium (1.966 mg<sup>l</sup>). The radiometric and Heavy metals analyses revealed that surface water and underground water quality and the physical environment is at risk if the leachate containing the element of heavy metals and radioactive elements are not managed well by the concerned authorities. It is important that local, state, federal government and other stakeholders pay attention to dumpsite leachates to provide safe facilities to control the wastewater and embark on daily orientation on the dangers associated with leachates to minimize the spread of diseases through water and air wherein the dumpsites are located.

*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 (Ojoawo, et.al, 2011), which occur as results of accumulation and reaction of different radioactive materials in the waste 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- $\gamma$ , Beta- $\beta$ , Alpha-  $\alpha$ , Ca-14, Uranium -U, and Thorium -Th) in the dumpsites as well as naturally occurring radionuclides in the soil.

According to Dusing et.al (1992), 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 spiral 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 (Tzoup&Zouboulis, 2010). Leachate quality are different and these differences are caused by several factors such as composition and depth of solid waste, availability of moisture and oxygen content, design and operational 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 are higher (Maleki et.al, 2009).

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 (1999), reported that 71.4% of local authorities are facing serious ground water pollution, while 57.2% are dealing with the problem of leachate management (Nasir et.al 1999).

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 sitting 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 (Ghafari et.al, 2009).

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 (Li et.al 2009).

Dumpsite leachates are an important potential contamination source of ground and surface waters. When the water is not properly collected, treated and safely disposed, causes extensive contamination of streams, creeks and water wells (Li, et.al 2010), the effluents are difficult to deal with and biological processes are totally inefficient for the toxic nature of stabilized leachates.

Radiometric methods rely on radioactive beta-decay, 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",  $t_{1/2}$ , the average time it would take for a population of radioactive particles to decline by one-half, or its inverse, the decay constant  $\lambda$ . Also, Heavy metal in the other hand tend to be leachate out of fresh landfill or dumpsites, they later became largely associated with massive solid waste derived from dissolved organic matter which plays an important role in heavy metal speciation and migration (Baumann et. al., 2006, Baun and Christensen, 2004; Li et. al., 2009).

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.

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## 2. MATERIAL 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 ABS<sub>2</sub> analytical weighing balance.

Lechate 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). The dumpsites were identified within Port Harcourt metropolis for this study. 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 non-ionic detergent, rinsed with tap water and later soaked in 10%HNO<sub>3</sub> 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

### 2.1 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<sub>3</sub> for 2hrs and later rinsed with demineralize water and kept in air-tight 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.

### 2.2 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 spectrometer nuclear radiation monitoring 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 ( <sup>40</sup>K, <sup>238</sup>U, <sup>232</sup>Th ) in the samples after the incubation period, were determined by gamma ray spectroscopy using a 7.62cmx 7.62cm NaI (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( <sup>40</sup>K) for <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup> K respectively.

### 2.3 Heavy Metal Analysis

The heavy metal present in the samples were analyzed using atomic absorption spectrophotometer. Two (2) grams of the respective sample was transferred into a Kjeldahl; 20ml of concentrated nitric acid (HNO<sub>3</sub>) 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

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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 (WHO, 2011).

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### 3. 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)

#### 3.1 Radiometric Parameters

##### Potassium ( $^{40}\text{K}$ )

The potassium ( $^{40}\text{K}$ ) shows the ratings of  $58.772 \pm 0.4 \text{ mg}^{-1}$ ,  $77.892 \pm 0.45 \text{ Bqkg}^{-1}$ ,  $78.542 \pm 0.05 \text{ Bqkg}^{-1}$  and  $71.735 \pm 0.3 \text{ Bqkg}^{-1}$  (mg/l). And the standard value for the observed parameter rated  $4.08 \pm 1.84 \text{ Bqkg}^{-1}$ . These are above limits recommendation of World Health Organisation (WHO). This agrees with Jeevarenuka et al. (2014) that shows  $\text{K}^{40}$  has a higher mean level when determined with gamma-ray spectrometer with rating dose of  $199.1 \text{ Bqkg}^{-1}$ .

##### Uranium ( $^{238}\text{U}$ )

The results revealed that rating dose of  $^{238}\text{U}$  were  $11.019 \pm 0.02 \text{ Bqkg}^{-1}$ ,  $14.439 \pm 0.028 \text{ Bqkg}^{-1}$ ,  $7.930 \pm 0.015 \text{ Bqkg}^{-1}$  and the mean of  $11.129 \pm 0.021 \text{ Bqkg}^{-1}$ . And the standard value for the parameter rated  $6.4 \pm 2.01 \text{ Bqkg}^{-1}$ . This is below the permission limits recommendation of World Health Organisation at  $< 50 \text{ Bqkg}^{-1} (55 \text{ Gynh}^{-1})$ . This result agrees with Abdelaal and Rove (2015) that worked on the characteristics of low-level leachates in North America, reported that Uranium ( $\text{U}^{238}$ ) was dominant radionuclides with low concentration in leachates.

##### Thorium ( $^{238}\text{Th}$ )

The results revealed that the rating dose value of leachates of  $^{238}\text{Th}$  are  $2.106 \pm 0.18 \text{ Bqkg}^{-1}$ ,  $1.416 \pm 0.021 \text{ Bqkg}^{-1}$ ,  $1.918 \pm 0.017 \text{ Bqkg}^{-1}$  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  $< 50 (55 \text{ Gynh}^{-1})$  and at the permissible level of World Health Organisation (WHO). This result also agrees with Saffanah et al. (2021) which reported that the radioactivity levels of thorium was below limiting index of below  $50 \text{ Bqkg}^{-1} (55 \text{ Gynh}^{-1})$ .

#### 3.2 Heavy Metals

##### Iron (Fe)

The result revealed that the mean of 17.232, 33.343, 12.322 mg/l. 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 (2015) 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 mg/l. This is above the (WHO) World Health Organisation permissible limit of  $< 2,000 \text{ mg}^{-1}$ . It is also above the standard value. Copper has density  $8.96 \text{ g/cm}^3$  and atomic weight  $63.5 \text{ g.cm}^3$ . The average concentration in crystal forms are  $8.1 \times 10^3 \text{ km}^{-3}$  and  $55 \text{ mgkg}^{-1}$  respectively. This indicates negative since it's above its permissible range.

##### 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) at 0.151.

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#### Zinc (Zn)

The Zn concentration ranges from 123.455, 98.564, 167.546 mg/l- respectively. The values were higher than the World Health Organisation (WHO) at 5.000mg/l-. This result agrees with Al-Yaaout'Hamoda (2003) who recorded high levels of zinc in a landfill.

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#### Manganese (Mn)

The Mn concentration ranges from 1.145, 0.587, 1.453 mg/l-, 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 0.050mg/l-.

#### 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 mg/l-. Therefore the Pb study sampling was recorded higher than the acceptable limit. This argues with Mahdi et al. (2021) that high concentration of Pb in the environment can be detrimental to human health.

#### 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 mg/l-. This is very dangerous to the environment. This negative trend agrees with Mahdi (2021) that the high concentration of Cr in the environment can cause anaemia to humans.

**Table 1: Radiometric parameters in leachates in samples of the study area and WHO standard value**

	<sup>40</sup> K (Bq/kg) Potassium	<sup>238</sup> U (Bq/kg) Uranium	<sup>232</sup> Th (Bq/kg) Thorium
Site I(Egbelu)	58.772 ± 0.4	11.019 ± 0.02	2.106 ± 0.18
Site II(Aluu)	77.892 ± 0.45	14.439 ± 0.028	1.416 ± 0.021
Site III(Elioizu)	78.542 ± 0.05	7.930 ± 0.015	1.918 ± 0.017

Counting Time 25,280 seconds

S/N	Parameters	Units	Site I (Egbelu)	Site II (Aluu)	Site III (Elioizu)	Mean $\bar{x}$	Standard Value	WHO Average
	Potassium ( <sup>40</sup> K)	Bq/kg	58.772± 0.4	77.892 ±0.45	78.542± 0.05	71.735± 0.3	4.08±1.84	<50/55 Gynh-1
	Uranium ( <sup>238</sup> U)	Bq/kg	11.019± 0.02	14.439 ±0.028	7.930±0 .015	11.129± 0.021	6.4±2.02	<50/55 Gynh-1
	Thorium ( <sup>232</sup> Th)	Bq/kg	2.106±0. 18	1.416± 0.021	1.918±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 (x)	(FEPA)Standard Values	WHO Standard
Iron	17.232	33.343	12.322	20.966	7.500	1.000
Fe (mg/l)						
Copper	7.476	23.897	45.987	25.787	3.020	2.000
Cu (mg/l)						
Cadmium	3.345	4.543	2.889	3.592	0.151	0.005
Cd (mg/l)						
Nickel	0.878	2.696	1.098	1.557	0.010	<10.00
Ni (mg/l)						
Zinc	123.455	98.564	167.546	129.855	57.510	5.000
Zn (mg/l)						
Manganese	1.145	0.587	1.453	1.062	0.050	0.050
Mn (mg/l)						
Lead	1.334	0.687	1.785	1.269	0.057	0.01
Pb (mg/l)						
Chromium	0.089	3.476	2.333	1.966	0.500	0.05
Cr (mg/l)						

Source: Researchers' Field Work, 2022

#### 4. 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.

#### 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.

#### REFERENCES

1. Abdelaal F. &Rawe, K. (2015) Effect of high pH found in low-level radioactive waste leachates on the autoxidant depletion of a HDPE geomembrane. *Journal of Hazard, Toxic Radioactive Waste*. 12(4), 2153-5515.
2. Al-Yagout, A. &Hamoda (2013) Evaluation of landfill leachate in arid climate – A case study. *Environ Int*. 29(5), 593-600.
3. Baumann, T., Fruhstorfer, P., Klein, T. and Niessner, R. 2006. Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Research*. 40, 2776-2786.

4. Baun, A., Ledin, A., Reitzel, L. A., Bjerg, P. L. and Christensen, T. H. 2004. Xenobiotic organic compounds in leachates from ten Danish MSW landfills-chemical analysis and toxicity tests. *Water Research*. 38, 3845-3858.
5. Baun, D. L. and Christensen, T. H. 2004. Speciation of heavy metals in landfill leachate: A review. *Waste Management and Research*, 22: 3-23.
6. Dusing, D.C. Bishop, P.I. & Keener, T.C. (1992) Effect of redox potential on leachate from stabilized/solidified waste materials. *J. Air Waste Management. Assoc.* 42, 56-62.
7. Edokpayi, J.N, Odiyo, J.O., Msagati, T.A.M. & Popoola, E.O. (2015) Removal of efficiency of faecal indicator organisms, nutrients and heavy metals from a peri-urban waste water treatment plant in Thohoyandau. *International Journal*. 29(12), 7-73.
8. Gbafari, S., Aziz, H.A., Isa, M.H. & Zinatizadeh, A.A. (2009) Application of response surface methodology (RMS) to optimize coagulation – flocculation treatment of leachate using poly-aluminium chloride (PAC) and alum. *Journal of Hazardous Materials*. 163, 650-656.
9. Jeevarenuka, K., Sankaran, P.G., Shahul, H.S.H.P. & Mathiyarasu, R. (2014) Evaluation of natural gamma radiation and absorbed gamma dose in soil and rocks of perambalur district. *Journal of Radio Analytical and Nuclear Chemistry*. 302, 245-252.
10. Jensen, D. L., Ledin, A. & Christensen, T. H. (1999). Speciation of heavy metals in landfill leachate polluted groundwater. *Water Research*, 33: 2642-2650.
11. Li, R., Yue, D., Liu, J. and Nie, Y. 2009. Size fractionation of organic matter and heavy metals in raw and treated leachate. *Waste Management*, 29: 2527-2533.
12. Mahdi, M.B., Kobra, N., Zoya, T., Mohammed, R.K. & Mahmood, S. (2021) Toxics mechanisms of five heavy metals: Mercury, lead, chromium, cadmium and arsenic. <https://doi.org/10.3389/fphv.2021.643972>.
13. Maleki, A., Zazuoul, M.A., IZanloo, H. & Rezaee, R. (2009) Compositing plant leachate treatment by coagulation – flocculation process. *American – European J. Agric and Environ. Sci.* 5(5), 538-643.
14. Ojoawo, S., Agbede, O. & Sangodoyin, A. (2011) On the physical composition of wastes in selected dumpsites of Ogbomoso land. *South – Western Nigeria. J. Water Resource. Protection*. 3, 661-666.
15. Omale, P.E, OKeniyi, S.O., Favuruwa, M.D. & Ngokat, A.B. (2014) Determination for levels of radionuclides of uranium, Thorium and potassium in water, sediments and algae samples from selected coastal areas of Lagos. *Global Journal of Pure and Applied Chemistry*. 2(1), 1-24.
16. Omale, P.E. (2012) *Physiochemical parameters and levels of radionuclides or potassium-40, Uranium-238, and Thorium-232 series in sediments, green algae and water samples from selected coastal areas of Lagos*. A Ph.D thesis submitted to the Nigeria Defence Academy.
17. Saffanach, A., Rubina, R., Sannatul, F. & Mahfuz, S.M.M. (2021) Assessment of radiometric standard and potential health risks from building materials used in Bangladesh dwellings. *International Journal Environmental Analytical Chemistry*, 1080-3067.
18. Tzonpanos, N.D. & Zouboulis, A.I. (2010) Characterization and application of novel coagulant reagent (Poly aluminum silicate chloride) for the post treatment of landfill leachates. *Water treatment technologies for the removal of high toxicity pollutants*, 24-252.

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