

Evaluation of Polycyclic Aromatic Hydrocarbons (PAHS) Levels in Soil Contaminated with Electronic Waste (E-Waste), South-Eastern, Nigeria

*** ¹Eyenubo, O. B., ²Odeh P. I.. ²Ataire, O. D. and ³Avwioro O. G.**

Received: July 8, 2024 /Accepted: September 10, 2024

© REJOST 2024

Abstract

E-waste is an emerging environmental problem, as it is composed of a heterogeneous mix of different metals, metalloid, glass and plastic, which are useful and hazardous to the environment. The article aimed at evaluating the levels of Polycyclic Aromatic Hydrocarbons (PAHs) in soil contaminated with e-waste obtained at different depths $(0 - 10 \text{ cm}, 10 - 20 \text{ cm} \& 20 - 30 \text{ cm})$ and the evaluation was done in soil samples with the help of gas chromatograph coupled with a mass analyzer. The concentrations of the 16 Polycyclic Aromatic Hydrocarbons ranged from $404 - 32$, 250 μ g/kg, There was significant variation in the mean values of the 16 PAHs under study across seasons. At $0 - 10$ cm in the dry season, the mean values ranged from 30.0 µg/kg (benzo(k)fluoranthene) High Molecular Weight (HMW) PAHs to 1,675 µg/kg (acenanphthylene) Low Molecular Weight (LMW) PAHs. While in wet season, it ranged from non detectable limit (naphthalene) LMW PAHs to 3,934 μ g/kg (phenanthalene) LMW PAHs. The trend of PAHs percentage distributions was 3-rind PAHs > 7-ring PAHs > 2 -ring PAHs > 4 -ring PAHs > 5 -ring PAHs > 6 -ring PAHs. The hazard index HI-non carcinogenic risk for children was > 1 and for adult is < 1 . The trends of ILCR concentrations for both children and adults follow ingestion $>$ dermal $>$ inhalation. The PAHs cancer risk in this study revealed moderate to very high level. It can be concluded that the e-waste dumping activities have contributed contaminant of PAHs to the soil. Hence dumping activates should be properly monitored.

✉ Eyenubo, O.B[: eyenokero2013@gmail.com](mailto:eyenokero2013@gmail.com)

² Osten Laboratory, Port Harcourt, River State, Nigeria

³Department of medical Laboratory Science, Delta State University, Abraka, Nigeria

¹Department of Science Laboratory Technology, Delta State University, Abraka, Nigeria

Keywords: E-Waste; Polycyclic Aromatic Hydrocarbon; Dump Site; Contamination; Cancer risk.

1.0 Introduction

In Nigeria, like other countries, PAHs contamination via e-waste has spread all over the country. Persistent organic pollutants (POPs) like PAHs are very ubiquitous in nature due to their volatility, and contamination from this source is widespread due to high level of population growth, indiscriminate dumping of e-waste and burning of material containing POPs compounds (Eyenubo *et al.*, 2024). Contamination from ewaste as a result of uncontrolled disposal has become a general health issues in Nigeria since it is associated with hazardous substances. Uncontrolled burning releasing highly toxic fumes which impact on the neighborhood aesthetics, dismantling, and dumping leads to a variety of issues in our environment like the contamination of groundwater, atmospheric pollution and water pollution through immediate discharge or as a result of surface runoff . The rate of growth of domestic and imported e-waste in Nigeria, as reported by researchers, is on the average of 500 shipping containers with 400,000 computer monitors that enter Lagos port, Nigeria per year (Adebola and Peter, 2017).

Persistence organic pollutants like PAHs generated from e-waste accumulate in the soil as a result of their poor water solubility and strong chemical stability (Xi, *et al.,* 2022), other sources like particulate matter from the atmosphere can increase the concentration of PAHs in the soil via sedimentation, as such soil is known to be a major source of PAHs in the environment that affects plants, animals and humans health (Liu *et al.,* 2018, Xi, *et al.,* 2022). Pollution generated by PAHs has become a major environmental challenge across the world as a result of their potential carcinogenic, tetratogenic and mutagenic effects (Cao, *et al.*, 2019, Xi, *et al.,* 2022). Waste from electronics generally known as e-waste is a generic term referring to those electrical electronics equipment that becomes obsolete or disposed of by the original users; phones, television, computer monitors, laptops, printers, scanners with their associated wiring (Khadijah, 2016). Emerging environmental issues like e-waste, composed of a heterogeneous mix of different metals, metalloids, glass and plastics from which some valuable metals such as aluminum, copper, gold, silver and iron are recovered via recycling which serve as environmental sustainability management (Robinson, 2019). Different hazardous substances like nickel (Ni), lead (Pb) plybrominated diphenyl ethers (PBDEs), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs) etc has been released into the environment due to the inability to monitor the dumping of e-waste (Eyenubo, e*t al.*, 2022)

Improper practices of e-waste disposal and dismantling like open dumping, open burning, acid baths and heating of circuit boards, have led to the emission and release of hazardous pollutants, including heavy metals, persistent organic pollutants (POPs), and volatile organic pollutants (VOCs) (Shengtao*, et al.,* 2021). During the past two decades, several research studies have been done on the environmental occurrence and fate, transformation and potential adverse health consequences of these hazardous chemicals from e-waste sites (Shengtao *et al.,* 2021). They found that dismantling employees and resident houses near the e-waste sites are highly exposed through dermal contact, inhalation and ingestion with this hazardous material, toxic fumes and toxic chemicals from contaminated soil, water and food. E-waste dismantlers are exposed to environmental pollutants via inhalation which is one of the

important exposure pathways (Shengtao*, et al.,* 2021).

The e-waste generates a large volume of toxic substances that affect the ecosystem. The material composition of e-waste contains various substances which are known to be hazardous and non-hazardous (Richard *et al.*, 2013). Occupational exposure to PAHs in Epidemiological studies has shown that they can generate induction of skin and lung cancers. Report have also shown that some PAH metabolites interact with deoxyribonucleic acid (DNA) and are genotoxic, generating malignancies and heritable genetic problems in humans (Adebola et al., 2017). Lower molecular weight PAHs like naphthalene, fluorene, phenanthrene and anthracene (2 to 3 rings) generated significant acute toxicity to aquatic organisms, on the other hand higher molecular weight PAHs like chrysene and coronene (4 to 7 rings) do not generate acute toxicity, but are carcinogenic (Adebola et al., 2017). The Food and Agriculture Organization of the United Nations and the Intergovernmental Technical Panel on Soils reported that many of world's soil resources will only be in better condition with 33% of the land resources being moderately to highly degraded [\(Panatda](https://pubmed.ncbi.nlm.nih.gov/?term=Pibul%20P%5BAuthor%5D) *et al*., 2023). The dumping, recycling and even burning of e-waste lead to the leaching of toxic metals into the soil which then affect humans through ingestion or direct dermal exposure, combustion of e-waste at low temperature released toxic chemicals such as PAHs (Adebola and Peter, 2017). Limited information has been reported on the transformation and distribution of PAHs from ewaste dumpsite in Nigeria, but PAHs are lipophilic and accumulate in food chains associated with the contaminated dumpsites (Oliveira *et al.,* 2014, Adebola and Peter, 2017).

There are several studies of PAH contamination in soil contaminated with e-waste in decades dumpsite associated with burning and other refuge, currently there is no comprehensive seasonal variation analysis of PAHs in soil contaminated with e-waste without combustion and other interfering refuge in Nigeria. Hence this study is to evaluate levels of PAHs in soil obtained from an impacted e-waste dumpsite free from interference of other refuge, ascertaining the level of pollution the e-waste has impacted on the soil at tender age of 2 years.

2.0 Material and Methods

2.1 Description of the study Area

Abraka is a University town and is one of the most developed areas in Ethiope East Local Government Area of Delta State, Nigeria. South-South, The town is bounded at the north by Obiaruku, at the south by Salubi in Eku, at the west by Edo state and at the east by Aragba Orogun. Abraka has low topography, and its geographical location is Latitude 06.23'01 450 N and Longitude 007.73'09 800 E. The town has an annual rainfall of 2324 mm.

2.2 Collection and preparation of Soil samples

A piece of land of 8 feet by 8 feet was impacted with an electronics waste for the period of 2 years, free from interference of other refuge. Eighteen soil samples were collected to form a composite of 9 samples at $0 - 10$ cm, $10 - 20$ cm and 20 – 30 cm. for each season, from an impacted dumpsite in Abraka communities from December – February (dry season) and May – July (wet season). A stainless hand held soil auger was used to collect the samples. Thereafter, they were conveyed to the laboratory, dried for 7 days, pulverized with mortar and pestle, sieve with 2 mm mesh sieved and then stored in a deep freezer at -20° C prior to further analysis.

Fig. 1: Map of the study area showing the sampling location

2.2.1 Analytical Procedures

Three steps were involved in the determination of PAHs in samples collected from the dumpsite and these are extraction, purification/ fractionation of the chromatographic separation and quantification.

2.2.2 Samples Extraction

10 g of the stored soil samples was mixed with 10 g of anhydrous sodium sulfate; 5 g aliquot was extracted three times by sonication with 15 ml of dichloromethane (1:1) in 20 min. Then there was concentration and fractionation of the

organic extract as water sample after centrifugation.

2.2.3 Extract clean - up

This was done with strong acid, thereafter partitioning was carried out with florisil; 2 ml of concentrated sulphuric acid was mixed with 1 ml of the extract with thorough shaking to avoid coextract interfering. The whole exercise was done severally until a colourless was observed in the acid phase. The extract was dried with anhydrous sodium sulfate before fractionation with florisil. The packing of the glass column was done with 10 g of florisil $(60 - 100 \text{ mesh})$ with addition of 2 g of anhydrous sodium sulfate at upper part of the column to eliminate any amount of water present. 1 ml of the extract was inserted into the column followed by the elution of PAHs with 80 ml of hexane. The concentration of elute was carried out with a rotary evaporator and a gradual nitrogen stream. 1 ml of hexane was used to dissolve the PAH fraction and conveyed to vials of gas chromatograph awaiting gas chromatography analysis. $GC - MS$ analysis was done in single ion monitoring (SIM) mode for assessing and quantifying of PAH congeners.

2.2.4 PAHs Congeners Determination

PAHs determination was done in soil samples with the help of Hewlett-Packard 7890 gas chromatograph coupled with a Hewlett Packard Model 5975 mass analyzer: quadrupled and automatic sampler. The column made up of fused silica capillary was a 30 m DB $- 1$ m (100%) dimethylsiloxane) (Cյ & W Scientific, CA, USA) $(0.25 \text{ mm i.d. x } 0.25 \text{ µm of the thickness of film}).$ The temperature of the oven was initially programmed at 100 $^{\circ}$ C (standing for 1 min) – 325 $\rm{^{\circ}C}$ at the ratio of 15 $\rm{^{\circ}C/min}$ and last for 5 min. The conditions under which the gas chromatograph was carried out were $250 \degree C$ injection temperature and $280\degree$ C transfer line temperature. Helium is used as a carrier gas through a steady flow count of 1.2 ml/min, with an elevated oven temperature of 120° C for 0.5 min to 210 $\mathrm{^{\circ}C}$ at 30 $\mathrm{^{\circ}C/min}$ to 6 $\mathrm{^{\circ}C min}$ for 5 mins. The running conditions of the mass spectrometer were 250° C used for transfer line and ionization source temperature, 70 eV is used ionization voltage, the time used for scanning was 0.3s with 0.5s scanning delay and 5 min delay solvent. Statistical analysis for all data obtained were done using Microsoft excel (Microsoft Inc., USA) and SPSS 22.0 (SPSS Inc., Chicago II., USA).

2.2.5 PAHs Identification and Quantification

The analyzed compounds identification was based upon the ion ratio, the spectra and the retention time which was done by an internal standard procedure using peak areas. The MS analysis was done using single ion monitoring mode where by 2 masses were monitored in the mass spectrum. The chromatogram retention time shift was corrected with the use of internal standard retention time and agreement of about \pm 0.1 min of the retention time expected, for the positive confirmation of the analyte. The linear range of the detector, were evaluated by preparing several standard solutions which are injected at various concentration. The calibration curves are within the range of $10 - 200$ ng/ml, the correlation coefficient (r^2) was above 0.999 for all compound analyzed.

2.3 Human Health Risk

2.3.1 Non-carcinogenic risk assessment using Hazard Index (HI)

The hazard index of PAHs in the soils was evaluated by using the USEPA standard methods assuming the three major routes of exposure; ingestion, dermal and inhalation (IDI) (USEPA, 2011). The hazard index was calculated from the summation of the individual hazard quotients through each route of exposure. The evaluation of the hazard index in terms of IDI was carried out by using the equations below.

$$
\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm} \tag{1}
$$

where;

$$
HQ_{ing} = \frac{CDI_{nc}}{RfD}; \ HQ_{inh} = \frac{CDI_{nc}}{RfC_{inh}}HQ_{derm} = \frac{CDI_{nc}}{RfD \times ABS_{GI}}
$$
 (2)

$$
CDI_{\text{ing}} = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}_{nc}} \times 10^{-6}
$$
 (3)

$$
CDI_{inh} = \frac{c \times InhR \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}}
$$
\n(4)

$$
CDI_{\text{derm}} = \frac{c \times SA \times AF \times ABS \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6}
$$
 (5)

where CDI_{ing} , CDI_{inh} , CDI_{dermal} are the chronic daily intake or dose contacted through ingestion, inhalation and dermal contact with soil respectively. RfD is the reference dose, RfD_{ing} (chronic oral reference dose), RfCinh (chronic inhalation reference concentration), RfD_{dermal} (chronic dermal reference dose = $RfD \times ABS_{GI}$) through the three exposure pathway, CSF_{inc} is the chronic oral slope factors via ingestion, IUR is the chronic inhalation unit risk, ABS is dermal absorption factor, PEF is soil to air particulat emission factor, AT_{nc} is average time for non carcinogenic and C is the concentration of PAHs in soil. Hazard index value less than 1 indicate there is no adverse non-carcinogenic risk while hazard index value greater than 1 indicates the presence of adverse non-carcinogenic risk (USEPA, 2011).

2.3.2 Carcinogenic risk assessment using Total Cancer Risk

Like the hazard index, total cancer risk of PAHs in the soil samples was evaluated by using the USEPA standard methods assuming the three major routes of exposure; ingestion, dermal and inhalation (IDI). The total cancer risk was calculated from the summation of the individual risks through each route of exposure. The equations and parameters for the evaluation of the total cancer risk are shown below.

$$
CDI_{\text{ing - ca}} = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{AT}_{\text{ca}}} \times 10^{-6}
$$
 (6)

$$
IngR_{adj} = \frac{ED_{child} \times lingR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child})}{BW_{adult}} \times IngR_{adult}
$$
 (7)

$$
CDI_{inh - ca} = \frac{c \times InhR \times EF \times ET \times ED}{PEF \times 24 \times AT_{ca}} \times 10^3
$$
\n(8)

$$
CDI_{\text{derm - ca}} = \frac{c \times SA \times AF \times ABS_d \times EF \times ED}{AT_{\text{ca}}} \times 10^{-6}
$$
 (9)

$$
DFS_{adj} \text{ - ca} = \frac{ED_{child} \times SA_{child} \times AF_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times SA_{adult} \times AF_{adult}}{BW_{adult}}
$$
(10)

$$
Risk = CDI_{ca} \times CSF \tag{11}
$$

$$
Total Cancer Risk = Risk_{ing} + Risk_{inh} + Risk_{derm}
$$
\n(12)

where, AF is soil to skin adherences factor BW is average body weight, ED is exposure duration, EF is exposure frequency, ET is exposure time

ATca is average time for carcinogenic, CfS_{ing} is chronic oral slope factor via ingestion and C is the concentration of PAHs in soil respectively.

Generally, total cancer risk value 1×10^{-6} is also considered the carcinogenic target risk (USEPA, 2011, Luo *et al.,* 2012). Total cancer risk value

less than 1×10^{-6} indicate no cancer risk but greater than 1×10^{-6} indicates the presence of adverse cancer risk.

Parameters	Unit	Values	References		
		Child	Adult		
EF	Day/Year	313	313	USEPA,2001	
ED	Year	6	30	USEPA,2001	
ET	h/d	8	8	USEPA, 1987	
IngR	Mg/d	200	100	USDOE, 2011	
SA	Cm^2 /event	2800	5700	USDOE, 2011	
ABS		0.13	0.13	USEPA, 2011	
AF	mg/cm ²	0.2	0.07	USEPA, 2011	
BW	Kg	15	60	Iwegbue <i>et al.</i> , (2014)	
ATnc & ATca	D	ED x 365 & LT x 365		USDOE, 2011	
LT	Year	52 Years		World Bank, 2014	
PEF	m^3/Kg	1.36×10^{9}		USDOE, 2011	

Table 1: Values of variable for estimation of human health risk assessment

2.4 Quality Assurance and Data Analysis

Blank sample analysis with recoveries of surrogate standard for each sample was done as a monitoring measure for all procedures. Each batch (4 per batch) was run with blank across all analytical phases. The mean recoveries for all the PCBs congeners were calculated. For extraction purpose, 10 g of muscle tissue and 2 g of soil were used to extract the PAHs. The data analysis was done with Microsoft excel Inc., USA by evaluating the principal component analysis, Pearson's correlation analysis, and assessing the relationship between the contaminant, the mean, median and standard deviation. The detection and quantification limit (LODs & LOQs) were determined with the ratio of 3 and 10 for signalto-noise for all the concentrations, which ranged from $0.003 - 0.013$ mg/kg (LODs) and $0.01 -$ 0.04 mg/kg (LOQs). From all the PCBs investigated, the blank were totally cleared. Calibration was done via injections of standard solutions of mixed PAHs at 6 concentration level.

3.0 Results and Discussions

The concentrations and statistical variations of PAHs with respect to months and depths are presented in Tables 2 and 3. The percentage distribution of PAHs on the soil collected from the e-waste dump site across depths and months is presented in Figure 2. Individual PAHs concentrations (Table 2) were analyzed for six months (3-months dry season and 3-months wet season). It was observed that high concentration of the individual PAHs with respect to depths and months were prominent in January and December at $0 - 10$ cm and $10 - 20$ cm for lower molecular weight (LMW) PAHs (naphthalene, acenaphthylene, acenaphthene, fluorine, anthracene and phenanthrene), which ranged from 78.0 μ g/kg – 3588 μ g/kg. The non detectable limit observed in some depths in February, May, June and July for LMW PAHs might have been evaporated from the soil as a result of their high volatility (Nganje *et al*, 2014).

	Compounds	Nap	Achy	Ace	Flu	Ant	Phe	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	DahA	IndP	BghiP	TOTAL 2R		3R	4R	5R	6R	7C
	$0-10$ cm	1326	1332	398	1154	876	266	276	896	532	1854	276	70	98	916	1484	734	3718	ND	2350	1286	50	42	1326
JAN.	$10-20$ cm	1536	804	236	324	726	468	176	796	522	494	274	792	914	1112	1786	1838	4440	3126	844	436	16	26	444
	20-30 cm	362	620	492	328	308	1624	1626	1766	1244	544	486	1116	1408	1512	1628	208	404	ND	246	94	52	22	136
	$0-10$ cm	$\mathbf{0}$	$\overline{0}$	974	1070	94	50	162	1284	ND	ND	2	$\overline{4}$	28	8	10	32	3718	ND	2350	1286	50	42	1326
FEB.	10-20 cm	1902	1224	714	ND	ND	ND	130	206	230	ND	ND	ND	ND	8	8	18	4440	3126	844	436	16	26	444
	20-30 cm	ND	ND	ND	ND	ND	ND	246	42	48	2	2	18	8	16	10	12	404	ND	246	94	52	22	136
	$0-10$ cm	ND	32	ND	ND	ND	ND	ND	824	222	ND	250	274	ND	ND	ND	168	1770	ND	32	1046	524	168	1570
MAY	10-20 cm	ND	114	264	256	222	384	3652	544	256	452	420	208	258	48	ND	104	7182	ND	1240	4904	934	104	2186
	20-30 cm	ND	28	186	204	624	42	460	980	596	976	984	994	284	1236	656	1010	9260	ND	1084	3012	3498	166 6	6050
	$0-10$ cm	ND	328	2342	1722	46	1724	712	886	1540	1282	810	216	1866	1136	838	1676	17124	328	6546	4518	4056	251	7736
JUN.	10-20 cm	ND	$\overline{2}$	ND	ND	ND	1910	ND	430	268	ND	ND	ND	ND	ND	ND	ND	2610	2	1910	698	ND	ND	698
	20-30 cm	ND	28	166	166	ND	ND	ND	ND	ND	ND	360	28	332	ND	ND	ND	ND						
	$0-10$ cm	ND	328	ND	206	ND	6144	6712	6492	1540	1790	2498	2746	2118	ND	ND	1676	32250	328	1306 \mathfrak{D}	12320	4864	167 6	17184
JUL.	10-20 cm	ND	6	ND	21	11	19	483	27	13	23	23	6	713	ND	ND	$\overline{2}$	1347	6	534	86	719	$\overline{2}$	805
	20-30 cm	ND	-1	9	10	41	102	397	802	240	175	92	150	108	62	94	$\rm ND$	2283		559	1309	414	94	1629
	$0-10$ cm	352	3692	296	294	3588	888	464	138	98	34	20	16	154	24	24	138	10220	352	8758	754	214	162	410
DEC.	$10-20$ cm	392	78	894	894	3228	874	828	310	294	50	474	80	40	18	28	36	8518	392	5968	1956	612	64	726
	20-30 cm	100	356	100	100	72	156	122	86	138	60	110	256	64	90	106	76	1992	100	784	516	520	182	762

Table 2: The PAHs (µg/kg) concentrations with respect to months and depths

Naphthalene (Nap), Acenaphthylene (AcY), Acenaphthene (Ace), Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phen), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo(a)anthracene (DahA), Indeno 1,2,3-ed)perylene (IndP) and Benzo(ghi)perylene (BghiP), $R =$ Rings.

Naphthalene (Nap), Acenaphthylene (AcY), Acenaphthene (Ace), Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phe), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo (a) anthracene (DahA), Indeno 1, 2, 3-ed) perylene (IndP) and Benzo (ghi) perylene (BghiP), R = Rings

Figure 2: Displayed the percentage distribution of PAHs in six months (three months dry & threes month wet) on soil from the e-waste dumpsite. JAN = January, FEB = February, May, JUN = June, JUL = July, DEC = December.

The highest PAHs concentration $(6,144 \mu g/kg)$ was observed in phenanthrene at July for LMW PAHs and in fluoranthene at July $(6,712 \mu g/kg)$ for higher molecular weight (HMW) PAHs. The trend of concentration across months was that high concentrations occur in wet season than in wet season across low and high molecular weight PAHs. These higher concentrations might be ascribed to too much deposit of these PAHs from the e-waste to the soil. Table 3 displays significant variation in the mean values of the 16 PAHs under study across the seasons. At $0 - 10$ cm in dry season, the mean values ranged from 30.0 µg/kg (benzo (k) fluoranthene) HMW PAHs to 1,675 µg/kg (acenanphthylene) LMW PAHs. While in wet season, it ranged from non detectable limit (naphthalene) LMW PAHs to 3,934 µg/kg (phenanthalene) LMW PAHs. At depths $10 - 20$ cm in dry season, the values varied from non detectable limit on both high and low molecular weight PAHs to 2,068 µg/kg (fluoranthene). At depth 20 -30 cm in dry season, the values ranged from 98.7 µg/kg (benzo (g), h, i) perylene to 890 µg/kg (phenanthrene, while in the wet season, the values varied from non detectable limit to 802 µg/kg (pyrene). In all, the highest mean concentration was observed in the wet season. The mean and median values displayed relative closeness across depths and season, which implies that the data set was normally distributed. The percentage distribution of the 16 PAHs was presented in Figure 2.

The 2- ring PAHs constitute below detectable limit to 70.41 % (10 – 20 cm) at February of Σ 16, the PAHs, 3 – ring PAHs constituted 1.81% $(0 - 10 \text{ cm}) - 92.2$ % $(20 - 30 \text{ cm})$ at June, 4 – ring of below detectable limit to 68.28% (10 – 20 cm) at May. The percentage distribution of the 5-ring PAHs constitute below detectable limit – 53.38 % ($10 - 20$ cm) at July and the percentage distribution for the 6 – ring of Σ 16 PAHs constitute below detectable limit – 27.69 % (10 –

20 cm) at January, while for 7 Ring PAHs, also constitute from below detectable limit to 88.7 % $(0 - 10$ cm) at May. The highest percentage was observed in the wet season at $10 - 20$ cm and there is no definite trend in the percentage distribution across depths and months. The trend of PAHs percentage distributions was 3-rind PAHs > 7 -ring PAHs > 2 -ring PAHs > 4 -ring $PAHs > 5$ -ring $PAHs > 6$ -ring $PAHs$. The highest percentage observed in the wet season might be ascribed to rainfall and the poor drainage system of the site. The calculated PAHs hazards index in this work is displayed in Table 4.

			PAHS CHILD NON CANCER RISK				PAHS ADULT NON CANCER RISK		
Months	Depths	HQing	HQinh HQDermal		\mathbf{H}	HQing	HQinh	HODermal	H
DEC.	$0-10cm$	0.68	$1.50x10^{-4}$	0.25	0.93	0.09	$6.00x10^{-4}$	0.04	0.13
	10-20cm	1.68	$6.36x10^{-3}$	0.61	2.30	0.21	0.03	0.11	0.35
	20-30cm	0.08	$1.80x10^{-5}$	0.03	0.11	0.01	$7.00x10^{-5}$	$5.00x10^{-3}$	0.02
JAN.	$0-10$ cm	0.04	$9.30x10^{-6}$	0.02	0.06	0.01	$3.00x10^{-5}$	$3.00x10^{-3}$	0.01
	10-20cm	1.53	$3.40x10^{-4}$	0.56	2.08	0.18	$1.40x10^{-3}$	0.09	0.28
	20-30cm	0.34	$7.50x10^{-5}$	0.13	0.47	0.07	$3.00x10^{-4}$	0.02	0.10
FEB.	$0-10$ cm	0.45	$3.40x10^{-4}$	0.16	0.61	0.04	$1.40x10^{-3}$	0.03	0.07
	10-20cm	0.05	$4.80x10^{-5}$	0.02	0.06	$6.00x10^{-3}$	$2.00x10^{-4}$	$3.00x10^{-3}$	0.01
	20-30cm	0.04	$4.00x10^{-5}$	0.01	0.05	$4.00x10^{-3}$	$2.00x10^{-4}$	$3.00x10^{-3}$	0.01
MAY	$0-10$ cm	1.86	$4.59x10^{-3}$	0.68	2.54	0.27	0.02	0.12	0.41
	10-20cm	1.63	$5.20x10^{-3}$	0.59	2.23	0.22	0.02	0.11	0.34
	20-30cm	1.87	$1.55x10^{-3}$	0.68	2.56	0.16	0.01	0.12	0.29
JUN.	$0-10cm$	2.12	$4.70x10^{-4}$	0.77	2.89	0.18	$1.90x10^{-3}$	0.14	0.32
	10-20cm	0.83	$1.80x10^{-4}$	0.30	1.14	$2.00x10^{-3}$	$8.00x10^{-4}$	0.05	0.06
	20-30cm	0.09	$2.10x10^{-5}$	0.03	0.13	0.01	$8.00x10^{-5}$	0.01	0.02
JUL.	$0-10cm$	5.18	$1.14x10^{-3}$	1.88	7.06	0.32	$4.70x10^{-3}$	0.34	0.66
	10-20cm	0.17	$3.80x10^{-5}$	0.06	0.23	0.02	$2.00x10^{-4}$	0.01	0.03
	20-30cm	0.21	$4.70x10^{-5}$	$0.08\,$	0.29	$0.02\,$	$2.00x10^{-4}$	$0.01\,$	$0.04\,$

Table 4: Hazard index of PAHs exposure in the soil from the dump site

The hazard quotient values for HQ_{ing} ranged from 0.08 in December at depth $20 - 30$ cm to 5.18 in July at $0 - 10$ cm depth, HQ_{inh} values ranged from 9.30×10^{-6} in January at $0 - 10$ cm to 5.20×10^{-3} in May at 10 – 20 cm and HQ_{dermal} values ranged from 0.01 in February at $20 - 30$ cm to 1.88 in July at $0 - 10$ cm for children. While for adult, HQing values ranged from 2.00×10^{-3} in June at $10 - 20$ cm to 0.32 I July at 0 -10 cm, HQ_{inh} values ranged from 3.00×10^{-5} in January at $0 - 10$ cm to 0.03 in December at $10 -$ 20 cm and HQ_{dermal} values ranged from 3.00×10^{-3} to 0.14 across depths and months. The hazard

quotient follows the trend of $HQ_{ing} > HQ_{dermal} >$ HQinh for both children and adult. The total non cancer risk for children spanned from0.05 at February to 7.06 at July, while for adult, the values ranged from 0.01in February to 0.06 in July of which both follows the same trend. The hazard index obtained for children was > 1 in some depths and months, indicating that there is non- carcinogenic risk with PAHs exposure in this work at across some depths and months. While for adult, the hazard index is < 1 indicating that there is no non-carcinogenic risk associated with PAHs exposure across depths and months.

The ILCR across soil depths and months via ingestion, inhalation and dermal for children and adult were presented in Table 5, the recorded values spanned from 1.43×10^{-3} to 3.05×10^{-3} ¹(ingestion), 3.29×10^{-11} to 6.57×10^{-9} (inhalation), 8.96x10⁻⁴ to 7.79x10⁻² (dermal) and $1.83x10^{-5}$ to 2.50×10^{-3} (ingestion), 1.12×10^{-10} to 2.40×10^{-8}

(inhalation), 4.44×10^{-5} to 9.57×10^{-3} (dermal) across depths and months for both children and adults. The trends of ILCR concentrations for both children and adults follow ingestion > dermal > inhalation. The total cancer risk across depths and months ranged from 2.25×10^{-3} to $4.16x10^{-1}$ and $6.49x10^{-5}$ to $1.11x10^{-2}$ for both

children and adults of which the total cancer risk for adults is lower than that for children. This might be as a result of the high tendency of dermal contact of children with soil particles (Emoyan, 2020). Considering the life time cancer risk based values classified by New York State Department of Health (NYS DOH, 2007), $(≥ 10^{-4}$ = very high, > 10^{-3} to 10^{-1} = high, $\geq 10^{-4}$ to 10^{-3} =

moderate, $\geq 10^{-6}$ to 10^{-4} = low and $\leq 10^{-6}$ = very low). The PAHs cancer risk observed in this study indicate moderate to very high level for both children and adults. Since the values of cancer risk in this study are greater than approved value of $1x10^{-6}$, this implies that the dump site is subject to generation of cancer to human via ingestion and derma contact routes.

Table 6: BaP_{TEQ} and BaP_{MEQ} concentrations (µg/kg) for the e-waste dump site across depths and months

Months	Depths	BaA	Chry	BbF	BkF	BaP	DahA	IndP	BaP _{TEO}	BaA	Chry	BbF	BkF	BaP	DahA	IndP	BaP _{MEO}
DEC.	$0-10$ cm	11.2	0.10	6.60	10.0	218	20.4	208	474	9.18	1.73	16.5	110	218	63.2	60.3	479
	10-20 cm	2.40	0.08	0.20	2.10	10.0	1.00	16.0	31.8	1.97	1.33	0.50	23.1	10.0	3.10	4.64	44.6
	20-30 cm	17.0	0.29	2.80	3.18	148	34.6	324	529	13.9	4.96	7.00	35.0	148	107	94.0	410
JAN.	$0-10$ cm	9.80	0.03	2.00	0.16	154	2.40	24.0	192	8.04	0.58	5.00	1.76	154	7.44	6.96	184
	10-20 cm	29.4	0.05	47.4	0.80	40.0	1.80	28.0	147	24.1	0.85	119	8.80	40.0	5.58	8.12	206
	20-30 cm	13.8	0.06	11.0	2.56	64.0	9.00	106	206	11.3	1.02	27.5	28.2	64.0	27.9	30.7	191
FEB.	$0-10$ cm	15.4	0.21	10.6	0.94	72.0	12.2	122	233	12.6	3.50	26.5	10.3	72.0	37.8	35.4	198
	$10-20$ cm	1.60	0.01	1.20	0.22	8.00	0.60	6.00	17.6	1.31	0.24	3.00	2.42	8.00	1.86	1.74	18.6
	20-30 cm	0.80	0.01	2.00	0.06	6.00	0.60	4.00	13.5	0.66	0.10	5.00	0.66	6.00	1.86	1.16	15.4
MAY	$0-10$ cm	53.2	1.85	27.6	0.70	98.0	91.6	1484	1757	18.2	ND	62.5	30.1	ND	ND	ND	111
	10-20 cm	52.2	0.49	27.4	7.92	914	111	1786	2899	20.9	7.68	105	22.9	258	14.9	ND	429
	20-30 cm	124	0.54	48.6	11.2	1408	151	1628	3372	48.9	16.6	246	109	284	383	190	1278
JUN.	$0-10$ cm	ND	ND	0.20	0.04	28.0	0.80	10.0	39.0	43.6	31.5	69.0	7.70	98.0	284	430	964
	10-20 cm	23.0	ND	ND	ND	ND	0.80	8.00	31.8	42.8	8.39	68.5	87.1	914	345	518	1983
	20-30 cm	4.80	ND	0.20	0.18	8.00	1.60	10.0	24.8	102	9.25	122	123	1408	469	472	2704
JUL.	$0-10$ cm	22.2	ND	25.0	2.74	ND	ND	ND	49.9	ND	ND	0.50	0.44	28.0	2.48	2.90	34.3
	10-20 cm	25.6	0.45	42.0	2.08	258	4.80	ND	332	18.9	ND	ND	ND	ND	2.48	2.32	23.7
	20-30 cm	59.6	0.98	98.4	9.94	284	124	656	1233	3.94	0.03	0.50	1.98	8.00	4.96	2.90	22.3

Table 6, displayed the estimated BaP equivalence (BaP_{TEO}) and mutagenic equivalence (BaP_{MEO}) values in relation to exposure to PAHs in soil obtained from e-waste dumpsite which spanned from $13.5 - 3.372$ μ g/kg, with significant contribution from BbF, BaP, DahA and IndP. The highest BaP_{TEO} value was observed in May at depth $20 - 30$ cm which shows that those PAHs contents penetrate into the soil due to rainfall and the poor drainage system of the site. While the lowest value was observed in February at 20 - 30 cm depth which indicate high

penetration ability and strong binding capacity of the soil to the PAHs contaminants. These values were similar to those reported by Chukwujindu *et al.* (2019) in a similar study. The values of BaP_{MEO} observed in this study ranged from 18.6 – 2,704 µg/kg, the significant contribution of these values was also obtained from BbF, BaP, DahA and IndP as in the case of BaPTEQ. These values corroborated the report of Emoyan (2020). The PCA results of PAHs in the soil are presented in Table 7. Four components were found and accounted for 90.111 % of the

variability in the data. Component 1 accounted for 31.902 % of the total variance and was characterized by high positive loading of Phen, Flt, Chry, BaA, BkF, IndP and DahA. BaA,

Chry, BkF and DahA are indicators for dieselpowered engines (Wang *et al.,* 2013; Yu *et al.,* 2014).

Component 2 explained 22.649 % of the total variance and was characterized by high positive loading of Nap, Pyr, BaP and BghiP. Nap is a tracer for incomplete combustion processes (Yu *et al.,* 2014) while BaP and BghiP are indicative of automobile emissions (Liu *et al*., 2017; Iwegbue *et al*., 2017). Component 3 explained 19.109 % of the total variance and was characterized by high positive loading of Ace, Acy and Flu and moderate loading of Phen. These compounds are indicative of low temperature combustion processes such as burning of wood/biomass and liquidified petroleum gas, natural gas and coal (Guo *et al.,* 2003; Wang *et al.,* 2013). Component 4 was characterized by high positive loading of Ant and BbF and moderate loading of Nap and Chry and accounted for 16.451 % of the total variance. Nap is related to incomplete combustion processes

while Ant, Chry and BbF are tracers of coal combustion (Dong and Lee, 2009). All numbers appearing bold shows that those compounds generate the highest concentrations among the 16 PAHs under considerations. Figure 3 displays a significant and highly significant correlation between the sixteen (16) PAHs congeners at $p <$ 0.05 and $p < 0.01$ levels. These correlations across the 16-PAHs at dry season certified the presence of hydrocarbon congeners with each other and gave a clear knowledge and insight of the PAH congeners on the surface of the soil. Phenanthrene (Phe) showed more positive correlation in relation to all other compound of PAHs, while Benzo (a) anthracene (BaA) showed a more negative correltion in relation to all other compounds of PAHs. The non-correlation observed implies that there is no significant effect with their persistence in the soil surface.

Figure 4 shows a strong, significant correlation (p < 0.01) between the sixteen (16) PAH congeners across all compounds, except for Anthracenc (Ant), during the wet season compared to the dry season. The correlation level here certified the presence of hydrocarbon across each compound which gives a better understanding and a better insight into PAHs congeners' movement within the soil surface. The non-significant correlation observed at Anthracene (Ant) might be an indication that there is no significant effect with the persistence of Ant congeners across the soil surface.

Figure 3: Pearson's correlation matrix of PAHs in relation to dry season

Figure 4: Pearson's correlation matrix of PAHs in relation to wet season

4.0 Conclusion

Due to the increase rate in dumping activities, ewaste contaminated soil deserved much concern to handle. The PAHs highest mean concentrations were observed in wet season with relative closeness to the median values, the highest percentage distributions were also observed in wet season across depths. The hazard quotient follows the trend of HQ Ing > HQ Derm > HQ Inh., for both children and adult and the total cancer risk for adult is lower than that of children in ths study. It can be affirmed that ewaste dumping has contributed much contaminants of PAHs to the soil. Hence proper legal action in observing the environment should be put in place to avoid indiscriminate dumping of e-waste.

References

- Adebola, A. A. and Peter, O. (2017). Heavy metals and polycyclic aromatic hydrocarbons in soil from e-waste dumpsites in Lagos and Ibadan, Nigeria. *Journal of health and pollution,* 7 (15): 71 – 84.
- Aliveira, R. F., Varandas, F. and Arbilla, G. (2014). Characterization of polycyclic aromatic hydrocarbons levels in the vicinity of a petrochemical complex located in a densely populated area of Rio de Janeiro, Brazil. Aunos Pollution Research, $5(1): 87 - 95$
- Cao, W., Yin, L., Zhang, D., Wang, Y., Yuan,J., Zhu, Y. and Dou, J. (2019). Contamination, sources, and health risk associated with soil PAHs in Rebulh Land from a Coking Plant, Beiging, China. *International Journal of Environmental Research Public Health,* 16, 4.
- Chukwujindu, M.A.I, Grace, O., Stephen, A. U, Francis, E. E., Eze, W. O., Godswill, O. T., Godwin, E. N. and Bice, S. M. (2019). Distribution, sources and risk exposure to polycyclic aromatic hydrocarbons in indoor dust from electronic repair workshop in Southern Nigeria. Emerging Contaminants, $5: 23 - 30$
- Dong, T. T. T., & Lee, B. K. (2009). Characteristics, toxicity and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea. *Chemosphere, 74*, 1245- 1253.
- Emoyan, O. O. (2020). Quantification and cancer risk evaluation of polycyclic aromatic hydrocarbons in soil around selected Telecom Masts in Delta State, Nigeria. Egyptian Journal of Chemistry, 63 (2): $433 - 448.$
- Eyenubo, O. B., Peretomodea, V. O., Egharevba, F., Osakwe, S. A.and Avwioro, O. G. (2014). Polychlorinated biphenyls (pcbs) in sediments and fish from dredged tributaries and creeks of river ethiope, south-south, Nigeria: sources, risk assessment and bioaccumulation, 6 , $1 - 8$, DOI:10.46481/jnsps.2024.1951.
- Eyenubo, 0. B., Augustine, A., Osakwe S, A. and Egharevba F. (2022). Assessment of pollution potentials and chemical interaction of polybrominated diphenyls ethers on soil and bitter leaf around dumpsite in Abraka. *Nigeria. Nigeria Journal of Pharmaceutical and Applied Science Research,* 11 (2): 9 – 18.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., &Zou, S.C. (2003).Particle-associated

polycyclic aromatic hydrocarbon in urban air of Hong Kong. *Atmospheric Environment, 37*, 5307-5317

- Iwegbue, C. M. A., Bassey, F. I, Tesi, G. O., Overah, L. C., Onyeloni, S. O. and Martincigh, B. S (2014). Concentration and health risk assessment of metals in chewing gums, peppermint and sweet in Nigeria. Journal of Food Measurement and Characterization, DOI 10.1007/s11694-9221-4
- Iwegbue, C. M. A., Tesi, G. O., Overah, L. C., Emoyan, O. O.,Nwajei, G. E., & Martincigh, B. S. (2017). Effects of flooding on the sources, spatiotemporal characteristics and human health risks of polycyclic aromatic hydrocarbons in flood plain soils of the lower parts of the River Niger, Nigeria. *Polycyclic Aromatic Compounds*. [https://doi.org/10.1080/-](https://doi.org/10.1080/-10406638.2017.1403329) [10406638.2017.1403329.](https://doi.org/10.1080/-10406638.2017.1403329)
- KhadiJah, A. I. (2016). Environmental Risk Assessment for an informal recycling site in Lagos State, Nigeria Middlesex University research at [http://emprints,](http://emprints/) mdx.ac.uk/22233/
- Liu, H., Yu, X. L., Liu, Z. R. and Sun, Y. (2018). Occurrence, characteristics and sources of polycyclic aromatic hydrocarbons in arable soils of Berging, China. *Ecotoxicology and environmental safety*, $159:120-126.$
- Liu, W., Ma, L., Abuduwaili, J., & Li, Y. (2017).Distribution,source analysis, and ecological risk assessment of polycyclicaromatic hydrocarbons in the typical topsoil of theIssyk-Kul Lake Basin.*Environmental Monitoring andAssessment*, 189,

398[.https://doi.org/10.1007/s10661-017-](https://doi.org/10.1007/s10661-017-6113-1) [6113-1.](https://doi.org/10.1007/s10661-017-6113-1)

- Luo, X.S., Ding, J., Xu, B., Wang, Y.J., Li, H.B., & Yu, S., (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils, *Science of the Total Environment*, 424, 88–96.
- New York State Department of Health (NYS DOH) (2007). Hopewell precision area contamination. Appendix C-NYS DOH, In: Procedure for evaluating potential health risk for contaminants of concern. [http://www.health.ny.gov/environmental/i](http://www.health.ny.gov/environmental/investigations/hopewell/appendc.htm) [nvestigations/hopewell/appendc.htm](http://www.health.ny.gov/environmental/investigations/hopewell/appendc.htm)
- Panatda, P., Siriuma, J. and Supabhorn, Y. (2023). Soil heavy metal pollution from waste electrical and electronic equipment of repair and junk shops in southern Thailand and their ecological risk. National Library Medicine, 9(10): e20438. doi: [10.1016/j.heliyon.2023.e20438](https://doi.org/10.1016%2Fj.heliyon.2023.e20438)
- Richard, A.O., John, K.B. and Stephen, O. (2013). Assessment of soil contamination through e-waste recycling activities in texma community one environment pollution, 2**(**2), 210-215.
- Robinson, B. A. (2009). E-Waste: An assessment of globral production and environmental impacts. *Science of the Total Environment.* **408**: 183-191.
- Shengtao, M., Meiqing, L., Jian, T., Ranran, L., Yan, Y., Yingxin. Y., Guiying, L. and Taicheng, A. (2021). Occurrence and fate of polycyclic aromatic hydrocarbons from electronic waste dismantling activities: A critical review from environmental

pollution to human health. *Journal of Hazardous Materials*, https://doi.org/- 10.1016/j.jhazmat.2021.127683

- USDOE (United State Department of Energy). (2011). The risk assessment information system (RAIS); U.S. Department of Energy's Oak Ridge Operation office (ORO): Oak Ridge, TN, USA.
- USEPA (United States Environmental Protection Agency). (1989). Risk Assessment guidance for superfund, Vol. 1: Human health Evaluation Manual EPA/se0/1- 89/002, office of solid waste & emergency Response, Washington, DC.
- USEPA (United States Environmental Protection Agency) (2001). Risk assessment guidance for superfund. Volume 1: Human evaluation Mannual (Part E, Supplemental guidance for defined risk assessment. EP/540/R/99/005.7. Washington, DC, USA: Office of

Emergency and Remedial response, United State Environmental Protection Agency.

- Wang, X. T., Miao, Y., Zhang, Y., Li, Y. C., Wu, M. H., & Yu,G. (2013). Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: Occurrence, source apportionment and potential human health risk. *Science ofthe Total Environment*, 447: 80–89.
- World Bank (2014). Life expectancy data. Retrieved on May 2, 2014 from [http://data.worldbank.org/indicator/SP.D](http://data.worldbank.org/indicator/SP.DYN.LE00.IN) [YN.LE00.IN](http://data.worldbank.org/indicator/SP.DYN.LE00.IN)
- Xi, C., Nuerla, A., Yusuyunjiang, M., Naifu, Z., Wenhu, C., Nanxin, L., Qlongfang, Z. and Miao, P. (2022). Pollution levels, sources and risk assessment of polycyclic aromatic hydrocarbons in farmland soil and crops, near Urumgui Idustrial Pak, Xinjiang, China. *Research square*, 1 : 1- 17.

