



Evaluation of polycyclic aromatic hydrocarbons in soil samples around Umuerim Nekede refuse dumpsite Owerri West, Imo State, Nigeria

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are very toxic and persistent environmental contaminants. This study assessed the concentration, distribution and environmental implication of polycyclic aromatic hydrocarbons in soil samples collected from Umuerim Nekede refuse dump. Soil samples were collected at four distances (0, 50, 100 and 200m) and three depths (0-15, 15-30 and 30-45cm). The soil samples were analyzed for 16 US EPA priority using Gas Chromatography-Flame ionization detector (GC-FID). Total PAHs concentration in soil sample from Umuerim refuse dump was 43.971mg/kg in topsoil (0-15cm) at a distance 50m. Total PAHs concentration at 100m in topsoil (0-15cm) was 30.524mg/kg. At 200m distance total PAHs concentration in bottom soil (30-45cm) was 6.425mg/kg. The order of carcinogenic PAHs concentration in soil samples from Umuerim refuse dumpsite were as follows: Benzo(b) Fluoranthene>Benzo(k)fluoranthene>Chrysene>Benzo(a)pyrene>Benzo(a) anthracene>Benzo(ghi)perylene>Dibenzo(a,h)anthracene>Indeno(1,2,3-cd) pyrene. The values of the cancer risk dermal pathway for adults ranged from 1.37E-10 to 3.42E-6 and dermal pathway for children ranged from 2.47E-10 to 6.15E-6. Also, the values of the cancer risk ingestion pathway for adults ranged from 2.5E-10 to 6.23E-6 and ingestion pathway for children ranged from 3.20E-10 to 1.99E-5.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), soil contamination, dermal pathway, ingestion pathway, carcinogenic

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are group of chemicals that are formed during the incomplete burning of coal, oil gas, wood, garbage or other organic substances (Muendo *et al*; 2006^[26], Zhang and Tao, 2009; Sharkour *et al.*, 2011; Korosi *et al*; 2013; Olayinka *et al*, 2015)^[22, 32, 35]. PAHs belong to the group of persistent organic pollutants (POPs). These are organic contaminants that are resistant to degradation, can remain in the environment for long periods, and have the potential to cause adverse environmental effects. POPs are contaminants which occur in all parts of the environment such as atmosphere, inland and sea waters, sediments, soils and vegetation. They are mainly of anthropogenic origin and have no significant natural source. The combustion of fossil fuels, including motor vehicle emission and power generation, wood burning, municipal and industrial waste incineration are examples of anthropogenic sources (Chiu *et al*; 2012)^[13].

PAHs are included in the "priority pollutants" listing of the US Environmental protecting Agency (US EPA). PAHs are grouped as low molecular weight PAHs or high molecular weight PAHs as a result of their chemical structure (Abdel – Shafy and Mansour, 2016)^[1]. The low molecular weight PAHs contain 2 or 3 benzene rings, while the high molecular weight PAHs contain 4 to 6 benzene rings. The low molecular weight PAHs are highly soluble in water than high molecular weight PAHs. Different types of PAHs, are formed based on combustion temperature. High temperature form simple PAHs, while low temperature form more complex PAHs.

The presence of PAHs in soils have been an issue of concern to researchers because some of the PAHs are known to have carcinogenic, mutagenic and teratogenic effects (Joa *et al.*, 2009)^[20]. A lot of research have been carried out on PAHs in soil samples. Results obtained

showed that soil contamination by PAHs were considered to be good indicator of level of environmental pollution by human activities. Adsorption and leaching of PAHs from the soil are complex processes that depend on numerous variables, such as soil type, soil moisture, the presence of molecules of other soluble compounds, pH of soil etc (Jaroslaw *et al*; 2010)^[19]. PAHs can enter plants through plant leaves or settle in the soil from atmosphere. PAHs accumulation in plants through roots, the PAHs will get to human beings through food chain, thereby threatening human health. The greater amounts of PAHs observed in most urban soils and the close proximity of these soils to humans may increase the probability of human exposure to these pollutants via inhalation, ingestion or dermal contact (Abrahams, 2002)^[2]. Reports have shown that exposure to trace amount of PAHs can accelerate cancer risks in human beings (Chen *et al.*, 2015). Alawi and Azeez (2016)^[7, 12] have reported vulnerability of PAHs exposure on people living close to waste dump. Okechukwu *et al* (2021) conducted a research on the environmental effects of the use of unlined dumpsite on the environment. Aralu *et al* (2022) reported PAHs accumulation in soil samples obtained from soil waste dumpsite in Awka, Nigeria during wet season and dry season. Anyahara *et al* (2023)^[8] investigated PAHs contamination of agricultural soil of Imo river watershed in Okigwe and Obowo zones of Imo State, Nigeria. They reported highest number of individual PAHs were detected in the soil samples from Obowo Zone.

Open dumpsites are characteristics of Nigeria cities especially Umuerim in Owerri West Local Government of Imo State, Nigeria. Low income people farm around the dumpsite of Umuerim where they are exposed to PAHs generated by burnt waste. The pollutants are discharged in the air, water and soil leading to environmental health risk of individuals farming near the dumpsite.

This study is aimed at determining PAHs in soil samples in the vicinity of Umuerim refuse dump and to study the variation in their concentration along the soil profile.

Materials and Method

Soil samples were collected from Umuerim Nekede refuse dumpsite, Owerri West Local Government, Imo State, Nigeria. This study is based on the prevalence open dumpsite situated close to cultivated farm lands that may create a pathway for contaminant transfer into the food chain. The locations of soil sample collection are shown in Fig. 1.

Collection of Soil Sample

Soil samples were collected using stainless-steel auger at different distances namely 0m, 50m, 100m and 200m. The soil samples were collected from the top soil (0-15cm), middle soil (15-30cm) and bottom soil (30-45cm) depths at each distance. After collection, the soil samples were homogenized in clean plastic containers that were previously washed. The homogenized portion of soil samples were taken into a clean amber bottle and stored in an ice-chest until use.

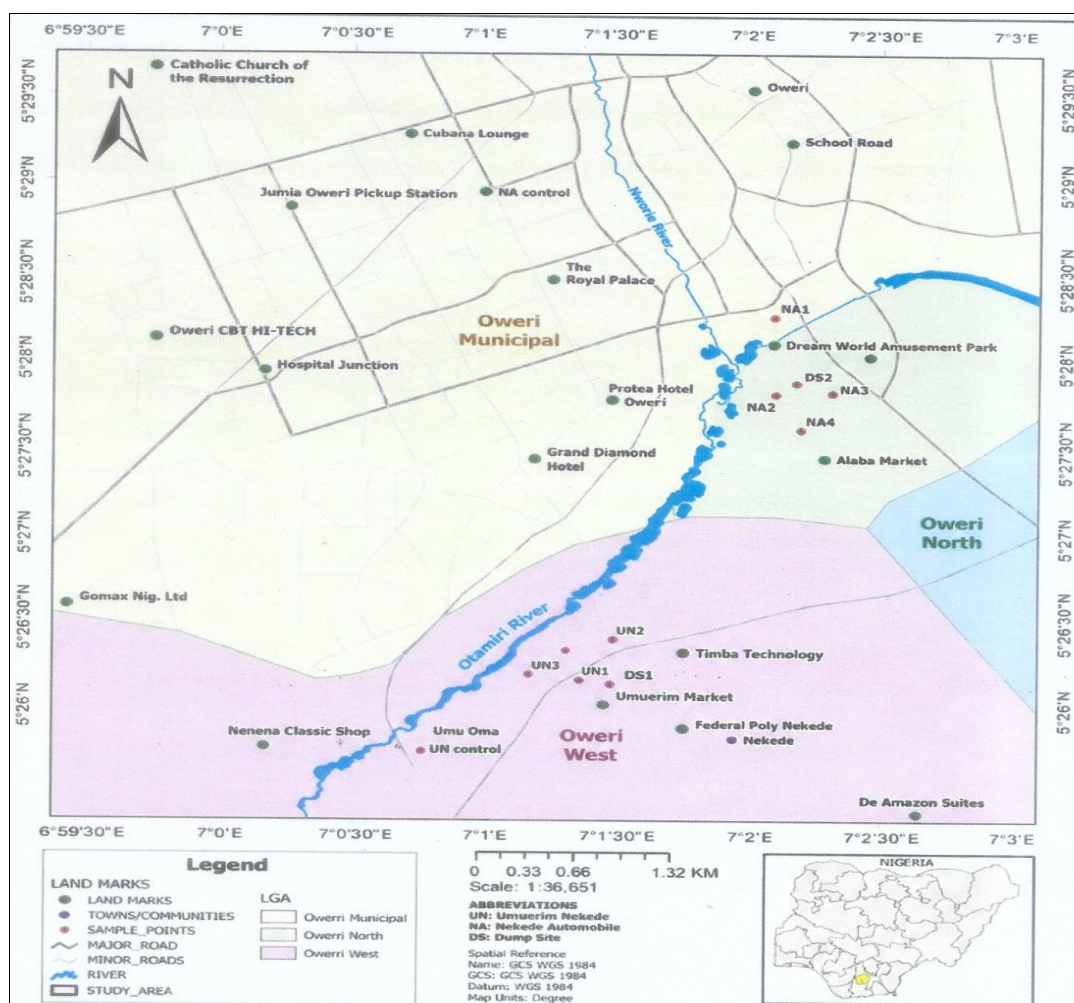


Fig 1: Map of the study area showing sampling stations, land marks, and local government boundaries

Sample Preparation

The homogenized soil samples were air-dried at room temperature for 72hrs to remove moisture. The dried soil samples were then sieved through a 2mm mesh to remove any debris, stones or roots that could interfere with the extraction process. The dried soil samples were ground into fine powder and sieved through a 0.2mm mesh and stored into a container.

Soil Sample Extraction

10g portion of the sieved soil samples were placed in a Soxhlet extractor and extraction was performed using 20ml of methanol and 50ml of dichloromethane for 24hrs at 80 °C under continuous reflux. The resulting extract were collected in a 250ml flask and purified with dichloromethane. The concentration of the extract to 50ml

was achieved using rotary evaporator. Further purification of extract was carried out in a 50ml flat bottom flask by addition of 15ml pentane. The extract was reduced to 20ml through rotary evaporation. Then the extract was concentrated to 0.5ml with a gentle stream of nitrogen gas. The concentrated extract was passed through a slurry-packed activated silica gel column for 8hrs at 200 °C to remove interfering hydrocarbons. Non-PAHs were now separated using pentane. Then PAHs were eluted using dichloromethane (UNEP, 1996, ASTM, 2011).

Sample Clean-up

Sample clean-up was performed using glass column. Column preparation was carried out by inserting glass cotton into the column. Silica gel was activated in an oven at 105 °C for 2hrs before use. Silica gel was dissolved with

dichloromethane (DCM) to form slurry, and the slurry was added into the column. Anhydrous Na₂SO₄ was added into the column to remove moisture from the sample extract, followed by addition of pentane. After preparation of the column, the concentrated sample extract was mixed with cyclohexane in a beaker and transferred into prepared column. The sample extract was eluted using pentane as solvent and eluted sample collected in a beaker below the column. The sample was eluted further by adding more pentane into the column. After elution the column was rinsed with DCM. The eluted sample was allowed to stand overnight at room temperature in a fume cupboard for evaporation to take place (LAWI, 2011).

Sample Separation and detection

The determination of PAHs were carried out using a high – resolution gas chromatograph (Agilent 5890 Series II) equipped with a flame ionization detector (GC-FID), an on-column capillary injection system and a Hewlett-Packard Model 7673 auto sampler. 1µl of sample was injected in splitless mode. Chromatographic separation was achieved using a fused –silica capillary column (DB-5; 5%

phenyl/95% methyl polysiloxane), 30mx0.25mm internal diameter, with a 0.25µm film thickness (ASTM, 2011). High purity nitrogen served as the carrier gas at flow rates of 1ml/min (column) and 30ml/min, respectively. The oven temperature programme was as follows: initial temperature at 80 °C for 2mins, increased to 190 °C at 5 °C/min, and then increased to 280 °C at 10 °C/min. The injector and detector temperature were set at 250 °C and 300 °C, respectively. Identification of individual PAHs were based on comparison of retention time between sample peaks and certified PAH standard.

Results and Discussion

The concentration of the 16 US EPA priority PAHs were analyzed in the soil samples obtained at various depths and distances at Umuerim refuse dump and surroundings. The results are presented in table 1. The result showed that 15 PAHs were detected in the soil samples out of 16 US EPA priority PAHs. The mean levels and standard deviation were also calculated for individual and total PAHs for each depth and distance from the dumpsite.

Table 1: PAH Concentration (mg/kg) at Umuerim Refuse Dump Soil

Distance	Depth (cm)	BaA	BaF	Acy	BkF	BaP	Phe	BghiP	Ace	Ant	DbA	Pyr	Nap	Fla	Chr	IcdP	Flu	Total PAHs
	0-15	0.006	0.159	0.034	0.452	0.048	0.159	0.056	0.053	0.105	0.005	0.058	0.048	0.246	0.096	0.008	ND	1.533
	15-30	0.002	0.054	0.006	0.117	0.052	0.012	0.004	0.013	0.057	0.002	0.006	0.007	0.054	0.098	0.053	ND	0.534
0m	30-45	0.001	0.059	0.003	0.063	0.056	0.055	0.027	0.066	0.058	0.007	0.053	0.053	0.060	0.101	0.003	ND	0.663
	Mean	0.003	0.091	0.014	0.211	0.052	0.075	0.029	0.044	0.073	0.004	0.039	0.036	0.120	0.098	0.021	ND	0.910
	SD	0.003	0.059	0.017	0.211	0.004	0.076	0.026	0.027	0.027	0.003	0.028	0.025	0.109	0.003	0.028	ND	0.543
	0-15	0.538	4.960	1.278	6.394	2.491	4.909	1.172	1.206	9.226	0.529	1.813	0.904	2.876	5.360	0.318	ND	43.971
	15-30	0.009	0.110	0.041	0.898	0.100	1.125	0.059	0.189	1.676	0.048	0.053	0.063	0.966	5.055	0.044	ND	5.434
50m	30-45	0.059	1.016	0.576	1.158	0.150	1.016	0.350	0.774	0.635	0.068	0.621	0.484	0.538	0.565	0.068	ND	7.810
	Mean	0.202	2.029	0.632	2.817	0.913	2.350	0.527	0.723	3.846	0.215	0.829	0.484	1.460	3.660	0.143	ND	19.071
	SD	0.292	2.578	0.620	3.101	1.366	2.217	0.577	0.510	4.689	0.272	0.898	0.420	1.245	2.685	0.152	ND	21.596
	0-15	1.593	8.050	0.560	5.815	1.520	2.005	0.106	1.531	1.254	0.019	1.046	1.033	4.955	0.827	0.212	ND	30.524
	15-30	0.007	5.373	1.090	6.183	2.310	0.212	1.056	2.166	0.096	0.096	2.130	0.215	3.750	1.977	0.578	ND	25.280
100m	30-45	0.053	4.954	0.800	2.648	0.059	4.955	0.086	5.013	0.265	0.054	1.620	0.318	0.105	1.520	0.056	ND	21.045
	Mean	0.551	6.126	0.817	4.882	1.296	2.390	0.416	2.903	0.538	0.056	1.599	0.522	2.936	1.441	0.282	ND	25.616
	SD	0.903	1.680	0.265	1.943	1.142	2.395	0.554	1.855	0.626	0.039	0.542	0.446	2.525	0.579	0.268	ND	4.749
	0-15	0.020	0.085	1.016	1.535	0.086	0.187	0.111	1.974	0.085	1.040	0.102	0.058	0.203	0.203	0.008	ND	4.425
	15-30	0.013	0.190	0.028	0.112	0.059	0.293	0.025	0.145	0.118	0.007	0.103	0.039	0.069	0.089	0.076	ND	1.369
200m	30-45	0.012	0.181	0.123	0.015	0.015	0.148	0.525	1.045	0.956	0.092	0.150	0.043	1.302	0.148	0.291	ND	6.425
	Mean	0.015	0.152	0.389	0.554	0.053	0.209	0.220	1.054	0.386	0.380	0.118	0.047	0.524	0.146	0.125	ND	4.073
	SD	0.004	0.058	0.545	0.851	0.036	0.075	0.268	0.915	0.494	0.574	0.027	0.010	0.677	0.057	0.148	ND	2.546
Control		0.006	0.057	0.082	0.018	0.052	0.0169	0.005	0.047	0.059	0.006	0.060	0.084	0.064	0.098	0.052	ND	0.962

Total PAHs: Total Polycyclic Aromatic Hydrocarbons; SD: Standard Deviation, BaA: Benzo (a) anthracene, BaF: Benzo (b) Fluorathene, Acy: Ancenaphthylene, BkF: Benzo (k) fluorathene, BaP: Benzo(a) Pyrene, Phe: Phenanthrene, BghiP: Benzo(ghi) Perylene, Ace: Acenaphthalene, Ant: Anthracene, DbA: Dibenzo (a,h) anthracene, Pyr: Pyrene, Nap: Naphthalene, Fla: Fluorathene, Chr: Chrysene, IcdP: Indeno (1, 2, 3-cd) Pyrene., Flu: Fluorene. ND: Not detected.

The result of Benzo(a) anthracene (BaA) concentrations are presented in table 1 at various depths and distances from Umuerim refuse dumpsite. At 0m distance, Benzo (a) anthracene values obtained at topsoil (0-15cm), middle soil (15-30cm) and bottom soil (30-45cm) were 0.006, 0.002 and 0.001 mg/kg, respectively. The result showed that BaA decreased as depth increases at 0m (dumpsite) distance. At 50m distance from dumpsite, the topsoil recorded BaA concentration 0.538mg/kg more, than the value obtained at middle soil and bottom soil. However, high concentration of benzo(a) anthracene was recorded at topsoil (0-15cm) at 100m distance with a value 1.593mg/kg. Adeniji *et al* (2024) ^[3] working on soil sample around Ojoou-Olayanju's dumpsite at Ada, South Western, Nigeria recorded benzo(a)

anthracene concentration 1.34mg/kg. Aralu *et al* (2023) ^[9] working around solid waste dumpsite at Awka, Nigeria reported BaA 0.3±0.60µg/kg. The benzo (a) anthracene concentration obtained in this study was higher than values obtained at Ada dumpsite South western, Nigeria. The maximum permissible limited for individual PAH in soil is 0.5mg/kg as stipulated by Nigeria's National Environmental Standard and Regulation Enforcement Agency (NESREA). This study revealed that soil sample obtained at Umuerim refuse dumpa at 100m distance (0.-15cm) was contaminated with 1.593mg/kg benzo(a) anthracene. There are farm lands at the distance of 100m from the dumpsite. Benzo(a) anthracene presence in the soil may be transferred through the food chain to human beings. Benzo(a) anthracene is a

carcinogenic PAH and its health effect is detrimental to human.

The distribution of benzo (b) fluoranthene (BbF) concentration as shown in table 1 varies across depths and distances from the refuse dumpsite. At the dumpsite (Om) the benzo (b) fluoranthene concentration was 0.159mg/kg at 0-15cm depth. At 50m distance from dumpsite BbF recorded higher values of 4.96 mg/kg and 1.016mg/kg at 0-15cm and 30-45cm, respectively. These values were higher than values obtained at Om distance. At 100m distance, BaF concentrations were 8.050, 5.373 and 4.954 mg/kg at topsoil, middle soil and bottom soil, respectively. At 200m distance from dumpsite BaF concentrations were low when compared to values obtained at 100m distance. The BaF values obtained at 100m distance were above permissible limit 0.5mg/kg stipulated by NESREA. The increase in BaF at 100m distance might be attributed to percolation of BaF at various depths. It might also be attributed to leachate movement, runoff and atmospheric deposition. Adeniji *et al*; (2024) and Mohammed *et al*; (2020) [3, 25] reported similar pattern of distribution of PAH. The decrease in BaF at 200m distance might be attributed to reduced dumpsite influence and natural attenuation process such as degradation and dilution. Okedere and Elehinafe (2022) and Akporhonor *et al* (2022) [6, 31] reported similar trend in soil samples. Benzo (b) fluoranthene is a carcinogenic PAH and its health effect is detrimental to human beings through food chain since so many farm lands are being cultivated at that distance of 100m by rural farmers.

The result of this study revealed that acenaphthylene (Acy) concentrations were low at Om distance from dumpsite. At 50m distance Acy concentration was 1.278mg/kg at topsoil. Also Acy concentration was 1.090mg/kg at middle soil at 100m distance from dumpsite. At 200m distance Acy concentration recorded 1.016mg/kg at topsoil. Eneji *et al*; (2017) [16] reported elevated concentration of acenaphthylene 394µg/kg in topsoil at Auto-mechanic workshop in Makurdi, Benue State, Nigeria.

Benzo (k) fluoroanthene (BKF) concentrations are presented in table 1. At Om distance the values of BKF were low at various depths. At 50m distance the concentration of BKF increases at topsoil with value 6.394mg/kg and decreases to 1.158mg/kg at 30-45m depth. At 100m distance the BKF concentration recorded 5.815, 6.183 and 2.648mg/kg at topsoil, middle soil and bottom soil, respectively. At 200m distance BKF content was 1.535mg/kg at topsoil and decreases as depth increases. The result of this study revealed that the soil samples were contaminated at 0-15cm, 15-30cm and 30-45cm depths at 50m distance. Also at 100m distance all the depths of the soil samples were contaminated. At 200m distance from dumpsite the soil sample was contaminated at topsoil. Benzo (k) fluoranthene is a carcinogenic PAH. Its effect in the soil is detrimental to human. It can easily be transferred to man through food chain. Olayinka *et al*; (2015) [32] working on Saje dumpsite at Abeokuta metropolis Southwestern, Nigeria reported benzo (k) fluoranthene concentration 1.29mg/kg at 0-15cm depth.

Benzo(a) pyrene (BaP) are presented in table 1. At Om distance BaP concentrations were similar at various depths studied. At 50m distance, BaP recorded 2.491mg/kg at topsoil. At 100m distance from dumpsite BaP content was 1.520 and 2.310mg/kg at topsoil and middle soil, respectively. However, at 200m distance the BaP

concentrations were low at various depths. The increase of benzo(a) pyrene at some depths at 50m and 100m might be attributed to redistribution through leachate movement through soil profile. Adeniji *et al*, (2024) [3] working on dumpsite around Ojoou-Olayanju's in Ada, South western, Nigeria reported similar trend. The High concentration of BaP at 50m and 100m distance is detrimental to man in view of BaP being a mutagenic and carcinogenic PAH. Also the high concentration of BaP especially at 50m and 100m distances where people farm is very dangerous in terms of its health hazard. However, hydrophobic nature of BaP might be attributed to its strong adsorption to soil particles, especially in organic rich layers, leading to accumulation in topsoil and middle soil at 50m and 100m distances, respectively.

The results of the analysis as shown in table 1 showed that phenanthrene (Phe) concentrations were low at various depth at Om distance. At 50m distance, Phe concentrations decreases as depth increases with values 4.909, 1.125 and 1.016 mg/kg at topsoil, middle soil and bottom soil, respectively. At 100m distance Phe recorded 2.005 and 4.955mg/kg at topsoil and bottom soil, respectively. However, at 200m distance the phenanthrene concentrations were low at all depths. The result of the analysis revealed that some of the soil samples were contaminated at 50m and 100m distances since the values obtained were higher than stipulated permissible limit of 0.5mg/kg by NESREA. The decrease in Phe concentration at 200m distance reflects reduced dumpsite influence and natural attenuation processes such as degradation and dilution (Ehigbor *et al*; 2020) [14].

Benzo (ghi) perylene (BghiP) concentration in table 1 showed that the values were low at all depths at Om distance. However, at 50m distance (0-15cm) the benzo (ghi) perylene concentration was 1.172 mg/kg. At 100m distance from dumpsite BghiP was 1.056mg/kg at 15-30cm depth. At 200m away from dumpsite BghiP recorded low concentration at topsoil and middle soil, whereas bottom soil recorded 0.525mg/kg concentration. As a high molecular weight, benzo (ghi) perylene is more persistent and strongly adsorb to soil particles, especially in organic-rich layers, leading to accumulation at topsoil and middle soil at 50m and 100m distances. Aralu *et al* (2023) [9] recorded benzo (ghi) perylene concentration 0.98µg/kg on soil around solid waste dumpsite in Awka, Nigeria. Benzo (ghi) perylene is a carcinogenic PAH. Its effect is detrimental to human beings through food chain. Otamiri river is very close to the dumpsite and the PAH compound might percolate through the soil profile into the river. The presence of the PAH in the river might affect the fish life in the river and other aquatic animals.

Acenaphthene (Ace) concentration as presented in table 1 showed low values at all depths at Om distance (dumpsite). At 50m distance Ace recorded 1.206mg/kg concentration at topsoil. At 100m distance, Ace content increases as depth increases with values 1.531, 2.166 and 5.013mg/kg at topsoil, middle soil and bottom soil, respectively. At 200m distance acenaphthene concentration recorded 1.974 and 1.045mg/kg at topsoil and bottom soil, respectively. Eneji *et al* (2017) [16] working around auto-mechanic workshop soil in Gboko, Benue State, Nigeria recorded acenaphthene concentration 381.5µg/kg at topsoil. The result of the analysis revealed that soil sample was contaminated with Ace at 30-45cm depth with high value at distance 100m

from dumpsite. All the values of acenaphthene obtained at 100m were higher than the maximum permissible limit of 0.5mg/kg for individual PAH in soil as recommended by NESREA.

Anthracene (Ant) content presented in table 1 showed that concentrations were low at various depths at Om distance. At 50m distance, anthracene concentration decreases rapidly as depth increases with values 9.226, 1.676 and 0.635mg/kg at topsoil, middle soil and bottom soil, respectively. At 100m distance, the anthracene concentration recorded 1.254mg/kg at 0-15cm depth, then decreases at 15-30m and 30-45cm depth. At 200m distance, Ant content was high at bottom soil when compared to values obtained at topsoil and middle soil. The increase in anthracene concentration at 50m distance might be attributed to redistribution through surface runoff, leachate and air dispersion from burning of waste. Adeyi and Oyeleke (2017) working on e-waste dumpsite in Lagos and Ibadan, Nigeria recorded similar result.

Table 1 showed low concentrations of dibenzo (a, h) anthracene (DbA) at Om distance. At 50m distance, DbA content was 0.529mg/kg within the acceptable standard of NESREA. At 100m distance the content of dibenzo (a, h) anthracene were low at various depths. At 200m distance from dumpsite DbA increases to 1.04mg/kg at topsoil. Ekpote *et al* (2019) ^[15] working on Rumuokuta dumpsite in Port Harcourt, Rivers state, Nigeria recorded dibenzo (a, h) anthracene concentration 1.248mg/kg. The value from Rumuokuta dumpsite was slightly higher than the value obtained in this study. Dibenzo (a, h) anthracene is a carcinogenic PAH and its presence in the soil will pose health hazard.

Pyrene (Pyr) concentrations presented in table 1 were low at Om distance in all the different depths studied. At 50m distance, the pyrene content was 1.813mg/kg at topsoil. At 100m distance Pyr concentration recorded 1.046, 2.130 and 1.620 mg/kg at topsoil, middle soil and bottom soil, respectively. However, at 200m distance Pyr content increases slightly as depth increases. The result revealed that the soil was contaminated at 50m distance (0-15cm) and 100m distance at topsoil, middle soil and bottom soil, respectively. Eneji *et al* (2017) ^[16] working on soil around auto-mechanic workshop in Makurdi, Benue State, Nigeria recorded Pyrene concentration 29.00µg/kg at topsoil.

Table 1 presented naphthalene (Nap) concentration at Om distance with low level of Nap at different depths. At 50m distance from dumpsite naphthalene concentration increases to 0.904mg/kg at topsoil. At 100m distance, naphthalene concentration increases at topsoil with value 1.033mg/kg and then decreases at middle soil and bottom soil. At 200m distance, Nap content were low in all the depths. Olayinka *et al* (2015) ^[32] working on Saje dumpsite in Abeokuta metropolis, South Western, Nigeria recorded Nap content 1.56mg/kg at 0-15cm depth. The result of the analysis revealed that the soil samples were contaminated at 50m distance at topsoil and 100m distance at topsoil, respectively. The decrease at 200m distance might probably be due to natural attenuation, microbial degradation and dilution (Adeyi and Oyeleke, 2017). This pattern highlights the influence of both distance and soil depth on the mobility of low molecular weight PAH in contaminated soil.

The results of the analysis presented in table 1 showed fluoranthene (Fla) concentrations were low at all depths studied at Om distance. At 50m distance, the fluoranthene concentration was 2.878mg/kg at topsoil. At 100m distance from dumpsite fluoranthene concentration decreases as depth increases with values 4.955, 3.750 and 0.105mg/kg at

topsoil, middle soil and bottom soil, respectively. At 200m distance Fla concentration increases at bottom soil with value 1.302mg/kg. The increase in the bottom soil at 200m distance reflects percolation overtime, demonstrating fluoranthene's persistence and hydrophobicity. This pattern highlights both distance from the dumpsite and soil depth as key factors controlling fluoranthene mobility in contaminated soil. This study revealed that the soil was contaminated with fluoranthene at 50m distance (0-15cm) and (15-30cm) depths and at 100m distance (0-15cm) and (15-30cm) depths. Also, at 200m distance from dumpsite there was contamination of fluoranthene at 30-45cm depth.

Table 1 showed the Chrysene (Chr) concentration in soil samples at Umuerim refuse dump. At Om distance, the Chrysene concentration increases gradually as depth increases. At 50m distance, Chr content increases at topsoil and middle soil with values 5.360mg/kg and 5.055mg/kg, respectively. At 100m distance, Chrysene concentrations were 1.977 and 1.520mg/kg at middle soil and bottom soil, respectively. At 200m distance from dumpsite the chrysene concentration decreases at various depths. This study revealed that the soil was contaminated at topsoil and middle soil at 50m distance. Also, at 100m distance all the soil samples obtained at various depths were above permissible limit as stipulated by NESREA. Chrysene is a carcinogenic PAH. Its presence in soil will constitute health hazard. The cultivation of any food crop in the contaminated soil, the chrysene will be transferred to man through food chain. Ekpote *et al* (2019) ^[15] working on Chakiricha dumpsite within Port Harcourt metropolis, Rivers state, Nigeria reported chrysene concentration 3.380mg/kg in soil sample from the dumpsite.

The result of indeno (1,2,3-cd) pyrene (IcdP) shown in table 1 showed that indeno (1,2,3-cd) pyrene a high molecular weight PAH, has low concentrations across all distances and depths. The result of his study revealed that the soil samples were not contaminated with indeno(1,2,3-cd) pyrene. All the values at various depths and distances were below permissible limit as recommended by NESREA except at 100m distance where IcdP recorded concentration 0.578mg/kg, this value was slightly above 0.5mg/kg NESREA standard.

The total PAH recorded at Umuerim refuse dumpsite was 43.971mg/kg at 50m distance (0-15cm). However, at 50m distance, total PAH recorded were 5.434 and 7.81mg/kg at middle soil and bottom soil, respectively. At 100m distance, the total PAH across various depths were 30.524, 25.28 and 21.045mg/kg for topsoil, middle soil and bottom soil, respectively. This study revealed that total PAH at 50m distance (0-15cm depth) was slightly above Dutch guide line limit. The Dutch stipulated value for intervention for PAHs contamination in any soil is 40mg/kg (Kaszubkiewicz *et al*, 2010) ^[21]. The result revealed that Umuerim refuse dumpsite was contaminated with polycyclic aromatic hydrocarbon and needed intervention by Government Environmental Agency.

Diagnostic and Sources of PAHs in Umuerim Soil Sample

The PAH composition of soil can provide necessary information about their sources using diagnostic ratios (Yunker *et al*, 2002, Wang *et al*, 2004) ^[2, 44]. The ratio of Ant/Ant + Phe <0.1 denotes petrogenic inputs, while > 0.1 denotes pyrolytic inputs (Adeniji *et al*, 2019) ^[4]. The ratio Fla/Pyr <1 denotes petrogenic sources of contamination while Fla/Pyr > 1 denotes pyrogenic sources (Neff *et al*;

2005, Pies *et al*, 2008) [28, 33]. Furthermore, the ratio of fluoranthene to fluoranthene + Pyrene (Fla/Fla + Pyr) was used to confirm whether the dominant source of PAHs in the dumpsite soils originated from pyrogenic process. The ratio of Ant/Ant + Phe obtained in this study was 0.3977 determined at topsoil (0-15cm) at Om distance which denotes pyrogenic source. The ratio of Fla/Fla + Pyr was 0.809 at topsoil (0-15cm) indicating pyrogenic source. The ratio of B[a]A/B[a]A + Chr obtained in this study at topsoil (0-15cm) was 0.06 indicating petrogenic source. This study was also carried out at ratio of I[c,d]P/I[c,d]P + B[ghi]P at topsoil (0-15cm) the value obtained was 0.125 indicating petrogenic source. The low molecular weight (LMW) PAH and High Molecular weight (HMW) PAH were used to determine the sources of contamination of the soil sample of Umuerim refuse dump. LMW/HMW ratio higher than 1 indicates petrogenic sources, while <1.0 confirms pyrolytic PAHs input (Jiao *et al*; 2017). The ratio Acy/Fla obtained in this study was 0.138 at topsoil (0-15cm) which indicates pyrogenic source, while ratio Ant/BaA recorded 17.5 at topsoil (0-15cm) which indicates petrogenic source. The Pyrogenic source could be attributed to the incomplete combustion of non –petroleum substances such as refuse, wood and biomass. However, petrogenic sources made minor contributions due to the location of the dumpsite along major transport route. The emissions from vehicles within the area might have contributed to the pollution of the soil. The emissions from incomplete burning of petroleum product and surface runoff from the environment might be sources of PAHs pollution. The result of the analysis indicates that mixed sources of contamination were observed at Umuerim refuse dumpsite with pyrolytic sources being dominant.

Incremental Life Cancer Risk Assessment

The incremental life cancer risk assessment was determined for eight carcinogenic PAH detected at Umuerim refuse dumpsite. The two pathways for the incremental life cancer risk (ILCR) soil exposure used in this study were ingestion and dermal pathways. The two pathways are expressed as follows (US EPA, 2002)

$$ILCR_{ingest} = C \times IR \times EF \times ED \times CF \times CSF \quad (1)$$

$$BW \times AT$$

$$ILCR_{derm} = C \times SA \times AF \times ABS \times EF \times ED \times CF \times CSF \quad (2)$$

$$BW \times AT$$

The summation of the risk index (RI) was determined using equation (3) (US EPA, 2015)

$$RI = \sum IL CR \quad (3)$$

Where C stands for the PAHs concentration, cancer slope factor is represented by CSF for individual PAH. 7.3mg/kg/d is the CSF for benzo (a) pyrene (US EPA, 2015). The CSF for benzo (a) pyrene was multiplied by the respective toxic equivalent factor for each PAHs. The toxic equivalent factor of the PAHs parameters is: BKF (0.1), BbF (0.1), BaP (1), BghiP (0.01) BaA (0.1), DBaA (1), Acp (0.001), Acy (0.001), Fla (0.001), Flur (0.001), Ant (0.01), Nap (0.001), Pyr (0.001) and Phen (0.001) (US EPA, 2012)

Table 2 shows the cancer risk parameter for evaluating dermal and ingestion exposure (US EPA 2004, 2011 [39, 40], 2014, 2015)

The incremental life cancer risk (ILCR) ingestion pathway for adults and children are presented in table 3 and 4, respectively. The calculations were carried out for eight carcinogenic PAH detected at Umuerim refuse dumpsite. The ILCR ingestion pathway obtained for adults for benzo(a) pyrene (BaP) at 50m and 100m distance were 6.23E-6 (topsoil) and 5.78E-6 (middle soil), respectively. The ILCR ingestion pathway for children recorded in this study were high for BaP at 50m and 100m distances with values 1.99E-5 (topsoil) and 1.85E-5 (middle soil), respectively more than ingestion pathway for adults.

The incremental life cancer risk dermal pathway for adults and children are presented in tables 5 and 6, respectively. The ILCR obtained in this study for BaP for adults were 3.42E-6 (topsoil) at 50m distance and 3.17E-6 (middle soil) at 100m distance, respectively. However, dermal pathway ILCR for children recorded high value 6.15E-6 for BaP at 50m distance at topsoil and 5.70E-6 (middle soil) at 100m distance, respectively more than adult's dermal pathway.

Generally, ILCR values between 1.0E-06 and above are assumed adequate. However, 1.0E-05 values are safe, but not recommendable, while a value of 1.0E-04 indicates potential risk (US EPA, 2001). The result of the analysis showed that ingestion pathway for children for BaP at 50m and 100m distances are not recommendable and should be monitored because of its closeness to potential risk value. Since BaP is a mutagenic and carcinogenic PAH it should be seriously monitored at Umuerim refuse dumpsite.

Table 3: Cancer risk of Ingestion pathway ILCR for Adult

Distance	Depth (cm)	BaA	BbF	BKF	BaP	BghiP	DbA	Chr	IcdP	RI
Om	0-15	1.49E-9	3.975E-8	1.13E-7	1.20E-7	1.40E-8	1.25E-8	2.40E-9	2.0E-9	2.93E-7
	15-30	5.0E-10	1.35E-8	2.93E-8	1.30E-7	1.00E-9	5.0E-9	2.45E-9	1.33E-8	1.94E-7
	30-45	2.5E-10	1.475E-8	1.58E-8	1.40E-7	6.75E-9	1.75E-8	2.53E-9	7.49E-10	1.91E-7
50m	0-15	1.345E-7	1.24E-6	1.60E-6	6.23E-6	2.93E-7	1.32E-6	1.34E-7	7.95E-8	1.1E-5
	15-30	2.25E-9	2.75E-8	2.25E-7	2.50E-7	1.48E-9	1.20E-7	1.26E-7	1.10E-8	7.63E-7
	30-45	1.475E-8	2.54E-7	2.90E-7	3.75E-7	8.75E-8	1.70E-7	1.41E-8	1.70E-8	1.13E-6
100m	0-15	3.98E-7	2.01E-6	1.45E-6	3.80E-6	2.65E-9	4.75E-8	2.07E-8	5.30E-8	7.78E-6
	15-30	1.75E-9	1.34E-6	1.55E-6	5.78E-6	2.64E-8	2.40E-7	4.94E-8	1.45E-7	9.13E-6
	30-45	1.325E-8	1.24E-6	6.62E-7	1.48E-7	2.15E-9	1.35E-7	3.80E-8	1.40E-8	2.25E-6
200cm	0-15	5.0E-9	2.13E-8	3.84E-7	2.15E-7	2.78E-9	2.60E-6	5.08E-9	2.0E-9	3.24E-6
	15-30	3.25E-9	4.75E-8	2.8E-8	1.48E-7	6.25E-9	1.75E-8	2.23E-9	1.90E-8	2.66E-7
	30-45	3.0E-9	4.53E-8	3.75E-9	3.75E-8	1.31E-8	2.30E-7	3.70E-9	7.28E-8	4.09E-7

Table 4: Cancer risk of Ingestion pathway ILCR for Children

Distance	Depth (cm)	BaA	BbF	BKF	BaP	Bghip	DbA	Chr	IcdP	RI
Om	0-15	4.8E-9	1.27E-7	3.62E-7	3.84E-7	4.48E-9	4.00E-8	7.68E-9	6.40E-9	9.36E-7
	15-30	1.60E-9	4.32E-8	9.36E-8	4.16E-7	3.20E-10	1.60E-8	7.84E-9	4.24E-8	6.21E-7
	30-45	8.0E-10	4.72E-8	5.04E-8	4.48E-7	2.16E-9	5.60E-8	8.08E-9	2.40E-9	6.15E-7
50m	0-15	4.30E-7	3.92E-6	5.12E-6	1.99E-5	9.38E-8	4.23E-6	4.29E-7	2.54E-7	3.44E-5
	15-30	7.20E-9	8.79E-8	7.18E-7	8.00E-7	4.72E-9	3.84E-7	4.04E-7	3.52E-8	2.44E-6
	30-45	4.72E-8	8.13E-7	9.26E-7	1.20E-6	2.80E-8	5.44E-7	4.52E-8	5.44E-8	3.66E-6
100m	0-15	1.27E-6	6.44E-6	4.65E-6	1.22E-5	8.48E-9	1.52E-7	6.62E-8	1.69E-7	2.50E-5
	15-30	5.60E-9	4.30E-6	4.95E-6	1.85E-5	8.45E-8	7.68E-7	1.58E-7	4.62E-7	2.92E-5
	30-45	4.24E-8	3.96E-6	2.12E-6	4.72E-7	6.88E-9	4.32E-7	1.23E-7	4.48E-8	7.20E-6
200m	0-15	1.60E-8	6.80E-8	1.23E-6	6.88E-7	8.88E-9	8.32E-6	1.62E-8	6.40E-9	1.04E-5
	15-30	1.04E-8	1.52E-7	8.96E-8	4.72E-7	2.00E-9	5.60E-8	7.12E-9	6.08E-8	8.50E-7
	30-45	9.60E-9	1.45E-7	1.20E-8	1.20E-7	4.20E-8	7.36E-7	1.18E-8	2.33E-7	1.30E-6

Table 5: Cancer risk of Dermal Pathway ILCR for Adult

Distance	Depth (cm)	BaA	BbF	BKF	BaP	BghiP	DbA	Chr	IcdP	RI
Om	0-15	8.23E-10	2.18E-8	6.20E-8	6.59E-8	7.68E-10	6.86E-9	1.32E-9	1.10E-9	1.61E-7
	15-30	2.74E-10	7.41E-9	1.61E-8	7.14E-8	5.49E-11	2.74E-9	1.34E-9	7.27E-9	1.07E-7
	30-45	1.37E-10	8.10E-9	8.65E-9	7.68E-8	3.71E-10	9.61E-9	1.39E-9	4.12E-10	1.05E-7
50m	0-15	7.37E-8	6.81E-7	8.77E-7	3.42E-6	1.61E-8	7.26E-7	7.36E-8	1.89E-8	5.89E-6
	15-30	1.23E-9	1.51E-8	1.23E-7	1.37E-7	8.10E-10	6.59E-8	6.94E-8	6.04E-9	4.18E-7
	30-45	8.08E-9	1.39E-7	1.59E-7	2.06E-7	4.80E-9	9.33E-8	7.75E-9	9.33E-9	6.27E-7
100m	0-15	2.18E-7	1.10E-6	7.98E-7	2.09E-6	1.45E-9	2.61E-8	1.13E-8	2.91E-8	4.27E-6
	15-30	9.59E-10	7.37E-7	8.48E-7	3.17E-6	1.45E-8	1.32E-7	2.71E-8	7.93E-8	5.01E-6
	30-45	7.26E-9	6.80E-7	3.63E-7	8.10E-8	1.18E-9	7.41E-8	2.09E-8	7.68E-9	1.24E-6
200m	0-15	2.74E-9	1.17E-8	2.11E-7	1.18E-7	1.52E-9	1.43E-6	2.79E-9	1.10E-9	1.78E-6
	15-30	1.78E-9	2.61E-8	1.54E-8	8.10E-8	3.43E-10	9.61E-9	1.22E-9	1.04E-8	1.46E-7
	30-45	1.64E-9	2.48E-8	2.06E-9	2.06E-8	7.20E-9	1.26E-7	2.03E-9	3.99E-8	2.24E-7

Table 6: Cancer risk of Dermal Pathway ILCR for Children

Distance	Depth (cm)	BaA	BbF	BKF	BaP	BghiP	DbA	Chr	IcdP	RI
Om	0-15	1.48E-9	3.92E-8	1.12E-7	1.18E-7	1.38E-9	1.23E-8	2.37E-9	1.97E-9	2.89E-7
	15-30	4.94E-10	1.33E-8	2.89E-8	1.28E-7	9.87E-11	4.94E-9	2.42E-9	1.31E-8	1.91E-7
	30-45	2.47E-10	1.46E-8	1.55E-8	1.38E-7	1.38E-9	1.73E-8	2.49E-9	7.40E-10	1.90E-7
50m	0-15	1.33E-7	1.22E-6	1.58E-6	6.15E-6	2.89E-8	1.31E-6	1.32E-7	7.85E-8	1.06E-5
	15-30	2.22E-9	2.71E-8	2.22E-7	2.47E-7	1.46E-9	1.18E-7	1.25E-7	1.09E-8	7.54E-7
	30-45	1.99E-9	2.51E-7	2.86E-7	3.70E-7	8.64E-9	1.68E-7	1.39E-8	1.68E-8	1.12E-6
100m	0-15	3.93E-7	1.99E-6	1.44E-6	3.75E-6	2.62E-9	4.69E-8	2.04E-8	5.23E-8	7.70E-6
	15-30	1.73E-9	1.33E-6	1.53E-6	5.70E-6	2.61E-8	2.37E-7	4.88E-8	1.43E-7	9.02E-6
	30-45	1.31E-8	1.22E-6	6.54E-7	1.46E-7	2.12E-9	1.33E-7	3.75E-8	1.38E-8	2.22E-6
200m	0-15	4.94E-9	2.10E-8	3.79E-7	2.12E-7	2.74E-9	2.57E-6	5.01E-9	1.97E-9	3.20E-6
	15-30	3.12E-9	4.69E-8	2.76E-8	1.46E-7	6.17E-10	1.73E-8	2.20E-9	1.88E-8	2.63E-7
	30-45	2.96E-9	4.47E-8	3.70E-9	3.70E-8	1.30E-8	2.27E-7	3.65E-9	7.18E-8	4.04E-7

Conclusion

The present study of Umuerim soil samples revealed that out of 16 US Environmental Protection Agency (EPA) priority PAHs, 15 PAHs were detected at Umuerim refuse dumpsite. The order of carcinogenic PAHs concentrations in soil samples from Umuerim refuse dumpsite are as follows:

- Benzo(b)fluoranthene>Benzo(k)fluoranthene>Chrysene>Benzo(a)pyrene>Benzo(a)anthracene>Benzo(ghi)perylene>Dibenzo(a, h) anthracene>Indeno (1,2,3-c, d) pyrene.

The high-level concentration of PAH in the soil samples at various distances and depth might be as a result of nature and level of activities carried out around the study area. PAHs in soil contaminate underground water when leached into it, which might lead to pollution of nearby water bodies and aquatic ecosystem. It might cause great loss in aquatic lives such as fishes and other marine species which when consumed by human might lead to serious health effects. The incremental life cancer risk assessment was high for

benzo(a) pyrene for ingestion pathway for children when compared to other PAHs studied.

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