

Source Apportionment and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Black Carbon Monitored in Port Harcourt, Rivers State, Nigeria

Muhyideen Oloyede¹, Precious Nwobidi Ede²

¹Institute of Geoscience and Space Technology, Rivers State University, Port Harcourt, Nigeria

²Department of Geography and Environmental Management, Rivers State University, Port Harcourt, Nigeria

Abstract:- The purpose of this study was to determine concentrations of polycyclic aromatic hydrocarbons (PAHs) in air samples in Port Harcourt metropolis, Rivers State, Nigeria, evaluate their potential risks to human health and identify pollution sources by characterizing the PAHs. Sixteen polycyclic aromatic hydrocarbons were measured with a total concentration range of 0 to 9,589 mg/kg in the rainy season and 0.46 to 131mg/kg range in the dry season. High molecular weight PAHs dominated the PAH profiles accounting for 91% in dry season and 45% in the wet season. The overall assessment of the ratios of LMW to HMW of minimum, maximum and mean concentrations indicated pyrogenic sources. Benzo (a) pyrene equivalent (BaP_{eq}) analysis showed that benzo (a) pyrene, DiBenzo (a,h) anthracene and Indeno (1.2,3-cd) pyrene contributed the highest cancer toxicity with 94% and 85% in wet and dry seasons, respectively. The total incremental lifetime cancer risks of PAHs ranged from 0 to 4.90 with a median value of 3.37×10^{-2} in wet season; while in the dry season, ILCR of PAHs ranged from 1.62×10^{-5} to 7.42×10^{-3} with a median value of 1.15×10^{-3} . These values showed pervasive pollution indicating a major carcinogenic risk of PAHs. Mean ILCR in wet season was 3.37×10^{-2} ($33,700 \times 10^{-6}$) meaning 1 in every 30 persons in the study area is estimated to develop cancer. In the dry season, mean ILCR was 1.15×10^{-3} ($1,150 \times 10^{-6}$) meaning 1 in every 870 persons in the study area is estimated to develop cancer.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds containing two or more benzene rings bonded in linear, cluster, or angular arrangements (Abdel-Shafy & Mansour, 2016). There are hundreds of different PAH congeners but U.S. EPA selected 16 PAH congeners as "priority pollutants" (Nisbet & Lagoy, 1992; Kamal *et al.*, 2016). These 16 PAHs are selected as the priority pollutants due to their frequency or risk by the U.S. Environmental Protection Agency (USEPA, 1993). These environmental pollutants compounds are widely distributed in the air, water, and soil according to Honda and Suzuki (2020) who also hold that they are categorized as general environmentally harmful pollutants which according to Yang *et al.* (2014) are introduced into the environment from both natural sources like oil seeps, forest fires and volcanic activity; and anthropogenic sources like

petrochemical industrial effluents, coal tar processing wastes and combustion processes.

PAH is an important pollutant contained in black carbon that are widely studied due to possible cancer and non-cancer risks it poses to its receptors particularly human. As particulate soot they are formed after incomplete combustion of carbon containing materials according to Niranjana and Thakur (2017) who regarded it as unwanted powdery mass of fine black particles. Gas-phase soot contains polycyclic aromatic hydrocarbons (Omidvarborna *et al.*, 2015).

Port Harcourt, the largest city in Rivers State and other settlements in that region of Nigeria suffer severe exposure to air pollution due to various industrial and non-industrial operations and processes. A study showed that the impact of air pollution is highest on Port Harcourt among the 16 communities in the Niger Delta whose air samples were analysed (Ede & Edokpa, 2015). In addition, since November 2016, residents of Port Harcourt and its environs have been experiencing discernible soot emissions in the atmosphere. The aim of this research is to analyse the PAHs contents of the samples and determine the concentrations for two seasons; identify the potential sources of PAHs diagnostic ratio analysis; and assess the carcinogenic risks of the particulate soot in the study area.

II. MATERIALS AND METHODS

Previous study by Ede and Edokpa (2017) has shown that the soot seen in Port Harcourt comes from outside the metropolis and that it is uniformly propagated over the city. Five sampling locations evenly spread across the city were therefore used in this study and air samples were collected during the day and in the night. The Air Metrix Minivolt Active Sampler (SN 3018 ver 4.2 10/01/02 by Environ Technology Services PLC 13028) was used to suck soot directly on to filters. The soot collected onto the filter was analysed in the laboratory for 16 priority pollutant PAHs.

In week one and two, samples were collected in both day and night. In each of the 5 sampling locations (L1 to L5), four samples were taken after every 6 hours and a total of 20 samples taken for the wet season and the sampling procedure was repeated for dry season. Each of these 40 samples were analysed for 16 U.S. EPA priority PAHs. The PAHs are naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe),

anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo (k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo(a,h) anthracene (DBA), benzo(ghi)perylene (BghiP). The filter was treated with 10 ml of dichloromethane in a 2oz S/S Jar Amber bottle and agitated

automatically with Orbital Genie for an hour. Then the extract was concentrated to below 1 ml by exposing it under a fume hood above it to reduce loss of the semi-volatile PAHs due to evaporation and then brought back to 1.0ml. The final extract was analysed for the 16 pollutant PAHs above and calibration curve was plotted for each PAH thereafter.

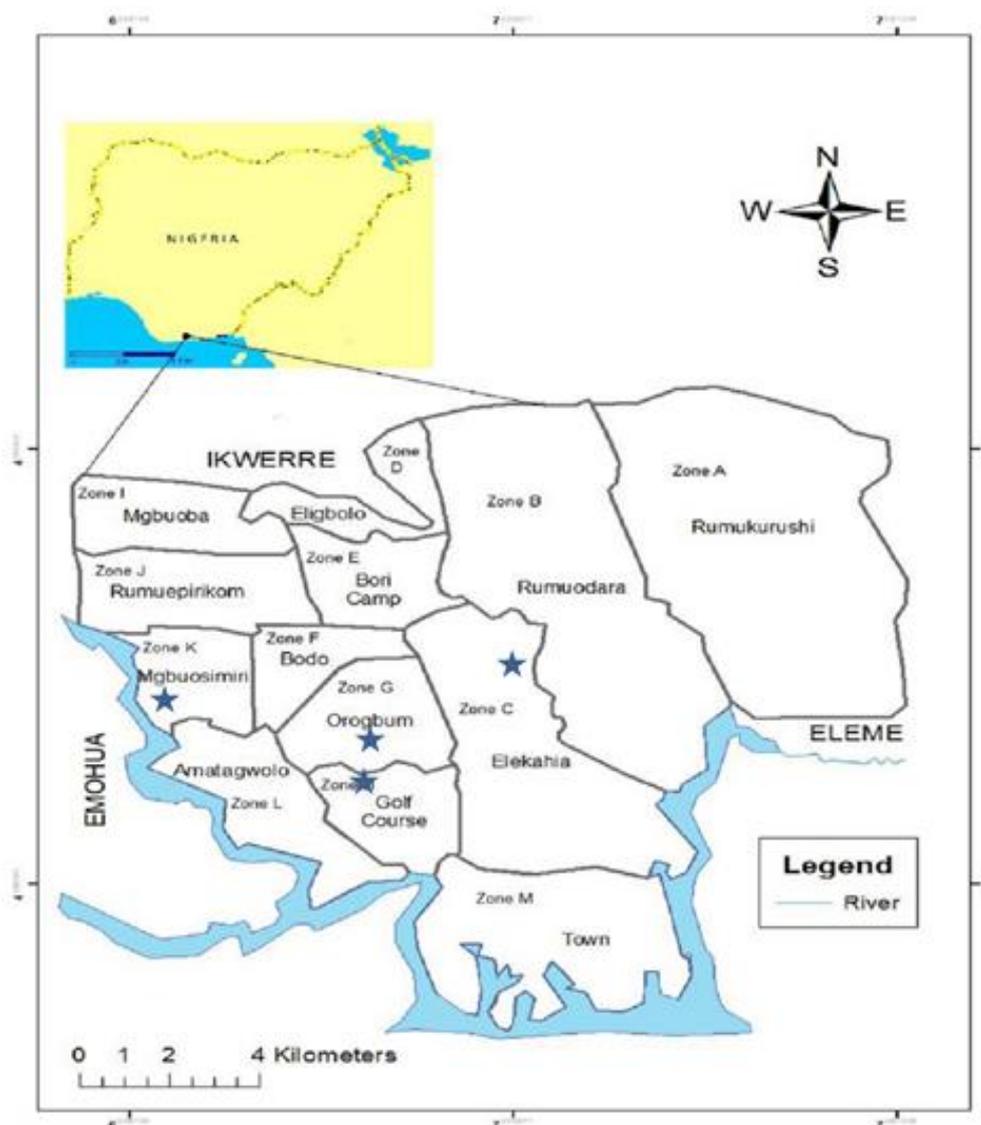


Fig 1:- Port Harcourt, Nigeria: showing the sampling locations Area

➤ PAH Diagnostic Ratios for Source Identification

PAH diagnostic ratios are commonly used as a tool for identification of PAHs emission sources. The concentration of different PAHs congeners depend on the source from which they are originated. The profile and composition of PAHs reflects the individual source of emission (Wang *et al.*, 2007). PAH diagnostic ratios therefore distinguishes petrogenic and pyrogenic sources of pollution. Also, the emission from petroleum products, petroleum combustion, biomass or coal burning can be distinguished by the diagnostic ratios of the following isomers anthracene & phenanthrene, and fluoranthene & pyrene in the combination $\text{Ant}/(\text{Ant} + \text{Phe})$ and $\text{Fla}/(\text{Fla} + \text{Pyr})$, respectively. The ratio $\text{Fla}/(\text{Fla} + \text{Pyr}) < 0.4$ indicates that the source of PAHs is from petroleum, the ratio between 0.4 and 0.5 implies fossil fuel combustion i.e., liquid fossil fuel, automobile emissions or crude oil. The ratio > 0.5 indicates grass, wood, coal combustion (De La Torre-Roche *et al.*, 2009). The $\text{Ant}/(\text{Phe} + \text{Ant}) < 0.1$ indicates petroleum emission source while the ratio > 0.1 indicates combustion (Pies *et al.*, 2008; Tobiszewski & Namiesnik, 2012).

PAHs (mg/kg)	Type	Wet Season			Dry Season		
		Minimum	Maximum	Mean	Minimum	Maximum	Mean
Naphthalene	LMW	0	2.66	0.74	0	1.1	0.15
Acenaphthylene	LMW	0	851.7	75.15	0	0.34	0.13
Acenaphthene	LMW	0	606.3	64.33	0.01	1.5	0.31
Flourene	LMW	0	957.9	116.55	0.02	1.57	0.47
Anthracene	LMW	0	1503	248.83	0.04	1.27	0.39
Phenanthrene	LMW	0	39.74	6.14	0.05	2.09	0.47
Flouranthene	HMW	0	184.5	10.76	0.04	1.14	0.39
Pyrene	HMW	0	707.2	69.45	0.04	1.24	0.42
Benz (a) antracene	HMW	0	207.5	26.94	0.08	4.17	0.97
Chrysene	HMW	0	43.82	4.31	0.01	6.98	1.32
Benzo (b) flouranthene	HMW	0	50.32	7.35	0.08	19.98	2.3
Benzo (k) flouranthene	HMW	0	35.73	6.71	0.05	19.4	2.73
Benzo (a) pyrene	HMW	0	69.81	5.52	0.04	12.78	1.92
DiBenzo (a,h) antracene	HMW	0	1522	100.17	0	6.43	1.02
Indeno (1.2.3-cd) pyrene	HMW	0	1653	118.58	0	37.47	6.8
Benzo (ghi) perylene	HMW	0	1154	71.71	0	13.71	2.33
LMW PAHs		0	3961.3	511.74	0.12	7.87	1.92
HMW PAHs		0	5627.88	421.5	0.34	123.3	20.2
Σ PAHs		0	9589.18	933.24	0.46	131.17	22.12
LMW/HMW			0.70	1.21	0.35	0.06	0.10

Table 1:- Concentrations of PAHs in the Particle Soot

LMW PAHs denote low molecular weight 2–3 ring PAHs; Nap, Acy, Ace, Flu, Ant and Phe.

HMW PAHs denote high molecular weight 4–6 ring PAHs; , Fla, Pyr, BaA, Chr, BbF,BkF, BaP, DahA, IcdP and BghiP.

High molecular weight PAHs dominated the PAH profiles accounting for 91% in dry season and 45% in the wet season. The overall assessment of the ratios of LMW to HMW of minimum, maximum and mean concentrations indicated pyrogenic sources.

➤ *Cancer Risk Assessment*

Total benzo (a) pyrene equivalent (BaPeq) of all the 16 PAHs was used in the cancer risk assessment. This is the summation of the product concentration and toxicity equivalent factor (TEF). Presently, over 2 million people live in Port Harcourt and are receptors of soot pollution. The incremental lifetime cancer risk (ILCR) was used to evaluate and calculate the potential risk of PAHs in the soot content of Port Harcourt air. The ILCRs for three pathways of exposures (ingestion, inhalation and dermal contact) were calculated using the following equations (Yang *et al.*, 2014).

• *Ingestion*

$$ILCR\ ing = \frac{C \times (CSF_{ing} \times \sqrt[3]{(BW/70)}) \times I_{Ring} \times EF \times ED \times CF}{BW \times AT} \tag{1}$$

• *Inhalation*

$$ILCR\ inh = \frac{C \times (CSF_{inh} \times \sqrt[3]{(BW/70)}) \times I_{Rinh} \times EF \times ED}{BW \times AT \times PEF} \tag{2}$$

• *Dermal Contact with Soot*

$$ILCR\ derm = \frac{C \times (CSF_{derm} \times \sqrt[3]{(BW/70)}) \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{BW \times AT \times PEF} \tag{3}$$

The total risk is given by the sum of risks of ILCRs from direct ingestion, inhalation and dermal contact.

$$Total\ ILCRs = ILCR\ ing + ILCR\ inh + ILCR\ derm \tag{4}$$

Where C is the PAH concentration of soot (mg/kg) used in calculating benzo (a) pyrene equivalent of each PAHs using their corresponding toxicity equivalent factor (TEF). The carcinogenic slope factor (CSF) measured in mg/ kg/ day was based on the cancer-causing ability of BaP: Cancer slope factor for the three main pathways of

exposure are CSFinhalation, CSFingestion and CSFDermal and of BaP were 3.85, 7.3 and 25 mg/kg/day, respectively. BW is body weight is 70kg; AT is average life span of 70 years (default); ED is the exposure duration 30 years and EF is exposure frequency 350 days per year. IRsoil is the soil intake rate which is 0.0001 kg/day; IRinh is the

inhalation rate which is 20 m³/day; SA is the dermal surface exposure is 5000 cm²/day, and cf is the conversion factor of 10⁶; AF is the dermal adherence factor (kg cm²²): 0.00001 kg/cm²; ABS is the dermal adsorption fraction of 0.1 and PEF is the soil dust produce factor of 1.32 x10⁹ m³/kg (USEPA, 1993; Wang *et al.*, 2007; Peng *et al.*, 2011).

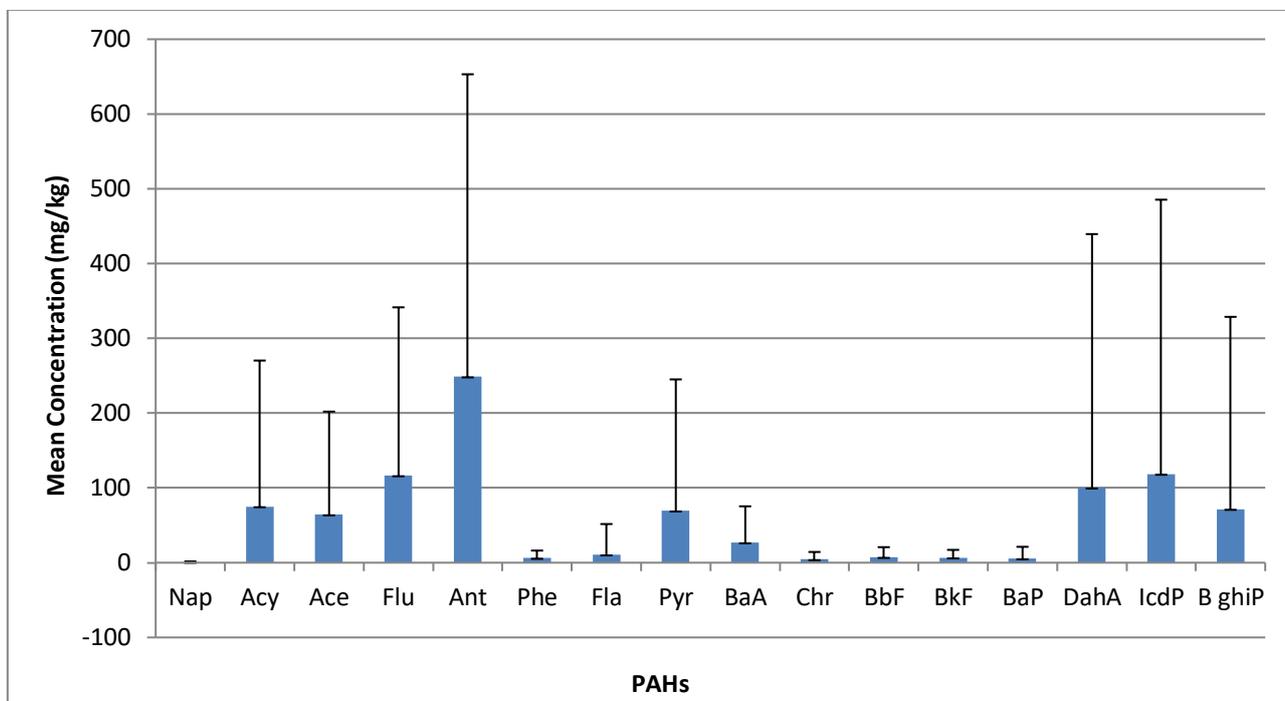


Fig 2:- Mean Concentrations of Individual PAHs in the Wet Season

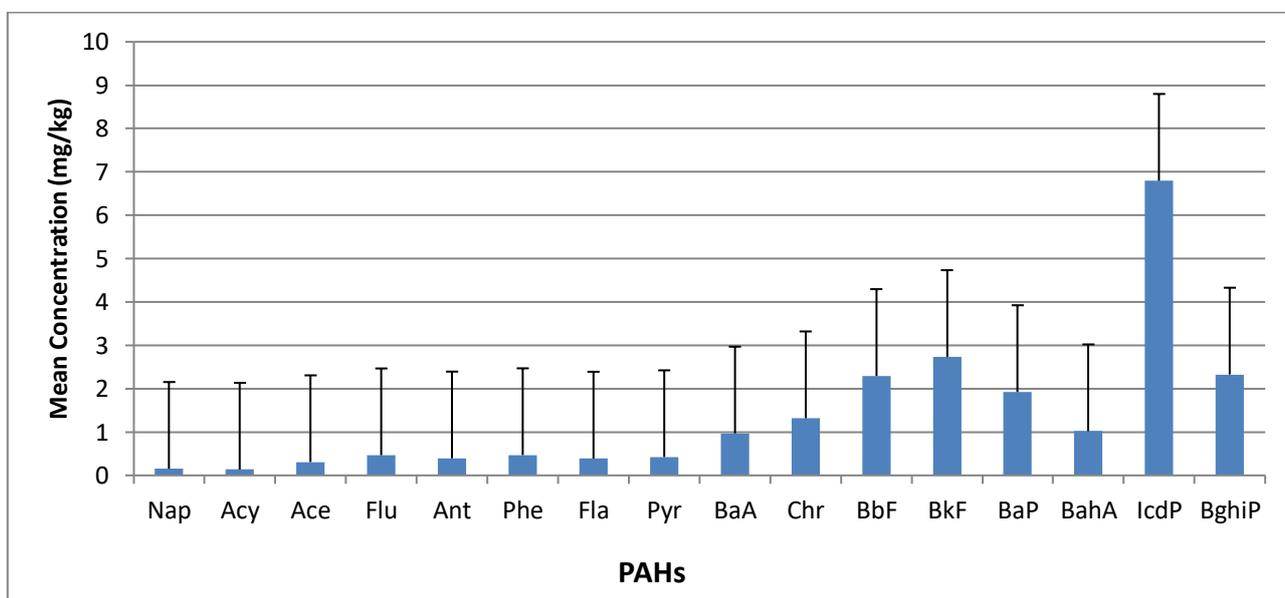


Fig 3:- Mean Concentrations of Individual PAHs in the Dry Season

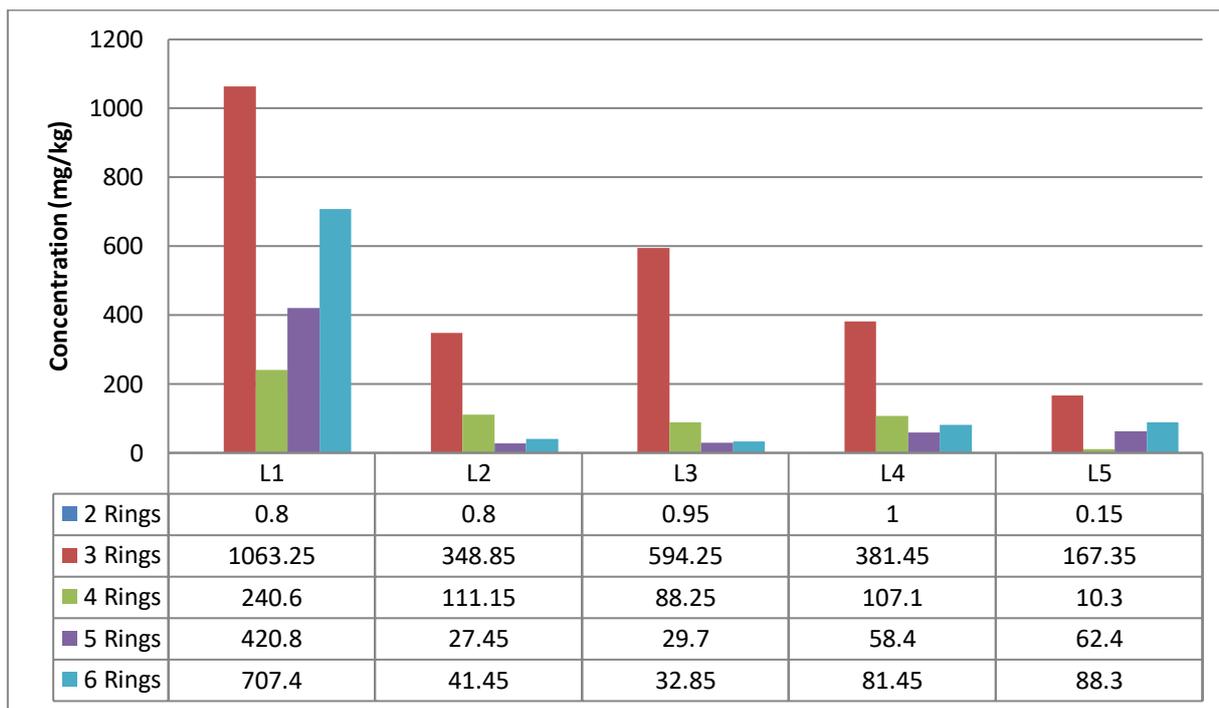


Fig 4:- Frequency Distribution of Different Ring PAHs in Wet Season

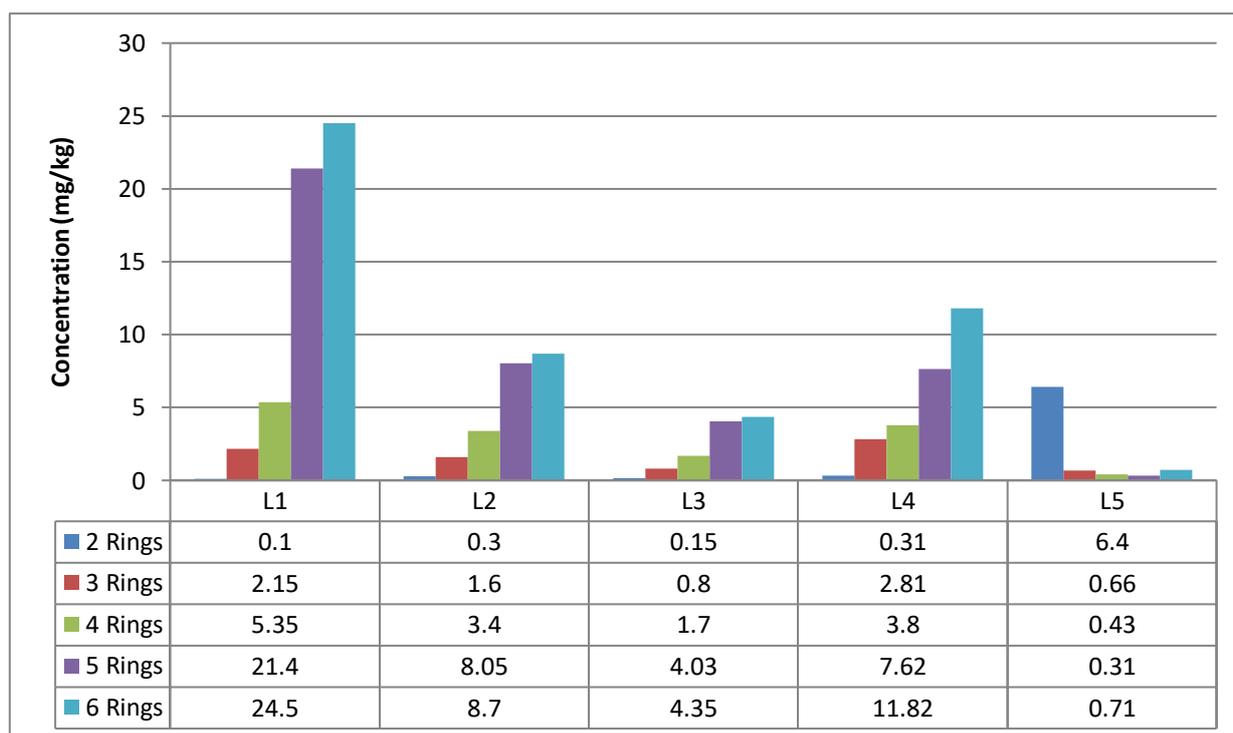


Fig 5:- Frequency Distribution of Different Ring PAHs in Dry Season

III. RESULTS AND DISCUSSION

➤ Seasonal PAH Profiles of Soot

The descriptive statistics for concentrations of PAHs determined in the soot in Port Harcourt is shown in Table 1. The overall total concentration of 16 US EPA priority pollutant PAHs in the atmospheric soot ranged from 0 to 5,589.18 mg/kg with a mean concentration of 933.24 mg/kg in wet season and from 0.46 to 131.17 mg/kg with a mean concentration of 22.12 mg/kg in the dry season.

Figures 1 and 2 showed the distribution of PAHs in the wet and dry seasons. While fluoranthene, anthracene, indeno (1,2,3-cd) pyrene and dibenzo (ah)anthracene were dominant in wet season with high concentration ($\geq 100\text{mg/kg}$), benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3-cd) pyrene and benzo (ghi) perylene were relatively higher in concentration ($\geq 2\text{mg/kg}$) than the remaining 11 PAHs in the dry season.

The concentrations of lower molecular weight PAHs (LMW, i.e., 2–3 ring PAHs) in the soot samples ranged from 0 to 3,961.3mg/kg with mean concentration of 511.74 mg/kg in the wet season while the concentrations of LMW PAHs in the dry season ranged from 0.12 to 7.87 mg/kg with mean concentration of 1.92 mg/kg. General assessment of the descriptive statistics showed that HMW PAHs were dominant in both the seasons. Maximum values in both the wet and dry seasons showed that HMW PAHs is higher and the HMW PAHs constituted 91% of total PAHs in the dry season with 45% of total PAHs in the wet season from pyrolytic sources and the rest from petroleum origin. The concentrations of higher molecular weight PAHs (HMW, 4–6 ring PAHs) in soils ranged from ND/0 to 5,627.88 mg/kg with a mean concentration of 421.5 mg/kg in the wet season while in the dry season the concentrations ranged from 0.34 to 123.3 mg/kg with a mean

concentration of 20.2 mg/kg. The concentrations of PAHs in wet season were higher than those in the dry season. The mean concentration of PAHs in the wet season is 42 times (in mg/kg) higher than the mean concentration in dry season.

Figures 3 and 4 showed that in the wet season the highest concentration of PAHs was found was 2,432.85 mg/kg with 3-ring PAHs accounted for 45% of this total value. Though the concentration in the dry season is relatively low compared to wet season, the highest in this dry season was still in the same location at 53.5 mg/kg concentration of which 6-ring PAHs accounted for 46% of this total. Implying that 3-ring PAHs were dominant in the wet season and 6-ring PAHs dominated the entire sampling sites in the dry season.

Islands and bays	Medium	Number of PAHs	Season/ Others	Range	Median/mean	Reference
Port Harcourt, Rivers State Nigeria	Air	16	Wet	0 – 9,589,180	933,240	This study
			Dry	460 -131,170	22,120	
Lagos Megacity, Nigerian	Dust		Industrial	545-10,785		<i>Iwegbue et al.</i> 2020
			Commercial	289 – 17,943		
			Residential	616 – 13,174		
Niger Delta of Nigeria	Soils	16	Σ16 PAH	188 - 684	N	<i>Iwegbue et al.</i> 2016
		7	ΣPAH _{7c}	28.5 - 571		
Guizhou, Southwest of China	Air	18	Indoor & Outdoor	0.0022- 0.0142	0.0068	<i>Yang et al.</i> , 2015
Vasilievsky, Russia	Soils	11		0.197–8.20	1.97	<i>Lodygin et al</i> 2008
Bermuda, Britain	Sediments	13		33.0–10200	1910/1070	Jones, 2011

N- No information; ΣPAH_{7c} carcinogenic PAHs

Table 2:- PAH concentrations in µg/kg in Different Media and places

Table 2 showed that the total PAHs concentrations in this study is much higher than those reported by *Iwegbue et al.* (2016) in Niger Delta of Nigeria soils and those obtained in indoor and outdoor air of Guizhou, Southwest of China by *Yang et al.* (2015). The minimum PAHs concentrations in dry season in this work were in the range similar to those reported by *Iwegbue et al.* (2020) in industrial, commercial and residential areas of Lagos. The total PAHs concentrations in soils and sediments of Vasilievsky, Russia and Bermuda, Britain are comparatively lower than the concentrations of PAHs in this study.

➤ *Potential Source of PAHs in the Study Area*

The molecular diagnostic ratios of PAHs are commonly used as a tool for the identification and characterization of PAHs emission sources and the profile and composition of the identified PAHs reflects the individual source of emission (*Yunker et al.*, 2002 and *Wang et al.*, 2007). PAHs can be from petrogenic or pyrogenic sources. Petrogenic PAHs are generally characterized by proportion of low molecular weight (LMW) while pyrogenic PAHs feature higher levels of high molecular weight (HMW) substance. The mass ratio of LMW/HMW has been widely introduced as a benchmark

for distinguishing petrogenic from pyrogenic PAH sources (*Socolo et al.*, 2000; *De Luca et al.*, 2005). The ratios of LMW/HMW higher than 1 indicates the petrogenic sources (petroleum emission) and the ratios of LMW/HMW lower than 1 indicates pyrogenic (e.g. petroleum combustion)

The LMW/HMW ratios in the wet season soot ranged from 0.43 to 4.68 with a mean value of 1.39. Seventy percent of the total samples had a ratio greater than 1, indicating existence of petrogenic sources of PAHs (Fig. 5). On the other hand, the ratios of LMW/HMW in the dry season samples ranged from 0.02 to 1.22 with a mean value of 0.39. Ninety percent of the total samples had a ratio less than 1, indicating existence of pyrogenic sources of PAHs (Fig. 6).

The results of the study showed that in the wet season, the value of the parent isomeric ratio Fla/(Fla + Pyr) were between 0.0 to 0.97 and the values of Ant/(Ant + Phe) were between 0.0 to 0.99 while in the dry season the values of the parent isomeric ratio Fla/(Fla + Pyr) were between 0.13 to 0.67 and the values of Ant/(Ant + Phe) were between 0.22 to 0.83. The cross plot of Fla/(Fla + Pyr) and Ant/(Ant + Phe) is as shown in Figure 7 indicates that the sources of PAHs in the soot during the wet season are four. The first

and second groups constitute 55% and 17% of the sampling sites depicted the characteristics of petroleum combustion i.e., crude oil, liquid fossil fuel and automobile combustion (Figs. 7A & 7B). The third group constituted 22% of the sampling sites with the characteristics of mixture both petroleum emission and combustion (Fig. 7C), while the remaining 6% for the fourth group (Fig. 7D) was of petroleum origin (petrogenic).

In the dry season, the cross plot of Fla/(Fla + Pyr) and Ant/(Ant + Phe) is as shown in Figure 8A indicated that the sources of PAHs in the soot exhibited the combustion origin with 82% grass, wood and coal combustion and the remaining 18% were of petroleum combustion (Fig. 8B). Therefore, the primary source of PAHs in Port Harcourt could be from biomass combustion.

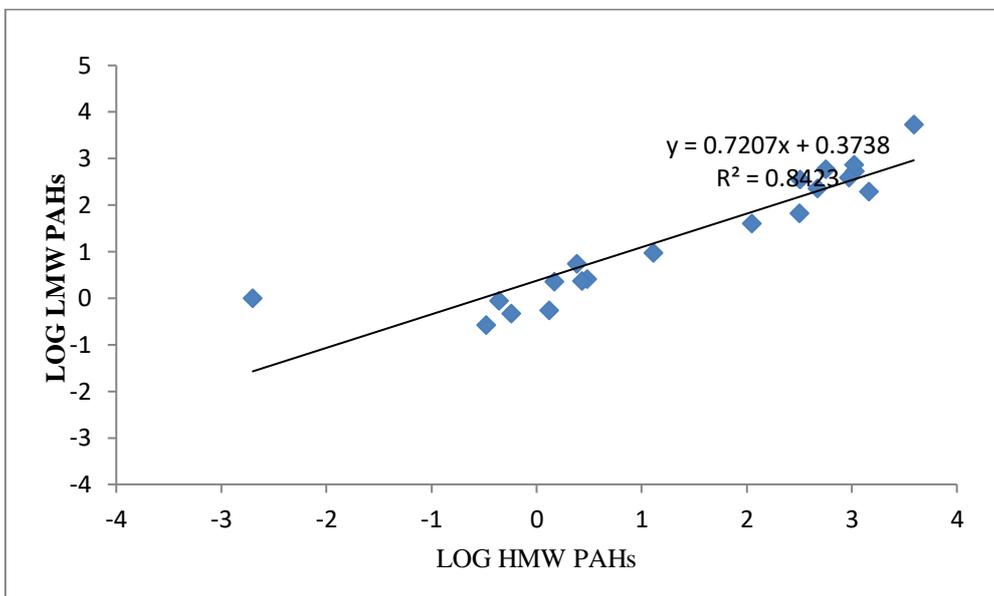


Fig 6:- The logarithmic plot of LMW and HMW PAH concentrations During Wet Season in Port Harcourt

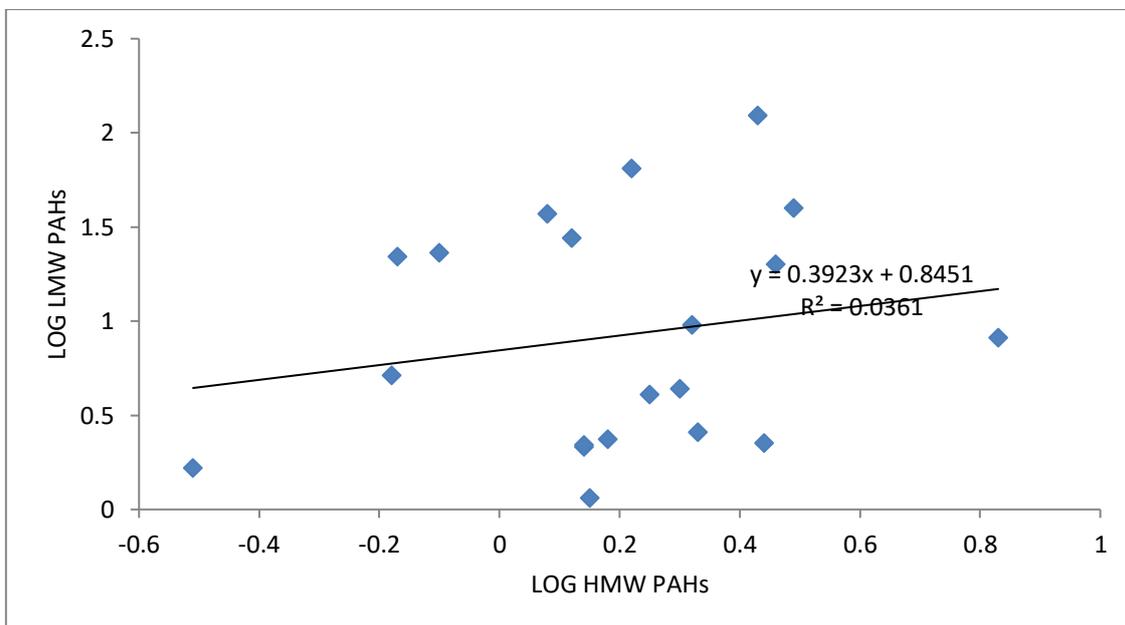


Fig 7:- The logarithmic Plot of LMW and HMW PAH Concentrations in the Dry Season

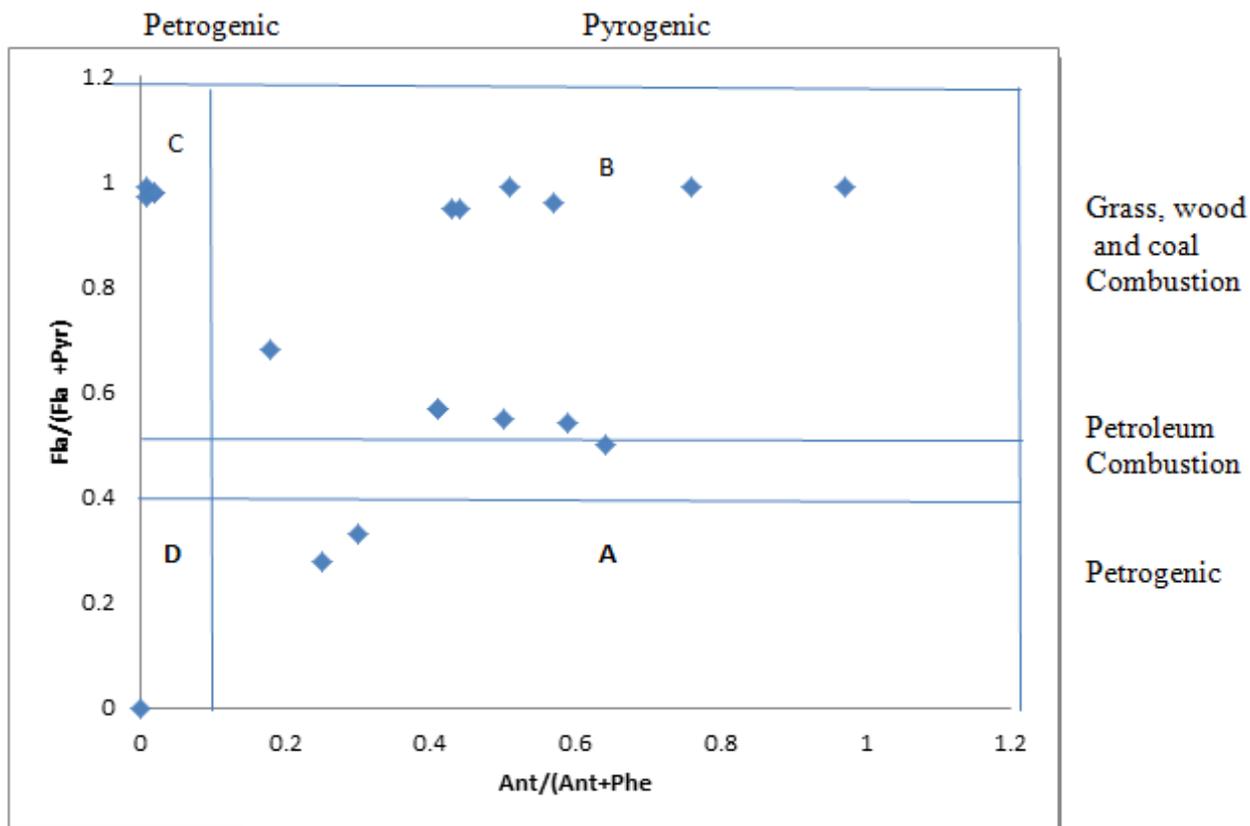


Fig 8:- Cross Plots for the Ratios of Fla/(Pyr+Fla) and Ant/(Phe+Ant) in the Wet Season
 Fla: fluoranthene; Pyr: pyrene; Ant: anthracene; Phe:phenanthrene

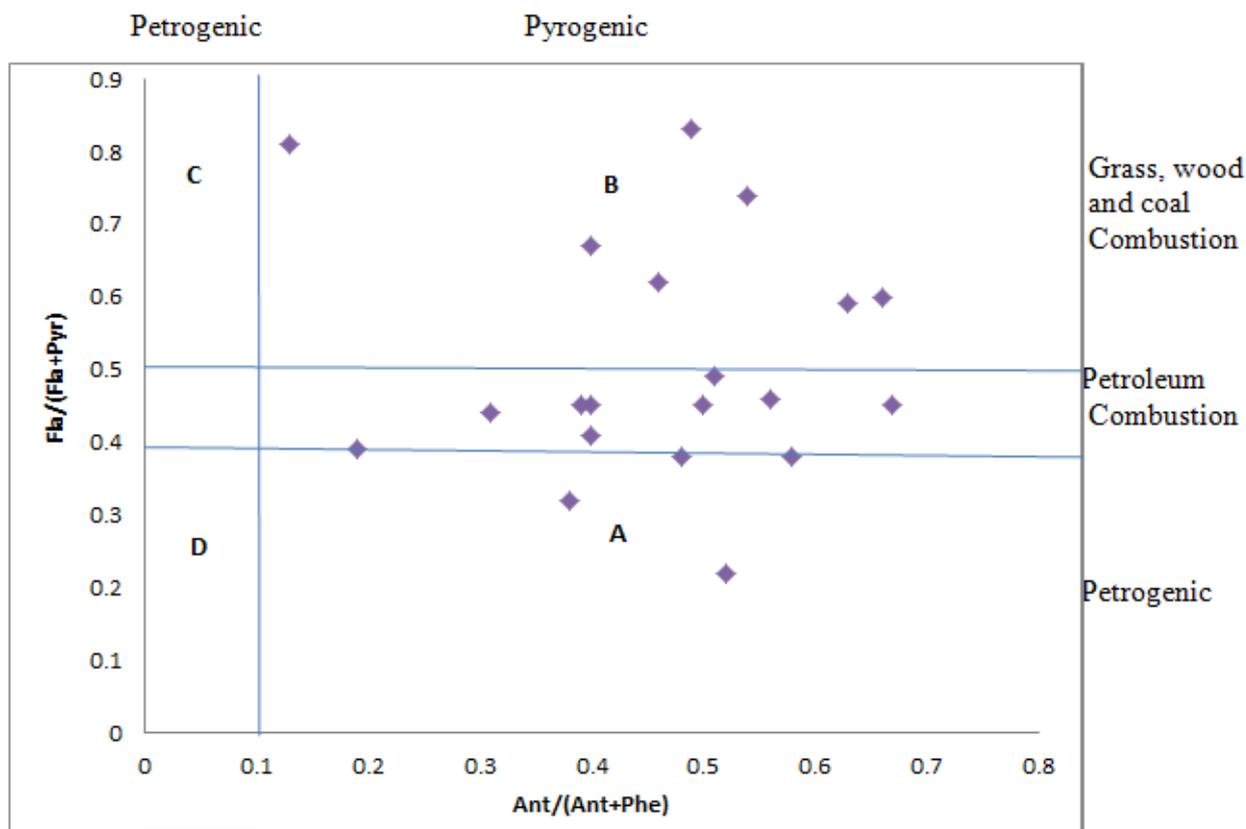


Fig 9:- Cross Plots for the Ratios of Fla/(Pyr+Fla) and Ant/(Phe+Ant) in the Dry Season
 Fla: fluoranthene; Pyr: pyrene; Ant: anthracene; Phe:phenanthrene

PAH	Type	TEF	Wet Season			Dry Season		
			Minimum	Maximum	Mean	Minimum	Maximum	Mean
Naphthalene	LMW	0.001	0	0.00	0.00	0.00	0.00	0.00
Acenaphthylene	LMW	0.001	0	0.85	0.08	0.00	0.00	0.00
Acenaphthene	LMW	0.001	0	0.61	0.06	0.00	0.00	0.00
Flourene	LMW	0.001	0	0.96	0.12	0.00	0.00	0.00
Anthracene	LMW	0.01	0	15.03	2.49	0.00	0.01	0.00
Phenanthrene	LMW	0.001	0	0.04	0.01	0.00	0.00	0.00
Flouranthene	HMW	0.001	0	0.18	0.01	0.00	0.00	0.00
Pyrene	HMW	0.001	0	0.71	0.07	0.00	0.00	0.00
Benz (a) antracene	HMW	0.1	0	20.75	2.69	0.01	0.42	0.10
Chrysene	HMW	0.01	0	0.44	0.04	0.00	0.07	0.01
Benzo (b) flouranthene	HMW	0.1	0	5.03	0.74	0.01	2.00	0.23
Benzo (k) flouranthene	HMW	0.1	0	3.57	0.67	0.01	1.94	0.27
Benzo (a) pyrene	HMW	1	0	69.81	5.52	0.04	12.78	1.92
DiBenzo (a,h) antracene	HMW	1	0	1522.00	100.17	0.00	6.43	1.02
Indeno (1.2.3-cd) pyrene	HMW	0.1	0	165.30	11.86	0.00	3.75	0.68
Benzo (ghi) perylene	HMW	0.01	0	11.54	0.72	0.00	0.14	0.02
ΣBaP _{eq}			0.00	1816.82	125.24	0.06	27.54	4.26
LMW			0.00	17.49	2.75	0.00	0.02	0.01
HMW			0.00	1799.33	122.49	0.06	27.52	4.26

Table 3:- Cancer toxicity expressed in Berms of Benzo (a) pyrene Equivalent

TEF denotes toxic equivalency factor [33]; BaPeq denotes Bap equivalent concentration. ND: not detected.

Benzo (a) pyrene, DiBenzo (a,h) antracene and indeno (1.2.3-cd) pyrene contributed the highest toxicity with 94% and 85% in wet and dry seasons, respectively.

	Wet season			Dry season		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Ingestion	0.00E+00	2.84E-03	1.96E-04	9.39E-08	4.31E-05	6.66E-06
Inhalation	0.00E+00	2.27E-07	1.56E-08	7.50E-12	3.44E-09	5.33E-10
Dermal contact	0.00E+00	4.87E-01	3.35E-02	1.61E-05	7.38E-03	1.14E-03
Total ILCRs	0.00E+00	4.90E-01	3.37E-02	1.62E-05	7.42E-03	1.15E-03

Table 4:- Descriptive Statistics of Seasonal Incremental Lifetime Cancer Risks (ILCR) Data in Soot PAHs in Port Harcourt

Mean ILCR in wet season 3.37×10^{-2} ($33,700 \times 10^{-6}$) meaning 1 in every 30 persons in the study area is estimated to develop cancer. In the dry season, mean ILCR is 1.15×10^{-3} ($1,150 \times 10^{-6}$) meaning 1 in every 870 persons in the study area is estimated to develop cancer.

➤ Cancer Risk Assessment in Port Harcourt

Total benzo (a) pyrene equivalent (BaP_{eq}) of all the 16 USEPA priority pollutant PAHs was used. This the addition of each PAH toxicity equivalent (TEQ) which in turn is the product of concentration of PAH and its toxicity equivalent factor (TEF).

The results of this study showed that the total benzo (a) pyrene equivalent (BaP_{eq}) of 16 PAHs in the samples of soot ranged from 0 to 1,816.52 mg/kg with the mean value of 125.24 mg/kg BaP_{eq} in the wet season while the total BaP_{eq} of 16 PAHs in the dry season were in the range of 0.06 and 27.54 mg/kg with the mean value of 4.26 mg/kg BaP_{eq}.

Out of the 16 PAHs, benzo (a) pyrene, dibenzo (a,h) anthracene and indeno (1,2,3-cd) pyrene contributed highest cancer toxicity. These three PAHs contributed 94% of the total toxicity with the highest of this from Dibenzo (a,h) anthracene. Similarly, in the dry season these three PAHs (BaP, DahA and IcdP) accounted for 85% of the cancer toxicity out of the 16 PAHs with the highest contribution from benzo (a) pyrene. Using benzo (a) pyrene (BaP) which is an established marker of PAHs in the atmosphere, there is a pervasive pollution of PAHs in the study area as mean and maximum BAP concentrations in the wet season were 5.52 mg/kg (1.5 ng/m^3) and 69.81 mg/kg (18.8 ng/m^3), respectively greater than European Union guideline target value of 1 ng/m^3 . Similarly, 20% of the samples in the dry season had BaP concentrations greater than this standard with maximum value of 12.78 mg/kg (3.5 ng/m^3) where the maximum values were recorded.

Incremental lifetime cancer risk (ILCR) is a numerical value calculated and used to assess human health risk. ILCR value greater than 10^{-6} indicates a potential risk i.e., receptors are unsafe from cancer due to the intake of contaminant under consideration. Table 4 shows the ILCR values calculated in the soot in Port Harcourt covering the three main exposure pathways which are inhalation, ingestion and dermal contact. The total ILCR values ranged from 0 to 4.9×10^{-1} with mean value of 3.37×10^{-2} in the wet season and the total ILCR values in the dry season ranged from 1.62×10^{-3} to 7.42×10^{-3} with mean value of 1.15×10^{-3} . These values ($> 10^{-6}$) indicate high human health risk of cancer from the exposure to soot emission in Port Harcourt. Similar, high ILCRs were also observed by Olawoyin *et al.* (2014) in the Niger delta water and soil. In their report, the cumulative ILCR from the water and soil contaminations were found to be 1.13×10^{-4} and 6.42×10^{-4} for children, while values of 1.09×10^{-4} and 6.19×10^{-4} were determined for adult.

These seasonal mean value of ILCRs of 3.37×10^{-2} and 1.15×10^{-3} for wet and dry seasons for estimated 33,700 and 1,150 persons per million to develop cancer. This further means that the mean ILCR in wet season 3.37×10^{-2} ($33,700 \times 10^{-6}$) implies 1 in every 30 persons in the study area was estimated to develop cancer. In the dry season, mean ILCR is 1.15×10^{-3} ($1,150 \times 10^{-6}$) meaning 1 in every 870 persons in the study area was estimated to develop cancer.

IV. CONCLUSIONS

The total PAHs concentrations ranged from 0 to 5,627.88 mg/kg with the mean value of 421.5 mg/kg in the wet season and PAHs concentrations ranged from 0.46 to 131.17 mg/kg with mean value of 22.12 mg/kg in the dry season. Wet season soot had a higher $\Sigma 16$ PAHs concentration than the concentration in the dry season. In these two seasons, the HMW PAHs are predominant with BaP, DahA and IcdP accounted for over 80% of the total PAHs in both seasons. The PAHs profile and diagnosis in the study area showed that the soot is primarily from pyrogenic source characterised with petroleum combustion i.e., crude oil, liquid fossil fuel, automobile and biomass combustion. A smaller proportion were attributed to petroleum emissions (petrogenic). High concentration of soot PAHs indicate pervasive pollution of the area coupled with high benzo (a) pyrene equivalent and benzo (a) pyrene concentrations higher than European Union (2001) guideline value of 1 ng/m^3 . The mean incremental lifetime cancer risks (ILCRs) of PAHs showed that people in the research area are exposed to high carcinogenic risk with probability of 1 incidence of cancer in every 30 persons in the wet season and 1 incidence of cancer in 870 persons in the dry season. The results of this study showed the need for management strategies to address, control and regulate the levels and sources of soot emissions in Port Harcourt. It has also provided information for all stakeholders including policy makers for improving the environment and human health.

REFERENCES

- [1]. Abdel-Shafy, H. I, & Mansour, S. M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*. Volume 25, Issue 1, Pages 107-123.
- [2]. De La Torre-Roche, R.J., Lee, W. Y. & Campos-Díaz, S.I. (2009). Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. *Journal of Hazardous Materials* 163, 946-958.
- [3]. Ede, P.N. & Edokpa, D.O. (2015). Regional Air Quality of the Nigeria's Niger Delta. *Open Journal of Air Pollution* 4, 7–15.
- [4]. Ede, P. N. & Edokpa, D. O. (2017). Satellite determination of particulate load over Port Harcourt during black soot incidents. *Journal of Atmospheric Pollution*. 5 (2).

- [5]. European Commission, 2001. Ambient air pollution by Polycyclic aromatic hydrocarbon (PAHs) Position paper. Office of Official publications of the European Communities, Luxembourg.
- [6]. Iwegbue, C. M. A., Obi, G., Aganbi, E., Ogala, J. E., Omo-Irabor, O. O. & Bice S. Martincigh. B. S. (2016). Concentrations and health risk assessment of Polycyclic aromatic hydrocarbons in Soils of an urban environment in the Niger Delta, Nigeria. *Toxicology and Environmental Health Sciences* volume 8, pages221–233.
- [7]. Iwegbue, C. M. A., Ehigbor, M. J., Tesi, G. O., Eguavoen, O. I. & Bice S. Martincigh, B. S. (2020). Occurrence, Sources and Exposure Risk of Polycyclic Aromatic Hydrocarbons (PAHs) in Street Dusts from the Nigerian Megacity, Lagos. <https://doi.org/10.1080/10406638.2020.1716027>.
- [8]. Jones, R. J. (2011). Spatial patterns of chemical contamination (metals, PAHs, PCBs, PCDDs/PCDFS) in sediments of a non-industrialized but densely populated coral atoll/small island state (Bermuda). *Marine Pollution Bulletin* 62: 1362–1376.
- [9]. Kamal, A., Syed, J. H., Li J., Zhang, G., Mahmood, A. and Malik, R. N. (2016). Profile of Atmospheric PAHs in Rawalpindi, Lahore and Gujranwala Districts of Punjab Province, Pakistan. *Aerosol and Air Quality Research*, 16: 1010–1021.
- [10]. Lodygin, E. D., Chukov, S. N., Beznosikov, V. A. and Gabov, D.N. (2008). Polycyclic aromatic hydrocarbons in soils of Vasilievsky Island (St. Petersburg). *Eurasian Soil Science* 41: 1321–1326.
- [11]. Niranjana and Thakur (2017). The Toxicological Mechanisms of Environmental Soot (Black Carbon) and Carbon Black: Focus on Oxidative Stress and Inflammatory Pathways. *Front Immunol.* 2017; 8: 763. doi: 10.3389/fimmu.2017.00763 PMID: PMC5492873. PMID: 28713383.
- [12]. Nisbet, C. and Lagoy, P. (1992). Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* 16: 290–300.
- [13]. Olawoyin, R., Grayson, R. L. and Okareh, O. T. (2012). Eco-toxicological and Epidemiological Assessment of Human Exposure to Polycyclic Aromatic Hydrocarbons in the Niger Delta, Nigeria. The Korean Society of Environmental Risk Assessment and Health Science and Springer. DOI 10.1007/s13530-012-0133-6.
- [14]. Omidvarborna, H., Kumar, A. and Shikim, D. (2015). Recent studies on soot modelling for diesel combustion, *Renewable and Sustainable Energy Reviews*. 48: 635-647.
- [15]. Peng C, Chen WP, Liao XL, Wang ME, Ouyang ZY, et al. (2011) Polycyclic aromatic hydrocarbons in urban soils of Beijing: Status, sources, distribution and potential risk. *Environmental Pollution* 159: 802–808.
- [16]. Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere* 72, 1594-1601.
- [17]. Tobiszewski, M. and Namiesnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162:110–119.
- [18]. USEPA (1993) Provisional Guidance for Quantitative Risk Assessment of PAHUS Environmental Protection Agency (1993) EPA/600/R-93/089.
- [19]. Wang Z, Chen JW, Qiao XL, Yang P, Tian FL, et al. (2007) Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: A case study in Dalian, China. *Chemosphere* 68: 965–971.
- [20]. Yang, Q., Chen, H. and Li, B. (2015). Polycyclic Aromatic Hydrocarbons (PAHs) in Indoor Dusts of Guizhou, Southwest of China: Status, Sources and Potential Human Health Risk. *PLoS ONE* 10(2): e0118141. doi:10.1371/journal.pone.0118141. Maosheng Yao, Peking University, CHINA.