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RESEARCH ARTICLE

POLYCYCLIC AROMATIC HYDROCARBONS LEVEL FROM HVAC IN BONNY ISLAND

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) were studied with the aim of investigating the compositional profile of particulate matters in offices and residential areas in Bonny metropolis. A Gas-chromatography Mass spectrometer was used to evaluate PAHs bound in dust retained in air-conditioning unit filters from office and residential buildings in Bonny metropolitan. The results obtained show that office and residential areas had average summation (PAHs) of 39.52 and 21.14 mg/kg, respectively. Acenaphthalene and naphthalene were the most common PAHs in Bonny Metropolis. In addition, the carcinogenic summation (PAH) from the Bonny office and residential areas was found to be 14.87 and 8.10 mg/kg, respectively. Bonny metropolis has a greater concentration of PAH hazardous pollutants. This could be attributable to the metropolis's intense industrial operations and uncontrolled activities coupled with continuous gas flaring which contributed significantly to the concentration of PAHs within Bonny metropolis. Thus, the government should enact and implement environmental restrictions that regulate industrial emissions in the city under study.

KEYWORDS

Pollution, Dust, Concentrations Ratios, Chromatography, Indoor Air Quality, Particulate Matter, Source Apportionment

1. INTRODUCTION

To improve the quality of life, humans have tampered with and attempted to control natural processes. Which has frequently had the opposite effect, causing human health to deteriorate and environmental equilibrium to be disrupted. Pollution is reaching alarming levels as more countries become industrialized and urbanized. Even in developing countries, public knowledge of the severity of polycyclic aromatic hydrocarbons poisoning has grown in recent decades. Pollution is defined as the release of undesired substances into the environment that harms and negatively influences a person and his surroundings (Tripathi et al., 2007). Polluted air contains one or more dangerous compounds, such as PAHs, which are particulate matter (EPHA, 2009).

Air pollution (both indoors and outdoors) is a well-known threat to human health, even at low levels, because it has been linked to a variety of negative effects on human health, including increased mortality and morbidity rates, as well as ecosystem damage, impacts on the built environment, and climate change (EEA, 2017; Oliveira et al., 2011). According to the World Health Organization (WHO), hazardous surroundings cause 12.6 million deaths worldwide, accounting for 23% of total global mortality and 26% of fatalities in children under the age of five (Landrigan et al., 2017). Some air pollutants have the ability to remain for long periods and accumulate in the environment and food chain, impacting humans and animals through several routes of exposure (inhalation, dermal, ingestion).

Air conditioning (AC) has grown increasingly significant in metropolitan areas, and it is now used in almost all homes for cooling, heating, or dehumidifying indoor spaces, as well as improving the quality of indoor air and assisting in the filtering of particulate pollutants (Yu et al., 2019; Ali et al., 2018). The exchange process is strongly linked to indoor and outdoor air quality, with indoor air being cleansed by AC filters as outdoor air is cycled into the dwelling (Yu et al., 2019). Dust particles make up the majority of the residue left behind by AC filters. Most people are aware that outdoor air pollution can harm their health, but they are less aware that indoor air pollution can have serious consequences (Manisalidis, 2020).

Other major contributors to the overall amount of dust are cement works, ferrous and non-ferrous industries, petrochemical industries, coal combustion, scrap metal recovery, and ceramic industries (Balabanova et al., 2012). Dust released into the atmosphere from industrial plants (especially smelters and refineries) and mines frequently contains large amounts of toxic metals, polycyclic aromatic hydrocarbons, and produces a huge amount of waste (Balabanova et al., 2012; Davis and Gulson, 2005). The rapid pace of industrialization is gradually contaminating and deteriorating the environment, and pollution levels are expected to rise to alarming levels in the coming years. PAHs are a major contaminant, and public concern about their harmful consequences has risen rapidly as evidence of their toxicity, carcinogenicity, and teratogenicity has emerged. Among the PAHs, benzo(a)pyrene (BaP) has the highest carcinogenic potential (Pongpiachan et al., 2013).

PAHs (polycyclic aromatic hydrocarbons) are aromatic hydrocarbons containing two or more fused benzene rings arranged in different structural configurations (linearly, angularly, or in clusters) (Loganathan et al., 2014; Ong et al., 2007). PAHs with up to four rings are known as light PAHs, whereas those with more than four rings are known as heavy PAHs. Light PAHs are less stable and hazardous than heavy PAHs (Wang et al., 2017). For the qualitative determination of PAH sources, concentration ratios of specific pairings of PAHs are commonly used. PAHs molecular diagnostic ratios are routinely employed to determine PAHs

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concentrations in air, soils, and sediments. The use of PAH diagnostic ratios by environmental researchers for the detection of PAH pollutant emission sources has been evaluated (Teng et al., 2012; Sun and Zang 2013; Rajpara et al., 2017; Xing et al., 2016).

The ratios apply to PAHs found in many environmental media, including air (gas + particle phase), water, sediment, soil, and biomonitor organisms like leaves or pine needles, as well as mussels. Several investigations have found that diagnostic ratios fluctuate in value to varying degrees as phase transitions and environmental deterioration occur. A number of health issues (including an increased risk of skin, lung, bladder, and gastrointestinal malignancies) have been documented in workers exposed to combinations of PAHs compounds, including BaP and Pyrene, which have been linked to cancer in experimental animals (Armstrong et al., 2004; Diggs et al., 2011). Due to the continual addition of harmful compounds into the environment, scientific experts have identified the need for ongoing monitoring of environmental safety. PAHs are easily adsorbed through condensation and nucleation. And thus, are intercepted by the A-C filter with the continuous circulation of air and thus accumulate in the dust of the filter.

This study location has been reported to be heavily polluted, as evidenced by the considerable amount of soot present. Report from a high proportion of HPAH in river sediments (Ihunwo and Ibezim-Ezeani, 2021). A further report from Port Harcourt and Lagos attest to high-level PAHs pollution in water and sediment, but investigation of the chemical composition of air quality in offices/residential areas has not been explored thus is the originality of this research (Oloyede and Ede, 2020; Iwegbue et al., 2020). Even indoor activities and the nature of air available within offices and residential areas, the chemical makeup of particle air pollutants in the research region has not been investigated. However, there are numerous sampling methodologies for evaluating interior air quality that represent the effect of air pollution exposure. As a result, the dust collected on HVAC filters should provide information on the research area's indoor air quality, and the study's goal was to determine PAHs from air-conditioning dust in offices and residential areas in Bonny Island.

2. METHODOLOGY

2.1 Study of the Area

The study area is Bonny local governments area in Rivers State due to the heavy presence of multinational companies operation. Bonny Island lies about 40 kilometers south of Port Harcourt. It is the administrative headquarters of Bonny Local Government Areas in Rivers State (Figures 1). With latitudes 4°52'N and 5°02'N, and longitudes 6°56'E and 7°04'E, with a population of 270,000 people (NPC, 2006). The Island has a rather flat topography, with an elevation of 3.05 atmospheric mean sea level and a total land area of 214.52m^2, with tidal floods and land subsidence affecting around 70% of its size (NLNG, 2005). Ibani is the local language on Bonny Island. The island is directly connected to the Atlantic Ocean, where giant oil tankers export crude oil. According to previous studies, the seasonal fluctuation of rainfall in the Niger Delta ranges from 2301 to 3670 mm during the wet season (March to November) and 43 to 97 mm during the dry season (December to March) (Adejuwon, 2012).

2.2 Samples Collection, Extraction and Analysis

Dust samples from HVAC units are collected in two categories (office locations and residential locations), Three samples within an office location are mixed to form one sample, office location 1 (Federal Polytechnic of Oil and Gas Bonny) and location 2 (Nigeria Liquefied Natural Gas site) making up a total number of two composite samples for office area. And three different strategic locations for residential areas (as shown in table 1 below) were brushed into an airtight Polyethylene bag, and sealed, the samples were carried to Deslog Energy services located behind shell gate at old Aba road for analysis and stored at temperatures below 4°C for a maximum of 7 days before extraction and 40 days following extraction before analysis. Into a dried organic free and chromic acid pre-cleaned extraction vial, ten grams (10g) of the sample was carefully weighed, and ten grams (10g) of anhydrous Sodium Sulphate was added and stirred. A glass rod was used to thoroughly stir 30ml of Dichloromethane into the mixture. For 30 minutes, the sample was shaken at 500 revolutions per minute in an organic flask shaker.

Table 1: Bonny Island Sample Location with Coordinate

S/N	Sample Code	Name of Location	Gps Coordinate	
			Latitude	Longitude
1	Offices	N-Site	N4°30′20.812″	E7°12′12.477″
2		FPOG	4.423308	7.1997285
3	Residential	Cable Road	N4°27′31.09212″	E7°10′20.856″
4		Water Well 6	N4°25′23.90772″	E7°12′0.747′′
5		Oguede	4.4328192	7.1997385

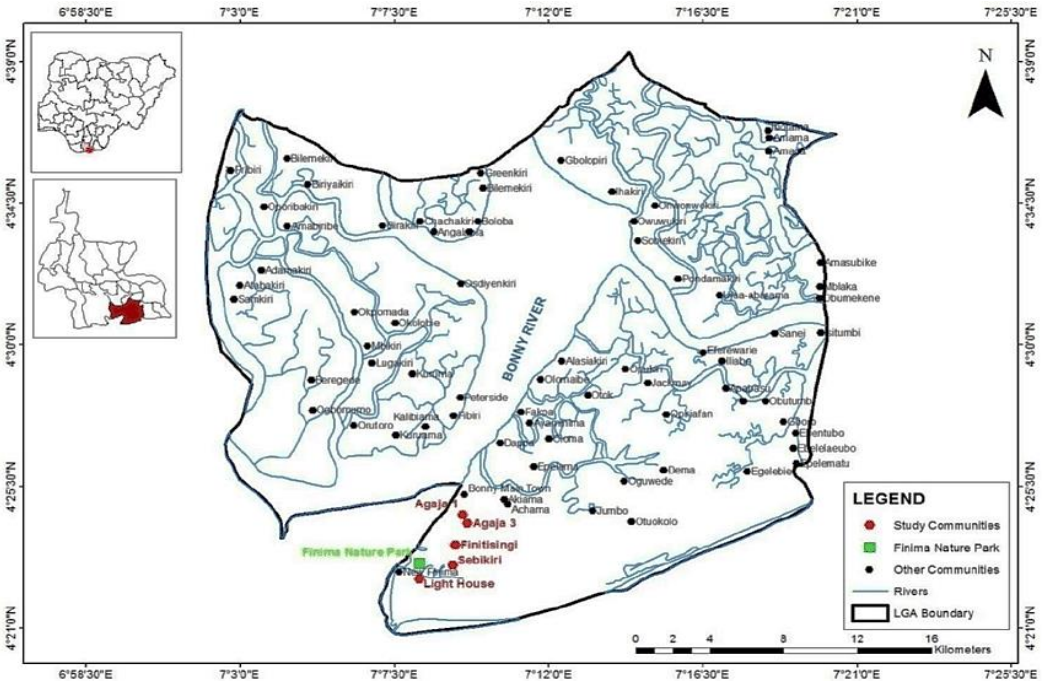

Figure 1: Mapping of Sampling Locations within Bonny Metropolis

The extract was filtered, and the filtrate was left in the extraction bottle for a minimum of 24 hours at laboratory room temperature to concentrate until about 2ml of the concentrated sample was left in the extraction bottle for separation into aliphatic and aromatic fractions using Dichloromethane and n-Hexane, respectively. The aromatic fraction was concentrated to approximately 1.0ml using rotary evaporators and stored in dried organic free and chromic acid pre-cleaned glass vials with Teflon rubber caps and kept refrigerated at -4°C until analysis. The standard reference method (figure 2) for PAH analysis was EPA8015-GC/MS, which was prepared by the manufacturer.

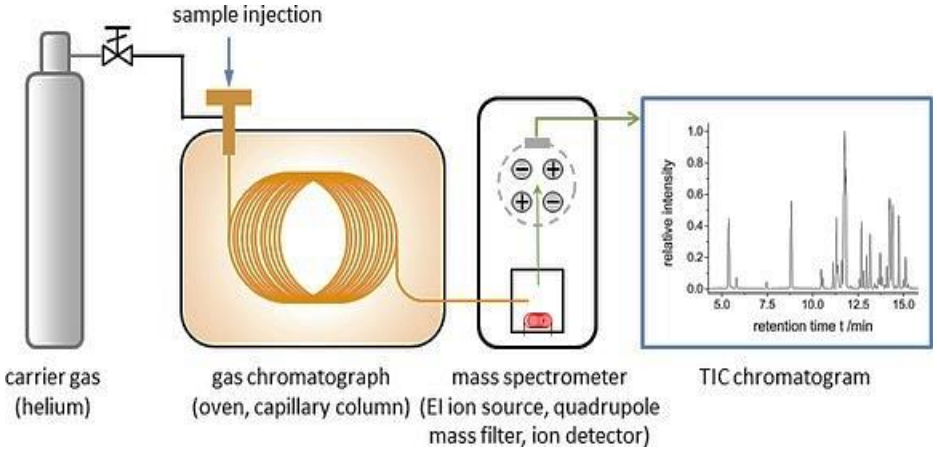

Figure 2: The principle of GC/MS Instrumentation (Jones, 2019).

2.3 Statistical Analysis

It involves Summation, mean and standard deviation using Microsoft excel 2016, Statistical Package for Social Sciences (SPSS). Pearson's correlation and Paired Sample T-test were conducted to study the significance of principal components across the sampling locations. In all cases, the level of significance was taken to be p <0.05.

3. Result and Discussion

Table 2 shows the quantity of polycyclic aromatic hydrocarbons in HVAC filter dust collected from the office and residential sampling sites in the Bonny metropolitan using a Gas Chromatography-Mass Spectrometer. The concentrations are presented as mean and standard deviation in mg/kg.

Table 2: Polycyclic Aromatic Hydrocarbon (PAH) Content Concentration of HVAC Filter Dust Particulate in Bonny metropolis

PAH Components	No of Rings	PAH Concentration (mg/kg)	
		Office	Residential
Naphthalene	2	4.276 ± 0.129	2.791 ± 0.332
Acenaphthalene	3	4.223 ± 0.098	4.481 ± 1.682
Acenaphthene	3	4.064 ±0.160	3.104 ± 0.06
Flourene	3	ND	6.661 ±0.000
Phenanthrene	3	4.303 ± 0.237	3.00 ± 0.05
Anthracene	3	3.974 ± 0.140	2.457 ± 0.015
Floureanthene	4	ND	ND
Pyrene	4	3.819 ± 0.204	2.199 ± 0.039
Benzo (a) Anthrocene	4	4.076 ± 0.214	2.664 ± 0.034
Chrysene	4	3.498 ± 0.144	2.239 ± 0.005
Benzo (b) flouranthene	5	3.645 ± 0.309	1.538 ± 0.014
Benzo (k) flouranthene	5	3.650 ± 0.292	1.663 ± 0.012
Benzo (a) pyrene	5	ND	ND
Indo (1,2,3-cd) pyrene	6	ND	ND
Benzo (g,h,I) perylene	6	ND	ND
∑PAH		**38.224**	**32.801**
∑PAH carc.		14.869	8.104
∑COMB		18.687	10.303
∑LPAH		20.84	22.499
∑HPAH		18.687	10.303

ND – Not Detected

The sources and dispersion of polycyclic aromatic hydrocarbons were identified by GC-MS analysis of filter dust in Bonny Island. About 7-11 PAHs compounds were discovered in these samples. Total PAHs readings ranged from 32.801 to 38.224 mg/kg at several sampling locations, with the following order of magnitude: Bonny Residential > Bonny Office. The overall PAH in the study area was higher than in a previous Lagos report (Iwegbue et al., 2020). As a result, the result displays pollutant levels at various sampling locations as well as the influence of various PAHs emissions sources in the research area.

Naphthalene was found in high concentrations in all of the samples. According to Naphthalene is the most abundant and water-soluble PAH in the environment (Ihunwo and Ibezim-Ezeani, 2021). It is also the most basic PAHs created from coal tar through the crystallization and distillation processes (Phale et al., 2019). However, ongoing industrial and exploration activity, as well as continual gas flaring from multinational petroleum corporations like NLNG, Shell, and Mobil, have greatly contributed to the accumulation of PAHs within the Bonny metropolis. The findings in this study are consistent with PAHs results reported in oil exploration settlements (Qi et al., 2014; Shen et al., 2020).

In this study, the fraction of LPAH was found to be higher than that of HPAH. This finding is consistent with previous research (Ihunwo and Ibezim-Ezeani, 2021), although it contradicts the results of river sediments (Ihunwo et al., 2019). Low molecular weight PAHs are volatile and typically come from diagenetic sources, whereas high molecular weight PAHs come from pyrogenic sources. The prevalence of LPAH implies recent contamination or direct PAH input from sources such as air deposition, both dry and wet. Through condensation and nucleation, these PAHs are easily adsorbed on the surface of particulate matter. As a result of the continual circulation of air, the PAHs are collected by the A-C filter and accumulate in the filter dust.

Table 3: PAH Ratio of HVAC Filter Dust from Bonny Metropolis

PAH ratio	Bonny Office	Bonny Residential	Value range	Source	Reference
ΣPAHs/ΣPAH carc.	2.571	4.048			
LPAH/HPAH	1.115	2.184	< 1 > 1	Pyrogenic Petrogenic	Zhang et al., 2008
∑COMB/∑PAHs	0.473	0.314	~ 1	Combustion	Ravindra et al., 2008a
PHE/ANT	1.083	1.221	>10 <10	Petrogenic Pyrogenic	Budzinski et al. 1997
FL/(FL + PYR)	0	0.7518	< 0.5 > 0.5	Petrol emissions Diesel emissions	Ravindra et al., 2008b
ANT/(ANT + PHE)	0.480	0.450	< 0.1 > 0.1	Petrogenic Pyrogenic	Pies et al., 2008
FLA/(FLA + PYR)	0.000	0.000	<0.4 0.4 - 0.5 >0.5	Petrogenic Fossil fuel combustion Grass, wood, coal	De La Torre-Roche et al., 2009
BaA/(BaA + CHR)	0.538	0.543	<0.2 0.2 - 0.35 > 0.35	Petrogenic Coal Combustion and Vehicular emissions	Akyüz and Çabuk, 2010 Yunker et al., 2002
BaP/(BaP + BeP)	0.000	0.000	< 0.2 > 0.35 ~ 0.5 < 0.5	Petrogenic Combustion Fresh particles Photolysis (aging of particles)	Oliveira et al., 2011
IcdP/(IcdP + BghiP)	0.000	0.000	< 0.2 0.2 - 0.5 > 0.5	Petrogenic Petroleum combustion Grass, wood, and coal combustion	Yunker et al., 2002
BbF/BkF	0.472	0.355	2.5 - 2.9	Aluminum smelter emissions	
BaP/BghiP	0.000	0.000	< 0.6 > 0.6	Non-traffic emissions Traffic emissions	Katsoyiannis et al., 2007

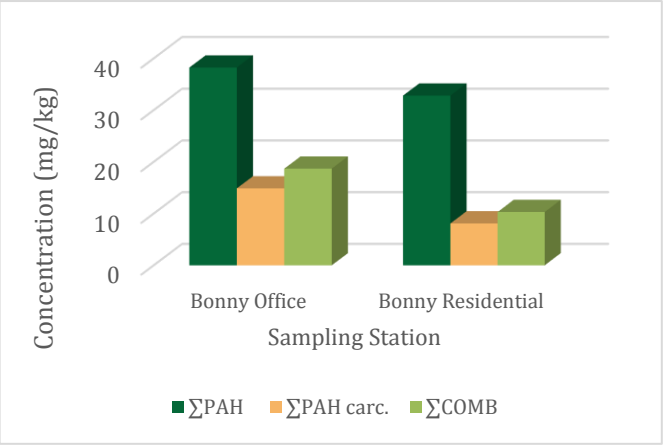

Figure 3: Total PAHs, Carcinogenic PAHs and Combustion PAHs

The graphical representation of the total PAHs concentration, combustion-related PAH, and carcinogenic PAHs are shown in Figure 3 above.

Among the PAHs, seven chemicals are probably human carcinogens which are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene (USEPA, 1994). The sums of the carcinogenic PAHs (ΣPAH carc.) are also presented in Table 1. However, studies of individual PAHs in their complex mixtures have shown that individual PAHs interact metabolically in a plethora of ways resulting in additive, synergistic or antagonistic effects to cause its tumorigenic actions (Montizaan, 1989). Thus, PAHs with four rings or more have been presumably used in the prediction of the tumorigenic potency of a number of emission condensates such as in dust particulates. Adverse haematological effects have been reported arising from the injection of PAHs in earlier research (Anselstetter and Hempel, 1986). Data from animal studies indicate that several PAHs may induce several adverse effects including immunotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity, and may also influence somatic mutation in the development of atherosclerosis (IARC, 1983; Wakabayashi, 1990).

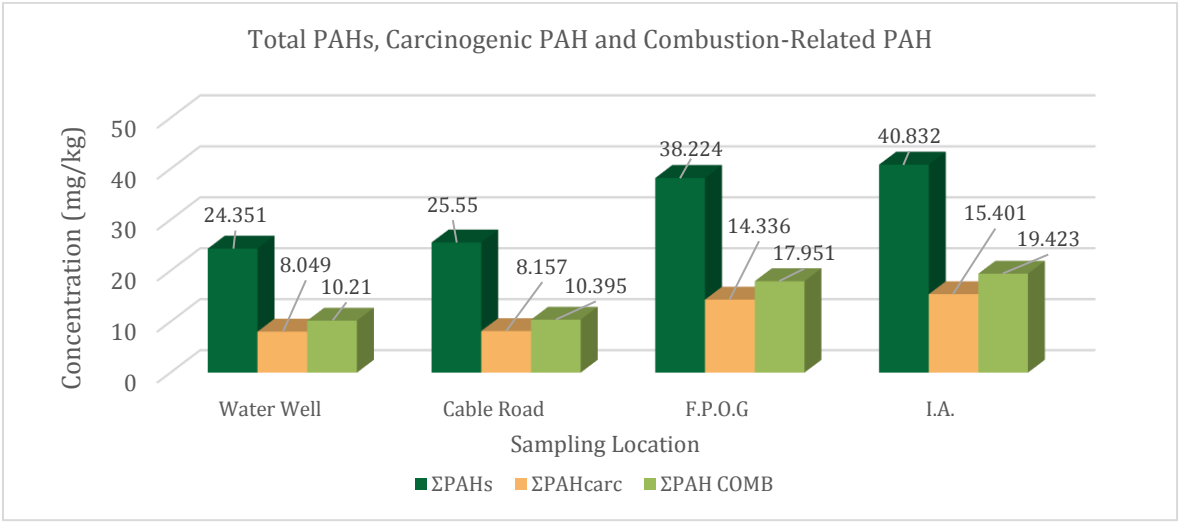

Figure 4: Summative Chart of PAH Constituent

Furthermore, combustion-related PAHs (COM) were observed to range between 0.233-18.687 mg/kg. It depicts the emission level of combustion-related industrial activities around the sampling location. Thus, a high percentage of combustion-related PAHs indicates the pyrogenic sourcing of PAHs as observed in the Bonny metropolis.

Table 4: Diagnostic PAHs Ratio of Filter Dust Bonny

PAHs Ratio	Water Well	Cable Road	F.P.O.G	Industrial Area	Value & Source	REF.
LPAH/HPAH	1.385	1.458	1.129	1.102	<1 Pyrogenic >1 Petrogenic	Zhang et al., 2008
ΣPAHcarc/ΣPAH	0.331	0.319	0.375	0.377		
ΣPAHcomb/ΣPAH	0.419	0.407	0.470	0.476		
PHE/ANT	1.210	1.236	1.061	1.104	>10 Petrogenic <10 Pyrogenic	Budzinski et al. (1997)
ANT/(ANT + PHE)	0.453	0.447	0.485	0.475	<0.1 Petrogenic >0.1 Pyrogenic	Pies et al., 2008
BaA/(BaA + CHR)	0.539	0.547	0.561	0.515	<0.2 Petrogenic >0.35 Combustion and Vehicular Emission	Akyüz and Çabuk, 2010
BbF/BkF	0.922	0.927	0.994	1.003		

The LPAH/HPAH ranged from 1.115-2.184 which were greater than 1 in all the sampling locations and PAHs could be attributed to sources of the petrogenic origin (Kerebba et al., 2017; Ravindra et al., 2008). However, Bonny metropolis has a relatively low LPAH/HPAH ratio owing to the negating influence of Pyrogenic activities taking place in the Industrial Area of the metropolis. Flt/(Flt+Pyr) ranged from 0.0-0.7518 which depicts emission of high molecular weight petroleum product (Ravindra et al., 2008b), Ant/(Ant+Phe) in Bonny was greater than 0.1 which also implied that PAHs had Pyrogenic sources.

Studies have identified the use of PAHs ratio in determining the source, distribution, and effect of PAHs which aids deductions from PAHs analyses (Costa and Sauer, 2005; Kerebba et al., 2017). Table 3 represents the calculated PAHs ratio of filter dust in the Bonny metropolis. The ratios obtained were subsequently used in the evaluation of dust particulate matter. The lowest ratio was observed for the Bonny Office location, thus having the highest carcinogen impact on humans within its densely concentrated environment when compared with the residential area. Diagnostic ratios (Table 4) are used to distinguish the originating sources of PAHs (Kerebba et al., 2017). PAHs have similar physicochemical and stability properties in the environment having the same molar mass, aqueous solubilities, and octanol-water partition coefficient.

Thus, the use of paired PAHs as a diagnostic source ratio suggests that PAHs with similar properties typically retain the same relative concentration in residues as in their sources (Kerebba et al., 2017). Earlier research has used these ratios to predict the sources of PAHs since they are highly consistent (Yunker et al., 2002; Kerebba et al., 2017). In this study, the calculated ratio include Phe/Ant, Flt/(Flt+Pyr), Ant/(Ant+Phe), IcP/(IcP+BgP), BaA/(BaA+Chr) and LPAHs/ HPAHs. Sampling from Bonny metropolis had a significantly high ratio. It implied that significantly high combustion-related activities take place within Bonny metropolis as evident in its continuous gas flaring activities in the petrochemical industries.

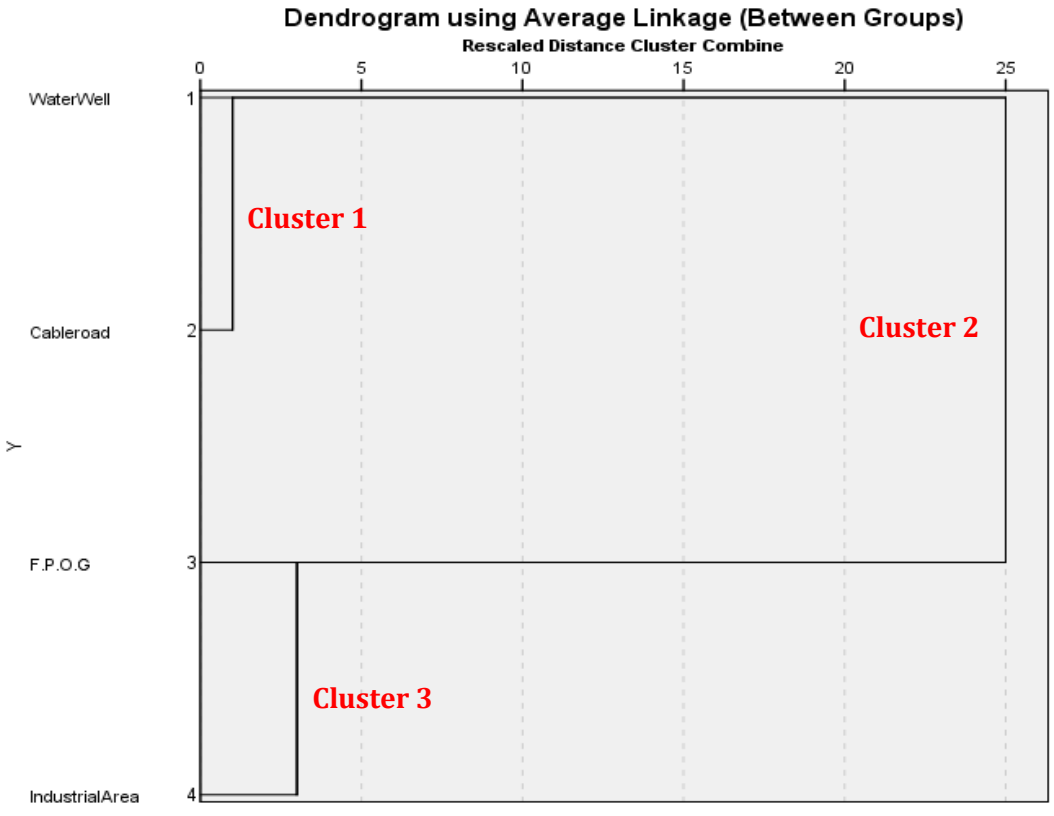

Figure 5: Dendrogram of Sampling Site Cluster analysis also established the grouping across the sampling location into Cluste

Table 5: Correlation between Sampling Sites

Pair	Location	N	Correlation	t	Sig. (2-tailed)
Pair 1	NLNG Water Well & Cable Road	16	.988	-1.892	.085
Pair 2	FPOG & IA	16	.981	-2.379	.037
Pair 3	NLNG Water Well & FPOG	16	.946	-6.491	.000
Pair 4	Cable Road & IA	16	.903	-5.845	.000
Pair 5	NLNG Water Well & IA	16	.904	-6.080	.000
Pair 6	Cable Road & FPOG	16	.944	-6.266	.000
Pair 7	Bonny Office & Bonny Residential	16	-0.111	0.815	0.432
Pair 8	Bonny Residential	16	0.635	-3.759	0.003

Bonny office and residential areas are negatively related and their concentration difference is insignificant (Table 5). Thus, the concentrations are trending toward opposing orders. The negative correlation implied that there might be additional uncommon sources of PAHs from the sampling location but its emission rates are similar. However, residential areas in Bonny metropolis showed a strong positive correlation, and their concentrations are significantly different. This depicts a common source of PAHs emission such as domestic and food processing emissions but these emissions have significantly different particle deposition rates, dilution areas, and other trans-evaporation influences.

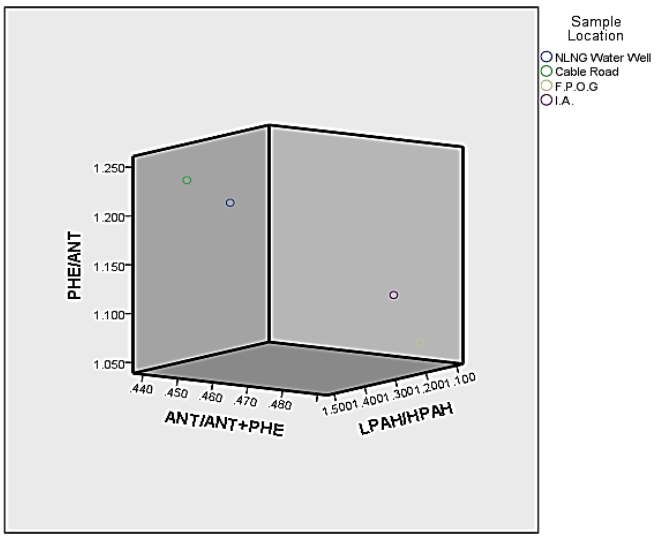

Figure 6: 3D Scatter Plot of Sampling Sites

Thus, considering the evaluated calculated ratios, a 3-D scatter plot of Phen/Anthra, Phe/(Phen+Anthra), and LPAH/HPAH are presented in Figure 6 above. The plot correlates with inference on the Pyrogenic source of PAHs in Bonny metropolis.

4. Conclusion

The sources and distribution of polycyclic aromatic hydrocarbons in Bonny Island were discovered using GC-MS analysis of filter dust. It has been suggested that Bonny Island has mostly pyrogenic PAHs and is more harmful using the diagnostic ratio to evaluate the PAHs composition. The offices (industrial areas) have a greater impact on human health due to their densely crowded environment. The outcomes of this study are critical to the citizens of Bonny metropolis' health, and the results obtained will also serve as a historical scientific record. As a result, monitoring PAHs in environmental assessments is critical. Future research should include surrounding communities away from the source as this work is restricted to offices and residential areas only within Bonny main town where industrial activities are centralized.

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