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POLYCYCLIC AROMATIC HYDROCARBONS: MEASURING THE AIR QUALITY OF THREE COMMUNITIES IN PORT HARCOURT, RIVERS STATE

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ABSTRACT

There are a good number of major oil-producing companies as well as numerous activities that involve the combustion of organic matter. These activities release enormous quantities of pollutants into the atmosphere and there seems to be a paucity of data that captures the concentration of pollutants in the air as well as their health implications. This study was aimed at determining the levels/concentrations of polycyclic aromatic hydrocarbons in the surrounding air of three communities in Port Harcourt, Rivers State. Rivers State houses two oil refineries, a fertilizer company, and numerous companies. Sampling was conducted using the EGASPIN 2018 sampling procedure. Air samples were collected unto sterilized filter paper from the three communities using a Bosean meter. Sample extraction and analysis were conducted using GC-FID (EPA 8270). The study was conducted over the dry and wet seasons in 2019. Dry season result showed the presence of majorly four low molecular weight polycyclic aromatic hydrocarbons - naphthalene, fluorene, phenanthrene, and anthracene; in Okrika, concentrations of were 2.766±1.429 mg/kg, 0.976±0.491 mg/kg, 0.014±0.007 mg/kg and 0.040±0.023 mg/kg respectively; in Mgbuodohia the concentrations were 0.822±0.668 mg/kg, 1.199±0.626 mg/kg, 0.008±0.004 mg/kg and 0.012±0.009 mg/kg respectively; in Chokocho the concentrations were 0.144±0.097 mg/kg, 1.074±0.738 mg/kg, 0.001±0.000 mg/kg, and 0.142±0.067 mg/kg respectively. Wet season results showed the concentration of naphthalene, fluorene, phenanthrene, and anthracene; in Okrika, the concentration was 0.271±0.034 mg/kg, 0.108±0.019 mg/kg, 0.055±0.009 mg/kg and 0.001±0.000 mg/kg respectively; in Mgbuodohia the concentrations were 0.014±0.002 mg/kg, 0.005±0.004 mg/kg, 0.009±0.002 mg/kg and 0.001±0.000 mg/kg respectively; in Chokocho the concentrations were 0.001±0.000 mg/kg, 0.001±0.000 mg/kg, 0.002±0.001 mg/kg and 0.001±0.000 mg/kg. Against the backdrop of past studies linking the concentration of PAHs to the presence of refineries and other anthropogenic human activities, the Chokocho study location was chosen as a control site. The result agrees with the premise that air around regions where there is relatively less human activity like the combustion of organic matter, tend to have lower concentration of polycyclic aromatic hydrocarbon content. The total concentrations of PAHs in the air during the dry season are 3.809 mg/kg, 2.045 mg/kg, and 1.375 mg/kg in Okrika, Mgbuodohia, and Chokocho respectively, showing Okrika to be the most polluted followed by Mgbuodohia and lastly Chokocho. Source apportionment points to petrogenic, pyrolytic, and other possible sources. The detection of just four out of the sixteen priority PAHs points to the fact that there seems to be more effect on other matrices like soil and water.

Keywords: polycyclic aromatic hydrocarbon, phenanthrene, naphthalene.

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INTRODUCTION

The Niger Delta region of Nigeria is famous for being the region where crude oil was first discovered in Nigeria. It is a region that has brought so much in the way of development because of the vast quantity of crude oil located in it. On the downside, the numerous exploratory activities have impacted negatively on the people as well as the environment, due to numerous activities of man. The region houses refineries and other chemical industries and is also a hotbed for the crude refining of crude oil. Several studies demonstrate the direct impact of the various activities in the region (Ogele and Egobueze, 2000; Yakubu 2018). These activities lead to the release of certain chemicals particularly polycyclic aromatic hydrocarbons which are heavy pollutants.

Polycyclic aromatic hydrocarbons, PAHs, are a well-studied class of compounds, easily recognized as organic compounds that contain two or more fused aromatic rings, typically 2 to 7 (Di-Toro *et al.,* 2000; Arey and Atkinson, 2003), and variously described as persistent with the possibility of alteration in their initial concentration by different diagenetic processes, so that PAHs can either be in the parent form or the substituted/altered form e.g., alkylated PAHs. They are well known as being carcinogenic Knox, 2005; Brody *et al*., (2007); Wang *et al.,* (2020); mutagenic, and ubiquitous in nature. Their ubiquity and adverse effects on human beings and the environment are reasonably well studied as well. Once released into the atmosphere, PAHs travel a long range and are eventually deposited on soil, sediments, and water and could be found even in the arctic regions Wang *et al.,* (2010); Friedman & Selin (2012); Kim *et al.*, (2013).

Polycyclic aromatic hydrocarbons originate from both natural and anthropogenic sources. Their widespread occurrence owes to both natural and anthropogenic sources such as volcanic eruptions, vehicular emissions, and burning of organic matter. Lima *et al*., (2005):

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Dalsøren *et al*., (2007). Natural sources of PAHs like volcanic eruptions and forest fires do not make a significant contribution to overall PAHs emission. Maliszewska-Kordybach (1999) subdivided the anthropogenic sources of PAHs into two categories namely; the first category - the combustion of materials for energy supply from stationary sources like industry (mainly coke and carbon production, petroleum processing, aluminium sintering, etc.), residential heating (furnaces, fireplaces, and stoves, gas and oil burners), power and heat generation (coal, oil, wood, and peat power plants) and mobile sources like cars, lorries, trains, airplanes, and sea traffic and the second category which covers incineration of municipal and industrial wastes. There are other miscellaneous sources containing unregulated fires such as agricultural burning, recreational fires, crematoria, etc., cigarette smoking as well as volatilization from soils, vegetation, and other surfaces. PAHs from anthropogenic that are discharged into the atmosphere either in the gaseous state or adsorbed onto particulate matter Gachanja (2005). Another important source of these compounds, peculiar to this region is the high incidence of crude burning of crude oil. Based on their sources, PAHs have also been classified as pyrolytic, i.e., as a result of the incomplete combustion of fossil fuels and organic matter, and petrogenic i.e., those associated with maturation of crude oil and coal at low temperatures.

Table-1. Classification of Polycyclic Aromatic Hydrocarbon (PAHs) Based on Molecular Weight Source: ATSDR (Agency for Toxic Substances and Disease Registry). Atlanta, GA, 458.

PAHs	Molecular Formula	Molecular weight	No. of Rings
Low Molecular Weight			
Naphthalene	$C_{10}H_8$	128	2
Acenaphthylene	$C_{12}H_8$	152	3
Acenaphthene	$C_{12}H_{10}$	154.21	3
Fluorene	$C_{13}H_{10}$	166.2	3
Phenanthrene	$C_{14}H_{10}$	178.2	3
Anthracene	$C_{14}H_{10}$	178.2	3
Medium Molecular Weight			
Fluoranthene	$C_{16}H_{10}$	202.16	4
Pyrene	$C_{16}H_{10}$	202.3	4
High Molecular Weight			
Chrysene	$C_{18}H_{12}$	228.3	4
Benzo[a]anthracene	$C_{18}H_{12}$	228.89	4
Benzo[k]fluoranthene	$C_{20}H_{12}$	251.3	5
Benzo[a]pyrene	$C_{20}H_{12}$	251.3	5
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.3	6
Benzo[g,h,i]perylene	$C_{22}H_{12}$	276.3	6

Polycyclic aromatic hydrocarbons possess different structural features, which may in turn be related to differences in their properties. For example, in their purest forms, PAHs are solids with low volatility at room temperature and range in colour from colourless to white or pale yellow-green. PAHs possess other physicochemical properties, which in turn impact the extent to which they affect man and his immediate and far environment. Their semi-volatility contributes to their being a major pollutant in the environment.

Clean air is intrinsic to healthy living, and the air around many regions of the world is severely polluted, with polycyclic aromatic hydrocarbons being a major culprit. Children are at high risk of exposure as they tend to spend more time outdoors compared to adults since their respiratory and immune systems are not as developed as those of adults Schwartz, (2004). Specifically, studies by Crosignani, *et al.*, (2004); Kim *et al.*, and (2005); Knox, 2005 ascribed the increased risk of cancer and asthma in children to exposure to PAHs. Pregnant women are thought to be vulnerable to PAHs. Animal studies have shown a possible association between exposure PAHs to and reproductive ability. Singh *et al*., (2008) associated negative fetal growth, fetal death, and other pregnancy-related outcomes to exposure to PAHs.

They are also classified as pollutants, and they affect both humans and the environment. In the mid-1970s, sixteen priority PAHs were chosen out of the

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several hundred based on their toxicity, ease of analysis, and their occurrence at the time Keith, (2015). These sixteen priority PAHs include acenaphthene, acenaphthylene, anthracene, benz (a) anthracene, benzo (a) pyrene, benzo (b) flouranthene, benzo (g, h, i) perylene, benzo (k) flouranthene, chrysene, dibenz (a,h) anthracene, flouranthene, flourene, indeno (1, 2, 3-c, d)pyrene, naphthalene, phenanthrene and pyrene. As per their impact on humans, USEPA (2002) has classified benzo[a]anthracene, benzo[b]pyrene, benzo [b] fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo [a, h] anthracene, and indeno [1, 2, 3-c,d] pyrene as probable human carcinogens (group B2) and the International Agency for Research on Cancer (IARC, 2004) has recognized benzo[a]anthracene and benzo [a] pyrene as probable human carcinogens, whereas benzo [b] fluoranthene, benzo- [j] fluoranthene, benzo [k] fluoranthene, and indeno [1, 2, 3-c, d] pyrene are labeled as possible human carcinogen. These sixteen PAHs are targeted for monitoring and used as a global standard. They are classified as low molecular and high molecular weight polycyclic aromatic hydrocarbons. Crude oil is a major staple of the economy of Rivers State, the Niger Delta, and Nigeria in general. Most pollution in River State is associated with the incomplete combustion of crude oil and other petrochemicals. Indeed, PAHs are produced in all processes of incomplete combustion of organic substances (Wilds and Jones, 1995) There are numerous activities of artisanal combustion of crude oil that have created a major problem which includes air pollution from the belching of black soot into the atmosphere, which when inhaled or ingested affects the wellbeing of humans and other organisms.

Though all PAHs that are released from natural and anthropogenic combustion get into the atmosphere, the concentration of PAHs in the air is still less (< 0.5%) compared to other matrices because most are eventually deposited into the soil and water. Oscar and Jones (1995) found less than 4% of total PAHs in air leading to the observation that the atmosphere is not a repository and collector of PAH but more likely to be a transporter, dilutor, and reactor.

Due to their physicochemical properties like volatility and environmental factors like relative humidity and prevailing ambient temperature, the concentration of PAHs in the air is affected by location and the season. Lai et al., (2011) collected a total of thirty-seven air samples using high-volume samplers, once a month over twelve months from May 2007 to June 2008 in the coastal area of southwest Taiwan and analyzed for total suspended particulates (TSP) and polycyclic aromatic hydrocarbons (PAHs). Air samples were collected using the procedure as outlined by NIEA A809.10B. Soxhlet apparatus was used for extraction over 24 hours using dichloromethane and petroleum ether for the extraction of gaseous and particulate PAHs respectively. On concentrating the extract, analysis was conducted using a capillary gas chromatograph (Agilent 6890N) and a mass spectrometer (Agilent 5973N), operating under the selected ion monitoring mode, to identify and quantify PAHs from samples. Results showed that they identified a total of 51 PAHs and found (for gaseous and particulate PAHs) a total concentration between 1.86 and 56.4 ng/m^3 with an average of 19.7 11.6 ng/m^3, with gaseous PAHs having the highest percentage. Lai et al., (2011) conducted their study over two seasons and found that the concentration of PAHs during the dry season (December to February) was higher compared with the concentration during the wet season, making the study align with the studies conducted by other researchers like Park *et al*. 2002, Guo *et al*., 2003, Fang *et al.*, 2003 and Tham *et al*., 2008. They found a notable exception though and found that the highest concentration of PAHs was noted in August (in the wet season) due to a ceremony in summer that involves incense and joss paper burning, both of which are significant sources of PAHs.

Communities that are near industrial locations are likely exposed to higher concentrations of pollutants. While Ana *et al.,* (2011) studied the air quality of Eleme and Ahoada East; Dibofori-Orji & Kalagbor (2019) studied the ambient air quality around Aba road, Iwofe, and Woji, both in Rivers State of Nigeria. Ana et al, (2011) sampled a total of fourteen (14) locations; seven in Eleme and seven in Ahoada East. Of the seven stations sampled in Eleme, the highest concentration of PAHs was found in Akpajo (3.3×10^4 ng/m^3) closely followed by that of Ebubu (2.2×104 ng/m^3) stations with both areas being near Shell Petroleum Development Company and Alesa refinery respectively. From all seven stations sampled in Ahoada East, the average total PAH concentration in the Ahoada LGA was 0.09 ng/m3 (range 2.30×10^5 to 7.40×10^2), well below the value for Eleme LGA of 8.34 µg/m3 (range 0.34–3.3 × 104 ng/ m^3). Dibofori-Orji and Kalagbor, (2019) attributed the high concentration of PAHs to the presence of numerous manufacturing, oil, gas, and mining industries in and around the stations that were sampled, as well as high incidence of major illegal activities of crude oil burning or refining and a large number of commercial activities like buying and selling of roasted meat, corn, fish yam, and other domestic activities. From their study, the concentrations of PAHs were highest in Woji (0.985 mg/m^3) followed by Iwofe (0.437 mg/m^3) and then Aba road (0.344 mg/m^3), with all values exceeding the recommended limit of 0.2 mg/m^3 set by OSHA (Occupational Safety and Health Administration) but within the limit of USA annual average of 0.3 -0.7 mg/m^3.

Environmental factors like temperature have been shown to impact the concentration of PAHs. Odabasi et al., (1999) measured the concentration of both gaseous and particulate PAHs between June and October of 1995 and found that total particulate PAHs decreased with increasing temperature. Also, in hot and humid summer days, the sun's radiation can easily degrade and/or volatilize PAHs because of photochemical reactions (Jiang *et al*., 2019).

The impact of suspended particulate matter on human and animal health is quite ginormous. Billions of people die yearly from the negative health effects of air pollutants. The relationship between suspended particulate

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matter and the concentration of PAHs could be significant. Akhbarizabeh *et al*., (2020) conducted studies to determine the possible relationship between suspended fine particulate matter ($PM_{2.5}$), microplastics, and polycyclic aromatic hydrocarbons as well as their health implications. Their study was conducted over the winter and summer seasons. A total of forty-six $PM_{2.5}$ samples were collected over 276 sampling days with 6-day intervals. The samples were collected on quartz microfiber filters (20.3 cm × 25.4 cm, Pall, USA, pore size: 2.5 µm). A quarter of the paper was used for PAH analysis. Results showed the total PAHs varied from 0.66 to 142.3 ng/m^3 with the median and average concentrations of 14.1 and 18.8 ng/m^3, respectively in the area where the study was conducted, and that the mean of total PAHs' concentration was the highest in winter (30.8 ng/m^3) and the lowest in summer (9.3 ng/m^3).

Considering the association of numerous industries based in the Niger Delta, and particularly Rivers State, there is the potential risk that inhabitants are exposed to the presence of PAHs in the atmosphere. Numerous studies concerning the concentration of PAHs in Rivers State have been conducted; in fresh water Inam *et al.,* (2016), in dumpsites (Ekpete *et al.*, 2019; Loremikan et al., 2019), in soil and sediments Parra et al., (2020) to mention but a few. In comparison, only a small amount of studies have been conducted to evaluate the air quality concerning the potential hazard of PAHs to humans and the environment, hence this current study.

2. MATERIALS AND METHODS

2.1 Study Area

Air samples were collected from three communities in Rivers State. These include Okochiri community in Okrika (latitude 04^o 45^I 0.7^{II}, longitude 007^o 06^I 7.6^{II}) local government area, Mgbuodohia (latitude 04^o 47^I 03.4^{II} longitude 006^o 57^I 56.0^{II}) in Obio-Akpor local government area, and Chokocho (latitude 04^o 59^I 37.4^{II} longitude 007^o 03^I 23.1^{II}) in Etche local government area

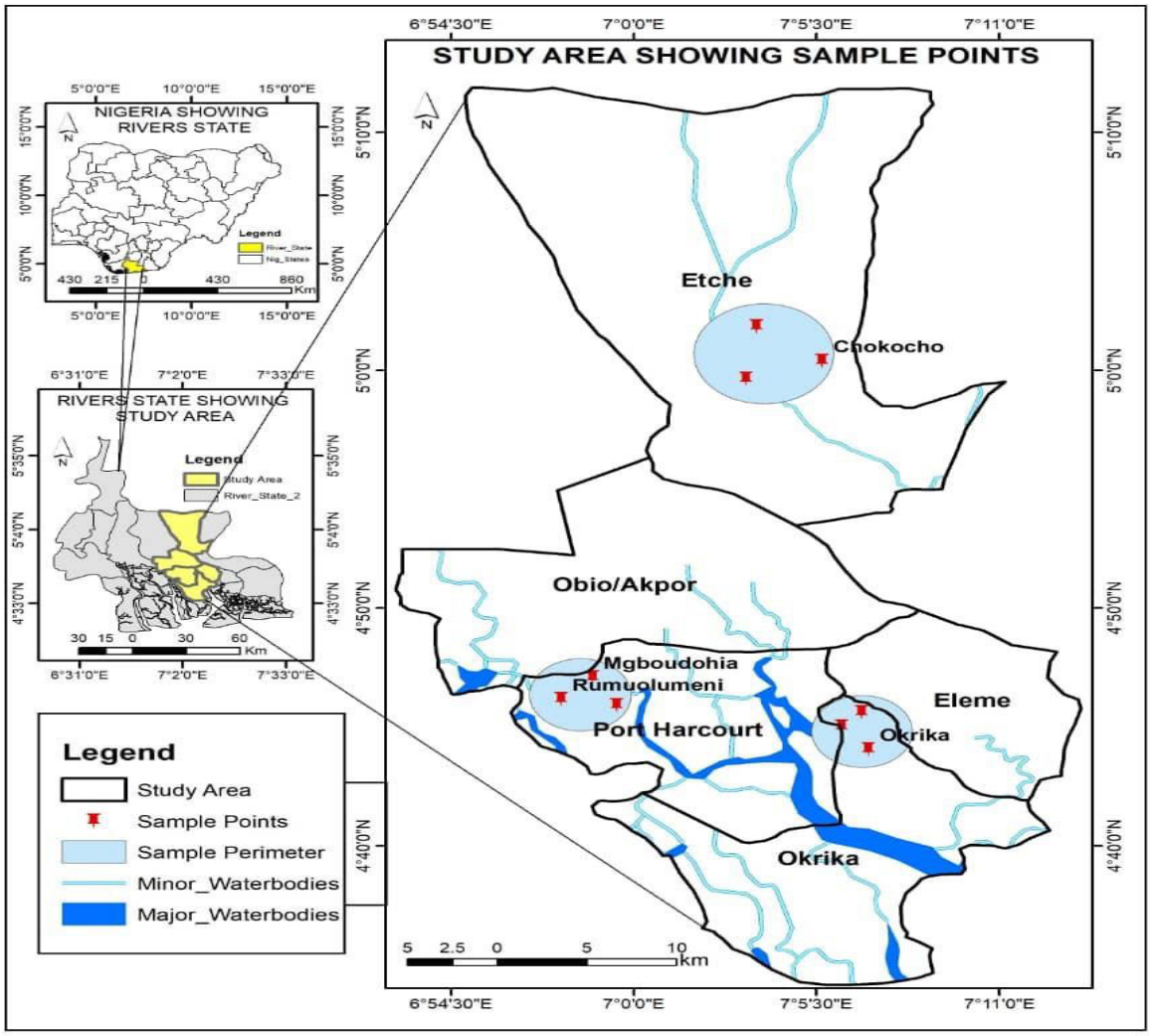

Figure-1. Map showing sampling points in Okrika (Okrika LGA), Mgbuodohia (Obio/Akpor LGA) and Chokocho, (Etche LGA) in Rivers State, Nigeria.

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2.2 Sample Collection

The Bosean multigas meter was used to provide information on the hydrocarbons present. The Extech 3-in-1 meteorological meter measures relative humidity, wind speed, and temperature. The Altimeter was used for the measurement of atmospheric pressure as well as wind direction. After locating the point source, the first and most important parameter that was determined was the wind direction.

At different distances from the point source, which corresponds to the different sampling points, the Bosean multigas meter is used at a fair distance away from the body and away from interferences. The meter is simply turned on. The meter first initializes and will give the exact reading of all possible pollutants, if present. Another device, Millivo, was used to trap air on a sterilized filter paper. The filter paper extracted from the Millivo was carefully transferred using forceps and was kept tightly covered in a Petri dish and taken back to the laboratory for PAHs analysis.

2.3 PAHs Extraction

The solvent that was used to extract the PAHs was dichloromethane. The filter paper was carefully transferred from the covered petri dish using clean, sterilized forceps. The filter papers were transferred into a beaker and the solvent, dichloromethane was added and left to stand for 30 minutes. The whole set up covered with aluminium foil to prevent loss of solvent by evaporation. Dichloromethane extracts the total organic content. After 30 minutes, the mixture is passed through a filtration setup. The mixture is passed through a mixture of granula sodium sulphate and silica gel to remove non-hydrocarbon compounds and water. The extract at this stage is taken to the GC for characterization and quantification of the possible priority PAHs

2.4 PAHs Analysis

The polycyclic aromatic hydrocarbons present in the extracted samples of soil, water, and air were passed in for analysis using the GC-FID. The basic GC parameters are as follows; The injector temperature was 270 ^{o}C while the detection temperature was 320 ^{o}C. The GC was heated for 1 minute to a temperature of 65^{o}C. The temperature was ramped at 25 ^{o}C/min to 140 ^{o}C at 0 minutes and later at 10 ^{o}C/minute to 290 ^{o}C at 11 minutes. The injection volume of standards and samples was 1 to 2 µL. Standards used for the calibration of the instrument were of industrial grade.

3. RESULT AND DISCUSSIONS

3.1 Polycyclic Aromatic Hydrocarbon Loading in Air During the Dry Season

Table-2. The concentration of PAHs (mg/kg) in air in the three communities during the dry season.

	Locations		
PAHs	**Okrika**	**Mgbuodohia**	**Chokocho**
Naphthalene	2.766±1.429^{b}	0.822±0.668 ^{a}	0.144±0.097 ^{a}
Acenaphthylene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Acenaphthene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Fluorene	0.976±0.491 ^{a}	1.199±0.626 ^{a}	1.074±0.738 ^{a}
Phenanthrene	0.014±0.007 ^{a}	0.008±0.004 ^{a}	0.001±0.000 ^{a}
Anthracene	0.040±0.023 ^{a}	0.012±0.009 ^{a}	0.142±0.067 ^{b}
Fluoranthene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Pyrene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Benzo(a)anthracene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Chrysene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Benzo(b)fluoranthene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Benzo(k)fluoranthene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Benzo(g,h,l)perylene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Benzo(a)pyrene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Dibenzo(a,h)anthracene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}
Indo(1,2,3)pyrene	0.001±0.000 ^{a}	0.001±0.000 ^{a}	0.001±0.000 ^{a}

Similar superscript means not significantly different (P>0.05) while different superscripts means significantly different

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3.2 Polycyclic Aromatic Hydrocarbon Loading in Air in the Wet Season

Table-3. The concentration of PAHs (mg/kg) in air in the three communities during the wet season.

	Locations		
PAHs	Okrika	Mgbuodohia	**Chokocho**
Naphthalene	0.271±0.034 [b]	0.014±0.002 [a]	0.001±0.000 [a]
Acenaphthylene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Acenaphthene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Fluorene	0.108±0.019 [b]	0.005±0.004 [a]	0.001±0.000 [a]
Phenanthrene	0.055±0.009 [b]	0.009±0.002 [a]	0.002±0.001 [a]
Anthracene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Fluoranthene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Pyrene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Benzo(a)anthracene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Chrysene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Benzo(b)fluoranthene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Benzo(k)fluoranthene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Benzo(g,h,l)perylene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Benzo(a)pyrene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Dibenzo(a,h)anthracene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]
Indo(1,2,3)pyrene	0.001±0.000 [a]	0.001±0.000 [a]	0.001±0.000 [a]

Similar superscript means not significantly different (P>0.05) while different superscripts means significantly different

3.3 Comparison of the Concentration of PAHs in Air over Seasons

The result of the analysis of polycyclic aromatic hydrocarbons (PAHs) in air samples collected from the three-sample location in the dry and wet seasons is shown in Table-1 and Table-2. The concentrations of PAHs observed were different in the three locations as well as different seasons. The result shows that the total concentrations of PAHs in the air during the dry season are 3.809 mg/kg, 2.045 mg/kg, and 1.375 mg/kg in Okrika, Mgbuodohia and Chokocho respectively, with naphthalene, fluorene, phenanthrene, and anthracene being significantly present in the air in the three locations studied. Of all sixteen priority PAHs studied, only four PAHs, naphthalene, fluorene, phenanthrene, and anthracene were detected in the air during the dry and wet seasons. The concentration of these four PAHs in the air was higher in Okrika compared to the other two areas during the dry season when the temperature was higher. This result is in tandem with that of Wang et al., (2008) who also found that the concentration of PAHs in air is higher during the dry season compared with the wet season. Important factors that were identified include residential heating emissions and inefficient photochemical degradation. In Okrika, the high concentration of PAHs in the air in Okrika during the dry season could be significantly linked to the anthropogenic activities of incomplete combustion or 'cooking' of crude oil. Another important factor affecting the air concentrations of PAHs was the rainfall. The rainfall in summer was higher than those in winter and the higher rainfall accompanied by higher wet deposition of PAHs in summer than in winter induced the air concentrations of all PAHs in summer to be lower than those in winter.

During the dry season, the concentrations of naphthalene (Np) were found to be 2.766±1.429 mg/kg, 0.822±0.668 mg/kg and 0.144±0.097 mg/kg; the concentrations of fluorene were found to be 0.976±0.491 mg/kg, 1.199±0.626 mg/kg and 1.074±0.738 mg/kg; the concentrations of phenanthrene were 0.014±0.007 mg/kg, 0.008±0.004 mg/kg and not detected in Chokocho; the concentrations of anthracene were 0.040±0.023 mg/kg, 0.012±0.009 mg/kg and 0.142±0.067 mg/kg all in Okrika, Mgbuodohia and Chokocho respectively. Park et al. (2001) studied the atmospheric distribution of polycyclic aromatic hydrocarbons and found also that phenanthrene and anthracene were dominant PAHs in air. In all three

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locations, all the other PAHs were below the detection limit.

During the wet season, only three of the PAHs; anthracene (An), fluorene (Fl), and phenanthrene (Ph) were identified. The concentrations of anthracene, fluorene, and phenanthrene in Okrika were 0.271±0.034 mg/kg, 0.108±0.019 mg/kg, and 0.055±0.009 mg/kg respectively. The concentration of anthracene, fluorene, and phenanthrene in Mgbuodohia was 0.014±0.002 mg/kg, 0.005±0.004 mg/kg, and 0.009±0.002 mg/kg respectively. In Chokocho, and of the three PAHs above, only phenanthrene was detected at a concentration of 0.002±0.001 mg/kg. Going by the low total concentration of the detected PAHs in Chokocho in the Etche local government area, the air quality concerning the presence of polycyclic aromatic hydrocarbon is cleaner than those of Okrika and Mgbuodohia. The reason for this could be due to the lack of certain activities like the burning of crude oil, which is very common in the other two study areas.

The low concentration of PAHs in particulate matter in this study could be a result of the findings from other studies that polycyclic aromatic hydrocarbons exist more in the gaseous phase than when they are adsorbed onto particulate matter Cheruiyot *et al.* (2015). The implication of this is that there is still a potential risk of these toxic compounds as they are abundant in the gaseous phase.

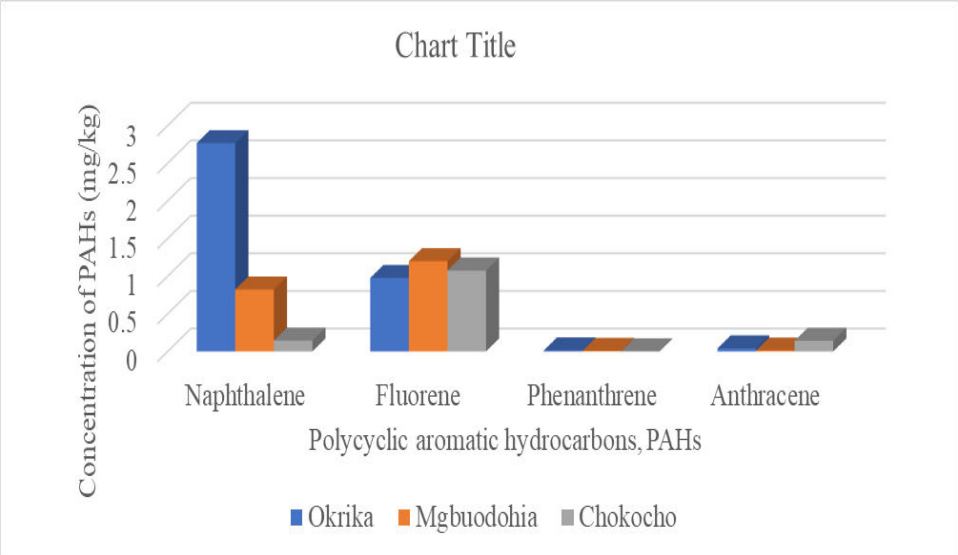

Figure-2. The concentration (mg/kg) of four detected PAHs in Okrika, Mgbuodohia and Chokocho during the dry season in 2019.

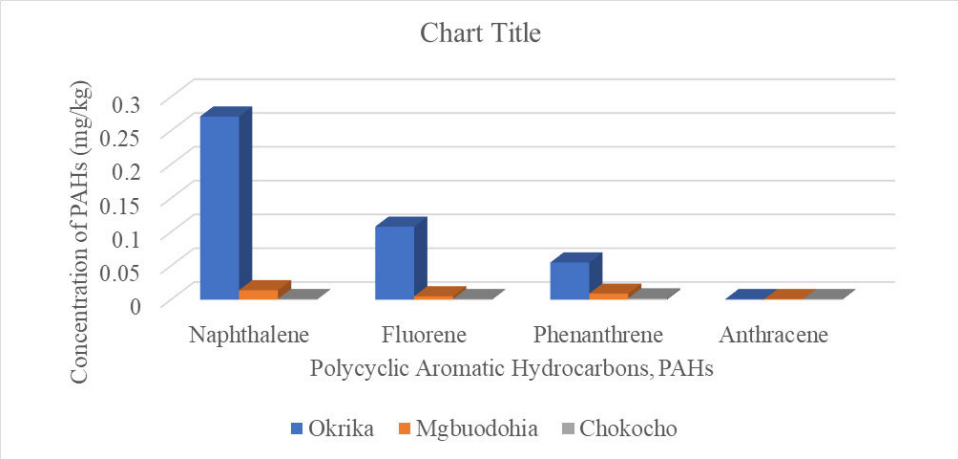

Figure-3. The concentration (mg/kg) of four detected PAHs in Okrika, Mgbuodohia and Chokocho during the wet season in 2019.

Figure-2 and Figure-3 clearly show that the category of polycyclic aromatic hydrocarbons present in the air samples collected from the three sites fall within the low molecular weight polycyclic aromatic hydrocarbons. High molecular weight PAHs were not detected in this study. This could be attributed to the nature of the sites from where air samples were collected. Gasoline vehicles are adjudged to be dominant sources of

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high molecular weight PAHs Juhasz and Naidu (2000) the sites at Okochiri (Okrika) and Mgbuodohia were not particularly noted for high vehicular motion. The siting of a major road close to the site at Chokocho in Etche LGA could account for the presence of the detected PAHs in the air. Moreso, unlike the sites at Okrika and Mgbuodohia, where there are high incidences of artisanal combustion of crude oil, there is no significant burning of crude at the Chokocho site. Rather the major activities include commercial drilling of sand from the nearby river for building purposes. That some low molecular weight PAHs were detected in the air around Chokocho could be attributable to the contribution from other sources.

3.4 Diagnosis Ratios and Source Apportionment of PAHs in Air

The diagnostic ratio shows the possible source of PAHs detected in the air surrounding the different study locations. The detected PAHs were naphthalene, fluorene, phenanthrene, and anthracene. Based on the detected PAHs in this study, the PAH concentration diagnostic ratios characteristic of the anthropogenic emissions that were calculated is An/(An + Phe) Hoseini *et al*., (2016). A comparison between the various diagnostic ratios obtained in this study with the standard values reported in the literature is shown in Table-3. Diagnostic ratios showed that PAHs in the atmosphere of the three study locations of Okochiri (Okrika LGA), Mgbuodohia (Obio/Akpor LGA), and Chokocho (Etche LGA) arose predominantly petrogenic, pyrolytic and possibly other sources.

Table-3. Diagnostic ratio and source apportionment of PAHs in Okrika, Mgbuodohia, and Chokocho.

	Dry Season	**Wet Season**
	An/(An + Ph)	An/(An + Ph)
Okrika	0.74	0.02
Mgbuodohia	0.60	0.10
Chokocho	0.99	0.33

Despite the nearness of the refinery at Okrika, and the intense activities of artisanal combustion of crude oil in both Okrika and Mgbuodohia, the study revealed that the loading of PAHs in air is not high. The reason for this could be several factors like the possible better interaction of PAHs with other matrices (soil and water), and the impact of other physicochemical parameters that could contribute to the fate of PAHs in the immediate environment compared to other places.

4. CONCLUSIONS

Of all the sixteen (16) polycyclic aromatic hydrocarbons (PAHs) studied, only four - low molecular weight PAHs - were present in the three selected study locations. The detected PAHs in this study include naphthalene, fluorene, phenanthrene, and anthracene. The presence of these 2-3-membered ring compounds indicates intense human activities. The study also revealed that polycyclic aromatic hydrocarbons tend to be more in the gaseous phase than in the particulate phase hence their low concentration. The diagnostic ratio shows the contribution of petrogenic, pyrolytic, and other possible sources. Though this study does show the presence of carcinogenic PAHs in the air in the three communities, the presence of these four PAHs in the air still constitutes a possible risk to humans on inhalation and authorities have the duty of taking steps to ensure that activities that infringe on the right of individuals to clean air is mitigated.

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