

## RESEARCH ARTICLE

## CHARACTERIZATION AND DISTRIBUTION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN WET PRECIPITATIONS, SURFACE WATERS AND SOILS FROM SOUTH-EASTERN NIGERIA

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## ARTICLE DETAILS

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## ABSTRACT

Polynuclear aromatic hydrocarbons (PAHs), are known as persistent organic pollutants (POP) which exist in different media as contaminants in parts of the environment's atmosphere, seawater, sediments, soils, and vegetation. PAHs have been known for their mutagenic, carcinogenic, and toxic properties to humans through the food chain. This study is aimed to characterize and investigate the distribution of PAHs in wet precipitations, surface waters, and soils from Ikot Abasi, Ibeno, and Eastern Obolo Local Government Areas of Akwa Ibom State, Nigeria. PAHs were determined in the environmental components by gas chromatography-mass spectrometry technique. Two soil and two surface water samples were taken from selected locations and wet precipitation samples were harvested on event basis from the study areas. The results reveal the presence of the following priority PAHs at different concentrations: naphthalene, (0.02-0.09 mg/L); benzo[k]fluoranthrene (0.001 -0.09 mg/L); benzo[e]pyrene (0.001-0.08 mg/L); benzo[a]pyrene (0.001 -0.09 mg/L); 3-methylcholanthrene (1.27-7.21 mg/L) during the rainy and dry seasons in Ikot Abasi. The concentrations of naphthalene ranges (0.02-0.06 mg/L), 3-methylcholanthrene ranges (2.40-3.65 mg/L), while other PAHs levels were below detection limits in rainwater from Ibeno in both seasons. The concentrations of naphthalene ranges (0.02-0.05 mg/L); 3-methylcholanthrene (2.30 – 5.65 mg/L), while other PAHs levels were below detection limits in rainwater from Eastern Obolo in both seasons. The PAHs levels indicated were higher than the World Health Organization (WHO) acceptable limit of PAHs (0.0007 mg/L) in drinking water. The PAHs detected in the surface waters were in the order: Ikot Abasi (11.09 ± 0.02 mg/L) > Eastern Obolo (3.87 ± 0.002 mg/L) > Ibeno (1.94 ± 0.004 mg/L), during the rainy season, while the PAHs detected in the surface waters were in the order: Ikot Abasi (13.79 ± 0.03 mg/L) > Eastern Obolo (3.95 ± 0.008 mg/L) > Ibeno (2.45 ± 0.011 mg/L), during the dry season. The PAHs obtained for the soils in the three study areas during the rainy season were in the order: Eastern Obolo (776 ± 5.92 ug/kg) > Ibeno (732 ± 8.33 ug/kg) > Ikot Abasi (8 ± 0.07 ug/kg), while, during the dry season, the results were in the order: Ibeno (872 ± 11.05 ug/kg) > Eastern Obolo (105 ± 9.03 ug/kg) > Ikot Abasi (20 ± 1.95 ug/kg). Soils from Eastern Obolo and Ibeno have PAHs levels greater than 700 ug/kg, which is categorized as slightly polluted, with toxic equivalent concentrations (TEQ) higher than permissible limit (33 ug/kg). This may cause ecological risk and raises public health concern that should attract more attention. Molecular diagnostic ratio analyses show that the sources of PAHs in the three study area are mainly pyrogenic.

## KEYWORDS

Petrogenic; pyrogenic; carcinogenic; mutagenic; organic pollutant, toxicity

## 1. INTRODUCTION

Development and technology have negative impacts of contamination of the ecosystem and damage to human health. Consequently, polynuclear aromatic hydrocarbons (PAHs) are a group of environmental pollutants classified as persistent organic pollutants (POPs), being resistant to degradation and can remain in the ecosystem for long periods, with the potential to cause adverse environmental effects (Liang et al. 2022; Wang et al., 2010).

Due to the fact that PAHs are resistant to environmental degradation, thus

leading to ubiquitous distribution (V. Wanjeri et al, 2013). PAHs have been widely found everywhere on earth, such as water, soil, air and food (Y. Yang et al. 2014; W. Wilcke, 2000 ; E. Christopher, 2017).

Some of the PAHs are capable of being dispersed on a global scale and, in addition to being persistent in the environment, are semi-volatile, moving between the atmosphere and the earth's surface in repeated temperature-driven cycles of deposition and volatilization (Gray and Hall, 2014; Othman et al., 2012).

Polynuclear aromatic hydrocarbons (as persistent organic pollutants) are

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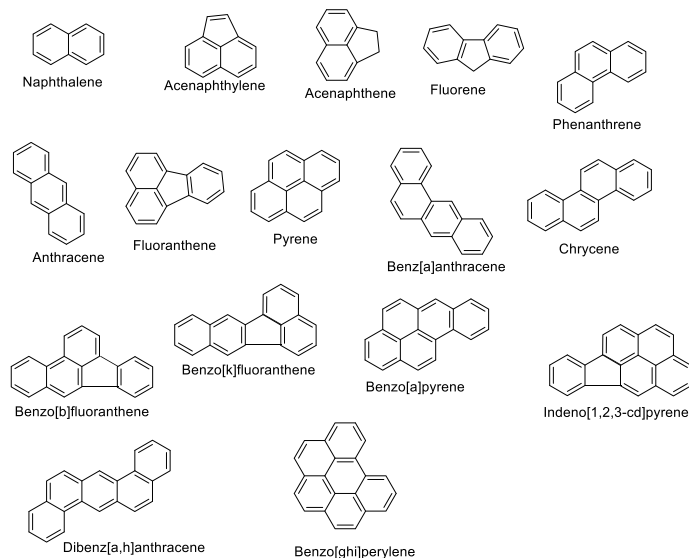
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truly multimedia contaminants that occur in parts of the environment's atmosphere, in land and seawater, sediments, soils, and vegetation, although they are mainly anthropogenic in origin with negligible natural sources (Kim et al., 2011; Bihanic et al., 2015; WHO, 2003; Anderson, 2009)

PAHs have been known for their mutagenic, carcinogenic, and toxic properties (Wang et al., 2011; Igwe et al., 2020; Bolden et al., 2017).



**Figure 1:** Structure of USEPAs Sixteen priority PAHs ( Bojes and Pope, 2007 )

The major sources of PAHs are from burning of coal, oil, gas, wood, tobacco, coal tars, crude oil, and petroleum products such as creosote and asphalt. However, some natural sources such as forest fires and volcanoes, have been well documented (Gupte et al., 2016; Chaloupka et al., 1993; Liu et al., 2007; Sahoo et al., 2020). The USEPA and the European Commission have implicated and listed PAHs as priority pollutants (Tong et al., 2020; IARC, 2004). PAHs released into the atmosphere go over long distances with attendant deposition with atmospheric precipitation on soils, vegetation, the sea, and inland waters (Diggs et al., 2011; IARC, 2010).

In addition, these agencies namely, International Agency for Research on Cancer (IARC), Agency of Toxic Substances and Diseases Register (ATSDR), the Environmental Protection Agency (EPA), and the European Union have enlisted PAHs as the priority pollutants on account of exhibiting carcinogenic and mutagenic (genotoxicity) properties (Patel et al., 2014). PAHs in the atmosphere may undergo photochemical and chemical reactions with oxides of nitrogen, sulphur (IV) oxide, oxygen, and hydroxides, which may likely produce more toxic compounds (Bojes and Pope, 2007).

A major study indicated that inhalation accounts for two to twelve percent of PAHs, while dietary exposure contributes 88 to 98 percent of PAHs intake mostly, among non-smoking populations (Chuang et al., 2003). Also studies indicated that benzo[a]pyrene (BaP) dietary exposure is in the range of 2–500 ng/day. On a global scale, the estimated average intake of PAHs is 0.02–3.6 ug/person/day, while other nations such as India, Nigeria, and China have 11 ug/person/day, 6 ug/person/day, and 3.56 ug/person/day, respectively (Diggs et al., 2011).

There are three major classes of PAHs which differ mainly in their origin to have petrogenic, biogenic, and pyrogenic (Dahle et al., 2003). PAHs can further be categorized into low molecular weight (LMW) PAHs that consist of two or three fused benzene rings and higher molecular weight (HMW) PAHs, consisting of four or more fused benzene rings, and having higher tendency for stability and persistence for long in the environment than the LMW PAHs (Dahle et al., 2003). The ratio of low molecular weight PAHs (LMW-PAHs) to high molecular weight PAHs (HMW-PAHs) has been used to characterize the origin of PAHs in the environment. According to Rocher et al. (2004), PAHs from petrogenic source show a characteristically higher proportion of LMW-PAHs such as naphthalene and acenaphthenes, while pyrolytic PAHs have a characteristically higher proportion of HMW-PAHs such as pyrene and benzo[a]pyrene.

Thus, PAHs from petrogenic source exhibit LMW/HMW ratios greater than one, whereas PAHs from pyrogenic source exhibit LMW/HMW ratios less than one. As an additional tool, PAH molecular diagnostic ratios used

PAHs have mainly carbon and hydrogen atoms as constituents of fused benzene rings of various structural linear, cluster, and angular arrangements (Abdel-Shafy and Mansour, 2016; Andrade et al., 2017).

So far, sixteen listed polynuclear aromatic hydrocarbons have been practically characterized (Fig. 1), with benzo [α] pyrene (BaP) rated an indicator contaminant due to frequent occurrence in a mixture of PAHs (García-Sánchez et al., 2018; Mojiri et al., 2019).

for sources of PAHs are as follows :

- $BaA/(BaA + Chrycene) < 0.2$  indicates a petrogenic source,  $2-0.35$  indicates mixed sources (petrogenic and pyrogenic), and  $> 0.35$  indicates a pyrogenic source (Unwin et al., 2006).
- $Ant / (Ant + Phe) < 0.1$  indicates a petrogenic source;  $> 0.1$  indicates a pyrogenic source (Tobiszewski and Namieśnik, 2012; Pies et al., 2008).
- BaA is benzo[a]anthrene, Ant is anthracene, and Phe is phenanthrene.

The pollution of soil by PAHs is virtually classified into three categories: unpolluted ( $\sum PAH < 200$  ug/kg), weakly polluted ( $\sum PAH 200-600$  ug/kg), and heavily polluted ( $\sum PAH > 1,000$  ug/kg), in accordance with Wu et al. (2019) classification .

In general, PAHs have low water solubility and high hydrophobicity, have a high affinity for the organic fraction of the sample, and in solution, are adsorbed on particulate matter, which can be deposited as sediments (Vione et al., 2004). In addition, PAHs are accumulated in the fat tissue of filtering organisms such as mussels, oysters, clams, etc., which for a long time have been used as bio-indicators (Nendza et al., 1997).

There has not been any reported study of polyaromatic hydrocarbons in environmental components in the study areas; therefore, to fill the knowledge and information gap, this study is designed to investigate the presence of sixteen priority PAHs in wet precipitations, surface waters, and soils from the three local government areas of Akwa Ibom State, Niger Delta, South-eastern Nigeria. Our objectives are to (1) identify the presence of priority PAHs in the study area, (2) determine PAH molecular diagnostic ratios, and (3) determine the concentrations of the pollutant species in the environmental components in comparison with the set standards by international regulated agencies. We hypothesize that there is no variation in the levels of the pollutants in the study areas and no seasonal variation of the pollutants compared to the previously published data in the Niger Delta, Region, Nigeria.

## 2. MATERIALS AND METHODS

### 2.1 Study Area Description

The study areas which consist of Ikot Abasi, Eastern Obolo and Ibeno Local Government Areas of Akwa Ibom State , Nigeria are located in

the mangrove swamp forest, with occurrence of rain throughout the year, which peaked between May and September (Figure 2). The climatic conditions prevailing in the study area are favourable throughout the year for fishing and farming. The landscape of the area consists generally of low-lying plains and riverine areas, with no portion exceeding 175 m above mean sea level (Amadi, 2014).

Ikot Abasi Local Government Area located between latitude 4.3111 ° to 4.4512 ° North, and between longitude 7.5213 ° to 8.0219 ° East, plays host to major multinational companies such as the Aluminium Smelter Company of Nigeria (ALSCON), Septa Energy Company Limited, Ibom Power Company, and Sterling Global Oil Drilling Company. Ikot Abasi is also a coastal area bounded by Imo River and the Bight of Bonny estuary, where the major economic activities include farming, artisanal fishing, trading (Etesin and Inim, 2021; Ikot Abasi: The Aluminium Town, 1997).

Ibenu is located in South-eastern Nigeria and lies within the coordinates: 4.57° N and 7.98° E (Figure 2). It lies on the eastern side of the Qua Iboe River, which is about 3 kilometers from the Atlantic, and is one of the largest fishing settlements on the Nigerian coast (Description of Fisheries, 2011). In the west, Ibenu is located along the Mangrove Forest Belt of the Niger Delta region of Nigeria and bounded by the Eastern Obolo Local Government Area. To the north, it is bounded by Onna, Esit Eket, and Eket

LGAs and to the south by the Atlantic Ocean. It occupies the largest Atlantic coastline, more than 129 km, in Akwa Ibom State. It also occupies a vast coastal area of over 1,200 km<sup>2</sup> (Description of Fisheries, 2011).

Eastern Obolo is a local government area (LGA) in Akwa Ibom State of South-eastern Nigeria, with headquarters at Okoroete and lies between latitudes 4° 28' and 4° 53' and longitudes 7° 50' and 7° 55' East (Figure 2). It is a coastal area under great tidal influence from the Bight of Bonny. Eastern Obolo is located in the Niger Delta fringe between the Imo and Qua Iboe River estuaries. It is bounded to the north by Mkpato Enin Local Government Area, northeast by Onna LGA, west, by Ikot Abasi LGA, Southeast by Ibenu Local Government Area, and in the south by the Atlantic Ocean (Etesin et al. 2013).

These areas are underlain by sedimentary formations of late Tertiary and Holocene ages (Magnus et al., 2014; Amadi, 2014). Deposits of recent alluvium and beach ridge sand occur along the coast and the estuaries of the Imo and Qua Iboe Rivers, as well as along flood plains of creeks. The study areas are also characterized by coastal plain sands. The sands are mature, coarse, and moderately sorted. The Coastal Plain sands, otherwise known as the Benin formation, overlies the Bende-Ameki formation and dip south-westward (Mbonu and Ebeniro, 1991; Akankpo and Igbokwe, 2011).

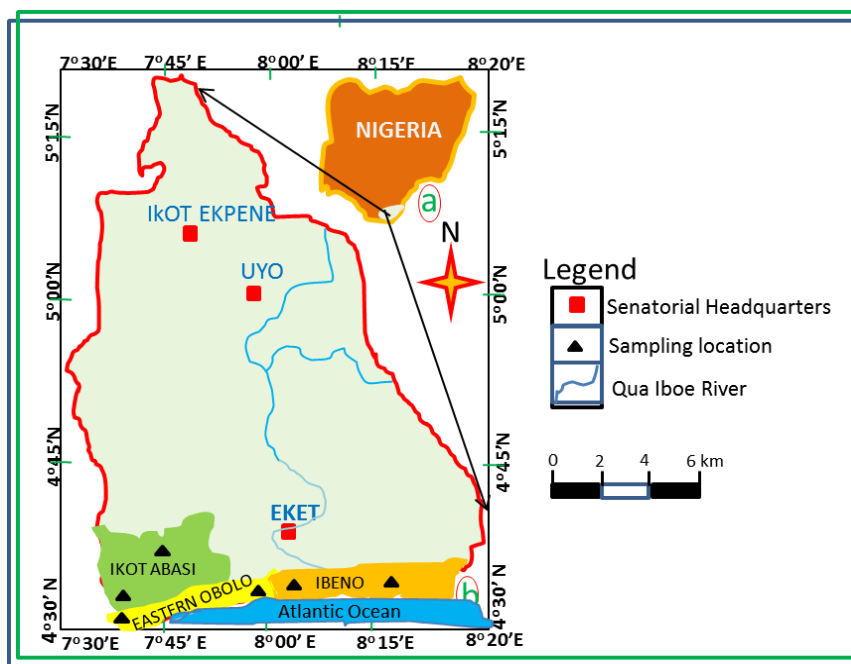


Figure 2: Map showing Nigeria (a) and Akwa Ibom state describing the study areas, sampling locations and Atlantic Ocean

2.2 Collection and Preparation of Samples

2.2.1 Rainwater Samples

Rainwater samples were collected manually using a clean aluminium plate on a tripod iron stand about 1.5 meters above the ground in an open field, as depicted in Figure 3. In order to avoid the effects of fine particle

deposition in the atmosphere in the absence of rainfall, the aluminium plate was removed and returned before precipitation. The harvested rainwater was decanted into glass bottles and stored in a refrigerator in the laboratory until analysis. Rainwater samples were collected for each season in the three study areas to cover January, February, and March 2022 during the dry season and May, June, and July 2022 during the rainy season, according to the method of APHA (2005).



Figure 3: Rainwater collection stand

2.2.2 Surface Water Sample

Twelve (12) surface water samples were collected from streams in the

three local government areas using glass bottles, consisting of two water samples from each area, to cover January, February, and March 2022 during the dry season and May, June, and July 2023 during the rainy

season. No preservative was added to any of these samples. The water samples were stored in ice-cooled coolers while in transit to the laboratory for physico-chemical and PAH analysis according to the method of APHA (2005).

### 2.2.3 Soil Samples

Twelve (12) soil samples were collected for each season in the three study areas to cover January, February, and March 2022 during the dry season and May, June, and July 2022 during the rainy season. Soil samples were collected using an auger, stored in black polyethylene bags, air-dried, and sieved to 63 micron sizes and stored in polyethylene bags until analysis, according to the method of APHA (2005).

## 2.3 Digestion of Samples And Determination of Pahs

### 2.3.1 Digestion and Determination of PAHs in Rainwater

The gas chromatograph used was an Agilent 5977 GC-MSD (method code: MTH010). Prior to calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of m/z 69, 219, 502, and other instrument optimal and sensitivity conditions.

The levels of PAHs in rainwater samples were determined using GC-MS with MSD operating in selective ion monitoring (SIM) and scan mode to ensure low-level detection of the target constituents (Ehsan et al., 2022).

An Agilent 8860A gas chromatograph coupled to a 5977C inert mass spectrometer (with a triple-axis detector) with an electron-impact source (Agilent Technologies) was used. The stationary phase of separation of the compounds was a HP-5 capillary column coated with 5% phenylmethyl siloxane (30m length x 0.25mm diameter x 0.25 µm film thickness) (Agilent Technologies).

The carrier gas was helium, used at a constant flow rate of 1.2 mL/min at an initial nominal pressure of 026 psi and an average velocity of 40.00 cm/sec. 1µL of each sample was injected in a split less mode at an injection temperature of 250 °C. The purge flow to spilt vent was 30.0 mL/min at 0.35 min with a total flow of 31.24 mL/min; the gas saver mode was switched off. The oven was initially programmed at 50 °C (2 min) and then ramped at 10 °C/min to 300 °C (5 min). The run time was 32 minutes with a 3-minute solvent delay (Andrianova and Quimby, 2019).

The mass spectrometer was operated in electron-impact ionization mode at 70 eV with an ion source temperature of 230 °C, a quadrupole temperature of 150 °C, and a transfer line temperature of 300 °C. Acquisition of ions was via scan mode (scanning from m/z 50 to 500 amu at 2.0 s/scan rate) and selective ion mode (SIM). After calibration, the samples were analyzed and corresponding PAH concentrations obtained (Quimby et al., 2013).

### Calibration Procedure

PAHs standard, 1000 ppm (Catalog Number: H-QME-01), containing 23 environmental PAH components, was purchased from AccuStandard. Four (4) point serial dilution calibration standards (0.1, 0.05, and 1.5 mg/L) were prepared from the stock and used to calibrate the GC-MS.

### 2.3.2 Digestion And Determination of Pahs in Surface Waters

Surface waters were digested and PAHs determined according to the method in Section 2.3.1.

### 2.3.3 Digestion And Determination of Pahs in Soil Samples

Sample preparation was carried out by ultrasonic extraction (Method Code: MTH, 004). The instruments used were ultrasonic baths: CLEAN 120-HD (China). Rotary Evaporator: BUCHI Rotavapor R-215 (Switzerland); Analytical Balance: ADAM AAA250LE Weighing Balance (UK);

The reagents used were of analytical grade: Acetone: GC Ultratrace Scharlau (Spain); n-Hexane: 96% GC Ultratrace Scharlau (Spain); Silica Gel: Loba Chemie (India); Anhydrous Sodium Sulphate: Merck (US).

### Extraction Procedure

Properly homogenized samples (5 g) were weighed into beakers and mixed with 10 ml of n-hexaneacetone (1:1). The beakers were then placed in an ultrasonic bath and sonicated for 20 minutes. The mixture was

allowed to settle, and the solvent layer was decanted and concentrated to 2 ml using a rotary evaporator.

### Clean-Up Procedure

Granular silica gel (Mesh Size 60–200A) was activated by heating at 130<sup>o</sup> C for 16 hours and stored in a desiccator. A glass column was packed with 5g of silica gel, and 1g of anhydrous Na<sub>2</sub>SO<sub>4</sub> was added. 20 ml of n-hexane was added to the column and eluted into a beaker. The 2 ml sample extract was quantitatively added to the top of the column. Another 10 ml of n-hexane was added to the column and eluted into waste. Before the column head dried, 10 ml (1+1) of dichloromethane and hexane were added, and the eluent was collected. The eluent was then concentrated to 2 mL using a rotary evaporator and analyzed for PAHs.

## 2.4 Ecological Risk Assessment of Pahs in Soil

Benzo[a]pyrene is an indicator PAH and has the highest carcinogenicity among the sixteen (16) PAHs. Therefore, toxic equivalent concentrations of Benzo[a]pyrene (TEQB[a]P) are utilised to assess the ecological risk of PAHs in the soil (G.-C. Fang et al, 2004).

The formula for calculating the total toxic equivalent concentration of PAHs in the soil is:

$$TEQB[a]P = \sum_i (w_i \times TEF_i)$$

W<sub>i</sub> is the concentration of the "i" PAH component,

TEF<sub>i</sub> is the toxic equivalent factor of the "i" PAHs.

TEQB[a]P is the toxic equivalent concentration of total PAHs.

TEQB[A]P is a standard reference chemical since it has the highest carcinogenicity among the

sixteen PAHs. Its lethal equivalent factor is set at 1. The TEF values for the PAHs utilised are

listed in Appendix 1. The TEF value can show the toxicity and environmental risks of PAHs.

There were no standard threshold values of PAHs in the soil quality of Nigeria, even Africa, so

the allowable values of PAHs in quality from the Netherlands were also applied to analyse the

pollution level of PAHs in soils from the study areas (Appendix 1).

## 3. RESULTS AND DISCUSSION

### 3.1 Results of Rainwater Samples

Rainwater results during the rainy season in Ikot Abasi revealed the presence of the following PAH compounds: viz, naphthalene, benzo[k]fluoranthrene, benzo[e]pyrene, benzo[a]pyrene, and 3-methylcholanthrene.

The levels of PAHs were in the following order: Conveyor Belt (7.24 mg/kg) > ALSCON (3.503 mg/L) > Ibom Power (1.295 mg/L) > Ikpetim (0.39 mg/L), these are depicted in Table 1.

The results for the rainwaters during the rainy season in Eastern Obolo LGA reveal the presence of the following PAHs: naphthalene and 3-methylcholanthrene only. The PAHs were in the order: Iko (5.65 mg/L) > Okoroete (2.34 mg/L), these are depicted in Table 2.

The results for the rainwater during the rainy season in Ibene showed the presence of naphthalene, benzo[e]pyrene, 3-methylcholanthrene, and benzo[a]pyrene only. The PAHs were in the order: Ibene Hall (3.67 mg/L) > Ukpeneikang (2.42 mg/L), as depicted in Table 2.

The results obtained from the analyses of the rainwater during the dry season in Ikot Abasi reveal the presence of the following PAH compounds: viz, naphthalene, benzo[k]fluoranthrene, benzo[e]pyrene, benzo[a]pyrene, and 3-methylcholanthrene. The PAHs were in the following order: Conveyor Belt (6.64 mg/kg) > ALSCON (3.464 mg/L) > Ibom Power (1.278 mg/L) > Ikpetim (0.38 mg/L), and these results are presented in Table 3.

**Table 1: Concentrations of PAHs in Rainwaters from Ikot Abasi During Rainy Season**

PAH	Iketim	ALSCON	Ibom Power	Conveyor Belt
	Ikot Abasi	Ikot Abasi	Ikot Abasi	Ikot Abasi
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	0.05	0.09	0.02	0.02
Acenaphthylene	ND*	ND	ND	ND
Acenaphthene	ND	ND	ND	ND
Fluorene	ND	<0.001	ND	ND
Phenanthrene	ND	ND	ND	ND
Anthracene	ND	< 0.001	ND	ND
Fluoranthene	ND	< 0.001	0.001	ND
Pyrene	ND	< 0.001	0.001	ND
Benzo[c]phenanthrene	ND	ND	ND	ND
Benz[a]anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND
Benzo[k]fluoranthene	0.09	< 0.001	0.001	< 0.001
Benzo [e]pyrene	0.09	0.002	0.001	0.01
Benzo [a]pyrene	0.09	0.001	0.001	< 0.001
3-Methylcholanthrene	ND	3.41	1.27	7.21
Indeno (1,2,3-cd)pyrene	ND	< 0.001	ND	< 0.001
Benzo[ghi]perylene	0.07	< 0.001	ND	< 0.001
SUM( PAHs)	0.39	3.503	1.295	7.24

ND , below detection limit

The results of the analyses of rainwater during the dry season from Eastern Obolo show the presence of naphthalene, 3-methylcholanthrene, and benz[a]anthracene only. The PAHs were in the following order: Iko (5.46 mg/L) > Okoroete (2.37 mg/L). These results are presented in Table 4.

The results of rainwater analyses during the dry season in Ibeno reveal the presence of naphthalene, benzo[e]pyrene, 3-methylcholanthrene, and benzo[a]pyrene only. The PAHs were in the order: Ukpeneikang, Ibeno (3.67 mg/L) > Ibeno, Hall (3.61 mg/L), as presented in Table 4.

**Table 2: Concentrations of PAHs in rainwaters from Eastern Obolo and Ibeno during rainy season**

PAH	Eastern Obolo	Eastern Obolo	Ibeno, Hall	Ibeno,
	( Iko )	( Okoroete )		Ukpeneikang
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	0.02	0.02	0.09	0.02
Acenaphthylene	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND
Phenanthrene	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	ND	< 0.001	ND	< 0.001
Pyrene	ND	ND	ND	< 0.001
Benzo[c]phenanthrene	ND	ND	ND	ND
Benz[a]anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND
Benzo[k]fluoranthene	< 0.001	< 0.001	< 0.001	< 0.001
Benzo [e]pyrene	< 0.001	0.01	0.01	< 0.001
Benzo [a]pyrene	< 0.001	0.01	0.01	< 0.001
3-Methylcholanthrene	5.65	2.30	3.56	2.40
Indeno (1,2,3-cd)pyrene	ND	< 0.001	< 0.001	ND
Benzo[ghi]perylene	ND	< 0.001	< 0.001	ND
SUM( PAHs)	5.65	2.34	3.67	2.42

The levels of PAHs in the rainwater in the two seasons were higher than the WHO acceptable limit for PAHs (0.0007 mg/L) in drinking water (Skupinska et al., 2004). Though, there is paucity of data and background

levels of PAHs in rainwater in Nigeria for comparison , opined that gas flaring is the major factor that precipitates acid rain in the Niger Delta region, of which these study areas are part of (Alakpodia, 2000; Efe, 2006).

3.2 Results of Surface Water Samples Analyses

The surface waters from the three study areas during the rainy season have been shown to have the presence of naphthalene and 3-

methylcholanthrene only; all other priority PAHs were below the detection limit . The PAHs levels in the surface waters were in the following order: Ikot Abasi (11.09 mg/L) > Eastern Obolo (3.87 mg/L) > Ibeno (1.94 mg/L), and presented in Table 5.

**Table 3: Concentrations of PAHs in Rainwaters from Ikot Abasi During the Dry Season**

PAH	Ikpetim	ALSCON	Ibom Power	Conveyor Belt ,
	Ikot Abasi	Ikot Abasi	Ikot Abasi	Ikot Abasi
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	< 0.001	0.07	0.05	0.02
Acenaphthylene	< 0.001	ND	ND	ND
Acenaphthene	ND	ND	ND	ND
Fluorene	ND	<0.001	ND	ND
Phenanthrene	0.06	ND	ND	ND
Anthracene	0.07	< 0.001	ND	ND
Fluoranthene	ND	< 0.001	0.002	ND
Pyrene	ND	< 0.001	0.002	ND
Benzo[c]phenanthrene	ND	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	< 0.001	0.001	< 0.001
Benzo [e]pyrene	0.09	0.001	0.001	0.01
Benzo [a]pyrene	0.09	0.003	0.002	< 0.001
3-Methylcholanthrene	ND	3.39	1.22	6.39
Indeno (1,2,3-cd)pyrene	ND	< 0.001	ND	< 0.001
Benzo[ghi]perylene	0.07	< 0.001	ND	< 0.001
SUM(PAHs)	0.38	3.464	1.278	6.42

Surface waters from the three study areas during the dry season reveal the presence of naphthalene, 3-methylcholanthrene, and benzo[a]pyrene only; all other priority PAHs were below detection limit. The PAHs detected in the surface waters were in the following order: Ikot Abasi (13.79 mg/L) > Eastern Obolo (3.95 mg/L) > Ibeno (2.45 mg/L), and presented in Table 6.

PAHs concentrations in drinking and surface waters vary between 1 ug/L and 11 µg/L, with the highest permissible concentration of benzo[a]pyrene (0.7 µg/L) by WHO (Skupinska et al., 2004). The PAHs in the surface waters of the three study areas were found to be higher than the acceptable limit of 0.7 ug/L set by WHO. The results obtained for the concentration of PAHs in surface waters are higher than those obtained by who determined the concentrations of PAHs in drinking water samples and found that the PAH compounds in all samples were below the limits proposed by the Portuguese legislation limiting the total concentrations of four PAHs (IcdP, BghiP, BkF, and BbF) to 0.10 µg/L and BaP limited to the maximum level of 0.010 µg/L. In comparison, this study has higher PAH values (Cardoso et al., 2008). To evaluated the concentration of PAHs in water in Brazil and reported that the mean total concentrations of PAHs were 51.20–162.37 µg/L, which are lower than the results obtained in this study, thus raising a serious public health concern (Froehner et al., 2018).

The predominance of PAHs of higher molecular weight congeners has demonstrated that petroleum and the combustion products of gas flaring,

as well as other pyrogenic sources, may have contributed to the main input of PAHs in the surface waters in the study areas.

On the overall, the levels of PAHs determined in soils of the study areas are lower than those reported in Kenya and China (Guo,2007; Liang, 2022)

3.3 Results of Soil Samples Analyses

The results for the analyses of soil samples from Ikot Abasi, Ibeno, and Eastern Obolo LGAs during the rainy season are presented in Table 7.

Soils from Ibeno LGA showed the presence of naphthalene (920 ug/kg), fluorene (4 ug/kg), phenanthrene (52 ug/kg), fluoranthrene (64 ug/kg), pyrene (196 ug/kg), benzo[c]phenanthrene (20 ug/kg), benzo[a]anthracene (24 ug/kg), chrysene (24 ug/kg), benzo[k]fluoranthrene (40 ug/kg), benzo[e]pyrene (40 ug/kg), benzo[a]pyrene (44 ug/kg), indeno (1,2,3-cd)pyrene (52 ug/kg), and 3-Methylcholanthrene (72 ug/kg), with only indeno (1,2,3-cd)pyrene (780 ug/kg) recorded in Eastern Obolo and only naphthalene (8 ug/kg) recorded in Ikot Abasi. The PAHs levels obtained for the soils in the three study areas during the rainy season followed the following order: Eastern Obolo (776 ug/kg) > Ibeno (732 ug/kg) > Ikot Abasi (8 ug/kg).

The results obtained for soil samples from Ikot Abasi, Ibeno, and Eastern Obolo LGAs during the dry season are presented in Table 8.

**Table 4: Concentrations of PAHs in Rainwaters from Eastern Obolo During Dry Season**

PAH	Eastern Obolo	Eastern Obolo	Ibeno	Ibeno
	Iko	Okoroete	Hall	Ukpeneikang
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	0.03	0.01	0.07	0.04
Acenaphthylene	< 0.001	< 0.001	< 0.001	< 0.001
Acenaphthene	ND	ND	0.01	< 0.02
Fluorene	ND	ND	ND	ND
Phenanthrene	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	< 0.001	< 0.001	< 0.001	< 0.001
Pyrene	ND	ND	< 0.001	< 0.001
Benzo[c]phenanthrene	ND	ND	< 0.001	< 0.001
Benzo[a]anthracene	0.01	0.01	ND	ND
Chrysene	ND	ND	ND	ND
Benzo[k]fluoranthene	< 0.001	< 0.001	< 0.001	< 0.001
Benzo [e]pyrene	< 0.001	0.01	0.01	< 0.001
Benzo [a]pyrene	< 0.001	0.01	0.01	< 0.001
3-Methylcholanthrene	5.42	2.33	3.51	3.63
Indeno (1,2,3-cd)pyrene	ND	< 0.001	< 0.001	< 0.001
Benzo[ghi]perylene	ND	< 0.001	< 0.001	< 0.001
SUM( PAHs)	5.46	2.37	3.61	3.67

**Table 5: Concentrations of PAHs in Surface Waters During Rainy Season**

PAH	Eastern Obolo	Ibena	Ikot Abasi
	Okoroete	Nkpanak	Ikpetim
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	0.02	ND	0.02
Acenaphthylene	ND	ND	ND
Acenaphthene	ND	ND	ND
Fluorene	ND	ND	ND
Phenanthrene	ND	ND	ND
Anthracene	ND	ND	ND
Fluoranthene	< 0.001	ND	ND
Pyrene	< 0.001	ND	ND
Benzo[c]phenanthrene	ND	ND	ND
Benz[a]anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo[k]fluoranthene	< 0.001	< 0.001	< 0.00
Benzo [e]pyrene	< 0.001	< 0.001	< 0.001
Benzo [a]pyrene	< 0.001	< 0.001	0.01
3-Methylcholanthrene	3.85	1.94	11.06
Indeno (1,2,3-cd)pyrene	< 0.001	ND	< 0.001
Benzo[ghi]perylene	< 0.001	ND	< 0.001
SUM(PAHs)	3.87	1.94	11.09

The concentrations of PAHs in soils from Ibena were as follows: naphthalene (92 ug/kg), fluorene (14 ug/kg), phenanthrene (72 ug/kg), fluoranthrene (52 ug/kg), pyrene (172 ug/kg), benzo[c]phenanthrene (36 ug/kg), benzo[a]anthracene (32 ug/kg), chrysene (36 ug/kg), benzo[k]fluoranthrene (48 ug/kg), benzo[k]fluoranthrene (48 ug/kg), benzo[e]pyrene]pyrene (68 ug/kg), benzo[a]pyrene (60 ug/kg), indeno (1,2,3-cd) pyrene (68 ug/kg), 3-Methylcholanthrene (60 ug/kg), fluoranthrene (52 ug/kg), pyrene (172 ug/kg), benzo[c]phenanthrene (36 ug/kg), benzo[a]anthracene (32 ug/kg), chrysene (36 ug/kg), benzo[k]fluoranthrene (48 ug/kg), benzo[e]pyrene (68 ug/kg), benzo[a]pyrene (60 ug/kg), indeno (1,2,3-cd) pyrene (68 ug/kg), 3-Methylcholanthrene (60 ug/kg), and benzo[ghi]perylene (52 ug/kg), with only indeno (1,2,3-cd) pyrene (105 ug/kg) recorded in Eastern Obolo and only naphthalene (20 ug/kg) recorded in Ikot Abasi. The PAHs levels in the soils in the three study areas during the dry season followed the order:

Ibena (872 ug/kg) > Eastern Obolo (105 ug/kg) > Ikot Abasi (20 ug/kg).

From the results of PAHs in the soil samples, soils from Eastern Obolo and Ibena could be slightly polluted (> 700 ug/kg) during the rainy season; however, during the dry season, soils from Ibena LGA could be slightly polluted (> 700 ug/kg), while soil from Ikot Abasi is said to be unpolluted (< 200 ug/kg) in both seasons, based on the classification by (Wu et al.2019).

**3.4 PAH Molecular Diagnostic Ratio Analyses**

The PAH molecular diagnostic ratio analyses using LMW/HMW for rainwater during the rainy season are presented in Table 9. The results were in the following order : Ikot Abasi (0.05) > Ibena (0.02) > Eastern Obolo (0.01)

**Table 6: Concentrations of PAHs in Surface Waters During Dry Season**

PAH	Eastern Obolo	Ibena	Ikot Abasi
	Okoroete	Nkpanak	Ikpetim
	Conc. (mg/L)	Conc. (mg/L)	Conc. (mg/L)
Naphthalene	0.04	< 0.001	0.02
Acenaphthylene	< 0.001	ND	ND
Acenaphthene	< 0.001	ND	ND
Fluorene	ND	ND	ND
Phenanthrene	ND	ND	ND
Anthracene	ND	ND	ND
Fluoranthene	< 0.001	ND	ND
Pyrene	< 0.001	ND	ND
Benzo[c]phenanthrene	ND	ND	ND
Benz[a]anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo[k]fluoranthene	< 0.001	< 0.001	< 0.001
Benzo [e]pyrene	< 0.001	< 0.001	< 0.001
Benzo [a]pyrene	< 0.001	< 0.001	0.04
3-Methylcholanthrene	3.91	2.45	13.73
Indeno (1,2,3-cd)pyrene	< 0.001	< 0.001	< 0.001
Benzo[ghi]perylene	< 0.001	< 0.001	< 0.001
SUM(PAHs)	3.95	2.45	13.79

**Table 7: Concentrations of PAHs in Soils During Rainy Season**

PAH	IbENO	Eastern Obolo	Ikot Abasi
	Ukpeneikang	Iko	Iketim
	( µg/kg )	( µg/kg )	( µg/kg )
Naphthalene	920	ND	8.00
Acenaphthylene	< 0.001	ND	< 0.001
Acenaphthene	< 0.001	ND	< 0.001
Fluorene	4.00	ND	< 0.001
Phenanthrene	520	ND	< 0.001
Anthracene	8.00	ND	< 0.001
Fluoranthene	640	ND	< 0.001
Pyrene	196	ND	< 0.001
Benzo[c]phenanthrene	20.00	ND	ND
Benz[a]anthracene	240	ND	ND
Chrysene	240	ND	ND
Benzo[k]fluoranthene	40.0	< 0.001	ND
Benzo [e]pyrene	40.0	< 0.001	ND
Benzo [a]pyrene	440	< 0.001	ND
Indeno (1,2,3-cd)pyrene	520	776.0	ND
3-Methylcholanthrene	720	ND	ND
Benzo[ghi]perylene	< 0.001	ND	ND
SUM(PAHs)	4548	776	8.00

**Table 8: Concentrations of PAHs in Soils During Dry Season**

PAH	IbENO	Eastern Obolo	Ikot Abasi
	Ukpeneikang,	Iko ,	Iketim , SS 3
	Conc. (µg/kg )	Conc. (µg/kg )	Conc. (µg/kg )
Naphthalene	92.00	ND	20.00
Acenaphthylene	< 0.001	ND	< 0.001
Acenaphthene	< 0.001	ND	< 0.001
Fluorene	4.00	ND	< 0.001
Phenanthrene	72.0	ND	< 0.001
Anthracene	20.0	ND	< 0.001
Fluoranthene	52.0	ND	< 0.001
Pyrene	172.0	ND	< 0.001
Benzo[c]phenanthrene	36.0	ND	ND
Benz[a]anthracene	32.0	ND	ND
Chrysene	36.0	ND	ND
Benzo[k]fluoranthene	48.0	< 0.001	ND
Benzo [e]pyrene	68.0	< 0.001	ND
Benzo [a]pyrene	60.0	< 0.001	ND
Indeno (1,2,3-cd)pyrene	68.0	105.00	ND
3-Methylcholanthrene	60.0	ND	ND
Benzo[ghi]perylene	52.0	ND	ND
SUM( PAHs)	872.0	105.0	20.0

The LMW/HMW PAH ratios for rainwater in the three study areas during the rainy season are less than one, indicating a petrogenic source, according to Rocher et al. (2004). The BaA/(BaA + Chrysene) ratios calculated for rainwater for all study areas during the rainy season was less than 0.2, indicating a petrogenic source of PAHs. The Ant/(Ant + Phe) ratios calculated for rainwater for all the study areas during the rainy season were less than 0.1, indicating a petrogenic source of PAHs.

Surface water samples from the three study areas during the rainy season gave an LMW/HMW ratios of less than 1 (Table 9), indicating a pyrogenic source of PAHs. BaA/(BaA + Chrysene) ratios were less than 0.2, and Ant/(Ant + Phe) were less than 0.1, indicating a petrogenic source of PAH.

PAH molecular diagnostic ratio using LMW/HMW for soil samples during the rainy season for Ikot Abasi was 0.001, IbENO 0.47 and Eastern Obolo 8.0, as presented in Table 9. According to LMW/HMW ratios for soils in Ikot Abasi and IbENO were less than one, indicating a pyrogenic source from incomplete combustion of organic substances, while Eastern Obolo soils had values greater than one, indicating petrogenic source from petroleum leakages (Rocher et al., 2004). This also corroborates the observation by S. Liang et al. 2022, in their studies of PAHs in Kenya.

PAH molecular diagnostic ratios using LMW/HMW for rainwater during the dry season in Ikot Abasi was 0.05, IbENO 0.02 and Eastern Obolo 0.01, and are presented in Table 10.



Table 9: Molecular Ratio of PAHs During the Rainy Season					
Molecular Ratio	Sample	Ikot Abasi	Ibeno	Eastern Obolo	Standard / indication
LMW /HMW		0.05	0.02	0.01	< 1, Pyrogenic
BaA/(BaA + Chrysene)	Rainwater	< 0.01	< 0.01	< 0.01	< 0.2, Petrogenic
					0.2 - 0.35, Petrogenic
					and pyrolytic
Ant / (Ant + Phe )		< 0.001	< 0.01	< 0.01	< 0.1, Petrogenic
LMW /HMW	Surface water	0.01	< 0.01	< 0.01	< 1,Petrogenic
BaA/(BaA + Chrysene)		< 0.01	< 0.01	< 0.01	Petrogenic
Ant / (Ant + Phe )		< 0.01	< 0.01	< 0.01	Petrogenic
LMW /HMW	Soil	0.469	< 0.001	> 8	< 1, Pyrogenic
BaA/(BaA + Chrysene)		< 0.001	0.5	< 0.001	
Ant / (Ant + Phe )		< 0.1	< 0.1	< 0.1	Petrogenic

Table 10: Molecular Ratio of PAHs During the Dry Season					
Molecular Ratio	Sample	Ikot Abasi	Ibeno	Eastern Obolo	Standard / indication
LMW /HMW	Rainwater	0.05	0.02	0.01	< 1, Petrogenic
BaA/(BaA + Chrysene)		< 0.01	< 0.01	< 0.01	< 0.2, Petrogenic
					0.2 - 0.35, Petrogenic
					and pyrolytic
Ant / (Ant + Phe )		< 0.001	< 0.01	< 0.01	< 0.1, Petrogenic
	Surface water	0.01	< 0.01	< 0.01	pyrogenic
LMW /HMW					
BaA/(BaA + Chrysene)		< 0.01	< 0.01	< 0.01	Petrogenic
Ant / (Ant + Phe )		< 0.01	< 0.01	< 0.01	Petrogenic
LMW /HMW	Soil	20	0.27	< 0	
		pyrogenic	pyrogenic	pyrogenic	
BaA/(BaA + Chrysene)		< 0	0.47	< 0	
		pyrogenic	pyrogenic	pyrogenic	
Ant / (Ant + Phe )		< 0	0.22	< 0	
		pyrogenic	pyrogenic	pyrogenic	

The PAH molecular ratios for the three study areas are less than one, indicating a pyrogenic source, according to Rocher et al. (2004). The BaA/(BaA + Chrysene) ratio calculated for rainwater during the dry season was all less than 0.2, indicating a petrogenic source of PAHs. The ant/(Ant + Phe) ratio calculated for rainwater during the dry season was less than 0.1, indicating a petrogenic source of PAHs.

Surface water samples from the three study areas during the dry season, had an LMW/HMW ratio of less than 1 (Table 10), indicating a petrogenic source of PAHs. BaA/(BaA + Chrysene) ratio was less than 0.2, indicating a petrogenic source and Ant/(Ant + Phe) ratios were less than 0.1, indicating a petrogenic source of PAH.

PAH molecular diagnostic ratio analyses by LMW/HMW for soil samples during the dry season were Ikot Abasi (> 20), Ibeno (0.27), and Eastern

Obolo (< 0), as presented in Table 10. The ratios for Eastern Obolo and Ibeno were less than one, indicating a petrogenic source, while the ratio for Ikot Abasi was greater than one, indicating a pyrogenic source probably from incomplete combustion of organic substances (Rocher et al. 2004).

### 3.5 Physicochemical Parameters of Rainwater

The physicochemical parameters of rainwater from the three study areas in the dry and rainy seasons are presented in Table 11. During the rainy season, the pH values were in the following order: Ibeno (6.76 ± 0.05) > Ikot Abasi (6.38 ± 0.02) > Eastern Obolo (5.87 ± 0.07), while the pH values during the dry season were in the following order: Ikot Abasi (6.58 ± 0.06) > Eastern Obolo (6.55 ± 0.07) > Ibeno (6.49 ± 0.09).

**Table 11: Physicochemical Parameters of Rainwater**

Parameter	Wet Season			Dry Season		
	Ikot Abasi	Ibena	Eastern Obolo	Ikot Abasi	Ibena	Eastern Obolo
pH	6.38 ± 0.02	6.76 ± 0.05	5.87 ± 0.07	6.58 ± 0.06	6.49 ± 0.08	6.55 ± 0.07
Conductivity (µ S/cm)	7.99 ± 0.03	187.1 ± 2.85	102.5 ± 3.06	8.63 ± 0.14	202 ± 4.95	82.4 ± 3.95
Salinity (‰)	0.00	0.02 ± 0.001	0.00	0.00	0.01 ± 0.003	0.00
Total dissolved solids ( mg /L)	6.05 ± 0.02	125.2 ± 2.76	53.09 ± 2.84	4.37 ± 0.03	101.2 ± 2.92	41.5 ± 2.66
Temperature( ° C)	24.72 ± 1.09	24.75 ± 0.74	25.62 ± 1.52	25.92 ± 0.34	26.4 ± 0.84	26.5 ± 0.67

During the rainy season, conductivity was in order: Ibena ( 187.1± 2.85 uS/cm) > Eastern Obolo (102.5 ± 3.06 uS/cm) > Ikot Abasi (7.99 ± 0.03 uS/cm), while during the dry season, conductivity was in the order: Ibena (202 ± 4.95 uS/cm) > Eastern Obolo (82.4 ± 3.95 µS/cm) > Ikot Abasi (8.63 ± 0.14 µS/cm).

The salinity determined in the rainwater from the three study areas was Ikot Abasi (0.0 ‰), Ibena (0.02 ± 0.001‰), and Eastern Obolo (0.0‰), whereas during the dry season, the salinity was Ikot Abasi (0.0 ‰), Ibena (0.01 ± 0.003‰), and Eastern Obolo (0.0‰), indicating less impact of salt water evaporation.

The total dissolved solids in the rainwater during the rainy season were in the order: Ibena (125.2 ± 2.76 mg/L) > Eastern Obolo (53.09 ± 2.84 mg/L) > Ikot Abasi (6.05 ± 0.02 mg/L), while the total dissolved solids in the rainwater during the dry season were in the order Ibena (101.2 ± 2.92 mg/L) > Eastern Obolo (41.5 ± 2.66 mg/L) > Ikot Abasi (4.37 ± 0.03 mg/L), as presented in Table 11. The variation in the results in the two seasons was not significant ( P < 0.01) in the three locations.

**3.6 Ecological Risk Assessment of Pachs In Soil**

The method used to calculate the benzo[a]pyrene toxic equivalent concentration (TEQB[a]P) was as adopted by S. Liang et al.(2022), to evaluate the risk of PAHs in the soil. The total TEQB[A]P determined during the rainy season were in the order (Table 12) ; Ibena (747µg/kg ) > Eastern Obolo ( 77.6 µg/kg ) > Ikot Abasi ( 0.008 µg/kg ) , while the TEQB[A]P values for the dry season were in the order : Ibena ( 114 µg/kg ) > Eastern Obolo ( 10.6 µg/kg ) > Ikot Abasi ( 0.02 µg/kg).

These values were lower than the total TEQB[A]P of sixteen PAHs in semiarid soils of India (650 µg/kg, A. Masih and A. Taneja, (2006).), except Ibena, during the rainy season. However, the values were higher than the total TEQB[A]P of Visevu (24 µg/kg) and Ribens soil of Portugal (S. Rodrigues, 2006).

Presently, there is no evaluation standard for soil PAHs in Nigeria, hence the threshold value of TEQB[a]P (33.0 µg/kg) from Dutch soil management regulations was applied to test the potential risk of PAHs in soils from the study areas. The TEQB[a]P values of soils in this study are higher than 33.0 µg/kg, indicating that the soil PAHs in these locations has potential

carcinogenic risks to the human body.

Table 12: TEQ of PAHs in Soil		
Rainy Season		
Ibena ( µg/kg )	Eastern Obolo (µg/kg )	Ikot Abasi (µg/kg )
747	77.6	0.008
Dry Season		
Ibena (µg/kg )	Eastern Obolo (µg/kg )	Ikot Abasi (µg/kg )
114.	10.5	0.02

**4. CONCLUSION**

The study reveals the following polyaromatic hydrocarbons in rainwater and surface waters in Ikot Abasi, Ibena, and Eastern Obolo LGAs during the rainy and dry seasons: naphthalene, benzo[k]fluoranthrene, benzo[e]pyrene, benzo[a]pyrene, and 3-methylcholanthrene. Most of the other sixteen priority PAHs, like acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene, were not present in the rainwater and surface waters. The levels of the PAHs in the rainwater and surface waters from the three study areas of Ikot Abasi, Eastern Obolo, and Ibena were higher than the WHO permissible limits for PAHs (0.7 µg/L) in drinking water.

From the results obtained, the levels of the PAHs in the soil samples, from

Eastern Obolo and Ibena are slightly polluted (> 700 ug/kg) during the rainy season, whereas during the dry season, soils from Ibena are slightly polluted (>700 ug/kg). In comparison, soils from Ikot Abasi are most likely to be unpolluted (< 200 ug/kg) in both seasons, based on the classification by (Wu et al., 2019).

PAH molecular diagnostic ratios using LMW/HMW, BaA/(BaA + Chrysene) ratio, and Ant/(Ant + Phe) ratios for rainwater and surface waters from the three study areas revealed a petrogenic source of PAHs during the rainy and dry seasons.

PAH molecular diagnostic ratios using LMW/HMW for soil samples during the rainy season in Ikot Abasi and Ibena show that the PAHs are from a petrogenic source, while the Eastern Obolo ratios show a pyrogenic source of PAHs from incomplete combustion of organic substances from anthropogenic activities. However, PAH molecular diagnostic ratios using LMW/HMW for soil samples during the dry season in Eastern Obolo and Ibena show a petrogenic source, while Ikot Abasi PAH molecular ratios show a pyrogenic source from incomplete combustion of organic substances from anthropogenic activities as a result of the power plant located in the area.

The variation in the physicochemical parameters of the rainwaters from the three study areas in the two seasons was not significant (P< 0.05); however, the total dissolved solids of the rainwater from Ibena were significantly higher than those from Ikot Abasi and Eastern Obolo, probably because of the intense anthropogenic activities in the area.

Generally, there is no evaluation standard for PAHs in Nigeria, hence the threshold value of TEQB[a]P (33.0 µg/kg ) from Dutch soil management regulations was applied to test the potential risk of PAHs in soils from the study areas. The TEQB[a]P values of soils in this study are higher than 33.0 µg/kg, indicating that the soil PAHs in these locations has potential carcinogenic risks to the human body.

Therefore, there is need for close monitoring of PAHs levels in the study areas and the need to minimise gas flaring activities by appropriate legislation in Nigeria.

**CONFLICT OF INTEREST**

The authors express no conflict of interest in the study

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<b>Appendix 1: TEF Values of Pahs and Allowable Values of Soil Quality in the Netherlands (A. Srivastava and Som, 2007)</b>								
<b>Pollutant</b>	<b>Nap</b>	<b>Acy</b>	<b>Ace</b>	<b>Fle</b>	<b>Phe</b>	<b>Ant</b>	<b>Flu</b>	<b>Pyr</b>
TEF Value	0.001	0.001	0.001	0.001	0.001	0.01	0.001	0.001
Standard(ng/g)	15				50	50	15	
<b>Pollutant</b>	<b>BaA</b>	<b>Chr</b>	<b>B[b]F</b>	<b>B[k]F</b>	<b>B[a]P</b>	<b>Dib</b>	<b>B[ghi]P</b>	<b>Ind</b>
TEF Value	1	0.01	0.1	0.1	1	1	0.01	0.1
Standard(ng/g)	20	20	25	25			25	