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Occurrence, Source Apportionment and Health Risk Assessment of Polycyclic Aromatic Hydrocarbons in Rainwater from Niger Delta Oil-Producing Communities: Policy and Management Implications

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ABSTRACT

Oil extraction activities, particularly gas flaring and artisanal refining, have contributed to the contamination of rainwater in the Niger Delta, potentially increasing human exposure to toxic chemicals. Given the limited information on the occurrence, distribution, and sources of PAHs in rainwater across multiple emission pathways, this study investigated sixteen USEPA priority PAHs in rainwater samples from seven oil-producing communities in Ogbia Local Government Area (LGA), Bayelsa State, Nigeria. Eleven PAH congeners were detected, with total PAH concentrations ranging from 0.22 to 1.27 µg/L and an overall mean of 0.519 ± 0.360 µg/L. Mean environmental concentrations (MEC) ranged from 0.0300 µg/L for acenaphthene to 0.3860 µg/L for phenanthrene, while RWIM1 was identified as a spatial hotspot. Phenanthrene exceeded the USEPA chronic water quality criterion (0.2 µg/L) and its ERL (0.240 µg/L), while acenaphthene exceeded its ERL (0.016 µg/L). Diagnostic molecular ratios indicated mixed petrogenic and pyrogenic inputs, while PCA identified petroleum- and combustion-related influences, with the first two components explaining 88.13% of the total variance. Carcinogenic risk assessment showed elevated cumulative Risk Index (RI) values, with the highest value of 7.47×10^{-1} observed in children through dermal exposure, while Hazard Index values remained below the USEPA threshold. The findings highlight rainwater as an important pathway for PAH exposure and support stronger enforcement of emission standards for gas flaring and artisanal refining, alongside household-level measures to reduce exposure from untreated rainwater, particularly among children.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs); Niger Delta; Rainwater Contamination; Atmospheric Deposition; Source Apportionment; Environmental Health Risk

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of global persistent organic pollutants (POPs) that are highly persistent in the environment, lipophilic in nature and known to cause cancer and mutations (Zhao *et al*., 2017; Patel *et al*., 2020). They are mainly generated by the incomplete combustion of hydrocarbon materials and the release of unburned petroleum products, which makes them good markers of anthropogenic influences in environmental systems (Sun *et al*., 2022).

Atmospheric concentrations of PAH in oil-producing areas like the Niger Delta, which is attributed to the combined effect of gas flaring, artisanal refining, biomass burning and motorized activity are high (Shimada *et al*., 2022). Once released, PAHs are redistributed and deposited over great distances by wet and dry deposition. Rainwater is an important sink for gaseous and particle-bound PAHs (Hu *et al*., 2021; Li *et al*., 2016). In Bayelsa State, rainwater is routinely used for domestic and agricultural purposes thus, a potential exposure route for inhabitants of the state.

While several researchers have documented soil and surface water contamination in the Niger Delta (Leizou *et al*., 2022; Ezekwe *et al*., 2025), limited information is available on the presence, distribution, and sources of PAHs in rainwater, particularly across multiple emission pathways. This study therefore investigated PAH source-to-sink dynamics in rainwater systems in the Niger Delta using an integrated approach combining diagnostic molecular ratios and Principal Component Analysis (PCA). The study aims to improve understanding of PAH contamination in rainwater systems in the Niger Delta and provide a basis for environmental management, emission control, regulatory enforcement, and improved protection of rainwater quality. Specifically, the study aimed to quantify and map USEPA priority PAHs in rainwater samples collected from seven communities in Ogbia Local Government Area (LGA); identify PAH sources using diagnostic molecular ratios and Principal Component Analysis (PCA); and assess the associated human health risks to adult and child populations under non-carcinogenic and carcinogenic exposure scenarios

MATERIALS AND METHODS

Study Area and Sampling Strategy

The study was conducted in Ogbia Local Government Area (LGA), within the rainforest and coastal swamp ecosystem of Bayelsa State, Nigeria. The area has a long-wet season (February to November), with high rainfall and humidity. Economic activities in the region include farming, fishing, and oil prospecting, which have contributed to environmental stress in the area. Samples were collected from carefully selected communities where oil exploitation and associated activities, including gas flaring and artisanal refining, are major sources of hydrocarbon emissions in the Niger Delta. The selected communities were Otuasega (4.93°N, 6.40°E), Imiringi (4.80°N, 6.30°E), Iberiberi (4.90°N, 6.40°E), and Otuoke (4.79°N, 6.32°E). A total of seven sampling locations were established: Otuasega (OTG1 and OTG2), Imiringi (IM1 and IM2), Iberiberi (IB1 and IB2), and Otuoke (OTU). For rainwater samples, the prefix “RW” was added to the site codes, resulting in RWOTG1, RWOTG2, RWIM1, RWIM2, RWIB1, RWIB2, and RWOTU. Otuoke was used as the reference site, while the other sites were impacted by petroleum-related activities and associated hydrocarbon emissions. Table 1 provides the coordinates and descriptions of the sampling sites. Rainwater was collected on site during rainfall to capture atmospheric deposition. Sterilized glass funnels were attached to raised platforms to prevent contamination from splashing and contact with other surfaces. Samples were collected in 1-L amber glass bottles and stored at 4 °C until extraction and analysis in the laboratory.

Analytical and Quality Control Procedures

The sample preparation using sonication aided extraction method was used as described by Wild & Jones (1995). Rainwater samples (250ml) were dried by adding 10 g anhydrous Na_2SO_4 then extracting them by 1:1 acetone/dichloromethane (DCM) extracted, in 45-minute intervals, twice. The concentrated solution (5ml) was purified through silica gel column (10mm x 250mm). PAH fractions were then eluted with methylene chloride and then evaporated to 1ml with a slow flow of nitrogen gas. The quantification was carried out with HP 6890 Series GC-FID equipped with HP-5 columns (30m x 0.25mm x 0.25um).

Table1: Geographic and Environmental Characteristics of Sampling Sites

Station Code	Community	Coordinates	Local Activities & Environmental Risks
RWOTU	Otuoke	4.79° N, 6.32° E	Semi-urban University town; institutional interface; close proximity to oil infrastructure and related anthropogenic activities of the Niger Delta
RWOTG1/2	Otuasega	4.93° N, 6.4° E	Active crude oil flow stations; pipeline corridor; high risk of spill-rebated contamination
RWIM1/2	Imiringi	4.8° N, 6.3° E	Intensive gas-flaring infrastructure; long-term atmospheric hydrocarbon exposure
RWIB1/2	Iberiberi	4.9° N, 6.4° E	Legacy hydrocarbon contamination; frequent oil spills, agricultural and fishing hub

The thermal program included holding the oven at 80°C for 1 minute then ramping up to 280°C for 2 minutes and finally increasing to 300°C at a rate of 2.5°C/minute. All concentrations listed were in µg/L per sample. The individual PAHs species were identified and quantified by matching retention time with those of certified standard. Accuracy was assured by Surrogate Recovery that gave from 85% to 110% and method detection limits calculated were within µg/L range. The amount of each PAH congeners was estimated using Peak Area Ratio (PAR) as detailed below according to Uzoekwe & Ikpesu (2019).

Concentration of analyte (µg/L) =

$$(A_x)(I_s)/(A_{is})(RRF)(V_s) \times 1/SF \quad _____ 1$$

Where:

Ax= area of the analyte
I_s = concentration of internal standard injected (µg)
RRF = relative response factor derived from the calibration curve
V_s = volume of the rainwater sample extracted (L), and SF is the Split factor

The concentration of PAHs in the rainwater of Ogbia Local Government Area was presented as mean ± Standard Deviation (SD). Data analysis, including multivariate receptor modeling, was carried out using IBM SPSS Statistics (Version 29).

Source Identification Using Diagnostic Molecular Ratios

PAH sources in Ogbia LGA were investigated using diagnostic molecular ratios based on the relative stability and structural characteristics of selected PAH congeners. These ratios provide source fingerprints that can be used to distinguish between predominantly petrogenic and pyrogenic inputs. The diagnostic ratios applied in this study and their corresponding source interpretations are presented in Table 2.

Table 2: PAH Diagnostic Ratios and Source Interpretation

PAH Ratio	Threshold Value	Source Interpretation	Reference
LMW/HMW	< 1.0 >1.0	Pyrogenic (combustion) Petrogenic (crude oil)	Zhang *et al*. (2008); Tobiszewski & Namieśnik (2012)
ANT / (ANT+ PHE)	< 0.10 > 0.10	Petrogenic Pyrogenic	Pies *et al*. (2008); Yunker *et al.* (2002)
FLT / (FLT+PYR)	< 0.40 0.40 – 0.50 > 0.50	Petroleum / Petrogenic Liquid Fossil Fuel Combustion Biomass (Wood, Grass) and Coal Burning	Yunker *et al*. (2002)
∑COMB/∑PAH	< 0.50 ≈ 1.0 (> 0.50)	Petrogenic / Non-combustion Dominant Combustion Dominant	Ravindra *et al*. (2008)

∑COMB (summates Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd] pyrene, and Benzo[ghi]perylene)

Multivariate Statistical Analysis

For all statistical analyses, a significance level of $p \leq 0.05$ was adopted. Pearson correlation analysis was used to examine the relationships among the PAH congeners and identify patterns of shared variability that could indicate common or related emission influences. Principal Component Analysis (PCA) was subsequently used to identify dominant patterns in the PAH dataset and provide further evidence for possible emission sources.

Prior to PCA, the Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity were performed to assess the suitability of the dataset for multivariate analysis. Components with eigenvalues >1.0 were retained, following the criterion of Hair *et al*. (2018). Varimax rotation was applied to facilitate interpretation of the extracted components. The resulting component loadings and score patterns were used to identify possible source-related groupings and assess spatial differences in PAH profiles among the sampling locations.

Multi-criterial Risk Assessment Framework

The ecological and human health risks were analysed in this study using a Multi-criterial risk assessment approach for the deposition of PAHs in rainwater. The framework included characterization of ecological risk, mixture toxicity assessment, estimation of exposure dose and assessment of non-carcinogenic and carcinogenic risk. Eco-risk quantification was done using the internationally recognized water quality guidelines of USEPA and sediment quality criteria (ERL/ERM) as reference values for the environmental concentrations.

Ecological Risk Quotients (RQ)

The ecological risk to aquatic environment was estimated with RQ method, in which measured environment concentrations (MECs) of individual PAHs in rainwater were compared to that of predicted no-effect concentrations (PNECs) for aquatic systems.

$$RQ = \frac{MEC_{PAH}}{PNEC_{PAH}} \quad 2$$

Where:

MEC_{PAH} = measured concentration of the PAH congener in rainwater (µg/L)

$PNEC_{PAH}$=predicted no-effect concentration for aqueous matrix (µg/L)

The risk classifications were according to benchmark thresholds presented in Table 3.

Table 3: Aqueous Ecological Risk Benchmarks (PNEC) and Characterization Scale

PAH Component	PNEC (µg/L)	Risk Characterization Scale	Reference
Naphthalene	1.20	RQ < 0.1: Negligible/Low Risk	USEPA/EU WFD
Phenanthrene	0.50	0.1 ≤ RQ < 1.0: Moderate Risk	Negri *et al*. (2020)
Benzo[a]pyrene	0.05	RQ ≥ 1.0: High/Extreme Risk	EU EQS (2013)

Toxic and Mutagenic Potency (TEQ & MEQ)

Overall toxicity and mutagenicity of PAH mixtures were evaluated with Toxic Equivalency Quotients (TEQ) and Mutagenic Equivalency Quotients (MEQ), relative to Benzo[a]pyrene.

$$TEQ = \sum (C_n \times TEF_n) \quad 3$$

$$MEQ = \sum (C_n \times MEF_n) \quad 4$$

Where:

C_n = concentration of the nth PAH congener in the sample (µg/L)

TEF_n = toxic equivalency factor

MEF_n = mutagenic equivalency factor

Exposure Dose Estimation (DAD & CDI)

Using DAD and CDI measures, human exposure to all pollutants were measured for dermal absorption and ingestion pathways.

$$DAD = \frac{C \times SA \times K_p \times CF \times ET \times EF \times ED}{BW \times AT} \quad 5$$

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad 6$$

Where:

C = PAH concentration in rainwater (µg/L)

SA = exposed skin surface area (18,000 cm^2 for adults; 6,600 $cm^{2\ for}$ children)

K_p = dermal permeability coefficient (cm/h)

CF = volumetric conversion factor (0.001 L/cm^3)

ET = exposure time (0.58 h/day adults; 1 h/day for children)

EF = exposure frequency (350 days/year)

ED = exposure duration (30 years adults; 6 years children)

BW = average body weight (70 kg adults; 15kg children)

AT = averaging time (ED x 365 days)

IR = Ingestion Rate (0.05 L/day adults; 0.1 L/day children)

Carcinogenic and Non-Carcinogenic Risk (HI & ILCR)

Non-carcinogenic risk was assessed by using the Hazard Index (HI), which was the sum of individual Hazard Quotients (HQ).

$$HQ_i = \frac{DAD_i \text{ or } CDI_i}{RfD_i} \quad \text{7a}$$

$$HI = \sum HQ_i \quad \text{7b}$$

Where:

HQ_i= hazard quotient for i^{th} PAH congener

DAD_i = dermal absorption dose

CDI_i = chronic average daily intake

RfD_i = reference dose (mg/kg/day)

HI > 1 = potential for adverse health effects

Incremental Lifetime Cancer Risk (ILCR) model was used to represent the possibility of cancer development:

$$ILCR = LADD \times CSF \quad \text{8}$$

Where:

LADD = Lifetime Average Daily Dose (mg/kg/day)

CSF = Cancer Slope Factor $(mg/kg/day)^{-1}$

Cumulative Cancer Risk Index (RI)

Overall carcinogenic risk was expressed as a cumulative Risk Index (RI), obtained by summing ILCR values across exposure pathways and PAH congeners:

$$RI = \sum ILCR_{pathway} \quad \text{9}$$

Each of the PAH concentration has been adjusted with respect to benzo[a]pyrene equivalents (BaPeq) to consider different carcinogenic potencies. A CSF value of 7.3 $(mg/kg/day)^{-1}$ was taken into account for highly toxic congeners, like dibenzo[a,h]anthracene (DahA), while BaA was standardized on its toxic equivalency factor (TEF = 0.1), resulting in CSF = 0.73 $(mg/kg/day)^{-1}$.

Categorization of the risks was performed by U.S. EPA standards (Table 4), whereby levels less than 10^{-6} mean insignificant risk, 10^{-6} to 10^{-4} mean acceptable risk and levels above 10^{-4} mean high/unacceptable risk requiring intervention.

Table 4: USEPA Carcinogenic Risk Characterization Scale

Calculated RI Value	Risk Level/ Category	Interpretation/Action
$< 10^{-6}$	Negligible	Risk is considered insignificant; no regulatory action required
10^{-6} to 10^{-4}	Acceptable/ Tolerable	Within the generally acceptable range for regulatory purposes
$>10^{-4}$	Unacceptable/ High Risk	Indicates a significant public health threat and requires immediate intervention

RESULTS AND DISCUSSION

Atmospheric Scrubbing: Effect of Meteorology on PAH Sequestration

Atmospheric scavenging was identified as the dominant pathway controlling the removal of gaseous and particle-bound PAHs in Ogbia LGA. Persistently high humidity and prolonged rainfall in the Niger Delta region enhance wet deposition processes, facilitating efficient transfer of atmospheric pollutants into precipitation. The water solubility and volatility of two- and three-ring PAHs promotes their preferential removal from the atmosphere during rainfall events (Casas *et al*., 2021). This mechanism is corroborated by the presence of low molecular weight (LMW) PAHs in the study, with a mean concentration of 0.384 µg/L (Table 5).

The ring-class distribution of PAH concentrations revealed that the 2–3 ring PAHs consistently dominated in the water sample in the study locations, suggesting good PAH partitioning into the gas phase followed by rapid wet deposition. In contrast, high molecular weight (HMW) PAHs are less soluble, more likely to be associated with particles, and less likely to be transferred into the aqueous phase. These lead to lower scavenging efficiency (Li *et al.*, 2016). However, occasional enrichments of high ring PAHs at certain locations may be due to episodic sources of combustion from the local area and not necessarily as a result of regional atmospheric background conditions. The distribution is the consequence of a combination of physicochemical properties and humid tropical weather conditions that favor efficient removal of LMW PAH while limiting the deposition of heavier fractions to the atmosphere. Uzoekwe and Ikpesu (2020) and Tarawou *et al.* (2021) reported similar patterns in humid tropics, suggesting that the rainfall was effective in scavenging low molecular weight PAHs.

Spatial Distribution and Composition of PAHs in Rainwater

Eleven of the sixteen USEPA priority PAHs were detected across the seven sampling locations (Table 5), indicating the widespread occurrence of PAHs in rainwater within the study area. Total PAH concentrations (∑16 PAHs) ranged from 0.22 µg/L at RWIB1 to 1.27 µg/L at RWIM1, with an overall mean concentration of 0.519 ± 0.360 µg/L. Naphthalene was detected at all sampling locations and showed considerable spatial variation, with concentrations ranging from 0.04 to 0.42 µg/L, while acenaphthene ranged from 0.04 to 0.09 µg/L and phenanthrene from 0.012 to 0.15 µg/L. Dibenz[a,h]anthracene (DahA) also showed a pronounced spatial pattern, reaching 0.36 µg/L at RWIM1 compared with 0.04 to 0.06 µg/L at the other sites.

The spatial distribution of total PAHs derived from these measurements is presented in Figure 1. Significant spatial variations were observed across the study area, with Imiringi Site 1 (RWIM1) identified as the hotspot. The concentration at RWIM1 was approximately three times higher than that at RWIM2 (0.43 µg/L) and nearly six times higher than that at RWIB1 (0.22 µg/L), indicating marked spatial variability in PAH distribution. The differences in total concentration were accompanied by differences in PAH composition. RWIM1 recorded the highest concentrations of both LMW and HMW PAHs, with ∑LMW and ∑HMW concentrations of 0.79 and 0.48 µg/L, respectively.

Table 5: Concentrations (µg/L) of Polycyclic Aromatic Hydrocarbon

PAH	RWOTU	RWOTG1	RWOTG2	RWIM1	RWIM2	RWIB1	RWIB2	Mean ± SD
Naph	0.04	0.09	0.04	0.42	0.04	0.04	0.33	0.143 ± 0.161
Amy	0.04	0.04	0.04	0.06	0.06	0.04	0.04	0.046 ± 0.010
Ane	0.06	0.09	0.04	0.06	0.04	0.04	0.09	0.060 ± 0.022
Phe	0.04	0.04	0.012	0.15	0.09	.06	0.04	0.062 ± 0.046
Ant	0.04	ND	0.04	0.04	0.04	ND	0.04	0.034 ± 0.015
Flu	0.04	0.04	0.04	0.06	0.04	0.04	0.06	0.046 ± 0.010
Pyr	ND	ND	0.04	ND	0.04	ND	0.04	0.017 ± 0.021
BaA	ND	ND	ND	0.04	ND	ND	ND	0.006 ± 0.015
Flt	0.04	ND	0.04	0.04	0.04	ND	ND	0.023 ± 0.019
BkF	ND	ND	ND	0.04	ND	ND	ND	0.006 ± 0.015
DahA	0.04	0.06	0.04	0.36	0.04	ND	0.04	0.083 ± 0.123
*Others	ND	ND	ND	ND	ND	ND	ND	0.000
∑ 16 PAHs	0.34	0.36	0.332	1.27	0.43	0.22	0.68	0.519 ± 0.360
∑ LMW	0.26	0.30	0.212	0.79	0.31	0.22	0.60	0.384 ± 0.225
∑ HMW	0.08	0.06	0.12	0.48	0.12	0.00	0.08	0.134 ± 0.164
∑ 2-Rings	0.04	0.09	0.04	0.42	0.04	0.04	0.33	0.143 ± 0.162
∑ 3-Rings	0.22	0.51	0.172	0.37	0.27	0.18	0.27	0.285 ± 0.120
∑ 4-Rings	0.04	0.00	0.08	0.08	0.08	0.00	0.04	0.046 ± 0.036
∑ 5-Rings	0.04	0.06	0.04	0.40	0.04	ND	0.04	0.037 ± 0.018
∑ 6-Rings	0	0	0	0	0	0	0	0

Naphthalene (Naph); Acenaphthylene (Any); Acenaphthene (Ane); Phenanthrene (Phe); Anthracene (Ant); Fluorene (Flu); Pyrene (Pyr); Benz[a]anthracene (BaA); Fluoranthene (Flt); Benzo[k]fluoranthene (BkF); Dibenzo[a,h]anthracene (DahA); *Others (Benzo(a)Pyrene (BaP); Benzo(b)Fluoranthene (BbF); Indeno(1,2,3, -Cd)Pyrene(IcdP); Benzo(g,h,i)Perylene(BghiP); Chrysene (Chry)). ND: not detected.

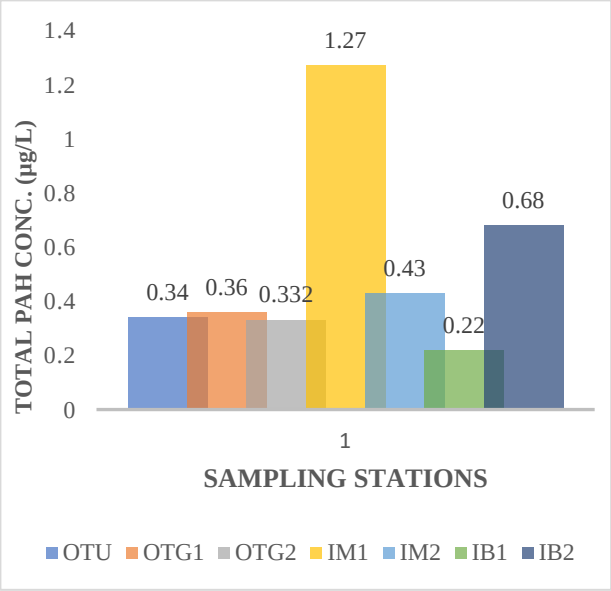


Figure 1: Spatial Distribution Profile

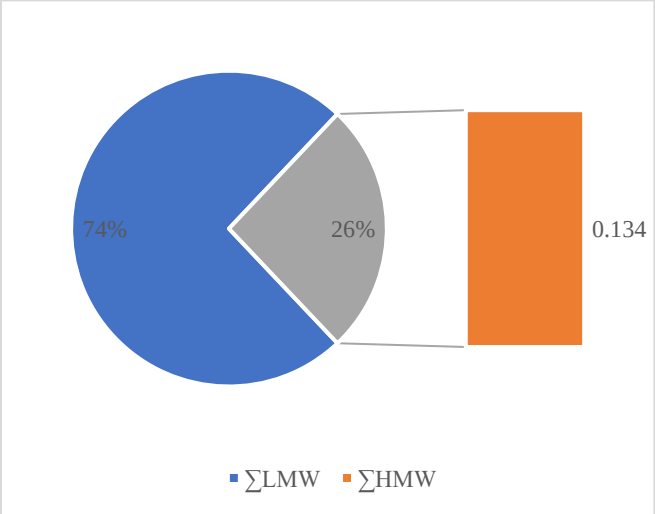


Figure 2: Percentage distribution of Low Molecular Weight (LMW) and High Molecular Weight (HMW) PAHs in rainwater.

Molecular-Weight and Ring-Size Distribution of PAHs

The molecular-weight and ring-size distribution of PAHs provided further insight into the composition of the rainwater samples (Table 5; Figure 2). LMW PAHs, comprising the 2–3 ring compounds, accounted for approximately 74% of the total PAH concentration, while HMW PAHs (4–5 ring compounds) contributed 26%. The predominance of LMW PAHs indicates that lower molecular-weight compounds constituted the major fraction of PAHs detected across the study area. Naphthalene and acenaphthene were detected at all sampling locations, consistent with the widespread occurrence of volatile PAH fractions. Although HMW PAHs contributed a smaller proportion overall, their higher contribution at RWIM1, where both LMW and HMW concentrations were highest, suggests a localized influence of combustion-related inputs. The molecular-weight profile therefore indicates that lower molecular-weight PAHs predominated overall, with localized enrichment of higher molecular-weight compounds at RWIM1. Source attribution based on diagnostic molecular ratios and PCA is presented in the subsequent section.

The detection of naphthalene and acenaphthene at all sampling points further supports this pattern. Both PAHs are commonly associated with recent petroleum inputs and volatile fuel fractions rather than high-temperature combustion products. The ubiquitous occurrence of these compounds indicates continued effect of petroleum-related activities in the study area. The limited contribution of high molecular weight (HMW) PAHs indicates modest influence of high-temperature combustion processes such as biomass burning. The compositional profile thus demonstrates the dominance of petroleum-derived inputs in the study area, which is typical of the oil producing area of Southern Nigeria (Akinnusotu *et al*., 2023; Leizou *et al*., 2022).

Multivariate Analysis and Source Identification

A hierarchical multivariate statistical approach was used to examine relationships among the PAH congeners and identify possible emission influences in Ogbia LGA. The Pearson correlation matrix (Table 6) showed several significant positive correlations among the PAHs, indicating shared variability among some congeners and supporting the use of principal component analysis (PCA).

Phenanthrene and dibenz[a,h]anthracene (DahA) showed the strongest correlation ($r = 0.97$, $p < 0.01$) despite differences in molecular weight and volatility. Naphthalene also showed strong positive correlations with phenanthrene ($r = 0.88$, $p < 0.01$), fluorene ($r = 0.82$, $p < 0.01$) and DahA ($r = 0.81$, $p < 0.01$). Phenanthrene and fluorene were also strongly correlated ($r = 0.78$, $p < 0.05$). These relationships indicate that several PAHs varied similarly across the sampling locations, suggesting common or related emission influences.

Table 6: Pearson Correlation Coefficient (r) among PAH Congeners

PAH	Naph	Any	Ane	Phe	Ant	Flu	Flt	DahA
Naph	1.00							
Any	0.44	1.00						
Ane	0.32	0.65	1.00					
Phe	0.88**	0.51	0.28	1.00				
Ant	0.15	0.23	0.41	0.18	1.00			
Flu	0.82	0.61	0.54	0.78**	0.36	1.00		
Flt	0.12	0.48	0.14	0.25	0.76**	0.33	1.00	
DahA	0.81	0.49	0.22	0.97**	0.14	0.75**	0.21	1.00

Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed)

Principal component analysis showed that Component 1 (PC1) explained 70.25% of the total variance, with an eigenvalue of 11.24 (Table 7). The presence of both LMW and HMW PAHs in this component indicates a mixed PAH profile, consistent with contributions from petroleum-related and combustion-related activities. The PCA score plot (Figure 3) showed spatial differentiation among the sampling locations. RWIM1 was distinctly separated from the other sites, consistent with its elevated PAH concentrations and suggesting a stronger localized influence at this location. RWIM2 was also separated from the cluster formed by RWIB1, RWIB2 and RWOTU, although less distinctly than RWIM1. RWIB1, RWIB2 and RWOTU were closely positioned, indicating similar PAH profiles, while RWOTG1 and RWOTG2 also formed a closely positioned pair.

Component 2 (PC2) accounted for 17.88% of the total variance, with an eigenvalue of 2.86 (Table 7). Anthracene was the dominant contributor to this component. Its relatively weak correlation with naphthalene (r = 0.15) suggests that the variation represented by PC2 was less closely associated with the dominant PAH pattern observed in PC1. This component may therefore represent a separate emission influence, potentially associated with pyrogenic activities. PC1 and PC2 together explained 88.13% of the cumulative variance, indicating that most of the variation in the PAH dataset was captured by the two principal components. The PCA results are consistent with previous findings in the Niger Delta, where petroleum-related activities, including gas flaring and industrial operations, have been identified as important contributors to atmospheric PAH emissions (Tarawou *et al*., 2021; Ezekwe *et al*., 2025). The diagnostic molecular ratios and PCA results point to a mixture of petroleum-related and combustion-derived sources of PAHs in the study area.

Table 7: PCA for PAH Pollutants in Ogbia LGA Rainwater

Component	Eigenvalue	% Variance	Cumulative %
1 Gas Flaring/Industrial	11.24	70.25	70.25
2 Vehicular/Pyrogenic	2.86	17.88	88.13

The PCA score plot (Figure 3) showed spatial differentiation among sampling locations, with RWIM1 distinctly separated from the remaining sites, indicating stronger localized influence. RWIB1, RWIB2, and RWOTU clustered together, reflecting similar background conditions. The second principal component dominated by anthracene loading accounted for 17.88% of the total variance. Its weak correlation to other PAHs (r = 0.15) points to an independent emission pattern associated with lower-temperature processes such as vehicular emissions, domestic combustion, and artisanal refining activities. Components 1 and 2 accounted for 88.13% of the cumulative variance, showing that the PAH profile is largely structured by identifiable anthropogenic sources rather than random variability. These results are consistent with previous findings in the Niger Delta, where petroleum-related activities, particularly gas flaring and industrial operations, have been identified as key contributors to atmospheric PAH emissions (Tarawou *et al*., 2021; Ezekwe *et al*., 2025).

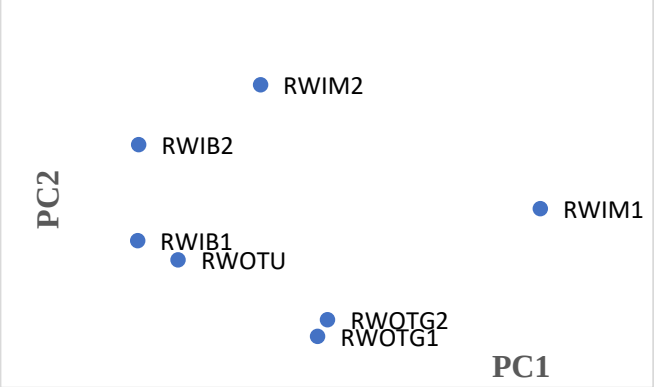


Figure 3: PCA Score Plot of Sampling Stations representing the spatial distribution of sampling stations through PAH fingerprints.

Multi-Criteria Risk Assessment: A Tiered Toxicological Suite

Ecological Risk and Biotoxicity

Ecological risk varied significantly among the PAH congeners, as evaluated by the risk quotient analysis (Table 8). Mean environmental concentrations (MEC) ranged from 0.0300 µg/L for acenaphthene to 0.3860 µg/L for phenanthrene. Benchmark comparisons revealed that phenanthrene exceeded the USEPA chronic water quality criterion (0.20 µg/L), while phenanthrene and acenaphthene exceeded their respective Effects Range Low (ERL) thresholds (0.240 µg/L and 0.016 µg/L respectively). The risk severity recorded in Table 8 increased significantly across individual congeners, driven by a combination of ambient concentrations and inherent compound toxicity. Naphthalene exhibited negligible ecological risk (RQ = 0.0058), primarily because its high-water solubility results in a relatively high safety threshold (PNEC} = 12.0). Low ambient levels of acenaphthene kept its risk profile low (RQ = 0.0789). On the contrary, phenanthrene posed a moderate risk (RQ = 0.3509). This can be attributed to its elevated concentration across the study area. Most notably, Dibenz[a,h]anthracene (D(a,h)A) with an RQ of 26.20, posed an extreme ecological risk indicating the highest potential for ecological hazard. This severe risk classification is driven not by massive environmental concentrations, but by the compound's high lipophilicity and toxic potency, which dictate an exceptionally strict safety threshold (PNEC = 0.0015 µg/L). The distribution of risk among individual congeners indicates continued PAH contamination across the study area, with high-molecular-weight PAHs contributing disproportionately to the estimated risk.

Table 8: Ecological Risk Assessment of PAHs in Rainwater

PAH Congener	MEC (Mean µg/L)	PNEC (µg/L)	RQ (MEC/ PNEC)	Risk Category
Naphthalene	0.070	12.0	0.0058	Negligible Risk
Acenaphthene	0.300	0.380	0.0789	Low Risk
Phenanthrene	0.386	1.1	0.3509	Moderate Risk
D(a,h)A	0.0393	0.0015	26.20	Extreme Risk

Biological Activity: Toxic (TEQ) and Mutagenic (MEQ) Equivalence

The weighted equivalency analysis indicates that HMW PAHs contributed disproportionately to the estimated toxicity and mutagenicity of the PAH mixture despite their lower contribution to total PAH mass (Table 9). This demonstrates that the most abundant PAHs are not necessarily those with the greatest toxicity potential. Phenanthrene contributed 8.72% of the total TEQ, whereas dibenz[a,h]anthracene (DahA) contributed 88.8%. DahA also accounted for 95.4% of the total MEQ, indicating that this high-potency congener dominated both the estimated toxic and mutagenic equivalence of the detected PAH mixture. Thus, while LMW PAHs constituted the greater proportion of the total PAH mass, HMW PAHs, particularly DahA, contributed most to the toxicity and mutagenicity indices. Similar patterns have been reported in petroleum-impacted environments (Mallah *et al*., 2022; Howard *et al*., 2021; Odesa and Olannye, 2025). These findings highlight the importance of considering PAH potency, rather than concentration alone, when evaluating the potential biological significance of PAH contamination in rainwater.

Table 9: Toxic (TEQ) and Mutagenic (MEQ) Equivalency of Priority PAHs

PAH Components	TEF	TEQ (mg/L)	% TEQ	MEF	MEQ (mg/L)	% MEQ
Phenanthrene	0.001	0.00386	8.72%	-	-	-
Dibenz[a,h]A	1	0.0393	88.8%	0.29	0.011397	95.4%
Total	-	0.04425	100%	-	0.01195	100%

Human Health Risk: Systemic and Carcinogenic Outcomes

The human health risk assessment showed a clear contrast between non-carcinogenic and carcinogenic outcomes (Table 10). Hazard Index (HI) values for ingestion (0.00015) and dermal exposure (0.00002) remained below the USEPA threshold of 1.0, indicating no significant non-carcinogenic hazard under the exposure conditions assessed. Naphthalene recorded the highest individual hazard quotient, although its value remained well below the threshold.

Table 10: Non-Carcinogenic Hazard Index (HI) Summary

PAH Congener	Mean Conc. (µg/L)	RfD (mg/kg-day)	HQ (Ingestion)	HQ (Dermal)
Naph	0.070	0.02	0.00010	0.000015
Ace	0.030	0.06	0.00001	0.000002
Flu	0.024	0.04	0.00002	0.000003
Anth	0.013	0.3	0.00000	0.000000
Flt	0.011	0.04	0.00001	0.000001
Pyr	0.009	0.03	0.00001	0.000001
∑HI	-	-	0.00015	0.00002

Note: RfD values sourced from US-EPA IRIS (2011). Calculations assume a 70kg adult body weight and 2L/day ingestion rate. A conversion factor of 10^{-3} was applied to align analytical µg/L units with mg/kg-day reference units.

The carcinogenic risk estimates, expressed as Incremental Lifetime Cancer Risk (ILCR) and cumulative Risk Index (RI), indicated elevated long-term health concerns associated with exposure to carcinogenic PAHs (Tables 11 and 12). Benz[a]anthracene was the major contributor to the dermal risk, particularly among children, while dibenz[a,h]anthracene, despite its lower concentration, contributed substantially because of its high cancer slope factor (CSF = 7.3).

As shown in Table 12, cumulative RI values exceeded the USEPA benchmark of 1×10^{-6} across both exposure routes and population groups. Dermal exposure produced higher RI values than ingestion, with 2.53×10^{-1} for adults and 7.47×10^{-1} for children. For ingestion, the corresponding values were 9.93×10^{-3} for adults and 1.44×10^{-2} for children. The highest cumulative RI was therefore observed in children through dermal exposure, indicating greater susceptibility under the exposure conditions considered. This finding is consistent with Marris *et al.*, (2020), who associated increased susceptibility in children with factors such as a higher surface-area-to-body-weight ratio and differences in metabolic capacity.

The predominance of high-molecular-weight PAHs in the carcinogenic risk profile indicates that relatively low concentrations of highly potent congeners can make substantial contributions to the estimated risk. Similar observations have been reported in petroleum-affected environments, where high-potency PAHs may contribute disproportionately to carcinogenic risk despite their lower concentrations (Mallah *et al.*, 2022). The marked difference between dermal and ingestion risks, particularly among children, suggests that reducing direct contact with untreated rainwater should be a priority in communities where rainwater is used for domestic purposes.

CONCLUSION AND RECOMMENDATIONS

Conclusion

Eleven USEPA priority PAHs were found in the rainwater samples collected from different points in the Ogbia LGA, indicating pollution of the atmosphere of the Niger Delta as a result of human activities. The non-carcinogenic risk estimates remained below regulatory limits, suggesting a low potential for acute systemic toxicity for the exposures evaluated.

Table 11: Individual ILCR Breakdown for Carcinogenic PAHs

PAH	TEQ	CSF	DAD (adult)	DAD (child)	CDI (adult)	CDI (child)
B(a)A	0.00029	0.73	2.424×10^{-1}	7.147×10^{-1}	7.25×10^{-5}	1.06×10^{-4}
DahA	0.0393	7.3	1.108×10^{-2}	3.268×10^{-2}	9.855×10^{-3}	1.431×10^{-2}
Cumulative (RI)	-	-	2.53×10^{-1}	7.47×10^{-1}	9.93×10^{-3}	1.44×10^{-2}

Table 12: Cumulative Risk Index (RI) for Carcinogenic PAHs by Population and Exposure Route

Population	Exposure Route	Cumulative Risk Index (RI)	Safety Limit (US-EPA)
Adult	Dermal (DAD)	2.53×10^{-1}	1.0×10^{-6}
Child	Dermal (DAD)	7.47×10^{-1}	1.0×10^{-6}
Adult	Ingestion (CDI)	9.93×10^{-3}	1.0×10^{-6}
Child	Ingestion (CDI)	1.44×10^{-2}	1.0×10^{-6}

However, the carcinogenic risk indices suggested elevated long-term risk with higher susceptibility seen in the pediatric population through dermal routes. The findings revealed that although the concentrations of high molecular weight PAHs are low, they are most responsible for the carcinogenic risk. This emphasizes that assessments based solely on concentration can underestimate the significance of highly toxic HMW PAHs. The overall biological impact of compounds in the study area is thus more dependent on compound potency than on mass concentration.

Policy and Management Recommendations

Effective mitigation of PAH exposure risks in Ogbia LGA requires coordinated environmental management strategies targeting emissions control, exposure reduction, and public health protection. These measures include:

a. Regulatory enforcement: Existing standards concerning gas flaring and artisanal refining need to be enforced. The regulatory authorities like NESREA and NOSDRA should further intensify compliance monitoring and guarantee compliance with emission limits. Environmental penalties should be strengthened to deter infractions, and the penalties imposed may be channeled into environmental cleanup and community mitigation efforts.

b. Exposure reduction strategies: Use of untreated rainwater to satisfy domestic water requirements should be minimized using simple technologies at the household level. Activated carbon filters and first flush diversion systems can be used to decrease exposure to high potency PAH fractions before they are consumed and are commonly used for low-cost interventions.

c. Public health surveillance: Regularly monitoring these health outcomes associated with PAH exposure is recommended, particularly respiratory, dermatological and long-term cancers. The increased exposure susceptibility and relative risk of children identified in this study should be considered in surveillance systems.

d. Environmental monitoring systems: The monitoring of atmospheric deposition and rainfall chemistry should be made continuous, with the use of accredited analytical laboratories. A comprehensive environmental-health database that correlates pollutant levels with health effects will help monitor risks over time and be useful for evidence-based decision-making.

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