

ECOLOGICAL RISK OF POLYCYCLIC AROMATIC HYDROCARBON DISTRIBUTION IN SEDIMENTS FROM GORONYO DAM, NORTHWESTERN NIGERIA

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ABSTRACT

This study investigated the concentrations, sources, and ecological risks of 16 priority polycyclic aromatic hydrocarbons (PAHs) in the sediments of Goronyo Dam, Nigeria, across five sampling stations during the rainy and dry seasons. Analysis was conducted via Gas Chromatography-Mass Spectrometry (GC-MS). Total PAH concentrations were relatively low, ranging from 1.1×10^{-2} to 4.41×10^{-2} mg/kg, suggesting a sparse industrial footprint and predominantly agricultural land use. High-molecular-weight (HMW) congeners, such as benzo[k]fluoranthene (4.95×10^{-3} mg/kg), dominated the profiles, while low-molecular-weight (LMW) congeners like naphthalene were frequently below detection limits. Diagnostic ratios identified a predominantly pyrogenic signature, specifically biomass and domestic fuel combustion, which transitioned to a mixed-source profile during the rainy season due to increased surface runoff. Although the dry season exhibited higher localized concentrations (notably at S1 and S4), likely due to reduced dilution and evaporative concentration, independent t-tests and ANOVA revealed no significant spatial or temporal variations ($p > 0.05$). Ecological risk assessment using the mean effect range medium quotient (m-ERMQ) yielded values significantly below the 0.1 threshold (5.36×10^{-11} to 1.87×10^{-5}), indicating a low probability (<12%) of adverse biological effects. These results establish a baseline for the dam, highlighting a current state of low-level contamination that requires routine monitoring to manage diffuse anthropogenic inputs.

Keywords: Goronyo, PAHs, Sediments, Seasonal, Goronyo

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants comprised of fused aromatic rings, known for their potential carcinogenicity, mutagenicity, and toxicity to aquatic life. Because of their hydrophobicity, PAHs often accumulate in sediments, which act as long-term reservoirs or sinks of contamination within aquatic ecosystems (Okonkwo et al., 2025). Seasonal variations, particularly between the rainy and dry seasons, exert a strong influence on PAH concentrations in sediments, primarily through processes such as surface runoff, sediment resuspension, and dilution effects (Areguamen et al., 2023; Edjere et al., 2020). Given the increasing environmental and public health concerns linked to PAHs many of which are identified by the U.S. Environmental Protection Agency (US EPA) as probable human carcinogens it is crucial to monitor their occurrence and behavior in sediments, especially in areas where dams serve as vital sources of water for irrigation and domestic purposes (US EPA, 2008; UNEP, 2022). While PAH dynamics in humid, tropical, and industrialized river systems are well-documented particularly in southern Nigeria significant data gaps persist regarding semi-arid dam reservoirs. Unlike perennial river systems, semi-arid reservoirs like the Goronyo Dam experience extreme hydrological fluctuations and distinct dust-loading cycles. It remains unknown how the unique interplay of high evaporation rates, harmattan-driven atmospheric deposition, and seasonal agricultural runoff governs the loading and bioavailability of PAHs in these specific catchment types. Existing literature lacks a mechanistic understanding of how these climatic drivers influence PAH fractionation in the Sahelian savannah belt.

In Nigeria, several studies have demonstrated that PAH levels in sediments vary significantly between wet and dry seasons. For instance, in the Ikpoba River, South-South Nigeria, total PAH concentrations were generally higher during the dry season than in the wet season, accompanied by notable variations in ring composition and source diagnostic indicators (Areguamen et al., 2023). Similarly, studies conducted in the Niger Delta (e.g., River Ethiope) have revealed that sediment samples collected during dry season typically contain higher concentrations of both low and high molecular weight PAHs compared to those from the rainy season, likely due to reduced dilution and increased contributions from atmospheric deposition and land-based sources (Edjere et al., 2020).

As a strategically important water body used for irrigation, flood control, and domestic supply, the Goronyo Dam's ecological significance is underscored by inflows from the Rima River. Unlike perennial river systems, semi-arid reservoirs like the Goronyo Dam in northwestern Nigeria experience extreme hydrological fluctuations and distinct dust-loading cycles. It remains unknown how the unique interplay of high evaporation rates, harmattan-driven atmospheric deposition, and seasonal agricultural runoff governs the loading and bioavailability of PAHs in these specific catchment types, as existing literature lacks a mechanistic understanding of how these climatic drivers influence PAH fractionation in the Sahelian savannah belt. This river traverses landscapes characterized by intensive agricultural practices, artisanal fishing, and seasonal human settlements land-use patterns that facilitate the introduction of organic pollutants through surface runoff and atmospheric deposition (Abdulrahman et al., 2023). As anthropogenic pressures on the catchment intensify, the dam becomes increasingly vulnerable to sediment-bound contamination (Okonkwo et al., 2025). Given that seasonal variations in Nigeria have been shown to exert a strong influence on PAH concentrations through processes such as resuspension and dilution (Areguamen et al., 2023; Edjere et al., 2020), a detailed investigation into the spatial and seasonal dynamics of PAH accumulation in this semi-arid system is critically warranted (US EPA, 2008; UNEP, 2022).

Despite growing research on PAHs in aquatic environments across southern Nigeria, there remains a notable paucity of data from northern regions, particularly within dam reservoirs such as Goronyo Dam in Sokoto State. This gap is significant given that

environmental conditions in the north characterized by semi-arid climates, intensive seasonal agriculture, and variable hydrology may influence the transport, deposition, and transformation of PAHs in markedly different ways compared to more humid southern systems. Goronyo Dam plays a vital role in irrigation, flood control, and domestic water supply for surrounding communities. However, no comprehensive study has yet quantified the influence of seasonal variability specifically the contrast between rainy and dry seasons on PAH accumulation in its sediments. Understanding these dynamics is essential for evaluating ecological risks, informing pollution control strategies, and ensuring the sustainable management of this critical water resource.

By employing gas chromatography mass spectrometry (GC-MS) for the accurate detection of PAHs, alongside diagnostic ratio analysis and ecological risk assessment, this study aims to elucidate the sources of contamination and evaluate the potential environmental risks posed to aquatic ecosystems. The outcomes are expected to provide valuable baseline data for water resource managers, environmental regulatory agencies, and public health authorities, supporting evidence-based decision-making and sustainable management of the Goronyo Dam catchment.

Description of the Study Area

The Goronyo Dam (13.5395°N, 5.956°E), managed by the Sokoto-Rima River Basin Development Authority (SRRBDA), is a cornerstone of agricultural resilience in Nigeria's semi-arid Sahelian zone (DAHITI, 2025). Constructed across the Rima River, the reservoir possesses a storage capacity of approximately 976 million cubic meters, making it one of the largest savanna-region reservoirs. Its hydrological regime is defined by extreme seasonal variability; during the dry season, high evaporation rates concentrate solutes, while the rainy season introduces massive inflows from a catchment characterized by intensive agricultural and pastoral land use. The benthic environment of the reservoir serves as a critical "chronological sink" for persistent organic pollutants. The sediments are predominantly composed of fine-grained silts and organic-rich clays, which exhibit high sorption capacities for hydrophobic compounds like PAHs. These characteristics facilitate the long-term sequestration of contaminants transported via the Rima River, which traverses a landscape shaped by artisanal fishing, seasonal human settlements, and intensive "fadama" farming. The dam is subject to diverse anthropogenic pressures that act as diffuse sources of PAH loading. Domestic energy reliance on fuel wood, open-waste burning, and the combustion of agricultural residues (biomass burning) provide significant pyrogenic inputs. Localized petrogenic contributions from motorized artisanal fishing vessels supplement these. As these pressures intensify, the dam's role in flood control and domestic water supply becomes increasingly vulnerable to sediment-bound toxicity (Abdulrahman et al., 2023; Okonkwo et al., 2025).

Map of the Study Area

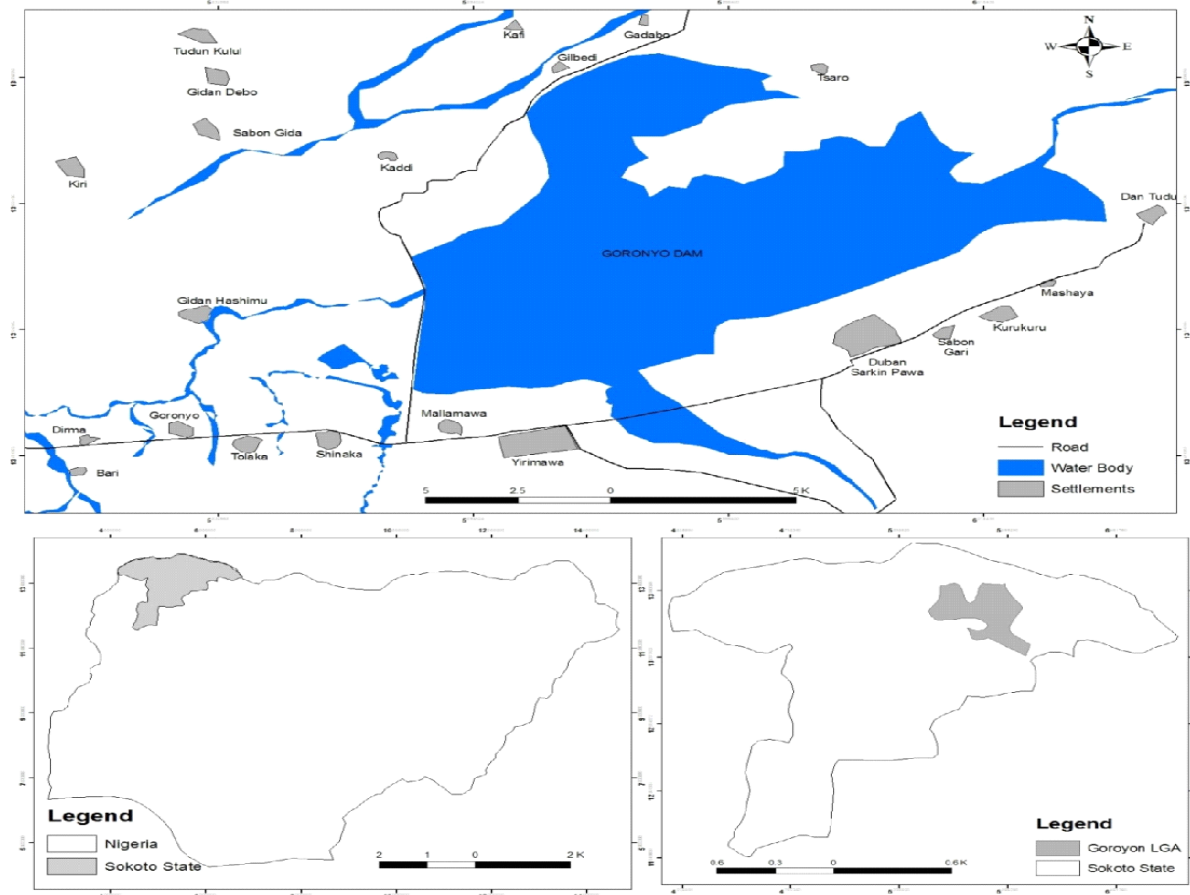


Figure 1: The Study Area (Goronyo Reservoir) ;**Source:** NASRDA, 2012

Materials and Methods

Sample Collection, Site Selection, and Preservation

Sediment samples were collected from Goronyo Dam, Sokoto State, Nigeria, at five designated locations (S1–S5) characterized by varying hydrodynamic features and anthropogenic pressures, including agricultural runoff and domestic waste discharge. To account for temporal fluctuations in PAH concentrations, sampling was conducted across two distinct seasons: the rainy season (July–September) and the dry season (January–March) (Abida et al., 2014; Umeghalu et al., 2019).

To ensure statistical representativeness, sampling was conducted in triplicate at five locations (N=5) across two seasons, resulting in a total sample size of n=30. These replicates were analyzed individually, and the data summarized in Tables 1 and 2 represent the arithmetic means of the triplicate sets for each sampling point. At each station, triplicate surface sediments were retrieved using a stainless-steel Ekman grab sampler or sediment corer, following standard protocols (García et al., 2012). Approximately 200–300 g of sediment from each replicate was homogenized in a stainless-steel bowl and transferred to pre-cleaned, solvent-rinsed amber glass jars.

To maintain sample integrity and prevent photodegradation, jars were wrapped in aluminum foil, transported in an icebox at 4 °C, and immediately stored at –20 °C upon arrival at the laboratory (Zhang et al., 2018). Before extraction, samples were freeze-dried (lyophilized) to remove moisture while minimizing the volatilization of low-molecular-weight PAHs (Maliszewska-Kordybach, 1999; US EPA, 2001). All replicates were analyzed

individually, and the data presented in Tables 1 and 2 represent the arithmetic means of these triplicate analyses.

Sample Preparation and Extraction

Sediment samples were stabilized and prepared according to modified US EPA Method 3540C protocols, as described by Zhang et al. (2018). To maintain the integrity of volatile low-molecular-weight compounds, the samples were freeze-dried (lyophilized) rather than air-dried, effectively removing moisture without compromising the PAH profile (Maliszewska-Kordybach, 1999). The dried sediments were gently homogenized using an agate mortar and pestle to a uniform powder and sieved through a 2 mm stainless-steel mesh to ensure a representative matrix.

Extraction was conducted via Soxhlet apparatus using a 1:1 (v/v) mixture of dichloromethane and acetone for 16–24 hours. The resulting extracts were concentrated using a rotary evaporator and purified via silica gel column chromatography to eliminate lipid and pigment interferences (Ravindra et al., 2008). The final cleaned eluates were reduced to a volume of 1.0 mL under a gentle nitrogen stream in preparation for instrumental analysis (US EPA, 2001).

Instrumental Analysis and GC-MS Parameters

Quantification of PAHs was performed using a Gas Chromatograph coupled to a Mass Spectrometer (GC-MS). Chromatographic separation was achieved on a high-performance capillary column (e.g., HP-5ms; 30 m × 0.25 mm i.d. × 0.25 μm film thickness). Ultra-high purity Helium served as the carrier gas at a constant flow rate of 1.0 mL/min.

Quality Assurance, Calibration, and Analytical Precision

To mitigate matrix effects and verify analytical accuracy, a comprehensive Quality Assurance (QA/QC) framework was implemented. Analytical calibration was performed using a seven-point internal standard method, spanning a concentration range of 0.01 to 5.0 mg/kg. All target analytes demonstrated high linearity, with correlation coefficients (R^2) exceeding 0.995. To account for volumetric losses and instrument drift, each extract was fortified with a suite of five deuterated internal standards (including Naphthalene $-d_8$, Phenanthrene $-d_{10}$, and Chrysene $-d_{12}$) before injection.

Method performance was validated through the assessment of recovery and precision. Surrogate recoveries remained within the acceptable range of 82% to 110%, ensuring minimal analyte loss during the extraction and cleanup phases. Instrument precision, determined via triplicate injections of the midpoint standard, yielded a Relative Standard Deviation (RSD) of < 5%. The sensitivity of the method was established through the calculation of the Limit of Detection (LOD) and Limit of Quantification (LOQ), which were rigorously defined at signal-to-noise (S/N) ratios of 3:1 and 10:1, respectively.

Risk Assessment of PAHs in Sediment Samples

To evaluate the relative toxicological potency of the PAH assemblages within the sediment, a screening-level ecological risk assessment was performed. This evaluation utilized the Toxic Equivalency Factor (TEF) approach (Nisbet and LaGoy, 1992) to normalize the varying toxicities of specific PAH congeners relative to benzo[a]pyrene (BaP).

In this comparative framework, BaP is assigned a reference value of 1.0, with other congeners scaled according to their relative potency. The cumulative toxic equivalent concentration ($\sum BaP_{eq}$) represents the theoretical potency of the mixture as if it were composed entirely of the reference compound. The BaP_{eq} for individual congeners was calculated using the following equation:

$$BaP_{eq} = C_i \times TEF_i$$

Where:

C_i : The concentration of the individual PAH congener (mg/kg).

TEF_i : The toxic equivalency factor assigned to the specific congener.

Identification of PAH Sources in Sediment Samples

In order to distinguish between naturally occurring and anthropogenically produced PAHs in the environment, a diagnostic ratio has been used as a technique for identifying the sources of PAHs in an ecosystem. Several researchers have applied this technique to identify the point sources of PAH contamination in various environmental media (Muze et al., 2020). The following diagnostic ratios are commonly used to determine the likely sources and origins of hydrocarbon pollution (Ilechukwu et al., 2016).

- i. **Flua/Flua + Pyr:** when the calculated ratio between Fluoranthene and Fluoranthene + Pyrene is greater than 0.5 ($\text{Flua}/\text{Flua}+\text{Pyr} > 0.5$), it is an indication that the origin is from pyrogenic sources, but if the ratio calculated is less than 0.4 ($\text{Flua}/\text{Flua}+\text{Pyr} < 0.4$), it suggests that it is of petrogenic origin.
- ii. **Ant/Ant + Phe:** Anthracene/anthracene + phenanthrene ($\text{Ant}/\text{Ant} + \text{Phe}$) ratio calculations show that anthracene has a petrogenic origin when the ratio is less than 0.1 and a pyrogenic origin when the ratio is greater than 0.1.
- iii. **BaAnt/BaAnt + Chr:** When this ratio is less than 0.2 ($\text{BaAnt}/\text{BaAnt} + \text{Chr} < 0.2$), it is an indication of petrogenic input, but when the ratio is greater than 0.35 ($\text{BaAnt}/\text{BaAnt} + \text{Chr} > 0.35$), it reveals that it originated from pyrogenic input sources
- iv. **IcdP/(IcdP + BghiP):** The $\text{IcdP}/(\text{IcdP} + \text{BghiP})$ ratio is a diagnostic tool for distinguishing between petrogenic and combustion-derived PAH sources. Values < 0.20 typically indicate petrogenic origins (crude oil or fuel spills), while ratios between 0.20 and 0.50 suggest petroleum combustion (vehicle exhaust). Values exceeding 0.50 point to pyrogenic sources, such as the combustion of biomass, coal, or wood.

Ecological Risk Assessment of PAHs in Sediment Samples Using the Mean ERM Quotient Method

The mean Effect Range Median quotient (m-ERM-q) approach, developed by Long et al. (1998), is widely applied to assess the potential ecological risk posed by multiple PAHs in sediments. This method involves comparing the measured contaminant concentrations with their respective Effect Range Median (ERM) sediment quality guideline values, which indicate thresholds associated with adverse biological effects.

$$\text{m-ERM}_i\text{-q} = \sum \left(\frac{C_i}{\text{ERM}_i} \right) / n$$

Where C_i represents the measured concentration of PAH i in sediment (mg/kg dry weight), ERM_i denotes the Effect Range Median value for PAH i (mg/kg dry weight), n is the number of PAHs assessed, and m-ERM-q refers to the mean ERM quotient.

The m-ERM-q values are interpreted according to risk thresholds established by Long et al. (1998), where an m-ERM-q of less than 0.1 indicates a low risk (~9% probability of adverse biological effects), values between 0.11 and 0.5 indicate a moderate risk (~21%), values between 0.51 and 1.5 suggest a high risk (~49%), and values greater than 1.5 correspond to a very high risk (~76%) of adverse biological effects.

Results

Table 1: Mean PAH Concentrations in Sediments (mg/kg) During the Rainy Season

PAHs	S1	S2	S3	S4	S5
Nap	ND	ND	ND	ND	ND
Acen	ND	ND	ND	3.27E-08 ± 1.3E-09	ND
Acep	ND	ND	ND	6.16E-08 ± 2.5E-09	ND
Flu	ND	ND	ND	2.11E-08 ± 8.4E-10	1.42E-05 ± 5.7E-07
Ant	8.67E-07 ± 3.4E-08	1.81E-06 ± 7.2E-08	ND	7.47E-09 ± 3.0E-10	1.69E-04 ± 6.7E-06
Phe	2.20E-06 ± 8.8E-08	2.17E-07 ± 8.6E-09	2.15E-07 ± 8.6E-09	2.10E-07 ± 8.4E-09	5.03E-05 ± 2.0E-06
Fluo	7.45E-08 ± 2.9E-09	1.28E-07 ± 5.1E-09	9.84E-08 ± 3.9E-09	2.71E-08 ± 1.1E-09	1.23E-04 ± 4.9E-06
Pyr	2.94E-07 ± 1.1E-08	9.38E-08 ± 3.7E-09	6.77E-08 ± 2.7E-09	7.77E-08 ± 3.1E-09	2.61E-04 ± 1.0E-05
B[a]A	1.44E-08 ± 5.7E-10	2.56E-09 ± 1.0E-10	ND	9.69E-09 ± 3.8E-10	ND
Chr	5.82E-08 ± 2.3E-09	3.15E-07 ± 1.2E-08	2.28E-08 ± 9.1E-10	3.16E-09 ± 1.2E-10	1.29E-03 ± 5.1E-05
B[b]F	ND	ND	ND	ND	2.57E-04 ± 1.0E-05
B[k]P	4.95E-03 ± 1.9E-04	ND	ND	ND	4.11E-03 ± 1.6E-04
B[a]P	8.94E-06 ± 3.5E-07	ND	4.97E-07 ± 1.9E-08	8.38E-09 ± 3.3E-10	ND
D[a,h]A	1.06E-05 ± 4.2E-07	3.78E-06 ± 1.5E-07	2.95E-06 ± 1.2E-07	4.19E-08 ± 1.7E-09	ND
I[1,2,3-cd]P	7.17E-04 ± 2.8E-05	3.27E-07 ± 1.3E-08	5.77E-07 ± 2.3E-08	9.32E-08 ± 3.7E-09	ND
B[g,h,i]P	1.41E-03 ± 5.6E-05	2.05E-06 ± 8.2E-08	1.32E-06 ± 5.3E-08	ND	ND
ΣPAHs	7.10E-03 ± 2.8E-04	8.72E-06 ± 3.5E-07	5.75E-06 ± 2.3E-07	5.94E-07 ± 2.3E-08	6.27E-03 ± 2.5E-04

Keys: ND = Not Detected ($< 1.0 \times 10^{-9}$ mg/kg). Nap, Naphthalene; Acen, Acenaphthylene; Acep, Acenaphthene; Flu, Fluorene; Ant, Anthracene; Phe, Phenanthrene, Fluo, Fluoranthene; Pyr, Pyrene; B[a]A, Benzo(a)anthracene; Chr, Chrysene; B[b]F, Benzo(b)fluoranthene; B[k]P, Benzo(k)fluoranthene; B[a]P, Benzo(a)pyrene; D[a,h]A, Dibenzo(a,h)anthracene; I[1,2,3-cd]P, Indeno(1,2,3-cd)pyrene; B[g,h,i]P, Benzo(g,h,i)perylene

Table 2: Mean PAH Concentrations in Sediments (mg/kg) During the Dry Season

PAHs	S1	S2	S3	S4	S5
Nap	ND	ND	ND	ND	4.76E-10 ± 1.9E-11
Acen	6.84E-06 ± 2.7E-07	ND	ND	ND	ND
Acep	ND	6.17E-05 ± 2.5E-06	ND	ND	ND
Flu	ND	ND	ND	ND	2.11E-05 ± 8.4E-07
Ant	ND	5.31E-04 ± 2.1E-05	ND	ND	ND
Phe	ND	ND	ND	ND	1.74E-03 ± 6.9E-05
Fluo	3.37E-04 ± 1.3E-05	ND	ND	ND	ND
Pyr	ND	2.93E-03 ± 1.2E-04	ND	ND	ND
B[a]A	ND	ND	ND	1.55E-03 ± 6.2E-05	ND
Chr	2.58E-03 ± 1.0E-04	ND	ND	ND	ND
B[b]F	ND	3.28E-03 ± 1.3E-04	ND	ND	ND
B[k]P	ND	ND	ND	ND	3.11E-03 ± 1.2E-04
B[a]P	ND	ND	ND	ND	4.96E-04 ± 1.9E-05
D[a,h]A	2.28E-03 ± 9.1E-05	ND	ND	ND	ND
I[1,2,3-cd]P	ND	ND	ND	1.96E-03 ± 7.8E-05	ND
B[g,h,i]P	ND	ND	ND	3.56E-03 ± 1.4E-04	ND
∑PAHs	7.54E-03 ± 3.0E-04	6.77E-03 ± 2.7E-04	ND	1.10E-02 ± 4.4E-04	5.38E-03 ± 2.1E-04

Table 3: Benzo(a)pyrene Equivalent in Sediment Samples from Different Sampling Points from Goronyo Dam During the Rainy Season

PAHs	TEF	S1	S2	S3	S4	S5
Nap	0.001	ND	ND	ND	ND	ND
Acen	0.001	ND	ND	ND	3.27×10^{-11}	ND
Acep	0.001	ND	ND	ND	6.16×10^{-11}	ND
Flu	0.001	ND	ND	ND	2.11×10^{-11}	1.42×10^{-8}
Ant	0.001	8.67×10^{-10}	1.81×10^{-9}	ND	7.47×10^{-12}	1.69×10^{-7}
Phe	0.001	2.20×10^{-9}	2.17×10^{-10}	2.15×10^{-10}	2.10×10^{-10}	5.03×10^{-8}
Fluo	0.01	7.45×10^{-10}	1.28×10^{-9}	9.84×10^{-10}	ND	1.23×10^{-6}
Pyr	0.001	2.94×10^{-10}	9.38×10^{-11}	6.77×10^{-11}	7.77×10^{-11}	2.61×10^{-7}
B[a]A	0.1	1.44×10^{-9}	2.56×10^{-10}	ND	9.69×10^{-10}	ND
Chr	0.001	5.82×10^{-11}	3.15×10^{-10}	2.28×10^{-11}	3.16×10^{-12}	1.29×10^{-6}
B[b]F	0.1	ND	ND	ND	ND	2.57×10^{-5}
B[k]P	0.1	4.95×10^{-4}	ND	ND	ND	4.11×10^{-4}
B[a]P	1	8.94×10^{-6}	9.81×10^{-10}	4.97×10^{-7}	8.38×10^{-9}	ND
D[a,h]A	1	1.06×10^{-5}	3.78×10^{-6}	2.95×10^{-6}	4.19×10^{-8}	ND
I[1,2,3-cd]P	0.01	7.17×10^{-6}	3.27×10^{-9}	5.77×10^{-9}	9.32×10^{-10}	ND
B[g,h,i]P	0.01	1.41×10^{-5}	2.05×10^{-8}	1.32×10^{-8}	5.26×10^{-8}	ND
Σ BaP _{eq}		5.36×10^{-4}	3.81×10^{-6}	3.47×10^{-6}	1.08×10^{-7}	5.38×10^{-4}
(\pm SD)		2.4×10^{-5}	1.5×10^{-7}	1.4×10^{-7}	2.4×10^{-9}	1.8×10^{-5}

Table 4: Benzo(a)pyrene Equivalent in Sediment Samples from Different Sampling Points from Goronyo Dam During the Dry Season

PAHs	TEF	S1	S2	S3	S4	S5
Nap	0.001	ND	ND	ND	ND	4.76×10^{-13}
Acen	0.001	ND	ND	ND	ND	ND
Acep	0.001	6.84×10^{-9}	6.17×10^{-8}	ND	ND	ND
Flu	0.001	ND		ND	ND	2.11×10^{-8}
Ant	0.001	ND	ND	ND	ND	ND
Phe	0.001	ND	ND	ND	ND	1.74×10^{-6}
Fluo	0.01	ND	ND	ND	ND	ND
Pyr	0.001	ND	2.93×10^{-6}	ND	ND	ND
B[a]A	0.1	ND	ND	ND	1.55×10^{-4}	ND
Chr	0.001	2.58×10^{-5}	ND	ND	ND	ND
B[b]F	0.1	ND	3.28×10^{-4}	ND	ND	ND
B[k]P	0.1	ND	ND	ND	ND	3.11×10^{-4}
B[a]P	1	ND	ND	ND	ND	4.96×10^{-4}
D[a,h]A	1	2.28×10^{-3}	ND	ND	ND	ND
I[1,2,3-cd]P	0.01	ND	ND	ND	1.94×10^{-4}	ND
B[g,h,i]P	0.01	ND	ND	ND	3.56×10^{-5}	ND
Σ BaP _{eq}		2.31×10^{-3}	3.36×10^{-7}	0.00	3.87×10^{-4}	8.09×10^{-4}
(\pm SD)		9.2×10^{-5}	1.3×10^{-5}	0.00	1.5×10^{-5}	3.2×10^{-5}

Table 5: Diagnostic Ratio of PAHs in Sediment Samples from Different Points of Goronyo Dam During the Rainy and Dry Seasons

Season	Ratio Type	S1	S2	S3	S4	S5	Source Indication
Dry	Ant/(Ant + Phe)	-	1.00	-	-	0.00	Pyrogenic
	Flua/(Flua + Pyr)	1.00	0.00	-	-	-	Biomass
	BaAnt/(BaAnt + Chr)	0.00	-	-	1.00	-	Pyrogenic
	IcdP/(IcdP + BghiP)	-	-	-	0.35	-	Mixed
Rainy	Ant/(Ant + Phe)	0.28	0.89	-	0.03	0.77	Pyrogenic
	Flua/(Flua + Pyr)	0.2	0.58	0.59	0.26	0.32	Mixed
	BaAnt/(BaAnt + Chr)	0.2	0.01	-	0.75	-	Pyrogenic
	IcdP/(IcdP + BghiP)	0.34	0.14	0.3	1.00	-	Mixed

Table 6: Mean Effect Range Medium (m-ERM) Quotient of PAHs in Sediment from Goronyo Dam, During the Rainy Season

PAHs	ERM SSG	S1	S2	S3	S4	S5
Nap	2100	ND	ND	ND	ND	ND
Acen	640	ND	ND	ND	9.57×10^{-13}	ND
Acep	500	ND	ND	ND	3.01×10^{-12}	ND
Flu	540	ND	ND	ND	7.25×10^{-12}	1.55×10^{-9}
Ant	1500	ND	7.10×10^{-11}	ND	2.30×10^{-12}	6.63×10^{-9}
Phe	1100	1.18×10^{-10}	1.16×10^{-11}	1.15×10^{-11}	2.93×10^{-13}	2.69×10^{-9}
Fluo	5100	8.59×10^{-13}	1.48×10^{-12}	1.13×10^{-12}	1.12×10^{-11}	1.42×10^{-9}
Pyr	2600	6.65×10^{-12}	2.12×10^{-12}	1.53×10^{-12}	ND	5.90×10^{-9}
B[a]A	1600	5.29×10^{-13}	9.41×10^{-14}	ND	1.76×10^{-12}	ND
Chr	2800	1.22×10^{-12}	6.62×10^{-12}	4.79×10^{-13}	3.56×10^{-13}	2.71×10^{-8}
B[a]P	1600	3.29×10^{-10}	3.61×10^{-14}	1.83×10^{-11}	ND	ND
D[a,h]A	260	2.40×10^{-9}	8.55×10^{-10}	6.67×10^{-10}	3.08×10^{-13}	ND
I[1,2,3-cd]P	330	1.28×10^{-7}	5.83×10^{-11}	1.03×10^{-10}	9.48×10^{-12}	ND
B[g,h,i]P	950	8.73×10^{-8}	1.27×10^{-10}	8.17×10^{-11}	1.66×10^{-11}	ND
Σ m-ERMQ		2.18×10^{-7}	1.13×10^{-9}	8.85×10^{-10}	5.36×10^{-11}	4.53×10^{-8}

Table 7: Mean Effect Range Medium (m-ERM) Quotient of PAHs in Sediment from Goronyo Dam, During the Dry Season

PAHs	ERM SSG	S1	S2	S3	S4	S5
Nap	2100	ND	ND	ND	ND	2.27×10^{-13}
Acen	640	1.07×10^{-8}	1.15×10^{-7}	ND	1.48×10^{-8}	ND
Acep	500	1.61×10^{-8}	1.23×10^{-7}	ND	7.68×10^{-9}	4.48×10^{-9}
Flu	540	3.52×10^{-8}	2.24×10^{-8}	ND	ND	3.91×10^{-8}
Ant	1500	ND	3.54×10^{-7}	1.21×10^{-9}	7.93×10^{-9}	1.43×10^{-7}
Phe	1100	ND	2.47×10^{-7}	1.97×10^{-10}	ND	1.58×10^{-6}
Fluo	5100	ND	6.61×10^{-8}	2.51×10^{-11}	ND	ND
Pyr	2600	1.53×10^{-8}	1.13×10^{-6}	3.61×10^{-11}	3.10×10^{-7}	ND
B[a]A	1600	2.03×10^{-8}	2.74×10^{-8}	1.60×10^{-12}	9.69×10^{-7}	ND
Chr	2800	9.21×10^{-7}	ND	1.13×10^{-10}	4.07×10^{-7}	3.24×10^{-9}
B[a]P	1600	1.11×10^{-7}	8.31×10^{-8}	6.13×10^{-13}	ND	3.10×10^{-7}
D[a,h]A	260	8.77×10^{-6}	5.42×10^{-7}	1.45×10^{-8}	7.38×10^{-6}	7.38×10^{-6}
I[1,2,3-cd]P	330	4.00×10^{-6}	ND	9.91×10^{-10}	5.94×10^{-6}	ND
B[g,h,i]P	950	2.14×10^{-6}	ND	2.16×10^{-9}	3.75×10^{-6}	1.99×10^{-6}
Σ m-ERMQ		1.60×10^{-5}	3.01×10^{-6}	2.08×10^{-8}	1.87×10^{-5}	1.15×10^{-5}

Discussion

Concentration of PAHs in Sediments

The concentration of individual 16 PAHs in sediment samples from Goronyo Dam exhibited significant variability across sampling points (S1–S5) and between dry and rainy seasons. The highest concentration of individual PAHs was recorded at point S1 during the rainy season, where benzo[k]fluoranthene (B[k]F) reached 4.95×10^{-3} mg/kg. As a high-molecular-weight (HMW) congener, the prevalence of B[k]F is indicative of high-temperature fossil fuel combustion and reflects the compound's characteristic environmental persistence and resistance to degradation.

Conversely, naphthalene (Nap) a highly volatile low-molecular-weight (LMW) congener was predominantly below detection limits (ND) or present only at trace levels (4.76×10^{-10} mg/kg at S5) during the dry season. This depletion is likely attributable to accelerated volatilization kinetics and enhanced microbial mineralization, both of which are facilitated by the elevated ambient temperatures characteristic of the dry period. Across the sampling sites, LMW PAHs (e.g., Nap, Acep, and Flu) consistently exhibited lower mass fractions compared to their high-molecular-weight (HMW) counterparts, such as B[a]P, D[a,h]A, and I[1,2,3-cd]P. This diagnostic distribution the dominance of 4- to 6-ring congeners over 2- to 3-ring structures is a hallmark of pyrogenic signatures. These results underscore a contamination profile driven by high-temperature combustion processes, including biomass burning, vehicular exhaust, and domestic fuel combustion, as opposed to petrogenic inputs like unrefined crude oil (Areguamen et al., 2023; Odali et al., 2024).

The higher concentrations observed for Phe, Pyr, and Chr in several locations, especially during the rainy season, may be linked to increased atmospheric deposition and surface runoff, which carry PAHs from terrestrial sources into aquatic systems (Iwenofu et al.,

2023). Rainfall facilitates the wash-in of particulate-bound PAHs from surrounding catchment areas, thereby increasing sediment contamination a phenomenon similarly reported in studies of the Ikpoba River and Dadin Kowa Dam in Nigeria (Chellube et al., 2023).

The total PAH concentrations recorded in sediments from the Goronyo Dam ($1.1 \times 10^{-2} \pm 4.41 \times 10^{-2}$ mg/kg) fall within the lower-to-moderate spectrum when compared to other Nigerian aquatic ecosystems. These levels are consistent with those reported by Olayinka et al. (2019) for the Ogun River (1.02×10^{-4} to 2.35×10^{-2} mg/kg) and Adegbola and Fagbemigun (2020) for the Lagos Lagoon ($3.75 \times 10^{-4} \pm 1.5 \times 10^{-5}$ mg/kg and $1.56 \times 10^{-2} \pm 6.2 \times 10^{-4}$ mg/kg). Similarly, Okoro et al. (2017) observed concentrations between $4.50 \times 10^{-4} \pm 1.8 \times 10^{-4}$ mg/kg to $2.10 \times 10^{-2} \pm 8.4 \times 10^{-4}$ mg/kg in the Niger Delta creeks, where elevated levels were attributed to chronic hydrocarbon spills and industrial effluents.

In contrast, the relatively lower concentrations observed at Goronyo Dam likely reflect the region's sparse industrial footprint and the predominantly agricultural land use. On a global scale, these values align with reported ranges in emerging industrial regions. For instance, Zhang et al. (2021) reported concentrations from $8.45 \times 10^{-4} \pm 3.38 \times 10^{-5}$ mg/kg to $3.26 \times 10^{-4} \pm 1.30 \times 10^{-3}$ mg/kg in the Yangtze River, China, while Lee et al. (2018) recorded levels between 6.2×10^{-4} and 1.47×10^{-2} mg/kg in South Korean River sediments. Consequently, the moderate PAH burden in Goronyo Dam suggests a contamination profile dominated by diffuse anthropogenic inputs, specifically surface runoff, atmospheric deposition from biomass burning, and localized pyrogenic activities, rather than concentrated industrial discharge."

Overall, the observed seasonal pattern characterized by higher PAH concentrations during the dry season aligns with findings from other Nigerian studies (Olayinka et al., 2019; Okoro et al., 2017). This trend suggests that factors such as reduced rainfall, lower dilution rates, and increased atmospheric deposition during the dry period contribute to greater PAH accumulation in sediments.

Similarly, statistical evaluation via independent t-tests and Analysis of Variance (ANOVA) revealed no significant temporal or spatial variations in PAH concentrations ($p > 0.05$). This lack of statistical divergence suggests a relatively uniform distribution of contaminants across the study area. Furthermore, the observation of weak, non-significant correlations between specific congeners points toward a complex mosaic of emission sources rather than a single, dominant point source.

BaP-Equivalent Concentrations of Individual PAHs

The BaP_{eq} concentrations presented in Tables 3 and 4 illustrate a significant contrast in the toxicological profile of sediments from Goronyo Dam, varying by season and location. During the rainy season, Benzo(k)fluoranthene [B(k)P] at sampling point S1 recorded the highest concentration at 3.16×10^{-12} , while Chrysene [Chr] at point S4 presented the lowest. In the dry season, Dibenzo(a,h)anthracene [D(a,h)A] at point S1 showed the highest concentration of 2.28×10^{-3} , whereas Naphthalene [Nap] at point S5 had the lowest at 4.76×10^{-13} . The BaP-equivalent concentrations were notably higher in the dry season (2.28×10^{-3}) at S1 compared to the peak values observed during the rainy season. In contrast, the lower values during the rainy season imply that while rainfall facilitates the mobilization of contaminants through runoff, the increased hydraulic energy of the dam may lead to the scouring and dilution of contaminated sediments at specific points. This nuanced dynamic challenges the simplistic perspective that "rain equals more pollution," instead suggesting that Goronyo Dam functions as a dynamic sink, where seasonal flow influences the residence time of high-molecular-weight (HMW) PAHs. This finding contradicts previous studies (Ekpo et al., 2022; Olayinka et al., 2021), which attribute higher PAH levels during rainy periods to enhanced mobilization and dispersion processes. The presence of high-molecular-weight and carcinogenic PAHs, including B[a]A, B[b]F, B[k]P, D[a,h]A, and I[1,2,3-cd]P, indicates a

pyrogenic origin primarily linked to waste burning, vehicular emissions, and industrial discharges, consistent with observations from other urban environments in Nigeria (Oluseyi et al., 2022; Nwaichi & Onyema, 2023). Elevated BaP concentrations at sampling points S1, S2, S4, and S5 further indicate localized contamination hotspots, supporting global studies that correlate BaP enrichment with anthropogenic activities near dumpsites (Zheng et al., 2021; Long et al., 1998).

Identification of PAH Sources

Table 5 present the diagnostic ratios of PAHs determined from Goronyo Dam during the rainy and dry seasons. The diagnostic ratios of PAHs in Goronyo Dam sediments reveal a dynamic pollution profile driven by seasonal hydrology and anthropogenic pressure. Evaluation of isomer pairs including Ant/(Ant + Phe), Flua/(Flua + Pyr), BaAnt/(BaAnt + Chr), and IcdP/(IcdP + BghiP) identifies a predominantly pyrogenic signature that shifts toward a mixed-source transition during the rainy season.

Across both seasons, the Ant/(Ant + Phe) ratio consistently exceeded the 0.1 threshold (notably at S1, S2, and S5), signaling high-temperature combustion. During the rainy season, Flua/(Flua + Pyr) values at S2 (0.58) and S3 (0.59) surpassed 0.5, specifically fingerprinting the combustion of biomass (wood/grass) and coal. This reflects the regional socio-economic reliance on fuel-wood and agricultural bush burning. The data suggest the dam serves as a primary sink for atmospheric soot and charred organic matter transported from the catchment area. Seasonal harmonization reveals that the rainy season introduces a more heterogeneous pollution profile than the dry season. While dry-season signatures were sporadic likely due to lower water levels and sediment burial the rainy season exhibited a distinct "mixed" signature. Evidence of petrogenic (petroleum-derived) input merging with pyrogenic residues is found in the IcdP/(IcdP + BghiP) ratios (0.14–1.00) and Flua/(Flua + Pyr) values at S1 and S4 (< 0.4). Seasonal variations show that dry-season samples exhibited higher pyrogenic signatures than those collected during the rainy season. This trend may be attributed to increased biomass burning, fossil-fuel combustion, and atmospheric deposition during the dry period, when temperature inversion and low precipitation enhance PAH accumulation. In contrast, rainy-season samples reflected more petrogenic characteristics, likely due to surface runoff carrying petroleum residues, lubricants, and vehicular emissions into the water body. Similar observations have been reported in other Nigerian and West African aquatic systems, where combustion processes dominate during the dry season while mixed sources prevail in the wet season (Adeniji et al., 2022; Anyika et al., 2023; Obafemi et al., 2024).

Although diagnostic ratios are widely used for source identification, they may be affected by photo-oxidation, microbial degradation, and differential solubility of isomers. Therefore, the interpretation of PAH sources should be supported by complementary multivariate or isotopic analyses for more accurate apportionment (Yunker et al., 2023; Zhao et al., 2024).

Ecological Risk Assessment and Sediment Toxicity

The potential for adverse biological effects in the Goronyo Dam was evaluated using the Mean Effect Range Medium Quotient (m-ERM_Q) as presented in Tables 6 and 7. This standardized index allows for the comparison of complex PAH mixtures against consensus-based sediment quality guidelines, providing a probability of toxicity to benthic organisms (Long et al., 1995; McCready et al., 2006). The sum m-ERM_Q values for both the rainy season (Table 6) and dry season (Table 7) were significantly below the critical threshold of 0.1. According to the classification system established by Long et al. (1998). The values in this study, ranging from 5.36×10^{-11} to 1.87×10^{-5} , indicate that the sediments of Goronyo Dam currently pose a low ecological risk. The probability of adverse biological effects on the aquatic biota is minimal ($< 12\%$), suggesting that PAH concentrations have not yet reached

levels associated with acute sediment toxicity. This is consistent with findings in similar freshwater reservoirs where anthropogenic impact is largely diffuse rather than industrial (Adedosu et al., 2015). A comparative analysis of the seasons reveals a distinct increase in the risk quotients during the dry season. During the rainy season, m-ERMQ values ranging from 10^{-11} to 10^{-7} suggest a dilution effect caused by increased water volume and high sedimentation rates of clean terrigenous mineral matter (Anyakora et al., 2011). In contrast, the dry season m-ERMQ values increased to a range of 10^{-8} to 10^{-5} , with the quotient at S4 reaching 1.87×10^{-5} . This suggests that during low-flow periods, evaporative water loss and a lack of flushing lead to the concentration of persistent high molecular weight (HMW) PAHs in the benthic layer.

Conclusion

The assessment of PAHs in the sediments of Goronyo Dam reveals an ecosystem currently characterized by low-level hydrocarbon contamination. The dominance of four- to six-ring HMW PAHs over LMW congeners indicates that the primary pollutant drivers are pyrogenic in nature, stemming from regional biomass burning and diffuse domestic combustion rather than point-source industrial or petrogenic discharges. Seasonal variations, while numerically present, were not statistically significant, suggesting a relatively uniform and stable distribution of these contaminants throughout the year.

The ecological risk indices (m-ERMQ and BaP_{eq}) consistently fall well below international thresholds for toxicity, confirming that the sediment currently poses a minimal threat to benthic organisms. However, the recorded increase in risk quotients during the dry season suggests that the dam functions as a dynamic sink where pollutants concentrate during low-flow periods. Given the persistence of the carcinogenic HMW PAHs detected, these results support the need for established baseline monitoring and the implementation of localized strategies to manage agricultural runoff and biomass burning in the catchment area to prevent future ecological degradation.

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