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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants with significant ecological and public health implications, particularly in urban wetlands exposed to chronic anthropogenic stress. This study evaluates the occurrence, spatial distribution, seasonal variability, and ecological risk of three low molecular weight PAHs (naphthalene, phenanthrene, and anthracene) in surface waters of Caño La Malaria, the main freshwater source of Cucharillas Marsh, Puerto Rico's largest urban wetland. Samples were collected at four locations across multiple seasons. Liquid-liquid extraction, rotary evaporation, and GC-MS were used for quantification. naphthalene was the dominant compound, with total PAH concentrations ranging from 7.4 to 2,198.8 ng/L, and most wet season samples falling within the mild-to-moderate contamination range. PAH levels were significantly higher in the wet season (mean = 4,434.66 ng/L) than in the dry season (mean = 1,245.08 ng/L), confirmed by Friedman test ($p < 0.000001$). Compositional shifts indicated increased levels of phenanthrene and anthracene during the wet season. No significant spatial differences were found ($p = 0.753$), and high correlations between sites ($r = 0.96$) suggest uniform input sources. Diagnostic ratios, inter-species correlations, and principal component analysis (PCA), all support a predominant pyrogenic origin. High correlations between phenanthrene and anthracene ($r = 0.824$) further suggest shared combustion-related sources. PCA revealed a clear separation between dry- and wet-season samples, with the latter showing greater variability and stronger associations with naphthalene and anthracene. Ecological risk assessment using hazard quotients (HQ) indicated insignificant acute toxicity risk across all sites and seasons, with all HQ values <0.01. The highest HQ (0.0095) occurred upstream during the wet season, approaching the threshold for low ecological risk. These findings support integrated watershed management practices to control PAH pollution and ensure long-term ecological health in this tropical urban wetland.

Keywords: Polycyclic aromatic hydrocarbons; urban wetland; surface water; distribution; PAH

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a diverse group of semi-volatile organic compounds composed of two or more fused aromatic rings. PAHs are typically categorized into low molecular weight (LMW) PAHs—comprising 2 to 3 aromatic rings—and high molecular weight

(HMW) PAHs, which contain 4 or more rings [1]. This classification influences their behavior in the environment, as LMW-PAHs tend to be more soluble and volatile, while HMW-PAHs are more persistent and prone to sediment accumulation [2,3]. These compounds originate from a variety of natural and anthropogenic sources [1,4], including incomplete combustion of fossil fuels and biomass (pyrogenic) [5], petroleum refining and spillage (petrogenic), and biological synthesis by microorganisms and plants (biogenic) [1]. Combustion-related activities—such as the burning of fossil fuels [6] and wildfires—are among the primary environmental sources of PAHs globally, contributing to their widespread occurrence across atmospheric [7], terrestrial [8], and aquatic systems [9,10]. After their release into the environment, PAHs are transported between environmental compartments via pathways such as atmospheric deposition [11], urban runoff [12,13], and wastewater discharge [14]. These processes lead to their accumulation in sediments [15] and their transfer through food webs via bioaccumulation [16,17], ultimately resulting in biomagnification [18]. Due to their low solubility in water, high hydrophobicity [19], and chemical stability [20], PAHs are considered persistent organic pollutants (POPs) that exert toxic effects on biota following bioaccumulation [21].

The environmental persistence and ubiquity of PAHs has raised global concern due to their mutagenic, teratogenic, and carcinogenic effects [22,23] on ecosystems and human health [24,25]. Accordingly, regulatory agencies such as the United States Environmental Protection Agency (USEPA) have designated 16 PAHs as priority pollutants [26,27], based on their toxicity and ecological impact [28]. In aquatic environments, PAHs can affect a broad spectrum of organisms across trophic levels [29] and have been associated with sublethal effects such as oxidative stress, immunotoxicity, and reproductive impairment [30]. Such impacts are especially concerning in shallow, urban-influenced wetlands where PAH exposure is amplified by stormwater inputs [31] and limited dilution capacity [32].

Urban wetlands, located within or near densely populated areas, function as transitional ecosystems that provide critical services such as water filtration, flood control, and habitat for aquatic organisms [33]. Located in close proximity to anthropogenic emission sources, they are particularly vulnerable to contamination by persistent organic pollutants like PAHs [34,35]. In tropical urban regions, wetlands frequently receive inputs from traffic emissions, industrial discharges, atmospheric deposition, and unregulated stormwater runoff, often acting as both reservoirs and conduits for these contaminants [36–38]. Despite their role as pollutant sinks, they can also function as natural ecological filters, attenuating PAHs through microbial degradation, sedimentation, and plant uptake under favorable conditions [39].

Elevated concentrations of PAHs have been reported in urban rivers, lakes, and drainage canals across Asia, Africa, and Latin America, frequently surpassing international water quality standards [40–43]. Enclosed or semi-enclosed wetlands—such as urban marshes—often retain higher PAH loads due to restricted hydrological exchange and elevated organic matter content, which increase the potential for sedimentary accumulation and long-term ecological impacts [44–46]. Their shallow waters, organic-rich sediments, and limited flushing can enhance pollutant retention and ecological exposure [33,35]. However, in tropical urban wetlands, where environmental dynamics are intensified by climatic variability and human pressures—integrated assessments that capture the spatial and seasonal behavior of mobile PAH fractions, such as LMW-PAHs, remain scarce.

Spatial and seasonal assessments of PAHs—LMW-PAHs such as naphthalene (NAP), phenanthrene (PHEN), and anthracene (ANT)—remain limited in tropical urban wetlands [47,48]. Due to their phase behavior and environmental mobility, these compounds are readily transported during rainfall events, which facilitates their dispersion but makes them difficult to monitor through sediment-based approaches [49,50]. In tropical urban environments, high temperatures and intense land-use pressures may amplify their ecological risks, through seasonal microbial degradation dynamics and transient contamination pulses [3,51–53]. However, studies that also quantify the ecological risk associated with LMW-PAH concentrations in tropical island wetlands remain notably absent.

Caño La Malaria is a tidal-influenced urban waterway within the highly urbanized Cucharillas Marsh watershed in Cataño, Puerto Rico, which plays a critical role in connecting upland runoff with the San Juan Bay Estuary [54–56]. It receives runoff from roads, informal settlements, and industrial zones before discharging into the San Juan Bay Estuary. Prior studies have reported elevated levels of fecal coliforms, heavy metals, and untreated sewage [56–58], yet the occurrence and seasonal behavior of PAHs in its surface waters remains uncharacterized. Given its location within a protected natural reserve and the lack of PAH monitoring in tropical urban channels in Puerto Rico, Caño La Malaria offers a relevant case study for evaluating spatial and seasonal variability of these compounds in an ecologically vulnerable wetland system.

Although PAHs are widely recognized as significant aquatic pollutants, comprehensive field assessments in tropical island environments are still scarce. Particularly in Puerto Rico, existing research has focused primarily on estuarine sediments and amphibian habitats [59–62], with no studies addressing the occurrence or seasonal variability of PAHs in waters of urban channels like Caño La Malaria, despite previous recommendations [63] and recent evidence of human exposure [64,65]. This urban waterway represents a critical yet understudied conduit of pollutant transfer into a protected tropical urban wetland. Within this context, this study addresses a critical knowledge gap by evaluating the occurrence, spatial distribution, seasonal trends, and potential sources of three LMW-PAHs—NAP, PHEN, and ANT—in Caño La Malaria. In addition, it integrates an ecological risk assessment (ERA) based on measured surface water concentrations and toxicity thresholds to estimate potential impacts on aquatic organisms. These findings support future monitoring and restoration efforts in tropical urban wetlands under similar anthropogenic pressures. This need is further emphasized by the lack of region-specific studies and long-term environmental assessments of PAH contamination in Caribbean urban wetlands, underscoring the urgency of sustained monitoring and management efforts [66].

2. Materials and Methods

2.1. Study Area and Sampling Design

Caño La Malaria is a tidal-influenced estuarine channel located in the municipality of Cataño, on the northern coast of Puerto Rico (18.4450° N, 66.1178° W). It functions as the primary hydrological conduit for surface water flow from the Cucharillas Marsh watershed into the San Juan Bay Estuary [56]. The channel receives year-round surface water inputs from upland tributaries such as the Santa Catalina and San Diego streams [67], which contribute to its continuous outflow into San Juan Bay. Its hydrological regime is artificially regulated by tide gates and a pump system located at the outlet, which limit marine–terrestrial exchange, block tidal inflow, and promote freshwater retention under seasonal rainfall conditions [54,55]. The region follows a bimodal precipitation pattern characteristic of Puerto Rico and the wider Caribbean, with a dry season (December–March), early rainfall (April–July), a brief midsummer drought, and late rainfall season (August–November) [68,69].

Surface water samples were collected at four fixed sampling sites—upstream (U), midstream (M), downstream (D), and outlet (O)— representing spatial variation from upstream headwaters to the canal's outlet. Site selection was based on proximity to stormwater discharge points, urban infrastructure, and accessibility during both dry and wet seasons. A total of four sampling campaigns were conducted in March, September, and November 2022, and February 2023, corresponding to two dry- and wet-season events. At each sampling station and campaign, duplicate surface water samples were collected. Figure 1 illustrates the geographic context of the study area, including watershed boundaries, drainage features, and the spatial distribution of surface water sampling sites along Caño La Malaria.

2.2. Materials and Reagents

Surface water samples were collected in pre-assembled amber wide-mouth glass bottles (LabForce®, Thomas Scientific), equipped with PTFE-lined caps to prevent analyte adsorption and

minimize photodegradation of PAHs during transport and storage. All laboratory glassware used in sample collection, extraction, and concentration was thoroughly cleaned following a multi-stage protocol. This included sequential washing with 1 % (w/v) Alconox® detergent solution, rinsing with distilled water, repeated rinses with deionized water, acid rinsing with 50% nitric acid to remove metal and organic residues, followed by additional deionized water rinses, and a final rinse with acetone. The glassware was subsequently dried in a laboratory oven at 100 °C for a minimum of 2 hours prior to use. The liquid-liquid extraction procedure employed certified HPLC-grade dichloromethane (DCM; CAS No. 75-09-2; GFS Chemicals). Anhydrous sodium sulfate (CAS No. 7757-82-6; Thermo Fisher Scientific), was used to remove residual water from the organic extracts. Analytical standards of PAHs, including NAP, PHEN, and ANT, were obtained as a certified solution at 1,000 µg/mL in DCM (Agilent Technologies, Method 610-compliant), and were used for calibration and quality control of gas chromatography-mass spectrometry (GC-MS) quantification procedures.

2.3. Sample Preparation and Extraction

PAHs were extracted from 1-liter surface water samples within 48 hours of collection to minimize degradation, using a liquid–liquid extraction adapted from the USEPA standard method [70]. Each sample was transferred to a 2,000 mL separatory funnel and extracted with three portions of 60 mL of DCM. The combined organic phases were dried with anhydrous sodium sulfate, followed by gravity filtration through Whatman #1 filter paper to eliminate particulate matter and drying agent. The dried extract was concentrated to dryness using a rotary evaporator. The residue was then reconstituted in 5 mL of DCM and transferred to amber glass vials. Extracts were stored at 4–6 °C in a laboratory-grade refrigerator and analyzed within 7 days. Each extract was injected in triplicate into the GC–MS.
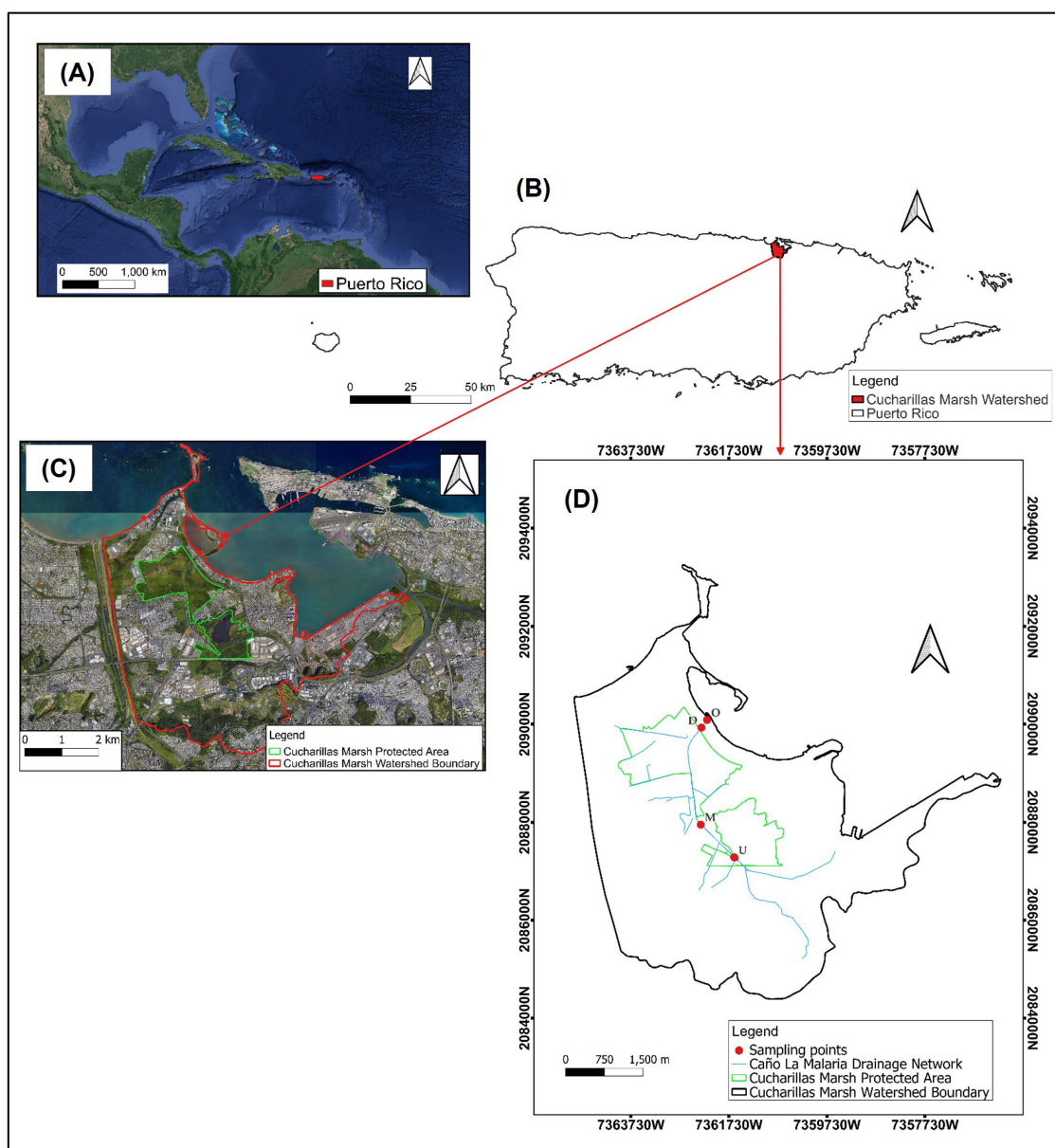
Figure 1. Geographic location and spatial context of the study area within the Cucharillas Marsh watershed, Cataño, Puerto Rico. Panel (A) shows the location of Puerto Rico within the Caribbean region. Panel (B) highlights the position of the Cucharillas Marsh watershed on the island of Puerto Rico. Panel (C) presents the watershed boundary (red) and protected wetland area (green) over satellite imagery. Panel (D) displays the drainage network of Caño La Malaria (blue), the Cucharillas Marsh Protected Area boundary (green), and the Cucharillas Marsh watershed boundary (black). Red dots indicate surface water sampling stations corresponding to U, M, D, and O segments along the Caño La Malaria system. Maps prepared using publicly available data from GIS Puerto Rico [71].

2.4. GC-MS Instrumental Analysis

LMW-PAHs were quantified by GC–MS using a Shimadzu GC-2010 Plus–QP2020 system (Shimadzu, Kyoto, Japan). Separation of the target compounds was achieved using a Restek Rxi-5Sil MS capillary column (30m × 0.25mm i.d., 0.25µm film thickness; Restek Corporation, Bellefonte, PA, USA) with high-purity helium (99.999%) as the carrier gas at a constant linear velocity of 43.7 cm/s. The injection was conducted in splitless mode with an injector temperature of 300 °C, and an injection volume of 1 µL was delivered using an AOC-20i autosampler (Shimadzu, Kyoto, Japan). The oven temperature program was set as follows: initial temperature of 90 °C (held for 2 min), ramped at 5 °C/min to 320 °C, with a final hold time of 12 min, for a total runtime of 60 min. The MS was operated

in electron ionization (EI) mode at 70eV, with an ion source temperature of 230 °C and an interface temperature of 300 °C. The solvent cut time was set at 3.5 min. Data acquisition was performed in Selected Ion Monitoring (SIM) mode, targeting characteristic m/z values of 128 (NAP), 178 (PHEN and ANT). Isomeric differentiation between PHEN and ANT was achieved by comparing retention times to those of certified standards.

2.5. Data Processing and Statistical Analysis

All GC-MS chromatograms were processed using the Postrun Analysis module of GCMSsolution software (Shimadzu Corporation, Japan) to quantify the peak areas and retention times of the target PAHs. External calibration curves were constructed using certified PAH standards (NAP, PHEN, and ANT) at known concentrations in DCM. The coefficient of determination (R^2) for each compound exceeded 0.99. Quantified concentrations were compared against national and international water quality guidelines to assess their ecological significance. The Shapiro–Wilk test indicated that $\sum 3PAHs$ concentrations were not normally distributed ($W = 0.76$, $p < 0.01$, $n = 16$), supporting the use of non-parametric statistical tests. Accordingly, the Friedman test was applied to assess spatial and seasonal differences in PAH concentrations, using a significance level of $\alpha = 0.05$. All statistical analyses were performed using Microsoft Excel (Microsoft 365; Microsoft Corporation, Redmond, WA, USA).

2.6. Quality Assurance and Quality Control

External calibration curves for each PAH were prepared daily using at least seven concentration levels (0.10–100.0 ng/L), achieving high linearity ($R^2 > 0.99$). The limits of detection (LOD) and limits of quantification (LOQ) were determined for each analyte and batch using the method based on the standard deviation of the intercept divided by the slope of the calibration curve [72]. LOD and LOQ were calculated using the formulas: $LOD = 3.3 \times SE / m$ and $LOQ = 10 \times SE / m$, where SE is the standard error of the y-intercept and m is the slope of the calibration curve. All reported concentrations above LOQ were considered quantifiable, while values between LOD and LOQ were labeled nonquantifiable (NQ). LOD values ranged from 1.72 to 433.14 ng/L, and LOQ values ranged from 5.22 to 1312.56 ng/L across the four sampling campaigns (see Supplementary Table S2).

Blanks consisting of HPLC-grade DCM were injected into GC-MS throughout each run to confirm the absence of carryover and instrument background contamination. No target PAHs were detected in the blanks. Analytical precision was assessed through duplicate sample acquisition and triplicate injections in the GC-MS. Relative standard deviation (RSD) and coefficient of variation values were calculated for each sample (see Supplementary Table S3). Nondetected (ND) values in individual injections were treated as zero for mean concentration calculations.

2.7. Ecological Risk Assessment

To estimate the potential ecological risk associated with NAP in surface waters of Caño La Malaria, we applied the Hazard Quotient (HQ) method [73–76]. The HQ was calculated as follows:

$$HQ_{water} = EC_{water}/PNEC_{water} \tag{1}$$

$$PNEC_{water} = L(E)C_{50}/AF \tag{2}$$

The EC_{water} represents the maximum concentration of NAP detected in surface water (ng/L). The predicted no-effect concentration in water ($PNEC_{water}$) was derived from acute toxicity data for *Callinectes sapidus* (blue crab), a native estuarine decapod crustacean widely distributed across Puerto Rico's coastal wetlands [77]. Based on the 96-hour LC_{50} (lethal concentration for 50% of test organisms), the lowest observed $L(E)C_{50}$ was 0.68 mg/L, applying an assessment factor (AF) of 10, and yielding a $PNEC_{water}$ of 0.068 mg/L (68,000 ng/L) [78]. Toxicity data for NAP, were obtained from the ECOTOX database [79].

HQ values were then calculated for each site and sampling date using the maximum observed NAP concentrations to reflect worst-case exposure scenarios. Ecological risk categories were assigned following the classification criteria by Li et al. [76]:

Table 1. Ecological risk classification based on HQ$_{water}$ values [76].

HQ$_{water}$ Range	Ecological Risk Category
HQ$_{water}$ < 0.01	Insignificant
0.01 ≤ HQ$_{water}$ < 0.1	Low
0.1 ≤ HQ$_{water}$ < 1.0	Moderate
HQ$_{water}$ ≥ 1.0	High

3. Results

3.1. Spatial and Seasonal Variability in PAH Concentrations

Table 2 presents the concentrations of NAP, PHEN, and ANT across four seasonal sampling campaigns and four stations along Caño La Malaria. PAH concentrations exhibited marked variability, with higher levels recorded during the wet season (September and November 2022) compared to the dry season (March 2022 and February 2023). For instance, Σ3PAHs during the dry season ranged from 7.40 ng/L (U, March) to 363.11 ng/L (O, February), while wet season values spiked up to 929.57 ng/L (M, September) and peaked at 2198.83 ng/L (U, November), driven by extreme ANT concentrations (up to 1313.60 ng/L). NAP was the most abundant compound, reaching 485.10 ng/L (U, September), although its dominance shifted to ANT in November. PHEN varied broadly (ND–557.43 ng/L), with notable peaks at M and U sites. The O consistently registered Σ3PAHs between 43.43–712.54 ng/L across all campaigns, underscoring its role as the final receptor before discharge into San Juan Bay.

Table 2. Mean concentrations (± standard deviation) and concentration ranges of NAP, PHEN, and ANT measured in surface water from four sites along Caño La Malaria, Puerto Rico, during four seasonal sampling campaigns conducted between March 2022 and February 2023.

Date	Site	NAP Mean (ng/L)±SD	Range	PHEN Mean (ng/L)±SD	Range	ANT Mean (ng/L)±SD	Range	Σ3PAHs (ng/L)
Mar, 2022	U	6.20±0.00	ND—6.20	1.20±0.00	ND—1.20	ND	ND	7.40
	M	30.13±28.46	10.00—50.25	8.10±1.91	6.75—9.45	ND	ND	38.23
	D	30.50±26.38	11.85—49.15	1.25±0.00	ND—1.25	0.50±0.00	ND—0.50	32.25
	O	34.73±32.99	11.40—58.05	8.70±0.00	ND—8.70	ND	ND	43.43
Sep, 2022	U	485.10±231.93	321.10—649.10	135.87±48.11	85.65—181.55	203.40±0.00	114.50—292.30	824.37
	M	337.60±32.39	308.60—372.55	364.72±47.34	321.55—415.35	227.25±109.39	149.90—304.60	929.57
	D	232.12±29.02	203.80—261.80	240.47±33.11	218.50—278.55	171.95±116.67	100.75—306.60	644.54
	O	281.62±67.63	230.50—358.30	297.17±81.43	224.35—385.10	133.75±36.98	108.90—176.25	712.54
Nov, 2022	U	327.80±183.92	197.75—457.85	557.43±0.00	554.05—560.80	1313.60±0.00	1285.15—1342.05	2198.83
	M	41.48±38.36	14.35—68.60	183.30±167.02	65.20—301.40	301.08±383.29	30.05—572.10	525.86
	D	34.35±0.99	33.65—35.05	5.00±0.49	4.65—5.35	27.68±3.22	25.40—29.95	67.03
	O	6.98±4.56	3.75—10.20	37.13±12.48	28.30—45.95	19.48±2.02	18.05—20.90	63.59
Feb, 2023	U	223.66±185.24	43.00—399.15	183.49±191.92	5.60—359.70	213.04±213.39	2.25—412.20	620.19
	M	43.76±1.29	41.75—45.75	46.04±9.44	31.95—54.90	20.57±17.34	2.45—39.10	110.37
	D	26.73±20.12	NQ—52.80	165.11±61.73	115.35—255.00	86.87±15.61	72.20—112.95	278.71
	O	16.12±11.70	3.60—28.80	228.98±24.01	204.50—251.00	118.01±4.33	112.30—123.50	363.11

Sites: upstream (U); midstream (M); downstream (D), and outlet to San Juan Bay (O). Values in the first column of each PAH represent mean ± standard deviation across replicates for each site and date. ND: Not detected; below limit of detection (LOD). NQ: Non-quantifiable; concentration detected below the limit of quantification (LOQ). Σ3PAHs = sum of NAP, PHEN, and ANT concentrations. Range = minimum-maximum concentrations measured per site.

Figure 2 presents the seasonal and spatial distribution of Σ3PAHs concentrations in surface waters of Caño La Malaria. Panel A illustrates that mean Σ3PAHs concentrations were elevated during the wet season, reaching 777.75 ng/L in September and 713.82 ng/L in November, in contrast to lower values observed in the dry season—31.44 ng/L in March and 343.09 ng/L in February. Panel B further underscores this seasonal trend, showing that overall mean concentrations during the wet season (4434.66 ng/L) were more than three times higher than those recorded during the dry season (1245.08 ng/L). Panel C depicts the spatial variation across the four sampling sites, with site U consistently exhibiting the highest concentrations, particularly in November 2022, whereas sites D and O showed persistently lower levels throughout the sampling period.
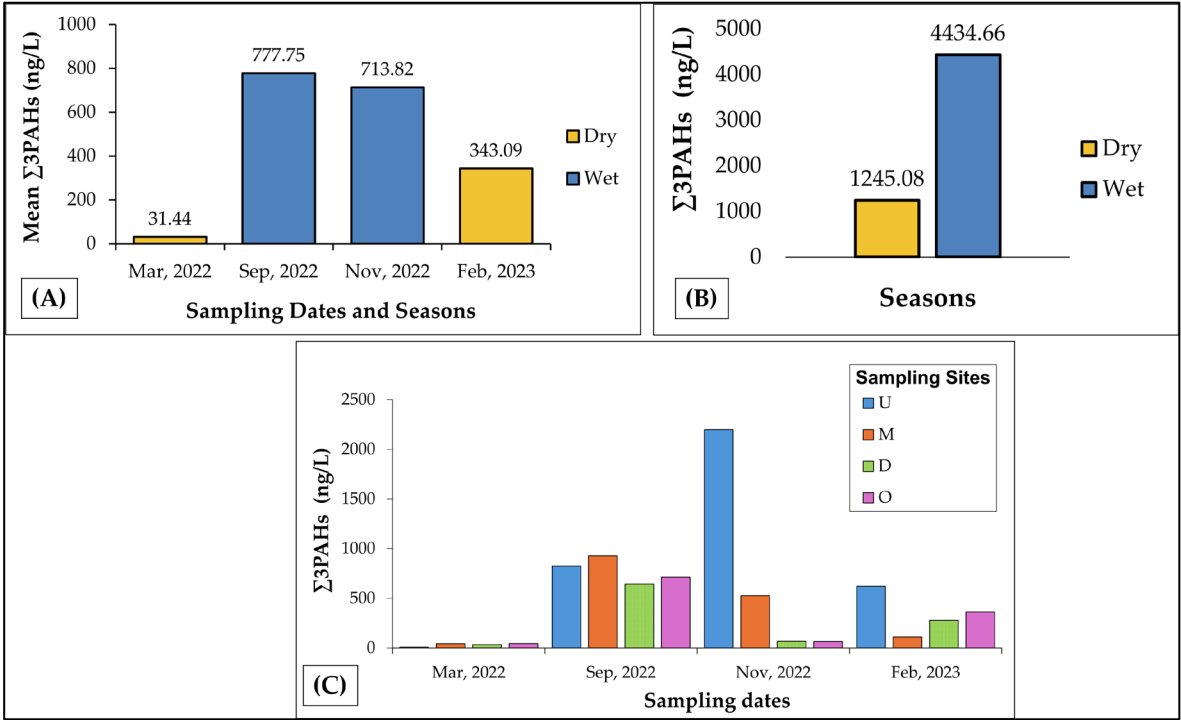

Figure 2. Seasonal and spatial variation of total LMW-PAHs (Σ3PAHs: NAP, PHEN, and ANT) in surface water samples collected from Caño La Malaria. (A) Mean Σ3PAHs concentrations (ng/L) per sampling campaign. (B) Comparison of overall mean Σ3PAHs concentrations by season. (C) Spatial and seasonal distribution of Σ3PAHs across four sampling sites (U, M, D, O) and four campaigns.

A Friedman test confirmed seasonal differences in Σ3PAHs concentrations across the four sampling campaigns ($\chi^2 = 21.00$, p = 4.59×10^{-6}), supporting the trend of elevated PAH levels during the wet season. In contrast, no significant differences were found among the sampling sites ($\chi^2 = 1.20$, p = 0.753), suggesting a homogeneous spatial distribution of PAHs across Caño La Malaria, despite marked seasonal variability.

3.3. PAH Sources and Compositional Patterns

3.3.1. Compositional Patterns

Figure 3 illustrates the relative percentage composition of the three LMW-PAHs across all sampling sites and dates. During the first sampling campaign (March 2022), NAP dominated the ∑3PAHs composition at all sites, representing 80–100% of the total concentration. PHEN contributed at sites M and O (16–20%), while ANT was either absent or accounted for less than 10%. By September 2022, the compositional profile became more balanced, especially at sites U and M, where NAP accounted for approximately 59% and 36%. PHEN and ANT showed increased contributions at these sites during the wet season (e.g., PHEN: 16-39%; ANT: 25–24%).
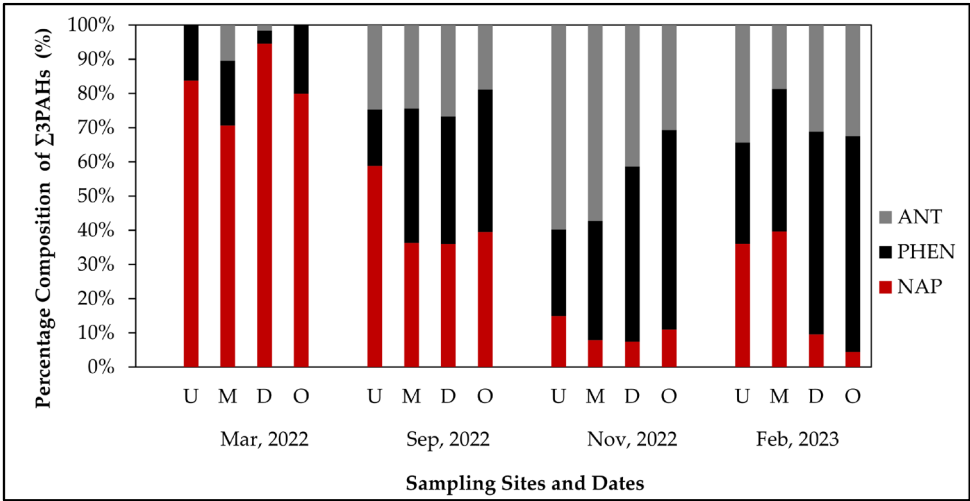
Figure 3. Percentage composition of individual LMW-PAHs — NAP, PHEN, and ANT—in surface water samples collected from Caño La Malaria. Data is shown for four sites: U, M, D, O, across four sampling campaigns. Each bar represents the relative contribution (%) of each PAH to the total Σ3PAHs concentration.

In November 2022, ANT became the dominant compound at all sites, notably at U and M, where it represented approximately 60% and 57% of $\sum3$PAHs. PHEN also remained elevated (25–58%), while NAP accounted for less than ~20% of the total. In February 2023, PHEN was the most abundant PAH at sites D and O, contributing approximately 59% and 63% of $\sum3$PAHs, followed by ANT with 31% and 32%. NAP contributions were highly variable: low in November and February (6–15%), but much higher in March (70–98%) and September (28–59%). Across all campaigns, NAP represented between 4% and 98% of Σ_3PAHs, dominating during the March 2022 campaign. PHEN and ANT showed greater seasonal and spatial variability, with ANT being notably higher during the peak wet season and PHEN becoming more dominant at downstream sites in the final sampling campaign.

3.3.2. Sources by Diagnostic Ratios

PAH source apportionment was evaluated using two diagnostic ratios: ANT/(ANT + PHEN) and PHEN/ANT. The former distinguishes petrogenic sources (<0.10) from pyrogenic ones (>0.10), while the latter indicates pyrogenic inputs when values are below 10. As illustrated in Figure 4, all ANT/(ANT + PHEN) values exceeded the 0.10 threshold, indicating a consistent pyrogenic signature across Caño La Malaria's surface waters. While PHEN/ANT ratios were also below 10, with most values under 2.5. Elevated values in both ratios aligned with periods of higher Σ3PAHs concentrations.
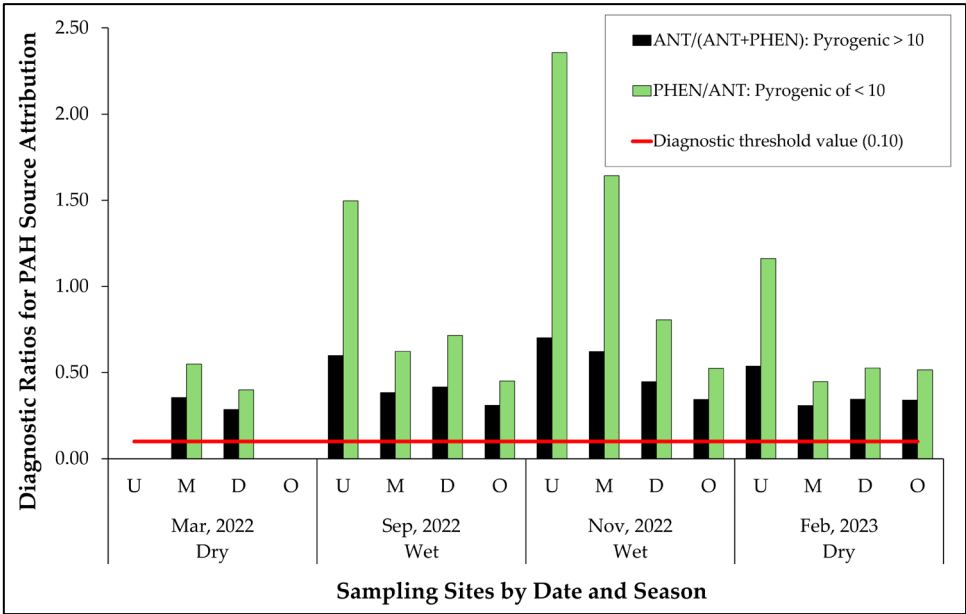
Figure 4. Diagnostic ratios of PAHs used for emission source attribution in surface water samples from Caño La Malaria, collected at four sites—U, M, D, O—during the seasonal campaigns (March, September, November 2022, and February 2023). Bars represent the value generated by the diagnostic ratios used: ANT/(ANT + PHEN) (black) and PHEN/ANT (green). The red line indicates the threshold value of 0.10 for ANT/(ANT + PHEN), above which pyrogenic sources are inferred. PHEN/ANT values below 10 also suggest a pyrogenic origin.

3.3.3. Sources by Principal Component Analysis

Principal Component Analysis (PCA) is a widely applied multivariate approach in PAH source apportionment, as it reduces complex datasets into a few principal components that explain most of the variance and reflect groups of correlated compounds [80]. The biplot of PC 1 and PC 2 (Figure 5), which together accounted for 96.7% of the total variance (84.8% and 11.9%, respectively), revealed a separation between samples collected during the dry and wet seasons. Dry-season samples clustered tightly in the lower-left quadrant, reflecting uniform PAH compositions and lower mean concentrations. In contrast, samples from the wet season exhibited greater dispersion and were oriented along the NAP and ANT vector directions. . Component loadings (Table S9) indicate that ANT had the strongest influence on PC1 (loading = 0.87794), followed by PHEN and NAP. Meanwhile, PC2 was primarily influenced by NAP (loading = 0.89129.
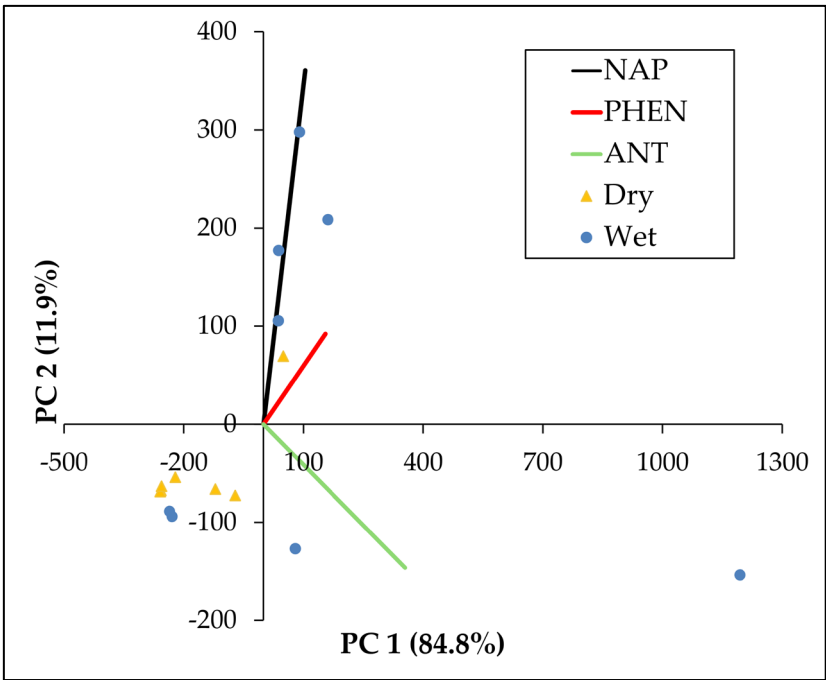
Figure 5. PCA biplot of surface water samples from Caño La Malaria based on concentrations of three LMW-PAHs: NAP, PHEN, and ANT. The plot displays the distribution of 16 samples grouped by season (Dry vs. Wet) along the first two principal components (PC 1 and PC 2), which explain 84.8% and 11.9% of the total variance, respectively. Vectors represent the directional contribution of each PAH to the multivariate pattern. Samples from the wet season exhibit greater variability and are more strongly associated with NAP and ANT concentrations.

3.4. Correlation Patterns

Pearson correlation analysis between sampling points supported the spatial and seasonal patterns observed. A positive correlation was found between sites U and M (r = 0.964), while moderate associations between U–O and M–O suggest similar contamination sources or hydrological connectivity among most sites. In contrast, weak or negative correlations with D indicate local variability, driven by distinct inputs or site-specific environmental processes (Supplementary Table S7). Inter-species correlation analysis also revealed strong relationships between individual PAHs. In particular, PHEN and ANT were strongly correlated (r = 0.824), while NAP showed moderate correlation with both compounds (Supplementary Table S8).

3.5. Ecological Risk Assessment

HQ_{water} values were calculated for each site and sampling event using the maximum observed NAP concentrations. Table 3 summarizes the HQ_{water} values calculated for each site–season combination. All HQ_{water} values were below 0.01 (Table 1), ranging from 9.12×10^{-5} to 9.55×10^{-3}, indicating insignificant ecological risk across the study area and seasonal sampling campaigns (Table 3). The highest HQ_{water} value (9.55×10^{-3}), was observed at the upstream site during the September 2022 sampling campaign—corresponding to the wet season and the peak NAP concentrations. Although, this value approached the upper limit of the "insignificant" ecological risk category, it did not cross into the "low ecological risk" range.

Table 3. Hazard Quotient Summary by Site and Sampling Date. PNEC value: 68,000 ng/L, based on acute toxicity data for *Callinectes sapidus* [79].

Date	Site	Max. NAP (ng/L)	HQ (ng/L)	Ecological Risk Classification

Mar, 2022	U	6.20	9.12E-05	Insignificant
	M	50.25	7.39E-04	Insignificant
	D	49.15	7.23E-04	Insignificant
	O	58.05	8.54E-04	Insignificant
Sep, 2022	U	649.10	9.55E-03	Insignificant
	M	372.55	5.48E-03	Insignificant
	D	261.80	3.85E-03	Insignificant
	O	358.30	5.27E-03	Insignificant
Nov, 2022	U	457.85	6.73E-03	Insignificant
	M	68.60	1.01E-03	Insignificant
	D	35.05	5.15E-04	Insignificant
	O	10.20	1.50E-04	Insignificant
Feb, 2023	U	399.15	5.87E-03	Insignificant
	M	45.75	6.73E-04	Insignificant
	D	52.80	7.76E-04	Insignificant
	O	28.80	4.24E-04	Insignificant

Spatial patterns showed that HQ_{water} values were higher at upstream locations (U and M), particularly during wet seasons. In contrast, downstream sites (D and O), consistently exhibited lower HQ_{water} values. Seasonally, wet season events (September and November) show elevated HQ_{water} relative to dry season campaigns (March and February). However, none of the HQs exceeded the threshold for "low risk".

4. Discussion

4.1. Influence of Seasonal Hydrology on PAH Dynamics

The pronounced seasonal variation in Σ3PAHs concentrations observed in Caño La Malaria (mean = 4434.66 ng/L during the wet season vs. 1245.08 ng/L in the dry season) underscores the dominant role of rainfall-driven hydrological pulses in mobilizing PAHs withing tropical urban wetlands. This enrichment during the wet period is consistent with findings from other tropical and subtropical freshwater systems, including Ho Chi Minh City, Vietnam [81], Sergipe State, Brazil [82], and the Cross River Estuary, Nigeria [32], where elevated PAH concentrations were linked to runoff-driven inputs during rainy seasons. Across these systems, LMW-PAHs—particularly NAP, PHEN, and ANT—were consistently dominant, reflecting the compositional pattern found in our study.

Contrasting seasonal trends have been reported. For example, Na et al. [83] and Jiang et al. [84] observed higher PAH concentrations during the dry season in the East Liao River and coal-mining-impacted groundwater systems, attributing the lower wet-season levels to dilution and hydrodynamic flushing. Similar dry-season peaks were reported in the Olt River [85] and the Han River [86], suggesting that regional climate regimes, flow variability, and land-use characteristics can lead to divergent seasonal behaviors. These patterns suggest that regional climate, hydrology, and land use drive seasonal PAH dynamics, with the extensive impervious cover and limited riparian vegetation in Caño La Malaria amplifying runoff-driven transport of LMW-PAHs during intense tropical rainfall.

The predominance of LMW-PAHs—especially NAP—during the wet season in Caño La Malaria reflects a trend reported in other tropical aquatic systems, including the Subarnarekha Estuary [87], Gaoqiao wetland sediments [88], and the Sombreiro River Estuary [89]. Elevated temperatures during warmer months may further enhance the dissolution and water-phase partitioning of lighter PAHs [76,90], contributing to the seasonal increase in aqueous concentrations observed in our study. Dominance of LMW-PAHs has also been reported in highly industrialized watersheds, such as the Kolo Creek [91] and the Kuye River [92], reinforcing their utility as indicators of recent pyrogenic input and their susceptibility to hydrological mobilization. In Caño La Malaria, Σ3PAHs

concentrations reached up to 2198.8 ng/L—exceeding values reported in many comparable tropical freshwater systems—highlighting the effects of sustained anthropogenic pressure, deficient stormwater infrastructure, and direct runoff inputs in this densely urbanized wetland catchment.

Compared to other global wetland systems, PAH levels in Caño La Malaria are elevated. For example, surface water concentrations of $\sum$3PAHs ranged from 50.1 to 365.8 ng/L in the Siahroud River Wetland, Iran [93], and between 7.95 and 122.41 ng/L in the Shadegan Wetland [94]—both well below our recorded peak concentrations of 2198.8 ng/L. Even in sediment-based studies such as the Anzali Wetland, PAH levels (52.3 to 408.2 ng/g) reflected moderate contamination compared to our surface water findings [95]. These comparisons reveal significant human impact in Cucharillas Marsh and support the need for pollution control strategies.

In summary, seasonal hydrology plays a pivotal role in shaping PAH dynamics in Caño La Malaria, primarily by facilitating the mobilization and aqueous partitioning of LMW-PAHs during periods of intense rainfall. These findings not only corroborate patterns of rainfall-driven PAH mobilization observed in other tropical systems [47,96], but also contribute novel data from a Caribbean urban wetland. While variability across studies reflects differences in regional hydrology, emission profiles, and land use, the strong influence of wet-season runoff on the transport of pyrogenic and petrogenic PAHs emerges as a consistent feature of tropical and subtropical aquatic systems.

4.2. Spatial Distribution and Attenuation of PAHs

Although the Friedman test revealed no statistically significant differences in Σ3PAHs concentrations across the four sampling sites (p = 0.753). Elevated concentrations at U and M sites—particularly during high-rainfall events—suggest local inputs from adjacent roadways and potential illicit discharges, in addition to diffuse runoff [53,97]. In contrast, D and O sites consistently showed lower concentrations, likely due to hydrological dilution , sorption to suspended particulates, and gradual deposition along the canal's flow path. [98].

This U-to-D gradient aligns with patterns observed in other urban aquatic systems. For example, elevated PAHs have been reported in the Imiringi River due to vehicular emissions and localized combustion [99], and along the Nile River downstream of wastewater and industrial discharge zones [80]. Similar upstream enrichment has also been observed in the Lipu River [100], the Damodar River Basin [101], and the Guanzhong River in the Danjiangkou Reservoir, where fossil fuel combustion dominates [76]. These spatial trends are further corroborated by findings in Ho Chi Minh City and the East Liao River, where PAH concentrations were higher in densely urbanized, high-traffic areas [81,83]. A consistent pattern emerges in which upstream and highly urbanized segments function as hotspots of PAH contamination, whereas downstream reaches reflect the combined influences of hydrological dilution, sedimentation, and pollutant attenuation, particularly within aquatic coastal environments.

Beyond hydrological controls, land-use patterns exert influence on the spatial distribution of PAHs in Caño La Malaria. As demonstrated in the Sombreiro Estuary and Kuye River, where extreme PAH concentrations were detected near oil activity [89,92]. Although Σ_3PAHs in Caño La Malaria were lower than in oil-impacted rivers, the system still exhibited spatial heterogeneity linked to anthropogenic pressure. This pattern parallels observations in Baiyangdian Lake, where coal and biomass combustion contributed to PAH variability modulated by both source proximity and hydrological retention [102]. Comparable trends in Dong and Tangxun Lakes, Wang Lake Wetland, and Brazilian estuarine systems further support that spatial PAH heterogeneity in urbanized tropical wetlands is shaped by a combination of land use and flow dynamics [103–105]. These studies indicate that the spatial heterogeneity observed in Caño La Malaria reflects broader patterns in which land-use intensity and hydrological processes modulate PAH distributions in urbanized wetland systems.

In summary, the spatial distribution of Σ3PAHs in Caño La Malaria reflects localized contamination at U and M sites, driven by road runoff, stormwater discharges, and surrounding land use. Although concentrations gradually decline toward D and O sites—suggesting attenuation

through hydrological dilution, sedimentation, or sorption—elevated upstream levels, particularly during the wet season, highlight the persistent influence of urban inputs near the canal headwaters. These findings may inform the prioritization of upstream pollution controls and stormwater management strategies in similarly urbanized wetland systems.

4.3. Source Apportionment of PAHs

Compositional profiles of PAHs in Caño La Malaria revealed distinct seasonal trends. NAP was the most abundant compound during the dry season, while PHEN and ANT increased notably during the wet season. This is consistent with our observations, where NAP contributed up to 98% of Σ3PAHs in March 2022, while PHEN and ANT together accounted for more than 70% at several sites in September and November. These shifts reflect changes in transport mechanisms: volatilization and solubility-driven movement dominate in dry periods [106], whereas particle-bound inputs and surface runoff prevail during rainfall events [32]. Diagnostic ratios [ANT/(ANT + PHEN) > 0.10; PHEN/ANT < 10] consistently pointed to pyrogenic sources, implicating vehicular emissions and biomass combustion [107]. The correlation between PHEN and ANT (r = 0.824) reinforces this common origin and behavior under combustion-influenced regimes. In late-season samples (February 2023), PHEN overtook ANT as the predominant PAH at downstream sites, indicating shifting dominance even within the wet-to-dry seasonal transition. Seasonal compositional shifts observed in Caño La Malaria suggest the combined influence of transport mechanisms and combustion-derived sources.

PCA was applied to differentiate seasonal variability in PAH profiles and support source apportionment. PC1 was primarily influenced by ANT, followed by PHEN and NAP, together explaining 96.7% of the total variance. ANT and PHEN are associated with pyrogenic emissions from industrial and residential combustion processes [108], while NAP is often considered a general marker of petrogenic inputs such as oil spills and petroleum leaks [93,109]. Comparable PCA-based approaches in other riverine systems have similarly identified combustion-derived PAHs as major drivers, with additional contributions from petroleum-related inputs depending on local activities and hydrological settings [53,99]. In Caño La Malaria, the loadings of ANT and NAP suggest pyrogenic and petrogenic influences, were the combined impact of combustion and petroleum sources influence PAH composition.

NAP dominated PC2 in our analysis, a pattern consistent with studies that linked strong NAP loadings to petroleum-derived inputs such as oil leaks and refined fuel residues [88,93]. Grmasha et al. [80] further emphasized that NAP is a major constituent of diesel fuels and gasoline, produced through incomplete combustion [110], and in their reported PCA, NAP appeared as a dominant component of PC1. The presence of NAP in PC2 indicates petroleum-derived sources, while the contributions of ANT and PHEN in PC1 reflect combustion markers, together accounting for the observed seasonal variations in PAHs. Overall, these findings demonstrate that PCA not only separates dry and wet season profiles but also highlights the dual influence of combustion and petroleum-related sources in shaping PAH dynamics in Caño La Malaria.

These diagnostic ratios, compositional profiles, and PCA-derived source attributions are consistent with broader reports from tropical and subtropical aquatic systems. In the Damodar River Basin and the East Liao River, 3- and 4-ring PAHs—including PHEN, fluoranthene, and pyrene—were associated with coal combustion and urban activity [83,101]. Similarly, PHEN and NAP were dominant in the Nile River and Ho Chi Minh City, reflecting urban runoff and motor vehicle emissions [81,111]. NAP was the most abundant PAH in the Danjiangkou Reservoir and the Taige Canal, attributed to petroleum combustion and diesel emissions, closely to the profiles observed in Caño La Malaria [76,112]. The compositional similarities between Caño La Malaria and other urban aquatic systems reveal that combustion-derived inputs are the dominant and persistent drivers of PAH behavior in this wetland.

Urban infrastructure facilitates the mobilization of combustion-derived PAHs, particularly in densely populated tropical catchments. Roads and stormwater systems promotes the transfer of

particle-bound compounds into aquatic systems, a dynamic also observed near PR-5 and PR-165 sampling sites in our study area [113]. This process is further amplified during the wet season, when increased runoff remobilizes PAHs previously adsorbed to soils and sediments [114]. Similar seasonal enrichment of LMW-PAHs—especially NAP—in urban watersheds suggest the influence of rainfall-driven inputs on PAH dynamics [115,116]. These patterns align with our findings in Caño La Malaria, where combustion-derived LMW-PAHs consistently dominated across both dry and wet seasons. The persistence of pyrogenic markers throughout the study period indicates chronic anthropogenic pressure from vehicular traffic, industrial activity, and stormwater discharge [53]. Altogether, the compositional and multivariate patterns observed in Caño La Malaria underscore the predominance of combustion-derived PAHs, with episodic petroleum inputs amplified by rainfall and stormwater infrastructure. These dynamics highlight the vulnerability of this tropical urban wetland to chronic anthropogenic pressure and establish the importance of source-specific management strategies.

4.4. Environmental Benchmarks and Management Recommendations

The concentrations of PAHs measured in Caño La Malaria frequently exceed established national and international environmental guidelines. The maximum concentrations for NAP (0.649 μg/L) remained below its benchmark of 1.1 μg/L, while PHEN (0.561 μg/L) and ANT notably exceeded their respective freshwater screening benchmarks (0.4 and 0.012 μg/L) [117]. Based on reported classification frameworks that define ∑PAH contamination levels as slight (0–100 ng/L), mild (100–1000 ng/L), moderate (1000–5000 ng/L), and severe (>5000 ng/L), most wet season samples in this study fall within the mild contamination category, with only one site in November 2022 reaching moderate levels [118,119]. When compared to chronic freshwater quality criteria, PHEN concentrations exceeded the 0.3 μg/L benchmark, reaching up to 0.561 μg/L, while NAP and ANT remained below their respective thresholds of 1 μg/L and 4 μg/L [120]. According to EU guidelines for inland surface waters, NAP concentrations did not exceed the threshold of 2,000 ng/L, whereas ANT surpassed the 100 ng/L limit, particularly during the wet season [121,122]. Several wet season samples also exhibited ANT concentrations well above the 120 ng/L threshold set for marine organisms, with maximum values reaching 1,342.05 ng/L [123]. These exceedances indicate potential ecological risk under multiple regulatory frameworks and justify the integration of alternative assessment models.

Beyond regulatory benchmarks, the ecological significance of the observed concentrations is further supported by thresholds derived from the target lipid model [124] and guidelines for human health protection [125]. Σ16PAHs concentrations in the Euphrates River ranged from 464 to 992 ng/L, with higher levels downstream of urban areas [80]. In Dong and Tangxun Lakes (China), Yao et al. [105] reported Σ16PAHs ranging from 42.9 to 434.7 ng/L. Σ3PAHs in Caño La Malaria exceeded 2,000 ng/L, even though only three compounds were analyzed, compared to the full set of USEPA priority Σ16PAHs in other studies [80]. Also, surface water concentrations often exceeded 1,000 ng/L, likely due to the canal proximity to urban areas upstream [126,127], shallow depth [128], organic-rich sediments [129], and hydrological connectivity [130] with the San Juan Bay Estuary. Together, these comparisons reinforce that current environmental benchmarks may underestimate site-specific risks in tropical urban wetlands and highlight the need for more comprehensive water quality standards for PAHs.

Effective mitigation of PAH pollution in Caño La Malaria requires a watershed-scale management approach that integrates urban planning, regulatory oversight, and ecosystem-based solutions. In highly urbanized watersheds, persistent PAH contamination has been linked to vehicular emissions and stormwater runoff, which are also prominent sources in the Cucharillas Marsh area [81]. Nevertheless, despite improvements in water quality, legacy pollutants and diffuse PAH sources remain challenging to control without long-term strategies [100]. Among recommended strategies, nature-based solutions offer promising low-cost and sustainable alternatives [131]. Constructed wetlands have proven effective in attenuating PAHs through plant uptake, microbial

degradation, and sedimentation [39]. Complementary stormwater management strategies, such as bio-swales [132] and infiltration basins [133] can further reduce runoff-borne PAHs before they enter the aquatic system. When implemented as small ponds or detention features along tributaries or upstream stormwater channels draining into Caño La Malaria, these interventions could intercept runoff during high-intensity rainfall events and significantly mitigate PAH inputs to the canal.

Findings from Caño La Malaria reveal that partial compliance with existing benchmarks does not guarantee ecological safety, because observed concentrations indicate risks that current standards do not fully capture. Traditional PAH assessments that focus solely on parent PAHs may underestimate total toxicity in aquatic systems by excluding substituted derivatives, such as nitrated and oxygenated PAHs, which have been shown to occur at higher concentrations and exhibit greater toxicity than parent compounds [108]. Expanding the analytical scope to include these compounds, alongside applying updated classification systems for PAH contamination [119,134], would strengthen future monitoring efforts. In parallel with improved monitoring, management interventions should not be limited to isolated hotspots [135,136]. Instead, efforts should also prioritize upstream pollution controls [137], the restoration of riparian buffers [138], and enhancements to stormwater infrastructure [139]. Ensuring long-term resilience in Cucharillas Marsh will require comprehensive, integrated monitoring and watershed-scale actions—rather than hotspot-only interventions—to mitigate chronic PAH pollution and protect ecological and hydrological functions.

4.5. Ecological Risk Assessment

The ecological risk associated with NAP in Caño La Malaria was found to be negligible across all sampling sites and seasons, with HQ_{water} values ranging from 9.1×10^{-5} to 9.5×10^{-3}. These values fall below the 0.01 threshold for "insignificant risk" suggesting negligible acute ecological threat under current environmental conditions. Even the highest HQ_{water}—recorded at the upstream site during the wet season (September 2022)—remained within the insignificant risk range. These findings are consistent with assessments conducted in subtropical systems, where PAH-related risks increased during wet-season runoff events due to pollutant mobilization and elevated concentrations [76]. Similarly, in coastal environments like tidal creeks, hydrological pulses during wet periods facilitated contaminant transport and led to higher ecological risk values [74].

Although HQ_{water} values in Caño La Malaria were consistently low, a clear spatial gradient was observed, with higher values upstream than downstream. This pattern aligns with findings from other river systems, where elevated upstream ecological risks are attributed to limited dilution capacity and closer proximity to pollutant sources [83]. Similarly, PAH-related risks in urbanized tidal creeks influenced by industrial and domestic discharges underscore the role of human activities in amplifying contaminant exposure [74]. Upstream sectors of urban wetlands serve as key vulnerability hotspots, where targeted ecological monitoring and management efforts are needed [140]. The elevated HQ_{water} values observed at the upstream site correspond to the most urbanized section of the watershed, located in the upper reach of Caño La Malaria, where dense residential development and major roadway infrastructure are present.

In the context of each study's ERA framework, findings across wetlands and estuarine systems under strong urban and industrial influence indicate a consistent pattern. In Shadegan Wetland (Iran), the risk of PAHs in water was classified as moderate for several compounds, with benzo[a]anthracene (BaA) reaching high risk levels at most sites, while overall sediment risk was lower [95]. Similarly, in the Hoor Al-Azim wetland (Iran), the authors reported high risk for BaA in water but generally low to moderate risk for most other PAHs, while sediments indicated low biological risk [94]. In Anzali Wetland (Iran), sediments overall showed no harmful biological effects, although site-specific exceedances occurred for fluorene and pyrene, and several compounds, including NAP and ANT, were frequently above negligible-effect thresholds [93]. Consistent with our finding of insignificant acute risk for dissolved NAP, Edku Wetland (Egypt) showed no observed ecological hazard during spring [141]. By contrast, in estuarine systems, several PAHs, including

PHEN, pyrene, and fluorene, frequently exceeded ecological risk thresholds, with clear seasonal variability [142]. More recently, studies demonstrated that, even when PAH water risk was negligible [141], sediment-bound PAHs can pose major ecological hazards in areas with dense urban infrastructure [143]. These comparisons indicate that while Caño La Malaria is not pristine, its present surface-water PAH levels imply insignificant ecological risk ($HQ_{water} < 0.01$) that those reported for other impacted wetlands; nonetheless, future risk assessments should integrate sediments and biota for a complete evaluation.

The ecological implications are particularly relevant when considering vulnerable benthic species such as the blue crab (*Callinectes sapidus*), which serves as a key ecological indicator in Puerto Rico's coastal wetlands. The negligible HQ_{water} values obtained in this study, calculated using toxicity thresholds derived from *Callinectes sapidus*, studies confirm a low acute ecological risk under current PAH concentrations [76]. However, evidence indicates that this species bioaccumulates PAHs in its tissues under long-term exposure conditions—particularly during wet seasons—with PHEN and ANT showing persistence that suggests slow metabolic degradation [144]. Other studies found no physiological or molecular effects after short-term exposure to PAH-contaminated sediments, highlighting the importance of exposure duration and compartment in ecological risk assessment [145]. Although *Callinectes sapidus* does not biomagnify PAHs across trophic levels, it is known to bioaccumulate these compounds from sediments, porewater, and diet in estuarine environments, showing its role in shaping PAH bioavailability within aquatic food webs [146]. Additionally, comparative assessments in rivers have shown that crustaceans and mollusks often exhibit higher ecological risk than fish, reinforcing their importance in monitoring frameworks [147]. These findings reaffirm the utility of *Callinectes sapidus* as a sentinel species and highlight the need to consider long-term exposure, seasonal variability, and sediment-phase contamination in future assessments.

Despite the insights gained from this study, several limitations must be acknowledged to contextualize the ERA more accurately. The risk assessment was restricted to dissolved NAP and focused solely on acute toxicity endpoints. It did not account for sediment-associated PAHs, high molecular weight congeners, or sublethal and chronic toxic effects—factors which have been shown to elevate ecological risk in similar wetland systems [8,103]. However, LMW-PAHs can induce oxidative stress and endocrine disruption even at concentrations below acute toxicity benchmarks, particularly under chronic exposure scenarios [28,148]. Similarly, in estuarine studies, PAHs such as fluoranthene, pyrene, and BaA were major contributors to total ecological risk, particularly when sediment-phase concentrations were considered [142]. These limitations underscore the need for integrative ERA approaches in Caño La Malaria that incorporate multiple PAH compounds, additional environmental compartments, chronic toxicity endpoints, and cumulative exposure pathways to characterize long-term ecological threats more accurately.

5. Conclusions

This study provides a comprehensive assessment of 3 LMW-PAHs (NAP, PHEN, ANT) in surface waters of Caño La Malaria, a canalized waterbody within a tropical urban wetland in Puerto Rico. Results revealed seasonal variability, with higher concentrations during the wet season, reflecting the influence of rainfall-driven runoff on PAH mobilization across the urban environment. Spatial patterns suggested localized inputs near upstream segments followed by downstream attenuation through dilution, sedimentation, and sorption processes. While compositional analyses consistently pointed to pyrogenic sources—primarily vehicular emissions and biomass combustion. These findings align with observations from other tropical and subtropical systems; however, Σ3PAH concentrations in Caño La Malaria frequently exceeded those reported in comparable regions.

To further evaluate the ecological implications of these concentrations, a formal HQ_{water} analysis was conducted using the highest measured NAP levels and conservative LC_{50}-based PNEC values. All calculated HQ_{water} values were below 0.01, indicating "insignificant risk" for acute toxicity across all sites and seasons, even under peak wet season conditions. The highest HQ_{water} (0.0095), observed

at the upstream site in September 2022, approached the upper boundary of the "insignificant" category but did not cross the "low risk" range. These results suggest that, under current environmental conditions, acute ecological risk from dissolved NAP remains negligible. However, potential risk increase during wet season rainfall events. Nevertheless, the system's ecological integrity may still be vulnerable to long-term PAH accumulation—particularly under scenarios of land-use change, climate-induced hydrological shifts, and continued contaminant inputs.

Although the acute risk assessment classified the system as low risk, the frequent exceedance of international water quality benchmarks raises concern regarding potential sublethal and chronic effects. Long-term exposure to LMW-PAHs can lead to disruptions in physiological processes. Peak concentrations measured during the wet season placed Caño La Malaria within moderate to heavy pollution categories, even though only three PAH compounds were analyzed. NAP and PHEN regularly exceeded freshwater guideline values, while ANT occasionally neared guideline values for marine organisms. These exceeding values indicate a potential risk of long-term disruptions to the health and functioning of aquatic organisms. Collectively, these findings indicate that current benchmark values may underestimate site-specific risks in Caño La Malaria, and that expanded monitoring strategies—accounting for chronic exposure scenarios and the system's complex environmental dynamics—are needed.

From a management perspective, this study reinforces the urgency of adopting integrated, watershed-scale interventions. Nature-based solutions such as constructed wetlands, along with stormwater infrastructure upgrades—including green roofs, permeable pavements, and vegetated swales—and the restoration of riparian buffers, could serve as effective strategies to reduce PAH inputs. In addition, monitoring programs should expand to include the USEPA priority listed 16PAHs and derivatives, with special account for groundwater–surface water interactions and atmospheric deposition to capture the full PAH dynamics in the system. Also, active engagement with local communities and stakeholders is essential to ensure that mitigation efforts are inclusive and address environmental justice concerns.

Overall, the insights gained from Caño La Malaria highlight the complex relationship between hydrological processes, urban infrastructure, and pollutant dynamics in a tropical urban wetland system. This study reports the spatial and seasonal dynamics of three LMW-PAHs—NAP, PHEN, and ANT—in an understudied Caribbean urban wetland and provides a framework for assessing and managing PAH pollution in other systems with similar characteristics, facing comparable anthropogenic pressures worldwide.

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Abbreviations

The following abbreviations are used in this manuscript:

PAHs	polycyclic aromatic hydrocarbons
LMW-PAHs	low molecular weight polycyclic aromatic hydrocarbons
HMW-PAHs	high molecular weight polycyclic aromatic hydrocarbons
NAP	naphthalene
PHEN	phenanthrene
ANT	anthracene
BaA	benzo[a]anthracene
Σ3PAHs	sum of three low molecular weight PAHs (naphthalene, phenanthrene, anthracene)
DCM	dichloromethane
PCA	Principal Component Analysis
USEPA	United States Environmental Protection Agency
GC-MS	Gas Chromatography–Mass Spectrometry
ng/L	Nanograms per Liter
U	upstream
M	midstream
D	downstream
O	outlet
RSD	relative Standard Deviation
EU	European Union
ND	nondetected
ERA	ecological risk assessment
HQ	hazard quotient
EC_{water}	environmental concentration in water
$PNEC_{water}$	predicted no-effect concentration in water
$L(E)C_{50}$	lethal (or effect) concentration for 50% of organisms
AF	assessment factor

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