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Variation Concentrations in Polycyclic Aromatic Hydrocarbons in the Northern Part of Shatt Al-Arab River, Basrah, Iraq

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are long-lasting organic pollutants with serious environmental implications in aquatic ecosystems, notably the Shatt al-Arab River system that sustains millions of residents in southern Iraq. The north branch of this important waterway is under extreme environmental stresses of industry and oil activities, but fluctuation patterns of PAHs by seasons remain unknown. The samples of water were collected at five strategic stations (Al-Qurna, Al-Shafi, Al-Dair, Karma Ali, and Al-Zuraiji) along the northern Shatt al-Arab River during summer (June-August 2024) and winter (December 2024-February 2025) seasons. Two replicate samples were collected at each station for each season, totaling 20 samples. PAH was determined by gas chromatography-mass spectrometry (GC-MS) following UNEP methodology. In situ environmental parameters like water temperature and pH were measured. Statistical analysis included ANOVA, cluster analysis, and correlation analysis to examine spatial and temporal variation. The PAHs ranged from 2.24 to 11.28 ŋg/L, far higher in summer (mean 9.46 ŋg/L) than winter (mean 7.20 ŋg/L). The most dramatic finding was the extreme seasonal variability in PAH composition, with higher molecular weight PAHs (4+ rings) dominating summer samples (78.4% total PAHs) and lower molecular weight PAHs (2-3 rings) dominating winter samples (82.7%). This provided a 17-fold seasonal difference in the low molecular weight/high molecular weight (LMW/HMW) ratio (summer: 0.28; winter: 4.81). Statistical correlation revealed a strong negative correlation between water temperature and the ratio of LMW/HMW ($r = -0.88$, $p < 0.001$), indicating temperature as a dominant factor governing seasonal patterns of PAH composition. Spatial distribution of PAH concentration revealed hotspots at Karma Ali and Al-Shafi stations, close to industrial activities and oil installations. Diagnostic ratios revealed predominantly petrogenic sources in winter and mixed petrogenic-pyrogenic sources in summer. This study provides key baseline data on the seasonality of PAH composition variation for the Shatt al-Arab River system. The extreme seasonality of PAH composition, together with elevated summer levels of carcinogenic PAHs, suggest potential hazards to aquatic life and human health. The findings highlight the imperative need for seasonally specific monitoring protocols and focused pollution abatement measures for this ecologically and economically important water body.

INTRODUCTION

Shatt al-Arab River, formed by the confluence of the Euphrates and Tigris rivers at Qurna in lower southern Iraq, flows through approximately 204 km before discharging into the Arabian Gulf. It sustains an estimated 4-5 million residents who depend on it for drinking water, domestic use, agriculture, and industrial activities. Despite its ecological and economic importance, the Shatt al-Arab River faces severe environmental stresses, primarily from polycyclic aromatic hydrocarbon (PAH) pollution (Al-Ghadban et al., 1994; Al-Hejuje et al., 2015).

PAHs are a group of organic compounds containing two or more fused aromatic ring systems, which are further categorized into low molecular weight PAHs (LMW, 2-3 rings) and high molecular weight PAHs (HMW, 4+ rings). PAHs are of particular concern in aquatic environments because they are persistent, bio accumulative, and exhibit toxic, mutagenic, and carcinogenic properties. Several HMW PAHs, including benzo[a]pyrene, benz[a]anthracene, and chrysene, are listed as probable human carcinogens by the International Agency for Research on Cancer (Al-Hejuje et al., 2015; Al-Saad et al., 2015). Aquatic PAHs originate from various sources that are traditionally classified as either petrogenic (petroleum-related) or pyrogenic (combustion-related). Petrogenic sources include the oil spill, oil refinery effluent, and storage tank leakage in underground storage, which are typically characterized by the predominance of LMW PAHs. Pyrogenic sources, such as incomplete combustion of fossil fuels, biomass burning, and industrial emissions, typically produce elevated ratios of HMW PAHs. In the Shatt al-Arab region, the intensely concentrated field of oil fields, refineries, industry, and heavy shipping leads to a complex pollution scenario, where both source categories may be significant contributors to PAH pollution (Al-Imarah et al., 2017; Adipah, 2019).

The LMW/HMW ratio of PAHs is also a good discriminator between the two sources, with values greater than 1 usually suggesting petrogenic origins while values less than 1 suggesting pyrogenic origins. Diagnostic ratios such as phenanthrene/anthracene (Phe/Ant) and fluoranthene/pyrene (Flo/Pyr) can also be employed to suggest PAH sources (Farid et al., 2014; Abo-Turab et al., 2024). Temperature, along with other environmental factors, significantly affects the distribution, partitioning, and fate of PAHs in aquatic environments. Temperature controls the solubility of PAHs, volatilization rates, microbial biodegradation, and photochemistry. Temperature, thus, as well as other environmental factors, may regulate temporal variations in PAH levels and compositional patterns in riverine systems (Said, 2007; Fagbote and Olanipekun, 2013).

The northern section of the Shatt al-Arab is especially vulnerable to PAH pollution due to the heavy density of oil operations and its location at the source of the river, affecting all locations downstream of the river. Despite its importance, few scientific analyses of seasonal PAH variation within this section have been conducted. Most studies conducted in this area investigated other regions of the river or reviewed general water quality parameters without conducting an extensive investigation of PAHs.

The findings of this research will provide valuable information on seasonal PAH pollution patterns in the Shatt al-Arab River, establish baseline data for future monitoring programs, and inform the development of season-dependent pollution control measures to protect this important water resource.

This study aims to bridge these gaps in knowledge by investigating seasonal variations in PAH concentration and composition in the northern Shatt al-Arab River. Specific targets are: (1) quantitative estimation of the levels at five strategic sites between summer and winter; (2) identification of seasonal trends in PAH composition, with special emphasis on LMW/HMW ratio changes; (3) establishment of diagnostic ratios as indices for recognition of PAH sources; (4) quantitative estimation of associations between environmental components and spatial distributions of PAH; and (5) appraisal of potential ecological and health impacts of estimated concentrations of observed PAH.

2. MATERIALS AND METHODS

2.1 Study Area Description

The study was conducted in the northern segment of the Shatt al-Arab River, which is formed by the confluence of the Tigris and Euphrates rivers at Qurna in southern Iraq (Figure 1). The river course is approximately 204 km in length prior to its emptying into the Arabian Gulf, having a width of approximately 1 km near Basrah city, increasing to more than 2 km at the mouth (Mohamed et al., 2008).

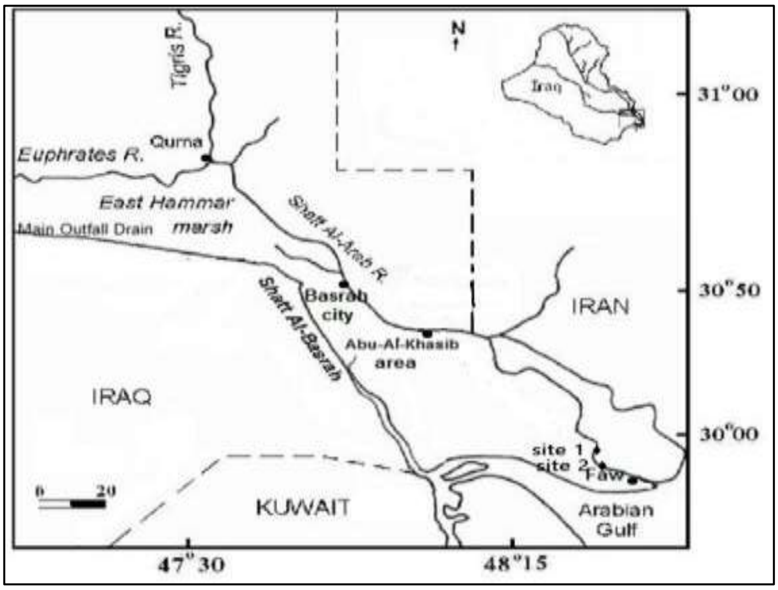

Fig. 1: Shatt al-Arab Map and its main tributaries (Mohamed et al., 2008).

The research area experiences a semi-tropical continental climate with dry and hot summers and wet and cold winters. The water temperature seasonal fluctuation from winter to summer varied between 15°C and over 40°C. The river comes under the influence of tidally controlled water from the Arabian Gulf, where the tidal cycle exceeds 24 hours, and produces cyclic fluctuations in water level and chemistry (Farid et al., 2014).

The surrounding landscape includes extensive agricultural fields supplied with river water, industrial and oil facilities that belong to the list of potential pollution sources, and urban agglomerations along the shores that form part of the complex anthropogenic pressures for this aquatic ecosystem (Abo-Turab et al., 2024).

2.2 Sampling Stations

Five sampling points were located in a strategic position on the northern bank of the Shatt al-Arab River to gather different environmental conditions and sources of PAHs (Figure 2):

- Al-Qurna Station: Located on the northern boundary of the study area, where the Tigris and Euphrates rivers meet. The station is a reference point for water quality before being affected by downstream sources of contamination, and is affected by the West Qurna oil field.
- Al-Shafi Station: Situated between Al-Qurna and Al-Dair, with a tributary network. The station is affected by an oil pipeline within the area and receives discharge from nearby residential and agricultural lands.
- Al-Dair Station: Situated within an intensive agricultural area with extensive farming along river banks. The station is near the Tank oil field and directly exposed to oil spills as a result of river shipping vessels.
- Karma Ali Station: Situated in the southern part of the study area, this station is directly impacted by industrial activities. It is strategically important with its proximity to oil export terminals and pumping stations, and under tidal influence from the Arabian Gulf.
- Al-Zuraiji Station: Located directly downstream of Karma Ali, this station is affected by three big industrial sources: a paper mill, the Hartha power plant that discharges heated water and pollutants, and the Majnoon oil field with secondary effects by drainage water.

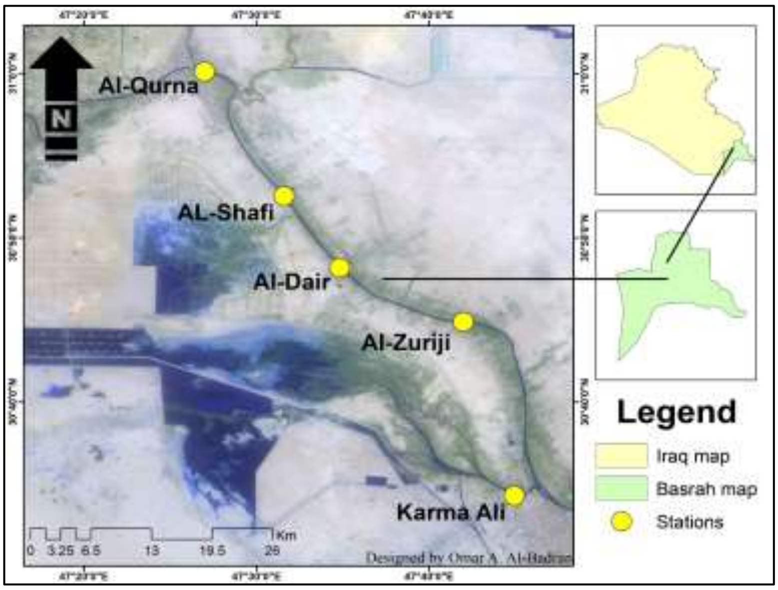

Fig. 2: Map of study locations.

The approximate distances between stations and their identifying features are presented in Table 1.

Table 1: Approximate distances between the five principal stations and their distinguishing features.

Station	Latitude & Longitude	Approximate Distance from Al-Qurna (km)	Key Characteristics
Al-Qurna	31.001639, 47.450056 (31°00'05.9"N 47°27'00.2"E)	0	Serves as a main collection point for water coming from northern areas, close to the West Qurna oil field
Al-Shafi	30.875707, 47.526504 (30°52'32.6"N 47°31'35.4"E)	About 15km	Affected by the system of water channels and oil pipeline, receives waste from surrounding residential and agricultural areas.
Al-Dair	30.802944, 47.580387 (30°48'10.6"N 47°34'49.4"E)	About 30 km	Intensive agricultural area, close to the Majnoon oil field, and exposed to oil leaks from river transportation means
Al-Zuraiji	30.571588, 47.749132 (30°34'17.7"N 47°44'56.9"E)	About 45 km	Exposed to three major industrial sources: the paper factory, the electricity station in Hartha, and the Nahr bin Umar oil field
Karma Ali	30.748067, 47.699877 (30°44'53.0"N 47°41'59.6"E)	About 60 km	Industrial and oil site, close to oil export ports and pumping stations, affected by tidal effects from the Arabian Gulf

2.3 Sampling Techniques and Frequency

Sampling was conducted from June 2024 to February 2025. Water sampling was conducted over a complete annual cycle, encompassing both summer (June-August 2024) and winter (December 2024-February 2025) seasons. Two sets of sampling events were conducted in each season in all five stations, totaling 20 samples (5 stations × 2 seasons × 2 replicates). The surface water was obtained from mid-river, 20-30 cm below the water surface, at low tide in pre-cleaned, dark glass bottles of 5-liter capacity. Samples were washed with sample water before filling the bottles, and sampling was carried out in a way that prevented air bubbles and sample contamination.

For PAH analysis, the samples were preserved by adding 15 mL of Chloroform. Preserved samples were transported to the laboratory in 4°C coolers. Each sample was labeled with sample number, location, date, type, added preservatives, collector's name, and special observations. Environmental conditions such as water temperature and pH were recorded in situ with a calibrated WTW multi-parameter probe.

2.4 Analytical Methods for PAH Detection

Analysis of petroleum hydrocarbons in water samples was conducted based on the methodology described by the United Nations Environment Program (UNEP, 1989) with appropriate modifications. The analytical procedure involved the following steps:

2.4.1 Extraction of PAHs

Four liters of each water sample were transferred into a clean beaker after washing with the sample water. Chloroform (15 mL for each 1 L of water) was added and shaken in an electric mixer for 20 minutes. The mixture was allowed to settle and then transferred into a separation funnel and left standing for 15 minutes to allow the layers to settle. The bottom part containing the PAHs was transferred to a clean beaker with an aluminum foil cover and left to air-dry at room temperature.

On drying, 5-10 mL of benzene was added to dissolve the sample with continuous stirring. The sample was then fractionated by filling a 20 cm glass column with glass wool, 8 g of silica gel (100-200 mesh), 4 g of alumina (Al_2O_3), and 4 g of anhydrous sodium sulfate (Na_2SO_4) at the top of the column.

2.4.2 Instrumental Analysis

The PAHs were analyzed and identified by using gas chromatography-mass spectrometry (GC-MS). The analysis was performed on an Agilent 7890B gas chromatograph equipped with an Agilent 5977A mass spectrometer. The column oven temperature program started at 40°C and was increased at a gradient of 10°C/min to 310°C. The injection temperature was set at 260°C with a split injection mode of 75:1. The flow control was maintained constant at a pressure of 7.0699 psi with a total flow of 79 mL/min, column flow of 1 mL/min, and purge flow of 3 mL/min. Operating conditions for the mass spectrometer were an ion source temperature of 250°C, a quadrupole temperature of 150°C, and an interface temperature of 283°C. Solvent cut time was 4.00 min, starting at 4.00 min, and ending between 35.00-40.00 min. Scan speed was 1562 (N_2) with the range of m/z 30-600.

PAHs were distinguished on the basis of retention time and mass spectrum with respect to authentic standards. The PAHs were quantified with the help of an internal standard technique involving deuterated PAHs as standards. The PAHs were split into low molecular weight (LMW, 2-3 rings) and high molecular weight (HMW, 4+ rings) fractions for analysis.

2.4.3 Quality Control and Assurance

Practices for quality control included frequent calibration of equipment with certified PAH standard solutions, procedural blank analysis, and certified reference material analysis. Duplicate analysis was also performed for approximately 10% of the samples, and recovery calculation was performed on spiked samples with a recovery percentage within 90-110%. Method detection limits for individual PAHs ranged from 0.001 to 0.005 ŋg/L. Comprehensive analytical validation parameters of the GC-MS technique are shown in Table 2*,* thus ensuring the suitability of the technique for PAH determination in environmental water

Table 2: GC-MS Analytical Validation Parameters.

Parameter	Value/Range
Detection limits (individual PAHs)	0.001-0.005 ng/L
Recovery percentages (spiked samples)	90-110%

Calibration curve coefficient (R^2)	≥ 0.90
Relative standard deviation	$\leq 10\%$
Method precision (duplicate analysis)	$<15\%$
Blank contamination	$<5\%$ of detection limit

2.5 Identification of PAH Source

In a way to recognize the potential PAH source(s), the following diagnostic ratios were calculated (Hong et al., 2008):

- LMW/HMW ratio: This is the comparison of low molecular weight PAHs (2-3 rings) with high molecular weight PAHs (4+ rings). Ratios > 1 typically indicate petrogenic (petroleum) sources, while ratios < 1 indicate pyrogenic (combustion) sources.
- Phenanthrene/Anthracene ratio (Phe/Ant): Values > 10 indicate petrogenic sources, while values < 10 indicate pyrogenic sources. Fluoranthene/Pyrene ratio (Flo/Pyr): Values < 1 are typically characteristic of petrogenic sources, while values > 1 suggest pyrogenic inputs.

2.6 Statistical Analysis

Statistical analysis was done with Minitab statistical software version 18. Descriptive statistics (minimum, maximum, standard deviation, and mean) were calculated to describe PAH concentration data. One-way Analysis of Variance (ANOVA) was used to test significant differences in PAH concentrations among sampling stations and seasons at a significance level of $p \leq 0.05$, and followed by Least Significant Difference (LSD) post-hoc tests where necessary. Pearson correlation coefficients were applied to identify correlations among PAH concentrations, composition patterns (the LMW/HMW ratio in specific), and environmental factors (temperature, pH and total dissolved solids). Hierarchical cluster analysis was performed to classify sampling stations by pattern similarity of PAH contamination.

To ensure the quality of statistical analysis, certain parameters were checked, including regression coefficient of variation (CV) $\leq 15\%$, regression coefficient of determination (R^2) ≥ 0.90, and relative standard deviation $\leq 10\%$.

Data were normalized using z-score transformation before cluster analysis to avoid scale bias. The z-score normalization was calculated using the formula $z = (x - \mu)/\sigma$, with x being an individual PAH concentration value, μ being the mean concentration, and σ being the standard deviation. This normalization ensures that all PAH compounds contribute equally to the clustering process regardless of their difference in concentration magnitude.

3. RESULTS

3.1 Physicochemical Parameters

3.1.1 Water Temperature

Water temperature varied significantly between summer and winter months at all sampling sites. Summer temperatures varied from 30.5°C at Al-Qurna to 31.2°C at Al-Zuraiji, with a mean of 30.9°C. Winters varied from 15.1°C at Al-Qurna to 16.2°C at Al-Zuraiji with a mean of 15.7°C. This explains a seasonal variation of approximately 15.2°C, or 97% higher in summer than in winter.

A highly minimal incremental increase in water temperature was observed from the most northern station (Al-Qurna) to the most southern station (Al-Zuraiji) during both seasons. The increment from Al-Qurna to Al-Zuraiji was approximately 2.3% during summer and 7.3% during winter. The average annual temperature across all stations was 23.3°C.

3.1.2 PH Values

The pH values of Shatt al-Arab waters ranged from 7.6 to 8.3, indicating slightly alkaline conditions. Winter pH values (mean 8.1) were greater than those of summer (mean 7.8), i.e., by a difference of ca. 3.8%. A gradual increase in pH was observed from Al-Qurna to Al-Zuraiji in both seasons, the increase being by 5.3% in summer and 5.1% in winter. The mean pH value for the year at all stations was 7.95.

3.2 Aromatic Hydrocarbons

3.2.1 Summer Distribution

Summer concentrations of aromatic hydrocarbons varied considerably among the sampling stations (Table 3). Al-Shafi had the highest concentration (11.28 ŋg/L, 23.8% of total), followed by Al-Qurna (10.13 ŋg/L, 21.4%), Al-Dair (9.91 ŋg/L, 20.9%), Al-Zuraiji (8.26 ŋg/L, 17.5%), and Karma Ali (7.73 ŋg/L, 16.3%).

Table 3: Mean concentrations of aromatic hydrocarbons (ŋg/L) in Shatt al-Arab waters in summer season.

Compound	Al-Qurna	Al-Shafi	Al-Dair	Karma Ali	Al-Zuraiji	Total
Naphthalene	0.20	0.94	0.93	0.61	0.71	3.39
Naphthalene, 2-methyl-	0.16	0.41	0.34	0.22	0.35	1.48
Naphthalene, 1-methyl-	0.14	0.28	0.25	0.17	0.25	1.09
Acenaphthylene	0.06	0.01	0.02	0.01	0.01	0.11
Acenaphthene	0.33	0.19	0.17	0.09	0.14	0.92
Fluorene	0.22	0.21	0.18	0.08	0.13	0.82
Phenanthrene	0.61	0.57	0.48	0.18	0.38	2.22
Anthracene	0.10	0.03	0.03	0.02	0.02	0.20
Fluoranthene	0.44	0.26	0.16	0.07	0.07	1.00
Pyrene	0.63	0.55	0.28	0.14	0.11	1.71
Benz[a]anthracene	1.60	1.65	1.38	1.12	0.98	6.73
Chrysene	1.76	1.87	1.60	1.34	1.22	7.79
Benzo[b]fluoranthene	0.87	0.97	0.91	0.82	0.84	4.41
Benzo[k]fluoranthene	0.95	1.07	1.02	0.94	0.92	4.90
Benzo[a]pyrene	0.84	0.97	0.87	0.72	0.74	4.14
Indeno[1,2,3-cd] pyrene	0.34	0.41	0.39	0.35	0.38	1.87
Dibenz[a,h]anthracene	0.39	0.42	0.41	0.40	0.45	2.07
Benzo[ghi]perylene	0.49	0.47	0.49	0.45	0.56	2.46
Total	10.13	11.28	9.91	7.73	8.26	47.31
LMW PAHs (2-3 rings)	1.82	2.64	2.40	1.36	1.99	10.21
HMW PAHs (4+ rings)	8.31	8.64	7.51	6.37	6.27	37.10
LMW\HMW	0.22	0.31	0.32	0.21	0.32	0.28
Phe/Ant	6.10	19.00	16.00	9.00	19.00	11.10
Flo/Pyr	0.70	0.47	0.57	0.50	0.64	0.58

The dominant individual constituents were Benz[a]anthracene (14.2% of total), Chrysene (16.5%), Benzo[k]fluoranthene (10.4%), and Benzo[b]fluoranthene (9.3%).

3.2.2 Winter Distribution

Winter concentrations of aromatic hydrocarbons also varied among stations (Table *4*). The concentration was highest in Al-Shafi (10.42 ŋg/L, 29.0% of the total), followed by Karma Ali (9.29 ŋg/L, 25.8%), Al-Qurna (8.84 ŋg/L, 24.6%), Al-Dair (5.19 ŋg/L, 14.4%), and Al-Zuraiji (2.24 ŋg/L, 6.2%).

Table 4: Average aromatic hydrocarbons concentrations (ŋg/L) in Shatt al-Arab waters during winter season.

Compound	Al-Qurna	Al-Shafi	Al-Dair	Karma Ali	Al-Zuraiji	Total
Naphthalene	1.98	0.85	0.02	3.41	0.58	6.84
Naphthalene, 2-methyl-	1.12	1.13	0.34	1.94	0.18	4.71
Naphthalene, 1-methyl-	0.87	0.87	0.32	1.39	0.12	3.57
Acenaphthylene	0.07	0.04	0.01	0.02	0.003	0.14
Acenaphthene	0.29	0.91	0.77	0.81	0.12	2.90
Fluorene	0.44	0.81	0.65	0.63	0.11	2.64
Phenanthrene	1.98	2.50	2.19	1.88	0.35	8.90
Anthracene	0.09	0.00	0.00	0.00	0.01	0.10
Fluoranthene	0.40	0.42	0.25	0.25	0.06	1.38
Pyrene	0.34	0.81	0.16	0.24	0.06	1.61
Benz[a]anthracene	0.58	0.68	0.16	0.08	0.11	1.61
Chrysene	0.68	0.55	0.17	0.14	0.08	1.62
Benzo[b]fluoranthene	0.00	0.51	0.03	0.23	0.19	0.96
Benzo[k]fluoranthene	0.00	0.29	0.05	0.09	0.07	0.50
Benzo[a]pyrene	0.00	0.05	0.07	0.08	0.06	0.26
Indeno [1,2,3cd] pyrene	0.00	0.00	0.00	0.00	0.03	0.03
Dibenz [a, h] anthracene	0.00	0.00	0.00	0.00	0.05	0.05
Benzo[ghi]perylene	0.00	0.00	0.00	0.00	0.07	0.07
Total	8.84	10.42	5.19	9.29	2.24	35.99
LMW (2-3 rings)	6.84	7.11	4.30	8.08	1.47	29.80
HMW (4+ rings)	2.00	3.31	0.89	1.21	0.77	6.19
LPAHs/HPAHs	3.42	2.15	4.83	6.68	1.91	4.81
Phe/Ant	22.00	-	-	-	35.00	28.50
Flo/Pyr	1.18	0.52	1.56	1.04	1.00	0.86

The principal individual compounds were Phenanthrene (24.7% of the total), Naphthalene (19.0%), Naphthalene, 2-methyl- (13.1%), and Naphthalene, 1-methyl- (9.9%).

3.2.3 PAH Ring Distribution

A distinct seasonal pattern was observed in PAH abundance based on ring number. In summer, high molecular weight PAHs (4 or more rings) dominated at 78.4% of the aromatic hydrocarbons, while low molecular weight PAHs (2-3 rings) accounted for only 21.6%. This trend was completely reversed in winter, when low molecular weight PAHs predominated 82.7% and high molecular weight PAHs only accounted for 17.3%. Figure 3 illustrates this extreme seasonality, where summer ratios are always less than 1 than winter.

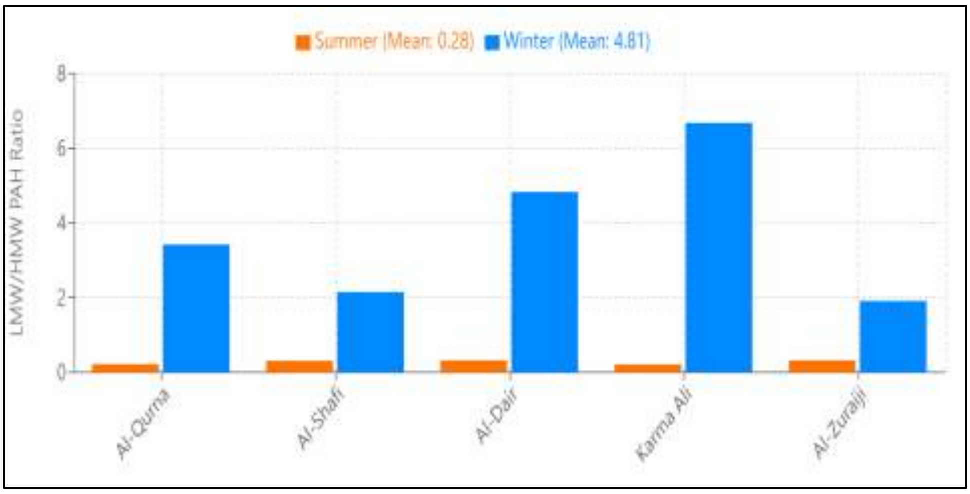

Fig. 3: Seasonal variation of LMW/HMW PAH ratios at sampling points in the Shatt al-Arab River.

Statistical modeling revealed a highly significant negative correlation between temperature and the LMW/HMW ratio ($r = -0.88$, $p < 0.001$), indicating that temperature is the primary reason for seasonal PAH compositional change. This correlation explains the drastic shift from HMW PAH dominance in summer (high temperature) to LMW PAH dominance in winter (low temperature). The most obvious seasonal fluctuation is that in the LMW/HMW PAH ratio distribution at all stations. The ratio is a very significant indicator of PAH source and transport direction. The single PAH compound analysis also illustrates the dramatic seasonal variation in PAH composition. Figure 4 presents the dominant PAH compounds of summer and winter samples. In summer, the high molecular weight PAHs with 4-6 rings dominated, particularly Chrysene (16.5%), Benz[a]anthracene (14.2%), and Benzo[k]fluoranthene (10.4%). Winter samples were characterized by low molecular weight PAHs with 2-3 rings, i.e., Phenanthrene (24.7%), Naphthalene (19.0%), and methylated naphthalene (23.0% in total). This seasonally varying composition of PAH reflects inherently different sources or transport patterns in seasons.

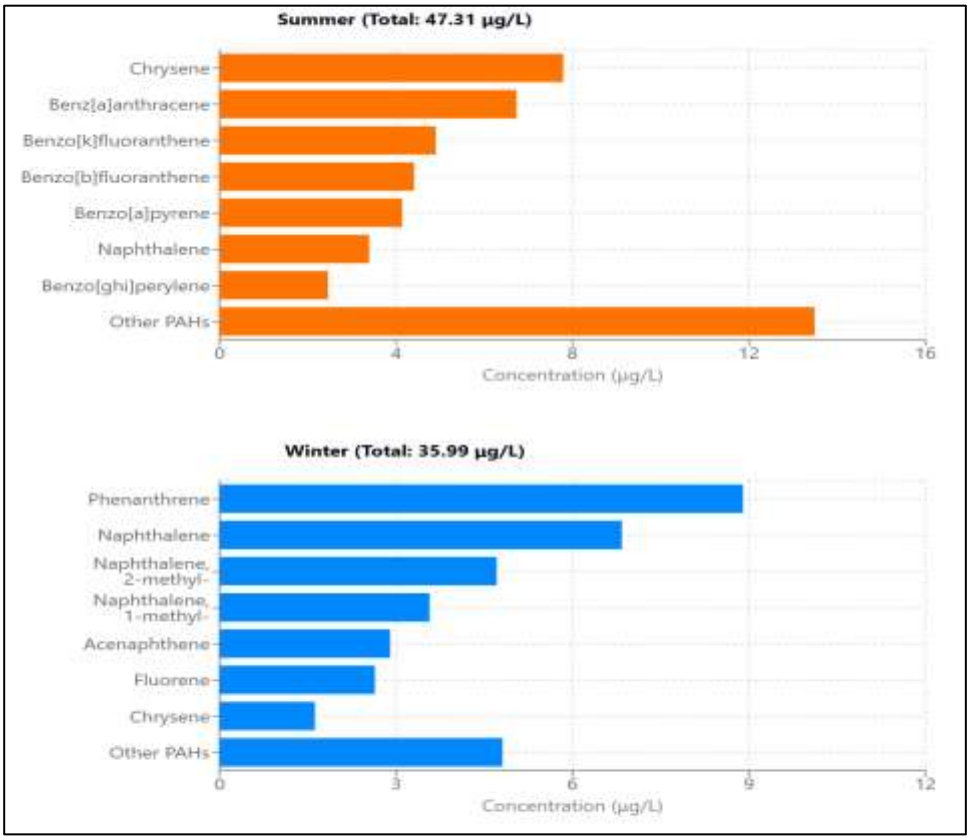

Fig. 4: Dominant PAH compounds in the Shatt al-Arab River during summer and winter seasons.

The personal distribution of PAHs by ring number is presented in Table 5.

Table *5*: Aromatic hydrocarbons distribution based on ring number (% total), summer and winter months.

Ring Number	Summer	Winter	Mean
2 rings	12.6	42.0	27.3
3 rings	9.0	40.7	24.9
4 rings	36.3	15.3	25.8
5+ rings	42.1	2.0	22.1
Total	100.0	100.0	100.0
LPAHs (2-3 rings)	21.6	82.7	52.2
HPAHs (4+ rings)	78.4	17.3	47.8

3.5 Indicators of Aromatic Sources

Diagnostic ratios were also used to establish the sources of aromatic hydrocarbons:

Phenanthrene/Anthracene Ratio (Phe/Ant): During summer, Phe/Ant values ranged from 6.10 to 19.00 (mean 11.10). In Al-Shafi, Al-Dair, and Al-Zuraiji stations, values were greater than 10, indicating petrogenic sources, while Al-Qurna and Karma Ali had values less than 10, indicating pyrogenic sources. During winter, Phe/Ant values were found only in Al-Qurna and Al-Zuraiji stations (22.00 and 35.00, respectively), both indicating petrogenic sources. **Fluoranthene/Pyrene Ratio (Flo/Pyr):** During summer, at all the stations, Flo/Pyr values were less than 1 (mean 0.58) with petrogenic sources. During winter, most of the stations had values greater than 1 (mean 0.86), indicating more input from pyrogenic sources. **LMW/HMW Ratio:** Summer ratio was less than 1 for all stations (average 0.28) and indicates a pyrogenic source. Winter ratio was greater than 1 for all stations (average 4.81) and indicates petrogenic inputs. Integrated analysis of numerous diagnostic ratios provides more comprehensive information regarding sources of PAHs in the Shatt al-Arab River. Figure 5 represents PAH source apportionment through a cross-plot of Phe/Ant and Flo/Pyr ratios. According to established criteria, Phe/Ant ratios greater than 10 typically indicate petrogenic sources, and Flo/Pyr ratios greater than 1 pyrogenic source.

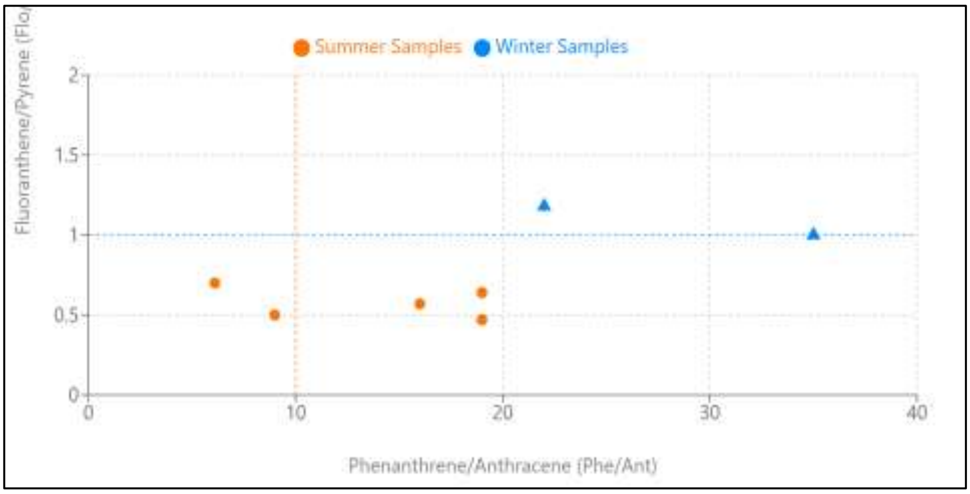

Fig. 5: Diagnostics ratios for PAH source apportionment in Shatt al-Arab River.

3.6 Statistical Analysis

3.6.1 Correlation Analysis

The Pearson correlation coefficients were calculated to identify correlations between the environmental parameters and hydrocarbon contents (Table 6).

Table 6: Correlation coefficients between measured variables in Shatt al-Arab waters.

Variable	Temperature	PH	TDS	Aromatic Hydrocarbons
Temperature	1.00	-0.52*	0.45*	0.62**
pH	-0.52*	1.00	0.33	-0.40
TDS	0.45*	0.33	1.00	0.12
Aromatic Hydrocarbons	0.62**	-0.40	0.12	1.00

*Significant at $p \leq 0.05$, **Significant at $p \leq 0.01$.

Temperature was positively and significantly correlated with concentrations of aromatic hydrocarbons ($r = 0.62$, $p \leq 0.01$), revealing that higher temperatures coincided with higher aromatic hydrocarbon concentrations. Such a relation is crucial in explaining PAH composition variations in different seasons. Temperature was significantly positively correlated with TDS ($r = 0.45$, $p \leq 0.05$) and significantly negatively correlated with pH ($r = -0.52$, $p \leq 0.05$), i.e., with rising temperature, TDS rose and pH fell.

3.6.2 Cluster Analysis

Hierarchical cluster analysis was performed for the grouping of sampling stations based on the degree of PAH contamination. Two significant clusters were derived from the results:

Cluster 1: This cluster consisted of Al-Shafi and Karma Ali stations, which are characterized by high PAH pollution levels. The mean concentration of aromatic hydrocarbons in this cluster was 9.68 ŋg/L (57.7% of the total concentration in all the stations). These stations showed the highest seasonal variation in LMW/HMW ratios.

Cluster 2: Includes Al-Qurna, Al-Dair, and Al-Zuraiji stations, which are relatively less contaminated with PAH. The mean concentration of aromatic hydrocarbons in this cluster was 7.10 ŋg/L (42.3% of total). The clustering illustrates the effect of human activity on PAH distribution, with Cluster 1 stations under the more direct influence of industrial and oil activities, while Cluster 2 stations are under the influence of less intense and more variable pollution sources.

3.6.3 Analysis of Variance

One-way ANOVA was used to examine significant differences in PAH concentration among sampling locations and seasons (Table 7).

Table 7: One-way ANOVA results for aromatic hydrocarbon concentrations by stations and seasons.

Source of Variation	Sum of Squares	df	Mean Square	F value	Significance
Between Stations	36.55	4	9.14	5.86	0.006**
Between Seasons	51.48	1	51.48	19.64	0.001**

**Significant at $p \leq 0.01$.

Wide variability was evident for aromatic hydrocarbon concentrations among stations of sampling ($p \leq 0.01$), which represents spatial heterogeneity in PAH contamination. Considerable seasonal variability was evident in aromatic hydrocarbons ($p \leq 0.01$), where summer had higher total PAH composition but highly distinct composition profiles concerning winter.

Post-hoc Least Significant Difference (LSD) tests revealed that Al-Shafi significantly differed from all the other stations, and Al-Zuraiji significantly differed from all the other stations for aromatic hydrocarbons.

3.6.4 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was used to supplement diagnostic ratios and to provide multivariate source apportionment of PAHs. Three principal components were derived that accounted for 78% of variance in PAH data.
Component 1 (42% of variance) was characterized by heavy molecular weight PAHs (Chrysene, Benz[a]anthracene, Benzo[k]fluoranthene), which indicates pyrogenic combustion sources. Component 2 (23% of variance) was indicated by light molecular weight PAHs (Naphthalene, Phenanthrene, Fluorene), which indicates petrogenic petroleum sources. Component 3 (13% of variance) had mixed molecular weight compounds, indicative of weathered petroleum products or mixed source inputs.

The PCA analysis confirms the diagnostic ratio evidence for mixed petrogenic and pyrogenic sources with alternating seasonal dominance modes for the two groups of sources. This multivariate method provides more quantitative source identification than application of arbitrary ratio-type methods.

4. DISCUSSION

The PAH concentrations measured in the Shatt al-Arab River demonstrated significant seasonal and spatial patterns with significant implications for interpreting pollution sources and processes. A significant positive correlation between water temperature and total PAH content ($r = 0.62$, $p \leq 0.01$) was observed, with summer (mean 9.46 ŋg/L) recording higher concentrations than winter (mean 7.20 ŋg/L). This temperature-dependent seasonal variation can be attributed to several temperature-dependent processes governing PAH behavior in aquatic environments. Higher temperatures increase the aqueous solubility of aromatic hydrocarbons, accelerate photodegradation rates, and enhance the activity of hydrocarbon-degrading microorganisms, which are typically most active at 20-35°C.

The most striking observation of this study was the drastic seasonal variation in PAH composition. High molecular weight PAHs (4+ rings) dominated in summer (78.4% of the total PAHs), and low molecular weight PAHs (2-3 rings) dominated in winter (82.7%). This resulted in a remarkable 17-fold seasonality in the LMW/HMW ratio (summer mean: 0.28; winter mean: 4.81). Such intense seasonality points to fundamentally different pollution sources or transport mechanisms between seasons. The significant negative correlation between the ratio LMW/HMW and water temperature ($r = -0.88$, $p < 0.001$) supports this association and indicates that temperature is a primary driver of PAH composition patterns in this river system.

Spatially, the trend of PAH pollution varied between sampling locations. Cluster analysis identified two groups: Cluster 1 (Al-Shafi and Karma Ali) with high concentrations of PAH pollution (mean 9.68 ŋg/L, 57.7% of total), and Cluster 2 (Al-Qurna, Al-Dair, and Al-Zuraiji) with relatively low concentrations (mean 7.10 ŋg/L, 42.3% of total). This spatial distribution reflects the influence of anthropogenic activity, where Cluster 1 stations cluster around oil export terminals, industrial areas, and urban centers, while Cluster 2 stations exhibit less intense industrial influences.

The total PAH concentrations in this study (ranging from 2.24 to 11.28 ŋg/L between stations and seasons) are of concern from ecological and human health perspectives. Some of the major PAHs detected, particularly the HMW compounds, which are rich in summer (Chrysene, Benz[a]anthracene, Benzo[k]fluoranthene, and Benzo[a]pyrene), are known carcinogens with bioaccumulation capacity in aquatic organisms. The seasonal change of PAH composition also implies various toxicological concerns, as different PAH compounds have different modes of toxic action and potencies. Table *8* shows comparison of PAH concentrations and LMW/HMW ratios in the current study with previous studies.

Other studies in Iraqi rivers have also recorded similar seasonal fluctuations. Al-Hejuje et al. (2015) recorded similar PAH levels in Shatt al-Arab, corroborating our results. Our LMW/HMW ratios, however, exhibit more erratic seasonal fluctuation than in studies by Al-Imarah et al. (2017) in southern parts.

Table 8: Comparison of PAH Concentrations with Previous Studies.

Study Area	**Total PAHs (ŋg/L)**	**LMW/HMW Ratio**	**Season**	**Source**
Northern Shatt al-Arab (Iraq)	9.46	0.28	Summer	Current study
Northern Shatt al-Arab (Iraq)	7.20	4.81	Winter	Current study
Shatt al-Arab (Iraq)	6.85 - 12.40	0.35 - 1.25	Annual	Al-Hejuje et al. (2015)
Southern Shatt al-Arab (Iraq)	4.25 - 8.72	1.46 - 2.34	Annual	Al-Imarah et al. (2017)
Euphrates River (Iraq)	3.56 - 5.98	2.15 - 3.40	Annual	Farid (2016)
Tigris River (Iraq)	2.85 - 6.12	1.95 - 3.85	Annual	Al-Saad et al. (2016)
Yangtze River (China)	0.42 - 1.35	0.85 - 1.73	Summer	Niu et al. (2017)
Yangtze River (China)	0.31 - 0.89	3.25 - 4.12	Winter	Niu et al. (2017)
Seine River (France)	0.05 - 0.27	0.62 - 1.15	Annual	Lorgeoux et al. (2016)
Yellow River (China)	0.18 - 0.67	2.45 - 3.87	Annual	Wang et al. (2011)
Pearl River Delta (China)	0.12 - 0.39	1.85 - 4.35	Annual	Wang et al. (2007)
Mediterranean Sea (Egypt)	0.08 - 0.23	1.26 - 2.41	Annual	Said (2007)
Arabian Gulf (Kuwait)	0.05 - 0.18	2.15 - 3.89	Annual	Al-Ghadban et al. (1994)

5. CONCLUSIONS

Large seasonal variations in PAH contamination occurred in the northern Shatt al-Arab River. Summer concentrations were larger than winter concentrations. Large seasonal variations in PAH composition occurred, with high molecular weight PAHs dominating summer samples and low molecular weight PAHs dominating winter samples. Spatial analysis identified hotspots of contamination related to industrial activity. Environmental conditions, particularly temperature, governed PAH patterns of distribution.

It is advisable to enhance industrial treatment facilities, emphasizing the control of high molecular weight polycyclic aromatic hydrocarbons (HMW PAHs) during the summer months and the regular monitoring of seasonal PAH patterns; and (3) to create comprehensive management frameworks that account for seasonal shifts in PAH levels induced by temperature changes. Additionally, further research should encompass the bioaccumulation of PAHs in aquatic organisms, the ecotoxicological effects resulting from summer variations in PAH concentrations, and the implications of global climate change on the behavior of PAHs within this crucial aquatic system.

Study Limitations

- Sparse temporal replication (two samples each season per site) and lack of alkylated PAH analysis, which could yield stronger source identification. Further, the emphasis on dissolved PAHs alone without regard to particulate-bound fractions would underreport total PAH loads. Future studies would do better to incorporate more intensive sampling, full PAH analysis encompassing alkylated species, and analysis of both dissolved and particulate phases to improve source apportionment certainty.

- The absence of hydrodynamic data such as river flow direction, discharge rates, and tidal or tributary influences. These factors can significantly affect the transport, dispersion, and deposition of PAHs in aquatic environments. While our study focused on spatial and seasonal variations in PAH concentrations, future research should incorporate hydrological modeling or flow measurements to better understand the mechanisms driving pollutant distribution and hotspot formation.
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