The University of Tehran Press

Pollution

https://jpoll.ut.ac.ir/

Print ISSN: 2383-451X
Online ISSN: 2383-4501

Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Seawater of the Gulf of Tobruk, Libya: Concentrations, Sources, and Environmental Risks

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Article Info

Article type:
Research Article

Article history:
Received: 17 July 2025
Revised: 12 November 2025
Accepted: 10 February 2026

Keywords:
Ecological risk
Diagnostic ratios
Principal component Analysis (PCA)
Pollution

ABSTRACT

There is limited data on the levels of polycyclic aromatic hydrocarbons (PAHs) in the waters of the Gulf of Tobruk, Libya. This study aims to establish a monitoring system to assess PAH concentrations, sources, and ecological risks in the region. Water samples were collected from seven sites during summer and winter. The concentrations of 16 PAHs ranged from 62.33 to 454.70 ng/L (Mean: 235.23 ± 152.37 ng/L) in summer and from 79.26 to 473.36 ng/L (Mean: 253.85 ± 151.49 ng/L) in winter, indicating high levels of pollution. Seasonal variations suggest lower PAH concentrations in summer due to differences in industrial activities, urban runoff, and hydrodynamic conditions. PAH diagnostic ratios and principal component analysis (PCA) revealed mixed petrogenic and pyrogenic sources. Tobruk Bay is under high ecological stress from PAH contamination. The ecological risk assessment classified the Gulf of Tobruk as a medium to high-risk area, posing potential harm to aquatic organisms. These findings underscore the need for long-term monitoring and pollution control strategies.

Cite this article: Okbah, M., El-Gammal, M., Bahnasawi, M., & Balal, B. (2026). Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Seawater of the Gulf of Tobruk, Libya: Concentrations, Sources, and Environmental Risks. *Pollution*, 12(1), 275-287.
https://doi.org/10.22059/poll.2025.398762.3029

DOI: https://doi.org/10.22059/poll.2025.398762.3029

INTRODUCTION

Populations near polluted water bodies, such as the Gulf of Tobruk, face health risks from consuming contaminated seafood. Polycyclic aromatic hydrocarbons (PAHs) are highly toxic pollutants with significant ecological and human health risks (Honda & Suzuki, 2020). PAHs accumulate in marine organisms, posing significant ecological and health risks, especially carcinogenic PAHs like benzo[a]pyrene. PAHs produce reactive oxygen species (ROS), causing oxidative stress and impairing vital behaviors in marine organisms. Due to their toxicity and bioaccumulation potential, PAHs present a major environmental challenge (Wei et al., 2022). Many countries have strict regulations to monitor and control PAH contamination in water, soil, and food (Han et al., 2019; Uddin & Xu, 2024). PAHs are widespread organic pollutants (Lee et al., 2021; Ambade & Sethi, 2021), and their long-term environmental presence is a growing

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concern (Zhang et al., 2020). PAHs, such as benzo[a]pyrene, are carcinogenic, posing health risks to wildlife and humans (Sosa et al., 2017).

Human activities, such as incomplete fuel combustion, oil spills, and vehicular emissions, contribute significantly to PAH contamination (Wang et al., 2021). The U.S. Environmental Protection Agency (USEPA) has grouped 16 PAHs as priority pollutants (Lamichhane et al., 2016). PAH contamination in aquatic ecosystems is concerning due to its high toxicity to marine life and potential carcinogenic effects on humans through seafood consumption (Fleming et al., 2006). Research has focused on the sources, distribution, transport, and fate of PAHs in aquatic environments (Jiang et al., 2022; Min et al., 2022).

Water pollution by PAHs is a global concern due to industrial and agricultural activities (Wang et al., 2019). Several studies have examined PAH concentrations and sources in Mediterranean waters (Zaghden et al., 2022; Pelin & Türetken, 2023). The Gulf of Tobruk, an economic hub, faces increasing pollution due to rapid urbanization and industrial growth. Coastal communities discharge untreated sewage, and industries release wastewater containing PAHs and heavy metals. This has degraded water quality, causing oxygen depletion, harmful algal blooms, and biodiversity loss. Ongoing wastewater discharge threatens the Gulf's long-term environmental health (Said et al., 2023).

Study objectives: This study aims to establish a monitoring system for polycyclic aromatic hydrocarbons (PAHs) in the waters of the Gulf of Tobruk. Specific objectives: 1- Evaluate PAH concentrations seasonally (summer vs. winter). 2- Identify PAH sources using diagnostic ratios and principal component analysis (PCA). 3- Assessing environmental and health risks using TEF, TEQ, and RQ methods.

The research will help policymakers design and implement more effective environmental regulations, prioritize intervention strategies, and allocate resources efficiently. The findings will provide valuable insights into pollution control measures, potentially leading to improved water quality, public health, and ecosystem sustainability in Gulf of Tobruk.

MATERIALS AND METHODS

Study Area and Sampling Design: This study was conducted in the Gulf of Tobruk, Libya, southeast of Tobruk city. The gulf spans approximately 5 km in length and narrows from 2 km at its entrance to 0.6 km inland (Figure 1), with depths ranging from 5 to 16 m. Sampling stations were selected to represent industrial discharge zones, municipal wastewater outlets and port activities sites (Table S1) (Said et al., 2023). This region is economically significant, hosting both commercial and fishing ports, yet faces escalating pollution from untreated domestic and industrial effluents. These inputs introduce various pollutants, notably polycyclic aromatic hydrocarbons (PAHs), leading to ecosystem stress such as hypoxia, algal blooms, and biodiversity loss.

Reagents and Equipment

Reagents were analytical grade, and standard PAH solutions and silica gel were used for cleanup and moisture removal. Ultrapure Milli-Q water (18.2 MΩ) was used to prevent ionic or organic contamination. Glassware was decontaminated by ultrasonic cleaning and solvent rinsing (acetone and hexane) to avoid interference.

Sample Collection and Preparation

Surface seawater samples (2 L) were collected seasonally (summer 2023 and winter 2024) from seven sites using Niskin samplers and amber glass bottles (Figure 1 & Table S1). Sampling was performed at 0–20 cm depth. Samples were transported at 4°C and filtered through pre-combusted Whatman GF/C filters (1.2 μm) prior to extraction. PAHs were extracted via liquid-

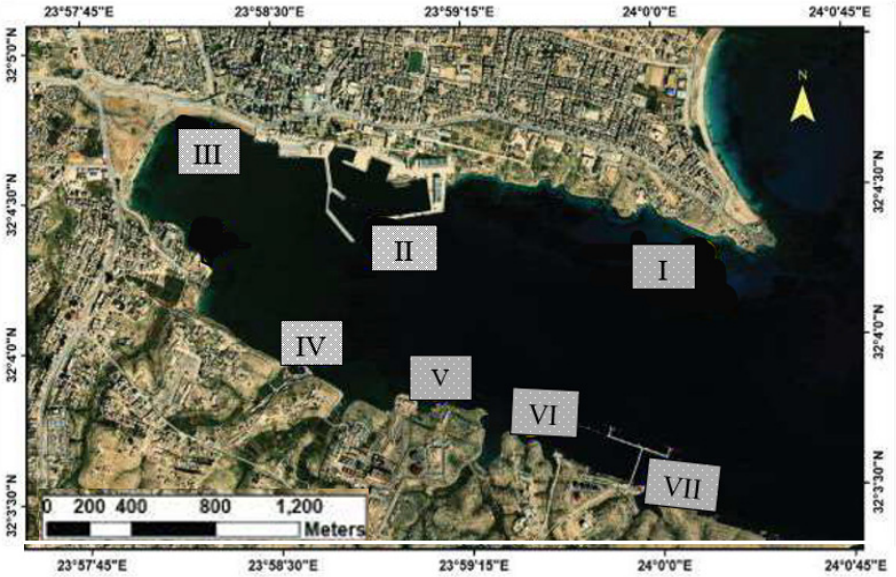

Fig. 1. Sampling sites in the Gulf of Tobruk, Libya

liquid extraction using hexane and dichloromethane (1:1 v/v), following established protocols (Okoli et al., 2011). PAHs were quantified using gas chromatography–mass spectrometry (GC-MS) (Agilent 7820A GC coupled with 5977A MS) operated in selective ion monitoring (SIM) mode, as per EPA Method 8270 (USEPA, 2010). The column used was HP-5ms (30 m × 0.25 mm × 0.25 µm), with helium as the carrier gas (1.5 mL/min). Oven temperature was programmed from 50°C to 290°C, optimizing separation of low and high molecular weight PAHs. Internal standard calibration used five deuterated PAHs to account for analytical variability. Calibration was achieved using six-point standard curves (5–1000 µg/mL), yielding $R^2 > 0.998$. Method detection limits ranged from 1.0 to 2.0 ng/L. Analytical quality control included method blanks (every six samples), spiked recovery tests (79–108% recovery), and certified standard reference material (SRM 2974, NIST). Internal standard recoveries were monitored for each batch to ensure method robustness. Descriptive statistics, ANOVA, and Pearson's correlation were performed using SPSS 16.0 at a 95% confidence level. Principal Component Analysis (PCA) was used to identify source patterns. The carcinogenic potential of PAHs was assessed via the Toxic Equivalent Quotient (TEQ), using BaP as the reference compound and applying toxic equivalency factors (TEFs) as proposed by Nisbet and LaGoy (1992). Ecological risk was evaluated using the Risk Quotient (RQ) method based on negligible (NC) and maximum permissible concentrations (MPC) per Jiang et al. (2022).

Toxicity equivalence assessment of PAHs in seawater samples

To assess the potential carcinogenicity of polycyclic aromatic hydrocarbons (PAHs) in seawater, the Toxic Equivalent Quotient (TEQ) approach was applied, using benzo[a]pyrene (BaP) as the reference compound due to its high carcinogenic potency. Toxic equivalent concentrations (TEQs) were calculated as the product of each PAH's concentration (Ci) and its corresponding Toxic Equivalency Factor (TEFi), following the method described by Nesbitt and LaGoy (1992). The cumulative TEQ was derived from eight high-risk PAHs: BaA, CHR, BbF, BkF, BaP, DBahA, BghiP, and IcdP, each with a TEF ranging from 0.001 to 1.0 (Sulung et al., 2019). Ecological risk was further evaluated using the Risk Quotient (RQ) method, as proposed by Jiang et al. (2022). RQs were determined by dividing the measured concentration of each PAH (CPAHs) by its corresponding quality value (CQV), based on Negligible Concentrations

(NCs) and Maximum Permissible Concentrations (MPCs). The total ecological risk was assessed by summing RQ values for all 16 priority PAHs. Risk classifications followed the thresholds established by Cao et al. (2010), allowing for a comprehensive evaluation of both carcinogenic and ecological impacts in the Gulf of Tobruk.

RESULTS AND DISCUSSIONS

PAHs composition in surface seawater in the Gulf of Tobruk:

Figure S1 displays the distribution of total PAHs and its composition in the seawater samples collected from the Gulf of Tobruk during the summer of 2023 and the winter of 2024. The results presented in Table S2 indicate slight variations in the total concentrations of 16 PAHs across different seasons during the study. Additionally, no significant differences were observed in the concentrations of individual PAH compounds, except for ANT, CHR, BaP, and BghiP, which showed variations in the seawater samples analyzed. Total concentrations of 16PAHs in seawater ranged from 70.95 ng/L at Station I to 454.70 ng/L at Station VII (mean: 255.4± 147.46 ng/L) in summer season and ranged from 96.57 to 473.36 ng/L at the same stations (mean: 275.17± 144.98 ng/L) in winter season. LMW concentrations of PAHs during the summer of 2023 ranged from 6.29-18.10 ng/L with an average of 10.52±0.22 ng/L, while in winter they ranged from 6.67 to 28.03 ng/L with an average of 15.05±1.75 ng/L. During the study period, these accounted for 3.96 to 8.87% and 5.92 to 6.91% of the total concentrations of PAHs (ΣPAHs), respectively. HMW concentrations of PAHs ranged from 64.66 to 436.60 ng/L with an average of 244.88±8.63 ng/L in summer, accounting for 91.13to 96.02% of the total concentrations of PAHs (ΣPAHs), while in winter they ranged between 89.90 and 445.33ng/L with an average of 260.12 ± 8.32 ng/L, accounting for 93.09 to 94.08% of the total concentrations of PAHs (ΣPAHs). The dominance of HMW PAHs suggests that the majority of PAHs in the Gulf are derived from pyrolytic sources, such as the combustion of fossil fuels or industrial processes, which are known to produce higher concentrations of 4-6 ring PAHs. These compounds tend to be more persistent in the environment due to their higher molecular weight and lower volatility, leading to their accumulation in the aquatic ecosystem. In contrast, LMW PAHs constitute a much smaller proportion of ΣPAHs (<10% for most sites), suggesting a smaller contribution from petrogenic sources, which typically produce more than 2–3-ring PAHs (e.g. crude oil or refined petroleum products). Combustion-related activities, particularly from oil refineries, are the main contributors to PAH contamination, supported by low LMW/ HMW ratios. It was observed that the increase in the total concentration of PAHs at sites IV to VII increased by 2 to 6 times compared to site I.

Temporal Variation and Concentration Levels of Priority PAHs:

The temporal variation of the 16 priority PAHs regulated by the US EPA during summer and winter was evaluated, and the values are presented in Table S2 and illustrated in Figure 2. The average concentrations of low molecular weight (LMW) PAHs were as follows: Naphthalene (NAP): 0.91 ± 1.12 – 0.91 ± 1.09 ng/L Acenaphthylene (ANY): 0.99 ± 1.21 – 0.98 ± 1.22 ng/L Acenaphthene (ANA): 1.01 ± 0.71 – 0.99 ± 0.69 ng/L Fluorene (FLU): 1.54 ± 0.82 – 1.53 ± 0.86 ng/L Phenanthrene (PHE): 2.78 ± 0.68 – 2.86 ± 0.64 ng/L Anthracene (ANT): 3.36 ± 0.92 – 7.84 ± 5.15 ng/L. Conversely, the average concentrations of high molecular weight (HMW) PAHs were as follows: Fluoranthene (FLT): 23.20 ± 15.76 – 24.27 ± 15.22 ng/L Pyrene (PYR): 24.12 ± 13.41 – 24.57 ± 13.06 ng/L Benzo[a]anthracene (BaA): 19.14 ± 13.02 – 18.35 ± 13.45 ng/L Chrysene (CHR): 27.71 ± 20.91 – 21.04 ± 13.59 ng/L Benzo[b]fluoranthene (BbF): 24.22 ± 17.08 – 20.37 ± 11.51 ng/L Benzo[k]fluoranthene (BkF): 36.55 ± 26.52 – 34.58 ± 24.39 ng/L Benzo[a]pyrene (BaP): 24.91 ± 13.70 – 33.50 ± 21.69 ng/L Dibenzo[a,h]anthracene (DBahA): 23.63 ± 15.43 – 25.13 ± 14.48 ng/L Benzo[g,h,i]perylene (BghiP): 19.13 ± 10.61 – 32.48 ±

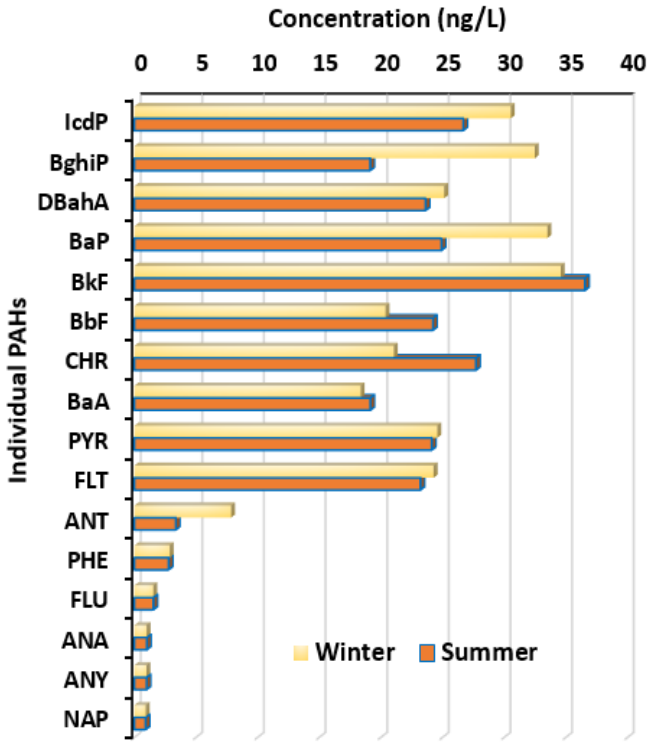

Fig. 2. mean concentration of individual PAHs (ng/L) in seawater in the Gulf of Tobruk, Libya

21.72 ng/L Indeno[1,2,3-cd]pyrene (IcdP): 26.68 ± 17.78 – 30.53 ± 16.19 ng/L.

According to the classification proposed by Mirrezaei and Orkomi (2020), PAH pollution levels in water are categorized as follows: Low pollution: ≤50 ng/L Slight pollution: 50–250 ng/L Moderate pollution: 250–1000 ng/L High pollution: ≥1000 ng/L Based on this classification, samples collected from Sites I–IV exhibited slightly polluted levels, whereas Sites V–VIII showed moderate pollution levels. The average concentrations of individual PAH compounds across all samples followed the descending order: BkF > CHR > IcdP > BaP > BbF > PYR > FLT > DBahA > BghiP > BaA > ANT > PHE > FLU > ANA > ANY > NAP (Figure 2). The total levels of polycyclic aromatic hydrocarbons (ΣPAHs) were systematically recorded and found to be lowest in the northwestern part of the Gulf of Tobruk (Sites I, II and III) during both summer and winter. The concentrations increased at Sites II and III (Commercial Port and Sewage Discharge) and continued to rise gradually towards the southern part of the Gulf (Sites IV, V, VI, and VII) Figure **2**. These variations in PAH levels were linked to differences in pollutant discharge and human activities. Many activities in the study area release untreated wastewater directly into the Gulf, contributing to PAH contamination at these sites. As shown in Table S2 and Figure 2, the highest concentrations were observed for 4-ring and 5-ring PAHs, which accounted for 60–77% of ΣPAHs across the study sites. The mean concentration of 2-ring PAH (NAP) in water samples ranged from 0.91±1.12 to 0.91±1.09 ng/L. The mean concentration of 3-ring PAHs (ANA, FLU, PHE, and ANT) varied from 0.98±1.22 to 3.36±0.92 ng/L. Among the PAH groups, 4-ring PAHs (FLT, PYR, BaA, and CHR) were significant pollutants, with mean concentrations ranging from 18.35±13.45 to 27.71±20.91 ng/L. Similarly, 5-ring PAHs (BbF, BkF, BaP, and DBahA) were notable pollutants, with mean concentrations between 20.37±11.51 and 36.55±26.52 ng/L. The average concentrations of 6-ring PAHs (BghiP and IcdP) ranged from 19.13±10.61 to 32.48±21.72 ng/L.

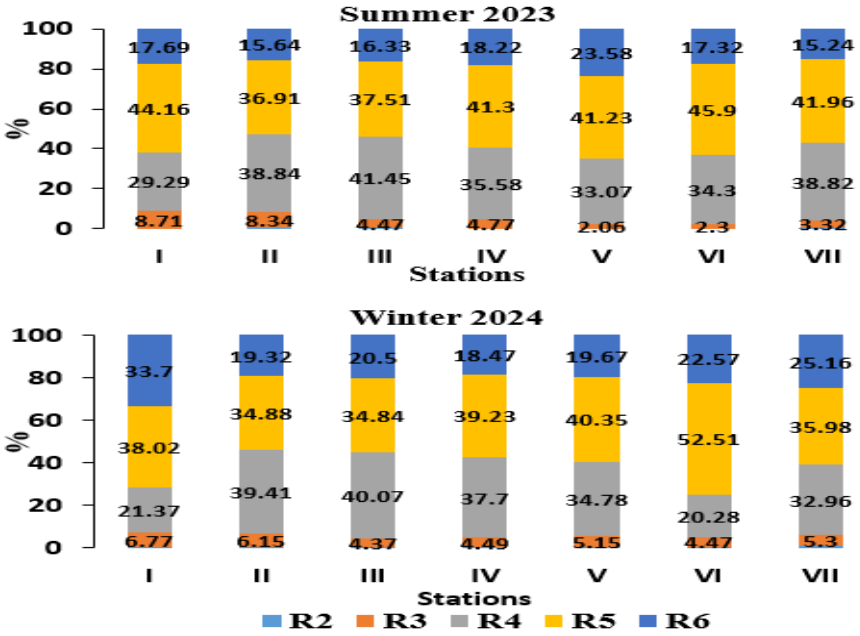

Fig. 3. Percentage of mean concentration of 2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs in seawater in the Gulf of Tobruk, Libya

Relative proportions of PAH individual PAHs in seawater:

The proportions of polycyclic aromatic hydrocarbons (PAHs) with different numbers of aromatic rings were investigated, as shown in Figure 3. The relative concentrations of PAHs varied across the seawater samples collected from the study area during the summer and winter seasons. The concentration of two-ring PAHs (e.g., naphthalene, NAP) ranged between 0.11 and 3.00 ng/L, contributing only 0.06 to 0.66% of the total PAHs. Three-ring PAHs (acenaphthylene, ANY; acenaphthene, ANA; fluorene, FLU; phenanthrene, PHE; anthracene, ANT) were found in concentrations ranging from 6.18 to 25.10 ng/L, representing 2.06 to 8.71% of the total PAHs. The four-ring PAH compounds (fluoranthene [FLT], pyrene [PYR], benzo[a]anthracene [BaA], and chrysene [CHR]) were detected at concentrations of 20.54-176.5 ng/L, representing 20.28-41.45% of total PAHs. Five-ring PAHs (benzo[b]fluoranthene [BbF], benzo[k] fluoranthene [BkF], benzo[a]pyrene [BaP], and dibenzo[a,h]anthracene [DBahA]) showed higher levels (31.33-214.0 ng/L) and constituted the dominant fraction (34.84-52.51%). Six-ring PAHs (benzo[g,h,i]perylene [BghiP] and indeno[1,2,3-cd]pyrene [IcdP]) exhibited lower concentrations (12.55-119.1 ng/L) and accounted for 15.64-25.16% of total PAHs. Overall, five-ring PAHs were the most abundant group, followed by four-ring, six-ring, three-ring, and two-ring PAHs. The dominant composition pattern observed was 5-rings > 4-rings > 6-rings > 3-rings > 2-rings (Figure 3). Notably, high-molecular-weight PAHs (4- to 6-rings) dominated the composition, accounting for over 95% of total PAHs in the seawater samples, while the low-molecular-weight PAHs (2-rings) contributed less than 0.5%.

Table S3 summarizes the relationships among individual PAHs across the study period. The correlation matrix shows strong associations among several compounds, pointing to potential common origins such as petrogenic and pyrogenic inputs. Exceptions were noted for some higher molecular weight PAHs (4–6 rings), which appear to derive predominantly from combustion-related (pyrogenic) sources. Seasonal patterns were generally consistent, though stronger correlations among five- and six-ring PAHs in winter suggest enhanced anthropogenic inputs. Significant correlations among high-molecular-weight PAHs suggest shared sources,

while weaker relationships among low-molecular-weight PAHs indicate mixed sources. Overall, the clustering of high-molecular-weight PAHs (CHR, BbF, BkF, BaP, DBahA, BghiP, and IcdP) reflects a strong pyrogenic signature, likely linked to incomplete fossil fuel combustion and biomass burning associated with industrial and commercial activity in the Gulf of Tobruk. These patterns are consistent with previous studies, which also reported strong interrelations among BaP, BbF, BkF, IP, and DahA, highlighting the persistence of HMW PAHs in the environment. Seasonal variability in correlation strength may be influenced by atmospheric deposition, sediment resuspension, and runoff from nearby urban and industrial areas. The stronger correlations observed among five- and six-ring PAHs suggest increased input from industrial and vehicular emissions during periods of higher energy demand.

Sources by Diagnostic ratio analysis of selected individual PAHs:

Effective mitigation of PAH emissions requires comprehensive source identification and quantitative contribution analysis. As shown in Figure S2, the diagnostic ratios of PAHs including LMW/HMW, FLT/PYR, NAP/PHE, PHE/ANT and BaA/CHR were used to separate the contributions of various sources of PAHs in the surface seawater of Gulf of Tobruk (Ambade et al.,2022). All seawater samples in this study yielded LMW/HMW ratios less than 1, in the range (0.03-0.12) in summer season, and the same range in winter, indicating the pyrolytic origin of the PAH contaminants. The values of the ratio. The results of the PHE/ANT ratio, as shown in Table2, ranged between (0.54 - 0.98) in the summer and (0.55 - 1.05) in the winter. The discrepancy is likely due to extensive mixing of PAH sources during transport and deposition of PAHs (Readman et al.,2002; Baumard et al.,1998). The FLT/PYR index > 1 was recorded at sites IV and VIII indicating a pyrolysis source during the winter and summer seasons, while the other sites revealed low index values < 1 indicating a petroleum source during the study period (Table **S**4). Most likely due to extensive mixing of different PAHs sources during transportation and deposition of PAHs. The NAP/PHE index was lower than 10 in all sites' samples, indicating a pyrolytic source (Ravindra et al., 2008). Because BaA/CHR ratios during the study period were greater than 1 at sites I, IV, V, and VI, indicating a pyrolytic source (Table **S**4), while PAHs in seawater at sites II, III, VII, and VIII recorded BaA/CHR ratios < 1 which indicates petroleum pollution (King et al.,2004). BaA/CHR ratio > 1, representing 44% of sampling sites that confirmed the association with pyrogenic materials, particularly liquid fossil fuel combustion, like the main sources of PAHs in the Bay of Tobruk. On the other hand, 66% of the sampling sites are characterized by containing petroleum sources. A BaA/CHR ratio greater than 1 also confirmed the diesel/gasoline combustion correlation, and all ratios highlighted pyrogenic materials, especially liquid fossil fuel combustion, as the main sources of targeted PAHs in the Bay. According to Hussein et al. (2016), the concentration ratio between BaP and BghiP serves as an effective molecular marker for apportioning vehicular versus non-vehicular PAH contributions. In the present study, the BaP/B(ghi)P ratio was more significant than 0.6 throughout the study, the ratio ranged from 0.70 at site IV to 2.98 at site V during summer, the same range was recorded in winter 2024 at the same sites (Table **S**4& Figure S2). Therefore, the potential for high traffic emissions may vary over the study period. Source apportionment using diagnostic molecular markers identified four primary PAH sources with seasonal variations: (1) gasoline combustion, (2) coal combustion, (3) general pyrogenic processes, and (4) vehicular emissions. These sources exhibited distinct temporal patterns, with combustion-related sources (gasoline/coal) predominating in winter months, while traffic emissions showed consistent year-round contributions.

Principal Component Analysis (PCA):

The PCA loading plot of Polycyclic Aromatic Hydrocarbons (PAHs) provides a clear distinction between petrogenic and pyrogenic PAHs, helping to pinpoint major pollution

sources in the studied area. Figure S3 shows two groups of PCA loading plots (PC1&PC2) for PAHs in both seasons, the summer 2023 and winter 2024. The plot identifies potential pollution sources based on how different PAHs cluster together. The right-handed group (PC1) accounts for 76% of the variance and includes the individual PAHs CHR (chrysene), BaA (Benz [a] anthracene),BkF (benzo[k]fluoranthene), BbF (benzo[b]fluoranthene), IcdP (Indeno[1,2,3-cd] pyrene), BaP (benzo[a]pyrene), BghiP (benzo[ghi]perylene), DBahA (Dibenzo [a, h] anthracene),PYR (pyrene), and FLT (fluoranthene). These are high-molecular-weight polycyclic aromatic hydrocarbons (PAHs), which are typically associated with pyrogenic sources and arise from the incomplete combustion of organic materials such as fossil fuels, biomass burning, and industrial emissions. Potential sources include industrial emissions, vehicle exhaust, and municipal waste incineration. The left-hand group (PC2) accounts for about 11% of the variance and includes the individual PAHs acenaphthene (ANA), naphthalene (NAP), Acenaphthylene (ANY), anthracene (ANT), fluorine (FLU), and phenanthrene (PHE). These hydrocarbons typically have low molecular weight (LMW) and are often associated with petrogenic sources such as oil spills, petroleum seeps, and unburned petroleum products. Potential sources in the Gulf of Tobruk include oil refineries, port activities, and shipping operations.

Potential toxicities of PAHs in seawater in the Gulf of Tobruk: Environmental risk: Ecological risk assessment using toxic equivalence approach (TEQ)

To evaluate the potential ecological and health risks associated with PAHs in the Gulf of Tobruk, we employed a methodology based on Toxic Equivalence Factors (TEFs) and the calculation of the Toxic Equivalent Quotient (TEQ). This method is particularly effective for estimating the relative toxicity of complex mixtures of PAHs in environmental matrices such as seawater in the Gulf of Tobruk. Benzo(a)pyrene (BaP) is widely recognized for its potent carcinogenic and mutagenic effects and is used as the reference compound in toxic equivalence assessments. The TEF value assigned to BaP is 1. Other PAHs are assigned TEFs based on their relative toxicity in comparison to BaP (Cheng et al., 2022). By applying these factors, we can translate concentrations of individual PAHs into a single BaP-equivalent value that reflects the overall carcinogenic potency of the PAH mixture. To assess ecosystem risks in the current study, we used a technique based on risk quotient (RQ) and toxic equivalence factors (TEFs). Table S5 showed Toxic Equivalent quotient (TEQ) of PAHs in seawater in the Gulf of Tobruk. Benzo (a) pyrene (BaP) is one of the most studied polycyclic aromatic hydrocarbons (PAHs) due to its strong carcinogenic and mutagenic properties. To evaluate the toxicity of PAH mixtures, toxic equivalence factors (TEFs) were used, using BaP as the reference compound with a TEF of 1. TEFs for other PAHs are determined based on their relative toxicity compared to BaP (Cheng et al., 2022). This approach enables a standardized assessment of the carcinogenic potential of PAH-contaminated environments, such as seawater. Focusing on PAHs in the Gulf of Tobruk, using toxicity equations, could be a useful method for assessing the health risks associated with PAH pollution in the region. Calculated Toxicity Equivalent Index (TEQ) values for PAHs in the Gulf of Tobruk using the US EPA TEQ criteria are shown in Figure S4. Winter TEQ values are generally higher than summer TEQ values at most locations, indicating seasonal variations in PAH contamination. Sites VI and VII had the highest TEQ values (122.88 and 108.70 ng/L in winter, respectively) (Table S5). This suggests a major contamination source in this area, possibly industrial effluents, port activities, or oil spills. Site V and Site VI also show high contamination, especially in winter has a peak in summer but drops in winter, possibly due to localized pollution sources. According to the US EPA and WHO, the drinking water limit for BaP (as a representative PAH) is 0.2 ng/L. All detected TEQ values exceed safe limits, indicating potential risks to marine life and human health, especially for desalination plants using seawater. To assess the ecological risk posed by PAHs in the Gulf of Tobruk, the Toxic Equivalent Quotient (TEQ) approach was applied using toxic equivalence factors (TEFs) with

benzo[a]pyrene (BaP) as the reference compound. TEQ values for both summer and winter seasons across all stations ranged between 18.06 and 91.67 ng/L in summer at sites I and VII, and from 21.63 and 122.88 ng/L in winter at sites I and VI, respectively (Figure S4), significantly exceeding established international guideline limits.

The risk grades for individual and total PAHs, adopted from Cao et al. (2010), Wang et al. (2018), and Lan et al. (2020), are presented in Table S6. As shown in Figure S4, the results of TEQ values appear tend to be higher in winter for most sites, especially for sites VI and VII. For comparison, the European Union Water Framework Directive sets an annual average EQS of 0.17 ng/L for BaP, while the Canadian Council of Ministers of the Environment (CCME) recommends a marine water quality guideline of 15 ng/L for the protection of aquatic life. Additionally, the USEPA ambient water quality criterion is 2.8 ng/L for carcinogenic PAHs, based on human health protection through the consumption of aquatic organisms. The TEQ values reported in this study exceed these limits by over 100 times (EU), over 6 times (USEPA), and slightly surpass (CCME) thresholds, indicating a high potential ecological and human health risk. These findings highlight the need for immediate pollution control measures, stricter regulatory enforcement, and comprehensive monitoring programs to mitigate the impact of PAH contamination in the marine environment of Tobruk Bay.

Ecological risk assessment of individual and ΣPAHs using risk quotient (RQ)

To evaluate the potential ecological threats posed by polycyclic aromatic hydrocarbons (PAHs) in Gulf of Tobruk, risk quotient (RQ) values were calculated based on both negligible concentrations (NCs) and maximum permissible concentrations (MPCs). These values denoted as RQ_{NCs} and RQ_{MPCs}, respectively, provide a measure of ecological risk by comparing observed PAH concentrations to established environmental thresholds. The mean seasonal values of RQ_{NCs} and RQ_{MPCs} for individuals and total PAHs in Gulf of Tobruk are summarized in Table S7. During the summer, RQ_{MPCs} for individual PAHs ranged from 0 to 2.42, while RQ_{NCs} ranged from 0.08 to 242.2. In winter, the RQ_{MPCs} ranged from 0 to 2.04, and the RQ_{NCs} from 0.08 to 203.70. Almost all of the 16 PAHs, except for naphthalene (NAP) and phenanthrene (PHE) showed RQ_{NCs} values greater than 1.0, indicating a high ecological risk throughout the study period. Notably, PAHs containing four and five aromatic rings such as benzo[a]anthracene (BaA) and benzo[b]fluoranthene (BbF) exhibited RQ_{MPCs} values exceeding 1.0, indicating that these specific compounds pose a higher risk to marine ecosystems. While most individual PAHs recorded RQ_{MPCs} values below 1.0, the cumulative ecological risk associated with total PAHs (∑PAHs) remained significantly elevated. Overall, based on both RQ_{NCs} and RQ_{MPCs} values, the ecological risk for total PAHs in the seawater of the study area was classified as high-risk. The seasonal results for both risk quotients were consistent, with minimal variation between summer and winter (Table S7). The total risk quotient values for PAHs were between 813–842 for $RQ_{TPAHs\ (NCs)}$, and between 8.14–8.42 for $RQ_{TPAHs\ (MPCs)}$. Furthermore, as illustrated in Table S7, the RQ_{NCs} values for acenaphthene (ANA), acenaphthylene (ANY), anthracene (ANT), fluorene (FLU), pyrene (PYR), fluoranthene (FLT),BbF, benzo[k]fluoranthene (BkF), BaA, chrysene (CHR), dibenzo[a,h]anthracene (DBahA), benzo[a]pyrene (BaP), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP) were all above 1.0, reinforcing a classification of medium to high ecological risk. In contrast, only NAP and PHE exhibited values below 1.0, indicating lower ecological risk. In contrast, for RQ_{MPCs}, values for most of the 16 PAHs fell below 1.0 in both seasons, suggesting lower individual risk, with the exception of BaA, BghiP and BbF, which remained above 1.0 and thus confirmed high risk. However, the ∑PAHs values exceeding 1.0 indicate a significant cumulative ecological risk. Figure S5 represents the ecological risk posed by individual PAHs in Tobruk Bay seawater during summer and winter. The chart includes both RQ values based on NCs (No-Effect Concentrations) and MPCs (Maximum Permissible Concentrations), with threshold lines highlighting low and high-risk levels (0.1 and 1.0). The

Risk Quotient (RQ) analysis of individual PAHs in Tobruk Bay seawater reveals significant ecological concerns, particularly in relation to the negligible concentrations (NCs) criteria. Most PAHs, including Pyrene (PYR), Benzo[a]anthracene (BaA), Benzo[b]fluoranthene (BbF), and Indeno[1,2,3-cd]pyrene (IcdP), exhibit RQ_{NCs} values far exceeding the high-risk threshold (RQ > 1) during both summer and winter seasons. This indicates a substantial potential for adverse ecological effects, especially from high molecular weight PAHs known for their toxicity and persistence. While RQ_{MPCs} values are generally lower, compounds such as BaA and BbF still surpass the high-risk threshold, suggesting that even under more tolerant regulatory limits, these PAHs pose a serious threat to marine biota. Seasonal variation is minimal, but certain PAHs such as Anthracene (ANT), Benzo[a]pyrene (BaP), and Benzo[ghi]perylene (BghiP) exhibit higher risk quotients in winter, potentially due to seasonal discharges or altered environmental conditions. Overall, the RQ results underscore the chronic and possibly acute ecological risks in Tobruk Bay, emphasizing the urgent need for environmental monitoring, pollution source control, and effective remediation efforts.

CONCLUSION

This study presents the first comprehensive evaluation of PAH contamination in the Gulf of Tobruk, revealing their presence in surface seawater across seven stations. Given their carcinogenicity, mutagenicity, and dominant anthropogenic sources, the findings highlight the need for ongoing monitoring and management. The concentrations of PAHs were measured using GC-FID, and diagnostic ratios such as LMW/HMW, FLT/PYR, NAP/PHE, PHE/ANT, and BaA/CHR were applied to identify the contributions of different PAH sources in the surface seawater of the Gulf of Tobruk. The results indicate substantial pollution levels, largely driven by industrial and urban activities. High-risk PAHs (BaA, BbF, BkF, BaP, DBahA, BghiP, and IcdP) were consistently detected in the Gulf of Tobruk, with overall ecological risks remaining elevated across both seasons. These results emphasize the urgency of continuous monitoring, stricter discharge regulations, and further studies on sediments and biota to safeguard marine ecosystems and human health.

ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to Dr. Alyaa A. Zidan, National Institute of Oceanography and Fisheries (NIOF), for her valuable assistance in paraphrasing and formatting the manuscript. Her contributions greatly improved the clarity and presentation of the work.

DATA AVAILABILITY

Data sharing is not applicable to this article, as no datasets were generated or analyzed during the current study.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATION

Term	Abbreviation
Low Molecular Weight	LMW

Term	Abbreviation
Naphthalene	NAP
Acenaphthylene	ANY
Acenaphthene	ANA
Fluorene	FLU
Phenanthrene	PHE
Anthracene	ANT
High Molecular Weight	HMW
Fluoranthene	FLT
Pyrene	PYR
Benzo[a]anthracene	BaA
Chrysene	CHR
Benzo[b]fluoranthene	BbF
Benzo[k]fluoranthene	BkF
Benzo[a]pyrene	BaP
Dibenzo[a,h]anthracene	DBahA
Benzo[g,h,i]perylene	BghiP
Indeno[1,2,3-cd]pyrene	IcdP
Toxic Equivalent Quotient	TEQ
Toxic Equivalency Factors	TEFs
Risk Quotient	RQ
Maximum Permissible Concentrations	MPC

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