Egyptian Journal of Aquatic Biology & Fisheries
Zoology Department, Faculty of Science,
Ain Shams University, Cairo, Egypt.
ISSN 1110 – 6131
Vol. 29(6): 1745 – 1770 (2025)
www.ejabf.journals.ekb.eg

Polycyclic Aromatic Hydrocarbons (PAHs) in Fish Species from the Northwestern Mediterranean Coast, Tobruk Bay, Libya: A Possible Risk Assessment

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ARTICLE INFO

Article History:
Received: Aug. 25, 2025
Accepted: Nov. 20, 2025
Online: Dec. 4, 2025

Keywords:
Fish muscle,
Bioaccumulation,
Marine pollution,
Carcinogenic risk,
Margin of exposure (MOE)

ABSTRACT

This study investigates the concentrations, sources, and potential health risks of 16 priority polycyclic aromatic hydrocarbons (PAHs) in four edible fish species: *Pagellus erythrinus*, *Lithognathus mormyrus*, *Diplodus vulgaris*, and *Liza aurata* collected from Tobruk Bay, Libya, during winter 2024. PAH concentrations were quantified in fish muscle using gas chromatography with flame ionization detection (GC–FID), revealing total levels ranging from 157.21 to 260.32ng/ g (wet weight), with *D. vulgaris* exhibiting the highest values. Distinct species-specific patterns were observed. Elevated levels of carcinogenic high-molecular-weight PAHs, such as indeno[1,2,3-cd] pyrene, dibenz [a, h] anthracene, benzo[b]fluoranthene, and pyrene, were found in both *P. erythrinus* and *D. vulgaris*. These compounds together accounted for more than 45% of total PAHs, indicating primarily pyrogenic sources from combustion and industrial emissions. In contrast, *L. aurata* and *L. mormyrus* showed higher contributions of low-molecular-weight compounds such as naphthalene, reflecting mixed petrogenic and pyrogenic sources. Benzo[a]pyrene concentrations in all fish exceeded the European UElevated levels of carcinogenic high-molecular-weight PAHs, such as indeno[1,2,3-cd] pyrene, dibenz [a, h] anthracene, benzo[b]fluoranthene, and pyrene, were found in both *P. erythrinus* and *D. vulgaris*. These compounds together accounted for more than 45% of total PAHs, indicating primarily pyrogenic sources from combustion and industrial emissions nion regulatory limit of 2.0ng/ g, suggesting potential carcinogenic concern. Although the estimated daily intake (EDI) and target hazard quotient (THQ) values for total PAHs remained below the safety threshold (THQ < 1), risk characterization based on the margin of exposure (MOE) yielded values below 10,000, indicating a possible carcinogenic risk to consumers. Overall, the results reveal moderate PAH contamination in Tobruk Bay fish and underscore the need for sustained environmental monitoring and strengthened pollution management to safeguard seafood quality and public health.

INTRODUCTION

Food is a fundamental human necessity, and its availability, accessibility, and affordability are central to global food security **(Sarkodie & Owusu, 2023; Chmangui *et al.,* 2025)**. Fish constitutes a major component of the human diet worldwide, supplying high-quality protein and essential nutrients. Because of their dietary importance, it is

critical to monitor fish for environmental contaminants to prevent the transfer of hazardous substances to consumers **(Blume *et al.,* 2025; Islam *et al.,* 2026)**. Libya, located in North Africa between latitudes 22°–32°N and longitudes 10°–25°E, borders the Mediterranean Sea with a coastline extending for approximately 1,970km **(Momen *et al*., 2024)**. Despite its oil-dominated economy, the country is nearly sufficient in fish production, with an estimated per capita consumption of 7 kg/person/year **(FAO, 2005)**. An estimated 95% of the country's total catch is used for direct human consumption (**European Commission, 2009**).

The Port of Tobruk, established in 1986 near the Egyptian border, is a key fisheries and economic hub in eastern Libya **(Idris *et al.,* 2025)**. However, outdated infrastructure, a fleet consisting mostly of small coastal vessels, and limited financial resources restrict fishing operations to approximately 120 days per year (**Blum *et al.,* 2025**). Despite ongoing investments to expand facilities, fleet modernization and improved financial support are crucial for enhancing productivity and sustainability. Although investments are underway to expand facilities, modernization of fleets and improved financial support are urgently needed to enhance productivity and sustainability. Globally, fish represent one of the most widely consumed sources of animal protein, with over 90% of harvested fish considered edible **(Verma & Prakash, 2020**). However, increased demand has led to unsustainable practices and overfishing, endangering marine biodiversity. To protect fish populations and guarantee food safety, effective fisheries management and strict environmental restrictions are crucial.

The effectiveness and sustainability of fishery operations are significantly impacted by the infrastructure quality of fishing ports, which serve as crucial intermediaries between capture and consumption. Anthropogenic activities are increasingly putting strain on coastal locations globally. Untreated municipal sewage, industrial discharges, and oil-related operations close to terminals and refineries are the main threats in Tobruk. These sources jeopardize the integrity of the ecosystem and the safety of seafood by introducing harmful pollutants into the marine environment, especially heavy metals and petroleum hydrocarbons **(Saad *et al*., 2025)**. The cumulative impact of these pollutants has contributed to declining fish stocks and ecological imbalance. **Bouzid *et al.* (2024)** draws attention to the pressing need for better fisheries management along the Tobruk coast. PAHs are persistent organic pollutants composed of two or more fused aromatic rings. They originate from natural processes such as forest fires and crude oil, as well as human activities including fossil-fuel combustion and petroleum refining **(Omar *et al.*, 2025; Saad *et al.,* 2025)**.

In Libya, extensive coastal petroleum operations are a major contributor to PAH contamination in marine environments. PAHs enter aquatic systems through atmospheric deposition, industrial and municipal wastewater discharges, road runoff, and oil spills. In marine environments, they readily bind to suspended particles and accumulate in sediments, where they can persist for long periods (**Dehvari *et al.,* 2023; Rahimi**

Moazampour *et al.,* 2023; Agranat, 2025; Omar *et al.,* 2025). PAHs are frequently detected in water, sediments, and marine organisms. Fish absorb them directly through gills and skin or indirectly via contaminated prey **(Singh *et al.,* 2023; Heydari, 2024)**.

Fish have metabolic routes for processing PAHs, but tissue concentrations usually indicate the degree of environmental contamination, particularly in areas close to pollution sources. In addition to posing major dangers to human health, such as endocrine disruption, respiratory illness, and cancer, elevated PAH levels can lower the quality and financial value of seafood (**Qishlaqi & Beiramali, 2019; Verheyen *et al*., 2020; Olasehinde *et al.,* 2022; Paquette *et al.,* 2023**). Due to their lipophilicity and persistence, PAHs bioaccumulate in organisms and biomagnify across food webs, ultimately entering the human diet. Exposure to PAHs is associated with cancer, genetic mutations, and other long-term health effects **(Honda & Suzuki, 2020)**. Therefore, assessing the health of ecosystems and the dangers of human exposure requires tracking PAHs in environmental matrices and biological markers.

Despite the significance of PAHs for the environment and public health, no prior research has examined PAH contamination in fish from the Gulf of Tobruk. Consequently, health risks associated with consuming PAH-contaminated fish in this region remain unknown. The present study addresses this critical gap by quantifying PAH concentrations in several commercially important fish species and evaluating potential risks to consumers. Global health agencies, including JECFA and EFSA, classify PAHs as priority contaminants because of their genotoxic, mutagenic, and carcinogenic properties **(Grigoriou *et al.,* 2022)**. Their persistence and toxicity make them a significant environmental concern in industrialized coastal zones such as Tobruk Bay.

This study aims to determine the concentrations of 16 priority PAHs in four commercially important marine fish species (*P. erythrinus*, *L. mormyrus*, *D. vulgaris*, and *L. aurata*) collected from the Gulf of Tobruk, and assess the potential health effects associated with human consumption of PAH-contaminated fish. In addition, it investigates possible sources and distribution patterns of PAHs in the Gulf of Tobruk marine environment, while providing essential baseline data on PAH pollution along the Libyan coast. Additionally, the study highlights the importance of continuous environmental monitoring and effective pollution control strategies to safeguard marine ecosystems and public health. As the first comprehensive evaluation of PAHs in commercially consumed fish species in Libya, this research offers crucial baseline information for pollution management and ecological risk assessment in the Gulf of Tobruk.

MATERIALS AND METHODS

Study area

Tobruk Bay is situated near the Egyptian border in northeastern Libya (32°4′N, 24°0′E), approximately 450km east of Benghazi (Fig. 1). The Gulf of Tobruk, located southeast of the city, extends for about 5.5km in length and 0.5– 2.0km in width, with an average depth of 16m (**Masoud *et al.,* 2022**; **Idris *et al.,* 2025**). The bay, which is almost

two nautical miles long, serves as a crucial maritime passage for ships and oil tankers. The southeastern section has large oil-related infrastructures, including the Hariga refinery, Brega Company's oil export terminal, and power and desalination plants working on heavy fuel. In contrast, the southwestern area contains economic and recreational locations such as the Al-Athrun fishing port and Al Masirah Hotel. Several beach resorts and a commercial port with 13 slots for cargo and fishing vessels may be found along the northern shoreline. The risk for marine contamination from oil discharges, heavy-fuel residues, heavy metals, salts, and untreated sewage is increased by these combined industrial, commercial, and recreational activities.

Reagent and chemicals

All reagents and chemicals were of analytical grade, including dichloromethane (DCM), n-hexane, CH_3OH, HCl, and KOH, obtained from Sigma-Aldrich (Steinheim, Germany) and Merck (Darmstadt, Germany). Millipore water was used for all analytical procedures. Glassware was soaked in 10% HNO_3 for 24 hours and thoroughly rinsed with millipore water to prevent contamination. Sigma-Aldrich provided certified standards with purities ranging from 97.9 to 99.9% for the sixteen priority PAHs classified as hazardous pollutants by the US EPA and WHO. The primary stock solutions were precisely diluted to create mixed standard solutions.

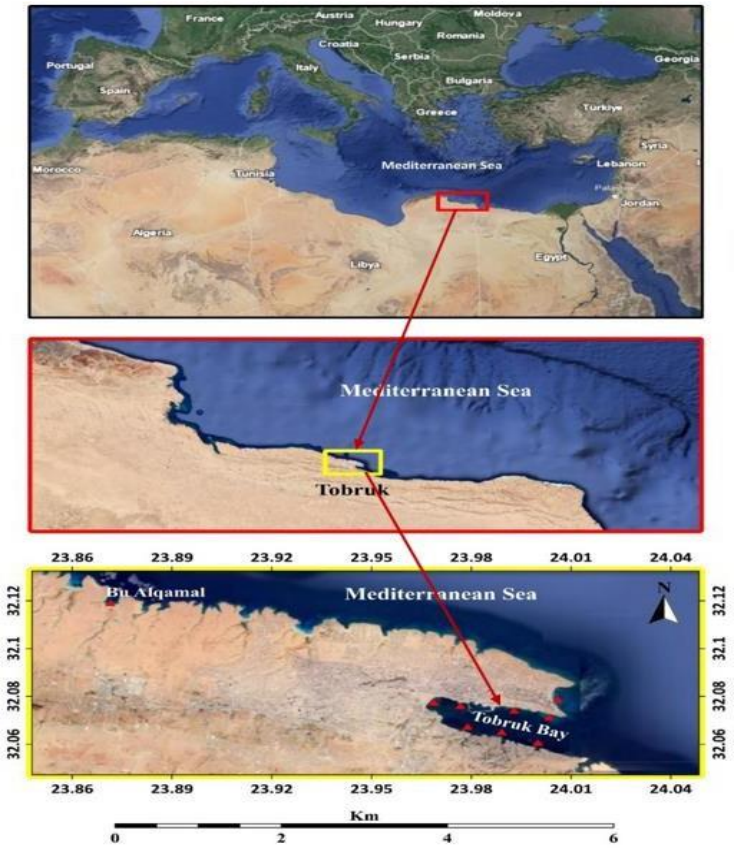

Fig. 1. Area of investigation

Sample collection

Fig. (2) presents a flowchart summarizing the procedure for PAH determination in fish samples. Four commercially important species, *P. erythrinus*, *L. mormyrus*, *D. vulgaris*, and *L. aurata*, were collected during winter 2024 from multiple locations across Tobruk Bay. Five individuals of each species (n = 10) were sampled, stored on ice, and transported to the laboratory within six hours. Upon arrival, samples were rinsed with deionized water, wrapped in hexane-cleaned aluminum foil, and frozen at –20°C to preserve tissue quality and prevent PAH deterioration. Before analysis, total length (17– 25cm) and weight (25–160g) were recorded. Biochemical analyses (moisture, proteins, lipids) were performed using three replicates from five individuals per species. After controlled thawing, only edible muscle tissues (filets) were retained, homogenized with a stainless-steel grinder, and stored in solvent-rinsed glass containers at –20°C. PAH extraction followed the **USEPA (1994)** standard protocol, and sixteen priority PAHs were quantified by GC–FID .

Chemical composition

Moisture content was determined by drying samples to constant weight at 105°C. Protein content was measured using the Kjeldahl method (6.25 × N), and ash content was obtained by incineration at 550 °C until a stable residue was formed. Lipids were extracted using a Soxhlet apparatus following the **AOAC (2002)**, where ~5g of dried sample was extracted with hexane for 4h at 70°C. The solvent was removed, and residue mass was used to calculate fat content.

Extraction and cleanup procedure

Chromatography-grade reagents (Merck) were used throughout. For each species, 10– 30g of muscle tissue was mixed with 5g of anhydrous sodium sulfate and homogenized for 5min. Soxhlet extraction was performed with n-hexane/dichloromethane (3:1, v/v) at 50°C for 8h according to the EPA Method 3540 **(USEPA, 1994; Nnaji & Ekwe, 2018; Chmangui *et al.,* 2025)**. An internal standard was added, and the extraction cycle was repeated three times. Combined extracts were filtered through sodium sulfate, concentrated by rotary evaporation (35°C) and saponified with 10mL of 1M KOH in ethanol for 3h **(Baumard *et al.,* 1997)**. After further concentration, residual solvents were removed using a Kuderna–Danish evaporator (< 30°C), and the extract was reduced to 1mL under nitrogen. Cleanup and fractionation were carried out using silica–alumina column chromatography. The column contained activated alumina (deactivated 1%), silica gel (deactivated 5%), and sodium sulfate. Acid-washed copper granules removed sulfur residues. Elution consisted of: F1: aliphatic hydrocarbons with 40mL n-hexane, and F2: PAHs with 40mL n-hexane/dichloromethane (90:10) + 20mL (1:1). The PAH fraction was concentrated to 1mL under nitrogen and was stored at –20°C.

Gas chromatographic conditions

PAHs were quantified using a Hewlett Packard 5890 Series II GC with a flame ionization detector (FID). Hewlett-Packard (HP) is an American company based in Palo Alto, California, USA. Splitless injection of 3µL was used at 290°C, with the FID operated

at 300°C. Separation was achieved on an HP-1 fused silica column (30 m × 0.32 mm, 0.17μm film). The oven program began at 60°C, increased with 3°C/ min to 290°C, and held for 25min. Nitrogen served as the carrier gas at 1.2mL/ min, ensuring adequate resolution and sensitivity for the 16 PAHs.

Analytical quality control and method validation

Recovery Efficiency**:** Using NIST SRM 2974, recoveries for the 16 PAHs ranged from 72–94% with CVs of 6–10%. Blank samples indicated no contamination (detection limit < 0.01μg/ mL). Clear chromatographic separation confirmed specificity. LOD: Three times the SD (n= 7) at 1.0 ng/L. LOQ: Nine times the SD. Linearity: Strong linear response across the calibration range.

Descriptive analysis

Data were analyzed using SPSS 21. Graphs were generated in SPSS and Microsoft Excel. Results are presented as mean ± standard deviation (SD) for samples from the various sampling locations.

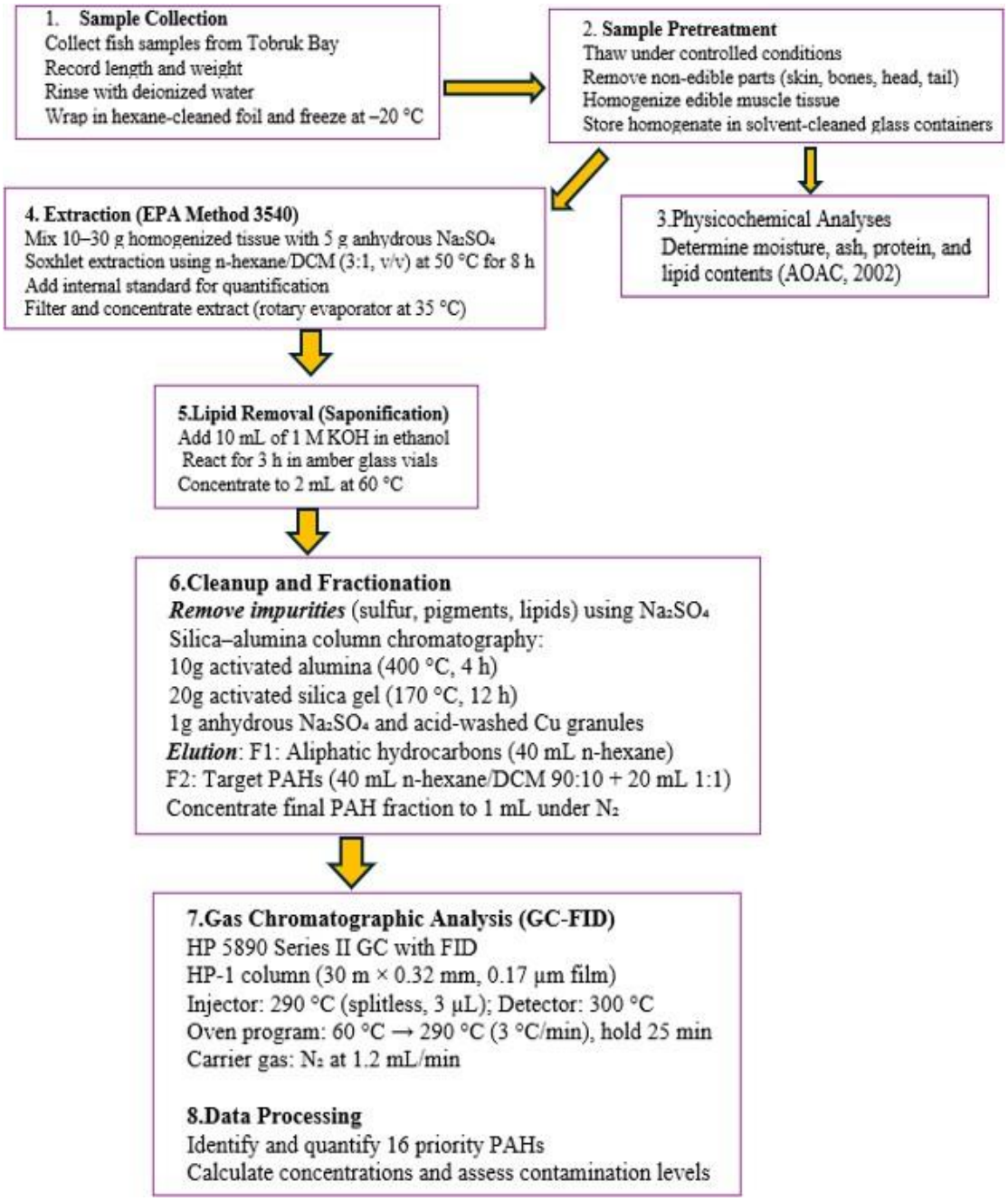

Fig. 2. Flowchart of the method for determining polycyclic aromatic hydrocarbons in fish samples

RESULTS AND DISCUSSION

Physical measurements and biochemical composition

The biochemical composition of fish species is a key area of study with broad relevance to nutrition, health sciences, and pharmaceutical research. Components such as moisture, ash, protein, and lipid content serve as essential indicators of nutritional quality and potential health benefits. These parameters are known to fluctuate seasonally, with variations affecting not only the nutritional value of fish but also their commercial quality and processing characteristics. In this study, four commercially and ecologically significant species, *P. erythrinus*, *L. mormyrus*, *D. vulgaris*, and *L. aurata*, were examined for their biochemical composition during winter 2024. The results of physical measurements and biochemical composition are shown in Table (1).

Physical measurements

The total length of the examined species varied as follows: *L. aurata* (25– 28cm (25 ± 0.15cm), *D. vulgaris* (16.17– 18.11cm ;17.00 ± 0.24cm), *L. mormyrus* (16– 20cm ;17 ± 0.23cm), *P. erythrinus* (19.41– 20.35cm ;19.82 ± 0.12cm) Body weight also differed between species: *L. aurata* **(**155– 168g ;160 ± 0.35g); *D. vulgaris* **(**26– 28g; 25.02 ± 0.22g); *L. mormyrus* **(**35– 38g; 36.14 ± 0.12g); and *P. erythrinus* **(**30.04– 31.25g; 30.34 ± 0.02g). These variations reflect interspecific differences in growth and body development, influenced by habitat conditions, feeding habits, and metabolic activity.

Biochemical composition

Analysis of muscle tissues revealed clear differences in the ash, moisture, protein, and lipid contents among the four species.

Ash content

Ash content, representing total mineral concentration, showed the following distribution (Table 1): *L. aurata* (1.87–2.06% ;1.92 ± 0.22%), *D. vulgaris* (2.11–2.28% ;2.17 ± 0.14%), *L. mormyrus* ;1.64–1.75% (1.69 ± 0.07%), *P. erythrinus* (2.11–2.44% ;2.14 ± 0.15%). *P. erythrinus and D. vulgaris* exhibited the highest mineral levels. Ash content is linked to the availability of essential minerals, which play vital roles in metabolic and physiological processes in humans.

Moisture content

Moisture content varies across species as follows: *L. aurata* (73.71–75.24%; 73 ± 0.27%), *D. vulgaris* (78.54–79.23%; 79.01 ± 0.12%), *L. mormyrus* (75.32–77.80%; 76.12 ± 0.30%), *P. erythrinus* (70.52–72.33%; 71.14 ± 0.04%).The descending order of moisture content was *D. vulgaris* > *L. mormyrus* > *L. aurata* > *P. erythrinus***.** As commonly observed in fish, an inverse relationship existed between moisture and lipid levels, where higher lipid content corresponded with reduced moisture within the muscle tissue.

Protein content

Protein concentrations in species under study were detected in the following order: *P. erythrinus* (20.1– 21.08%; 20.64 ± 0.32%), *L. aurata* (18.21–19.45%; 18.72 ± 0.17%), *L. mormyrus* (17.55– 17.92%; 17.32 ± 0.09%), *D. vulgaris* (17.11– 17.37%; 17.22 ± 0.09%).

P. erythrinus had the highest protein content, indicating strong nutritional value and making it an attractive dietary protein source, especially in regions where protein availability is limited.

Total lipids (TL)

Lipid levels differed significantly among the species: *L. aurata* (3.68–4.55%; 3.85 ± 0.32%), *D. vulgaris* (1.03–1.21%; 1.12 ± 0.10%) ,*L. mormyrus* (1.42–1.63% ;1.52 ± 0.05%),*P. erythrinus* (1.55–1.75%; 1.62 ± 0.08%). *L. aurata* showed the highest lipid content nearly three times greater than that of *D. vulgaris*, which had the lowest values. Species-specific factors such as metabolic rate, feeding habits, and habitat contribute to these differences.

Concentration of individual PAHs in tissues of fish species (ng/g; wet weight)

The concentrations of PAHs detected in the four fish species are presented in Table (2) and Fig. (3). The distribution patterns differed among species, reflecting interspecific variability in PAH exposure and accumulation. *D. vulgaris* recorded the highest ΣPAHs concentration (260.32ng/ g), suggesting greater susceptibility or exposure to PAH contamination, while *L. aurata* exhibited the lowest ΣPAHs level (157.21ng/ g), likely indicating reduced pollutant uptake or residence in less contaminated habitats.

Across all species, the PAHs PHE, BbF, BaP, DBahA, and IcdP were consistently predominant, indicating a common environmental contamination source. Notably, the carcinogenic PAHs BaP, DBahA, BbF, and IcdP were markedly elevated in *D. vulgaris* and *P. erythrinus*, highlighting potential ecological risks and concerns for human consumers. Among all compounds, Indeno[1,2,3-cd]pyrene (IcdP) showed the highest accumulation, reaching 37.89ng/ g in *P. erythrinus* and 32.43ng/ g in *D. vulgaris*. *P. erythrinus* also displayed particularly high levels of ANY and IcdP**.**

Table 1. Biochemical composition and biological characteristics (range, mean ± SD) of the fish species studied during winter 2024

Species Parameter	*L. aurata*	*D. vulgaris*	*L. mormyrus*	*P. erythrinus*
Weight (g)	155-168 (160±0.35)	26-28 (25.02±0.22)	35-38 (36.14±0.12)	30.04-31.25 (30.34±0.02)
Length (cm)	25-28 (25±0.15)	16.17 -18.11 (17.00±0.24)	16-20 (17±0.23)	19.41-20.35 19.82±0.12)
Moisture (%)	73.71-75.24 (73±0.27)	78.54-79.23 (79.01±0.12)	75.32-77.8 (76.12±0.30)	70.52-72.33 (71.14±0.04)
Ash (%)	1.87- 2.06 (1.92±0.22)	2.11-2.28 (2.17±0.14)	1.64-1.75 (1.69±0.07)	2.11-2.44 (2.14±0.15)
Protein (%)	18.21-19.45 (18.72±0.17)	17.37-17.11 (17.22±0.09)	17.55-17.92 (17.32±0.09)	20.1-21.08 (20.64±0.32)
Lipids (%)	3.68-4.55 (3.85±0.32)	1.03 - 1.21 (1.12±0.10)	1.42 - 1.63 (1. 52±0.05)	1.55 - 1.75 (1.62±0.08)

*Number of samples for each species (n: 10).

Fig. (4) illustrates the percentage contributions of individual PAHs to total ΣPAHs in the muscle tissues of the four species, revealing clear species-specific accumulation profiles. High-molecular-weight (HMW) and carcinogenic PAHs including IcdP**,** DBahA, BbF, and PYR were dominant in *D. vulgaris* and *P.erythrinus*, together with contributing more than 50% of their total PAH burden. This pattern suggests substantial exposure to pyrogenic sources, likely linked to combustion emissions, industrial effluents, and contaminated sediments in Tobruk Bay.

In contrast, *L. aurata* and *L. mormyrus* exhibited a more balanced distribution, characterized by higher proportions of low-molecular-weight (LMW) PAHs such as Naphthalene (NAP), indicating mixed petrogenic and pyrogenic sources. Overall, these findings emphasize the potential ecological and human-health implications associated with the bioaccumulation of carcinogenic PAHs in commercially important fish species inhabiting polluted coastal environments.

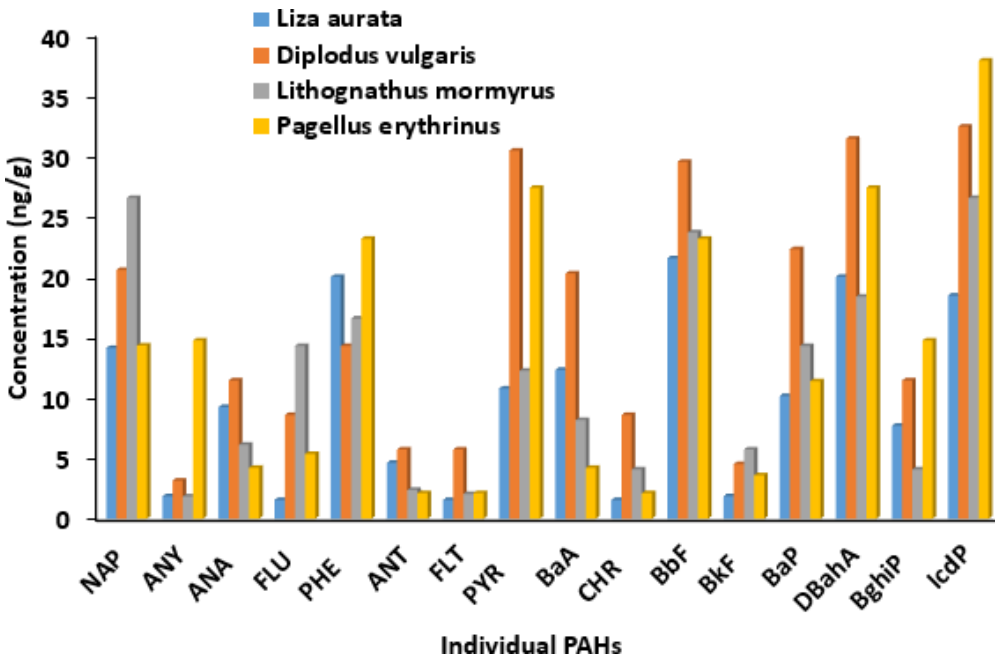

Fig. 3. Concentration of individual PAHs in tissues of fish species (ng/g wet weight)

Table 2. Mean concentration of individual PAHs in fish tissues species (ng/g; wet weight ± standard deviation, n=10)

PAHs	Concentration (ng/g ± SD)			
	L. aurata	*D. vulgaris*	*L. mormyrus*	*P. erythrinus*
NAP	14.12±0.12	20.57±0.78	26.53±4.23	14.32±2.58
ANY	1.85±0.14	3.14±0.25	1.84±0.05	14.74±2.52
ANA	9.23±0.07	11.43±2.63	6.12±0.12	4.21±1.23
FLU	1.54±0.09	8.57±0.13	14.29±0.89	5.36±1.22
PHE	20±0.12	14.29±1.15	16.55±2.48	23.16±2.42
ANT	4.62±0.04	5.71±0.52	2.38±0.22	2.11±0.23
FLT	1.54±0.18	5.71±0.43	2.04±0.13	2.11±0.11
PYR	10.77±0.11	30.44±2.36	12.24±1.45	27.37±0.87
BaA	12.31±0.13	20.27±3.59	8.16±1.54	4.21±0.21
CHR	1.54±0.20	8.57±1.54	4.08±0.81	2.11±0.08
BbF	21.540.15	29.52±4.36	23.68±2.53	23.16±2.58
BkF	1.85±0.23	4.52±0.08	5.71±1.05	3.58±1.22
BaP	10.15±0.41	22.29±2.36	14.29±2.08	11.37±3.45
DBahA	20±0.35	31.43±7.02	18.37±5.12	27.37±4.39
BghiP	7.69±0.23	11.43±0.52	4.08±1.09	14.74±3.85
IcdP	18.46±0.56	32.43±0.47	26.53±3.66	37.89±4.39
ΣPAHs	157.21±13.56	260.32±24.32	186.89±15.22	217.81±36.16

SD = Standrd Diviation ; naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), 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), and indeno[1,2,3-cd]pyrene (IcdP).

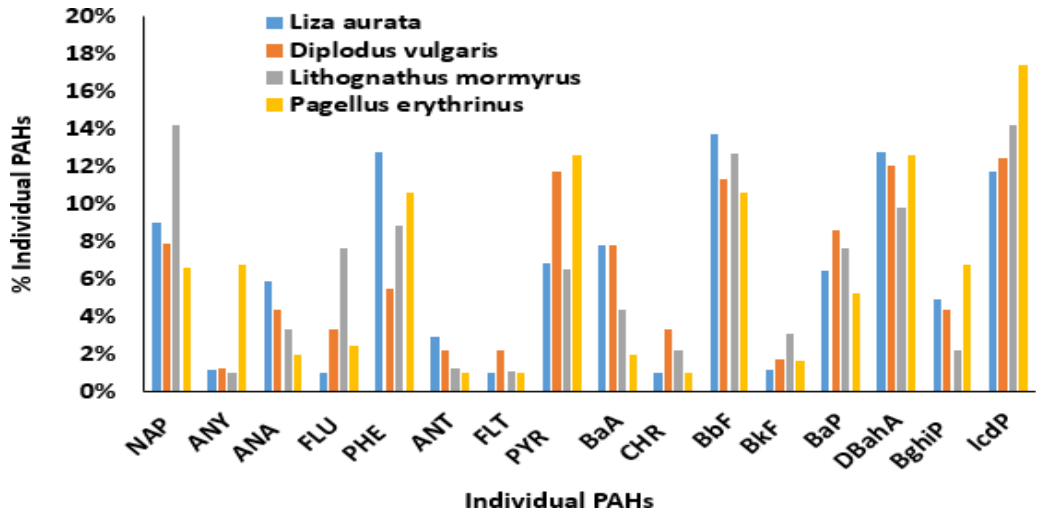

Fig. 4. Percentage contribution of each individual PAH to ΣPAHs (Total PAHs)

Number of PAHs rings)

The distribution of PAHs by aromatic ring number varied among the four examined fish species (Fig. 5). Overall, 5-ring PAHs dominated the profiles, contributing 30.06% to 34.06% of total PAHs. *L. aurata* exhibited the highest proportion (34.06%), followed closely by *D. vulgaris* (33.71%) and *L. mormyrus* (33.20%), highlighting a strong accumulation of high-molecular-weight PAHs in these species.

P. erythrinus showed the greatest proportion of 6-ring PAHs (24.16%), suggesting notable accumulation of the most persistent and carcinogenic PAH classes. In contrast, 2-ring PAHs were the least represented in all species, ranging from 6.57% in *P. erythrinus* to 14.20% in *L. mormyrus* (Table 3). These differences reflect species-specific PAH bioaccumulation patterns, likely associated with variations in habitat use, feeding strategies, and metabolic detoxification capacities.

Table 3. Percentage contribution of PAHs by number of aromatic rings (2–6 rings) in four fish species

Type of PAHs ring	*L. aurata*	*D. vulgaris*	*L. mormyrus*	*P. erythrinus*
2-ring	10.32	12.44	14.20	6.57
3-ring	18.11	17.32	19.45	16.28
4-ring	25.51	23.88	21.90	22.03
5-ring	34.06	33.71	33.20	30.96
6-ring	12.00	12.65	11.25	24.16

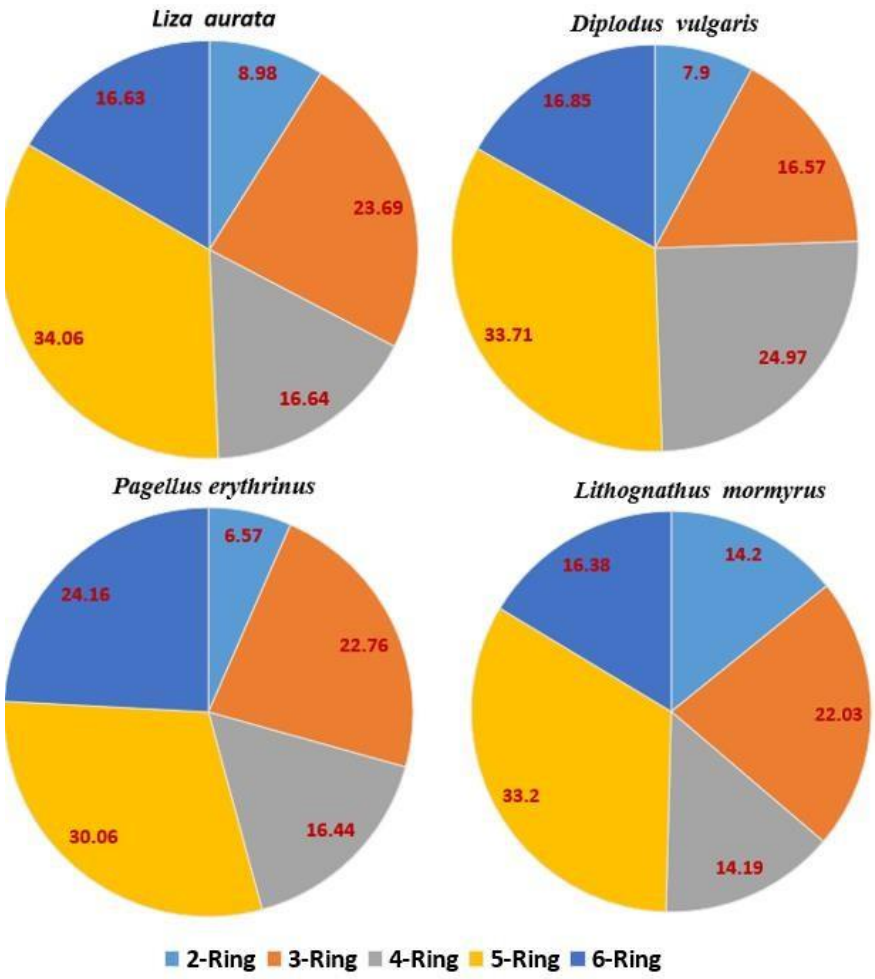

Fig. 5. Distribution of different PAHs ring structures in four fish species collected from the Gulf of Tobruk during the winter of 2024

Table (4) shows comparison of PAHs concentrations in fish from different surrounding regions. The concentrations measured in the present study were generally higher than those reported in several previous studies, including those from Suez Bay, the Bizerte Lagoon, Lake Togo Lagoon, Iraqi marine waters, the Persian Gulf, Hong Kong, and the Gulf of Guinea. However, they remained far lower than the exceptionally elevated levels documented by **Younis *et al.* (2018)** for fish from Suez Bay.

Table 4. Comparison of total PAH concentrations in fish and shellfish from different regions

Species / Sample Type	PAH Concentration (ng/g wet weight)	Notes	References
Four commercial fish species, Gulf of Tobruk	*157.21–260.32*	Moderate levels	Present study (2024)
Fish species, Suez Bay (Egypt)	*0.92–26.32*	Much lower than present study	Kottb *et al*., 2019
Mussels & fish, Bizerte Lagoon (Tunisia)	*9.41–14.42* (avg. 12.27)	Lower than present study	Barhoumi *et al*., 2016
Fish, Lake Togo–Lagoon (Togo)	*5.24–48.40* (avg. 14.51)	Lower	Ouro-Sama *et al*., 2023
Aquatic species, Iraqi marine waters	*50*	Lower	Al-Khion, 2018
Fish, Persian Gulf	*118*	Lower	Bastami *et al*., 2013
Marine fish, Hong Kong	*15*	Lower	Cheung *et al*., 2013
Fish, Gulf of Guinea	*165*	Lower–moderate	Bandowe *et al*., 2013
11 fish species, Suez Bay	*621–4207*	Much higher than present study	Younis *et al*., 2018
fish species, Suez Bay (Egypt)	*136.23-3087.9*	Higher than present study	Soliman *et al*., 2023
fish species, Catania Gulf (Sicily, Italy)	*0.25- 6.10*	Much lower than present study	Bua *et al*., 2021
muscles fish species Augusta Bay (Southern Italy)	9-21.7	Much lower than present study	Traina *et al*. (2021)
fish species, Marsa Matruh (Egypt	17-35	Much lower than present study	Said *et al*., 2023

Human health risk

PAH4 index in fish muscle

The PAH4 index, defined as the sum of benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and benzo[a]pyrene, is widely used as a marker of carcinogenic PAH exposure in seafood safety assessments (**Yang *et al.*, 2024**). The calculated PAH4 concentrations were 45.54µg/ kg in *L. aurata*, 80.65µg/ kg in *D. vulgaris*, 50.21µg/ kg in *L. mormyrus*, and 40.85µg/ kg in *P. erythrinus* (Table 5). All species exceeded the **European Union (2014)** maximum limit of 30ng/ g, indicating potential carcinogenic risks from regular consumption.

Among the species, *D. vulgaris* displayed the highest PAH4 burden, more than twice the regulatory limit, while *P. erythrinus* showed the lowest but still exceeded the threshold. Fig. (6) compares the PAH4 levels of the four species with the EU safety standard, further underscoring the dietary health risk.

Table 5. PAH4 Index ng/g, in the muscles of some fish species collected from Tobruk Bay

PAHs	*L. aurata*	*D. vulgaris*	*L. mormyrus*	*P. erythrinus*
BaA	12.31	20.27	8.16	4.21
CHR	1.54	8.57	4.08	2.11
BbF	21.54	29.52	23.68	23.16
BaP	10.15	22.29	14.29	11.37
PAH4 Index	45.54	80.65	50.21	40.85

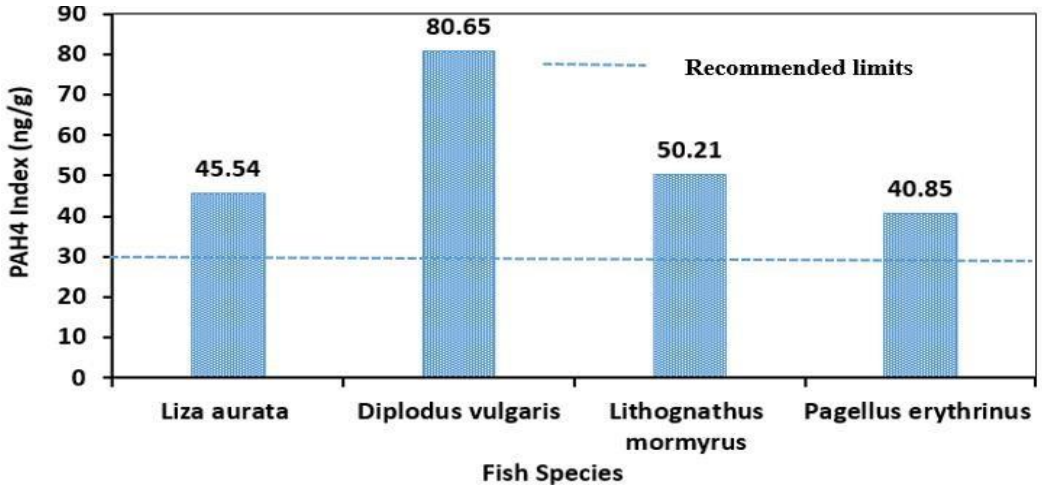

Fig. 6. PAH4 Index in Fish Species (ng/g)

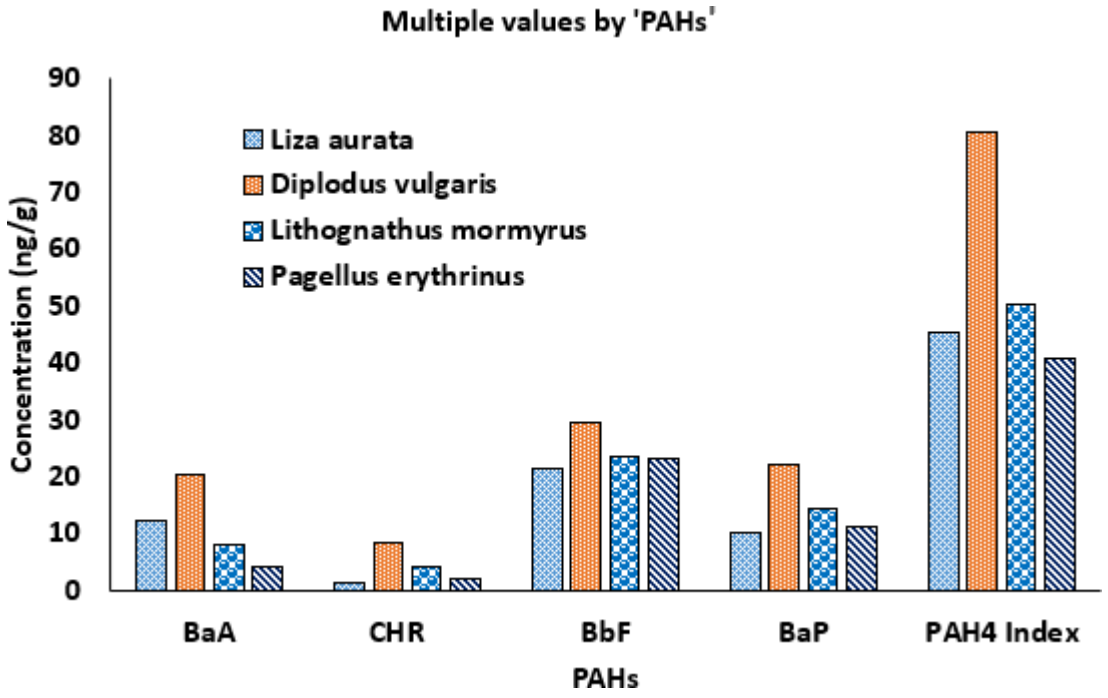

Fig. 7. Concentrations of BaA, CHR, BbF, BaP, and the PAH4 index in four fish species from the Gulf of Tobruk during winter 2024

The concentrations of key carcinogenic PAHs (BaA, CHR, BbF, and BaP) and the PAH4 index varied noticeably among the four fish species (Fig. 7). *D. vulgaris* recorded the highest levels of most PAH compounds, reflected in its elevated PAH4 index, indicating greater exposure to carcinogenic PAHs. *P. erythrinus* and *L. mormyrus* showed moderate concentrations, with similar patterns for BbF and BaP. In contrast, *L. aurata* exhibited the lowest value across all measured PAHs, suggesting reduced contamination or lower bioaccumulation potential. These differences highlight species-specific PAH accumulation influenced by habitat and behavior.

Carcinogenic potency (TEQ BaP) in fish muscle (ng/g*)*

The carcinogenic potencies of PAHs in fish muscle were evaluated using the toxic equivalency factor (TEF) method, which expresses toxicity relative to benzo[a]pyrene (BaP, TEF = 1). The TEFs applied (**Nisbet & LaGoy, 1992; WHO, 1998)** were: BaA (0.1), CHR (0.01), BbF (0.1), BkF (0.1), BaP (1.0), DBahA (1.0), BghiP (0.01), and IcdP (0.1).

As shown in Table (6), most individual PAH toxic equivalents (TEQ BaP) were below the recommended limit of 5.0ng/ g for fish muscle **(Tongo *et al.*, 2017; Guo *et al.*, 2022)**. However, BaP (10.15– 22.29ng/ g) and DBahA (18.37– 31.43ng/ g) consistently exceeded this threshold across all species. Consequently, total TEQ BaP values were 2–6 times higher than the permissible limit, ranging from 35.76µg/ kg in *L. aurata* to 62.75µg/

kg in *D. vulgaris*, with intermediate values in *L. mormyrus* (39.25µg/ kg) and *P. erythrinus* (45.90µg/ kg). These results indicate that *D. vulgaris* and *P. erythrinus* may present comparatively higher carcinogenic risks to consumers due to their elevated TEQ BaP levels.

Table 6. Individual TEQ BaP (ng/g) in fish species muscles off the Gulf of Tobruk

PAHs	*L. aurata*	*D. vulgaris*	*L. mormyrus*	*P, erythrinus*
BaA	1.231	2.027	0.816	0.421
CHR	0.0154	0.0857	0.0408	0.0211
BbF	2.154	2.952	2.368	2.316
BkF	0.185	0.452	0.571	0.358
BaP	10.15	22.29	14.29	11.37
DBahA	20.0	31.43	18.37	27.37
BghiP	0.0769	0.1143	0.0408	0.1474
IcdP	1.846	3.243	2.653	3.789
TEQ BaP (ng/g)	35.76	62.75	39.25	45.90

Dietary exposure to carcinogenic PAHs in fish

The daily dietary intake (DDI) of carcinogenic PAHs, expressed as benzo[a]pyrene toxic equivalents (TEQ BaP), was estimated for four fish species and compared with the **EFSA (2008)** safety threshold of 2.5ng/ kg body weight/day (Table 7 & Fig.7).

The DDI was calculated as:

$$\mathbf{DDI\ (ng/day) = C \times IR}$$

$$\boldsymbol{DDI\ (ng/kg\ bw/day) = (C \times IR)/BW}$$

Where, *C* is the PAH concentration (ng/g); *IR* the ingestion rate (100g/ day for adults); and *BW* the consumer's body weight (70kg). All four species exceeded the EFSA limit by 20–35 times. The highest value was observed in *D. vulgaris* (89.64ng/ kg bw/day), followed by *P. erythrinus* (65.57), *L. mormyrus* (56.07), and *L. aurata* (51.09). These results indicate a considerable carcinogenic risk from daily consumption, particularly with frequent or long-term intake. They underscore the need for strict monitoring and control of PAH contamination in commercially important fish from Tobruk Bay. (Sources and parameter justifications: Libya per-capita fish consumption 21.4kg yr^{-1}; child ingestion reference 16g/ day; EPA RfD for BaP = 3.0×10^{-4} mg/kg-day.) **(Thuraya *et al.*, 2020)**.

Table 7. Comparison of BaP-equivalent PAH DDI and MOE values at a 100g/ day fish intake relative to the EFSA benchmark of 2.5 ng/kg/day (**EFSA, 2008**)

Fish Species	TEQ $_{BaP}$ (ng/g)	DDI (ng/day)	DDI (ng/kg/day)	EFSA Limit (2.5 ng/kg/day)	Status	MOE	Risk Status
L. aurata	35.76	3576	51.09	> 2.5	Exceeds	1,370	Health concern
D. vulgaris	62.75	6275	89.64	> 2.5	Exceeds	781	Health concern
L. mormyrus	39.25	3925	56.07	> 2.5	Exceeds	1,248	Health concern
P. erythrinus	45.9	4590	65.57	> 2.5	Exceeds	1,068	Health concern

Margin of Exposure: MOE Value ≥10,000 Low concern for public health, MOE Value <10,000 Possible health concern – further action needed.

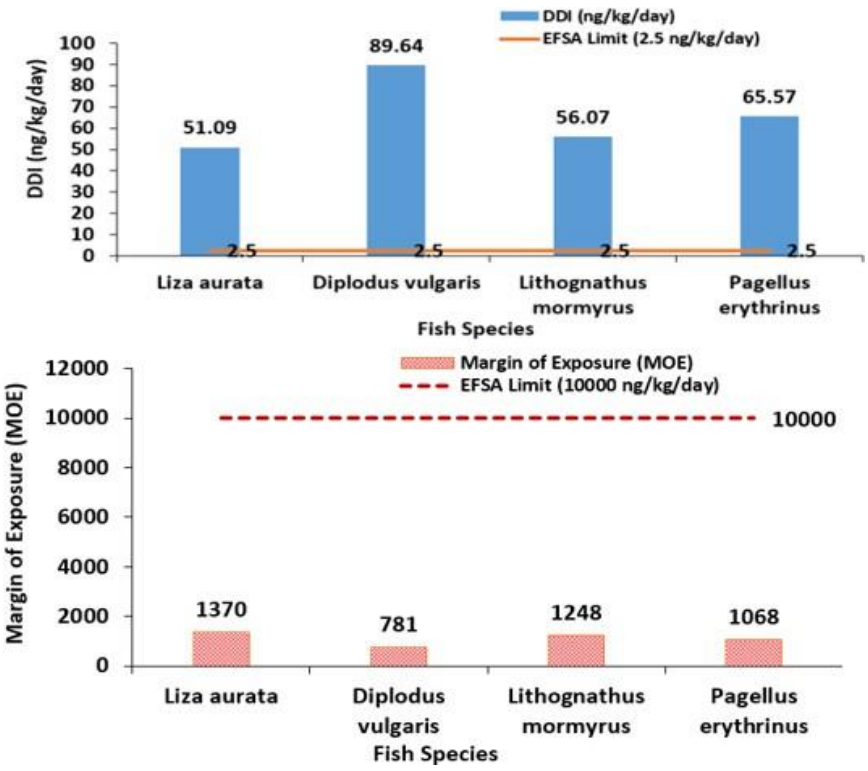

Fig. 8. Comparison of DDI as BaP toxic equivalents) and MOE with the EFSA limit for carcinogenic PAHs in fish species

Risk characterization using MOE

The carcinogenic risk from PAH exposure was further assessed using the Margin of Exposure (MOE) approach, as recommended by EFSA and JECFA for benzo[a]pyrene (BaP) and PAH mixtures. The MOE is defined as:

$$MOE = BMDL_{10} / Estimated\ Exposure\ (ng/kg/day)$$

Where, $BMDL_{10}$ represents the benchmark dose lower confidence limit for a 10% increased cancer risk. EFSA applies a $BMDL_{10}$ of 70,000 ng/kg bw/day for BaP.

As shown in Fig. (8), the calculated MOE values were 1,370 for *L. aurata*, 781 for *D. vulgaris*, 1,248 for *L. mormyrus*, and 1,068 for *P. erythrinus*. All values are well below the EFSA reference level of 10,000, indicating a potential carcinogenic risk, particularly under daily consumption of 100 g of fish **(EFSA, 2008)**.

These findings reinforce the DDI results, highlighting that PAH contamination in fish from Tobruk Bay poses a significant health concern and warrants urgent monitoring and mitigation measures.

Together, the DDI and MOE results highlight the significant dietary risk posed by PAH contamination in fish from Tobruk Bay and underline the need for continuous monitoring, stricter pollution control, and consumer protection measures. Comparable international assessments, such as those by the US EPA and WHO, also regard MOEs below 10,000 as a concern, reinforcing the global public health relevance of these findings.

Dietary exposure and non-carcinogenic health risk assessment

The non-carcinogenic health risks associated with PAH exposure through fish consumption were assessed using standard USEPA equations. Concentrations of 16 PAHs in fish muscle (ng g^{-1} Wet weight) were converted to mg kg^{-1} for risk calculation. The estimated daily intake (EDI, mg kg^{-1} day^{-1}) was determined as:

$$EDI = C \times IR / BW$$

Where, C is the PAH concentration (mg kg^{-1}), IR is the daily fish ingestion rate (0.0586 kg day^{-1} for adults; 0.016kg day^{-1} for children), and BW is body weight (70kg for adults; 15 kg for children). The target hazard quotient (THQ) was calculated for benzo[a]pyrene (BaP) as:

$$THQ = EDI_{BaP} / RfD_{BaP}$$

using an oral reference dose (RfD) of 3.0×10^{-4} mg kg^{-1} day^{-1} **(USEPA, 2017;USEPA, 2023)**. Values of THQ < 1 indicate no significant non-carcinogenic risk.

Mean ΣPAH concentrations ranged from 157.21ng g^{-1} dw in *L. aurata* to 260.32ng g^{-1} dw in *D. vulgaris*, with phenanthrene, pyrene, and dibenz[a,h]anthracene as the dominant compounds. Estimated EDI values for BaP were 8.5×10^{-6} – 1.9×10^{-5} mg kg^{-1} day^{-1} for adults and 1.1×10^{-5} – 2.4×10^{-5} mg kg^{-1} day^{-1} for children. Corresponding THQs for BaP ranged from 0.028–0.062 (adults) and 0.036–0.079 (children), all below unity (Table 8), indicating no appreciable non-carcinogenic health risk from BaP exposure through fish consumption in Tobruk Bay. ΣPAH-based EDI values were higher but are

presented only for comparison, as mixture toxicity assessment requires either individual RfDs or conversion to BaP-equivalents (BaP-TEQ). All THQ (BaP) estimates for adults are ≈ 0.028–0.062 (<< 1). All THQ (BaP) estimates for children are ≈ 0.036–0.079 (<< 1). under the stated assumptions (Wet-weight concentrations, IRs and BWs used), neither adult nor children show non-carcinogenic risk from BaP alone (THQ < 1). Children have higher EDI per kg and therefore somewhat higher THQs, but still below 1.

Table 8. EDI and THQ for BaP and ΣPAHs in fish species from Tobruk Bay, Libya

species	BaP (ng/g, dw)	ΣPAHs (ng/g, dw)	Adult EDI BaP (mg/kg-day)	Adult THQ (BaP)	Adult EDI ΣPAHs (mg/kg-day)	Child EDI BaP (mg/kg-day)	Child THQ (BaP)	Child EDI ΣPAHs (mg/kg-day)
L. aurata	10.15	157.21	8.50×10^{-6}	0.028	1.32×10^{-4}	1.08×10^{-5}	0.036	1.68×10^{-4}
D. vulgaris	22.29	260.32	1.87×10^{-5}	0.062	2.18×10^{-4}	2.38×10^{-5}	0.079	2.78×10^{-4}
L. mormyrus	14.29	186.89	1.20×10^{-5}	0.04	1.57×10^{-4}	1.52×10^{-5}	0.051	1.99×10^{-4}
P. erythrinus	11.37	217.81	9.52×10^{-6}	0.032	1.82×10^{-4}	1.21×10^{-5}	0.04	2.32×10^{-4}

CONCLUSION

All species show notable levels of carcinogenic PAHs, with species variation likely linked to feeding behavior, habitat, and trophic level. The findings highlight potential bioaccumulation of toxic PAHs in fish and the risk to human consumers, stressing the need for continuous monitoring and regulatory actions

This study investigates the contamination of four fish species (*Liza aurata*, *Diplodus vulgaris*, *Lithognathus mormyrus*, and *Pagellus erythrinus*) with PAHs in Tobruk Bay. Concentrations of carcinogenic PAHs, especially IPY, DBA, and BbF, were highest in *Diplodus vulgaris* and *Pagellus erythrinus*, indicating pyrogenic origins such as industrial activity and combustion. The PAH4 index in these species exceeded recommended safety thresholds, suggesting significant bioaccumulation and posing a potential human health risk through fish consumption. The data underscore the importance of continuous environmental monitoring and food safety regulation in coastal Libya.

1. In *Liza aurata*, the dominant PAHs were Benzo[b]fluoranthene (BbF) (~13.7%), Phenanthrene (PHE) and Dibenzo [a, h] anthracene (DBA) (both ~12.7%), and Indeno[1,2,3-cd] pyrene (IPY) (~11.7%). The balanced profile with moderate HMW

contributions indicates chronic exposure to mixed petrogenic and pyrogenic sources at relatively low levels.

2. In *Diplodus vulgaris*, Indeno[1,2,3-cd] pyrene (IPY) (~12.5%), Dibenzo [a, h] anthracene (DBA) (~12.1%), Pyrene (PYR) (~11.7%), and Benzo[b]fluoranthene (BbF) (~11.4%) predominated. Carcinogenic HMW PAHs dominated, reflecting strong exposure to combustion-related inputs, likely through bioaccumulation or contact with polluted sediments.

3. In *Lithognathus mormyrus*, Indeno[1,2,3-cd] pyrene (IPY) and Naphthalene (NAP) (both ~14.2%), BbF (~12.7%), and DBA (~9.8%) were most abundant. The mix of LMW (NAP) and HMW carcinogens suggests combined petroleum and combustion sources.

4. In *Pagellus erythrinus*, Indeno[1,2,3-cd] pyrene (IPY) (~17.4%), DBA and PYR (both ~12.6%), and PHE and BbF (both ~10.6%) dominated. The strong prevalence of carcinogenic HMW PAHs points to substantial pyrogenic contamination, likely from industrial or port-related activities.

Overall, the elevated DI and low MOE values demonstrate that PAH contamination in Tobruk Bay fish poses a clear carcinogenic risk to consumers. These findings, together with evidence of industrial discharges, port activities, and municipal inputs as major pollution sources, emphasize the urgent need for integrated coastal management strategies to reduce PAH emissions and safeguard both marine ecosystems and public health.

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