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Ecological Assessment of Polycyclic Aromatic Hydrocarbons in Water, Sediment, and Fish in the Suez Bay, Egypt, and Related Human Health Risk Assessment

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LEVELS of some polynuclear aromatic hydrocarbons (PAHs) were determined in water, sediment, and different organs of three commercial fish species (*Teraponputa*, *Rastrelliger kanagurta*, and *Nemipterus japonicus*) collected from the northern part of the Gulf of Suez. Pyrene (Pyr) was found to be the dominant PAH in water, sediment, and edible parts of fish species. Different indices were used to detect the PAH sources. Low ratio (low/high molecular weight) PAHs were observed in all samples, suggesting pyrogenic sources for water, sediment, and fish. However, other indexes that depend on the components ratios of the same molecular weight suggested petrogenic sources. PAH concentrations in water samples from sites in front of the Attaqa Electric Power and Petroleum Pipelines Company exceeded the maximum permissible concentration according to the European Union. In contrast, in sediment samples, only the Green Island site had high Pyrene concentrations (above effects range-low and below effects range-median) that may have mild undesirable biological effects. Based on the human health risk assessment, the high lifetime cancer risk values were higher than the threshold value (10^{-4}) suggested by the USEPA. the results declared the potential risk due to the consumption of studied fish for populations around the study area.

Keywords: Human health risk, Petrogenic sources, Polycyclic aromatic hydrocarbons, Pyrogenic, Suez Bay.

Introduction

PAHs are a class of compounds containing two aromatic rings or more. They are classified into low (LMW) and high molecular weight (HMW) compounds. LMW PAHs consist of two to three combined rings and HMW contains four to six rings (Kuppusamy et al., 2020). LMW compounds predominate in petrogenic sources, whereas HMW compounds that often originate from combustion are of pyrogenic sources (Bandowe et al., 2014; Saleh et al., 2021). The major sources of PAHs into marine environment are through oil spills from ship activities and incomplete combustion of fuel,in addition to biogenic sources such as bacteria, algae, and other aquatic organisms (Effiong et al., 2016; Belahmadi et al., 2021). High hydrophobic nature of these compounds made them be adsorbed on sediment particles and are more available to accumulate in biota (Moraleda-Cibrian et al., 2015; Nwaichi & Ntorgbo, 2016). However, any chemical change in the chemistry of sediments may release these compounds into the water column (Zhang et al., 2012; Ihunwo et al., 2021). The composition of PAHs in sediments may be indicative to their source. The USEPA (1993) classified 16 PAHs (Table 1), as dangerous pollutants in terms of toxicity.

Carcinogenic (CAR) polycyclic aromatic hydrocarbons (PAHs) include DBA,BaA,Chr, BbF,InP, BkF, Pyr, and BaP (USEPA, 1993).Thus, Identification of PAHs concentrations in the muscles may be helpful in estimation of possible

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risks associated with fish consumption (Barhoumi et al., 2016; Diop et al., 2017; Oliva et al., 2017). Suez Gulf is economically an important area for fishing. The expansion in different industries in Suez bay e.g; refineries of El-Nasr and Suez petroleum companies, fertilizer plant, power station, textile company caused the northern part of Suez Gulf to be polluted by their wastes in addition to ship activities in ports (El Nemr, 2013). The purpose of this paper is to infer to the level of the 16PAHs in water, sediment, and commercial fish of Suez Bay investigating their possible origin(s) based on their compositions, and assess the potential human health risk of some fish species in Suez Bay.

Experimental

Study area

Given that it serves as Egypt's crucial eastern gateway to the outside world, the Gulf of Suez and Red Sea is an important maritime region for Egypt. It symbolizes the left arm of the Red Sea that divides Egypt's Arabian Desert from Saudi Arabia's Sinai Peninsula. The Gulf of Suez stretches for around 280 km from its mouth at the Strait of Jubal to Suez City, and it is between 19 and 43 Km wide. Gulf water depths range from 16 m south of Suez Bay to 50–85m toward the open Gulf. The Suez Canal, a crucial route for international trade, is where the Gulf of Suez derives its significance. The SuezGulf can be regionally divided into two regions:the north part known as Suez Bay and the rest area of the Gulf known as the south part. Suez Bay is located between longitude 32°28′ and 32°34′ latitude 29°54′E and 29°75′N (El-Sikaily et al., 2005; Ibrahim et al., 2019). A shallow extension of the Gulf, Suez Bay has a primary axis that runs from northeast to southwest and is somewhat twisted in shape. There are several sources of pollution surrounding the bay; such as El-Zaitiyat (oil and gas tankers), Al-Adabiya and El-Sokhna goods, Attaqa (fishing), and Suez Bay harbors (cargo and passenger hunch) (GARSP, 2017; Elgendy et al., 2018; Tageo Geographic Database, 2018). Water samples were collected from outfalls of some factories (El-Zaitiyat, Elkabanon, Textile Egypt Iran Company, Suez Company for Fertilizer, sewage treatment plant, Al-Adabyia industrial treatment plant, and Sumed Pipeline Company Terminals) and analyzed for PAHs. The concentration values are reported in Annex1.

TABLE 1. Abbreviationof PAHcompounds and their TEF values (USEPA, 2011)

Compound name (IUPAC)	Abbreviation	No. of rings	Classes	Molecular formula	Source	TEF
Naphthalene	Naph	2	LMW	$C_{10}H_8$	Petro	0.001
Acenaphthylene	Acthy	3	LMW	$C_{12}H_8$	Petro	0.001
Acenaphthene	Ace	3	LMW	$C_{12}H_8$	Petro	0.001
Fluorene	F1	3	LMW	$C_{13}H_{10}$	Petro	0.001
Phenanthrene	Phe	3	LMW	$C_{14}H_{10}$	Petro	0.001
Anthracene	Ant	3	LMW	$C_{14}H_{10}$	Petro	0.01
Fluoranthene	Flu	4	HMW	$C_{16}H_{10}$	Petro	0.001
Pyrene	Pyr	4	HMW	$C_{16}H_{10}$	Petro	0.001
Benzo[a]anthracene	BaA	4	HMW	$C_{18}H_{12}$	Petro	0.1
Chrysene	Chry	4	HMW	$C_{18}H_{12}$	Petro	0.01
Benzo[b]Fluoranthene	BbF	5	HMW	$C_{20}H_{12}$	Pyro	0.1
Benzo[k] Fluoranthene	BkF	5	HMW	$C_{20}H_{12}$	Pyro	0.1
Benzo[a]Pyrene	BaP	5	HMW	$C_{20}H_{12}$	Pyro	1
Dibenzo[ah]anthracene	DBA	5	HMW	$C_{22}H_{14}$	Pyro	5
Benzo(ghi)perylene	BghiP	6	HMW	$C_{22}H_{12}$	Pyro	0.01
Indeno(1,2,3-cd)pyrene	InP	6	HMW	$C_{22}H_{12}$	Pyro	0.1

BaA, Chry, BbF and BkF are ++ carcinogenic and BaP, DBA and InP are +++ carcinogenic, petro: petrogenic and pyro:pyrolytic

Sampling

Seasonal samples of water were collected from 11 locations in the northern part of the Suez Gulf during 2017 (Fig. 1; Table 2). Three fish species (*Terapon puta, Rastrelliger kanagurta*, and *Nemipterus japonicus*) were collected from Suez Bay during winter and summer 2017. Ten fish were chosen indiscriminately from each species. Fish samples were individually wrapped in previously hexane-cleaned aluminum foil immediately after transport to the laboratory and then cleaned with distilled water. For analysis, the homogenized edible muscles, gills, and liver were extracted and kept in the refrigerator. In winter 2017, the upper 5cm of sediment samples were collected using Ekman Grab and stored at −20°C until analysis

Fig. 1.Map of the sampling sites of the study area

TABLE 2. Sampling sites in the Suez Bay

Site		Latitude	Longitude
1	El-Zaitiyat	32 32 44.6 N	29 57 12.5 E
2	Thermal Power Company	32 30 25.6 N	29 56 54.6 E
3	Textile Egypt Eran Company	32 29 27.9 N	29 56 27.9 E
4	Suez Company for Fertilizer	32 29 03.3 N	29 56 12.6 E
5	Attaka Power Station	32 28 06.3 N	29 56 48.0 E
6	Attaka Port	32 28 33 N	29 55 08.2 E
7	Al-Adabiya Effluent	32 28 21.4 N	29 53 52.5 E
8	AAl-Adabiya	32 28 44.1 N	29 53 39.6 E
9	Green Island	32 32 18.1 N	29 55 04.2 E
10	Petroleum pipeline company	32 26 56.0 N	29 47 26.0 E
11	Ain Sukhna	32 21 44.0 N	29 36 38.0 E

Sample preparation and methodology

PAHs in water were determined using the methods described by Parsons et al. (1985). The extraction of water samples was done twice with 60mL dichloromethane using a separating funnel,as the same manner distilled water was used as a blank. Anhydrous sodium sulphate was added to 10g of air-dried sediment samples, and the mixture was mixed at high speed for 5min before being extracted by 200mL methylene chloride in a Soxhlet extractor for ~8h (UNEP/ IOC/IAEA, 1992). For fish, 10g (mixed samples) were homogenized with 10g Na_2SO_4 for 5min . The homogenized samples were Soxhlet extracted using 200mL CH_2Cl_2 for 8h. Extracted Na_2SO_4 was used as a blank for sediment and fish samples.

At a low temperature (40°C), all samples were first concentrated to a few milliliters using a rotary evaporator, then, using a nitrogen stream, the samples were further concentrated to 1mL. Elimination of the samples using a silica/aluminum oxide column (10g silica, and 1g Na_2SO_4, and 10g Al_2O_3,) was used for sample cleaning and fractionation. All solutions underwent a 10-minute ultrasonic degassing procedure before being injected into the gas chromatography apparatus Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector). The injection port was kept at 290°C, and the detector was kept at 300°C while the instrument was run in splitless mode (5-L splitless injection). The samples were examined using a 100% dimethyl polysiloxane (30m length, 0.32mm i.d., and 0.17m film thickness) fused-silica capillary column HP-1. The oven's temperature was set to rise from 60°C to 290°C at a rate of 3°C per minute, and it was kept there for 25min. Nitrogen was the carrier gas, flowing at 1.2mL/min. To produce a series of calibration standards with a minimum detection limit of 0.12ng/mL, PAH compounds were quantified by dilution using a stock solution.

Analytical quality control

On all data, quality control methods were used. PAHs were measured using external standards, and calibration curves and correlation coefficients both exceeded 0.990. The USA National Institute of Standards and Technology provided the SRM 2974 PAHs mixed standard (purity > 99%). The average recovery for the 16 PAHs was between 74 and 112%, with most (RSD) values falling under 14%. The instrumental limit of detection (LOD) for a single PAH is 3 times the standard deviation of eight duplicate tests on spiked seawater samples. Blanks were examined after every five samples, and LODs were calculated using blank experiments that were run. The detection limits were 0.01g/L for naph, ace, f1, ant, flu, and phen, 0.02g/L for acthy, BaA, and BbF, and BaP, and 0.03g/L for BbF, pyr, InP, Chr, BghiP, and DBA.

Human health risk

The potential cancer risk due to the consumption of analyzes fish from the study area was tested using several indices including individual PAH carcinogenic potencies, the PAH_4 index, carcinogenic toxic equivalents (TEQs) in fish,and lifetime cancer risk (LCR) index. PAH_4 index is a more suitable indicator of PAHs in food (EFSA, 2008). PAH4 was evaluated as the sum of four different PAHs;BaA, Chr, BbF, and BaPusing Eq. (1).PAH4 index is acceptable until 30µg/kg in muscles (Eu, 2014).

$$PAH4\ Index = [BaA + Chr + BbF + BaP] \quad \textbf{Eq. 1}$$

The carcinogenic potencies of each PAH (B[a] Pteq) were calculated by Eq. (2):

$$B(a)Pteq = Ci \times TEFi \quad \textbf{Eq.2}$$

where C_i is the concentration of individual PAH in fish(ng/g) and The TEF compares the relative toxicity of individual PAH fractions compared to BaP (Nisbet & LaGoy, 1992). The TEFs values are presented in Table 2.Total Carcinogenic TEQs were then obtained by Eq. (3) (Ding & Zeng, 2012).

$$TEQs = \sum B(a)Pteq \quad \textbf{Eq. 3}$$

Daily intake (DI)

DI was calculated for individual PAH, ∑PAHs, and ∑ CAR PAHs according to Eq. (4 and 5):

$$DI = B(a)Pteq \times FC \quad \textbf{Eq. 4}$$

$$Total\ DI = \sum DI \quad \textbf{Eq. 5}$$

LCR

LCR is calculated by the following equation (Eq.6):

$$\mathbf{LCR} = \frac{DI \times ED \times EF \times CF \times SFB}{BM \times AT} \quad \textbf{Eq. 6}$$

where DI is the daily intake of PAHs via consumption of fish (ng/g), ED is exposure duration (years), EF is exposure frequency (days/ year), BM is the average body mass (70kg), AT is

the average time (days), and CF is the conversion factor (10^{-6} kg/mg). The cancer-causing ability of B[a]P was used to determinetheoral slope factor. The oral slope factor for BaP was 4.5, 5.9, 9.0, and 11.7, with a geometric mean of 7.3mg/kg/day (USEPA, 2001).

Results and Discussion

Water

∑PAHs varied from 2ng/L at Ain Sukhna during summer to 1007.47ng/L at Attaqa Electric Power during winter. ∑PAHs concentrations in Attaqa Electric Power and Petroleum Pipelines Company were higher than the acceptable concentrations (200ng/L) according to the European Union (EU) (Fig. 2). Table 2 indicates the abbreviation of each PAH in addition to the number of aromatic rings, molecular formula and weight, and level of carcinogenicity. Table 3 illustrates the seasonal range of each PAH (ng/L). These results were less than the range recorded of Alexandria's coastal seawater (13.4–6076ng/L) by El-Naggar et al. (2018). Our results detected low ratios of $\sum LPAH/HPAH$ (Table 3), which might be due to low number of aromatic rings that make them more volatile and lower stable in water (Ali et al., 2006; Obayori & Salam, 2010). Seasonally, $\sum_{16}$ PAHs recorded the highest value during the winter season due to low temperature values that decreased degradation and volatility and high emission sources and spreading of pollutants due to climate conditions (wind, current, and rain),whereas the lowest value was recorded during spring (Fig. 3). This seasonal variation agreed with seasonal variation of PAHs in Suez Gulf investigated by Kottb et al. (2019). The sitein front of Attaqa Electric Power (S 8) recorded the highest annual mean value of PAHs (476.22ng/L), and the lowest was at Site (S 3) opposite to Textile Egypt Iran Company(27.14ng/L).

The level of PAHs in this study was compared with some previous studies in Egypt and around the world in Table 4. Pyr was found to be the highest abundant hydrocarbon, followed by Chr and Flu, in this study suggesting the petroleum contamination by existing oil refineries in the study area. Flu and Pyr may be formed from the condensation of low aromatic rings of PAHs at elevated temperatures (Na et al., 2021). This also may be due to increasing hydrophobicity and decreasing biodegradation of HMW compounds (Ghandourah, 2022). This explains the cause of the low dominance of LMW PAHs (Fig. 4), such as Naph, Ace, and Fl, which are more soluble and degradable (Helfinalis et al., 2021). El-Naggar et al. (2021) detected higher levels of ∑PAHs of Red Sea Coast at marina Marsa Alam (about 54.47µg/L) which may be due to tourism activities in Marsa Alam area, followed by Safaga shipyard of (about 51.52µg/L) then Abou Tartour harbour, Safaga (48.18µg/L) and finally fishermen valley, safaga (31.82µg/L) that was near oil company, Ras Gharieb. CAR PAHs (BbF, BaA, InP, BaP, BghiP, BkF, DBA, and Chr) are eight PAHs typically considered as possible carcinogens. ∑CAR varied from 6.20 ng/L at Ain Sukhna to 200.55ng/L at the Petroleum Pipeline Companywith the highest percentage (95.51%) at AttakaPort (Table 3). The major combustion specific compounds (COMB) are BkF, Pyr, Flu, BbF, BaA, InP, BaP, BghiP, and Chr. %∑COMB/∑PAHs varied from 60.11% at El-Zaitiyat to 98.48% at the Petroleum Pipeline Company.

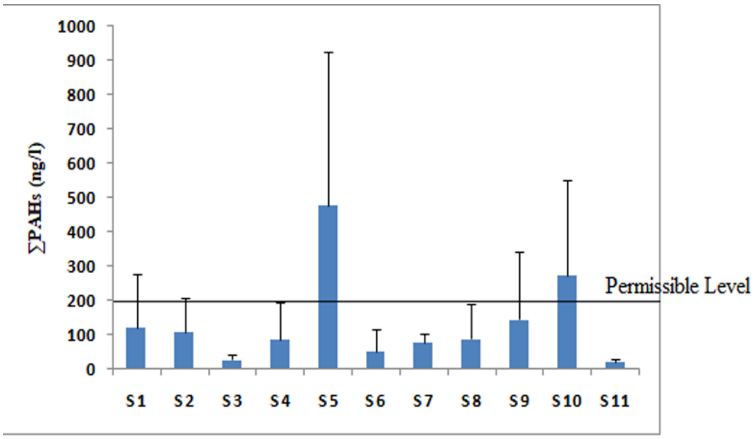

Fig. 2. Distribution of Annual mean concentration of PAHs (ng/L) in water samples of the Northern Part of Suez Gulf

TABLE 3. The range of PAH concentrations in water samples seasonally and sediments in Suez Bay during 2017

	Water (ng/L)				Sediment (ng/g dry wt)
	Winter	Spring	Summer	Autumn	
Naph	Nd-92.09	Nd-0.18	Nd-3.94	Nd-3.23	Nd-0.15
Ace	Nd-36.64	Nd-0.21	Nd-1.346	Nd-0.15	Nd-0.14
Acthy	Nd-28.21	Nd-0	Nd-0.62	Nd-0.15	Nd-1.62
F1	Nd-50.72	Nd-0.13	Nd-0.624	Nd-0.48	Nd-0.23
Phen	Nd-129.17	Nd-0.13	Nd-0.457	Nd-0.18	Nd-0.74
Ant	Nd-83.88	Nd-0.17	Nd0.3132	Nd-0.15	Nd-0.45
∑LPAHs	0.12-420.71	0.1-0.53	0.125.49	0.12-3.23	0.12-2.49
Flu	Nd-351.02	Nd-3.32	Nd-9.54	Nd-21.77	Nd-7.2
Pyr	Nd-90.17	Nd-8.84	Nd-173.84	Nd-173.84	Nd-841.11
BaA	Nd-43.12	Nd-0.97	Nd-10.57	Nd-8.86	2.2-26.66
Chr	Nd-53.53	Nd-0	Nd-308.54	Nd-8.96	3.4-95.88
BbF	Nd-12.32	Nd-0.64	Nd-41.28	Nd-2.87	Nd-2.09
BkF	Nd-67.57	Nd-0	Nd-41.28	Nd-4.71	Nd-26.7
BaP	Nd-51.78	Nd-0.15	Nd-22.5	Nd-3.46	0.12-0.79
InP	Nd-123.83	Nd-1.71	Nd-5.77	Nd-3.07	2.41-30.41
DBA	Nd-38.59	Nd-2.38	Nd-12.385	Nd-12.39	6.8-16.82
BghiP	Nd-80.62	Nd-0.7	Nd-29.065	Nd-0.49	Nd-38.55
∑HPAHs	6.98-586.76	3.3-12.16	2.6-564.42	1.88-19.16	8.93-981.5
∑PAHs	7.11-1007.47	3.91-12.6	2.80-569.91	2-190.63	9.1-981.99
∑COMB	5.99-580.65	1.57-12.16	2.6-562.76	1.88-177.77	8.798-971.74
%∑COMB	55.32-97.23	38.55-97.07	85.49-99.61	60.33-98.97	71.8-98.96
∑CARC	0-189.13	0-3.94	0-437.02	0-18.38	6.71-379.99
%∑CARC	0-99.75	0-97.05	0-99.61	0-95.9	14.05-97.39

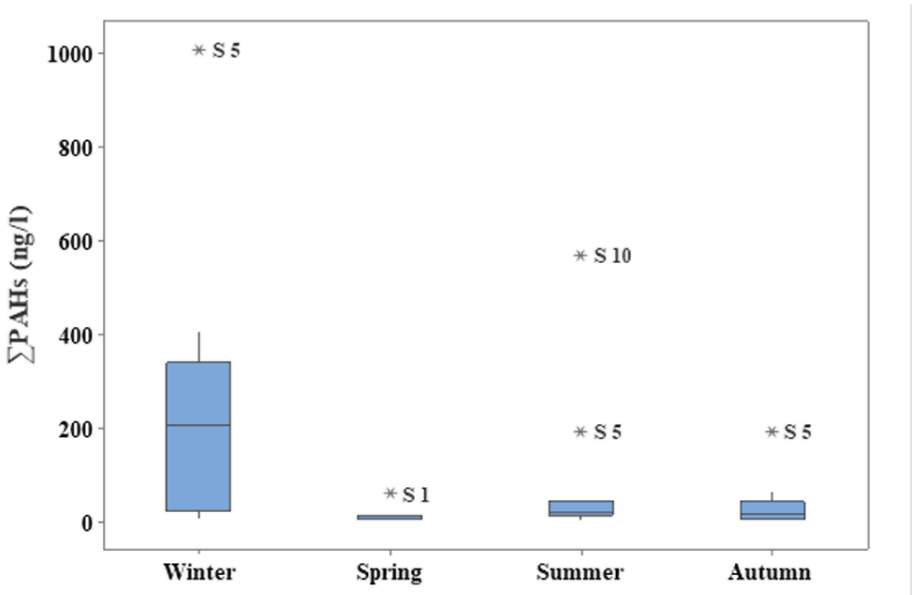

Fig. 3. Boxplot indicating Seasonal variations of PAHs in water samples of the study area

TABLE 4. Comparison of the present levels of PAHs in water with some previous studies

Location	Water (µg/L)	Reference
Suez Bay, Egypt	0.02-1.007	The present study
Suez Gulf, Egypt	0.002-0.025	Kottb et al. (2019)
Suez Gulf, Egypt	0.71–39.14	Emara et al. (2013)
Coastal Area of Suez Gulf, Egypt	0.013–205.40	Farid et al. (2015)
Suez Canal, Egypt	.012-0.5	Al-Agroudy et al. (2017)
Red Sea Coast	0.21-54.47	El-Naggar et al. (2021)
Red sea Coast	0.4–96.45	Said & Hamed (2006)
Persian Gulf, Iran	0.07–0.884	Jafarabadi et al. (2017)
North Atlantic Ocean and the Arctic Ocean	0.0003–0.0102	Liu et al. (2022)
Bahía Blanca Estuary, Argentina	ND–4.00	Arias et al. (2009)
Deep Bay, South China	0.025-0.069	Qiu et al. (2009)

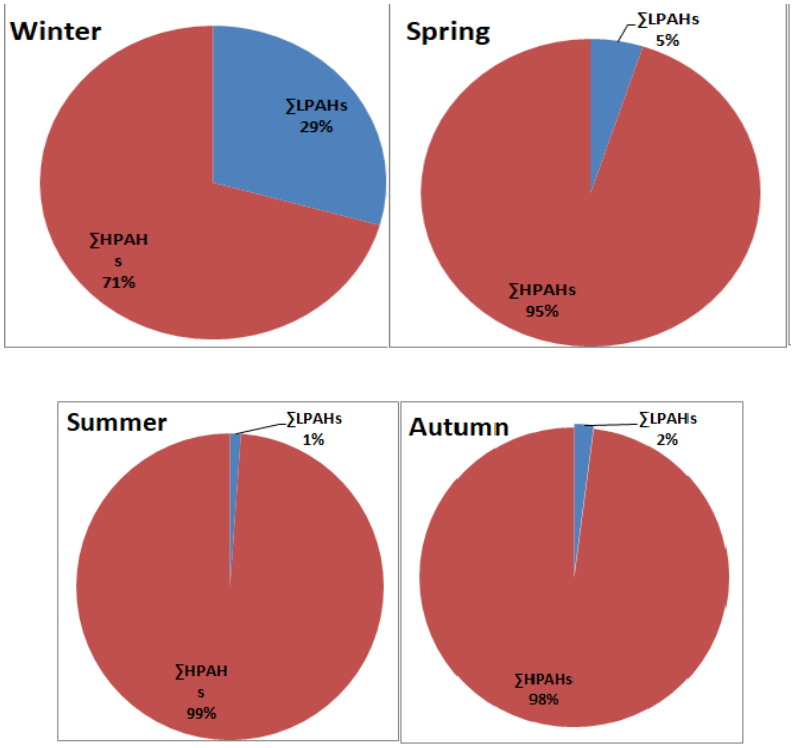

Fig. 4. Pie Chart illustrating the proportion of LPAHs and HPAHs in different seasons of the study area

Sediment

∑PAH concentrations fluctuated between 9.1 and 981.99ng/g in sediment samples (dry weight) of Suez Bay, with an average of 253.86 ng/g dry weight. The highest level of ∑PAHs was observed in Green Island (981.99ng/g) and El-Zaitiyat (839.17ng/g), whereas the lowest concentration was detected in Suez Company for Fertilizer (9.1ng/g). Pyr was the maximum dominant compound in the studied area, followed by Chr and B[a]A. ∑COMB ranged from 8.79to 971.74ng/gdry weight (Table 3). %∑COMB/∑PAHs ranged from 71.8% to 98.96% in the studied area.∑CAR fluctuated between 6.71 to 379.99 ng/g, with maximum %∑CAR of 97.39% at the Petroleum Pipeline Company. The relative pollution level of PAHs in sediment samples may be in low level with concentrations varying from (0–100ng/g), moderate level (100–1000ng/g), high level (1000–5000 ng/g),and very high level (>5000ng/g) of ∑PAH concentrations (Baumard et al., 1998; Bongiorno et al., 2022). Following this scale, the present study was slightly polluted in most stations, whereas El-Zaitiyat, Attaka Power Station, Al-Adabiya Effluent, and Green Island

were moderately Polluted. This contamination level agreed with that mentioned by Kottb et al. (2019) of Suez Bay and Salem et al. (2014) of the Red Sea. The range of ∑PAHs in this study was compared with some previous studies in Table 5.

Fish

The liver represented the maximum PAHs levels (on average) in *T. puta* and *R. kanagurta***,** while *N. japonicus* had the maximum content of PAHs (on average) in the muscles in the different fish species (Table 6). Where the levels of PAHs in the selected fish were (213.39 and 3087.9, 158.89 and 928.8, and 136.23 and 599.38ng/g wet weight) for the edible part, (539.01 and 2902.25,108.96 and 1318.92, and166.24 and 84.55ng/g wet)for the liver, and (859.51 and 893.47,58.7 and 581.08, and80.54and 22.34ng/g wet weight) for gills, in *T. puta*, *R. kanagurta*, and *N. japonicas* during winter and summer, respectively. Maximum level was at *T. puta*, and minimum was at *N. japonicus.* Summer represented the highest seasonal mean concentrations of PAHs in muscles, gills, and liver (Table 6). This study presented higher levels than those observed (0.92–26.32ng/g wet weight) by Kottb et al. (2019) of some fish species of Suez Bay but still lower than that recorded of 11fish species in Suez Bay (621–4207ng/g wet weight) by Younis et al. (2018). Pyr was the highly dominant PAH in muscles and gills of investigated species, followed by Chr and BaA, whereasliver showed the highest abundant concentration of Chr, followed by BaA. Chr and BaA are of petrogenic sources and are (++) strongly carcinogenic, showing the risk expected by these carcinogenic compounds (Omokpariola et al., 2022). The maximum ∑CAR was at the liver of *T. puta*, with a concentration of 2194.3ng/g wet weight. However, the highest CARPAH percentage (%∑CAR = 83.64%) was in liver of *N. japonicas*. For muscles, the highest %∑CAR was 69.95% at *N. japonicus* during summer. %∑COMB range from 85.84% to 99.59%, and ∑COMB concentrations were between 21.54 and 3069.02ng/g wet weight; high%∑COMB/∑PAHs was recorded in fish samples in this study.

Source identificationof PAHs

LMW PAHs predominate in a petrogenic source of PAHs (derived from petroleum) whereas pyrogenic PAHs have HMWs (Pouch et al., 2021). We found high presence of LMW PAHs in water during the winter season, whereas, in hot seasons, HMWPAHs (C4>C5 >C6) are dominant, which may be due to higher temperature, effect of photooxidation, volatilization, and bacterial degradation of light compounds. This study agreed with El-Naggar et al. (2018) that inferred to high occurrence of HMW PAHs of water samples collected from the coastal area of Alexandria.

In sediments, %C4 represented the highest abundant percentage in most stations due to high Pyr, BaA, and Chr concentrations. Only Suez Company for Fertilizer and Petroleum Pipeline Company showed the highest C5 abundance, indicating high BaP concentrations in these stations (Fig. 5).

TABLE 5. Comparison of the present levels of PAHs in sediment with some previous studies

Location	∑PAHs (µg/kg) dry weight	Reference
Suez Bay, Egypt	9.1-981.10	The present study
Suez Gulf, Egypt	1667.02-2671.27	Younis et al. (2018).
Suez Gulf, Egypt	19-97	Salem et al. (2014)
Aqaba Gulf, Egypt	0.37–0.74	Salem et al. (2014)
Red Sea Coast, Egypt	0.3-0.57	Salem et al. (2014)
Abu Qir Bay, Egypt	Nd-2.66	Khairy et al. (2009)
Rijeka Bay area, Croatia USA	0.032–13.681	Alebic-Juretic (2011)
Deep Bay, China	184.1–581.5	Qiu et al. (2007)
Masan Bay, Korea	207–2670	Yim et al. (2005)
Hsin-ta Harbour, Taiwan	1156–3382	Fang et al. (2003)
Boston Harbour, USA	7266–358,092	Wang et al. (2001)
Aquitaine Bay, France	3.5–853	Soclo et al. (2000)
Santander Bay, Spanish	20–344,600	Viguri et al. (2002)

TABLE 6. PAH concentrations (ng/g wet weight) in organs of different fish species collected from Suez Bay during winter and summer 2017

Sp.	*Terapon Puta*						*Rastrelliger kanagurta*						*Nemipterus japonicus*					
	Muscle		Gills		Liver		Muscle		Gills		Liver		Muscle		Gills		Liver	
Season / Parameter	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
Naph	Nd	Nd	N.D	Nd	Nd	Nd	Nd	1.31	0.38	0.28	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Ace	Nd	0.38	0.17	Nd	Nd	6.23	Nd	Nd	0.13	0.95	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.25
Acthy	Nd	0.25	Nd	Nd	0.25	0.57	Nd	Nd	0.45	1.02	Nd	Nd	Nd	Nd	Nd	0.12	Nd	Nd
F1	0.12	0.12	Nd	0.45	0.19	Nd	0.13	0.3	0.15	Nd	Nd	Nd	Nd	0.12	0.13	0.13	Nd	0.17
Phe	Nd	Nd	0.12	Nd	0.2	1.42	Nd	0.38	0.16	Nd	0.14	Nd	0.14	0	Nd	Nd	0.14	0.31
Ant	0.17	0.57	0.13	0.82	0.73	3.61	0.58	0.18	Nd	0.16	0.12	Nd	Nd	Nd	Nd	0.11	0.12	0.28
Fluo	1.57	91.37	31.18	8.34	11.88	148.91	15.4	9.81	2.59	4.66	0.21	4.13	9.95	Nd	Nd	2.23	Nd	3.67
Pyr	138.86	1427.8	590.96	408.33	416.82	547.17	642.03	35.76	9.84	114.93	88.26	664.82	456.4	64.37	48.55	1.09	102.02	9.15
BaA	17.54	759.26	25.04	92.09	1.09	85.37	15.14	19.67	3.28	136.91	2.31	Nd	0.67	10.17	14.41	1.52	45.59	4.41
Chr	22.36	729.21	130.2	304.04	40.27	2054.7	190.81	78.12	22.08	305.24	14.16	596.12	86.33	42.37	11.08	16.3	2.24	29.04
BbF	2.21	30.81	1.28	5.79	1.07	4.09	4.65	6.19	1.86	Nd	0.55	3.66	0.12	Nd	Nd	Nd	1.3	2.34
BkF	3.44	19.31	5.58	11.61	3.65	12.76	6.75	1.4	2.56	2.79	0.12	12.61	5.17	1.01	1.67	Nd	0.46	1.06
BaP	0.36	1.61	0.54	0.66	0.33	25.73	0.51	0.34	0.13	0.15	0.21	0.13	0.29	0.16	0.25	0.03	0.13	0.17
InP	12.3	9.63	32.44	24.37	20.02	2.22	14.91	1.98	4.48	6.94	1.18	17.42	10.98	0.99	1.88	0.23	6.66	10.27
BghiP	4.09	Nd	10.48	9.44	14.87	9.47	12.82	1.26	3.57	1.98	0.12	5.28	6.75	0.51	0.88	0.12	2.28	13.96
DBA	10.37	17.58	31.39	27.53	27.64	Nd	25.07	2.19	7.04	5.07	1.58	14.63	22.58	16.53	1.69	0.44	5.3	9.47
∑ PAHs	213.39	3087.9	859.51	893.47	539.01	2902.25	928.8	158.89	58.7	581.08	108.96	1318.92	599.38	136.23	80.54	22.34	166.24	84.55
∑ COMB	202.74	3069.02	827.71	864.67	510	2890.38	903.01	154.53	50.4	573.6	107.12	1304.17	576.66	119.57	78.72	21.54	160.68	74.07
%COMB	95.01	99.39	96.3	96.78	94.62	99.59	97.22	97.25	85.84	98.71	98.32	98.88	96.21	87.78	97.74	96.39	96.65	87.6
∑CAR	72.68	1567.42	236.95	475.53	108.94	2194.3	270.65	111.15	45	459.08	20.22	649.85	132.89	71.73	31.86	18.67	63.96	70.71
%CAR	34.06	50.76	27.57	53.22	20.21	75.61	29.14	69.95	76.65	79	18.56	49.27	22.17	52.66	39.56	83.55	38.48	83.64

W: winter; S: summer

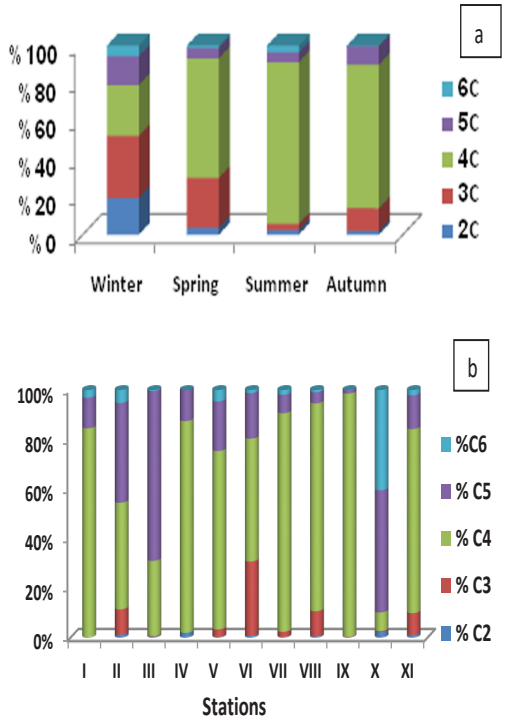

Fig. 5.Characterization of PAH sources in (a) water and (b) sediment of the Suez Bay during 2017

Different indices were used in our study to detect possible source of PAHs e.g; Flu/PyrPhen/Ant, Ant/(Phen+Ant), Flu/(Flu + Pyr) and BaA/(BaA + Chry) (Soclo et al., 2000; Magi et al., 2002; Yunker et al., 2002; Qiao et al., 2006; Stern et al., 2023) (7).

In water samples, most sites showed a Flu/Pyr ratio <1, suggesting petrogenic inputs, whereas Textile Egypt Iran Company, Suez Company for Fertilizer, Green Island, and Ain Sukhna showed values >1, indicating combustion sources at these sites. Most sites had BaA/(BaA+Chr) ratio more than 0.35, indicating pyrogenic inputs. Phen/Ant varied from 0.58 to 4.67 (10<) at all sites, indicating a pyrolytic source, except the thermal electric company that had Phen/Ant (81.17) >10, indicating petroleum contamination in this site. Calculating the mean values of these indices indicated mixed sources of pollution (Table 7). Liu et al. (2022) investigated the the levels of PAHs in surface water of the North Atlantic Ocean and the Arctic Ocean and detected vehicle emissions and biomass combustion as the major sources of contamination by PAHs.

In sediments, the Phen/Ant ratio lower than 10wasrecorded in all sites, indicating a pyrolytic source. Ant/(Ant +Phen) ratios in most sites were >0.1, indicating combustion sources, butThermalPower Company, Suez Company for Fertilizer, Attaka Power Station, and Green Island indicated petroleum contamination(Ant/(Ant+Phen)=0].The Flu/Pyr ratio 1< at all sites indicated petroleum contamination. The Flu/(Flu+Pyr) ratio for most sites was<0.4, indicating petroleum contamination. Only Thermal Power Company and Attaka Port recorded Flu/(Flu+Pyr) between 0.4 and 0.5, which detected mixed sources of pollution. Calculating the mean values of these indices indicated also mixed sources of pollution.

In fish species, the Phen/Ant index varied from 0 to 2.07 (<10), indicating a pyrolytic source in all organs of all species during winter and summer (Table 7). The Ant/(Phen+Ant) index was higher than 0.1 in most samples, indicating a pyrolytic source. As Flu/(Pyr+Flu) ratios were mostly <0.4, Flu/Pyr1< and BaA/(BaA + Chr)<0.35 at most samples, PAHs in fish may be from petroleum contamination.

Sediment Quality Guidelines

We used effects range-low (ERL) and effects range-median (ERM) to infer to the possible ecological risks of investigated PAHs (Li et al., 2012). All samples had individual concentrations lower than ERL (Table 8) with the exception of Pyr in Green Island and thus the present study was in low level of Risk except Green Island that needed a continuous monitoring to avoid increasing levels of Pyr than ERM.

Human health risk

DI

The estimated DI (ng/g/day) values for ΣPAHs in the assessed fish were6737.24, 4211.21, and 5722.85 for *T. puta*, *R. kanagurta*, and *N. japonicus*, respectively (Table 9), whereas the DI (ng/g/day) values for total CAR PAHs were 6689.71, 4190.90, and 5707.71 for *T. puta*, *R. kanagurta*, and*N. japonicus*, respectively (Table 4). The DI of total and carcinogenic PAHs was the highest in *T. puta*. These results indicated that the consumption of *T. puta*may expose humans to a greater hazard

of PAHs, especially CAR PAHs.

Carcinogenic risk

PAH4 index

The PAH4 indices were 866, 96, and 26 µg/kg for *T. puta*, *R. kanagurta*, and *N. japonicus*, respectively (Table 9). Both *T. puta* and *R. kanagurta* exceeded the recommended limits of the PAH4 index (30µg/kg) referred by the EU, suggesting possibility of cancer risk for consumers.

Carcinogenic potency

Individual carcinogenic Potency (BaPteq) values in fish muscles were lower than the acceptable level of BaP in fish (0.005mg/kg; (Guo et al., 22022; Tongo et al., 2017). DBA had the highest carcinogenic potency in all species and exceeded the maximum acceptable level at all species. BaA exceeded the maximum acceptable level for *T. puta*. The total carcinogenic potency (TEQs) in the fish species were 118.2, 73.88, and 100.40 ng/g in *T. puta*, *R. kanagurta*, and *N. japonicus*, respectively. The results indicated that *T. puta may cause*a higher risk for consumers than the other species.

LCR

LCR may be acceptable of 1 in a 1,000,000 (LCR = 10^{-6}), whereas a 10^{-4} value for LCR or more is in a serious level over 70 years (USEPA, 2001). In this study, LCR values in all fish species were 0.00070, 0.00044, and 0.00059. These results were higher than the U.S. Environmental Protection Agency threshold (10^{-4}; Table 9). This indicated that consumption of *T. puta*, *R. kanagurta*, and *N. japonicas* could result in a potential cancer risk of populations in Suez Bay.PAH concentrations (ng/L) discharged into the study area from some factories are listed in the appendix (Appendix Table 1).

Conclusion

This study discussed the concentrations and different PAHs sources in water, sediment, and some fish species collected from Suez Bay. The sources classification of PAHs indicated the mixed origin (petrogenic and pyrogenic) of the analyzed hydrocarbons in the water and sediment samples, while PAHs in fish were mainly derived from petrogenic sources. PAHs concentrations varied from 2ng/L at Ain Sukhna to 1007.47ng/L at Attaqa Electric Power for water samples. However, water samples are generally characterized by low ratios of LPAH/HPAH, where Pyr was found to be the dominant PAH in the water samples, followed by Chr and Flu. Based on the classification scale of sediment contamination, El-Zaitiyat, Attaka Power Station, Al-Adabiya Effluent, and Green Island were moderately contaminated, where PAHs varied between 9.1 and 981.99ng/g dry weight the maximum level at Green Island. According to sediment quality guidelines protocol, Green Island site had Pyr concentrations higher than ERL, which may cause mild adverse biological effects. On the other hand, in theedible part of different fish species, PAHs contents were in the ranges of 136.22 to 3087.92ng/g w/w and in the order of *T. puta>R.kanagurta>N. jponicus*. Indices of Carcinogenic risk assessment showed that LCR values in all fish species were higher than the USEPA threshold indicating the potential cancer risk due to the consumption of commercial *T. puta*, *R. kanagurta*, and *N. japonicas* caught from the Suez Bay.

TABLE 7. Index ratios of petrogenic and pyrogenic sources in water, sediment, and fish of the Suez Bay

Index	Petrogenic	Pyrogenic	Mixed sources	Water	Sediment	Edible part of Fish
Flu/Pyr	< 1	> 1		0-1.84 (0.6)	0-0.85 (0.188)	0-2.05 (0.195)
Phen/Ant	> 10	< 10		0.58-81.17 (1.36)	0-4.73 (0.889)	0-2.07 (0.392)
Ant/(Phen+Ant)	<0.1	> 0.1		0.012-0.64 (0.412)	0-1 (0.392)	0-1 (0.54)
Flu/(Flu+Pyr)	< 0.4	> 0.5	0.4-0.5	0.04-1 (0.375)	0-0.46 (0.121)	0-0.67 (0.103)
BaA/(BaA + Chry)	<0.2	>0.35	0.2-0.35	0-0.548 (0.327)	0.025-0.848 (0.386)	0-0.95 (0.233)

TABLE 8. Comparison of PAH levels in surface sediments (ng/g dry weight) with ERL and ERM values (Liu et al., 2009)

Compound	ERL	ERM	This study				
			Mean	Minimium	Maximium	>ERL	<ERM
Naph	160	2100	0.03	Nd	0.15	-	-
Ace	16	500	0.06	Nd	1.62	-	-
Acthy	44	640	0.23	Nd	0.15	-	-
F1	19	540	0.14	Nd	0.38		-
Phe	240	1500	0.19	Nd	0.71	-	-
Ant	853	1100	0.13	Nd	0.26	-	-
Fluo	800	5100	4.18	Nd	15.63	-	-
Pyr	665	2600	142.51	Nd	841.11	Green Island	-
BaA	261	1600	20.68	Nd	83.24	-	-
Chr	384	2800	28.38	1.64	95.88	-	-
BbF	320	1880	6.81	Nd	46.25	-	-
BkF	280	1620	3.45	Nd	26.7	-	-
BaP	430	1600	0.78	Nd	3.99	-	-
DBA	63.4	260	12.53	0.14	51.52	-	-
BghiP	430	1600	11.95	Nd	38.55	-	-
InP	-	-	7.32	0.86	48.09	-	-

TABLE 9. PAH4 Index, DI and LCRof total PAHs in muscles of some fish species collected from Suez Bay

Species / Season	*Terapon puta*		*Rastrelliger kanagurta*		*Nemipterus japonicus*	
	Winter	Summer	Winter	Summer	Winter	Summer
PAH4 Index	0.042	1.52089	0.21111	0.10432	0.087	0.052
B(A)Pteq	56.16575	180.2287	132.7047	15.05716	116.2813	84.52029
DI (Σ PAHs)	3201.448	10273.04	7564.166	858.25812	6628.034	4817.657
DI (ΣCAR)	3193.34	10186.08	7526.354	855.4446	6601.444	4813.981
LCR	0.000334	0.001071	0.000789	8.95E-05	0.000691	0.000502

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التقييم البيئي للهيدروكربونات متعددة الحلقات في مياه ورواسب وأسماك خليج السويس، مصر، وتقييم المخاطر الناجمة على صحة الإنسان

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قيمت الدراسة الحالية تركيزات ومصادر بعض الهيدروكربونات متعددة الحلقات في مياه ورواسب وبعض أنواع الأسماك التي تم جمعها من خليج السويس. وأوضحت الدراسة أن مصدر الهيدروكربونات في عينات كل من المياه والرسوبيات يرجع إلى كل من المصادر البترولية والبيروجينية، في حين أن الهيدروكربونات في الأسماك كانت مشتقة بشكل أساسي من مصادر بترولية. وقد تراوحت التركيزات من 2 نانوجرام/لتر في عينات المياه امام محطه العين السخنة إلى1007.47 نانوجرام/لتر في عينات المياه امام محطة عتاقة للطاقة الكهربائية ومع ذلك، تتميز عينات المياه عموما بنسب منخفضة من المركبات الأقل وزنا إلى المركبات الأعلى وزنا، حيث وجد أن البيرين هو أعلى مركب في عينات المياه، يليه الكيريسين والفلورين، وأوضحت الدراسة أن عينات الرواسب بمحطات الزيتيات و كهرباء عتاكة ومصرف الأدبية والجزيرة الخضراء كانت متوسطة التلوث بالهيدروكربونات حيث تراوحت التركيزات بين 9.1 و981.99 نانوجرام/جرام للوزن الجاف وكانت أعلى قيمة في عينات الرواسب بموقع الجزيرة الخضراء حيث احتوى هذا الموقع على تركيزات للبيرين أعلى من الحد المسموح به عالميا مما قد يسبب آثارا بيولوجية ضارة على الكائنات التى تعيش فى القاع. ومن ناحية أخرى احتوى لحم الأسماك المختلفة (الصرع والباغة والشخرم) على تركيزات للهيدروكربونات تراوحت بين 136.22 إلى 3087.92 نانوجرام/جرام بالوزن الرطب. وطبقا لمؤشر تقييم المخاطر، فإن احتمالية إصابة الإنسان بالسرطان من تناول هذة الأنواع الأقتصادية من الأسماك بخليج السويس كانت أعلى من الحدود المسموح بها.