



Risk assessment of polycyclic aromatic hydrocarbons in a Mediterranean semi-enclosed basin affected by human activities (Abu Qir Bay, Egypt)

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ARTICLE INFO

Article history:

Received 17 January 2009

Received in revised form 18 March 2009

Accepted 20 April 2009

Available online 3 May 2009

Keywords:

PAHs

Risk assessment

Sediments

Mussels

SLERA

Mediterranean Sea

Egypt

ABSTRACT

The contamination of sediments and mussels sampled from Abu Qir Bay by polycyclic aromatic hydrocarbons (PAHs) was investigated. Concentrations of PAHs recorded in the bay sediments ranged from <MDL to 2660 $\mu\text{g}/\text{kg dw}$. In general, concentrations of PAHs in mussels were higher than their corresponding sediment concentrations reflecting their great bioavailability (242–3880 $\mu\text{g}/\text{kg dw}$). The highest concentration was observed in the western part of the bay, a location affected by intensive shipping activities. The distribution pattern of PAHs was similar for mussels and sediments, particularly for sediments characterized by high contamination level, and they were dominated by the high molecular weight PAHs (4–6-rings). Applying different PAHs ratios, it was found that PAHs originated predominantly from the pyrogenic source either from the combustion of grass, wood and coal (majority of the samples) or from petroleum combustion (harbour area). The output of a Screening Level Ecological Risk Assessment (SLERA) on the bay sediments revealed that adverse ecological effects to benthic organisms are expected to occur in only one sample, and thus PAHs are not considered as contaminants of concern in Abu Qir Bay. Also adverse health effects are not expected to occur from the consumption of the investigated mussels with respect to PAHs in Abu Qir Bay.

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1. Introduction

Estuarine sediments are one of the major sinks for PAHs in the aquatic environment [1,2]. Thus the study of sediments is an important step in mapping possible exposure pathways to various aquatic organisms, since contaminants in sediments may be bioavailable to sediment dwelling organisms.

The use of sentinel organisms (mussels and oyster) to measure the levels of bioavailable contaminants has been established by various pollution monitoring programs [3–7]. The advantage of using these sentinel organisms (biomonitors) is the ability to concentrate many organic contaminants by a factor of 10 above the ambient sea water levels and even higher than sediments, providing a direct representation of pollutants bioavailability [8]. Besides, they are resistant to a wide range of contaminant concentration [9]. In addition, mussels and indeed invertebrates have only a limited ability to metabolize organic pollutants especially PAHs and are therefore often used to monitor PAHs contamination in the marine environment [10].

Studies on the environmental status of Abu Qir Bay have concentrated mostly on simple chemical and bulk analysis of sediments such as the analysis of selected heavy metals [11–15]. Few studies on the status of PAHs along the Egyptian coast have been conducted [16]. Thus the objectives of the present investigation are to assess the occurrence and distribution of PAHs in sediments and mussels of Abu Qir Bay, to identify the origin of PAHs in the bay, and conduct an environmental risk assessment to evaluate the possibility of occurrence of adverse ecological effects to benthic species due to the exposure to PAHs concentrated in the bay sediments. The study extends to evaluate the possibility of occurrence of adverse health effects from the consumption of the mussel species based on the current ingestion rate (0.270 g day^{-1}). The mussel species investigated in the present work are edible and can be found in the Egyptian market.

2. Materials and methods

2.1. Study area

Abu Qir Bay is a semicircular shallow basin about 35 km east of Alexandria city between Abu Qir Peninsula (West) and the Rosetta branch of the Nile (East), with a shoreline extending about 50 km (Fig. 1). It lies between 30° 4'–30° 21' East and 31° 16'–31° 30' North.

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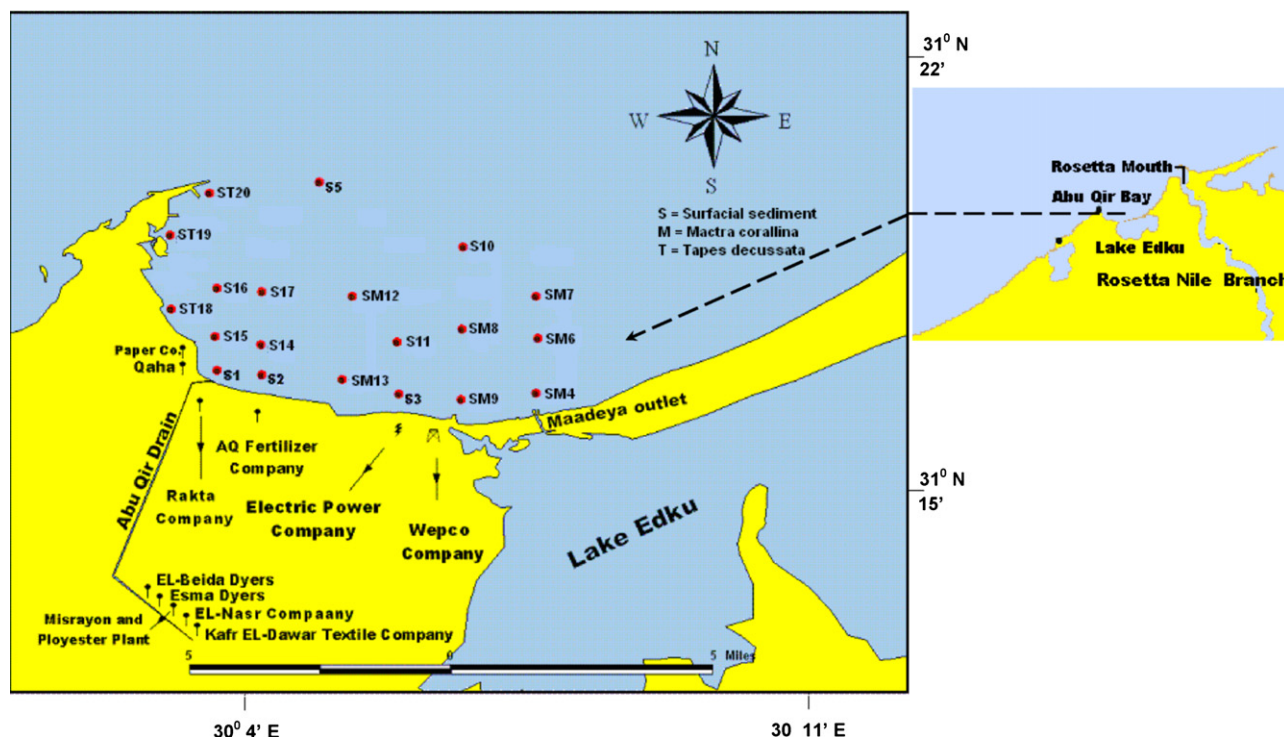


Fig. 1. Study area (Abu Qir Bay) with sampling sites.

It is relatively shallow with a depth ranging from less than 1 m along the coast, increasing gradually away from the shore to reach a maximum depth of about 15 m [17]. The bay has a surface area of 360 km² and the water volume is about 4.32 km³. Marine pollution originates from several land-based sources, mainly: Abu Qir Drain (AQD), Lake Edku and Rosetta branch of the River Nile in the eastern part of the bay (Fig. 1) [18]. AQD discharges industrial wastes from 22 different factories [11] including food processing and canning, paper industry, fertilizer industry and textile manufacturing [12]. In addition, brackish water is discharged to AQD from vast cultivated land in the north-eastern part of the Nile Delta, which is then discharged directly into the bay [13]. The bay also receives agricultural drainage water from Lake Edku through Maadeya Outlet. This is a shallow channel with an average depth of about 3 m and an average width of 20 m. The annual average of the drainage water discharged into the lake is about 1.00×10^9 m³ [12].

2.2. Sampling

In April 2006, 20 surficial sediment samples were collected from Abu Qir Bay covering the western part of the bay to Maadeya Outlet (Fig. 1). Station 5 in the northern part of the bay near the open sea, was selected as the reference site located 6 km from land-based activities. Surficial sediment samples were sampled with an Ekman grab sampler. Samples were preserved under dry ice and transferred to the laboratory, where they were stored at -20°C until processing. In addition, 10 mussel samples were collected from the bay through scuba divers (Fig. 1) representing two species: *Macra corallina* (collected from seven different locations in front of Maadeya Outlet, the Wepco Petroleum Company and between the Fertilizer Company and the Electric Power Plant) and *Tapes decussata* (collected from three different locations in the western part of the bay). Only broken shells instead of living mussels were found at all the other locations corresponding to the collected sediment samples. From each location, 30–40 specimens were collected and stored in hexane rinsed glass jars at -20°C until analysis.

2.3. Determination of the physico-chemical properties of the sediment samples

Sediment samples were oven dried at 40°C . Sediment grain size analysis was performed according to Sweet et al. [19]. Total organic carbon (TOC) was determined using DC-90 Total Organic Carbon Analyzer (Dohrmann, USA) after treating the samples with 12.5% HCl to remove the inorganic carbon fraction.

2.4. Sediment extraction and cleanup

60–70 g of each sediment sample homogenized with anhydrous Na₂SO₄ was extracted in a glass column (5 cm i.d. \times 50 cm) and each sample was eluted with 450 mL *n*-hexane/acetone (pesticide grade) (2:1, v/v) overnight according to Batarseh et al. [20]. Cleanup and fractionation procedures were performed with alumina and silica gel column chromatography according to Kolb et al. [21] with some modifications. At the first step, PAHs were eluted from the alumina column with 100 mL *n*-hexane/ethyl acetate (pesticide grade) (70:30, v/v) together with PCB and organochlorine pesticides (results of the chlorinated organic compounds are not reported here). Afterwards, the aliphatic hydrocarbons were separated from PAHs by silica gel column chromatography with 75 mL *n*-hexane (pesticide grade). Following, PAHs (F2) were eluted with 70 mL of ethyl acetate: *n*-hexane (1:1). Sulfur was removed from the eluate by using activated Cu powder. F2 was then concentrated filled up to 1 mL with *n*-hexane for GC analysis.

2.5. Mussel extraction and cleanup

Tissue samples were extracted and cleaned up according to Yunker et al. [22] with some modifications. *n*-Hexane (pesticide grade) was used instead of *n*-pentane in the original method to extract PAHs after digestion of the tissues with a mixture of methanol (HPLC grade) and 50% KOH solution.

Table 1
Concentrations of PAHs ($\mu\text{g}/\text{kg dw}$) in surficial sediments of Abu Qir Bay.

Station no.	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	InP	DibA	BghiP	\sum PAHs
1	16.5	21.4	25.8	51.8	59.1	52.9	122	66.0	44.2	41.6	25.7	20.8	24.1	<MDL	<MDL	<MDL	572
2	22.5	24.6	23.3	65.5	73.7	69.7	236	103	51.0	58.7	82.9	23.7	63.3	<MDL	<MDL	<MDL	898
3	37.4	25.8	23.4	32.1	39.6	34.4	53.1	41.9	44.2	26.0	34.2	23.6	36.0	35.3	75.3	37.1	600
4	19.9	24.6	24.9	34.9	65.0	58.7	98.1	80.7	69.9	44.9	60.8	30.6	61.4	48.1	15.7	27.8	766
5	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6	6.05	5.97	<MDL	9.75	24.4	12.0	45.5	33.1	27.3	21.0	30.4	13.2	25.2	12.6	4.33	18.1	289
7	4.18	4.91	4.04	6.21	5.78	7.07	3.93	4.76	3.10	4.21	5.92	4.56	4.44	3.34	<MDL	2.65	69.1
8	6.26	8.54	6.98	9.77	8.83	11.5	10.0	7.61	9.82	7.25	8.71	7.61	8.59	11.1	3.40	6.84	133
9	9.35	9.45	8.48	12.8	12.0	13.5	14.4	8.24	11.0	8.26	11.9	9.34	10.5	11.9	31.7	14.9	198
10	13.0	11.7	12.8	21.5	66.0	30.9	149	107	78.8	61.5	109	23.0	230	6.57	5.03	4.69	930
11	14.8	5.68	4.86	7.65	13.7	10.1	35.3	21.5	16.3	11.7	17.6	6.05	18.0	7.40	3.38	11.6	206
12	6.09	5.75	5.30	11.0	11.3	7.55	8.88	10.5	9.38	6.68	8.05	5.08	6.42	4.11	<MDL	2.85	109
13	17.1	13.0	12.6	<MDL	27.2	17.3	45.9	34.2	27.1	19.6	27.7	14.3	24.7	27.4	14.4	20.0	343
14	6.58	16.5	8.50	34.5	52.7	43.1	177	277	54.8	26.8	72.6	36.7	18.1	<MDL	<MDL	<MDL	825
15	<MDL	25.4	20.5	51.7	60.1	49.9	98.9	54.6	42.6	37.9	33.1	23.9	48.5	<MDL	<MDL	<MDL	547
16	<MDL	4.21	<MDL	6.93	7.52	6.23	12.5	6.67	8.15	7.40	9.07	6.98	6.24	3.94	8.31	<MDL	94.1
17	22.9	5.41	<MDL	10.9	36.6	11.5	55.5	36.9	31.0	20.1	31.9	11.2	24.8	11.9	9.03	8.07	331
18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20	5.17	20.1	35.6	496	470	211	357	490	185	297	28.3	35.9	29.8	<MDL	<MDL	<MDL	2660
Min	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Max	37.4	25.8	35.6	496	470	211	357	490	185	297	109	36.7	230	48.1	75.3	37.1	2660
Mean	10.4	11.7	10.8	43.1	51.7	32.4	76.2	69.1	35.7	35.0	29.9	14.8	32.0	9.19	8.53	7.73	478
SD	10.0	9.12	11.0	108	102	47.2	93.7	118	42.4	64.5	29.9	11.7	50.2	13.3	17.6	10.7	601
MDL	3.18	2.73	3.75	2.01	2.93	2.60	1.26	1.62	2.63	2.59	1.61	1.79	1.89	2.83	3.34	2.72	

<MDL = below the method detection limit; Nap = naphthalene; Acy = acenaphthylene; Ace = acenaphthene; Flr = fluorene; Phn = phenanthrene; Ant = anthracene; Fla = fluoranthene; Pyr = pyrene; BaA = benzo(a)anthracene; Chy = chrysene; BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; BaP = benzo(a)pyrene; InP = indeno[1,2,3-(c,d)]pyrene; DibA = dibenzo(a,h)anthracene; BghiP = benzo(g,h,i)perylene.

Further cleaned up of the extracts was performed with alumina column chromatography similar to the sediment samples. PAHs were eluted with 70 mL *n*-hexane. As the chlorinated organic compounds were not analysed like in sediments, elution with *n*-hexane was sufficient. The eluate was then evaporated and brought to a final volume of 1 mL. Lipid content was determined according to Qian et al. [23].

2.6. Instrumentation

The prepared samples were analysed for PAHs by a Shimadzu (GC-17A) gas chromatograph. The gas chromatograph was coupled to a Shimadzu QP 5050A mass selective detector (MSD) with electron ionization mode (EI ionization). The mass spectrometer was operated in selected ion monitoring mode (SIM). The ionization source was supplied with voltage at 70 eV. The GC was equipped with a DB-5 MS fused silica capillary column (J&W Scientific, USA) with 30 m length, 0.25 μm film thickness and 0.25 mm inner diameter. The oven temperature program was 60 °C (5 min) ramped at 10 °C/min to 300 °C, and finally holds for 10 min. The transfer line temperature was maintained at 280 °C and the carrier gas (He) flow rate was 1 mL/min.

2.7. Quality assurance

For every set of samples, a procedural blank and a standard solution consisting of all the reagents were run to check for interferences and cross-contamination. The instrument was calibrated by injection of the standard mixture at seven different concentrations to prepare the standard curve for the external calibration purposes. For checking the applied method of extraction and cleanup, spiked sediment samples were measured at two levels: 10.0 $\mu\text{g}/\text{kg dw}$ and 50.0 $\mu\text{g}/\text{kg dw}$ for sediments, and 25.0 $\mu\text{g}/\text{kg dw}$ and 100 $\mu\text{g}/\text{kg dw}$ for mussels. For each concentration, four spiked sediment samples were measured and the obtained recovery of each analyte was the average value of the four trials. Recoveries of the 16 PAHs in

these fortification experiments were in the accepted range from 70.0% to 110%. They ranged from 72.4% to 114% for sediments and from 76.6% to 116% for mussels. The method detection limits (MDLs) for the investigated organic pollutants were determined according to USEPA [24]. The MDL of PAHs ranged from the MDL of PAHs ranged from 1.26 $\mu\text{g}/\text{kg dw}$ to 3.75 $\mu\text{g}/\text{kg dw}$ for sediments (Table 1) and from 1.07 $\mu\text{g}/\text{kg dw}$ to 10.2 $\mu\text{g}/\text{kg dw}$ for mussels (Table 3). All the investigated PAHs had RSD (%) lower than 20.0% in the fortification experiment and in the replicates used to determine the MDL. All results were rounded to three significant figures.

3. Results and discussion

3.1. Spatial distribution of PAHs in sediments

Concentrations of PAHs in surficial sediments of Abu Qir Bay ranged from <MDL to 2660 $\mu\text{g}/\text{kg dw}$ with an average concentration of 478 $\mu\text{g}/\text{kg dw}$ (Table 1). The maximum concentration of PAHs was observed in station 20 at the western part of the bay, a location affected by intensive shipping activities. Contamination with PAHs in the sediments was observed all over the bay with higher concentrations recorded in the nearshore stations especially in front of the Fertilizer Company (station 2: 897 $\mu\text{g}/\text{kg dw}$ and station 14: 825 $\mu\text{g}/\text{kg dw}$), Abu Qir Drain (station 1: 572 $\mu\text{g}/\text{kg dw}$), in front of Maadeya Outlet (station 4: 766 $\mu\text{g}/\text{kg dw}$) and in front of the Electric Power Plant (station 3: 600 $\mu\text{g}/\text{kg dw}$). PAHs concentrations were generally lower in the remote stations (stations 5, 6, 7, 8, 9, 11, 12, 13, 16 and 15). An exception was station 10, which showed an elevated concentration of PAHs (930 $\mu\text{g}/\text{kg dw}$). Insignificant correlation was observed between PAHs concentrations and TOC% ($r = 0.18$; $p < 0.05$) in sediments of Abu Qir Bay.

High temperature combustion processes emit the high molecular weight PAHs (HMWPAH), which is represented by PAHs with 4 or more rings [25]. Concentrations of 4–6-rings PAHs typical for combustion (Fla + Pyr + BaA + Chy + BbF + BkF + BaP + InP + DibA + BghiP)

Table 2
Molecular indices of PAHs, TOC and clay content in surficial sediments of Abu Qir Bay.

Sample no.	\sum PAHs _{combust}	\sum PAHs _{toxic}	Phn/Ant	Fla/Pyr	Ant/Ant + Phn	Fla/Fla + Pyr	BaA/BaA + Chy	TOC (%)	Clay (%)
1	321	156	1.12	1.85	0.472	0.649	0.515	5.79	14.1
2	556	280	1.06	2.30	0.486	0.697	0.465	6.23	32.4
3	371	275	1.15	1.27	0.465	0.559	0.630	0.468	18.0
4	477	331	1.11	1.22	0.474	0.549	0.609	0.588	15.3
5	<MDL	<MDL	ND	ND	ND	ND	ND	0.093	0.600
6	206	134	2.03	1.37	0.330	0.579	0.565	1.12	14.0
7	32.5	25.6	0.818	0.826	0.550	0.452	0.424	0.001	3.75
8	72.4	56.5	0.769	1.32	0.565	0.569	0.575	0.023	4.33
9	122	94.6	0.887	1.74	0.530	0.635	0.572	0.052	8.00
10	544	514	2.13	1.40	0.319	0.583	0.562	2.42	2.00
11	131	80.5	1.36	1.64	0.424	0.621	0.581	0.030	15.0
12	55.5	39.7	1.49	0.848	0.401	0.459	0.584	0.034	4.33
13	231	155	1.57	1.34	0.389	0.573	0.581	0.293	8.36
14	645	209	1.22	0.641	0.450	0.391	0.672	1.47	12.3
15	291	186	1.21	1.81	0.453	0.644	0.529	12.1	19.0
16	63.0	50.1	1.21	1.87	0.453	0.652	0.524	0.162	5.06
17	216	140	3.18	1.50	0.239	0.601	0.607	0.368	5.32
18	<MDL	<MDL	ND	ND	ND	ND	ND	0.014	3.24
19	<MDL	<MDL	ND	ND	ND	ND	ND	0.031	2.26
20	1390	576	2.23	0.728	0.310	0.421	0.384	0.451	2.24
Min	32.5	25.6	0.769	0.641	0.239	0.391	0.384	0.001	0.600
Max	1390	576	3.18	2.30	0.565	0.697	0.672	12.1	32.4
Mean	286	165	1.23	1.18	0.366	0.482	0.469	1.59	9.48
SD	329	162	0.780	0.659	0.178	0.223	0.213	3.10	7.97

<MDL, below the method detection limit; ND, not detected.

[26] ranged from 32.5 $\mu\text{g}/\text{kg}$ dw to 1390 $\mu\text{g}/\text{kg}$ dw with an average concentration of 286 $\mu\text{g}/\text{kg}$ dw (Table 2). Concentrations of these PAHs represented from 47.0% to 78.2% of the total PAHs concentrations with an average value of 51.6%. The 3-rings PAHs represented a significant portion of the PAHs concentrations in front of the Abu Qir Drain (stations 1 and 15), the Fertilizer Company (stations 2 and 14), Maadeya Outlet (station 4) and station 20 in the western part of the bay, which may reflect recent input of PAHs.

The concentration of PAHs with a mutagenic and genotoxic potential (\sum PAHs_{tox}) (BaA, BbF, BkF, BaP, Chy, DibA and InP) [27] ranged from 25.6 $\mu\text{g}/\text{kg}$ dw to 576 $\mu\text{g}/\text{kg}$ dw with an average concentration of 164 $\mu\text{g}/\text{kg}$ dw (Table 2). These concentrations represented an average of 33.7% of the total PAHs concentrations and ranged from 21.6% to 55.2%.

3.2. PAHs in mussels

Concentrations of PAHs in the mussel samples are shown in Table 3. PAHs concentrations ranged from 11.4 $\mu\text{g}/\text{kg}$ dw (station 18) to 3880 $\mu\text{g}/\text{kg}$ dw (station 20) with an average concentration of 1300 $\mu\text{g}/\text{kg}$ dw in *T. decussata* and 242 $\mu\text{g}/\text{kg}$ dw to 2830 $\mu\text{g}/\text{kg}$ dw with an average concentration of 1070 $\mu\text{g}/\text{kg}$ in *M. corallina*. The highest detected concentration of PAHs was observed in *T. decussata* (station 20) in the western part of the bay reflecting the high concentration in sediments. Relatively high PAHs concentrations were also observed in front of Maadeya Outlet (stations 4 and 6) and between the Abu Qir Fertilizer Company and the Electric Power Plant (stations 12 and 13). Concentrations of PAHs in the mussel samples had a similar trend as for sediments. A significant

Table 3
Concentrations of PAHs ($\mu\text{g}/\text{kg}$ dw) in mussel tissues of Abu Qir Bay.

Station no.	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	InP	DibA	BghiP	\sum PAHs	Lipid (%)
<i>Macrta corallina</i>																		
4	120	110	102	147	216	141	313	277	211	181	224	113	200	195	119	159	2830	5.17
6	64.6	35.0	33.3	44.4	59.4	45.3	97.0	93.8	58.9	61.5	88.9	57.3	72.4	82.5	48.0	71.6	1010	4.79
7	14.5	17.9	15.7	22.7	26.4	23.1	33.8	31.4	24.5	28.5	28.9	25.1	29.1	36.7	27.5	32.9	418	4.28
8	9.75	11.9	12.6	11.9	12.6	15.3	16.4	17.5	13.9	16.2	17.8	17.6	16.1	19.6	16.5	16.4	242	4.06
9	20.8	18.8	18.9	23.7	39.2	27.7	40.1	52.0	34.0	44.4	39.2	30.8	34.1	42.0	31.3	36.5	534	4.26
12	45.3	40.4	40.6	54.4	83.3	57.0	126	118	95.4	94.8	102	73.2	87.2	94.6	60.6	84.0	1260	4.64
13	17.8	20.4	22.1	34.4	84.7	42.3	157	133	93.1	104	113	63.9	95.3	91.3	45.9	79.4	1200	4.83
Min	9.75	11.9	12.6	11.9	12.6	15.3	16.4	17.5	13.9	16.2	17.8	17.6	16.1	19.6	16.5	16.4	242	4.06
Max	120	110	102	147	216	141	313	277	211	181	224	113	200	195	119	159	2830	5.17
Mean	41.8	36.3	35.0	48.3	74.6	50.3	112	103	75.9	75.8	87.7	54.3	76.3	80.2	49.8	68.6	1070	4.57
SD	39.5	33.9	31.1	45.7	68.2	42.6	103	88.1	67.7	56.7	70.9	33.2	62.5	58.5	33.7	47.7	870	0.392
<i>Tapes decussata</i>																		
18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	11.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	11.4	8.19
19	<MDL	<MDL	9.46	<MDL	<MDL	<MDL	12.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	21.6	7.99
20	48.9	51.1	62.4	135	289	173	471	440	304	343	363	223	300	291	146	236	3875	8.83
Min	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	11.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	11.4	7.99
Max	48.9	51.1	62.4	135	289	173	471	440	304	343	363	223	300	291	146	236	3880	8.83
Mean	16.3	17.0	24.0	45.0	96.2	57.7	165	147	101	114	121	74.3	103	96.8	48.8	78.5	1300	8.33
SD	28.2	29.5	33.6	78.0	167	99.9	265	254	175	198	209	129	171	168	84.5	136	2230	0.439
MDL	2.56	1.07	2.51	3.62	2.02	2.97	2.42	3.23	3.04	5.20	1.75	3.94	2.12	10.2	8.49	5.78		

<MDL = below the method detection limit. For abbreviations of PAHs, see Table 1.

Table 4
Concentrations of PAHs ($\mu\text{g}/\text{kg dw}$) in sediments worldwide.

Location	Sampling year	PAHs ($\mu\text{g}/\text{kg dw}$)	Reference
Abu Qir Bay	2006	<MDL–2660	Present study
(1) Sediments worldwide			
Corsica, Italy	1987	3.90–53.5	[30]
Touloun, France		912–8530	
Casco Bay, USA	NA	16.0–21000	[31]
San Diego Bay, USA	NA	80.0–20000	[32]
Mediterranean Sea	1985–1986	20.0–960	[33]
	1995	680–4800	
	1996	550–18700	
Kyeonggi Bay, Korea	1995	9.10–1400	[34]
Arcachon Bay, France	1995	31.7–2390	[35]
French Coast, Mediterranean Sea	1995	1.47–20400	
Izmit Bay, Turkey	1999	30.0–1670	[36]
San Francisco Bay, USA	2001	18.0–2230	[37]
Inner Clyde Estuary, UK	2003	630–23710	[38]
(2) Alexandria Coast			
Western Harbour	1999	7.90–131150	[39]
Abu Qir Bay, Egypt	2004	94.9–1450	[16]
Western Harbour	1999	2000	[40]
Eastern Harbour		6340	
EL-Mex Bay, Egypt		4330	

NA, not available.

correlation was found between the total PAHs concentrations for sediments and mussels in the bay ($r=0.90$; $p<0.05$). At the same time, high degree of correlation was found between PAHs concentrations and lipid content in both species ($r=0.91$; $p<0.05$ in *M. corallina* and $r=0.97$; $p<0.05$ in *T. decussata*). Concentrations of PAHs in offshore and in the western part of the bay (stations 18 and 19) were obviously lower than the nearshore mussel samples (Table 3). In station 18, only Fla was detected, while in station 19 only Fla and Ace were observed.

Similar to sediments, PAHs in the mussel tissues were dominated by the HMWPAH (4–6-rings), which represented an average value of 67.4% of the total detected PAHs (56.0–100%). Several stud-

ies [5,28,29] have shown that bivalves preferentially bioaccumulate 4-, 5- and 6-ringed PAHs rather than 2- and 3-ringed PAHs following increase in K_{ow} and the more solubility of the lower molecular weight PAHs (LMWPAH) [28]. In waters of high turbidity, where particles are re-suspended regularly, filter-feeding bivalves will contain a higher proportion of the more hydrophobic 4- to 6-ring compounds due to accumulation of PAHs from the sediment [28]. Concentrations of PAHs recorded in sediments and mussels worldwide are shown in Tables 4 and 5 respectively.

Similar distribution pattern can be observed between sediments and *M. corallina* of stations 4, 6 and 13 and *T. decussata* of station 20. These four locations had sediment PAHs concentrations higher than $200 \mu\text{g}/\text{kg dw}$. On the other hand, all the sediment samples with PAHs concentrations lower than $200 \mu\text{g}/\text{kg dw}$ (stations 7, 8, 9 and 12) showed insignificant correlation with mussel PAHs concentrations. PAHs pattern in stations 7, 8, 9 and 12 was characterized by a marked increase in the HMWPAH in the mussel tissues compared to the respective sediment samples. In most of the investigated samples of both species, LMWPAH was in most cases much lower than the HMWPAH that could be possibly related to the metabolic pathway in the investigated mussels.

3.3. Origin of PAHs in Abu Qir Bay

The concentrations and pattern of PAHs found in sediments have been shown to reflect source characteristics [48]. This can be related to the physico-chemical properties of individual PAHs that influence sediment binding capacity. PAHs in urban areas, such as Abu Qir Bay originate from a variety of sources such as combustion of fossil fuels (e.g., cooking and heating oils, coal burning, vehicle emissions) and biomass burning (e.g., fireplaces, controlled burning). These are classified as PAHs of pyrogenic origin. Unburned fossil fuels (crude oil and its refined products formed by slow maturation of organic materials under the geochemical gradient conditions of temperature and pressure referred to as petrogenic PAHs) can also impart their PAHs signature to the marine environment [49–51], primarily by street surface runoff, accidental spills and intentional discharge by ships. In addition, PAHs can be formed from the short-term diagenetic degradation of biogenic precursors (diagenetic PAHs) [37].

Table 5
Concentrations of PAHs ($\mu\text{g}/\text{kg}$) in different mussel species worldwide.

Location	Sampling year	Species type	PAHs ($\mu\text{g}/\text{kg}$)	Reference
Abu Qir Bay, Egypt	2006	<i>Macra coral-</i> <i>Tropes decus-</i> <i>sata</i>	242–2830 ^x 44.5–526 ^y 55.0–3880 ^x 10.3–701 ^y	Present study
(1) Mussels worldwide				
Catalonia	NA	<i>Mytilus galloprovincialis</i>	670–5490 ^y	[41]
Arcachon Bay, France	1995	<i>Mytilus galloprovincialis</i>	279–2420 ^x	[35]
French coast, Mediterranean Sea	1995	<i>Mytilus galloprovincialis</i>	25.6–373 ^x	
Ebro Delta, NW Mediterranean	1989–1991	<i>Mytilus galloprovincialis</i> <i>Ostrea edulis</i> <i>Crassostrea gigas</i> <i>Rotula decussata</i>	70.0–150 ^y 10.0–220 ^y 20.0–50.0 ^y 20.0–120 ^y	[42]
Haifa Bay	1995–1998	<i>Macra corallina</i>	54.0–267 ^x	[43]
Bay of Fundy, Atlantic Canada	1996–1998	<i>Mytilus edulis</i>	ND–248 ^x	[44]
Baltic Sea, Poland	1997	<i>Mytilus edulis</i>	8.64–29.7 ^y	[45]
Corral Bay, Chile	1999–2000	<i>Mytilus chilensis</i>	138–876 ^x	[46]
Guanabara Bay, Brazil	1999	<i>Perna perna</i>	9.00–273 ^x	[47]
(2) Marine species along the Egyptian Coast				
Red Sea, Egypt	2000	<i>Brachiodonates sp.</i>	676–4670 ^y	[40]
Abu Qir Bay, Egypt	2004	<i>Donax trunculus</i>	1140 ^y	[16]

NA, not available; x, concentrations are given on dry weight basis; y, concentrations are given on wet weight basis.

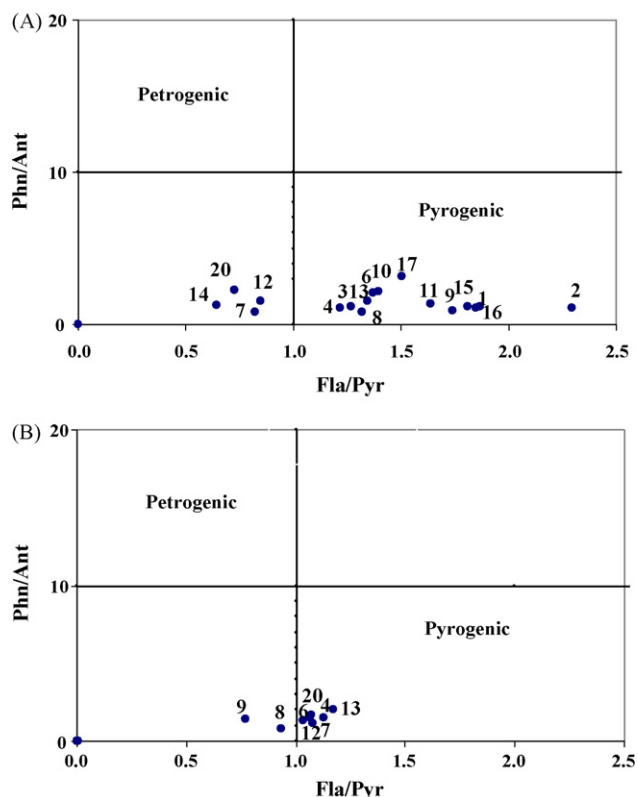


Fig. 2. Phn/Ant versus Fla/Pyr plots of PAHs in sediments (A) and mussels (B) of Abu Qir Bay.

PAHs of molecular mass 178 and 202 are commonly used to distinguish between pyrogenic and petrogenic sources [52,53]. Ratio values such as Phn/Ant ($m = 178$) and Fla/Pyr ($m = 202$) had been used by previous workers [5,54,55]. Petroleum often contains more phenanthrene relative to anthracene, which is a more thermodynamically stable tricyclic aromatic isomer, so that the Phn/Ant ratio is observed to be very high in the case of petrogenic pollution with PAHs but low in pyrolytic contamination cases [52–54]. Budzinski et al. [52] found that sediments with Phn/Ant > 10.0 were mainly contaminated by petrogenic inputs and Phn/Ant < 10.0 was typical of pyrolytic sources. In addition to the Phn/Ant ratio, Fla/Pyr ratio also indicated the origin of PAHs. Sicre et al. [54] found that a Fla/Pyr < 1.00 was attributed to petrogenic sources and values greater than 1.00 were obviously related to a pyrolytic origin. In order to estimate PAHs sources, the Phn/Ant ratios were plotted against Fla/Pyr according to Budzinski et al. [52] (Fig. 2A and Table 2). It was found that 80.0% of the investigated sediment samples have pyrogenic origin of PAHs. At the same time, only four samples (stations 7, 12, 14 and 20) showed a mixed pattern of contamination (petrogenic and pyrogenic). For the mussel samples (Fig. 2B and Table 6), the pyrolytic origin was the dominant source in most of the investigated samples however petrogenic sources cannot be excluded.

Another three PAHs ratios were used in the present study (Table 2): an Ant/Ant + Phn ratio < 0.100 usually is taken as an indication of petroleum while a ratio > 0.100 indicates a dominance of combustion [52]. A Fla/Fla + Pyr ratio of 0.500 is usually defined as the petroleum/combustion transition point. This boundary appears to be less definitive than 0.100 for Ant/Ant + Phn. The Fla/Fla + Pyr ratio is below 0.4 for most petroleum samples, between 0.400 and 0.500 for liquid fossil fuel (vehicle and crude oil) combustion and above 0.500 in kerosene, grass, most coal and wood combustion [52].

Table 6

Molecular indices of PAHs in the mussel tissues of Abu Qir Bay.

Sample no.	Phn/Ant	Fla/Pyr	Ant/Ant + Phn	Fla/Fla + Pyr	BaA/BaA + Chy
4	1.53	1.13	0.395	0.531	0.538
8	1.31	1.03	0.433	0.509	0.489
9	1.14	1.08	0.467	0.518	0.462
12	0.826	0.935	0.548	0.483	0.463
13	1.42	0.771	0.414	0.435	0.434
18	1.46	1.06	0.406	0.515	0.502
19	2.00	1.17	0.333	0.540	0.473
25	ND	ND	ND	1.00	ND
26	ND	ND	ND	1.00	ND
27	1.67	1.07	0.375	0.517	0.470
Min	0.589	0.771	0.333	0.435	0.233
Max	2.00	1.76	0.629	1.00	0.538
Mean	1.14	0.830	0.337	0.605	0.383
SD	0.673	0.449	0.186	0.210	0.204

ND, not detected.

The higher mass PAHs are usually minor contributors to refined petroleum products [55] and generally are present in significant amounts only in heavier fractions such as asphalt [56] and possibly in bitumen or coal [22]. Because very low proportions of BaA are rarely observed in combustion samples, a BaA/BaA + Chy less than 0.200 likely indicates petroleum, a ratio value of BaA/BaA + Chy between 0.200 and 0.350 indicates petroleum combustion, and a value higher than 0.350 is an indicative of grass, wood and coal combustion source [22].

Calculated PAHs ratios (Table 2) revealed that the dominant source of PAHs in sediments of Abu Qir Bay is the combustion process, either petroleum combustion (less frequent) or wood, coal and grass combustion (more frequent). At the same time, only station 14 (in front of the Fertilizer Company) shows a mixed pattern of petroleum and combustion sources. Petroleum combustion fingerprints are greatly observed in station 20 (in the western part of the bay), which could possibly be related to the shipping activity. Similar to sediments, the pyrogenic origin was the dominant source of PAHs in all the investigated mussels in the bay based on the calculated ratios (Table 6).

3.4. Risk assessment of PAHs in Abu Qir Bay

A Screening Level Ecological Risk Assessment (SLERA) was performed for the sediments to evaluate the possibility of occurrence of adverse ecological effects by PAHs concentrations according to the framework developed by the United States Environmental Protection Agency (USEPA) [57,58]. The protection of benthic species from generic adverse effects was selected as the assessment endpoint. In addition, a Human Health Risk Assessment (HHRA) was performed [59–61] to assess the occurrence of adverse health effects (carcinogenic and noncarcinogenic) as a result of the consumption of the mussel species.

3.4.1. Screening Level Ecological Risk Assessment (SLERA)

In SLERA, maximum concentration of each of the investigated 16 EPA PAHs in the bay sediments was selected as the exposure concentration in a conservative assumption (Tier 1 of a risk assessment). In the effect characterization step, sediment quality guidelines (SQGs), which were previously developed [62–65] and cited in literature, were used. A consensus based approach according to MacDonald et al. [66,67] was used in the present study to harmonize the different existing values of the sediment quality guidelines and to increase reliability. The consensus based sediment quality guidelines used in the present study were developed by calculating the geometric mean of the following SQGs: AETL and AETH of Barrick et al. [62]; ERL and ERM of Long et al. [63]; TEL and PEL of MacDonald et al. [64] and T20, T50 and T80 of USEPA/NOAA [65].

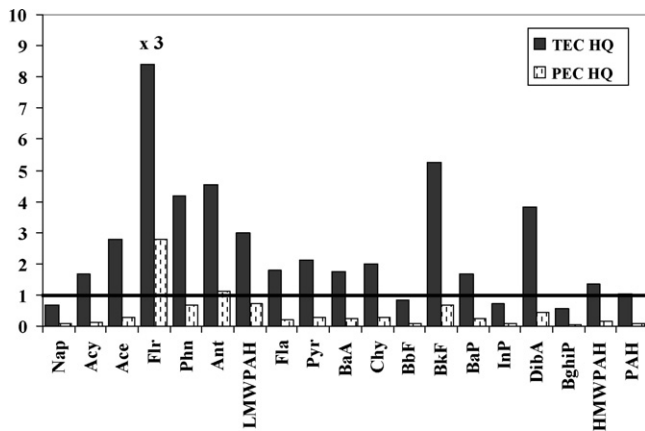


Fig. 3. TEC HQ and PEC HQ for PAHs in sediments of Abu Qir Bay.

In the risk characterization step, the generic hazard quotient (HQ) (pollutant concentration divided by the selected SQG) was calculated for each pollutant based on the maximum concentration of each pollutant and the calculated consensus based sediment quality guidelines according to the following equation:

$$HQ = \frac{\text{maximum concentration of PAH in sediments } (\mu\text{g/kg dw})}{\text{calculated consensus based sediment quality guideline of PAH } (\mu\text{g/kg dw})}$$

According to the consensus based approach, two HQs were calculated: one representing the threshold effect concentration (TEC HQ) and the other representing the probable effect concentration (PEC HQ). When TEC HQ < 1, rare adverse ecological effects are expected. When TEC HQ > 1 > PEC HQ, adverse ecological effects are possible but less frequent. Finally, when PEC HQ > 1, frequent adverse ecological effects are expected.

Results obtained from the risk assessment of PAHs in sediments of Abu Qir Bay are shown in Fig. 3. These results were based on the concentrations recorded in station 20, which showed the maximum concentration of PAHs. Except for Nap, all the lower molecular weight PAHs (Acy, Ace, Flr, Phn and Ant) showed TEC HQ > 1 indicating a possibility of occurrence of adverse ecological effects. At the same time, some of the high molecular weight PAHs (Fla, Pyr, BaA, Chy, BaP and DibA) showed TEC HQ > 1. Only Flr and Ant (low molecular weight PAHs), showed PEC HQ > 1, indicating a higher possibility of occurrence of adverse ecological effects. But rare adverse ecological effects are associated with the exposure to PAHs

Table 7
Calculated HQs and cancer risks in the performed Human Health Risk Assessment in Abu Qir Bay.

Analyte	<i>Mactra corallina</i>		<i>Tapes decussata</i>	
	HQ	Cancer risk	HQ	Cancer risk
Nap	2.400×10^{-6}	NA	1.640×10^{-6}	NA
Ace	6.660×10^{-7}	NA	6.970×10^{-7}	NA
Flr	1.410×10^{-5}	NA	2.270×10^{-5}	NA
Phn	2.850×10^{-7}	NA	6.440×10^{-7}	NA
Ant	1.870×10^{-7}	NA	3.860×10^{-7}	NA
Fla	3.210×10^{-5}	NA	7.880×10^{-5}	NA
Pyr	3.850×10^{-6}	NA	9.810×10^{-6}	NA
BaA	NA	6.590×10^{-8}	NA	1.550×10^{-7}
Chy	NA	6.140×10^{-10}	NA	1.750×10^{-9}
BbF	NA	7.290×10^{-8}	NA	1.850×10^{-7}
BkF	NA	4.390×10^{-9}	NA	1.130×10^{-8}
BaP	NA	6.390×10^{-7}	NA	1.530×10^{-6}
InP	NA	6.450×10^{-8}	NA	1.480×10^{-7}
DibA	NA	3.910×10^{-7}	NA	7.460×10^{-7}
BghiP	1.180×10^{-6}	NA	2.630×10^{-6}	NA

NA, not available. For abbreviations of PAHs, see Table 1.

in sediments of the rest of the bay (all the other samples showed TEC HQ < 1). Thus it can be concluded that PAHs are not contaminants of potential concern in Abu Qir Bay.

3.4.2. Human Health Risk Assessment of PAHs in Abu Qir Bay

The intake or dose for the ingestion of mussels is calculated based on the following equation [59,61]:

$$CDI = \frac{C_{tis} \times Rf \times IR \times Cf \times ABS \times Ef \times ED}{BW \times AT}$$

where CDI = chronic daily intake ($\text{mg kg}^{-1} \text{day}^{-1}$); C_{tis} = concentrations (mg/kg wet weight) of the investigated chemical pollutants in bivalve tissues; Rf = reduction factors (unitless): (1); IR = ingestion rate (g day^{-1}): $0.2700 \text{ g day}^{-1}$ [68]; Cf = conversion factor (10^{-3} kg/g); ABS = ingestion absorption factor (fraction absorbed): 100% (conservative); Ef = exposure frequency (days year^{-1}): $350 \text{ days year}^{-1}$ for noncarcinogenic effects and $365 \text{ days year}^{-1}$ for carcinogenic effects [61]; ED = exposure duration (years): 30 years for noncarcinogenic effects and 70 years (lifetime) for carcinogenic effects [61]; BW = body weight (kg): 70 kg [59]; AT = average time of exposure (days): 365×30 for noncarcinogenic effects and 365×70 for carcinogenic effects [61].

Dose–response information [oral reference dose (RfD) for noncarcinogenic effects and oral slope factor (OSF) for carcinogenic effect] used in this risk assessment was provided in the EPA's Integrated Risk Information System (IRIS) [58] or Health Effects Assessment Summary Tables (HEAST) [58].

Potential noncarcinogenic effects were evaluated by calculating a chronic hazard quotient (HQ). For a single compound, the hazard quotient (HQ) is the ratio of the CDI to a reference dose (RfD):

$$HQ = \frac{CDI}{RfD}$$

As the RfD is a threshold dose or intake, which is conservatively chosen so that if the estimated intake is less than the reference dose ($HQ < 0.1$), there is almost no possibility of an adverse health effect. However if the intake exceeds the reference dose ($HQ > 0.1$), this does not indicate an adverse health effect is expected, only that a conservative threshold is exceeded.

Carcinogenic effects were quantified by estimating the probability of contracting cancer based on a site related exposure. Cancer risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen. In order to estimate the cancer risk, the CDI is multiplied by the cancer oral slope factors (OSF) of the chemical investigated as shown in the following equation:

$$\text{risk} = CDI \times OSF$$

USEPA under superfund uses a risk level of 10^{-6} as the point at which risk management decisions can be considered. Risk management decisions most frequently made under superfund are in the cancer risk range of 10^{-6} to 10^{-4} [60].

Calculated HQs and cancer risks for the investigated PAHs in both species are summarized in Table 7. It was found that no adverse health effects (either carcinogenic or noncarcinogenic) are associated with the consumption of both mussel species from Abu Qir Bay with respect to PAHs.

4. Conclusion

The SLERA conducted on the PAHs data from the present study at Abu Qir Bay highlighted two major problems: the first problem was related to the scarcity of information on the PAHs concentrations in sediments and marine organisms of the bay, and thus no integrated and updated database was available. The second problem was related to the effects and guidelines, as no SQGs were available to the region or even to the Mediterranean Sea. Meanwhile, on-site ecotoxicological data were not available. In spite of these limitations, the adopted approach in the present study highlighted that no adverse ecological and human health effects are associated with the exposure to PAHs levels in Abu Qir Bay and, thus, a further detailed investigation based on site specific studies would be greatly required. Like many countries in the Mediterranean region, there are no emission inventories of sources or release of organic and inorganic pollutants in the Egyptian environment, or any official data on stockpiles and disposal. In order to determine and control the sources of the observed contaminants of potential concern, intense localized sampling and analysis of effluents and runoff patterns are needed.

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