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FULL LENGTH ARTICLE

Organic sources in the Egyptian seawater around Alexandria coastal area as integrated from polycyclic aromatic hydrocarbons (PAHs)

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KEYWORDS

Polycyclic aromatic hydrocarbons;
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Abstract This paper represents the first comprehensive survey and provides important data on PAHs concentration and composition in Alexandria coastal seawater. The compositions of PAHs determined in all samples are to be used as chemical markers for identifying different sources of PAH pollution in the surface seawater of Alexandria coastal area. The quantitative analysis of PAHs showed a concentration ranging from 8970.939 to 1254756.00 ng/L, which exceeds the maximum admissible concentrations of PAHs (200 ng/L) for the water standard of European Union. The calculated diagnostic ratios suggested that the sources of PAHs at the majority of the studied area are derived primarily from pyrogenic sources from incomplete fuel combustion of the boats and vehicle engines with lesser amounts of PAHs contributed from petrogenic sources. Some stations displayed mixed sources in comparison to many other studied marine systems, the PAH concentrations detected at Alexandria area were considered to be higher and pose health risks to aquatic bodies.

1. Introduction

The investigated area includes Alexandria shores located on the northern Mediterranean coast of Egypt. The investigated area lies between longitudes 29° 30′ W, 30° 30′ E and latitudes 31° 00′ S to 31° 30′ N (Fig. 1). This figure shows most of the coastal area of Alexandria, extending from EL-Montazah to Sidi Krier beach at the northeast with a shoreline of about 42 km long. The area includes three harbors; the two old harbors (Western and Eastern Harbors) and the newly constructed Aldekhela Harbor. The northeastern part of the area includes most of the old beaches of Alexandria. Two points of loading point, the east port of Alexandria site (4) and the west port of Alexandria site (5), respectively were chosen in the oil platform n. 52 where loading oil tankers is undertaken. Six locations in El-Agamy area were chosen as follows, EL-Nikhil beach (7), EL-Bitash beach (8), EL-Hanovill beach (9), Zahra El-A Gamy (10), 6-October beach (11) and the Center of drainage EL-A gamy (12). Finally, Sidi Krier beach site (13) which is located at 42 km. from EL-Montazah beach.

The coastal sea area of Alexandria, which comprises the biggest and main harbors in the country and is considered one of the most industrialized zones, receives considerable

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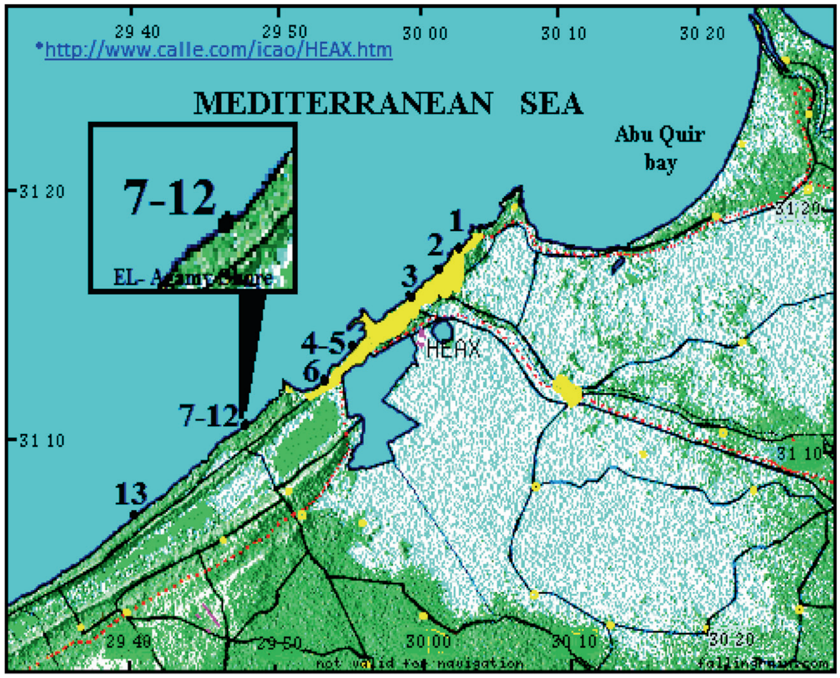

Figure 1 Map of the area of study around Alexandria coastal seawater.

amounts of petroleum and its products. A part of this is the summed pipeline which transports more than 100 million tons per year from crude petroleum of the Arabian Gulf countries. Another important source of oil contamination in the area is due to the discharge of huge amounts of land drainage water from the highly polluted Lake Mariut and the sewage water; these may include the wastes of lubricants and other mineral oils. Limited attention was given to follow up and evaluation of the petroleum-contamination problem in the coastal region of Alexandria [1]. Investigation of polycyclic aromatic hydrocarbons (PAHs) in the water bodies is a very important part of environmental quality assessment which determines the status of contamination and the impacts it may cause to the ecosystem.

This paper represents the first comprehensive survey of PAHs in seawater and provides important data on PAHs concentration and composition in Alexandria coastal seawater in order to provide a technical basis to evaluate and pursue pollution abatements in the coastal seawater by hygienic treatment of the industrial effluents before their drainage in the marine water coasts is highly recommended.

2. Materials and methods

The samples were collected from different sites in the studied area (Fig. 1). The surface seawater samples (0.2 cm) were taken along the coasts of Alexandria Sea using narrow neck borosilicate glass bottles with Teflon lined caps. The samples were acidified to pH = 2 using 10% HCl to preserve them against bacterial action during transportation and storage. At each location two samples were taken in a square of 2 m^2. Samples were stored at −20 °C until analysis. For each site, the samples were mixed and homogenized before analysis. Extraction began directly after collection to avoid microbial degradation [2] as the following procedure:

1. 100 ml of water sample was shaken with 100 ml of carbon tetrachloride in separating funnel for 15 min. After 30 s of agitation and a 3 min settling period, the aqueous layer was discarded.
2. The process was repeated twice for every 100 ml of brine until the entire brine sample has been extracted. The obtained extract was dried using anhydrous sodium sulfate (30 g).
3. The extract was then transferred to a weighted beaker and carbon tetrachloride solvent is evaporated at 60 °C.
4. After, cooling in desiccators, the samples were weighed till constant weight. The oil content in ng/L was calculated [3] as ng of oil/L = $(A - B) \times 10^{(9)}$/m L of water sample, where: A and B are the weights of the empty beaker and when containing the sample. PAH identification and quantification in the extracted oil were performed using HPLC (Perkin Elmer series 200) with photodiode array detector [4].

3. Results and discussion

3.1. Estimation of PAHs

Qualitative and quantitative estimation of the individual PAHs for the extracted oils from surface seawater of Alexandria coasts was done and representative model samples are shown in (Fig. 2). The HPLC chromatograms show that, each sample has its own distribution pattern and all have most of the target compounds. The concentrations of PAHs in Alexandria seawater at different sites are shown in (Table 1 and Fig. 3a). The total PAHs concentration in water ranged from 8970.939 to 1254756.0 ng/L with an average 323749.13 ng/L and gradually decreased along Alexandria coasts from EL-

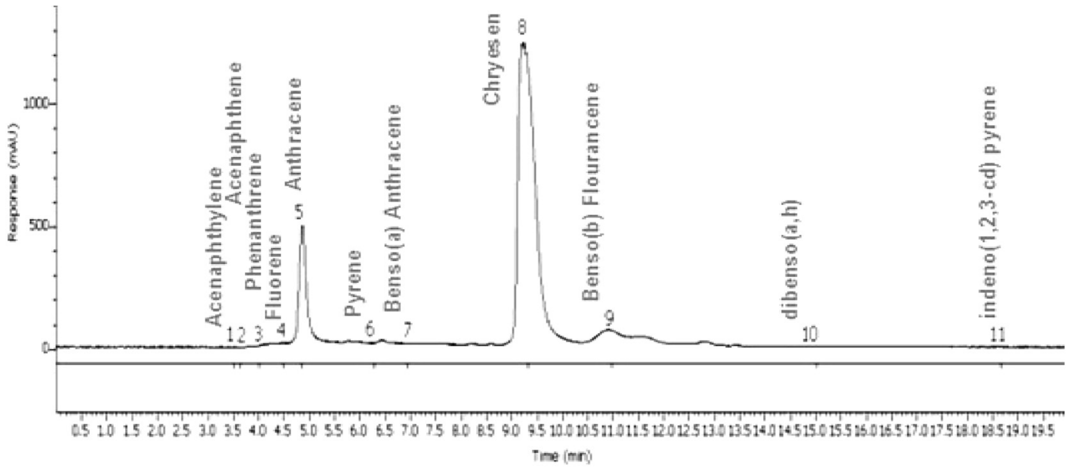

Figure 2 Representative HPLC chromatogram of extracted oil of sample no. 10.

Montazah beach to the west port of Alexandria. The results showed a high concentration of PAHs at the west port of Aldekhela (36690.611 ng/L) to Zahra EL-A gamy (1254756.0 ng/L) and EL-Bitash beach (181790.62 ng/L). This is consistent with the direction of the water currents and winds from the west to the east sides of Alexandria coasts with increasingly intense urban and industrial development around the watershed. The concentration of PAHs detected were obviously related to different reasons: (1) urban runoffs, sewage outfalls and wastewater from industrial area discharges, (2) releasing of petroleum wastes from passing ships and (3) parking at the waiting zone nearby the harbors and fuel catering processes, which were observed during the sampling. High concentrations of PAHs were detected as: 431645.56 ng/L and 441597.0 ng/L in site 11 (6-October and site 13 Sidi Krier) respectively.

In terms of individual PAHs in surface water, many of the PAH compounds were present at concentrations that exceed 10,000 ng/L for most samples (Table 2), suggesting that the

Table 1 Total PAHs concentration (ng/L) in extracted oil from Alexandria coastal area.

S. No.	Location		Conc. ΣPAHs (ng/L)
1	EL-Montazah Beach		286718.29
2	Miami Beach		190200.89
3	26-July Beach		165610.62
4	The east port of Alexandria		37571.71
5	The west port of Alexandria		8970.939
6	The west port of Aldekhela		36690.611
7	EL-Nikhil Beach	El-A Gamy region	568901.99
8	EL-Bitash Beach		181790.62
9	EL-Hanovill Beach		575799.62
10	Zahra El-A Gamy		1254756.0
11	6-October Beach		431645.56
12	Center of the drainage El-A Gamy (km.21)		28485.366
13	Sidi Krier Beach		441597.0
	Total average		323749.13

Conc.: Concentration (ng/L).

waters in this area were heavily contaminated by PAHs. On the other hand, no (Bap) was detected. Different sites were dominated by different compounds. The higher concentration of individual PAH varied from low molecular weight and was more volatile (Nap) 54755.347 ng/L, (Ace) 383796.580 ng/L at site 13 and (A) 13379.80 ng/L, (Phe) 3439.79 ng/L at site 11, besides the dominate of (F), (Ant) at sites 8 (1764.694 ng/L) and 10 (131784.14 ng/L) to the high molecular weight (Flu) 32149.12 ng/L and (Pyr) 9165.947 ng/L at sites 4, 8 in addition to (BaA), (Chr) at sites 12 (23996.586 g/L) and 10 (1078482.3 ng/L). High concentrations of BkF, BbF and Ip were observed in most sites.

There is a need to define the natural variation of the above mentioned aromatic hydrocarbons, but simple parametric statistics are not enough to give a good evaluation.

The mean concentration of individual PAHs including carcinogenic and non-carcinogenic PAHs, in all samples ranged from N.D. to 1078482.3 ng/L. These are either within or higher than that of the Annual Average Environmental Quality Standards (AA-EQS) of European Water Framework Directive (WFD) for individual PAHs, which state that the safe range for PAHs is from 2.0×10^{-2} to 2.4 μg/L [5], the mean concentrations of seven carcinogenic PAHs with high molecular weight (BaA, Chr, BbF, BkF, BaP, DahA, and IP) with mean values that ranged from N.D. to 187626.06 ng/L, accounting for 77.661% of total PAHs in all water samples. These results are higher than the safe limits of the EPA National Recommended Water Quality Criteria for the protection of aquatic life and human health 0.020 μg/L [6]. Benzo[a]pyrene (BaA), the most carcinogenic pollutant of all PAHs [5] was detected in all samples, with concentrations ranging from 7.055 to 23996.586 ng/L (a mean of 1938.137 ng/L), the levels were higher than those of the EPA National Recommended Water Quality Criteria for the protection of aquatic life 0.010 μg/L [6], which could have represented approximately equal contents of adverse ecological effect in these areas, particularly for the aquatic organism and humans health Table 3.

3.2. PAHs composition

The composition pattern of PAHs by ring size for the water samples around Alexandria coastal is shown in (Table 2 and

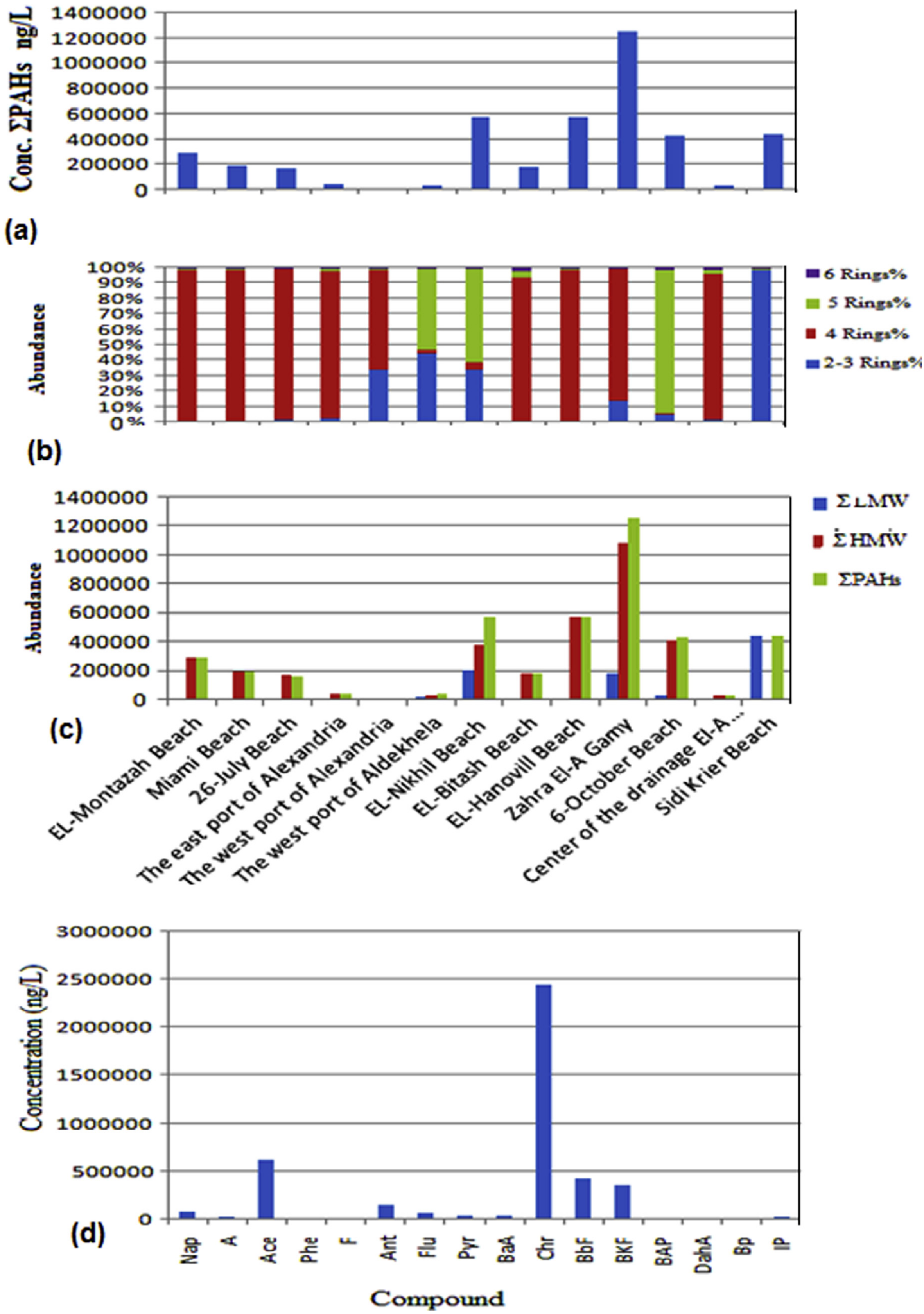

Figure 3 Histogram representing the variation of the total PAH concentrations (a), concentrations of PAHs% according to number of aromatic rings (b), total LMW, HMW and Σ PAHs concentrations (c), and the concentrations of individual PAHs determined (d) different sampling station around Alexandria coastal area.

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Table 2 Concentrations of PAHs in sampling stations around Alexandria coastal area by HPLC (ng/L).

	1	2	3	4	5	6	7	8	9	10	11	12	13	Mean
Nap	N.D	N.D	2298.227	N.D	2543.104	15911.005	92.231	N.D	N.D	N.D	N.D	N.D	54755.347	5815.378
A	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	5971.570	13379.80	N.D	N.D	1488.567
Ace	N.D	N.D	N.D	N.D	N.D	N.D	190534.67	N.D	N.D	35441.104	N.D	N.D	383796.580	46905.565
Phe	N.D	N.D	N.D	258.211	186.317	N.D	2573.786	N.D	127.191	180.0	3439.79	N.D	N.D	520.407
F	6.626	40.387	239.987	504.193	26.020	447.205	115.466	1764.694	93.00	739.295	2.523	371.381	N.D	334.675
Ant	N.D.	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	131784.14	6532.525	N.D	N.D	10639.743
Flu	N.D	N.D	N.D	32149.12	N.D	N.D	19279.041	N.D	N.D	N.D	N.D	901.018	N.D	4025.321
Pyr	571.786	30.277	233.983	3582.460	5966.778	435.515	6499.689	9165.947	4.453	589.825	500.254	1943.657	545.637	2313.097
BaA	11.338	130.118	12.870	183.051	117.482	382.965	16.935	113.763	7.055	11.375	155.703	23996.586	56.537	1938.137
Chr	283938.19	186580.9	161979.2	N.D	N.D	N.D	N.D	159267.08	568735.41	1078482.3	N.D	155.845	N.D	187626.06
BbF	116.176	26.088	582.698	N.D	98.105	167.174	23275.461	N.D.	2053.430	10.305	398202.48	672.371	34.808	32710.698
BkF	908.134	N.D	N.D	N.D	N.D	19210.339	326432.94	6442.337	N.D	N.D	1173.079	N.D	N.D	27243.6
Bap	N.D.	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D.
DahA	N.D	3169.430	N.D	490.288	N.D	N.D	N.D	N.D	N.D	1298.134	N.D	N.D	N.D	381.373
BP	N.D	N.D.	N.D	N.D.	N.D	N.D	N.D	1316.809	N.D	N.D	N.D	N.D	2314.475	279.330
IP	1166.055	223.706	263.673	404.386	32.583	136.409	81.802	3720.011	4779.094	248.162	8259.427	444.521	93.635	1527.190
Total PAH	286718.29	190200.89	165610.62	37571.71	8970.939	36690.611	568901.99	181790.62	575799.62	1254756.0	431645.56	28485.366	441597.0	323749.13

N.D: Under the limit of detection; Nap: Naphthalene; A: Acenaphthylene; Ace: Acenaphthene; Phe: Phenanthrene; F: Flourene; Ant: Anthracene; Flu: Fluoranthene; Pyr: Pyrene, BaA: Benzo [a] anthracene; Chr: Chrysene; BbF: Benzo(b)fluoranthene; BKF: Benzo (K) Fluoranthene; BaP: Benzo [a] pyrene; DahA: Dibenzo (a,h) anthracene; BP: Benzo [g,h,i] perylene; IP: Indo (1,2,3-cd) perylene[36,13], Average: Total average concentrations for each individual PAHs.

Table 3 Concentrations of PAHs% in Alexandria coastal according to number of aromatic rings.

S. No.	Location	2–3 Rings	4-Ring%	5-Ring%	6-Ring%
1	EL-Montazah Beach	0.002	99.234	0.357	0.407
2	Miami Beach	0.021	98.285	1.680	0.118
3	26-July Beach	1.533	97.956	0.352	0.159
4	The east port of Alexandria	2.028	95.592	1.304	1.075
5	The west port of Alexandria	30.713	57.826	1.093	0.368
6	The west port of Aldekhela	44.584	2.232	52.813	0.371
7	EL-Nikhil Beach	33.981	4.534	61.47	0.014
8	EL-Bitash Beach	0.971	92.715	3.544	2.771
9	EL-Hanovill Beach	0.038	98.775	0.357	0.830
10	Zahra El-A Gamy	13.876	85.999	0.104	0.020
11	6-October Beach	5.411	0.152	92.524	1.913
12	Center the drainage A Gamy (km.21)	1.302	94.776	2.359	1.562
13	Sidi Krier Beach	99.310	0.136	0.008	0.546

Fig. 3b). The high-molecular-weight PAHs of four rings (FIu, Pyr, BaA, and Chr), five rings (BbF, BkF, BaP, and DahA) and six rings (IP, BP) generally account for 99.234%, 92.524%, and 2.771% of the total PAH concentrations, respectively. The water samples were dominated by HMW-PAHs (4–6 rings) representing the range of 0.136–99.234%, 0.008–92.524%, and 0.014–2.771% which are likely derived from anthropogenic activities [5] such as incomplete fuel combustion of the boats, ships, and vehicle engines. However, the lower-molecular-weight PAHs of two rings (Nap) and three rings (A, Ace, F, Phe, and Ant) made up 0.002 and 99.31% of the total PAH concentrations, respectively. LMW-PAHs (2–3 rings) were the most abundant components in water samples from Sidi Krier beach, with value 99.31%. The compositional pattern of PAHs was investigated by ring number in the seawater and is shown in (Fig. 3b). The pattern of PAHs contamination on the basis of ring number was in order of 2–3 ring > 4 ring > 5 ring > 6 ring of the sixteen PAHs detected. The results suggest a relatively recent local PAHs source which introduced into Alexandria coastal seawater due to the inefficient two-stroke outboard engines of most boats beside, considerable amounts of petroleum and its products. The water sample from the west port of Aldekhela represented an approximately equal content of HMW-PAHs (55%) and LMW-PAHs (44%) (Table 4 and Fig. 3c) which probably reflect both anthropogenic activities and recent local PAH sources due to the tourism boats and ships activities that adsorbed on the surface of suspended matter and its high resistance to degradation. Some studies reported that the level of chrysene did not significantly change even after 12 years from oil spill, which reflects the resistance of chrysene in aquatic environment and its high increase compared to others. Benzo [ghi] perylene (BP), a compound that has the fingerprint of a combustion engine and which is more abundant in soot [7] was found to have 3631.284 ng/L in the water samples of Alexandria coastal. Other studies supported the phenomenon of BP emission coming from engines [8]. The study mentioned that the highest abundance of BP was recorded in the urban aerosols of Alexandria City which is caused by the incomplete fuel combustion. Therefore, the amount of BP measured in this study was most probably related to the incomplete fuel combustion of the boats and vehicle engines that were extensively used in the studied area.

Finally, the total distribution and separation of individual PAHs of 16 PAHs (Fig. 3d) were recorded in the studied area, higher levels of low molecular weight (Ace), (Ant), (Nap) and (A) beside, higher levels of high molecular weight Chr, Bbf, Bkf, Pyr, BaA and Ip. Generally, the PAHs found in decreasing order were Chr > Ace > Bbf > Bkf > Ant > Nap > Flu > pyr > BaA > IP > A > Phe > DahA > F > BP > Bap.

Table 4 Total LMW, HMW and ΣPAHs concentrations (ng/L) in seawater from different sampling stations.

S. No.	Location	Σ LMW	Σ HMW	ΣTPAHs
1	EL-Montazah Beach	6.628	286711.670	286718.29
2	Miami Beach	40.387	190160.510	190200.89
3	26-July Beach	2538	163072.62	165610.62
4	The east port of Alexandria	762.0	36809.7	37571.71
5	The west port of Alexandria	2755	6215.939	8970.939
6	The west port of Aldekhela	16,358	20332.611	36690.611
7	EL-Nikhil Beach	193,316	375585.99	568901.99
8	EL-Bitash Beach	1764.694	180025.930	181790.62
9	EL-Hanovill Beach	220.191	575799.400	575799.62
10	Zahra El-A Gamy	174,116	1,080,640	1,254,756
11	6-October Beach	23,356	408289.56	431645.56
12	Center of the drainage El-A Gamy (km.21)	371.381	28113.985	28485.366
13	Sidi Krier Beach	438,552	3045	441,597

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3.3. Identification of PAH sources

The identification of the pollution origin is also based on the identification of compounds with specific sources. The presence of Fluoranthene (Flu) and Pyrene (Pyr) indicates the importance of pyrolytic inputs since these compounds are considered as products formed from the condensation of aromatic compounds of low molecular weight at high temperature [9]. Chrysene is considered as a preserved biomarker of PAHs and it was selected to be a good marker of petroleum compounds because of its resistance to a biotic factors and bacterial degradation [10]. Chrysene (Table 5) showed relatively high concentration in sites 1(283938.19), 2(186580.9), 3 (161979.2), 8(159267.08), 9(568735.41) and 10(1078482.3) reflects a petrogenic contamination. To elucidate the details of PAH sources in the water samples, diagnostic ratios were applied, which are a useful tool to distinguish the petrogenic and pyrogenic sources of PAH in different media of the environment depending on their physical, chemical properties and stability against photolysis [11]. The petrogenic source is a result of the direct input from petroleum and its products, while the pyrogenic sources are a result of incomplete combustion of fossil fuels (i.e., exhausts of vehicles) [7]. Various PAH congener ratios that display the best potential to distinguish between the petrogenic and pyrogenic sources and the most consistently quantifiable compounds in the majority of these samples were selected as indication, for example, the ratios of Phe/Ant, Flu/Pyr, Flu/Flu + Pyr, Ip/Ip + Bp, BaA/BaA + Chr and PAHs [12]. Phe/Ant ratio less than 3 indicates pyrolytic origin and petrogenic origin when this ratio is higher than 3 [13]. On the other hand, a ratio Ant/Ant + Phe <0.1 indicates a petrogenic source, while this ratio indicates a combustion source when it is greater than 0.1. The ratio of Flu/Pyr <1 is characteristic of a petrogenic source and the ratio Flu/Pyr >1 characterizes a pyrolytic source. The ratio Flu/Pyr + Flu differentiates between petroleum, wood, coal and plants combustion. When Flu/Pyr + Flu <0.5, it is generally associated with petrogenic source as a characteristic of fuel combustion (gasoline, diesel and crude oil), while when this ratio exceeds 0.5 it characterized pyrolytic sources (kerosene, wood, terrestrial plants and coal combustion) [14]. Phe/Ant and Ant/Ant + Phe ratios indicate that PAHs present at all stations derived from pyrolytic sources (mean = 0.406, 0.1272) respectively (Table 5). This pyrolytic origin is however not exclusive since the values of Flu/Pyr and Flu/Pyr + Flu ratios show the contribution of oil sources (lubricating oils) in sites 4, 7 and 12 indicating mixed origin of PAHs. In spite of the well-established ratios found in the above literature for source indications, the Flu/Flu + Pyr and Ant/Ant + Phe ratios of this study did not give consistent information because Flu and Ant were usually low in some samples with a scarce peak in the chromatographic profile, thus leading to analytical errors and difficulties in quantification, the samples 10(0.999) and 11(0.655) suggesting pyrolytic origin for Ant/Ant + Phe ratio and this is confirmed by Flu/Flu + Pyr ratio in samples 4 (0.900), 7(2.966) and 12(0.317). However, Ip/Ip + Bp and BaA/BaA + Chr reported values of diagnostic ratios for a particular source were illustrated in (Table 5). The calculated ratios in this table exist between 0.039–1.0 and 0.00001–1.0 (mean = 0.906, 0.5387 respectively) which might favor contribution of both petroleum and coal combustion as PAHs origin. Usually, low molecular weight PAHs predominated in water samples. Based on characteristics in PAH composition and distribution pattern, the sources of anthropogenic PAHs, which are formed mainly via combustion processes and release of un-combusted petroleum products, can be distinguished by

Table 5 PAHs parameters (ng/L) used to detect the sources of PAHs in Alexandria coastal area.

S. No.	Location	Phe/Ant	Flu/Pyr	Flu/(Flu + Pyr)	Ant/(Ant + Phe)	BaA/(BaA + Chr)	IP/(IP + BP)	10LPAHs	10HPAHs	Σ6LPAHs/Σ10HPAHs
1	EL-Montazah Beach	< 1	< 1	< 1	< 1	0.00006	1.000	6.628	286711.67	0.00002
2	Miami Beach	< 1	< 1	< 1	< 1	0.0012	1.000	40.387	190160.51	0.0002
3	26-July Beach	< 1	< 1	< 1	< 1	0.00008	1.000	2538	163072.62	0.01556
4	The east port of Alexandria	< 1	8.974	0.900	< 1	1.000	1.000	762.0	36809.7	0.02070
5	The west port of Alexandria	< 1	< 1	< 1	< 1	1.000	1.000	2755	6215.939	0.4433
6	The west port of Aldekhela	< 1	< 1	< 1	< 1	1.000	1.000	16,358	20332.611	0.80454
7	EL-Nikhil Beach	< 1	2.966	0.748	< 1	1.000	1.000	193,316	375585.99	0.51471
8	EL-Bitash Beach	< 1	< 1	< 1	< 1	0.007	0.739	1764.694	180025.93	0.00980
9	EL-Hanovill Beach	< 1	< 1	< 1	< 1	0. 00,001	1.000	220.191	575799.4	0.00038
10	Zahra El-A Gamy	0.001	< 1	< 1	0.999	0.00001	1.000	174,116	1,080,640	0.16112
11	6-October Beach	0.527	< 1	< 1	0.655	1.000	1.000	23,356	408289.56	0.05720
12	Center the drainage a Gamy (km.21)	< 1	0.464	0.317	< 1	0.994	1.000	371.381	28113.985	0.01320
13	Sidi Krier Beach	< 1	< 1	< 1	< 1	1.000	0.039	438,552	3045	143.929
	Mean	0.406	0.542	0.1512	0.1272	0.5387	0.906	65704.328	258061.75	11.228
	Petrogenic sources	> 10	< 1	< 0.4	< 0.1	< 0.2	0.2–0.5	-	-	> 1
	Pyrogenic sources	< 10	> 1	> 0.4	> 0.1	> 0.35	> 0.5	-	-	< 1

< 1: under the limit of detection, concentration ng/L, LPAHs/HPAHs > 1 petrogenic, < 1pyrogenic, Flu/Flu + pyr < 0.4 petrogenic > 0.4 pyrogenic, Ant/Ant + phe < 0.1 petrogenic, > 0.1 pyrogenic, Flu/pyr < 1 petrogenic, > 1 pyrogenic, Phe/Ant > 10 petrogenic, < 10 pyrogenic, BaA/BaA + Chr < 0.2 petrogenic, > 0.35 pyrogenic, Flu/Flu + pyr 0.4–0.5 petrogenic, > 0.5 pyrogenic, Ipy/Ipy + Bp < 0.2 petrogenic, > 0.2pyrogenic, Ip/Ipy + BP 0.2–0.5 petrogenic, > 0.5 pyrogenic. Ant: Anthracene, Phe: Phenanthrene, BaA: Benzo[a] anthracene, Chr: Chrysene, Flu: Fluoranthene, BP: Benzo [g,h,i] perylene; BaP Benzo [a] pyrene, LPAHs: Low molecular weight PAHs, HPAHs: High molecular weight PAHs; IP: Indo [1,2,3-cd] perlyene; Pyr: Pyrene.

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ratios of individual PAH compounds of anthropogenic PAHs, the lower-molecular weight parents LMW PAHs have both petrogenic and combustion sources, whereas the high-molecular parents HMW PAHs have a predominantly pyrolytic source. Therefore, lower LMW/HMW (2 and 3 rings PAHs/4, 5 and 6 ring PAHs) ratio was observed in the pyrolytic source. In general, a ratio of LMW/HMW <1 suggests a pollution of pyrolytic origin [15]. The calculated ratios for the LMW/HMW for all stations were between 0.32 and 143.929 (mean = 11.228), which suggests that the sources of PAHs were both pyrogenic ratio of <1 and petrogenic ratio of >1 [15]. LMW/HMW ratio indicated that one station in the study area were contaminated mainly by petrogenic PAHs, revealed LMW/HMW ratio values higher than 1 at Sidi Krier beach site 13(143.929). This is likely to be due to inputs of hydrocarbons from shipping (e.g. ship discharges and oil spills into the coastal area of Alexandria). Examination of (Table 5) shows that the rest samples show values of LMW/HMW ratio lower than 1 (values between 0.00002 and 0.80454), indicating pyrolytic origin pollution.

4. Conclusion

This paper represents the first comprehensive survey of PAHs in seawater and provides important data on PAHs concentration and composition in Alexandria coastal seawater. Our results show that:

1. PAHs profile reveals that the dominant PAHs are high molecular weight compounds (4–6 rings); especially some suspected carcinogenic 4-ring PAHs were detected in all sites which should be concerned in the future.
2. The higher contents of low molecular weight PAHs (2–3 rings) in the water suggest a relatively recent local source of PAHs entered into the sea via wastewater discharge.
3. The spatial distribution of PAHs was site-specific, and the concentration of PAHs was higher in those samples collected near the effluents of sewage outfalls, industrial discharge, ballasting and de-ballasting operations of oil tankers and atmospheric rain-out which includes incompletely combusted oil products.
4. The calculated diagnostic chrysene ratio showed that the sources of PAHs are derived primarily from pyrogenic sources which originate from incomplete fuel combustion of the boats and vehicle engines with lesser amounts of PAHs contributed from petrogenic sources.

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