

## Origin and Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) In Surface Water of Suez Gulf

Mostafa M.Emara,<sup>1</sup>Nazik A. Farid,<sup>2</sup>Enas A.El-Sabagh,<sup>3</sup>Omayma E.Ahmed,<sup>2\*</sup> Eman M.Kama<sup>3</sup>

1- Chemistry department, Faculty of Science (Boys) Al-Azhar University, Nasr City, Cairo, Egypt.

2- Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt.

E-mail address: \*dr.omaymamosa@yahoo.com

3- Chemistry department, Faculty of Science (Girls) Al-Azhar University, Nasr City, Cairo, Egypt.

**Summary** The Suez Canal is the passage to the international trade between East and West, thus several waste pollutants are easily disposed and dumped into the boundaries of the studied area. The pollutant varies from raw sewage, oil spills, and industrial effluents to garbage which has tremendous impacts on the marine environment. Most of these sources in the investigated area mainly occurred from the human activities such as Industrial wastes, Domestic draining of the Suez City and Ship's oil. Distribution and origin of polycyclic aromatic hydrocarbons of (PAHs) in the collected water samples revealed the origin of (PAHs) is petrogenic and pyrogenic or mixture of (petrogenic and pyrogenic). Levels of PAHs varied between 1.640 - 39.139  $\mu\text{g} / \text{L}$  and 0.7317- 21.9373  $\mu\text{g} / \text{L}$  for summer and winter respectively. These results indicate high level of contamination, it is recommended that more effort and rules are carried out in order to govern, prevent or even minimize the sources of pollutants.

### Introduction

Hydrocarbons are a wide spread class of environmental chemical pollutants <sup>(1)</sup> which enter the marine environment through natural pathways and anthropogenic processes. Natural sources include forest fire, natural petroleum seeps and post – depositional transformation of biogenic precursors .The most important anthropogenic sources are petrogenic and pyrogenic, the latter usually being largely prevalent in aquatic environments. Anthropogenic sources include urban runoff, sewage disposal, industrial effluents, and oil production and transport activities. Polycyclic aromatic hydrocarbons (PAHs) a class of ubiquitous contaminants with two or more fused aromatic rings are mainly introduced into the environment via anthropogenic processes<sup>(2)</sup> such as the combustion of fossil fuels and the direct release of oil and oil products with a smaller

contribution arising from the forest fires and agricultural burn off . Anthropogenic inputs of PAHs have caused significant accumulation of PAHs in the marine environment <sup>(3)</sup>. PAHs are known to enter marine environment through the spillage of petroleum, atmospheric fallout and urban runoff upon entering the aquatic system PAHs distribute between different phases including truly dissolved, colloids, suspended particulate matter, surface sediment and biota. The way in which PAHs are distributed between these different phases is controlled by their intrinsic physicochemical properties including solubility, vapour pressure and lipophilicity. Because of their low water solubility and hydrophobicity, they tend to adsorb to particulate material and deposit in the sediments .In this form they are more persistent to biodegradation in comparison to dissolved PAHs. The degradation intensity differs depending on biological, chemical and physiochemical parameters <sup>(4)</sup>. Earlier studies indicates that hydrophobic organic compounds such as PAHs are often enriched in the sea surface and sediments .Accumulation of PAHs in sediments can be remobilized in the sea water and become bio-available to indigenous aquatic organisms. Concentrations of PAHs at the sea surface and in sediments are of toxicological importance to both benthic and pelagic marine organisms. Thus accumulation of pollutants represents a potential hazard to the organisms. As pollutants they are of great concern since some of them have been identified as carcinogenic and mutagenic. PAHs can induce oxidative stress and oxidative DNA damage through metabolic activation and the generation of reactive oxygen species <sup>(5-6)</sup>. Polycyclic aromatic hydrocarbon toxicity is very structurally dependent, with isomers varying from being non toxic to extremely toxic .Toxicity of these substances depends upon the number and configuration of the benzene rings and the presence and the position of their substituent<sup>(7)</sup>. Many high molecular mass PAHs are known to be carcinogenic and mutagenic. The composition of PAHs usually reflects the sources that produced the PAH. Some molecular indexes play a major role in establishing the origin of PAHs in marine water and sediments <sup>(8)</sup>. PAHs isomeric composition is temperature dependent because it is governed by thermodynamic properties in low temperature processes (e.g. formation of petroleum) or by kinetic factors in high temperature processes (e.g.

pyrolysis of organic matter). On the other hand, petrogenic contamination is characterized by the predominance of the lower molecular weight fraction, while the higher molecular weight PAHs prevails in pyrolytic PAHs(9).

## Experimental

### Materials and Methods

Collection of waste water samples: The samples are collected seasonally from the Different sites in the studied area as described in Table 1. The wastewater samples were taken from the drainages using plastic water sampler, the sample size was ( 3L.) for the petroleum analysis and samples were cleaned before use; they were rinsed several time in 0.1N hydrochloric acid for several days and then rinsed and protected in diluted acid to prevent degradation of oil to give proper result of analysis. During the period of study, the wastewater samples was collected from two sides of the location and mixed to make composite sample which represent one station. The study was done seasonally and samples collected twice from the studied sites one in summer season 7-2009 and another one in winter season 2-2010.

**Table 1.** The studied sites, their locations, activities and distance from Suez harbor  
Harb: harbor, km: Kilometer

Site No.	Locations	Activities for each site	Distance from Suez Harb.(km)
1	Suez Harbor.	Loading and discharge, marine transportation, including tanker operations	2 (km)
2	Al-Nasr oil Company	petroleum refinery of the crude oil	5 (km)
3	Inlet of Suez oil company	petroleum refinery of the crude oil	7 (km)
4	Outlet of Suez oil company.	petroleum refinery of the crude oil	9 (km)
5	Outlet of Electrical station company.	Industrial treatment- Unit for domestic sewage treatment	10 (km)
6	Fertilizer Factory	Unit for domestic sewage treatment	18 (km)
7	Al-Osra beach	Oil residue and solid wastes	20 (km)
8	Al-Melaha beach	Oil residue and solid wastes	21 (km)

## Procedure

100 mL of the seawater sample was shaken with 100mL of carbon tetrachloride in a separating funnel for 15 minutes. After 30 seconds agitation and 3 minutes settling period, the aqueous layer was discarded. The process was repeated until all of seawater sample has been extracted. The obtained extract was dried using anhydrous sodium sulphate (30 g). The extract was then transferred to a weighted beaker and finally evaporated by electrical furnace at 60 0C till constant weight (6).

## High performance liquid chromatography Analysis (HPLC)

All oil extracted from the studied samples was analyzed using HPLC technique (10).

### Apparatus

-Water HPLC 600, Auto sampler 616 plus, Dual Absorbance Detector 2487, attached to computerized system with Millennium 32 software.

### Condition for operation

-Sample: 1 $\mu$ I, Column: Supelcosill LC-PAHs .15 cm, 4.6 mm ID, 5  $\mu$  m particles

-Mobile phase: Acetonitrile: water 50:50 for 5 min .Changed gradually to 100% acetonitrile in about 25 min.

-Flow Rate: 0-2 min., 0-2 mL/min 0.2-45 min. 1.0 mL/min.

Detector: U.V 254nm.

## Results and discussion

The studied areas include Suez harbor, industrial zone in Suez and beaches in the Suez Gulf. These areas received pollutants from the shipping inputs which arise mainly from operational activities and from deliberating discharges of waste and water tankers. Oil is the most obvious contaminant in Suez Canal, dumping and accidents also contribute, but much less than in shelf waters. Other chemical contaminants from the synthetic organic compounds produced from the disposal of agricultural drains along the boundaries of the lakes and bay, as well as more directly via pipelines and dumping

operations. Sewage disposal, industry, and agriculture are the sources of nutrients. Waters were taken to cover most of the contaminated sites in studied area in two trips.

#### Seasonal Variation and distribution Patterns of Total PAHs in Surface Seawater

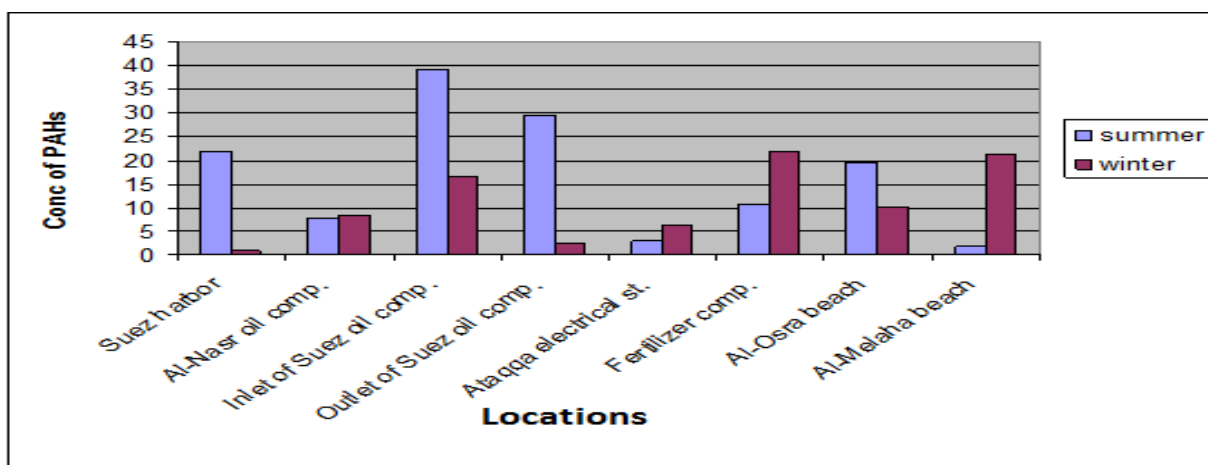
Eight surface seawater samples were collected during summer and winter 7 / 2009 and 2 \ 2010, in the Gulf of Suez, and analyzed by HPLC Table 2 and Figure 1. The total PAHS concentrations in surface seawater of the Gulf of Suez differ markedly in the summer and winter season's. The concentrations of total PAHs in summer ranged from 1.640 to 39.139  $\mu\text{g/L}$ . Highest concentrations was found at Inlet of Suez Petroleum Company, and the lowest concentration was recorded at Al-Melaha beach. Whereas, the concentration of total PAHs in surface seawater in winter ranged from 0.732 up to 21.937 $\mu\text{g/L}$ , the highest concentrations was observed at the Fertilizer company 21.937 $\mu\text{g/L}$ , and the lowest concentration 0.731  $\mu\text{g/L}$  was recorded at the Suez harbor Table 2, Figure1. Several previous studies (11-12) were carried out in order to determine the seasonal variability of PAH concentrations in Al-Nasr Petroleum Company, inlet outlet of Suez Petroleum Company, Electricity Station, Fertilizer Factory and both of AL-Osra and Al-Melaha beaches. The results suggest that seasonal variation in PAH concentrations are generally connected to temperature, lower concentrations of PAH were observed during summer, while higher concentrations during winter (12). The decreasing concentrations in summer could be a result of accelerated degradation due to the higher water temperature that affects the rate by which PAHs are degraded by micro-organisms or due to higher photo-oxidation. Additionally, other previous work also, suggested that seasonal variation in PAH concentration could be also attributed to hydrological and meteorological conditions. In contrast to previous studies, the results of our study show an average higher total PAH concentrations in summer compared to that in winter. Higher concentrations of PAHs detected in summer could be attributed to; PAHs of different degradation products present in surface seawater, while in general, the levels of PAHs determined in previous studies took into account only resolved PAH compounds. In accordance with our expectations, higher concentrations of PAHs were

obtained in semi-enclosed sites such as marine, harbors and petroleum companies. Results obtained proved that such location showed the most polluted ones. The reason lies in the more intensive pollution and limited circulation of seawater leading to higher accumulation of pollutants, arising from boats engine losses, atmospheric deposition and urban runoff. On the other hand, the offshore sites are less subjected to pollution pressure and at the same time. The mixing of waters leads to the dilution of dissolved, dispersed compounds<sup>(3)</sup>.

**Table 2.** Seasonal concentration ( $\mu\text{g/L}$ ) of Total PAHs in surface seawater at different sampling stations in Suez Gulf

S.No.	Location	Concentration	
		summer	winter
1	Suez harbor	21.98	0.732
2	Al-Nasr oil comp.	7.845	8.432
3	Inlet of Suez oil comp.	39.1392	16.758
4	Outlet of Suez oil comp.	29.5748	2.29406
5	Ataqqa electrical station	2.870	6.3855
6	Fertilizer company	10.92	21.9373
7	Al-Osra beach	19.72	10.2824
8	Al-Melaha beach	1.640	21.21

Concentration:  $\mu\text{g/l}$ .



**Figure1.** Histogram representing seasonal variation of total PAHs concentration  $\mu\text{g/L}$

### Concentration of individual PAH in surface seawater

The composition of PAHs in a particular sample usually reflects the source that produce the PAHs. There are three major types of PAH which differ by their genesis petrogenic, pyrogenic and biogenic. All samples Tables 3 and 4 are characterized by the presence of low poly-aromatic hydrocarbons (di, tri-aromatic ring) and 10 PAHs compounds, (tetra-penta and hexa-aromatic ring). HPAHs are more carcinogenic than either lower or longer ring system<sup>(13)</sup>.

**PAHs with 2-3 rings** are generally of petrogenic origin, including crude oil and its refined products<sup>(14)</sup>.

**Di-aromatic ring** show the presence of naphthalene at sites 2, 3, 7 and 8 for summer and 3, 4, 6 and 7 for winter water samples suggests fresh petroleum pollution. Close values 2.036 and 2.290  $\mu\text{g/L}$  were observed for sites 3 and 4 respectively in winter and predominance of Al-Osra beach site (7) 18.90  $\mu\text{g/L}$ .

**Tri-aromatic rings PAHs, were** below the detection limit of some samples except for sites 2 and 3 have Acenaphthylene (A) values 0.7084, 0.2406  $\mu\text{g/L}$  for summer and 0.5903, 1.4207  $\mu\text{g/L}$  for sites 6 and 7 in winter water samples. Acenaphthene (Ace) show high value at site (2) 6.5982  $\mu\text{g/L}$  in summer, while close values for sites (3) and (6) 5.875 and 5.6764  $\mu\text{g/L}$  in winter season. Phenanthrene (phe) explain matching values between sites 6, 8 and 2, 3 have values 0.025, 0.02  $\mu\text{g/L}$  and 0.1706, 0.2649  $\mu\text{g/L}$  for summer.

Also good matching for sites 2, 3 have values 0.0342, 0.0266  $\mu\text{g/L}$  at winter water samples Tables 3 and 4. Sites 7, 8 and 3 have values 0.1622, 0.194  $\mu\text{g/L}$  and 3.478  $\mu\text{g/L}$  for summer and winter season, respectively while the rest of samples were below the detection limit, for Fluorene (F). On the other hand, anthracene (Ant) recorded values for all samples except for sites 3,6 at summer and 1,2,4,7 & 8 were below the detection limit in winter.

**Tetra –aromatic rings**, PAHs with 4-6 ring hydrocarbons are generally of pyrogenic origin and generated by the combustion of fossil fuel and of recent organic material <sup>(14)</sup>. High concentrations Fluoranthene, Pyrene and Chrysene (Chr), Benzo (a) pyrene (BAP) for summer and winter season samples show a pyrogenic origin.

**Penta-aromatic rings**, only sample 4 have Benzo (k) Fluoranthene (BKF) with value 3.004  $\mu\text{g/L}$  whereas sites 3,4 and 6 have values 29.377 and 25.436, 10.44  $\mu\text{g/L}$ , respectively, from Benzo (a) Pyrene (BAP) for summer water samples and 6.2252, 11.8658 and 1.744  $\mu\text{g/L}$  for sites 2,6 and 8 respectively in winter. Indeed, each of Suez petroleum inlet and Al-Melaha beach sites 3 and 8 have Dibenzo (a,h) anthracene (DahA) 2.012 and 15.1861  $\mu\text{g/L}$  for summer and winter season respectively .

**Six aromatic rings** compound, from Benzo (ghi) Perlyene (BP) and Indeno (1, 2, 3-cd) perlyene (IP) are present in most samples with the predominance of (BP) 21.77  $\mu\text{g/L}$  for Suez Gulf in summer season. High poly- aromatic compounds (HPAHs) have high carcinogenic effect and show that the samples suffer high weathering effects.

### **Distinguishing between pyrogenic and petrogenic origin Hydrocarbon in Suez Gulf**

Several methods can be used to determine the most probable sources of PAHs <sup>(3)</sup>. In many studies <sup>(14, 2)</sup> the sources of PAHs in various environmental samples was determined by various molecular diagnostic ratios. One of the most used approaches is to compare the sum of several pyrogenic PAHs (4-6 ring PAHs) with a group of petrogenic PAHs (2-3 ring PAHs), since the 2-ring and 3-ring PAHs are more abundant in petroleum, while highly condensed PAHs (4-6 PAHs) are significant combustion products. pyrogenic sources, such as the combustion –derived particles present in urban atmospheric dust



**Table 3.** Concentration of individual PAH ( ug/L) in the oil extracted from summer water samples

Locations		S.NO.1	S.NO.2	S.NO.3	S.NO.4	S.NO.5	S.NO.6	S.NO.7	S.NO.8
Ring NO.	PAHs								
<b>2Ring</b>	<b>Nap.</b>	N.D	0.2814	0.6765	N.D	N.D	N.D	18.90	0.3141
	<b>Total</b>	<b>N.D</b>	<b>0.2814</b>	<b>0.6765</b>	<b>N.D</b>	<b>N.D</b>	<b>N.D</b>	<b>18.90</b>	<b>0.314</b>
<b>3Ring</b>	<b>A.</b>	N.D	0.7084	0.2406	N.D	N.D	N.D	N.D	N.D
	<b>Ace.</b>	N.D	6.5982	1.9090	N.D	N.D	N.D	3.095	N.D
	<b>Phe.</b>	N.D	0.1706	0.2649	N.D	0.0928	0.025	0.00705	0.020
	<b>F.</b>	N.D	N.D	N.D	N.D	N.D	N.D	0.1622	0.194
	<b>Ant.</b>	0.0129	0.0046	N.D	0.0279	0.00295	N.D	0.00514	0.010
	<b>Total</b>	<b>0.0129</b>	<b>7.481</b>	<b>2.4145</b>	<b>0.0279</b>	<b>0.0957</b>	<b>0.025</b>	<b>0.4838</b>	<b>0.225</b>
<b>4Ring</b>	<b>Flu.</b>	N.D	0.040	1.8822	0.2328	N.D	N.D	0.0239	0.102
	<b>Pyr.</b>	N.D	0.042	0.7722	0.2370	N.D	N.D	0.2545	0.079
	<b>BaA</b>	N.D	N.D	0.1518	N.D	N.D	N.D	0.0384	N.D
	<b>Chr.</b>	N.D	N.D	N.D	N.D	0.182	N.D	0.0171	0.048
		<b>Total</b>	<b>ND</b>	<b>0.083</b>	<b>2.8062</b>	<b>0.4698</b>	<b>0.182</b>	<b>ND</b>	<b>0.3339</b>
<b>5Ring</b>	<b>Bbf</b>	N.D	N.D	N.D	N.D	0.169	N.D	N.D	0.060
	<b>Bkf</b>	N.D	N.D	N.D	3.0039	N.D	N.D	N.D	N.D
	<b>BAP</b>	N.D	N.D	29.377	25.436	0.154	10.44	N.D	N.D
	<b>BahA</b>	0.131	N.D	2.012	ND	0.849	ND	N.D	N.D
		<b>Total</b>	<b>0.131</b>	<b>ND</b>	<b>31.389</b>	<b>28.4399</b>	<b>1.172</b>	<b>10.44</b>	<b>ND</b>
<b>6Ring</b>	<b>Bp</b>	21.77	N.D	N.D	0.5836	1.405	N.D	N.D	N.D
	<b>Ip</b>	0.068	N.D	1.853	0.0536	0.014	0.454	N.D	0.811
		<b>Total</b>	<b>21.84</b>	<b>N.D</b>	<b>1.853</b>	<b>0.63729</b>	<b>1.419</b>	<b>0.454</b>	<b>N.D</b>
<b>Total PAHs</b>		<b>21.98</b>	<b>7.845</b>	<b>39.1392</b>	<b>29.5748</b>	<b>2.870</b>	<b>10.92</b>	<b>19.72</b>	<b>1.640</b>

Concentration : (µg/L), N.D: Not Detected

**Table 4.** Concentration of individual PAH ( $\mu\text{g/L}$ ) in the oil extracted from winter water samples

Location		S.NO.(1)	S.NO.(2)	S.NO.(3)	S.NO.(4)	S.NO.(5)	S.NO.(6)	S.NO.(7)	S.NO.(8)
Ring NO	PAHs								
2Ring	Nap.	N.D	N.D	2.036	2.2904	N.D	1.2798	0.8628	N.D
	<b>Total</b>	<b>N.D</b>	<b>N.D</b>	<b>2.036</b>	<b>2.2904</b>	<b>N.D</b>	<b>1.2798</b>	<b>0.8628</b>	<b>N.D</b>
3Ring	A.	N.D	N.D	N.D	N.D	N.D	0.5903	N.D	1.4207
	Ace. Phe.	N.D 0.0803	N.D 0.0342	5.875 0.0266	N.D N.D	N.D 1.0876	5.6764 0.8503	2.5862 N.D	N.D N.D
	F.	N.D	N.D	3.478	N.D	N.D	N.D	N.D	N.D
	Ant.	N.D	ND	0.0234	N.D	0.0308	0.1273	N.D	N.D
	<b>Total</b>	<b>0.0803</b>	<b>0.0342</b>	<b>9.403</b>	<b>ND</b>	<b>1.1184</b>	<b>7.2443</b>	<b>2.5862</b>	<b>1.4207</b>
4Ring	Flu.	N.D	N.D	N.D	N.D	1.3524	N.D	3.3665	2.0055
	Pyr.	N.D	N.D	0.0843	0.00245	2.1076	0.3297	N.D	N.D
	BaA	N.D	N.D	4.1788	0.00121	0.5209	N.D	N.D	N.D
	Chr.	0.1918	N.D	0.00950	N.D	0.1351	N.D	N.D	N.D
	<b>Total</b>	<b>0.1918</b>	<b>N.D</b>	<b>4.2706</b>	<b>0.00366</b>	<b>4.116</b>	<b>0.3297</b>	<b>3.3695</b>	<b>2.0055</b>
5Ring	Bbf	N.D	N.D	0.1741	N.D	0.4491	N.D	N.D	N.D
	Bkf	N.D	0.7546	0.8746	N.D	N.D	1.2177	3.1367	0.8531
	BAp	N.D	6.2252	N.D	N.D	N.D	11.8658	N.D	1.7446
	<b>BahA Total</b>	<b>N.D N.D</b>	<b>N.D 6.9771</b>	<b>N.D 1.0488</b>	<b>N.D N.D</b>	<b>N.D 0.4491</b>	<b>N.D 13.0835</b>	<b>N.D 3.1367</b>	<b>15.1861 17.7838</b>
6Ring	Bp	N.D	0.2697	N.D	N.D	N.D	N.D	0.3272	N.D
	Ip	0.4596	1.1510	N.D	N.D	0.7020	N.D	N.D	N.D
	<b>Total</b>	<b>0.4596</b>	<b>1.4207</b>	<b>N.D</b>	<b>N.D</b>	<b>0.7020</b>	<b>N.D</b>	<b>0.3272</b>	<b>N.D</b>
<b>Total PAHs</b>		<b>0.7317</b>	<b>8.432</b>	<b>16.758</b>	<b>2.29406</b>	<b>6.3855</b>	<b>21.9373</b>	<b>10.2824</b>	<b>21.21</b>

Concentration :( $\mu\text{g/L}$ ), N.D: Not Detected

were depleted in low molecular weight 2-3 ring PAHs (LPAHs) and enriched in high molecular weight 4-6 ring PAHs (HPAHs), which led to an LPAHs \ HPAHs ratio  $<1$ . Petrogenic sources, such as fuel oil or light refined petroleum products, were dominated by low molecular weight PAHs and have LPAHs\ HPAHs ratio  $>1$ . Indeed, the higher the LPAHs\HPAHs ratio, the higher the prevalence of petrogenic sources<sup>(15)</sup>. The sources of PAHs may be assessed also by using the ratios of individual PAH concentrations<sup>(16)</sup>. Different authors use different methods for such purposes widely used ratios are Fluoranthene to pyrene (Flu/pyr), and phenanthrene to anthracene (phe/Ant). The Flu/pyr ratio  $>1$  suggests pyrogenic sources, while Flu/pyr  $<1$  indicate petrogenic sources<sup>(17)</sup>. The ratio between phenanthrene and anthracene was also extensively used to infer the nature of PAH pollution<sup>(8)</sup>. A phe/Ant ratio  $<10$  suggests pyrogenic origin while, contamination from petrogenic sources is characterized by phe/Ant  $>10$ . Besides the above mentioned ratio, some other PAH isomer ratios, such as anthracene to anthracene plus phenanthrene Ant/ (Ant+phe), Fluoranthene to Fluoranthene plus pyrene Flu/Flu+pyr, have been developed to a more detailed interpretation of PAH composition and the inference of possible sources<sup>(18)</sup>. Tables 5 show that phe/Ant ratio for S.NO. (5) 31.45 and 35.311 $\mu\text{g/L}$   $>10$  indicating mainly petrogenic origin, for summer and winter seasons, also S.NO. (2) 36.49 for summer water samples have the same origin. The ratios of Fluoranthene /pyrene (Flu/pyr) indicate the origin of PAHs. A predominance of Fluoranthene over pyrene is characteristic of pyrolytic sources, while in PAHs petrogenic origin, pyrene is more abundant than Fluoranthene. Table 5 shows that PAHs of samples (2,4 and 7) have values 0.9523, 0.9822 and 0.0939 respectively, mainly petrogenic origin while samples (3,8) have values 2.437 and 1.290 respectively, mainly pyrolytic origin for summer season also, S.NO.(5) have value 0.641 for winter season indicating petrogenic origin, while the rest of samples under low detections, Besides the above mentioned ratios some other PAHs isomer ratio such as Ant \ (Ant +phe ) and Flu / (Flu+pyr) have been developed for a more detailed interpretation of PAHs composition and inference of possible sources,<sup>(18)</sup> Table 5 displays values for Ant/Ant+phe ratio less than 0.1 except for S.NO. 7 and 8 for summer season have values 0.4215 and 0.3333  $\mu\text{g/L}$ .

**Table 5.** PAHs parameter used to detect the origin of PAHs for seasonal water samples

S. No	Phe/Ant	Flu/Pyr	Ant /Ant+phe	Flu/ Flu+Pyr	6LPA Hs	10HPA Hs	6LPAHs /10HPA Hs	Phe/Ant	Flu/Pyr	Ant /Ant+ph e	Flu/ Flu+Pyr	6LPA Hs	10HPA Hs	6LPAH /10HPAH s
	summer							winter						
1	N.D	N.D	N.D	N.D	0.0129	21.975	0.0006	N.D	N.D	N.D	N.D	0.0803	0.651	0.123
2	36.49	0.9523	0.0262	0.4878	7.7624	0.083	93.522	N.D	N.D	N.D	N.D	0.0342	8.397	0.0040
3	N.D	2.437	N.D	0.7090	3.091	36.048	0.0857	1.1367	N.D	0.4680	N.D	11.439	5.319	2.150
4	N.D	0.9822	N.D	0.4955	0.0279	29.546	0.0009	N.D	N.D	N.D	N.D	2.290	0.0040	572.5
5	31.45	N.D	0.0303	N.D	0.0957	2.775	0.0344	35.311	0.641	0.0275	0.3908	1.118	5.267	0.212
6	N.D	N.D	N.D	N.D	0.025	10.894	0.0022	6.679	N.D	1.1049	N.D	8.524	13.413	0.635
7	1.371	0.0939	0.4215	0.0858	19.389	0.333	58.225	N.D	N.D	N.D	N.D	3.449	6.833	0.504
8	1.951	1.290	0.3333	0.5635	0.5392	1.101	0.4897	N.D	N.D	N.D	N.D	1.420	19.789	0.071

PAHs parameter used to detect the origin of PAHs by  $\mu\text{g/L}$ , N.D: not determined. 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 BaA/Chr 0.9 petrogenic,<0.4 pyrogenic, Chr/BaA<1 petrogenic,>1 pyrogenic, Bap/BP < 0.6 petrogenic ,>0.6 pyrogenic, Flu/flu+pyr 0.4-0.5 petrogenic, > 0.5 pyrogenic, Ipy/Ipy+Bp <0.2 petrogenic,>0.2 pyrogenic, Ipy/Ipy+BPE 0.2-0.5 petrogenic, >0.5 pyrogenic <sup>(3)</sup>.

respectively also, S.NO. (3 and 6) have values 0.4680 and 1.1049  $\mu\text{g/L}$  indicating pyrogenic origin in winter in addition, values  $>0.4$  suggested pyrogenic origin while,  $<0.4$  indicating petrogenic sources for Flu / (Flu+pyr) ratio <sup>(6)</sup>. S.NO. (2, 4) in summer samples exhibit values 0.4878, 0.4955  $\mu\text{g/L}$  suggests fuel combustion from petrogenic origin, whereas S.NO. (3) 0.7090  $\mu\text{g/L}$  and (8) 0.5635  $\mu\text{g/L}$  indicating Grass, coal and wood combustion from pyrogenic sources <sup>(3)</sup>. Lower molecular weight compounds (LPAHs) are abundant in petrogenic (PAHs), which can easily undergo weathering as compared to the higher molecular weight (HPAHs). Thus attention has been paid to the distribution of Low and high molecular weight (PAHs) as a reliable tool origin of (PAHs). Studies have shown that high  $\Sigma\text{LPAHs} / \Sigma\text{HPAHs}$  ratios  $>1$  often indicate (PAHs) with petrogenic origin predominate sources, while low  $\Sigma\text{LPAHs} / \Sigma\text{HPAHs}$  ratios suggest PAHs of pyrolytic origin<sup>(19)</sup>, so samples Tables (5) display values for 6LPAHs /10HPAHs ranged between 0.00006 to 93.522  $\mu\text{g/L}$  and 0.0040 up to 572.5  $\mu\text{g/L}$  for summer and winter seasons respectively. These ratios were used for exhibit the pollution from the Gulf traffic through the port, as from the industry and sewage out falls from the city of Suez Gulf. Also, its semi-enclosed position and shallowness is an exceptionally sensitive ecosystem which is strongly influenced by human activities. The Gulf's peculiar geomorphologic and hydrologic conditions make it prone to the accumulation of pollutants which mainly enter the Gulf environmental through anthropogenic activities. For better determination and demonstration LPAHs / HPAHs ratio against Flu/pyr ratio were examined in Table 6 and suggested by<sup>(18)</sup> the PAH cross plots of the ratios of LPAHs/HPAHs against Flu/pyr indicate different PAH origins, Summer surface seawater S.No. (3, 8) with LPAHs / HPAHs ratio  $<1$  and Flu / pyr ratio  $>1$  suggested pyrogenic origin, while S.No. (4, 5, 7) with LPAHs \ HPAHs  $<1$  and Flu \ pyr ratio  $<1$  suggested mixed origin (pyrogenic and petrogenic) for summer and winter seasons samples <sup>(20)</sup>. The origin of PAHs in surface water samples were examined by phe/Ant against Flu/pyr ratios Table 7, the phe /Ant ratio  $<10$  and Flu/pyr ratio  $>1$  found in summer water S.No. (3) And suggested contamination from combustion processes, while phe/Ant ratio  $>10$  and Flu/pyr ratio  $<1$  found in water S.No.(2,5) confirmed mixed origin<sup>(21)</sup>. The phe/Ant

**Table 6.** Calculated ratios for source identification seasonal surface water samples

S.NO.	Locations	Phe/Ant		Flu/Pyr		LPAHs\HPAHs		Flu/Pyr	
		summer	winter	summer	Winter	summer	winter	summer	winter
1	Suez harbor	N.D	N.D	0.0006	0.123	0.0006	0.123	N.D	N.D
2	Al-Nasr oil company.	36.49	N.D	93.522	0.0040	93.522	0.0040	0.9523	N.D
3	Inlet of Suez oil company.	N.D	1.1367	0.0857	2.150	0.0857	2.150	2.437	N.D
4	Outlet of Suez oil company	N.D	N.D	0.0009	572.5	0.0009	572.5	0.9882	N.D
5	Ataqqa electrical station.	31.45	35.311	0.0344	0.212	0.0344	0.212	N.D	0.641
6	Fertilizer factor	N.D	6.679	0.0022	0.635	0.0022	0.635	N.D	N.D
7	Al-Osra beach	1.371	N.D	58.225	0.504	58.225	0.504	0.0939	N.D
8	Al-Melaha beach	1.951	N.D	0.4897	0.071	0.4897	0.071	1.290	N.D

LPAHS: Low polyaromatic hydrocarbons, H PAHs: High polyaromatic hydrocarbons: Flu: Fluoranthene, :Pyr: Pyrene.,Phe: Phenanthrene; Ant: Anthracene, N.D: under the limit of detection.

**Table 7.** Determination of PAH pollution sources of seasonal surface water samples

S.NO.	Locations	Ant\Ant+phe		Flu\Flu+pyr	
		summer	winter	summer	winter
1	Suez harbor	N.D	N.D	N.D	N.D
2	Al-Nasr oil comp.	0.0262	N.D	0.4878	N.D
3	Inlet of Suez oil company.	N.D	0.4680	0.7090	N.D
4	Outlet of Suez oil company.	N.D	N.D	0.4955	N.D
5	Ataqqa electrical station.	0.0303	0.0275	N.D	0.3908
6	Fertilizer factor	N.D	1.1049	N.D	N.D
7	Al-Osra beach	0.4215	N.D	0.0858	N.D
8	Al-Melaha beach	0.3333	N.D	0.5635	N.D

Ant: Anthracene, phe: Phenanthrene; Flu: Fluoranthene; Pyr: Pyrene, N.D: under the limit of detection

ratio against Flu/pyr ratio suggests mixed origin, while S.NO. (2, 5) indicates the predominance of petrogenic origin in summer and winter seasons respectively. In order to determined PAHs sources in surface seawater where different ratios and plots shows mixed origin, the ratios Ant / (Ant+phe) against Flu / (Flu/pyr) Table 7, were previously reported in this study indicating mainly pyrogenic origin and confirmed pyrogenic origin<sup>(22)</sup>.

#### **Distribution of PAHs (%) in surface seasonal seawater according to their number of aromatic rings**

The composition pattern of PAH by ring number is shown in Table 8. Usually, low molecular weight PAHs predominate in seawater while high molecular weight PAHs predominate in sediment samples<sup>(3, 22)</sup>. Such a difference in contaminant abundance by different PAH assemblages is expected due to at least two factors. First, the water column receives direct PAH inputs from various sources, including both petrogenic and pyrolytic. In the surface seawater of the Gulf of Suez, the petrogenic sources may be more widespread and dominate than pyrolytic ones, leading to the abundance of 3-ring PAHs in seawater. Second only those PAHs that are stable enough will reach the sediment bed. Such PAHs are quite likely to be of relatively high molecular mass and hence more resistant to degradation, evaporation and dissolution processes. In addition, processes such as biodegradation will attach PAHs leading to accumulation of those PAHs more resistant to degradation. Again, it is mainly the high molecular mass PAHs that are more

stable. As a result, the water samples were dominated by different PAHs. Generally, the most abundant 2-3 ring compounds of phenanthrene, anthracene, acenaphthene and naphthalene were present in both summer and winter season samples. Predominance of low molecular weight PAH (2-3 ring PAHs) over high molecular weight PAHs (4-6 ring PAHs) in seawater is accordance with some other studies<sup>(23)</sup>. 2-3 ring PAHs showed dominance at S.NO 2, 7, 8 and 3 respectively, with percentage between 0.09 to 98.9% for summer water samples whereas, winter samples recorded predominance for S.NO. 4, 3, 6, 7 and 8 respectively and exhibit percentage ranged between 0.41-99.8 %percent beside, four ring PAHs suggests value ranged between 0.083 upto 14.0 percentages for summer season. On the contrary, winter season samples represented an increasing percentage for 4-ring distribution at S.NO.5, 7 and 3 with values 64.5, 32.8 and 25.5% respectively penta aromatic ring percentage of higher molecular weight, PAHs has been commonly observed in summer and winter season samples ranged between 0.59-96.16% and 6.3-83.8% respectively. Benzo (ghi) perlyene (Bp) and Indeno (1,2,3cd) perlyene in six ring compounds prevailed at sites (1,5 and 8) with percentage (99.36, 49.4 and 49.5%) for summer season, and recorded values ranged between 3.2 up to 62.8% for winter samples and dominance for S.NO.(1,2) 62.8% and 16.9% respectively.



**Table 8.** Distribution of PAHs% in seasonal seawater of the Suez Gulf according to the number of aromatic rings

S.NO.	Location	2-3	4 Ring%	5 Ring%	6 Ring%	2-3	4Ring%	5	6
		Rings%				Rings%		Ring%	Ring%
		summer				winter			
1	Suez harbor	0.06	N.D.	0.59	99.36	11.0	26.2	N.D.	62.8
2	Al-Nasr oil company	98.9	0.083	N.D.	N.D.	0.41	N.D.	82.8	16.9
3	Inlet of Suez oil company.	7.89	7.16	80.19	4.73	68.3	25.5	6.3	N.D.
4	Outlet of Suez oil company.	0.09	1.58	96.16	2.15	99.8	0.16	N.D.	N.D.
5	Ataqqa electrical station.	3.3	6.3	40.8	49.4	17.5	64.5	7.03	11.0
6	Fertilizer factor	0.22	N.D.	95.6	4.15	38.9	1.50	59.6	N.D.
7	Al-Osra beach	98.2	1.7	N.D.	N.D.	33.5	32.8	30.5	3.2
8	Al-Melaha beach	32.7	14.0	3.6	49.5	6.7	9.4	83.8	N.D.

N.D: under the limit of detection

### **Conclusion and Recommendations**

The aim of the present study was to investigate and establish the pollution with PAHs in surface sea water of the Suez Gulf Egypt, HPLC was applied as screening method for the determination of total PAHs in surface seawater across the range of estuaries, marinas, coastal and offshore areas in order to identify hot spots and also, for the individual PAHs compounds identification at the most polluted sites. Because surface seawater samples often reflect the momental situation of PAH pollution which usually depends on hydrological and meteorological conditions. The study was focused on distribution, seasonal variation, composition and sources of PAHs in surface seawater of Suez Gulf. Different diagnostic ratios were applied to elucidate the sources of investigated compounds. Results of the present study provide information about the contamination of surface seawater, which are considered as one of the most dangerous group of environmental pollutants, in an industrial and very sensitive area Egypt. The results of this study show seasonal concentration of TPAHs ranged between 1.640-39.139 $\mu\text{g/L}$  and 0.7317-21.9373 $\mu\text{g/L}$  for summer and winter respectively, this will contribute to the better understanding of the state and sources of pollution with PAHs in the Suez Gulf. Because the Suez Gulf is used in many areas as a recipient of waste water from different sources this; study recommended that pollution control for wastewater disposing into it should be improved by separation of oils water Alsaourh before dumping into the Gulf, follow the accumulation of contaminants in the water and beaches to take the necessary precautions to reduce it, development of a system for rapid intervention in the event of oil disasters and Serious commitment to the application of environmental law 1994 on the protection of water and beaches.

### References

- 1- A. Valavanidis, Th. Vlachogianni, S. Triantafillaki, M. Dassenakies, F. Androutsos, M. Scoullou, *Coastal and shelf Science*, 79,733-739, (2008).
- 2- Y.w. Qiu, G. Zhong, G. O. Liu, L .L. Guo, X.D. Li, O. Wai, *Coastal and shelf Science*, 83, 60-66, (2009).
- 3- P. Ludvik, MSc. Thesis entitled, Nova Garcia, (2010).
- 4- B. Jovan-Cicevic, M. Vrvic, J. Schwarzbauer, H. wehner, G. Sheader, D. Vitorovic, *Water, air and soil pollution* 183, 225-23, (2007).
- 5- S. Ohnishi, S. Kawanishi, S. Double, *Biochemical and Biophysical research Communications*. 290, 778-782, (2002).
6. I. A. Mohamed .Thesis submitted for MSC, Azhar University, (2012).
7. R.G. Harvey, Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley New York, 8-11, (1996).
- 8- E. Magi, R. Bianco, C. Ianni, M. Di Carro, *Environmental pollution*.119, 91-98, (2002).
- 9- M. P. Zakaria, H. Takada, Si. Tsutsumi, K. Ohno, J. Yamada, E. Kouno, H. Kumata, *Environmental Science and Technology*, 36, 1907 - 1918, (2002).
10. S. Fengchen, A. Richard Mowery, A. Vanessa Castleberry, G. Peter Van Walsum Kevin Chambills, "Journal of Chromatography a, 1104, 54-61, (2006).
- 11- C. Halsall, L. A. Barrie, P. Fellini, D.C.G. Muir, B. N. Billeck, L. Lockhart, F. Rovinsky, Ya. EYA. Kononov, B. Pastukhov, *Environmental science and technology*, 31, 3593 -3599, (1997).
12. G. Witt, *Marine Chemistry* 79, 49-66, (2002).
13. J.M. Neff. *Fates and Biological effects* .7-33, applied science, London, u k. (1979).
14. L. Liu, Y. Chen, Z. Jianful, H. Qinghui, Z. Zhiliang, G. ttongwen, *Environmental pollution* .154, 298-305, (2008).
- 15- X. C. Wang, S. sum, H. O. Ma, Y. lu, *Marine pollution Bulletin*, 52, 129-138, (2006).
- 16- A. Katsoyiannis, E. Terzi, Q. Y. Cai, *Appropriate Chemosphere*, 69, 1337-1339, (2007).

- 17- M. Kim, Kennicutt, M.C. It, Y. Qian, *Science of total environment*, 289, 367-377, (2008).
- 18- M. Brandli, T.D. Bucheli, T. Kupper, J. Mayer, F.X. Stadelman, S. Taradellas, *Environmental pollution* 520-528, (2007).
- 19- G. De Luca, A. Furesi, G. Micera, A. Panzanelli, P. C. Piu, M. I. Pilo, N. Spano, G. Sanna, *Nature Marine Pollution Bulletin*, 50, 1223-1232, (2005).
- 20- S. Ali, N. Sh-El-Gendy, Y. Moustafa and S. Habib. 12<sup>th</sup> International Conference in petroleum, Mineral wealth and development, 7-9, Feb. Egypt, Cairo, (2009).
- 21- M. Notar, H. Leskovsek, and J. Faganeli, *Marine Pollution Bulletin*. 42, 36-44, (2001).
- 22- T. Cibic. A. Acquavita, F. Aleffi, N. Beltoso, O. Blasutto, C. De Vittor, C. Falconi, J. Fonda, S. Faresil predonzani, F. Tamberlich Fonda, S. umani, *Marine pollution Bulletin* 56, 1650-1657, (2008).
- 23- E. Health, N. Organic, J. Faganeli, S. Covelli, *Water, air and soil pollution focus*, 6, 241-250, (2006).