

DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN COASTAL WATER ALONG THE NORTH-WESTERN AREA OF THE GULF OF SUEZ

BY

MOURSY, A.S; IBRAHIM, M.B.M. * AND ABD EL-GHAFAR, H.H.

**Water Pollution Research Department, National Research Centre, Cairo, Egypt.*

ABSTRACT

Levels of polycyclic aromatic hydrocarbons (PAH's) were determined in the coastal seawater of the northwestern area of the Gulf of Suez (GOS). Sixty subsurface water samples were collected along the coastal area between EL-Adabya port near the Suez City and Ain Sokhna in the vicinity of the SUMED pipeline terminal. Monthly sampling was performed between October 1999 to November 2000 from five different locations. Seventeen compounds of PAH's were identified. Mean Σ PAH's levels ranged from 16.25 to 39.29 $\mu\text{g}/\text{l}$. Generally, high concentrations of the total PAH's (30.69 and 39.29 $\mu\text{g}/\text{l}$) were found in the locations 4 and 5 (Suez bay). The degree of pollution decreases southwards along GOS. Fluoranthene was abundant in all locations than other PAH's. The results from different seasons have also been compared. The levels of PAH's were lower in summer than during winter. This might be attributed to seasonal temperature variations and the intensity of degradation. The origin of hydrocarbons was identified using the distribution of individual compounds and by a set of parameters and ratios that are useful in distinguishing the contribution of biogenic (biological nature) and anthropogenic (petroleum nature). This study aimed to determine the petroleum hydrocarbon distribution along the northwestern region of GOS, estimate background levels and establish criteria for future monitoring strategies in the region.

INTRODUCTION

Marine pollution by oil has received global scientific interest, since it contributed to the deterioration of the marine environment. It has been estimated that the total annual influx of petroleum into marine environment is between 1.7 and 8.8 million metric tonnes (National Academy of Science, NAS, 1985). Hydrocarbons, which are the major

constitute of oil, are the most ubiquitous organic contaminants in the marine environment (Weber and Bicego, 1990; Madany *et al.*, 1998; Peña Méndez *et al.*, 2001).

Polycyclic aromatic hydrocarbons (PAH'S) are one of the most significance classes of organic pollutants in the marine environment (Harvey, 1996). The annual input of PAH's into marine environment is estimated as 230000 tonnes and they are ubiquitously distributed world wide (Law, 1986). PAH's arise from pyrogenic sources such as incomplete combustion of organic materials in flames , pyrolysis of fossil fuels (coal and petroleum), engines and industrial processes, or from petrogenic sources such as oil spills, emissions of noncombustion-derived petroleum or petroleum products (Wakeham *et al.*, 1980). PAH's are also produced during the diagenesis of biogenic precursors (e.g. plant matter) or synthesized by some organisms (e.g. bacteria, algae and fungi) (Volkman *et al.*, 1992; Witt, 1995). Levels of PAH's due to natural processes (biogenic) are generally very low compared to PAH's originating from anthropogenic sources. PAH's are known to enter aquatic environment through domestic and industrial discharges, oil spillage or leakage during the storage and transport of petroleum and petroleum products, and non-point sources such as urban run-off and atmospheric deposition (Latimer *et al.*, 1990; Lipiatou and Saliot, 1991; Sherblom *et al.*, 1995; Smick *et al.*, 1996).

Coastal oil pollution of the Gulf of Suez is a serious problem. The principal sources are anthropogenic and they include, (a) offshore oil production mostly in the southern regions, (b) wastewatare effluents from the industrial activities in the northern region which comprise oil refineries, fertilizer plants and petrochemical industries, (c) ballast and/or bilge water from tankers and huge vessels awaiting berth or those in transit through the Suez Canal, (d) sewage and domestic waste from the Suez City, (e) accidental oil spills and leakage, (f) tanker operations at SUMED pipeline terminals in Ain Sokhna and (g) atmospheric deposition.

The levels and distribution of petroleum pollution in water from the Gulf of Suez has been the subject of several studies (Meshal, 1970; Awad *et al.*, 1983; Mancy, 1983; Hanna, 1995),but no of these or others have focused on the level Of PAH's so, the study was undertaken to identify potential current problems and provide a baseline for future reference.

MATERIALS AND METHODS

Sixty subsurface water samples (1 m depth) were collected at approximately monthly intervals during the period from October 1999 to November 2000. The samples were taken from five different locations (Table 1 & Fig.1) along the coastal area of the northwestern part of the Gulf of Suez (GOS).

Table 1: Description of the sampling stations.

Station (1)	Ain Sokhna, in the vicinity of the SUMED pipelines terminal.
Station (2)	In front of the new commercial port (Ain Sokhna Port).
Station (3)	The middle point between the Suez City and Ain Sokhna (private beach called Miratex).
Station (4)	Inside the Suez Bay, 15 km away from the station 1 to the south.
Station (5)	Inside the Suez Bay at El-Adabya port.

The water samples were extracted twice using glass-separating funnel fitted with glass stopper and PTFE stopcock. Chromatography grade n-hexane was used to extract the water samples. The extracts were combined, dried with anhydrous Na_2SO_4 and concentrated to 2 ml using Rotary evaporator. The subsequent clean-up and fractionation of the extracts was carried out by column chromatography. A 20 cm length and 10 mm bore glass column were used. The column was slurry packed – the slurries of both aluminum and silica gel (5% deactivated) – being prepared in n-hexane. The packed column has 6 cm of aluminum over 12 cm of silica and 1 cm of anhydrous Na_2SO_4 on the top, then it washed with 20 ml of n-hexane. The concentrated extract quantitatively transferred to the top of the column using Pasteur pipette. The aliphatic fraction (F1) is eluted first with 40 ml of n-hexane, then the aromatic fraction (F2) which contain PAH's is eluted next with 20 ml of 10% dichloromethane in n-hexane followed by 20% dichloromethane in n-hexane.

The second fraction (F2) is reduced to 1 ml for further analysis by gas chromatography. Hewlett Packard HP 6890 series capillary gas chromatography equipped with Flame Ionization Detector (FLD) was used to identify and the quantify the polycyclic aromatic hydrocarbons. The column PH-1 was used and programmed from 80 °c – 280 °c/min with 2 min initial hold and 15 min final hold. The inlet and detector temperatures were isothermally maintained at 250 °c and 300 °c, respectively. Nitrogen was used as a carrier and make-up gas. All samples were injected in the splitless mode. Procedure blanks and standard were run systematically in association with samples. The lower detection limits for PAH's varied between 0.05 – 5 ng/l. Data acquisition and were controlled by HP windows-based Chemstation data system. Concentrations of the individuals PAH's were calculated by using the external standard calibration method. A standard of seventeen individual PAH Compounds in a mixture (priority pollutants specified on EPA method 610) obtained from Suppelco Inc. was used.

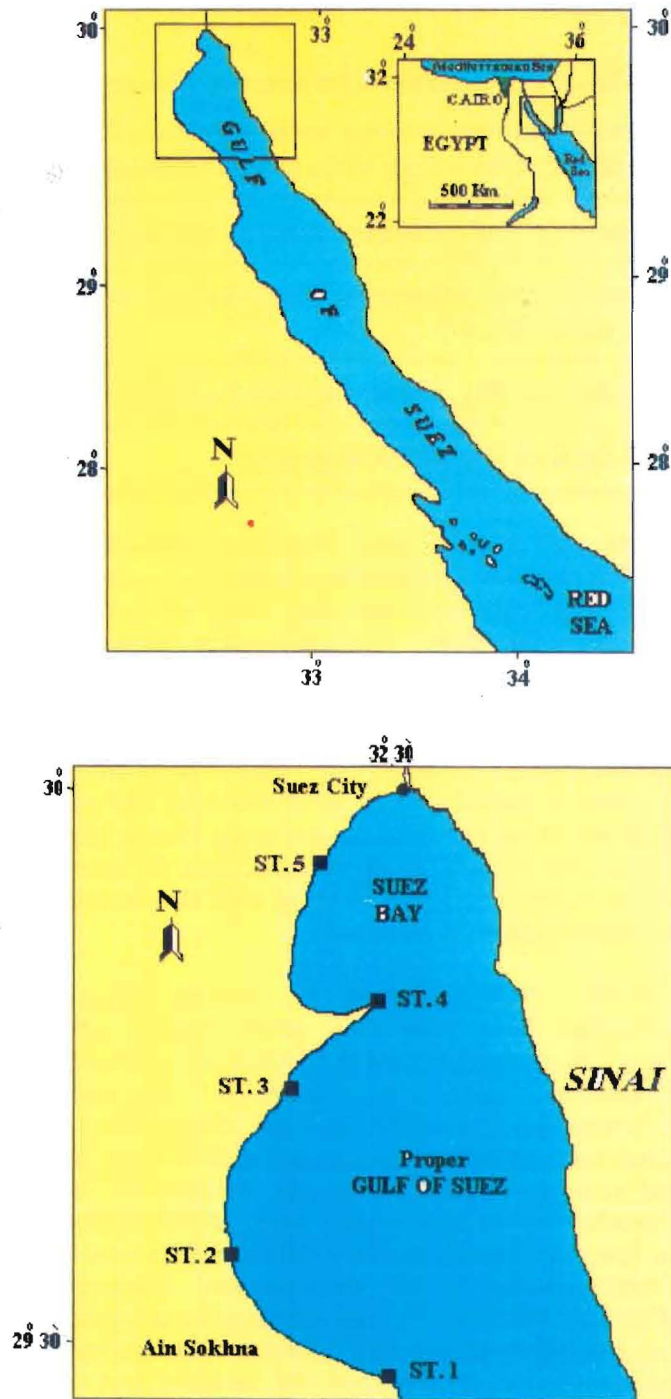


Fig. 1 Map of the Gulf of Suez showing the sampling stations.

Concentrations of PAH's in water are expressed in unit $\mu\text{g/l}$. Sum of PAH's, minimum levels, maximum levels, mean concentrations, standard deviation (\pm SD) and 95 % confidence intervals (95% CI) were used as statistical measurements to verify the accuracy of the results. Analysis of variance test (ANOVA) was used to determine the statistical significant variations of PAH's levels in water among the different locations and seasons.

RESULTS AND DISCUSSION

Seventeen individuals PAH's were identified and determined in the collected water samples. The mean concentrations of each compound as well as the total PAH's in the water from the different stations are presented in tables 2 & 3, respectively. The highest mean value was recorded in station 2 (16.25 $\mu\text{g/l}$). Means of the total PAH's in the stations 1 & 3 were the same (23.56 $\mu\text{g/l}$ & 23.85 $\mu\text{g/l}$, respectively).

The distribution of PAH's in the water samples from all stations during the period of study is shown in Fig. 2. The gradient of the total PAH's levels in the studied area is shown in Fig. 3 as well as the mean concentrations of the total PAH's with their 95% CI is seen in Fig. 4. The worst affected Locations are in the Suze Bay (stations 4&5), and the degree of pollution decreases southward. However, on one occasion, unusually high value of total PAH's was determined at station 4 on May 2000 (119.27 $\mu\text{g/l}$), probably due to recent pollution source.

Among the individual PAH's identified, the dominant compounds in the water were flouranthene, benzo [b] flouranthene, benzo [a] pyrene and benzo[a] anthracene, respectively (Table 2). Flouranthene was the abundant compound in all samples, where its mean values ranged from 7.02 – 30.11 $\mu\text{g/l}$. The PAH group profile shows the predominance of 4-rings compounds followed by 5-rings and 3-rings, respectively Fig.5.

When discussing the distribution of PAH's, or any other pollutants, in the Gulf of Suez, there are two factors should be taken into account. These are the sea level in the GOS and the direction of water current. In general, the Red Sea and the GOS level is higher than the Mediterranean Sea level all over the year, consequently the water current is northward most of the year. This could be explaining that why the degree of pollution during the period of study is higher at the northern part of the GOS compared with the southern part. Several authors have referred to this point and concluded the same results with different kind of pollutants (Meshal, 1970; Awad *et al.*, 1983; Mancy, 1983;).

Table (2) Mean values \pm SD of individual PAH's ($\mu\text{g/L}$) in water during the period of study (1999-2000)

Compounds	Site(1)			Site(2)			Site(3)			Site(4)			Site(5)		
	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max	Mean	Max	Mean \pm SD	
Naphthalene	0.018	1.219	0.531 \pm 0.313	0.146	1.857	0.584 \pm 0.485	n.d	1.071	0.419 \pm 0.386	0.026	1.017	0.531 \pm 0.379	0.059	1.276	0.546 \pm 0.415
Acenaphthylene	0.022	0.689	0.188 \pm 0.215	0.017	0.654	0.152 \pm 0.183	n.d	0.522	0.130 \pm 0.178	n.d	0.622	0.201 \pm 0.219	n.d	0.505	0.191 \pm 0.163
2-Bromonaphthalene	0.016	0.245	0.115 \pm 0.072	0.041	0.203	0.112 \pm 0.053	n.d	0.281	0.117 \pm 0.097	n.d	0.502	0.185 \pm 0.149	n.d	0.459	0.177 \pm 0.155
Acenaphthene	0.133	1.910	0.559 \pm 0.604	0.102	1.192	0.369 \pm 0.341	n.d	1.081	0.275 \pm 0.317	0.022	1.306	0.505 \pm 0.472	0.037	0.852	0.421 \pm 0.307
Fluorene	0.094	2.286	0.721 \pm 0.730	0.138	1.772	0.582 \pm 0.561	n.d	1.679	0.440 \pm 0.541	n.d	1.989	0.737 \pm 0.661	0.011	1.481	0.583 \pm 0.496
Phenanthrene	0.068	2.044	0.639 \pm 0.681	0.059	1.429	0.442 \pm 0.512	n.d	1.292	0.401 \pm 0.408	0.031	2.161	0.684 \pm 0.677	0.045	1.227	0.549 \pm 0.426
Anthracene	0.025	1.729	0.481 \pm 0.562	0.036	1.243	0.283 \pm 0.365	n.d	0.64	0.224 \pm 0.230	n.d	3.087	0.599 \pm 0.918	0.022	0.97	0.438 \pm 0.318
Carbazole	0.022	2.332	0.556 \pm 0.759	0.013	0.787	0.316 \pm 0.294	0.005	0.979	0.398 \pm 0.373	0.012	1.877	0.575 \pm 0.605	0.038	2.108	0.858 \pm 0.696
Fluoranthene	1.00	78.27	13.21 \pm 19.96	1.038	22.82	7.019 \pm 8.157	n.d	54.56	16.19 \pm 20.63	0.818	62.89	16.11 \pm 21.18	n.d	70.55	30.107 \pm 29.94
Pyrene	n.d	1.013	0.321 \pm 0.427	0.006	1.159	0.301 \pm 0.376	n.d	1.172	0.345 \pm 0.435	0.005	6.949	1.103 \pm 2.142	0.014	1.126	0.450 \pm 0.398
Benzo[a] Anthracene	n.d	8.508	1.469 \pm 2.701	0.011	8.648	1.307 \pm 2.632	0.019	6.931	1.094 \pm 2.175	0.001	11.09	2.030 \pm 3.526	n.d	2.988	0.856 \pm 1.011
Chrysene	n.d	4.322	0.839 \pm 1.489	0.024	5.698	0.795 \pm 1.731	n.d	5.303	0.808 \pm 1.660	0.014	11.88	1.732 \pm 3.613	0.012	1.999	0.655 \pm 0.724
Benzo[b] Fluoranthene	n.d	9.238	2.138 \pm 2.977	0.005	15.04	2.455 \pm 4.494	0.144	11.67	1.835 \pm 3.569	0.240	7.255	2.357 \pm 2.483	0.008	11.24	1.922 \pm 3.351
Benzo[a] Pyrene	n.d	10.37	1.799 \pm 3.742	n.d	14.85	1.527 \pm 4.680	n.d	9.867	1.059 \pm 3.099	n.d	16.89	2.671 \pm 5.503	n.d	2.975	0.572 \pm 0.999
Indeno[1,2,3-Cd]Pyrene	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2.455	0.248 \pm 0.775	n.d	2.591	0.259 \pm 0.819
Dibenz[a,h]Anthracene	n.d	n.d	n.d	n.d	0.037	0.004 \pm 0.012	n.d	0.675	0.121 \pm 0.257	n.d	3.72	0.383 \pm 1.173	n.d	0.087	0.015 \pm 0.032
Benzo[ghi]Perylene	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.185	0.037 \pm 0.078	n.d	4.976	0.692 \pm 1.612
Total PAH's	-	-	23.562	-	-	16.246	-	-	23.853	-	-	30.692	-	-	39.291

n.d : not detected

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Table 3: Levels of total PAH's (µg/l) in water during the period of study (1999 – 2000)

Sampling Stations	Year 1999			Year 2000							Min-Max	Mean	* 95% CI
	Ocl.	Nov.	Jan.	Feb.	Mar.	May	Jun.	Aug.	Sep.	Nov.			
Station (1)	80.9	85.3	3.70	33.4	10.9	4.96	4.24	2.65	3.98	5.57	2.65-85.3	23.56	23.4
Station (2)	76.6	10.4	5.90	4.20	29.0	9.92	4.18	4.34	2.21	15.8	2.21-76.6	16.25	16.2
Station (3)	94.7	5.60	68.0	0.97	4.71	14.4	19.7	4.41	21.8	4.22	0.97-94.7	23.85	22.7
Station (4)	45.4	7.60	1.70	2.04	7.85	119.3	6.85	53.2	52.8	10.1	1.7-119.3	30.69	26.9
Station (5)	75.8	88.1	83.8	5.69	24.6	12.7	3.91	8.08	41.6	48.7	3.91-88.1	39.29	23.9

* 95% CI : 95% Confidence interval.

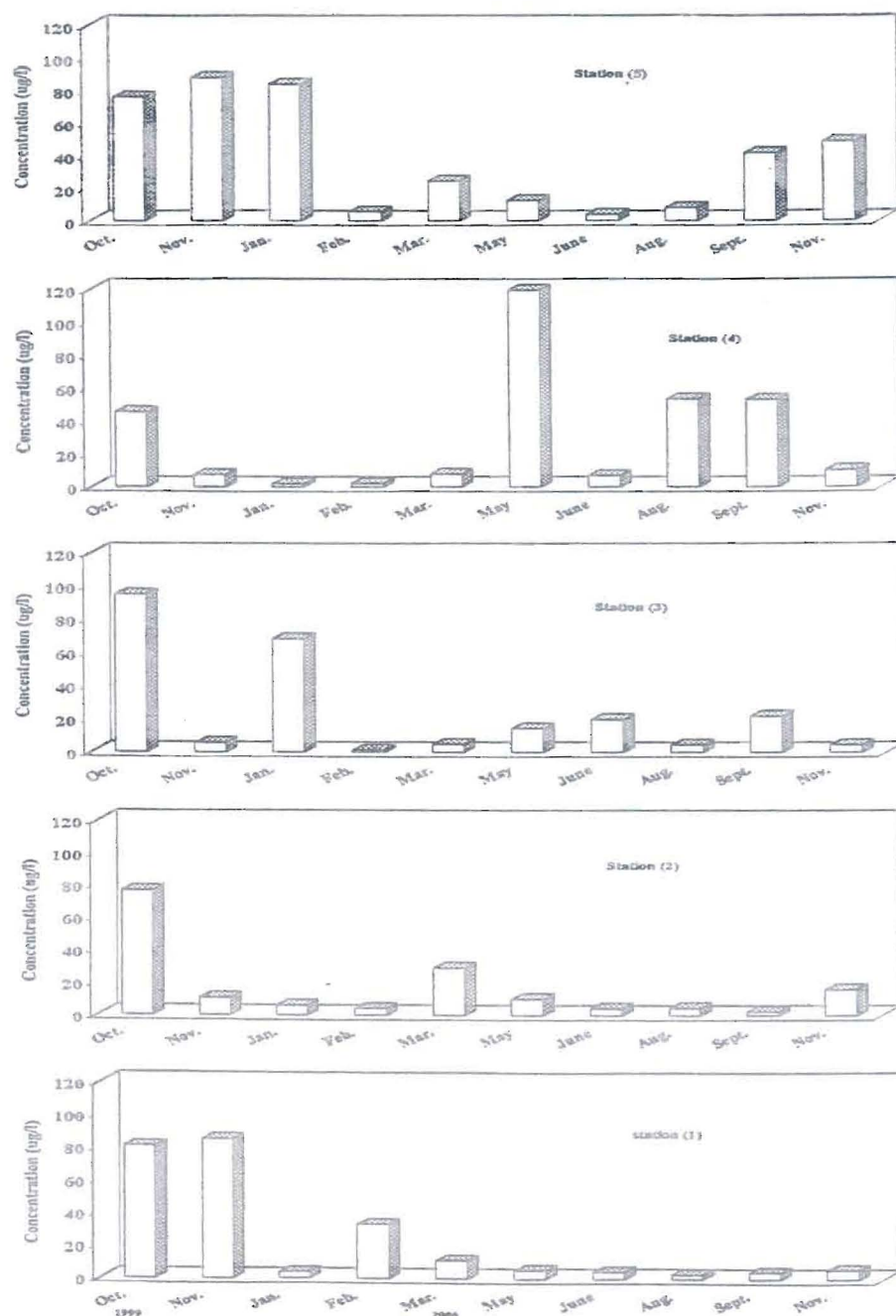


Fig. 2. Distribution of PAH's in the water at the different stations during the period of study.

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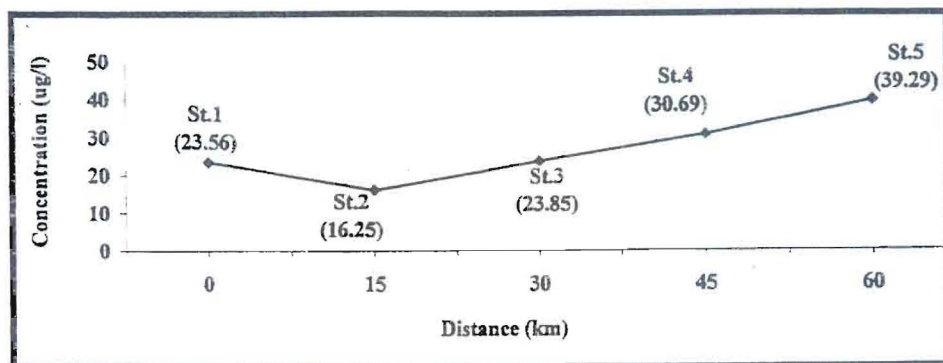


Fig. 3: Mean concentrations of PAH in the water at the different stations.

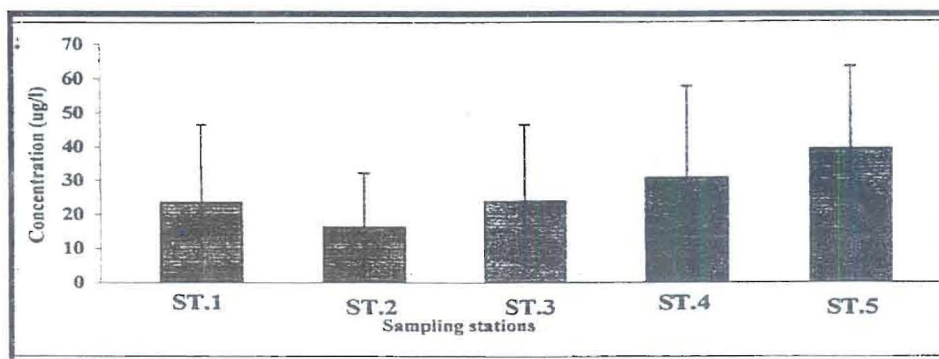


Fig.4 : Mean concentrations of PAH with their 95 % confidence intervals.

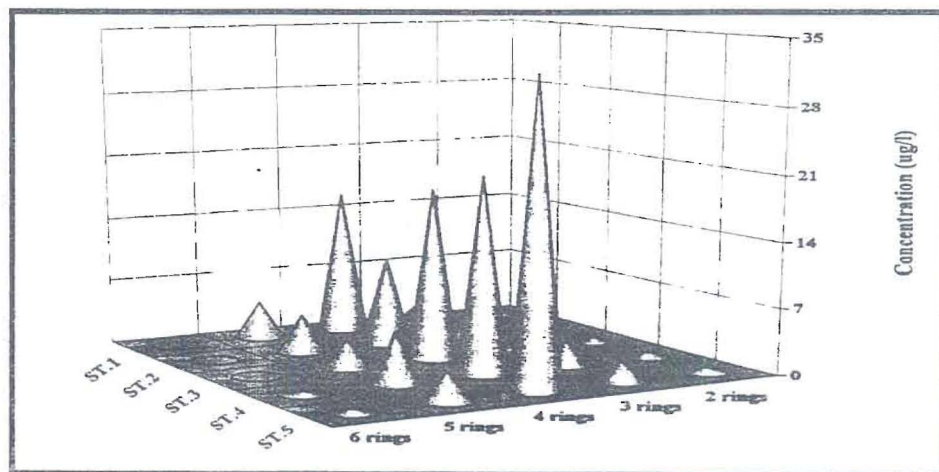


Fig. 5 : Group profiles of PAH in water at the different stations.

The degree of pollution in the studied area is obviously not uniform. This is evident as, the levels of total PAH's have shown statistical significant variation through the whole period of study ($P < 0.05$), although there is no statistical significant variation in the level of total PAH's between the stations as well as between the different seasons ($P > 0.05$). The presence of these pollutants in the water during the period of study was on interval. For example, the level of total PAH's in station 3 increased from 5.6 $\mu\text{g/l}$ in November 1999 to 68 $\mu\text{g/l}$ in January 2000, then declined significantly to 0.97 $\mu\text{g/l}$ in February 2000. Even in station 2 – the fairly contaminated location – the level of total PAH's was decreased from 76.5 $\mu\text{g/l}$ in October 1999 to 10.4 $\mu\text{g/l}$ in November of the same year, then increased again to 29 $\mu\text{g/l}$ in March 2000. This prove the unusual distribution trend of PAH's in the Gulf of Suez that could be attributed to the continuous input and removal of these pollutants at the studied area.

The result of this study indicate with no doubt that the sources of PAH's in the Gulf of Suez are anthropogenic rather biogenic due to the high concentrations of these compounds in all sampling station. This is in agreement with several studies worldwide (Sherblom *et al.*, 1995; Witt, 1995; Zanardi *et al.*, 1999; Notar *et al.*, 2001). The anthropogenic sources of PAH's in the Gulf of Suez have been presumed to be pyrogenic and petrogenic. Some useful indicators, such as the ratios of phenanthrene / anthracene (Phe/Anth) and flouranthene / pyrene (Flu/Py) have been applied to provide information on the sources of pollution. Hece, a ratio of Phe/Anth < 10 and Flu/Py > 1 indicated a contaminants due to pyrogenic origin (Raoux and Garrigues, 1993; Pereia *et al.*, 1999; Notar *et al.*, 2001). The ratios of Phe/Anth and Flu/Py have been calculated at all stations and they were < 10 and > 1 , respectively which reflects the contribution of pyrogenic sources. On the other hand, petrogenic hydrocarbons exhibit a characteristically high PAH's content. Zanardi *et al.*, (1999) found that the concentration of dissolved / dispersed hydrocarbons was fro 0.35 to 2.5 $\mu\text{g/l}$ in water from São Sebastião, Brazil and they concluded that the region is affected by petrogenic contribution. In the present study, a relatively high levels of PAH's (mean sum ranged from 16.25 – 39.29 $\mu\text{g/l}$, Table 3), suggests a petroleum source.

Considering the regional distribution, levels and composition of PAH's and source definition criteria, it can be concluded that the northern part of the Gulf of Suez (sampling area) is being exposed to a mixture of pyrogenic and petrogenic hydrocarbon sources. Sues Bay (stations 4 & 5) exhibits contribution from petrogenic sources rather pyrogenic. This can be attributed to be the values of PAH's and the lowest ratios of Ph/Anth. In addition, this area is characterized by intensive human activities. While station 2 exhibits contribution from pyrogenic source rather petrogenic, where the lowest concentration of PAH's were detected and the highest ratios of Ph/Anth was recorded.

This study documents the first comprehensive analysis of polycyclic aromatic hydrocarbons in the coastal seawater of the northwestern region of the Gulf of Suez. Relative to other urbanized coastal area worldwide, the measured PAH's content in the

GOS can be considered highly polluted (Law, 1986; Weber and Bicego, 1991; Witt, 1995; Ahmed *et al.*, 1999;). These data provide background information to evaluate the extent of impact from future development of this area, taking into account the area of station 2 where currently development projects are established including Ain Sokhna commercial port and the very huge industrial zone.

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