

POLYCYCLIC AROMATIC HYDROCARBONS AND AROMATIC PLASTICISER MATERIALS IN THE SEAWATER OF ALEXANDRIA COASTAL AREA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), the real contaminants of petroleum, were detected in the surface seawater of Alexandria coastal area in winter and spring seasons of 1995. Their order of predominance, particularly for the individual components were principally due to the processes of input, transport and fluxes. Variation of PAHs was not following seasonal changes but it was slightly affected by partial dissolution of the lower-boiling aromatic hydrocarbons. The most abundant component of aromatic hydrocarbons was pyrene (PAH), 112ngl^{-1} followed by naphthalene (56ngl^{-1}) and its alkylated derivatives (dicyclic), then phenanthrene (14ngl^{-1}) and its methylated derivatives (tricyclic). The potential fish carcinogenic PAH, dibenz [a & c] anthracene was found in extremely trace levels. Most aromatic hydrocarbons present in seawater were arised from combustion of various petroleum and non-petroleum products, while few aromatics were found as a result of petroleum pollution. PAHs were also detected in rain water (25ngl^{-1}). Plasticizer materials (phthalates) were determined everywhere at considerable levels in the coastal area of Alexandria; which is the first district in Egypt for producing and recycling polyethylene, plastics and nylons.

INTRODUCTION

Monitoring and pollution studies of seawater by petroleum hydrocarbons involve many aspects including biogenic and anthropogenic sources. Hydrocarbons derived from "biogenic sources" in some areas, may exceed others of petrogenic origin, and easily undergoes degradation as a result of their aliphatic nature. The real contaminants of oil are the polynuclear aromatic hydrocarbons (PAHs), they resist degradation and are retained in sediments and fatty tissues and may accumulate there as it passes up the food chain eventually to man (Dacker, 1981).

Hydrocarbons enter the sea at high and low levels of concentration. The first usually occurs as a result of oil spills which may happen due to accidents of oil tankers and

some minor spills from offshore oil production. Low level hydrocarbons in the sea are often found due to the effluents of sewage outfalls, industrial discharge, ballasting and deballasting operations of oil tankers and atmospheric rain-out which includes incompletely combusted oil products.

The coastal sea area of Alexandria, which comprises the biggest and main harbours in the country and is considered one of the most industrialized zones, receives considerable amounts of petroleum and its products. A part from this is SUMED pipeline which transports more than 100 million tons per year from crude petroleum of the Arabian Gulf countries. It was opened in December 1976 with its terminal at about 35 km west of Alexandria. Another important sources of oil contamination in the area are due to the

discharge of huge amounts of land drainage water from the highly polluted Lake Mariut and the sewage water, they may include the wastes of lubricants and other mineral oils.

Limited attention was given to follow up and evaluate the petroleum-contamination problem in the coastal region of Alexandria (Abou El-Dahab, 1980; Wahby and El-Deeb, 1980; Emara and Shriadah, 1995), while the present work is a step from a series of comprehensive detailed investigations carried out for the assessment of the problem in the whole ecosystem of the area.

MATERIAL AND METHODS

The investigated area lies between latitude $31^{\circ} 8', 00''$ & $31^{\circ} 17', 2''$ N and longitude $29^{\circ} 47', 00''$ & $30^{\circ} 4', 00''$ E (Figure 1) which shows also the location of sampling stations. It comprises most of the coastal area of Alexandria, extending from El-Dikheila Harbour at the southwest to Mandara at the

northeast with a shoreline of about 26 kilometers long. The area includes three harbours; the two old harbours (the Western and Eastern Harbours) and the newly constructed El-Dikheila Harbour. The northeastern part of the area comprises most of the old beaches of Alexandria. The southwestern part of the region is El-Mex Bay which represents semi-closed shallow basin with an average depth of about 9.0 m bordered from its northeastern side by the Western Harbour outlet and by El-Dikheila Harbour at the northwest. Its southern side is El-Mex area which receives about 2.4×10^9 m³ per year of drainage, sewage and industrial waste waters from Lake Mariut through El-Mex Pumping Station. At Qayet Bey area, which is close to the Eastern Harbour outlet, there is the main sewer outlet which discharges about 83.95×10^6 m³ annually of untreated sewage containing used refined oil products.

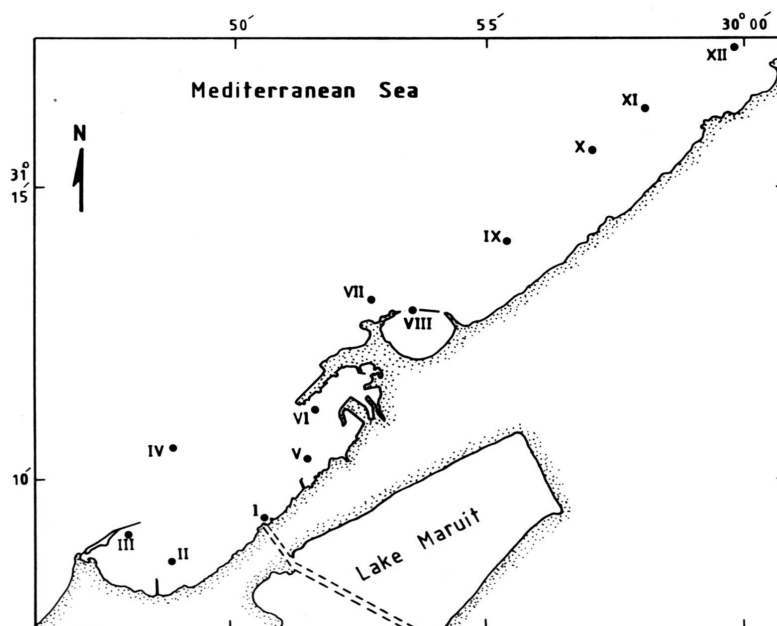


Figure 1. Area of study and position of sampling stations.

Surface water samples were collected in January and April-May 1995, extracted and analyzed using the method described by IOC (1984) with a solvent mixture of aromatic free hexane and dichloromethane (7/3, v/v). Extracts were purified and fractionated through chromatographic columns using silica gel and alumina. The gas chromatographic analysis was done using Fisons 8000 Series Gas Chromatograph (equipped with FID, injection splitter and a capillary column SGE, 25 meter length filled with stationary phase BPX5). Nitrogen was used as a carrier gas. Injector and detector temperatures were 210°C & 310°C, respectively. The temperature programming was: 4°C initial temperature for 4 minutes and the final temperature 280°C for 15 minutes with intervals of 5°C/minute. The peak areas were measured using an electronic system and identification is achieved by comparing the retention times with those of known standards. Quantification of the identified and integrated peaks is performed by comparing with nearest internal standards.

RESULTS AND DISCUSSION

The aromatic hydrocarbons detected in both surface sea water and rain water during winter and spring are listed in Table (1), while Figure (2) shows the mean PAHs profile with the most frequently occurring concentrations. The main observations obtained from this profile are the abundance of pyrene (112ngI⁻¹) which represents about 41.2% from the total PAHs determined, and pronouncedly elevated contents of naphthalene, 2 methyl phenanthrene and 1 ethylnaphthalene which are comprising 20.4, 10.3 and 8.3% from total PAHs, respectively. The following compounds were present in low concentrations ranging between 5.2 and 1.9% in a descending order: phenanthrene, 1 methylphenanthrene, fluorene, fluoranthene, acetaphthene and trimethylnaphthalene. Chrysene, perylene, dimethylphenanthrene and dibenzanthracene were found in very low

concentrations comprising less than 1% from the total PAHs. The distribution of total PAHs in surface water during winter and spring seasons is presented in Figure (3) showing the effects of the rain water outlet of Gleem (station 10) on the coastal area in winter. High concentration (952ngI⁻¹) was found there and gradually decreased in the southwest direction. The most striking feature is a pronounced drop of total PAHs content at this station in spring reached to 81.5% from winter values. A slight elevation was found in El-Mex Bay water during spring compared with that of winter (i.e., \approx from 113 to 162 ng I⁻¹) indicating the presence of local sources of contamination in the bay including the drainage water and Western Harbour water.

The average content of total PAHs in spring decreased to about 42.0% from its level in winter, reflecting the effect of temperature on dissolution of low-boiling aromatics besides the decrease of contamination from some other sources. After oil is released to marine environment, it will be subjected to normal degradation pathways. Ehrhardt and Douabul (1989) observed that the oxidation products of aromatic hydrocarbons can be present in higher concentrations than the parent hydrocarbons in surface seawater even in areas of relatively high petroleum input. Polycyclic aromatic hydrocarbons (PAHs) appear to persist for long periods (Boehm *et al.*, 1981). Thus, PAHs could provide a convincing guide to evaluate the state of pollution by oil. The correlation data matrix (Table 2) revealed the higher significance of the polycyclic aromatics: pyrene, chrysene and 1 methylphenanthrene than the dicyclic naphthalene and its derivatives. Polynuclear aromatic hydrocarbons are more difficult to biodegrade than one and two-ring aromatics (Atlas, 1981). Condensed ring aromatic hydrocarbons are even more resistant to enzymatic attack; for example, structures with four or more condensed rings are attacked, in some cases, by co-oxidation and degraded further as a result of commensalism

(Barnsley, 1975; Gibson, 1975; Cripps and Watkinson, 1978). In spite of naphthalene is more abundant than phenanthrene and its derivatives, its relation with other components in the matrix seems to be less than other PAHs due to the possibility of biodegradation and/or oxidation. The changing conditions in spring (e.g., temperature rises and increasing microbial activities) enhance biodegradation and oxidation processes which lead to remarkable decrease in the concentration of naphthalene. The average content of naphthalene in spring decreased to $\approx 44.4\%$ from that of winter (40ngl^{-1}). The microbial degradation of petroleum in the environment is limited primarily by abiotic factors, including temperature, oxygen and nutrients such as nitrogen, phosphorus (Atlas, 1981, 1984; Bartha, 1986). Microbial degradation of oil has been shown to occur by attack on the aliphatic or light aromatic fractions of the oil. Although some studies have reported their removal at high rates under optimal conditions (Rotani *et al.*, 1985; Shiaris, 1989), high molecular-weight aromatics, resins and asphaltenes generally exhibit only very low rates of biodegradation.

Table (1): Concentration of polynuclear aromatic hydrocarbons PAHs and phthalates(ng l^{-1}) in the surface water of three selected stations during winter and spring of 1995, and Qayet-Bey area and rain water during winter of 1995.

Compound	Station 1 El-Mex		Station 4 Offshore Mex		Station 10 Gleem		Station 7 Qayet-Bey	Rain water
	Winter	Spring	Winter	Spring	Winter	Spring	Winter	
- naphthalene	58	61	58	27	154	32	ND	ND
- 1 methyl naphthalene	ND	ND	ND	ND	ND	ND	ND	ND
- 1 ethyl naphthalene	24	22	21	31	ND	30	30	19
- acenaphthene	11	1	ND	ND	7	19	8	6
- 2,3,6 trimethyl naphthalene	ND	7	ND	ND	ND	ND	27	ND
- fluorene	6	17	ND	18	ND	12	ND	ND
- phenanthrene	1	23	22	25	ND	28	ND	ND
- 2 methyl phenanthrene	ND	ND	ND	ND	36	22	139	ND
- 1 methyl phenanthrene	ND	ND	ND	ND	61	3	ND	ND
- 3,6 dimethyl phenanthrene	ND	ND	ND	ND	ND	ND	6	ND
- fluoranthene	ND	9	ND	23	2	14	ND	ND
- pyrene	13	22	28	24	683	16	ND	ND
- 1 methyl pyrene	ND	ND	ND	ND	ND	ND	ND	ND
- benzyl butyl phthalate	28	47	3	3.3	ND	7	26	225
- chrysene	ND	ND	ND	ND	9	ND	ND	ND
- di-n-octyl phthalate	63	77	0.1	1.2	401	155	273	65
- perylene	ND	1	0.9	12	ND	ND	ND	ND
- 1234 dibenzanthracene	ND	0.5	ND	ND	ND	ND	ND	ND
Total PAHs	113	163.5	129.9	160.0	952	176	210	25
Total phthalates	91	124	3.1	4.5	401	162	299	290

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Table (2): Correlation matrix of PAHs in sea water.

	na.	2 na.	Ace.	3 na.	fl.	ph.	2 ph.	1 ph	3 ph.	fluo.	pyr.	chry.	per.	b. anth.
na.	1													
2 na.	-0.972	1												
ace.	-0.087	0.128	1											
3 na.	-0.498	0.301	-0.001	1										
fl.	-0.296	0.459	-0.11	-0.283	1									
ph.	-0.317	0.442	-0.154	-0.404	0.685	1								
2 ph.	-0.318	0.117	0.228	0.906	-0.497	-0.544	1							
1 ph.	0.887	-0.916	0.066	-0.224	-0.404	-0.458	0.066	1						
3 ph.	-0.505	0.304	0.09	0.966	-0.413	-0.478	0.96	-0.176	1					
fluo.	-0.287	0.428	-0.07	-0.313	0.856	0.706	-0.355	-0.224	-0.338	1				
pyr.	0.902	-0.93	0.008	-0.24	-0.399	-0.453	0.037	0.998	-0.197	-0.226	1			
chry.	0.891	-0.924	0.027	-0.212	-0.413	-0.478	0.068	0.999	-0.167	-0.239	0.999	1		
per.	-0.26	0.346	-0.485	-0.225	0.594	0.421	-0.289	-0.208	-0.197	0.796	-0.183	-0.193	1	
b. anth.	0.048	-0.023	-0.351	0.094	0.515	0.299	-0.244	-0.176	-0.167	0.106	-0.158	-0.167	-0.098	1

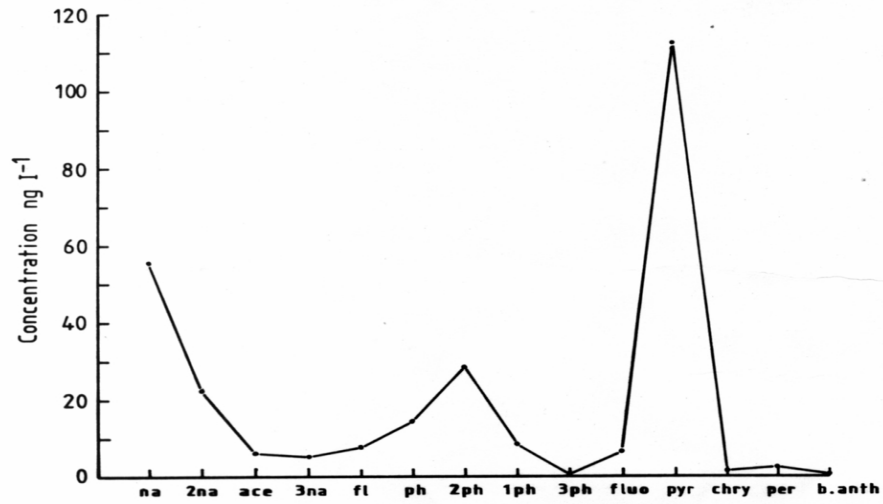


Figure 2. The mean PAHs profile for surface water in winter and spring with the most frequently occurring concentrations.

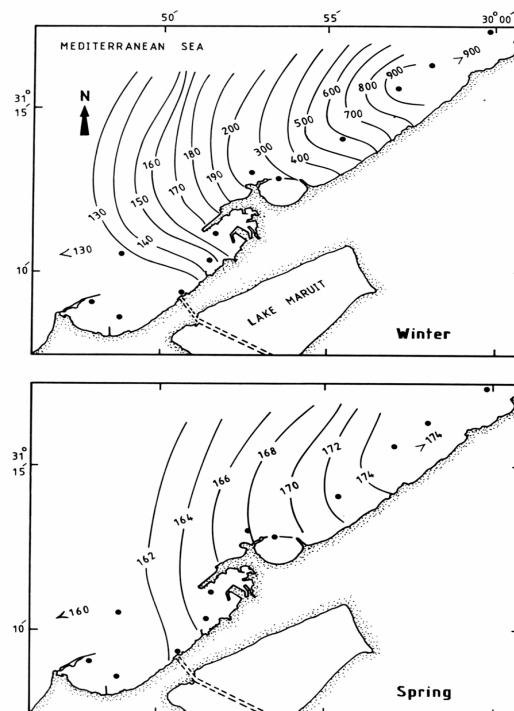


Figure 3. Distribution of total PAHs(ng l^{-1}) in surface water during winter and spring of 1995

The principal component in the matrix “pyrene” (PAH) shows a slight increase in spring than in winter at El-Mex Bay, if we exclude its high level found at the rain water outlet in January. This occasional rise of pyrene at that site may be changed to lower level as a result of the processes of transport originated from wind-derived currents, which will give an indication about its persistence to oxidation and degradation processes. Phenanthrene, a three-ringed aromatic compound, represents about 5.2% of total PAHs detected, might be expected to behave similarly to naphthalene. It is probably among the most biodegradable (Dean-Raymond and Bartha, 1975) and soluble hydrocarbon (May *et al.*, 1978) of the PAH group.

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. Table (3) shows a simple comparison between the mean levels of some aromatic hydrocarbons determined in the present study and other areas. By comparing our results with Saudi Red Sea coastal water and Gulf of Oman, it appears that “pyrene” is the most predominant PAH in the three coastal areas, it represents about 41.0, 71.0 and 46.0% from total PAHs measured in the three regions, respectively. Predominance of phenanthrene in these areas was about 5.0, 10.0 and 26.0% from total PAHs. This may give an assumption that PAHs in the three regions are

probably derived from nearly the same types of petroleum products and/or crude oils. Levels of PAHs in Alexandria coastal water are remarkably lower than that of the Saudi Red Sea and Oman waters. The ratio of measured mean concentrations of 1 ethylnaphthalene, 2 methylphenanthrene, naphthalene and pyrene (which are the dominant PAHs in the area) were 1:1.2:2.5:5.0 reveals the predominance of polycyclic aromatics than the dicyclic, particularly pyrene, phenanthrene and its methylated derivatives, while naphthalene represents a dicyclic aromatic hydrocarbon of pronounced medium occurrence of less importance among the total aromatics found in sea water. The ratio of parent aromatic hydrocarbons to alkylated derivatives was calculated and found to be 5:2. This indicates that the principal source of PAHs in the coastal sea water is expected to be from combustion of oil products, wood and coal. Meanwhile, the coastal water receives relatively little inputs of PAHs originated from crude oil and its products, waste oils arise from ships, run-off of road washings and refinery discharges. PAHs which consist of parent hydrocarbons and alkyl derivatives dominated by unsubstituted species, are mainly produced from combustion, while when alkylated compounds rise above parent aromatics, the PAHs are generally believed to originate from crude oil and petroleum products (Lake *et al.*, 1979; Cranwell and Kowl, 1989).

Table (3): Comparison between the mean levels of some aromatic hydrocarbons determined in the present study and other areas.

Area	Aromatic hydrocarbons (ng l-1)						Reference
	na.	ph.	flu.	pyr.	chry.	Benz (a) anth.	
- The Southern Ocean	6.3	5.5	4.4	3.3	1.1	0.9	Cripps, 1992
- Saudian Red Sea coastal waters	-	29.3-66.3	-	200.2-228.3	44.3-97.2	-	Awad, 1990
- Gulf of Oman	-	113	-	373	235	-	Awad <i>et al.</i> , 1990
- Alexandria coastal waters	55.7	14.1	6.9	112.3	1.3	0.1	Present study

The plasticiser materials "phthalates", which are derivatives of naphthalene that detected in the area, are characterized by the abundance of di-n-octyl phthalate than benzylbutyl phthalate. They were detected everywhere in the coastal area. Alexandria is considered the first zone in Egypt for producing and recycling polyethylene, plastics and nylons. The relative abundance of di-n-octyl phthalate than the benzylbutyl form (8.5:1) may give a sign that "toxicity" of these materials to the marine life of the area is still far from the dangerous limits, as it is well-known that benzyl aromatic hydrocarbons are more toxic than the corresponding octyl compounds. Mean concentrations and ranges of these compounds confirm this assumption [they were : $\bar{X} = 16.3 (3 - 47 \times 10^{-12})$ for the benzyl phthalate and $\bar{X} = 0.139 (0.0001 - 0.401 \times 10^{-9})$ for the octyl phthalate].

The aromatic hydrocarbons and phthalates found in the rain water during the study period showed the following (1) Absence of PAHs and presence of some low-boiling aromatics such as 1 ethylnaphthalene and acenaphthene in trace concentrations of 19 and 6 ng l⁻¹, respectively. Naphthalene and its alkylated derivatives are considered among the main components of the kerosene fraction of crude oils (Fieser and Fieser, 1963), while acenaphthalene was found between aromatics constituting the gas oil. The occurrence of these aromatics in rain water might be originated from incomplete combustion of kerosene in machine factories followed by dispersion into the atmosphere, in addition to dispersion of trace amounts of combusted gas oils in the form of vapours to the air. (2) The abundance of benzylbutyl phthalate than the octyl form, which is presumably found due to ignition of litter containing plastic bags, polyethylene containers in addition to the vapours of plastic-producing factories. The magnitude of phthalate dispersion into the atmosphere is judged by the benzyl

compounds which are more easily combusted and dispersed upwards than the octyl phthalates (ratio was 1:3.5).

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