

CONCENTRATION OF HYDROCARBON IN WATER AND SEDIMENT IN SUEZ BAY, EGYPT

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Polycyclic Aromatic Hydrocarbons (PAHs) were analyzed in water and sediment collected from some hot spots suffered from discharges of PAHs from many sources in Suez city like refineries, petroleum dock. PAHs were analyzed in water and sediment samples collected from six stations in Suez Bay during winter and summer 2019 by gas chromatography. In water total PAHs concentration ranged from 70.21 ng/L to 316.50 ng/L in winter and from 193.98 ng/L to 3210.0 ng/L in summer season while sediment samples ranged between 73.064 ng/g 3532 ng/g and from 77.97 ng/g to 12887.84 ng/g in winter and summer, respectively.

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Introduction

Suez Bay suffered negative impact from discharge of industrial wastes which come from different sources nearby the Suez Gulf (such as garbage from the city of Suez and from ships transit through the Suez Canal and other industrial sources including petroleum companies and sewage discharges) all these sources are dumped into the bay, either directly or indirectly[1]. Polycyclic aromatic hydrocarbons (PAHs) are the most environmentally hazardous fractions of petroleum hydrocarbons[2], which have been listed as persistent organic pollutants (POPs)[3]. It is organic chemicals composed of two or more aromatic rings arranged in angular, linear or clustered arrangement [4]. PAHs divided into two groups according to molecular weight, It's consist of two to three fused benzene rings are known as light PAHs they are 6 LPAHs and other PAHs containing four to six combined benzene rings are called heavy PAHs (HPAHs) which are 10 HPAHs, HPAHs are more stable and toxic than light PAHs [5]. PAHs compounds

characterized by hydrophobicity and low soluble in water and their concentration are low in water [6], PAHs accumulate in high concentration in the sediment and highly persistent on it due to weak degradation process so sediment consider the major sink of PAHs[7]. Sediment PAH analysis used as determine level of contamination and source of PAH input into the ecosystem [8]. Adsorbed PAHs release into the water column by biological and chemical process when environmental condition changes causes threaten in aquatic environment by bioaccumulation in food chain (Chen, C.-W. & Chen, 2011; Karacik et al., 2009; Lu, M., Zeng, D. C., Liao, Y., and Tong, 2012; Okay OS, Tolun L, Telli- Karakoç F, Tüfekçi V, Tüfekçi H, Olgun A, 2003)(Chen, C.-W. & Chen, 2011; Karacik et al., 2009; Lu, M., Zeng, D. C., Liao, Y., and Tong, 2012; Okay OS, Tolun L, Telli- Karakoç F, Tüfekçi V, Tüfekçi H, Olgun A, 2003)[9&10]. They may be released to the environment by natural processes, but anthropogenic activities consider the main input source into the environment [11]. Hydrocarbons that present in the environment by anthropogenic sources more than natural one [12]. US Environmental Protection Agency (USEPA) are

considered only 16 PAHs compounds as priority pollutants based on their toxicity, mutagenicity, and carcinogenicity, although hundreds of it are known to exist in the environment [13&14].

Materials and methods

Water and sediment samples were collected from six stations during winter and summer 2019 (Fig.1 & Tab.1). The study area extended from the western side of the bay in port-Tawfiq to Adabyia Harbour). Surface water (0.5 m depth), and sediment samples were collected on February 2019 (winter) and on August 2019 (summer) from six stations of study area and transported in ice box to the laboratory of National Institute of Oceanography and Fisheries for analysis of Hydrocarbons. Water samples stored in dark brown glass bottles covered by aluminium foil and transferred to laboratory for PAHs analysis. Sediment samples collected by using a stainless-steel spatula, stored at aluminium foil, then transported to the laboratory in ice box.

Extraction of water samples, 1 L of water sample was shaken with 40 ml of dichloromethane in a separating funnel for 10 min; strong shaking of the liquid sample occurs or put sample on stirrer after adding of dichloromethane, followed by the separation of the organic layer (extract) from the aqueous phase. The process was repeated until all of seawater sample has been extracted, before a final concentration and then the analytical stage on GC [15].

Extraction of Sediment samples, the extraction of sediment samples was taken place as follow: 30 g of dried mixed sediment sample with 20 g of anhydrous sodium sulphate and subjected to extraction by sonication twice in 100 ml n-hexane for 30 min, then sonicated in 100 ml dichloromethane (CH₂Cl₂). The collected extracts were concentrated by rotary evaporator at low temperature (40 °C), then concentrated to 1 ml by nitrogen stream [16&17].

Results and discussion

The 16 toxic PAHs which measured in water and sediment were as follows: Naphthalene (Nap), Acenaphthylene (A), Acenaphthene (Ace), Fluorene (F), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flu), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k] fluoranthene (BkF), Benzo[a] pyrene (BaP), Dibenzo [a,h] anthracene (DahA), Benzo[ghi]perylene (BP) and Indeno (1,2,3c,d) pyrene (IP).

PAH in water samples: The concentrations of individual PAH in surface water at different studied stations during winter and summer 2019 are shown in (Tab.2). The total PAHs concentrations ranged from 70.21 ng/L to 316.50 ng/L in winter and from 193.98 ng/L to 3210.04 ng/L in summer season. The variation between ΣPAHs readings were remarkably high (Fig.2). Summer season recorded

the highest concentration at all studied stations. The results showed the maximum ΣPAHs concentration at St 3 (Al-Kabanon beach) and St 6 (Near to Al-Adabyia Harbor) than other stations.

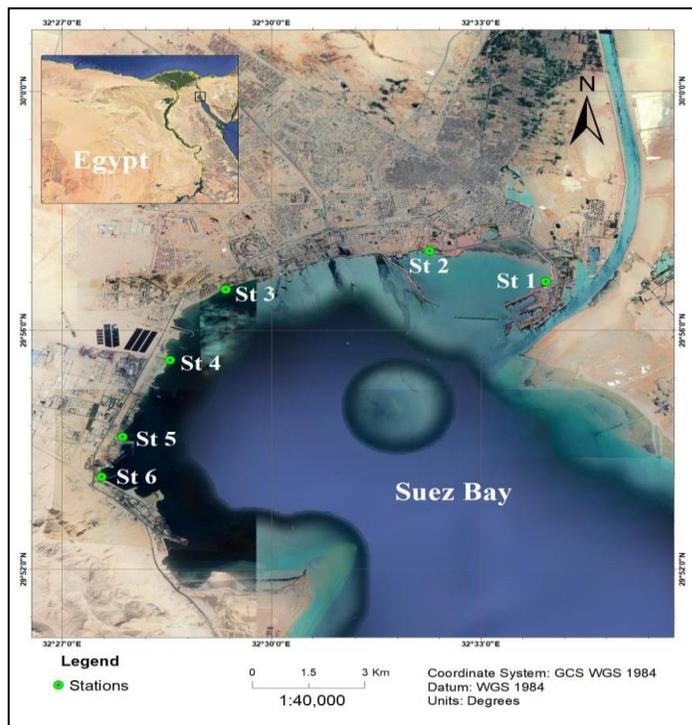


Fig.1: Map showing the study area in Suez Bay.

Tab 1: Studies stations and their locations

St. No	Location
1	El Tagdef beach (west of Port Tawfiq Harbor)
2	End of El-kornish near to El-Zeityia Harbor
3	Al-Kabanon beach
4	Beach of the National Institute of Oceanography and Fisheries (NIOF)
5	Al-Attaka fishing Harbor
6	Near to Al-Adabyia Harbor

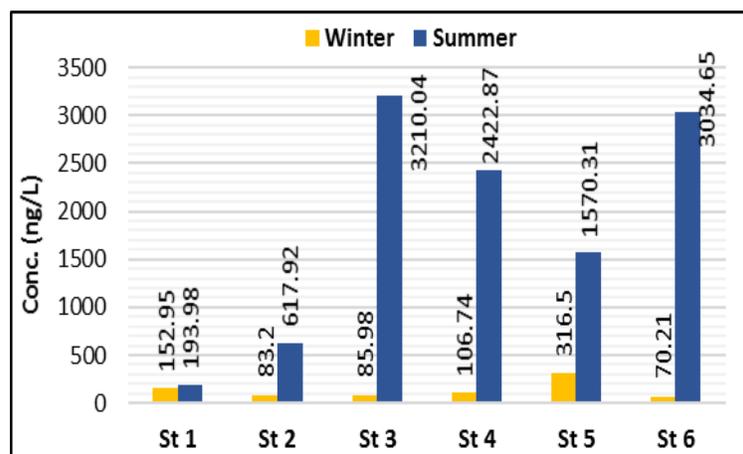


Fig. 2: Concentrations of ΣPAHs of in water samples (ng/L).

Tab 2: Individual PAHs in water samples (ng/L).

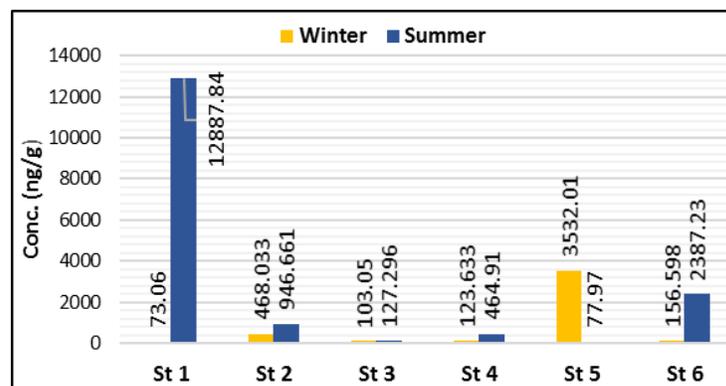
PAHs Compound	Station /Winter						Station /Summer					
	St 1	St 2	St 3	St 4	St 5	St 6	St 1	St 2	St 3	St 4	St 5	St 6
(Nap)	1.57	2.50	6.40	2.89	4.85	1.87	0.55	3.79	2.39	7.67	ND	ND
(A)	3.27	9.94	6.10	1.25	1.98	2.38	7.04	3.33	ND	17.91	1.20	0.31
(Ace)	26.09	18.77	6.09	2.37	0.69	2.23	5.99	6.10	ND	13.70	0.75	ND
(F)	2.71	6.25	15.34	3.38	2.72	3.78	15.35	8.34	ND	18.97	ND	2.58
(Phe)	4.68	1.98	10.22	12.90	11.21	4.79	28.51	5.79	ND	16.47	ND	4.67
(Ant)	2.41	2.08	20.59	18.43	12.62	3.88	21.91	8.25	ND	12.24	0.57	2.80
(Flu)	8.07	1.51	3.56	19.53	11.99	3.08	40.84	183.65	0.95	9.61	2.87	2.93
(Pyr)	10.32	1.30	4.70	7.43	15.35	3.30	41.61	246.55	1.54	7.17	2.11	1.58
(BaA)	11.31	3.50	1.47	4.81	80.20	10.43	14.78	ND	11.62	10.50	10.96	7.74
(Chr)	6.16	2.82	0.95	2.06	25.07	5.26	ND	114.12	3152.57	2271.65	1496.50	2975.90
(BbF)	13.04	10.36	1.49	4.26	30.26	7.63	11.13	4.37	13.49	9.91	24.86	6.98
(BkF)	9.34	6.01	1.09	4.94	18.05	5.70	0.59	6.37	4.07	8.48	5.73	1.66
(BaP)	19.38	8.29	1.75	6.59	22.83	4.80	0.13	14.05	7.60	9.89	3.57	4.51
(DahA)	14.39	3.86	2.76	7.09	42.11	4.62	2.69	8.36	7.14	4.21	11.77	8.90
(BP)	10.26	1.86	1.47	3.78	17.71	3.43	1.41	1.44	4.77	1.98	3.82	4.83
(IP)	9.97	2.18	2.02	5.04	18.87	3.04	1.45	3.43	3.91	3.34	5.62	9.27
Total PAHs	152.95	83.20	85.98	106.74	316.50	70.21	193.98	617.92	3210.04	2422.87	1570.31	3034.65

N.D.: under the limit of detection

There are different factors associated with high concentration of detected PAHs: 1) wastewater discharged from industrial process, 2) sewage discharge 3) petroleum pollution from transportation, oil refinery, spills, and lack of industrial process [18]. In present study the highest concentration of Σ PAHs in summer season may be due to the presence of HMW-PAHs 4-rings (Flu, Pyr, BaA and especially Chrysene compound which is detected at all studied stations except in St 1. In other word, Chrysene seemed to be the most important compound affect the total concentration of PAH. The above compounds originated from anthropogenic sources like incomplete fuel combustion in boats and ships [19]. According to some studies, the amount of chrysene did not change considerably after 12 years of oil spill, indicating the resistance of chrysene in the aquatic environment, as well as its high rate of increase when compared to others [20].

PAHs in sediment in samples: Tab 3 showing the concentration of individual PAHs in sediment samples at six stations during studied period they were ranged from 73.06 ng/g to 3532 ng/g and from 77.97 ng/g to 12887.84 ng/g in winter and summer, respectively (Tab 3). St 1 and St 5 recorded the highest Σ PAHs concentration (12887.84 and 3532.01) ng/g in summer and winter respectively (Fig 3). In winter Pyrene and Fluoranthene recorded the maximum concentration of individual PAHs while Benzo [a] Pyrene was the most dominant fraction in sediment samples in summer seasons, the second dominant fraction was Benzo [b] fluoranthene. Baumard et al. (1998) [21] divided the relative contamination level

into four categories or groups: (1) low (0–100 ng/g); (2) moderate (100–1000 ng/g); (3) high (1000–5000 ng/g); and (4) very high (more than 5000 ng/g). According to this classification scale most studied stations in winter season were moderately contaminated with a total PAHs except St 1 and St 5 were slightly and highly contaminated respectively. In summer season, St 1 was very high contaminated, St 6 was high contaminated while other stations were moderately contaminated with a total PAHs concentration and St 5 was slightly contaminated (78 ng/g). PAHs were contaminant in sediment than in water because of their hydrophobic nature (water solubility between 10^{-10} and 10^{-13} mol/l) and are easily adsorbed onto suspended particulate. PAHs present in sediment are resistant to bacterial degradation [22].

**Fig. 3:** Concentrations of Σ PAHs in sediment samples (ng/g).

Tab 3: Concentrations of Individual PAHs in sediment (ng/g).

PAHs Compound	Station /Winter						Station /Summer					
	St 1	St 2	St 3	St 4	St 5	St 6	St 1	St 2	St 3	St 4	St 5	St 6
(Nap)	ND	1.88	15.77	8.52	25.63	ND	123.61	1.78	1.04	11.62	1.65	2.02
(A)	0.76	8.53	6.63	8.37	154.60	2.34	170.00	4.33	3.25	1.72	1.20	8.32
(Ace)	1.43	20.85	8.22	6.18	81.85	0.95	134.20	2.91	3.90	3.11	ND	13.68
(F)	1.15	19.96	10.40	8.43	338.74	1.22	229.87	3.57	8.33	2.99	0.68	23.15
(Phe)	1.82	38.63	13.39	3.57	333.14	8.36	ND	8.47	7.34	62.93	ND	45.28
(Ant)	1.94	49.53	5.44	1.92	280.52	6.58	1120.34	11.33	7.79	37.53	0.43	32.70
(Flu)	14.54	56.50	5.75	7.018	987.07	4.10	1544.0	12.53	2.24	33.59	1.32	83.89
(Pyr)	7.73	73.16	6.75	3.55	1131.63	3.26	904.08	7.93	4.41	6.98	6.23	69.43
(BaA)	11.03	111.75	4.66	15.53	103.80	6.81	1889.37	13.69	14.19	77.05	2.00	79.98
(Chr)	6.42	77.51	2.30	6.28	86.46	4.18	1013.74	761.31	15.13	22.99	27.34	721.50
(BbF)	4.59	0.40	2.89	12.99	ND	4.66	1987.71	17.14	7.82	20.36	4.83	182.99
(BkF)	2.96	ND	2.59	5.90	ND	2.84	1246.98	11.68	4.63	26.86	3.24	96.13
(BaP)	4.56	ND	5.86	12.32	ND	10.88	2007.17	21.26	11.21	38.57	3.96	164.34
(DahA)	8.39	4.63	5.80	11.53	2.06	44.65	ND	37.69	8.50	51.30	11.99	418.90
(BP)	3.22	1.96	3.29	5.83	4.42	29.49	257.02	18.80	4.31	24.26	8.09	145.23
(IP)	2.54	2.74	3.32	5.67	2.09	26.29	259.76	12.24	22.23	43.07	5.01	299.69
Total PAHs	73.06	468.03	103.05	123.63	3532.01	156.60	12887.84	946.66	127.30	464.91	77.97	2387.23

N.D.: under the limit of detection

Conclusions:

The present study provided important data on concentrations of individual and total PAH in water and sediment samples at Six stations of Suez Bay. The concentration of PAHs varied from site to another and PAH is contaminant in sediment than in water due to its hydrophobicity. In water, the higher concentrations of total PAHs were observed at St3 (Al-Kabanon beach) followed by St 6 (Near to Al-Adabyia Harbor) in summer and it was dominant with HMW-PAHs 4-rings such as Chrysene. On the other hand, in sediment, St 1 (El Tagdef beach (west of Port Tawfiq Harbour) contaminated with higher level of the total PAH concentration followed by St 6 in summer, while in winter St 5 (Al-Attaka fishing Harbour) recorded the highest concentration of total PAH (high contaminated). Some region suffer from sewage discharges, industrial discharge and accident of oil spills and leaks and other area affected by fishing processes that's all reasons may contribute to PAH pollution. PAHs were observed at higher concentrations in semi-enclosed regions such as marinas and harbours, because of sever pollution and higher concentration of pollutants as a result of lower seawater circulation.

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