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Distribution and Sources of Polycyclic Aromatic Hydrocarbons in the Northern Persian Gulf as Indicated by Kinetic and Thermodynamic Criteria

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Polycyclic Aromatic Hydrocarbons (PAHs) are wide spread contaminants throughout the environment. They have received increasing attention in recent years because of their carcinogenic and mutagenic properties combined with their nearly ubiquitous distribution in depositional environments (Youngblood and Blumer 1975). There are several routes of entry of PAHs into the nearshore marine sediments including petroleum pollution, fallout from air pollution, effluents from industries and sewage treatment plants and storm drain runoffs (Dunn and Fee 1979). PAH exposure can cause mixed-function oxygenase (MFO) enzyme induction in certain tissues of various organisms (Hodson, PV et al 1997).

Over half of the world oil supply is transported from the Persian Gulf and offshore oil exploitation in this region is considered the most extensive in the world (Golob and Bruce, 1984). In addition, as a result of the 1991 war, the marine environment in the Persian Gulf was subjected to an estimated six million barrels of crude oil, making it the largest oil spill ever recorded (Burger 1997). In comparison, the much-publicized 1989 *Exxon-Valdez* tanker spill in Alaska released only 258,000 barrels of crude oil (Boehm et al. 1998). There have been few studies on PAHs in marine sediments, before Gulf War. In spite of some studies after the Gulf war (Fowler et al, 1993), only few of these have focused on the distribution and sources of PAHs in sediments of the northern part. The present work is an essential part of the Iranian marine aromatic hydrocarbon monitoring (IMAH) project. The purpose of IMAH was to establish baseline levels of selected PAHs, recommended by US-Environmental Protection Agency (US-EPA) as priority pollutants in four selected islands of the Persian Gulf. The criterion for selection of these islands is that they are unique and can be the representative of overall situation of pollution by PAHs. Kish Island is the first Iranian free trade zone and is under human impact. Hormoz Island is located in the strait of Hormoz, which is the passage of 20000-35000 individual tankers annually. Khark Island is the biggest Iranian oil-exporting terminal. Fourth island (Qaabr-e-Nakhoda) has been selected as control as it is non-residential without any land source human impact. Figure 1 shows the location of these islands and sediment sampling sites. Molecular indices based on PAH physical-chemical behavior covariability were developed to assess the various origins of these pollutants (Baumard et al. 1998) and where possible, the distribution and sources of PAHs has been compared with other sites. In addition the trend of PAH accumulation in sediments has been demonstrated.

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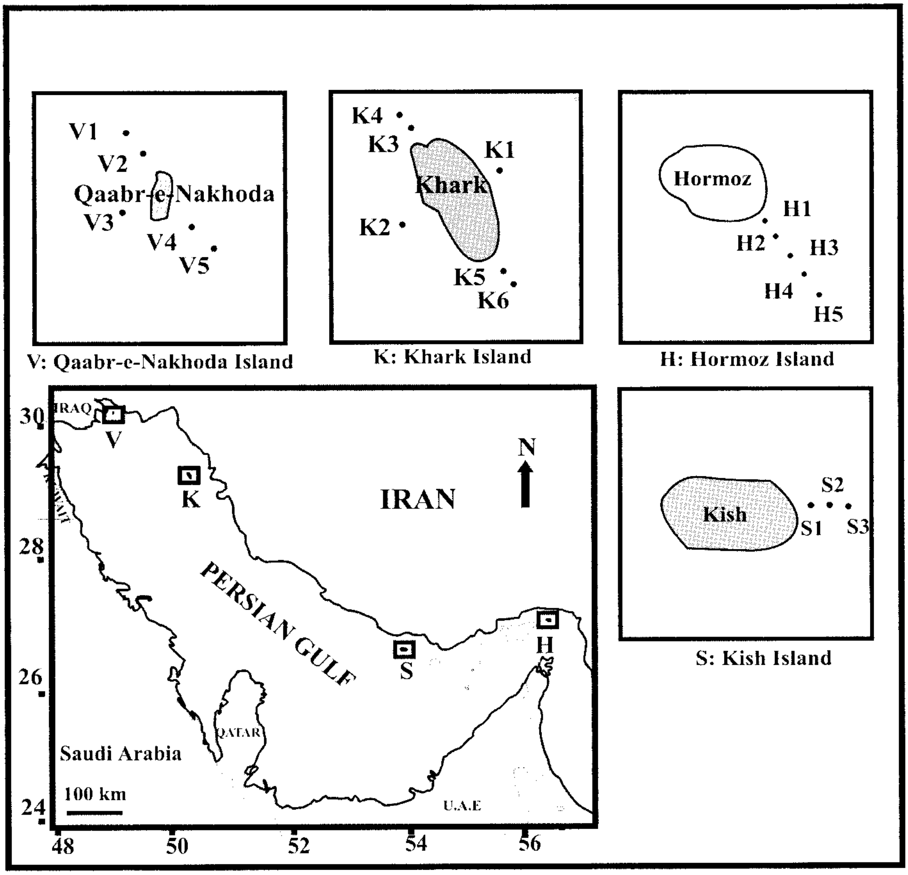

Figure 1. Locations of sampling stations in the northern Persian Gulf

MATERIALS AND METHODS

The sediment sampling sites are shown in figure 1. Samples were collected during four field trips to the regions in the spring of 1998. In all cases, the sampling stations were selected along a transect, parallel to the dominant clockwise water movement direction in the entire Persian Gulf. The position of sampling points was determined using a "Magellan" Global Positioning System (GPS). The locations and specifications of stations sampled are given in table 1. The surface (0-10 cm) sediments collected using a small stainless steel Van-Veen grab operated from a boat. Sediment samples were placed in aluminum pans (previously washed with methanol and heated at 400 °C for 3hr), and allowed to dry at room temperature for 5-6 days. The samples were then homogenized and sieved in a stainless steel sieve (62µm), returned to the laboratory, freeze-dried and analyzed by a capillary gas chromatography (flame ionization detector–FID), using a Unicam Model 610 equipped with a DB5 capillary column (30 m x 0.25 mm id) as previously described (EPA 1998). Nitrogen was the carrier gas at between 10-20 mL/min. Injection was performed on splitless mode at 280°C with

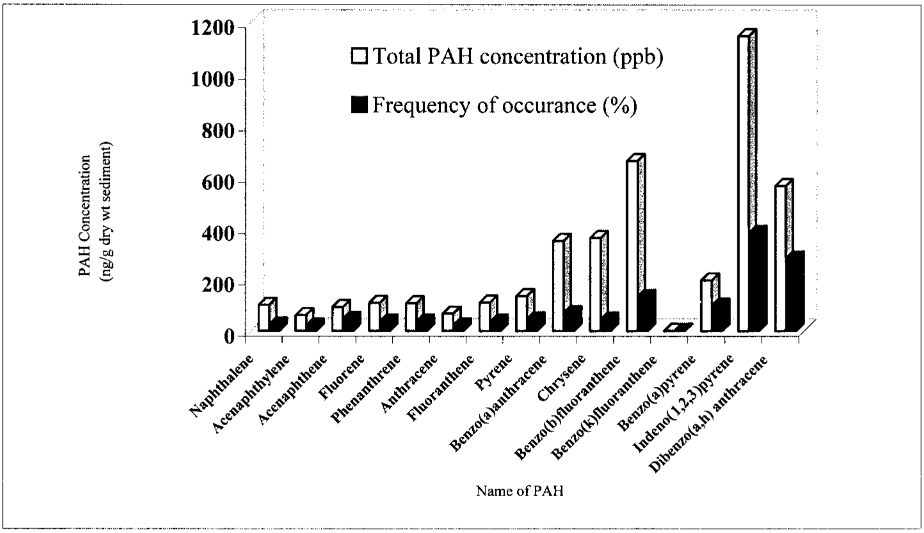

Figure 2. Frequency of occurrence of individual PAH in sediment

Table 2. PAH content in studied locations (ng g^{-1} dry wt sediment)

PAH no.	Molecular weight	Kish Island		Qaabr-e-Nakhoda Island		Khark Island				Hormoz Island			Sum of each PAH no.
		S1	S2	V3	V5	K1	K3	K4	K6	H3	H4	H5	
1	128	12		22					45	22			**101**
2	154	15	26						20				**61**
3	154	16							77				**93**
4	166	18	19						72				**109**
5	178	16	27						64				**107**
6	178	12	15						40				**67**
7	202	40	30						40				**110**
8	202	73	31						31				**135**
9	228	97	50			77	43			84			**351**
10	228		60	84	24		47	34		55	34	24	**362**
11	252	180	60	55		37	330						**662**
12	252												**0**
13	252		112				85						**197**
14	276	204	290				502						**1147**
15	278		225				340						**565**
Total PAH		**683**	**945**	**161**	**24**	**114**	**1374**	**34**	**389**	**161**	**34**	**24**	

PAH number 1: Naphthalene, 2: Acenaphthylene, 3: Acenaphthene, 4: Fluorene, 5:Phenanthrene, 6: Anthracene, 7: Fluoranthene, 8: Pyrene, 9: benzo(a)anthracene, 10: Chrysene, 11: Benzo(b)fluoranthene, 12: Benzo(k)fluoranthene, 13: Benzo(a)pyrene, 14: Indeno(1,2,3)pyrene, 15: Dibenzo(a,h) anthracene

Stations S3, V1, V2, V4, K2, K5, H1 and H2: not detected

Blank cells: not detected; detection limits: 10 ng g^{-1} dry wt sediment

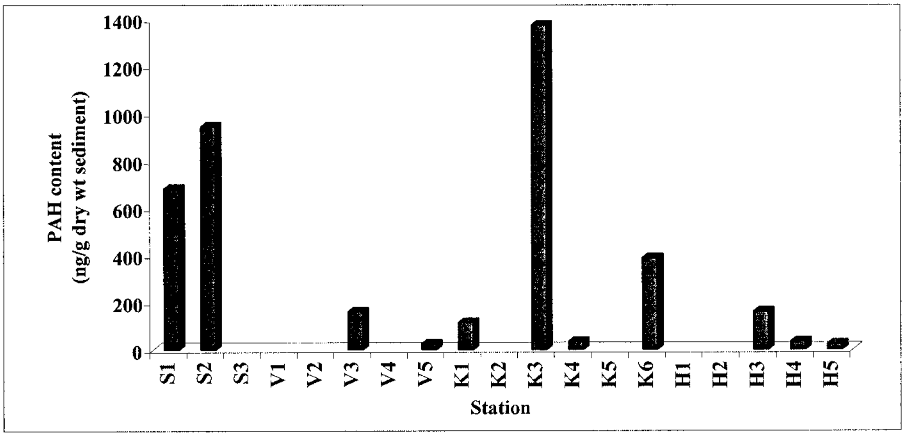

Figure 3. PAH content in the stations

Table 3. Concentration of PAHs in Northern (Iran) and Southern Persian Gulf following the Gulf War (ng g^{-1} dry wt sediment) in 1998 and 1991

Chemical	Iran	Saudi Arabia	Kuwait	Bahrain	UAE	Oman
	Spring 1998	Spring and summer of 1991*				
Pyrene	31.0-73.0	2.7-450.0	11.0	21.0-62.0	2.7-3.8	1.0-9.4
Phenanthren	16.0-64.0	10.0-53.0	0.8	3.0-9.0	1.7-3.3	0.8-3.0
Fluoranthene	30.0-40.0	1.9-130.0	3.0	3.0-21.0	2.2-4.2	1.1-8.3

*Source: Fowler et al 1993

analogous GC/FID data for pyrene, phenanthrene and fluoranthene, in the southern Persian Gulf, following the Gulf War (Fowler et al 1993). Semi-quantitative comparisons (i.e. orders of magnitude) of total PAHs concentrations across studies can be made. In all cases (except pyrene and fluoranthene in Saudi Arabia) all polluted stations in the northern Persian Gulf, have higher PAH content in 1998 than other littoral countries even in 1991, just after the Gulf War. The degree of sediment contamination by PAHs in the northern Persian Gulf is moderate in comparison with other aquatic systems (Table 3 and 4). Based on these comparisons, it appears that sediment PAH concentrations in the Persian Gulf are similar to those in parts of the Baltic Sea and Kyeonggi Bay in Korea, but are substantially less than those in some areas of urbanized industries in the Manukau Harbor, New Zealand and Western Mediterranean Sea. This is in spite of massive introduction of oil hydrocarbons to the Persian Gulf marine environment. This is likely due to the relatively warm climate of the region (i.e. high rates of volatility and photolysis) and natural dominance of oil degrading microbial communities which their presence is a result of large inputs of hydrocarbons.

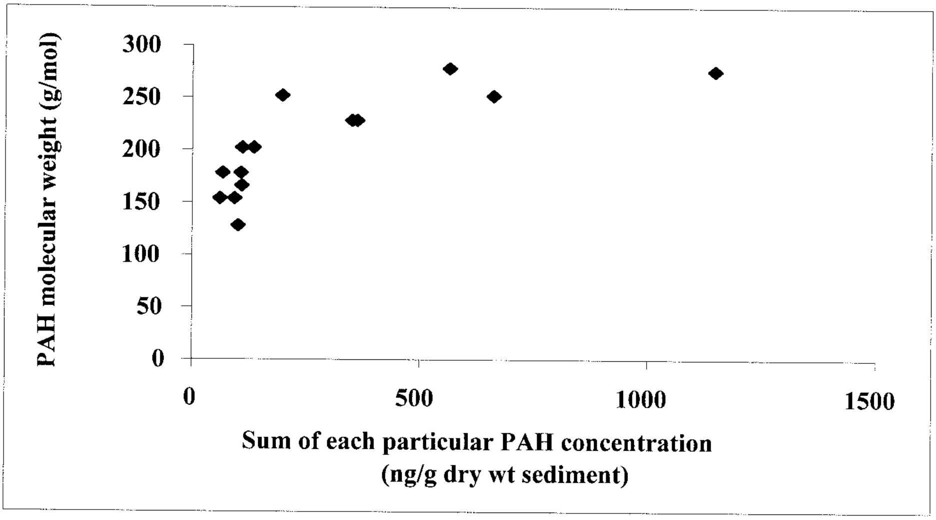

Figure 4- Regression correlation between total PAH concentration and their molecular weight in sediments of 18 sampling stations

Table 4. Comparison of sediment PAH concentrations (ng g^{-1} dry wt) measured in this study with those in other regions

Sites	*n*	Mean	Range	Reference
Northern Persian Gulf	15	358	24-1374	This study
Washington Coast, USA	13	200	29-460	Prahl and Carpenter (1983)
Chesapeake Bay, USA	15	52	0.56-180	Foster and Wright (1988)
Kyeonggi Bay, Korea	24	120	9.1-1400	Kim GB et al (1999)
Manukau Harbor, New Zealand	10	820	16-5300	Holland et al (1993)
Baltic Sea	15	1200	720-1900	Witt (1995)
Adriatic Sea	12	200	18-580	Caricchia et al (1993)
Western Mediterranean Sea	31	1300	180-3200	Lipiatou and Saliot (1991)

n Number of PAH compounds analyzed in each study

Table 5. PAH ratios in the sediment samples from the Persian Gulf

Location	Phen / Ant	Flt / Pyr
S2	16 / 12 = 1.3	40 / 73 = 0.55
S3	27 / 15 = 1.8	30 / 31 = 0.97
K6	64 / 40 = 1.6	40 / 31 = 1.29

Phen/Ant: phenanthrene/anthracene; Flt/Pyr: fluoranthene/pyrene

The acquirement of the ratio phenanthrene/anthracene (Phen/Ant) and fluoranthene/pyrene (Flt/Pyr) allows us to esteem the source of contamination (Mille et al. 1982). In fact, phenanthrene and anthracene are two structural isomers. Because of their different physico-chemical properties, they could behave differently in the environment and could lead to different values for their

Table 1. Specifications of sampling sites sediments

Site	Code	Sediment facies	Granulometry (µm)	Depth (m)	Latitude	Longitude
Hormoz	H1	Coarse sand	>500	15	27° - 02 N	56° - 27.7 E
	H2	Silt	30-63	20	26° - 59.9 N	56° - 27.7 E
	H3	Fine sand	2-30	25	26° - 57.7 N	56° - 28.7E
	H4	Fine sand	63-200	30	26° - 59.5 N	56° - 29.1 E
	H5	Fine sand	63-200	5	27° - 02 N	56° - 29.1 E
Khark	K1	Fine sand	2-30	19	29° - 14.22 N	50° - 20.40 E
	K2	Coarse sand	>500	23	29° - 14.50 N	50° - 17.48 E
	K3	Fine sand	63-200	21	29° - 16.65 N	50° - 17.4 E
	K4	Fine sand	63-200	26	29° - 16.98 N	50° - 17.00 E
	K5	Silt	30-63	15	29° - 12.51 N	50° - 20.02 E
	K6	Fine sand	2-30	19	29° - 11.8 N	50° - 20.50 E
Kish	S1	Fine sand	2-30	5	26°-30.7 N	54°-3.21 E
	S2	Fine sand	2-30	10	26°-31.1 N	54°-3.39 E
	S3	Fine sand	63-200	20	26°-31.6 N	54°-3.49 E
Qaabr-e-Na-khoda	V1	Fine sand	2-30	15	30°- 20.12	49°- 02.10
	V2	Fine sand	2-30	12	30°- 19.43	49°- 02.48
	V3	Silt	30-63	10	30°- 17.31	49°- 03.68
	V4	Fine sand	63-200	6.5	30°- 15.35	49°- 05.56
	V5	Fine sand	2-30	2	30°- 14.62	49°- 05.34

0.25 µm film thickness. The oven temperature was programmed 40 to 300 at 6°C/min. Detector temperature was 340 °C. A mixture of PAHs (Supelco Inc. Beafonte PA 16823) containing 15 aromatic compounds, was used as an external standard. The average recovery of both fractions was about 90%. Also, a series of blanks were carried out before and after chromatographic analysis to reconfirm the percentage of aliphatic and aromatic compounds. The identification and quantification of these organic compounds was carried out by its retention time compared with an internal standard (Supelco Inc. Beafonte PA 16823). Total organic carbon (TOC) content was determined using the back-titration method (Wakley and Black 1934).

RESULTS AND DISCUCSSION

To date, the literature regarding the presence of polycyclic aromatic hydrocarbons in the northern Persian Gulf has been very sparse. Eleven individual stations manifested between 2 and 8 PAH compounds with a mean of 3.21 to 8.47 ppb dry wt sediment (Figure 2). Table 2 shows the PAHs contents expressed in ngg^{-1} of dry sediment in nineteen samples. Concentrations above 1000 ppb were limited to one station (K3) in Khaark Island which is the biggest Iranian oil exporting terminal. Intermediate values, between 683 and 943 ppb were found at Kish Island (S1 and S2), that possesses the most intensive tourist activities (figure 3). This is suggestive of localized, anthropogenic inputs. Chrysene is the most frequently seen PAHs (it has been present in 42% of the samples). Table 3 shows the

Phen/Ant ratio that give useful information on the PAH origin (Gschweng and Hites 1981). Phenanthrene is more thermodynamically stable than anthracene, thus Phen/Ant ratio is observed to be high in petrogenic PAH pollution. In the same way, fluoranthene and pyrene were often associated during natural matrices analyses and were considered as typical pyrogenic products derived from high temperature condensation of lower molecular weight aromatic compounds. Hence a ratio of Phen/Ant<10 and Flt/Pyr<1 indicated that the contamination by PAHs would arise from petrogenic sources (Table 5). A significant correlation ($r = 0.781$, $n = 19$, $P<0.00096$) was observed between the sum of each particular PAH concentration on a dry weight basis and their molecular weight (Table 2 and Figure 4). Low molecular weight compounds such as naphthalene, phenanthrene and anthracene were found at low concentrations, while the high molecular weight compounds were found at high concentrations, showed a very good correlation with their molecular weight. One plausible explanation for this correlation is that persistence of PAHs in the estuarine sediments seems to be related to their molecular weights (Readman et al. 1982). Low molecular weight compounds tend to be volatile and subject to rapid microbial degradation, hence they have short residence times. High molecular weight PAHs, have a high particulate affinity and low microbial degradation rate and hence tend to accumulate in sediments. This suggests a trend of accumulation for the higher molecular weight PAHs in sediments of the Persian Gulf. Total PAHs on a dry weight basis, were positively correlated with total organic carbon (TOC) content (data not shown) which is consistent with PAH phase associations reported for field collected sediments from coastal environments (Prahl and Carpenter 1983). This study documents the first known analysis of PAHs in sediments from the northern Persian Gulf, an area of most spacious oil exploitation and largest oil spill ever recorded. At their present levels, PAHs in the northern Persian Gulf sediments do not appear to impose a biological/ecological threat. However, periodic monitoring of persistent sediment associated contaminates such as PAHs should be instituted as an indicator of environmental quality in this region.

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