



Distribution and Sources of Polycyclic Aromatic Hydrocarbons in the Sediment of Bushehr Coastal Zone-Iran

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) concentrations in sediments were measured from five stations in coastal area of Bushehr-Iran. Total PAHs concentration ranged from 844.9 to 4790.3 ng g⁻¹ in summer and 935.0 to 4972.0 ng g⁻¹ in winter. Significant difference was observed between total PAHs concentration in studied stations ($P < 0.05$). Among the studied stations, tPAHs concentration was higher in Rafael followed by Sheghab station. The lowest level of tPAHs observed in Abshirikon station. There was no significant difference between tPAHs concentration in August and February ($P > 0.05$). Based on the number of aromatic rings in the molecular structure, the composition pattern of PAHs was different within studied stations. The studied stations received their PAHs from both petrogenic and pyrolytic sources. The level of PAHs contamination in the Bushehr coastline founded to be moderate to high compared to other studied locations. Regular monitoring of PAHs contaminant in the region is recommended.

Key words: PAHs; Sediments; Bushehr coast; Pollution; Pyrolytic; Petrogenic

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the major group of marine contaminants which are made of two or more benzene rings. The solubility of these compounds in the seawater is low and they tend to be bounded to suspended organic matter in the water column and finally accumulate in the marine sediment [1]. There in the sediment, they would be more available to benthic organisms and may enter food chain via ingestion or direct uptake from surrounding environment.

Forest and grass fires, natural oil spills, volcanoes and atmospheric deposition are natural sources of PAHs input into the environment. Anthropogenic sources of these compounds include petroleum spills (resulted from direct discharges, oil accidents and leakages), power plants, garbage incineration, combustion of fuels,

industrial and municipal waste discharge and urban runoff [2].

Based on their formation mechanisms, PAHs are divided into two different categories; pyrolytic and petrogenic types. Pyrolytic PAHs originate from incomplete combustion of fuels while petrogenic PAHs originate from crude oil and its products [3].

Bushehr province has a long shoreline of 625 Km in north Persian Gulf. This is equal to one third of the total Iranian shorelines along the Persian Gulf. Many human activities particularly those which are related to oil industries such as oil exploration, oil exploitation and transportation increase the risk of PAHs pollution in this area. For example, Khark Island, the most important site for Iranian oil exportation, is located in this province and a great volume (about 3 million barrels) of oil is loaded into four tankers daily in order to export. Therefore, local

oil spills and leakages are common forms of PAHs input in Bushehr marine environment. Moreover, other anthropogenic sources such as urban wastes and shipping products could contaminate this area by PAHs compounds as well.

Since there is a lack of information concerning PAHs contamination in Bushehr coastal area, this study was carried out to determine the level of PAHs in the coastal sediments of Bushehr and to identify the possible origins of contamination in the studied area.

MATERIALS AND METHODS

Study Area and Sampling: Sediment samples were collected from five different stations along Bushehr shoreline including Rafael, Sheghab, Abshrinkon, Lian and Helyleh, during August 2008 and February 2009 (Fig. 1). The geographical position and major sources of input contaminant in each station are presented in Table 1.

Sediment samples were collected from 0-2 cm surface sediment [4, 5]. They were covered with aluminum foil and transferred to the laboratory-using icebox. After gravel discarding, the samples were freeze-dried [6] and stored in glass containers in a -20°C freezer.

PAHs Extraction: PAHs were extracted using US-EPA (United States Environmental Protection Agency) SW846 methods 3540C [7]. About 10 g of freeze-dried sediment was spiked with 1 ml decachlorobiphenyl ($16 \mu\text{l}^{-1}$) as surrogate standard [8] and Soxhlet-extracted with 250 ml hexane-dichloromethane (50: 50) for 16 h. Elutes were concentrated to 15 ml using rotary evaporator. About 2-3 g activated copper was added to the extracts in order to eliminate the sulfur and its compounds then the mixture was filtered after 24 h. The extracts were passed through clean up column containing 10 mg silica, 10 mg activated alumina and 10 mg anhydrous sodium sulfate. The elutes were concentrated to 5 ml by rotary evaporator again and were put in scaled vials. After the solvent was evaporated completely, the remainder was rinsed with 1ml acetonitrile to prepare the sample for HPLC injection [9].

Instrumental Analysis: The PAHs analysis was performed by HPLC system (KANUER) equipped with a UV detector and reversed-phase C_{18} (4.5×250mm) column. The operating software was Chrome Gate version 3.1.7. The mobile phase was acetonitrile 60% and water 40%, which was shifted to 100% acetonitrile using a linear gradient within 31 min. The constant flow rate of 2.0 ml/min was set throughout the instrument running.

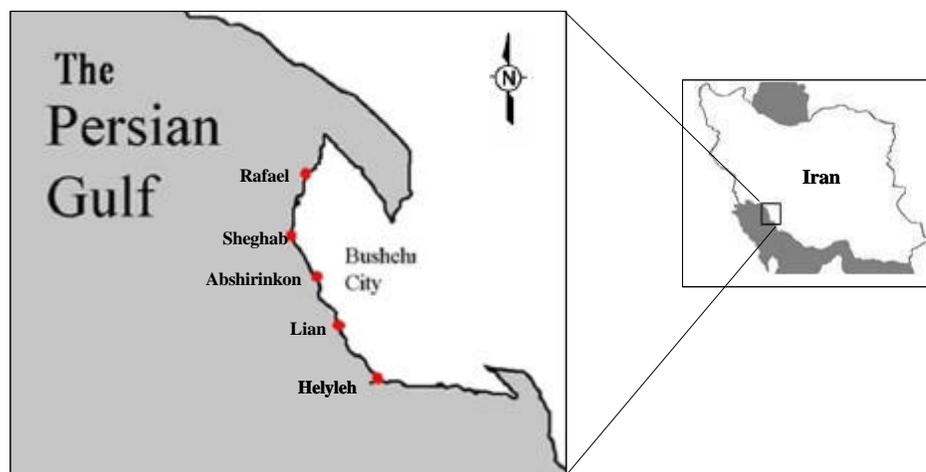


Fig. 1: Map showing the sampling stations

Table 1: Geographical positions of the studied station and the major sources of contaminants

Station	Latitude	Longitude	Explanation
Rafael	28° 57' 49.5"	50° 48' 43.2"	Fishery and shipment
Sheghab	28° 55' 38.7"	50° 48' 26.7"	Residential and aircraft reparation effluents
Abshrinkon	28° 54' 12.7"	50° 49' 9.0"	Urban wastes dumping
Lian	28° 52' 20.0"	50° 50' 33.3"	Fishery port, small industries
Helyleh	28° 50' 3.3"	50° 52' 31.9"	Fishery port, urban waste dumping

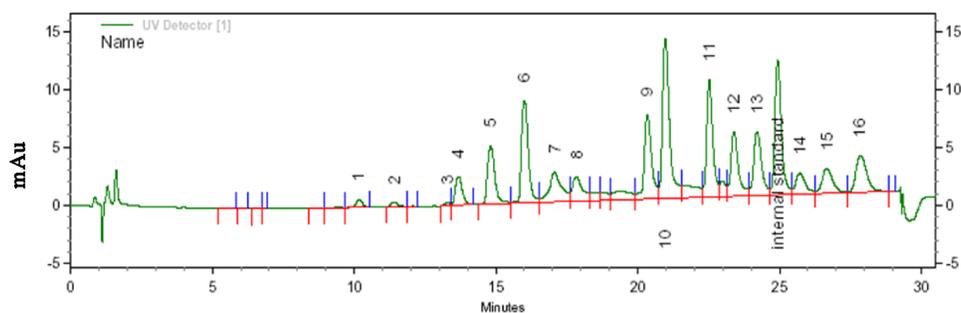


Fig. 2: Chromatogram of standard solution.

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-dibenzo[a,h]anthracene and 15-benzo[ghi]perylene, 16-indeno[1,2,3-cd]pyrene. Internal standard: decachlorobiphenyl

A linear internal standard calibration procedure was employed to obtain the calibration curves and to measure the PAHs. The standard solutions used for this purpose were decachlorobiphenyl (48318-catalogue number) and PAH calibration mix (47940-U catalogue number) from Supelco. PAHs calibration mix contained 16 different aromatic compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. The chromatogram of the standard calibration curve is shown in Fig. 2.

RESULTS AND DISCUSSION

The results of PAHs analysis in the sediment showed that the total PAHs (tPAHs) concentration ranged from 844.9 ng g⁻¹ in Abshirinkon to 4790.3 ng g⁻¹ in Rafael in August. In February, tPAHs concentration ranged 935.0 ng g⁻¹ to 4792.0 ng g⁻¹ in Abshirinkon and Rafael, respectively. The concentration of PAHs and tPAHs in the sediment of different stations are shown in Table 2. The PAHs components were distributed in various stations with different patterns. This difference in PAHs composition might be related to the extent and the nature of inputs in each station. In addition, the sediment

Table 2: PAHs concentration in sediments from studied stations in August and February (mean ± standard deviation)

Compound	Rafael	Sheghab	Abshirinkon	Lian	Helyleh
August					
Phenanthrene	344.7±23.6	276.3±11.0	61.0±2.4	223.9±9.9	490.3±24.5
Anthracene	145.9±9.8	60.7±2.4	17.9±0.7	255.0±10.3	20.9±1.4
Fluoranthene	277.8±15.3	151.2±5.9	78.1±3.1	191.1±7.9	100.3±6.94
Pyrene	865.3±41.7	309.1±11.7	180.4±7.0	514.9±21.4	291.0±12.8
tPAHs	4790.3±278.3	3078.4±118.3	844.9±33.3	2988.0±122.5	2430.6±119.7
Phe/Ant	2.36	4.54	3.40	0.91	23.40
Flu/Pyr	0.32	0.48	0.43	0.35	0.38
February					
Phenanthrene	360.5±14.0	324.8±12.5	68.6±2.7	247.3±9.4	559.0±22.9
Anthracene	165.7±8.2	77.9±3.5	35.8±1.2	273.0±8.8	26.8±1.0
Fluoranthene	207.0±8.3	148.2±5.7	70.5±28.2	206.4±8.0	112.6±4.5
Pyrene	942.1±33.9	398.6±14.9	187.1±7.3	535.6±20.6	297.9±11.3
tPAHs	4972.0±186.7	3399.8±123.8	935.0±63.9	3146.8±121.8	2651.6±100.1
Phe/Ant	1.67	4.16	1.97	0.87	20.86
Flu/Pyr	0.21	0.37	0.40	0.38	0.37

Internal standard recovery was 87%

Phe/Ant: Phenanthrene/Anthracene, Flu/Pyr: Fluoranthene/Pyrene

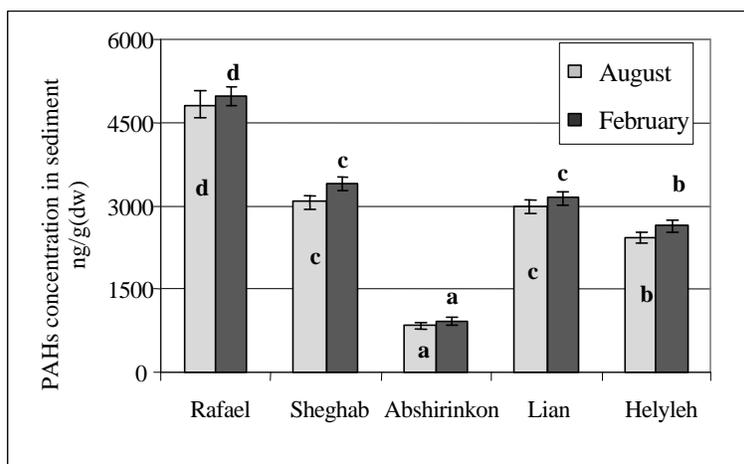


Fig. 3: Concentration of PAHs in the studied stations during August 2008 and February 2009. Various characters indicate significant difference of PAHs content between stations ($P<0.05$).

characteristics such as organic carbon content, structure and diameter of sediment particles have also been recognized as important factors influencing the abundance and distribution of PAHs in the sediment [10].

A significant difference was found between tPAHs concentration in the sediments from different stations both in August and February ($P<0.05$). The concentration of tPAHs was higher in Rafael followed by Sheghab. The station Rafael is exposed to high volume of urban sewage and seems to receive great load of organic materials all over the year. Since organic materials could serve as PAHs transmitter from water to sediment [1, 11], the prevalence of organic matter in Rafael station could be considered as a reason for the presence of high PAHs concentration in the sediment. Like Rafael, Sheghab is also located in urban area. It seems that harbour activities, marine transportation as well as urban discharges negatively affect this station.

The lowest concentration of PAHs was detected in Abshirinkon. Being far from harbors and urbanized areas and the absence of direct discharges might be the main reasons keeping this station cleaner than others.

The temporal variation of tPAHs concentrations in the sediment of the studied stations are shown in Fig. 3. Since no significant change was observed between tPAHs concentrations in August and February ($P>0.05$), it is suggested that PAHs are released into the marine environment with a more or less constant rate or PAHs are relatively persistent contaminants which could remain in the sediment for long time. In addition, water temperature change during summer and winter was not so high to cause a significant change in PAHs deposition or decomposition in the sediment.

Table 3: PAHs concentration range in various marine sediment of the world

Location	tPAHs ng g ⁻¹ (dw)	Reference
Cartagena Bay, Colombia	495-3210	[12]
Mediterranean sea, France	34-13870	[13]
Izmit Bay, Turkey	118-8937	[14]
Mobile Bay, Alabama	55-2230	[15]
Black Sea, Ukraine and Russian	7.2-635	[16]
Santander Bay, Northern Spain	20-25800	[17]
Taranto Gulf, Italy	335-5193	[18]
Oman sea	1271-3539	[19]
Gulf and Gulf of Oman, Bahrain	13-6600	[20]
Gulf and Gulf of Oman, UAE	110-4000	[20]
Persian Gulf, Iran, Bushehr	844-4792	This study

UAE- United Arab Emirates

The concentration of tPAHs in the sediment of Bushehr coastal area found in this study was compared to the previous studies on the Persian Gulf and other locations of the world as summarized in Table 3. According to this data, Bushehr sediments are more contaminated by PAHs than Cartagena Bay, Oman Sea, Mobile Bay and Black Sea sediments and is less contaminated by PAHs compared to Izmit Bay, Taranto Gulf, Santander Bay and coastal sediment of Bahrain. Generally, compared to the other location, PAHs contamination in the Bushehr coastal area was found to be moderate or severe.

Based on the number of benzene rings in molecular structures of PAHs components, the relative abundance of PAHs compounds in each station is presented in Fig. 4. The overall order of PAHs abundance in the sediment was: 5+6 rings>4rings>3rings. The pattern of the relative abundance of 3, 4 and 5+6 rings compounds were

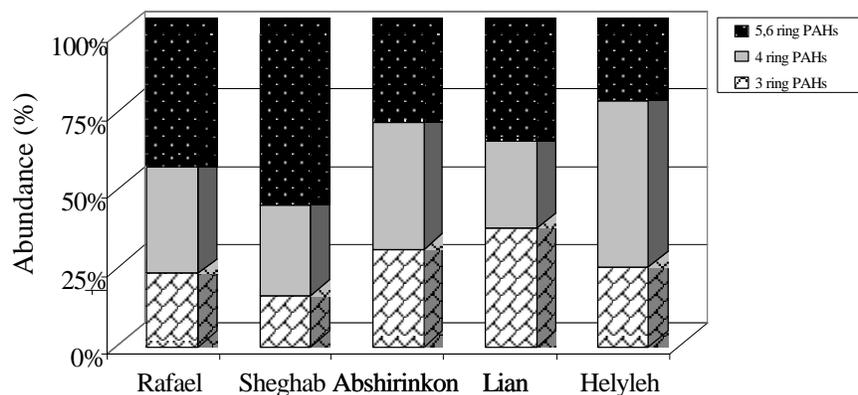


Fig. 4: The relative abundance of PAHs compounds in the Bushehr sediment (Based on the number of rings).
 3 ring PAHs (summation of acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene).
 4 ring PAHs (summation of fluoranthene, pyrene, benzo[a]anthracene and chrysene).
 5,6 ring PAHs (summation of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene).

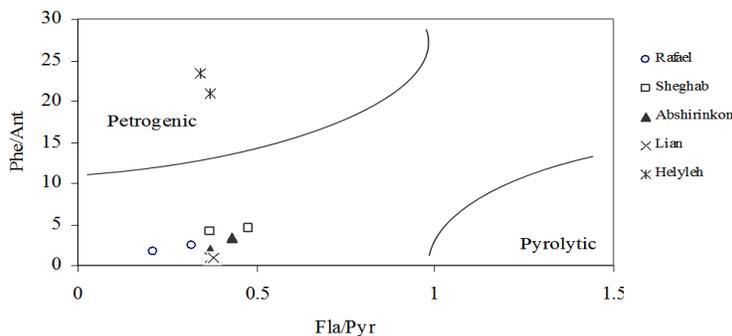


Fig. 5: Phenanthrene/Anthracene (Phe/Ant) against Fluoranthene/Pyrene (Fla/Pyr) plot ratio in the coastal sediment of Bushehr

Table 4: Isomer ratio values for identification PAHs origin [13]

Molecular indices	Pyrolytic origin	Petrogenic origin
Phe/Ant	<10	>10
Fla/Pyr	>1	<1
An/Ant+Phe	>0.1	<0.1
Fla/Fla+Pyr	>0.5	<0.5

not similar in all stations. Such variation might be related to the input sources of PAHs in each location [11]. However, the percentage of 4 ring compounds was maximum in station Abshirinkon and Helyleh, while the maximum percentage of 5, 6 rings were observed in Rafael and Sheghab. The amount of 3 rings PAHs in Lian was found to be higher than other compound in this station.

Since the major part of heavy PAHs are formed by fuel combustion [21], the neighboring of Rafael and Sheghab stations to the Bushehr harbor and their close distance to the roads could result in elevated heavy PAHs in the mentioned stations. On the other hand, Helyleh

where is located far from the city or heavy traffic roads, is less impacted with urbanization and industrialization, therefore the dominance of 4 rings PAHs is expected there. Environmental factors affecting potential bounding of PAHs to suspended organics and sedimentation rate in each station are other explanations about different patterns of PAHs abundance observed between studied stations. It has been emphasized by other researchers that even PAHs with the same molecular weight have different transport dynamics [22].

Investigations on the isomers ratio of PAHs compounds in recent years helped investigators to identify the source of PAHs in the marine sediment [6, 13, 16, 23]. Values of molecular indices for the pyrolytic and petrogenic PAHs are shown in Table 4. Comparison between the PAHs isomers ratio in the Bushehr sediment (Table 2) with values shown in Table 4 indicates that PAHs compound in the Bushehr sediment originate from both; pyrolytic and petrogenic sources (Fig. 5).

Bushehr is an elongated city with a long shoreline located in the north Persian Gulf. It could receive PAHs from both the land-based and sea-based sources. Unlike other stations, Helyleh receives PAHs only from petrogenic sources. This station is a less urbanized area where is located far from harbors and ports. However, it could be concluded that coastal sediment of Bushehr receives PAHs from both the petrogenic and pyrolytic sources.

CONCLUSIONS

The concentration of PAHs in Bushehr sediment was found to be moderate to high compared to other marine sediments from different parts of the world. The urbanized and industrialized stations were more contaminated than those located far from the city. No significant difference was found between PAHs concentrations in sediment during winter and summer indicating the steady condition of the PAHs input in the studied area. The station Helyleh receives PAHs from petrogenic sources, while the major part of PAHs in the sediment originated from both the pyrolytic and petrogenic sources. Due to the elevated levels of PAHs compounds in the sediment, regular monitoring of PAHs in marine ecosystem of Bushehr is recommended.

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