

Contamination of Polycyclic Aromatic Hydrocarbons in Surface Sediments of Khure-Musa Estuarine, Persian Gulf

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Abstract: To assess the status of polycyclic aromatic hydrocarbons (PAHs) contamination in the Khure Musa estuaries of Persian Gulf, samples of sediment were collected from five sampling sites and analyzed for PAHs by gas chromatography-spectrometry (GC-MS). The total concentrations of 15 PAHs varied from 703 to 3302 ng/g dry weight in surface sediments. Sediment samples are dominated by the presence of high molecular weight PAHs, especially four, five and six-ring PAHs. The samples of sediment were calculated using phenanthrene/anthracene and fluranthene/pyrene ratios to determine the sources. The results of study suggested that the main sources of PAHs in sediment in the studied region were mixed pyrolytic and petrogenic inputs.

Key words: Persian Gulf % Petrogenic % Polycyclic Aromatic Hydrocarbons % Pyrolytic

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic contaminations generated by natural and anthropogenic process. They can be introduced into marine environment by various ways such as oil spills, ship traffic, urban runoff, wastewater and industrial discharge, as well as combustion fossil fuel, forest fires, volcanic eruption and atmospheric fallout of vehicle exhaust [1-4].

The largest concentrations of PAHs have been reported in coastal sediments near urban and industrial areas [3, 5, 6]. They are present in both dissolved in particulate phases. Because of their low solubility and hydrophobic nature, PAHs tend to associations with inorganic and organic suspended particles with eventual deposition in the sediments of aquatic system [6,7]. The resulting elevated concentrations can mean increased exposure risk to resident benthic biota.

Sixteen individual PAHs compound have been indentified priority pollutants by United States Environmental Protection Agency (EPA) due to carcinogenic, mutagenic and toxic to marine organism and

their larvae [3,8,9] and the toxicity is increased by several orders of magnitude when combined with exposure to the ultraviolet portion of sunlight [10].

According to the formation mechanism, PAHs can be classified as petrogenic and pyrolytic. petrogenic PAHs are mainly derived from spillage of crude oil and its refined products whereas Pyrolytic PAHs are formed as a consequence of incomplete combustion [1,11]. PAHs ratio profiles based on PAHs' physical-chemical behavior have been commonly used to assess the differences between those of pyrolytic and petrogenic origin [4, 11-13].

The Persian Gulf is a shallow semi-enclosed marginal sea between the Arabian Peninsula and Iran. With little natural fresh water drainage makes the spilled oil to accumulate in its environment rather than being dispersed and degraded in the open gulf. Persian Gulf represents a stressed ecosystem due to its location within the richest oil province in the world hosting more than 67% of the world oil reserve.

Khure-Musa is the biggest bay in the Persian Gulf and its very importance with respect to biological and ecological properties. This region, due to geography special situation recipient wastewater of many several

industries such as Imam Khomeini Petrochemical Plant, Razi Petrochemical Plant, Farabi Petrochemical Plant and the Petrochemical Special Economic Zone. Because of the activities associated with transportation oil tanker by ships and discharge ballast water, this area heavily contaminated with oil residues, tar ball and heavy metals.

Few studies have been carried out to assess the concentration and origin of PAHs in coastal sediment of Khure-Musa estuarine where industrialization and urbanization have proceeded rapidly during the past two decades. In present study therefore we investigated the concentration levels, distribution and the possible origin of PAHs found in recent sedimentary material at Khure-Musa estuaries.

MATERIALS AND METHODS

The study was carried out in the Khure-Musa estuaries. Samples of sediments were collected from five sampling sites, namely Jafari esuarine, Ahmadi estuarine, Ardoleh estuarine, Ghazaleh estuarine and Merimos estuarine as indicated in Figure 1. The positions of sampling sites were recorded using GPS (Table 1). All samplings were conducted during July 2010.

Surface sediment (0-5 cm) samples were collected during low tide using a Van veen grab, from the five locations. Collected samples were immediately transferred to hexane rinsed glass bottle with aluminum foil cap and transported in dry ice to the laboratory and kept frozen at -20°C prior to analysis. The extraction and clean-up of sediments was carried out according to the procedure by Zakaria *et al.* [14]. Briefly, samples of sediment were taken for dry weight determination. The samples were dried with anhydrous sodium sulphate (muffled at 300°C for 4h) and mix together for a homogenous. A solution of four surrogated internal standard mixture (Phenanthrene-d₁₀-

P-terphenyl-d₁₄-Chrysene-d₁₂-Perylene-d₁₂) was added directly to the samples prior to extraction. Samples were extracted by soxhlet for more than 8 hours using DCM following activated copper treatment for elemental sulfur removal. The extracted samples were concentrated until near dryness using rotary evaporator for further clean up. The concentrated extracts were charged to 1st step column chromatography (1 cm inner diameter) packed with 5% silica gel deactivated to remove polar compound. The eluants were collected, volume reduced to near dryness and charged to 2st step column chromatography (0.45 cm inner diameter) packed with 100% fully activated silica gel to fractionate hydrocarbons. Then the mixture of DCM and hexane (3:1 v/v) was passed through the 2st step column chromatography to elute the PAHs fraction. The PAHs fractions were evaporated to near dryness under gentle nitrogen stream and taken up to 200 μ l using iso-octane.

The analysis each extract was carried out with a GC-MS system using a HP 6890 series gas chromatography with mass detector equipped with a split/split less injector. The capillary column used was a 30m long HP-5MS with 0.25 mm ID. The carrier gas used was helium at a constant flow rate of 1mL min⁻¹. The temperature program had an initial temperature of 70°C for 2min. The temperature was increased at a rate of 4°C/min to a final temperature of 310°C which was maintained for 10 min. The injector was maintained at 280°C. A selected ion monitoring mode (SIM) was employed using molecular ions of studied PAHs. Quality control study was carried out by monitoring recovery surrogate standards. The four surrogate standards were used for recovery correction of PAHs. The acceptable range of recovery was between 40 to 120%. The relative standard deviations (RSD) of individual PAHs identified in sample extracts were <10%.

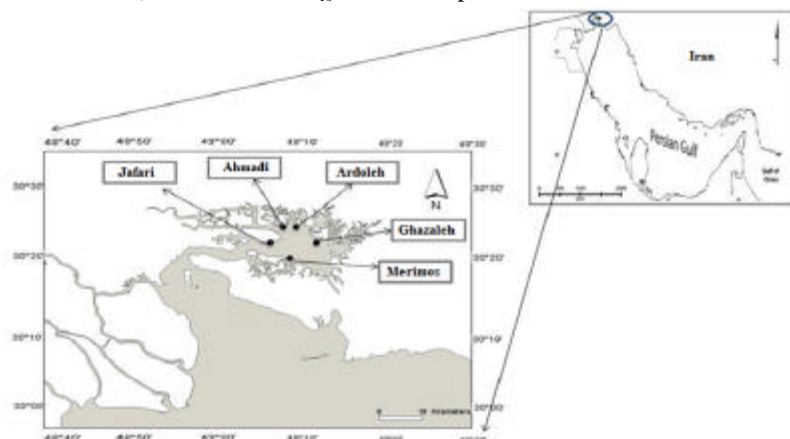


Fig. 1: Sampling sites in Khure - Musa estuaries

Table 1: Locations of sampling stations

Station	Site no.	Date	Location
Jafari	1	18/7/2010	30° 25' N, 49°06' E
Ahmadi	2	18/7/2010	30° 27' N, 49°07' E
Ardoleh	3	18/7/2010	30° 27' N, 49°09' E
Ghazaleh	4	18/7/2010	30° 25' N, 49°11' E
Merimos	5	18/7/2010	30° 22' N, 49°08' E

RESULTS AND DISCUSSION

The concentrations of the 15 compounds of PAH in surface sediments in Khure-Musa estuarine are shown in Table 2. They ranged from 703 ng/g dry weight to 3302 ng/g dry weight. The high concentration was obtained in Jafari, Ahmadi and Ardoleh estuaries respectively. The high pollution in these stations is found as a result of their proximity to industrial installations such as Imam Khomeini Petrochemical Plant, Razi Petrochemical Plant, Farabi Petrochemical Plant and heavy traffic of tanker and commercial cargo boats. The stations are also located near the ship lift, dry dock as well as the naval ships facilities.

According to a classification system suggested previously Baumard *et al.* [13], PAH levels can be described as low, moderate, high and very high when Σ PAH concentrations are 0-100, 100-1000, 1000-5000 and >5000 ng g⁻¹, respectively. On the basis of classification adapted by Baumard *et al.* [13] the sediment samples from the Khure- Musa estuaries can be considered moderate to high polluted with PAHs. Due to their non-solubility, hydrophobic character and long-lasting persistence, PAHs rapidly become associated with sediments and suspended particles [15]. The total concentrations PAHs in sediment samples were similar to international studies

worldwide such as coastal sediment in Tabasco state Mexico, Caspian Sea Azerbaijan and Masan Bay Korea (Table 3).

The PHE/AN index reflect was extensively used to infer nature of PAH pollution in sediments [11, 16-19] over Ant supports petrogenesis for PAHs in sediments. Similarly, fluoranthene (Fl) is less thermodynamically stable than pyrene (Py); they are often associated with each other in natural matrices and a predominance of Fl over Py is characteristic of a pyrolytic process, while in petroleum-derived PAHs, pyrene is more abundant than fluoranthene. Generally, a PHE/ANT < 10 and FLU/PYR > 1 indicates that the contamination by PAHs from a pyrolytic origin, whilst the PAH from petrogenic is characterized by PHE/ANT > 10 and FLU/PYR < 1 [2,11,13,17,20].

Our results showed that of samples of sediment in all sites have PAHs from mixed of pyrolytic and petrogenic origin with predominant petrogenic input at Jafari estuarine Table (2).

Distribution patterns of PAHs in sediments were dominated by 4-5 and 6 aromatic rings (mainly Fluranthrene, Pyrene, Benzo [a] anthracene, Benzo [b] fluranthrene Benzo [a] pyrene, Dibenzo [gh] anthracene and Indeno [1,2,3-cd] pyrene) PAHs along the

Table 2: Concentrations of PAHs in surface sediments in Khure-Musa estuarine, Persian Gulf (ng g⁻¹dw).

Compounds	Jafari	Ahmadi	Ardoleh	Ghazaleh	Merimos
Acenaphthylene	86	71	107	63	38
Acenaphthene	37	10	12	11	10
Fluorene	101	17	68	20	21
Phenanthrene	386	69	145	72	61
Anthracene	22	24	24	20	20
Fluranthrene	337	75	113	94	74
Pyrene	616	153	252	175	132
Benzo[a]anthracene	43	53	58	51	147
Chrysene	502	51	52	42	38
Benzo[b]fluranthrene	690	73	64	61	55
Benzo[k]fluranthrene	24	30	30	28	25
Benzo[a]pyrene	127	53	53	51	46
Dibenzo(gh) anthracene	118	46	44	42	37
Indeno[1,2,3-cd]pyrene	140	64	61	55	51
Benzo[ghi]perylene	73	52	49	49	48
Phe/Ant	15.55	2.87	6.04	3.6	3.05
Flu/Pyr	0.54	0.49	0.44	0.53	0.56
GPAHs (ng/g dry weight)	3302	841	1131	834	703

Table 3. Worldwide concentrations of ÓPAHs in coastal sediments (ng g⁻¹ dw).

Area	GPAHs (ng/g dw)	Pollution level	References
Tabasco state, Mexico	454-3120	Moderate to high	[21]
Kyeonggi Bay, Korea	10-1400	Low to moderate	[22]
West Mediterranean Sea	1.5-20440	Low to very high	[13,20]
Northwest Coast Mediterranean Sea	86.5-48090	Low to very high	[23]
Todos Santos Bay, Mexico	7.6-813	Low to moderate	[24]
Caspian sea, Azerbaijan	338-2988	Moderate to high	[25]
Masan Bay, korea	207-2670	Moderate to high	[26]
Gulf and the Gulf of Oman, Oman	1.6-30	Low	[27]
Gulf and the Gulf of Oman, Bahrian	13-6600	Low to very high	[27]
Gulf and the Gulf of Oman, Qatar	0.55-92	Low	[27]
Gulf and the Gulf of Oman, UAE	0.6-9.4	Low	[27]
Marine environment, Korea	8.80-18,500	Low to high	[28]
Niger Delta, Nigeria	21-72	Low	[29]
Coastal of Bushehr, Persian Gulf	41.7-227.5	Low to moderate	[4]
Khure - Musa estuarine, Persian Gulf	703-3302	Moderate to high	Present study

The Pollution levels are assigned as low: 0-100, moderate: 100-1000, high: 1000-5000, very high: >5000 ng g⁻¹ [13].

Table 4: ERL and ERM values for some PAHs in surface sediments of Khure - Musa estuaries, Persian Gulf (ng g⁻¹).

Compounds	ERL	ERM	Jafari	Ahmadi	Ardoleh	Ghazaleh	Merimos
Acenaphthylene	160	2100	86	71	107	63	38
Acenaphthene	44	640	37	10	12	11	10
Fluorene	16	500	101	17	68	20	21
Phenanthrene	240	1500	386	69	145	72	61
Anthracene	85	1100	22	24	24	20	20
Fluranthrene	600	5100	337	75	113	94	74
Pyrene	665	2600	616	153	252	175	132
Benzo[a]anthracene	260	1600	43	53	58	51	147
Chrysene	380	2800	502	51	52	42	38
Benzo[b]fluranthrene	430	1600	690	73	64	61	55
Benzo[a]pyrene	430	2800	127	53	53	51	46
Dibenzo(gh) anthracene	63	260	118	46	44	42	37
Indeno[1,2,3-cd]pyrene	240	950	140	64	61	55	51
Benzo[ghi]perylene	85	330	73	52	49	49	48

contamination gradient. The abundance of high molecular weight PAHs in sediment samples are more likely to be transported to the sediment bed due to their increased sorption and resistance to degradation. The importance of high molecular weight PAHs has been commonly observed in sediments from marine or estuarine environments [30-34].

Sediment chemistry data alone do not provide an adequate basis for assessing the hazards posed by sediment associated contaminants to aquatic organisms. Interpretive tools are also required to determine if sediment-associated contaminants are present at concentrations which could, potentially, impair the designated uses of the aquatic environment. PAHs level

in sediment were assessed for possible hazards to marine benthic community using the compared with effects-based sediment guideline values, such as the effects range-low (ERL), that was calculated as the lower 10th percentile of effects concentrations and the effect range-median (ERM) as the 50th percentile of effects concentrations [35]. The ERL and ERM values for some PAH compounds are listed in (Table 4).

The high value recorded of investigated pollutants were 690 and 616 ng g⁻¹ for Bezo (a) fluranthrene and Pyrene respectively. Thus concentrations of PAHs found in this study are not expected to be a threat to benthic marine organisms along the khure-Musa estuarine except for Jafari estuarine.

CONCLUSIONS

This study has provided data on the levels and origin of PAHs in the surface sediments of Khure - Musa estuaries. The obtained results demonstrate high contamination levels for PAHs in sediments of Khure - Musa estuaries. The total concentrations of PAHs in sediments were similar to or lower than those found in many other marine environments, which were considered moderate to high polluted with PAHs. PAHs sources for samples of sediment were mixed anthropogenic sources, due to combustion emissions from industrial activities, ships and atmospheric deposition, effluents from Imam Khomeini Petrochemical Plant, Razi Petrochemical Plant, Farabi Petrochemical Plant, oil seeps, discharges ballast water from oil tanker and other ship, dry dock as well as the naval ships facilities. The profile reveals that the dominant PAHs were high molecular weight (4,5 and 6 ring). The concentrations of total PAH and most individual PAH compounds were below the ERM guidelines, suggesting that PAHs accumulated in Khure - Musa sediments were unlikely to cause serious toxicity except for jafari estuarine.

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