



## Aliphatic and Aromatic Hydrocarbons in the Coastal Sediments of the Kharg Island in the Persian Gulf

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### ABSTRACT

Kharg Island in the Persian Gulf is the place for the major oil export terminals of Iran and hosts several large oil related industries. Coastal environment of the Kharg Island is rich in coral reefs. This paper presents concentrations and sources of aliphatic and aromatic hydrocarbons in the sediments from the coastal area of the island. The concentration of hydrocarbons in 14 seabed sediment samples from water depths of 13-20 m around the island were measured by gas chromatography (GC). Total Petroleum Hydrocarbon (TPH) concentrations in sediment samples ranged from less than 1 to 133  $\mu\text{g/g}$  indicating low to moderate levels of oil pollution. Spatial distributions of TPH concentrations indicated no oil pollution in the southern part of the island, higher oil pollution levels near oil terminals and correlation with fine particles. Total Polycyclic Aromatic Hydrocarbons ( $\Sigma\text{PAHs}$ ) concentrations in sediment samples ranged from near zero to 6210 ng/g, indicating non to highly, but mainly moderately polluted levels.  $\Sigma\text{PAHs}$  concentrations, except at one station, were all less than the NOAA sediment quality guideline value for the effects range low. Developed indices for pollutant origins showed that hydrocarbons in all sediment samples collected in the study area had petrogenic origin. The results also indicated that the emissions from gas flares in the island were the main source of aromatic compounds in the sediment samples.

**Keywords:** Sediment; Oil Pollution; TPH, PAH, Petroleum hydrocarbon

### INTRODUCTION

Kharg Island is located in the northern part of the Persian Gulf (Fig. 1) at  $29^{\circ} 14' \text{ N}$  and  $50^{\circ} 18' \text{ E}$ . It has a length of about 8 km and a width of about 4 to 5 km (Fig. 2). The coastal environment of the Kharg Island is rich with coral reefs. The coral reefs of the Kharg Island are the host to many types of fishes of the Persian Gulf (Mirvakili et al., 2013; Jafarabadi et al., 2018).

More than 90% of the Iranian crude oil is exported from two major oil terminals in the eastern and western side of the Kharg Island. Considerable oil related industrial development and operations including petroleum extraction, crude oil tank farms, oil terminals and petroleum refineries have been the major sources of oil pollution of the coastal environment of the island. In addition, damages to oil facilities and oil tankers during Iraq-Iran war caused several large oil spills in Kharg coastal waters. However, there are only a few studies conducted on the oil pollution of the coastal environment of Kharg Island (Mirvakili et al., 2013; Mirvakili and Zaker, 2014; Akhbarizadeh, 2016; Jafarabadi et al., 2018).

The occurrence of any oil spill in a coastal area is associated with damages to its environment and ecosystems. Depending on the time, place, toxicity, and concentration of the oil spill, exposure to oil spill can lead to the death of various organisms and could cause

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harmful effects such as reduced reproduction, inappropriate growth, difficulty in feeding mechanisms, and diminished defense capacity against diseases (Clark, 2001; Law and Klungsoyr, 2000).

Aliphatic and aromatic hydrocarbons in coastal sediments could have petrogenic origin or could be the result of natural inputs from terrestrial plant waxes, marine phytoplankton, volcanic eruptions, biomass combustion and natural oil seeps (Tolosa et al., 2004; Meyers, 2003).

Aliphatic hydrocarbons include straight chain alkanes, branched chain alkanes, cyclo alkanes and isoprenoids compounds, including biomarkers (Clark, 2001; Tolosa et al., 2004). Biomarkers can be used to provide information on the source of hydrocarbons and the extent of weathering of the oil spill in coastal sediments (Pu et al., 2017; Wang et al., 2014; Peng et al., 2016; Tarasov et al., 2013)

Some polycyclic aromatic hydrocarbons (PAHs) are known to be highly pollutant and potent carcinogens with destructive effects on human health (Clark and Finley, 1973; Abdel-Shafy and Mansour, 2016). PAHs in coastal sediments could have several origins including incomplete combustion of fossil fuels, discharge of petroleum and its products, and biological processes. (Tolosa et al., 2004; Lourenço et al., 2013).

The study on concentrations and sources of hydrocarbons in sediments is a common and effective way for understanding the level of oil pollution in coastal environment (Tolosa et al., 2004; 2005, 2009, Mirvakili and Zaker, 2014; Melé et al., 2018; Taghavi et al., 2021).

Tolosa et al. (2005) investigated composition and distribution of aliphatic and PAHs in biota and coastal sediments from four countries of Bahrain, Qatar, UAE and Oman in the Persian Gulf. The levels of TPH and PAHs in sediments and biota were relatively low compared to world-wide locations reported to be chronically contaminated by oil. However, in sediments collected near an oil refinery in Bahrain, TPH and PAHs concentrations indicated a chronically contaminated coastal area. The results also indicated that PAHs were mainly from fossil sources with one exception near BAPCO refinery produced by combustion.

Akhbarizadeh et. al. (2016) investigated potential sources and ecotoxicological risk of aliphatic and polycyclic aromatic hydrocarbons in coastal water and sediments of Kharg Island. Sediment samples were collected in shallow waters very close to shoreline of the island. The results showed petroleum and petroleum combustion as the major sources of contamination in the samples. In addition, the ecological risks of both individual and multiple PAHs were found low.



**Fig. 1.** Kharg Island in the Persian Gulf

Mirvakil et al. (2013), investigated oil pollution and origin in surface coastal sediments of Kharg Island collected from very shallow coastal waters near the shoreline. TPH concentration showed highly polluted samples near the oil terminals and non-polluted samples in the northern part of the Island.

In this paper, using lab analysis, concentrations of aliphatic and aromatic hydrocarbons in 14 sediment samples collected in the coastal area around the Kharg Island in water depths of 13-20 m (Figs. 1 and 2) are presented and sources of hydrocarbons and levels of oil pollution are discussed.

## MATERIALS AND METHODS

Seabed surface sediment samples were collected at 14 points around the Kharg Island in 2010 (Figs.1 and 2). The samples were collected from water depths of 13 to 20 meters. Geographical coordinates, water depth and percentage of fine particles (<63 microns) at the sampling stations are presented in Table 1. The positions of the sampling stations were selected in a way to cover all parts of the coastal waters of the Kharg Island with more samples in the areas which were more exposed to oil pollution in the east and west of the island in particular around the two major oil terminals.

The sediment samples were collected using a standard Van Veen Grab Sampler with 25x25 cm cross section. The UNEP/IOC/IAEA standard method (No. 20) (UNEP, 1992) was employed for sediment sampling. About 200 to 300 grams of wet sediment was taken from the top 5 centimeter of surface seabed sediment. The collected samples were packed and transferred to laboratory using the USEPA-sw-846 standard method. The standard method of American Association of Environmental Protection (USEPA-SW-846#3540C) named SOXHLET was used for the preparation of samples and extraction of petroleum hydrocarbons from them. The samples were passed through a 63 microns sieve (<63) before the lab analysis. A Varian gas chromatography device (GC-FID) was used for determining the concentrations of Total Petroleum Hydrocarbons (TPHs) and Aliphatic compounds in the sediment samples. PAHs concentrations were measured using an Agilent GC/MS model 6890N. Quality assurance and quality control (QA/QC) for PAHs analysis were conducted according to the method of Tolosa et al (2005).

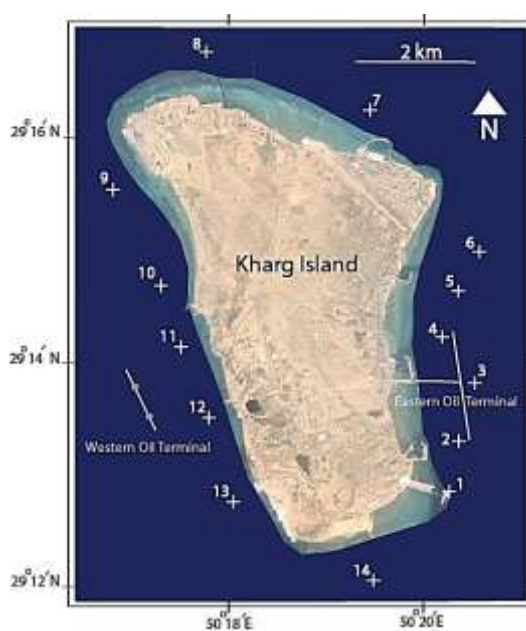


Fig. 2. Location of sediment sampling stations

## RESULTS AND DISCUSSIONS

TPH concentrations in the sediment samples ranged from less than 1  $\mu\text{g/g}$  to 133 $\mu\text{g/g}$  (Fig. 3). The highest concentrations were observed at stations 1, 3 and 5, located adjacent to the eastern oil terminal (Fig. 2), with values of 82, 53 and 133  $\mu\text{g/g}$  respectively and also at station 12, near the western oil terminal with value of 94 $\mu\text{g/g}$ . The eastern and western oil terminals in the island have been the places for frequent discharges of oil into marine environment from different sources including leakages from loading activities, oil tanker accidents and illegal discharges of oily wastes from ships.

In the southern part of the island at stations 13 and 14 (Fig. 2), TPH concentrations in the samples were very low and less than 1  $\mu\text{g/g}$ . TPH concentrations at stations 6 and 9 were 3 and 16  $\mu\text{g/g}$ , respectively and in all the other sediment samples ranged between 30 and 38  $\mu\text{g/g}$ .

**Table 1:** Location and depth of sediment sampling stations.  
H = Water depth (m); p (%) = Percentage of fine particles (<63 microns)

Station	Latitude N	Longitude E	H (m)	P (%)	Station	Latitude N	Longitude E	H (m)	P (%)
1	29° 13.06	50° 20.37	17	69.3	8	29° 16.84	50° 17.85	15	15.5
2	29° 13.32	50° 20.34	20	62.1	9	29° 15.56	50° 17.15	18	0.3
3	29° 13.83	50° 20.44	20	59.7	10	29° 15.02	50° 17.47	18	11.4
4	29° 14.32	50° 20.37	17	37.3	11	29° 14.33	50° 17.64	18	3.0
5	29° 14.72	50° 20.39	17	29.6	12	29° 13.75	50° 17.801	18	26.0
6	29° 15.38	50° 20.50	18	1.3	13	29° 12.69	50° 18.211	18	1.5
7	29° 16.69	50° 19.01	13	1.3	14	29° 12.07	50° 19.165	18	1.3

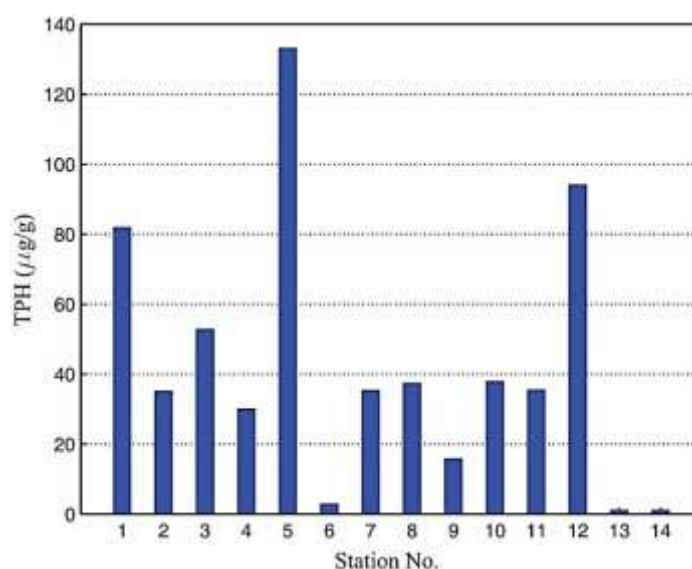
Commendatore and Esteves (2007) considered three TPH concentration levels for oil pollution in coastal sediments: low (< 10  $\mu\text{g/g}$ ), low to moderate (10-100  $\mu\text{g/g}$ ) and moderate to high (100-1000  $\mu\text{g/g}$ ). Readman et al. (2002) considered the sediments with TPH concentrations above 100  $\mu\text{g/g}$  as polluted. Tolosa et al. (2004) considered TPH concentrations higher than 500  $\mu\text{g/g}$  indicative of significant pollution and values below 10  $\mu\text{g/g}$  as unpolluted sediments. Considering the above criteria, the level of oil pollution at stations 6, 13 and 14 were low (unpolluted) and in all other stations were low to moderate. The results showed that percentage of fine particles had considerable effect on the value of TPH concentration in the sediment samples. This is evident in a much lower TPH concentration at station 6, with a coarse nature of sediment, in comparison to the one at station 5 (Fig 3, Table 1).

The study by Mirvakili et al. (2013) showed that the levels of TPH concentrations in the sediment samples collected near the coastline around eastern and western oil terminal were very high and indicative of chronically significant oil pollution. The much lower levels in the sediments collected in the present study from the same area but further from the coastline in water depths of 13-20 m were the results of environmental conditions in the nearshore open waters including strong local waves and tidal currents and also a low percentage of fine-grained materials in seabed sediments in an area that is mainly covered with coral reefs.

Compared to other regions in the world, the TPH concentrations observed in our study were within the same range of magnitude with those observed in sediments collected from coastal areas such as Qatar (2.2-84  $\mu\text{g/g}$ ) (Tolosa et al., 2005), Bahrain (16.6-41.8  $\mu\text{g/g}$ ) (Tolosa et al., 2005) and southern coastal area of the Caspian Sea (115-201  $\mu\text{g/g}$ ) (Taghavi et. al., 2021) and more than the ones observed in UAE (0.1-16.4  $\mu\text{g/g}$ ) (Tolosa et al, 2005), Eastern Aegean Sea (Turkey)

(0.52–4.85  $\mu\text{g/g}$ ) (Gonul and Kucuksezgin, 2012), Oman (0.01–7.6  $\mu\text{g/g}$ ) (Tolosa et al., 2005), Izmir Bay (0.09–4.50  $\mu\text{g/g}$ ) (Darilmaz and Kucuksezgin, 2007), Australia (0.5–2.0  $\mu\text{g/g}$ ) (Volkman et al. 1992), Eastern Mediterranean (0.5–5.7  $\mu\text{g/g}$ ) (Gogou et al., 2000), Ukraine (2.1–6.6  $\mu\text{g/g}$ ) (Readman et al., 2002), Antarctica (0.25–23  $\mu\text{g/g}$ ) (Martins et al., 2004) and Northeast Caspian Sea (0.052–34.09  $\mu\text{g/g}$ ) (Tolosa et al., 2004) and less than the ones collected in locations reported to be chronically contaminated by oil, e.g. Baku Bay in the Caspian Sea (600–1820  $\mu\text{g/g}$ ) (Tolosa et al., 2004), Hong Kong (60–646  $\mu\text{g/g}$ ) (Hong et al., 1995) and New York Bight (35–2900  $\mu\text{g/g}$ ) (Farrington and Tripp, 1977).

Fifteen PAH compounds were analyzed included Pyrene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Benzo[a]anthracene, Chrysene, Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, Indeno[123-cd]pyrene, Dibenzo[ah]anthracene, Benzo[ghi]perylene and Naphthalene. These compounds are all among the 16 PAH compounds that have carcinogenic and mutagenic effects on humans and animals and are considered as the leading pollutants (Tolosa et al., 2005; Bengert et al., 2010; Gao et al., 2018)



**Fig. 3.** TPH concentration in sediment samples.

The concentrations of the PAH compounds ranged from <10 to 2402 ng/g. PAHs concentrations at stations 6, 13 and 14 were negligible. Among the 15 measured PAH compounds, Benzo[a]pyrene, Indeno[123-cd]pyrene and Dibenzo[ah]anthracene were not found in the sediment samples. Fossil PAHs of Acenaphthylene, Phenanthrene and Anthracene (Tolosa et al., 2004), with considerable amounts of concentration, were found in most stations indicating oil as the main source of PAHs in the study area. Other higher concentration of PAH belonged to Pyrene, Benzo[a]anthracene and Benzo[k]fluoranthene. Naphthalene with significant amount of 1111 ng/g concentration was found only at station 3.

Naphthalene was observed only at 2 stations of 3 and 5 (Fig. 2) with concentrations of 1111 and 108 ng/g respectively. Naphthalene is considered as a predominant component in a typical profile of petrogenic PAHs, however a more physical weathering of petrogenic profile is indicated by the loss of naphthalene as a more volatile PAH (Tolosa et al., 2005). Therefore, the high concentration of Naphthalene at station 3 near the eastern terminal could be the result of fresh leakage of petrochemical products in that area.

Acenaphthylene, Fluorene, Chrysene, Benzo[b]fluoranthene and Benzo[ghi]perylene concentrations were very small and each observed at only a few stations.

$\Sigma$ PAHs concentrations, except at station 5, were all less than the NOAA (1999) Sediment Quality Guideline value for the effects range low of 4000 ng/g dry weight, representing a "Minimal-effects" range with condition in which effects rarely be observed (Long et al., 1995). Baumard et al. (1998) considered 2 levels for  $\Sigma$ PAHs concentration in the sediments: low to moderately polluted (100-1000 ng/g) and highly polluted (>5000 ng/g). Considering these levels, sediment samples at station 6, 13 and 14 were unpolluted, at station 5 highly polluted and at the other stations moderately polluted (Table 2).

Sediments in the coastal areas near major oil terminals and industries could have PAHs concentrations both derived from combustion processes and the spillage of petroleum or its products (Tolosa et al., 2004 and 2005). The ratios of Ant/(Ant + Phe) and BaA/(BaA + Chr) have been used to distinguish the sources of anthropogenic PAHs. A ratio of Ant/(Ant + Phe) < 0.1 suggests an origin of petroleum while a ratio > 0.1 indicates a source of combustion (Li et al. 2006, Hu et al., 2010). A ratio of BaA/(BaA + Chry) < 0.2 indicates petroleum sources, ratio between 0.2 and 0.35 indicates mixed origin and ratio > 0.35 implies combustion origin (Yunker et al., 2002; Mai et al., 2002; Guo et al., 2006, Hu et al., 2010; Aghadadashi et al., 2017).

In this study the ratio of Ant/(Ant + Phe) could not be computed at stations 6, 13 and 14 because the concentrations of Phe and Ant at these stations were lower than the method detection limits (Table 2). The ratios of Ant/(Ant + Phe) at all other stations were > 0.1 and ranged from 0.16 to 0.36 with a mean value of 0.33 (Table 2) suggesting pyrolytic origins. The ratios of BaA/(BaA + Chry) at all stations, except stations 4, 6, 13 and 14 which could not be computed, were > 0.35 (Table 2), further confirming pyrogenic sources. There are a large number of gas flares in the Kharg Island that continuously burn the sour gases separated from crude oil. The results showed the combustion of gases from these flares as the main source for the PAHs concentrations in the nearshore coastal sediments of the island.

**Table 2:** Concentration of the main PAH compounds in the sediment samples (ng/g)

PAH (ng/g)	Stations													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pyrene	89	234	96	155	179	*	93	93	189	107	135	224	*	*
Acenaphthene	904	527	821	214	2402	*	742	742	432	534	533	520	*	*
Acenaphthylene	123	*	*	*	180	*	*	*	*	*	*	*	*	*
Fluorene	0	*	*	*	*	*	*	*	*	*	*	*	*	*
Phenanthrene	1168	790	909	362	1725	*	534	534	443	528	528	289	*	*
Anthracene	647	156	434	163	1085	*	358	358	143	213	211	286	*	*
Benzo[a]anthracene	322	151	314	*	50	*	242	242	111	227	161	234	*	*
Chrysene	88	*	*	*	64	*	*	*	*	*	*	*	*	*
Benzo[k]fluoranthene	58	76	796	92	64	*	159	159	207	154	181	379	*	*
Benzo[b]fluoranthene	67	*	*	*	81	*	73	73	0	*	75	0	*	*
Benzo[a]pyrene	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Indeno[123-cd]pyrene	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Dibenzo[ah]anthracene	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzo[ghi]perylene	68	54	*	60	62	62	21	21	0	18	16	*	*	80
Naphthalene	*	*	1111	*	108	*	*	*	*	*	*	*	*	*
$\Sigma$ PAHs (ng/g)	3530	1990	3690	1050	6210	62	2220	2220	1530	1780	1840	2100		80
Ant/(Ant + Phe)	0.36	0.16	0.32	0.31	0.39		0.40	0.40	0.24	0.29	0.28	0.50		
BaA/(BaA + Chr)	0.78	1	1		0.44		1	1	1	1	1	1		

\* <10 ng/g

Sources of aliphatic hydrocarbons in the sediments from the study area were investigated using a set of indexes. Aliphatic hydrocarbons in the coastal sediments could be resulted from human activities or biological sources such as algae, bacteria, marine animals and terrestrial vascular plants (Tolosa et al., 2004; Meyers, 2003).

Figure 4 shows the distribution of n-alkanes in the sediment samples in the study area. The n-C16 index is computed from division of total n-alkanes concentrations to the concentration of n-C16. The amount of n-C16 index is small (<15) for oil-contaminated samples, while samples contaminated by biological hydrocarbons have larger n-C16 ratios (>50) (Clarke and Finely., 1973; Tolosa et al., 2004). The n-C16 index of sediment sample at station 12 was 17 and in all other stations were less than 15 (Table 3), indicating that all the samples were contaminated with fossil hydrocarbons.

**Table 3:** Index quantities calculated for sediment samples

Station	CPI	n-C16	Odd/even
1	0.3	3.8	0.7
2	0.1	3.8	0.4
3	0.0	11.8	0.1
4	0.1	12.9	0.3
5	0.4	3.6	0.5
6	0.0	0.0	0.0
8	0.2	6.9	0.4
9	0.1	7.5	0.5
10	0.3	9.1	0.5
11	0.4	8.7	0.6
12	0.3	17.0	0.3
13	0.1	0.0	0.2
14	0.4	0.0	0.1

$$\text{CPI} = \frac{1}{2} \left( \frac{\sum C_{21-33} (\text{odd carbon})}{\sum C_{20-32} (\text{even carbon})} + \frac{\sum C_{23-35} (\text{odd carbon})}{\sum C_{22-34} (\text{even carbon})} \right)$$

The Carbon Priority index (CPI) is about 1 for crude oil hydrocarbons, while it varies from 3 to 6 for the hydrocarbons originated from vascular plants (Colombo et al., 1989). As shown in Table 3, the CPI index at all stations were less than 1, indicating oil contamination in the sediment samples.

The Odd/Even index (Volkman et al., 1992) is the ratio of the total concentrations of odd carbon number alkanes to the total concentrations of even number ones. This ratio is about 1 for petrogenic hydrocarbons and varies between 8 and 10 for plant waxes. The Odd/Even index for the sediment in the study area (Table 3) were in the range of 0.1 to 0.7, indicating petrogenic hydrocarbons.

According to the results shown by all the presented indices, petrogenic inputs were the source of hydrocarbons in all of the sediment samples collected in the study area.



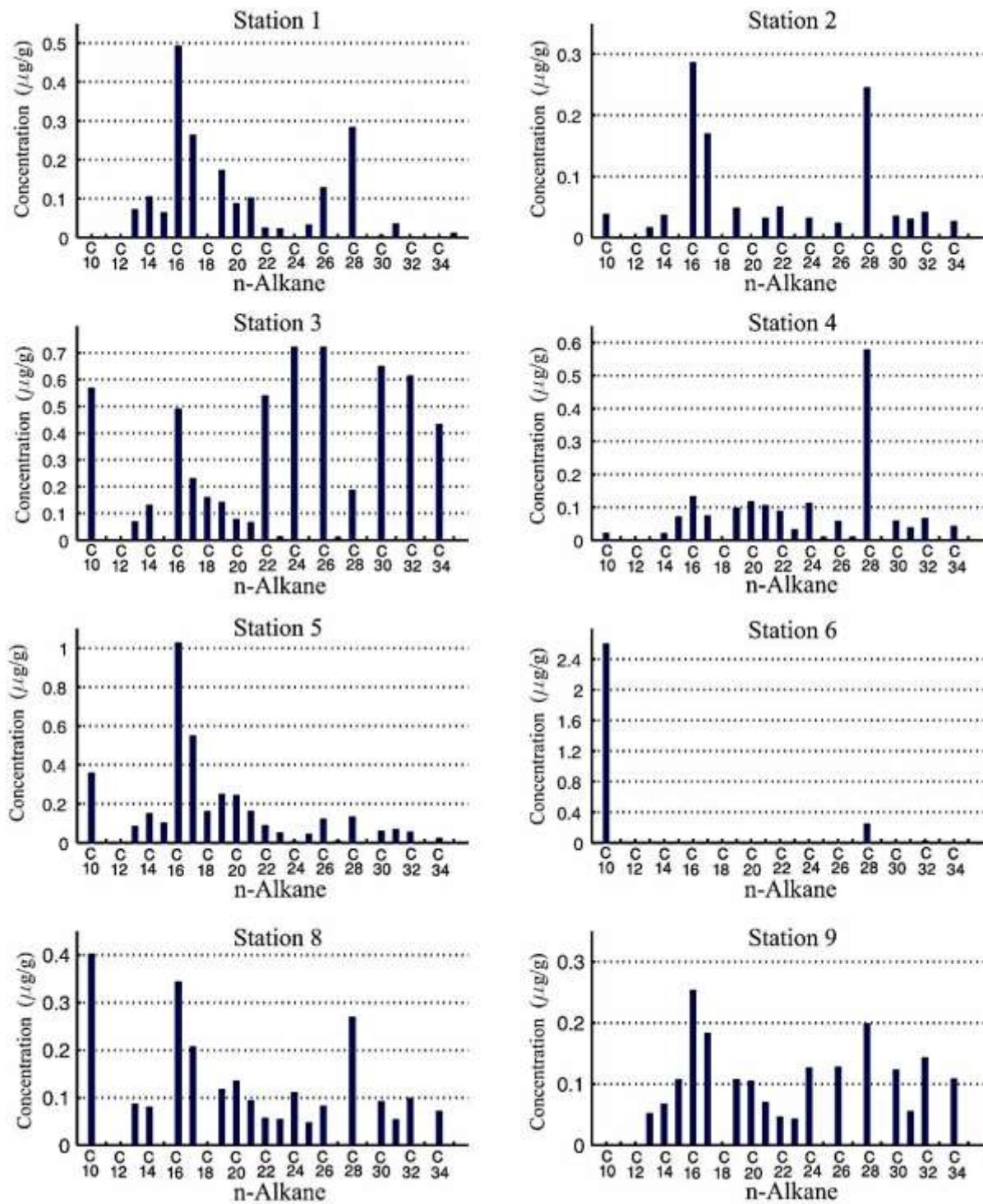


Fig. 4. Values of n-alkanes concentrations in sediment samples ( $\mu\text{g/g}$ )



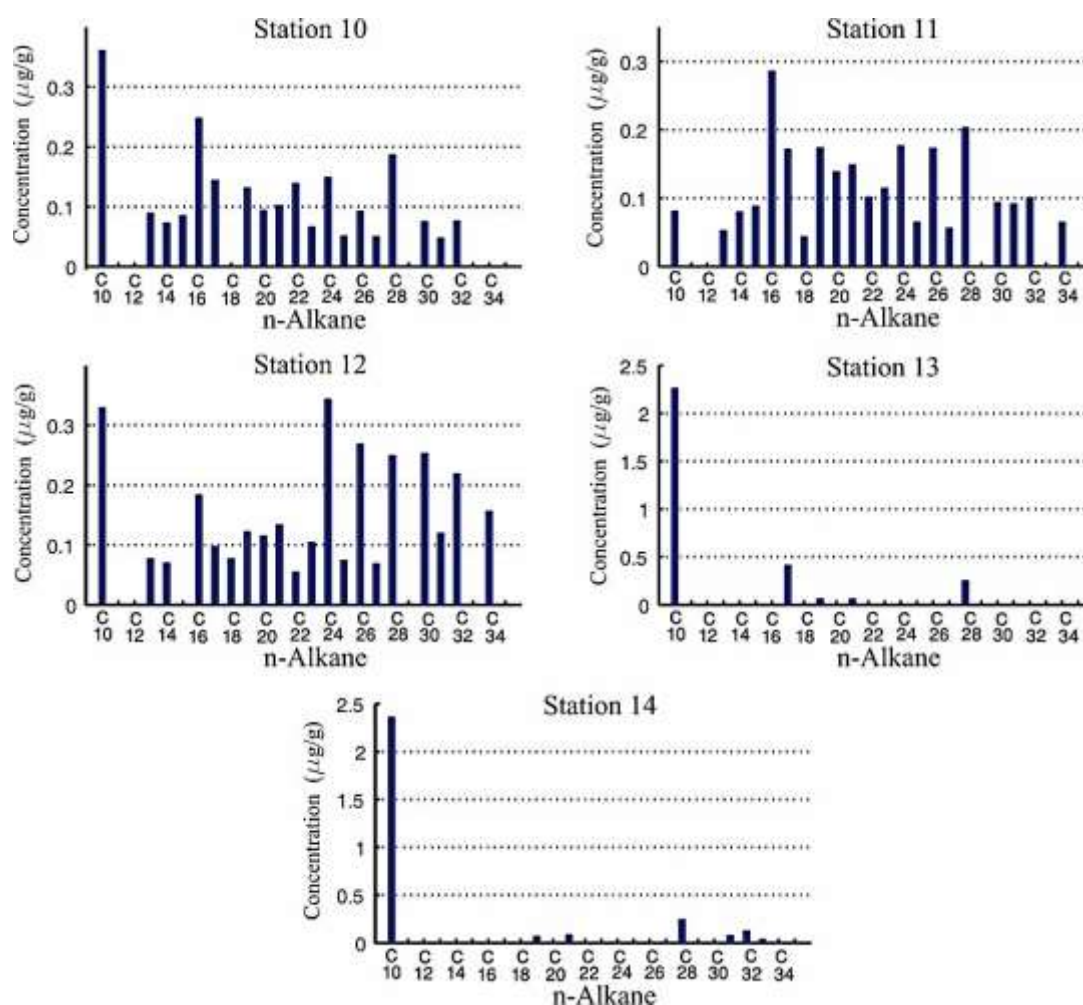


Fig. 4 (continue). Values of n-alkanes concentrations in sediment samples (µg/g)

## CONCLUSIONS

Concentrations and sources of aliphatic and aromatic hydrocarbons in the sediments from the coastal area of Kharg Island in the Persian Gulf were studied by laboratory analysis. This study provided a better understanding about the level and source of pollution in a marine environment which is rich in coral reefs, but is located close to one of the most active and operational oil industrial areas in the Persian Gulf. Oil and oil products discharged into coastal waters or entered the water through atmosphere, were found as the major sources of hydrocarbons in the sediment samples. The results showed low to moderate levels of oil pollution in the study area. Highest concentrations of hydrocarbons were found near eastern and western oil terminals in the island.

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The present research did not receive any financial support.

## CONFLICT OF INTEREST

The author declare that there is no conflict of interests regarding the publication of this manuscript. In addition, ethical issues, concerning plagiarism, informed consent, misconduct,

data fabrication and/ or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research

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