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Petrogenic Events as The Dominant Source of Petroleum Pollution in Sediment Cores Of Industrial Environment in The Northwest of the Persian Gulf

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ABSTRACT

Given the entrance of oil to the northwest of the Persian Gulf from the oilfields in this ecosystem, an investigation was carried out in 2017 to evaluate the historical records of hydrocarbons, source identification, and chemical fingerprinting. To these purposes, sediment core samples were collected from the northwest of the Persian Gulf. Then, compounds (*n*-alkanes, PAHs, hopane, and sterane) were extracted with a Soxhlet system and two-step column chromatography and were analyzed by a GC-MS instrument in a laboratory. Also, oil samples from five oilfields in the study area were analyzed for the chemical fingerprinting goal. Overall, the results showed petrogenetic sources in recent years in the Persian Gulf. Common petrogenic hydrocarbon source was strongly suggested in all layers by the presence of unresolved compounds resolved (UCM), lower molecular weight/higher molecular weight (LMW/HMW) and carbon preference index (CPI) ratios of <1. The typical profile of petrogenic PAHs with various PAH ratios and multivariate analysis showed that PAHs were mainly derived from petrogenic sources. Simultaneous use of *n*-Alkanes and PAHs in source identification can be effective in precisely specifying hydrocarbon sources in complicated mixtures ecosystems. Furthermore, multivariate analysis and chemical fingerprinting of *n*-alkanes, PAHs, hopanes, and sterane confirmed that the Hendijan crude oil can be a source of the sediment pollution in the study site.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), with two or more fused aromatic rings, are ubiquitous semi-volatile organic pollutants that are included in lists of hazardous substances and belong to one of the most common families of micro-organic pollutants that are significant public health and environmental concern (Xu et al., 2014). Petroleum hydrocarbons have serious dangers to human health and marine organisms and find their way into the food chain due to their wide distribution, complex compositions, and toxicants, along with bioaccumulation, and biomagnifications (Li et al., 2016; Xia et al., 2015). Both natural and anthropogenic activities are sources of hydrocarbons and are transferred to marine ecosystems in a solution form via urban runoffs, domestic wastewater, industrial dumps, land-based industrial activities, offshore oil exporting and extraction facilities, oil terminals, tanker accidents, ballast water, and spills due to wars (Sheppard et al., 2010). Due to their hydrophobic nature, hydrocarbons tend to associate with particles, resulting in their downward transport through the water column and final accumulation in marine sediments, so sediments have complex compositions of hydrocarbons (Deyme et al., 2011; Parinos et al., 2013). The chemical fingerprinting of petroleum is made possible by the multitude of individual hydrocarbon compounds that are present and by the great variability in the relative abundances of these compounds among different crude oils. Hydrocarbons in sediment cores have been used to identify their source and to reconstruct the historical records of these hydrocarbon inputs for studies on their environmental impact (Gao et al., 2007). Abundant and enormous oil spills in recent years have menaced the Persian Gulf, and the most noticeable events of the Persian Gulf pollution are related to the Gulf War spill of 1991 (Mora et al., 2010) and the Nowruz oilfield oil spill associated with the Iran-Iraq War (NOAA, 2010). Although the Persian Gulf has always been exposed to oil spills and oil events, no report can be found that identifies the origin and reconstructs the history of oil pollutions in sediment cores in the Northwestern Persian Gulf by using biomarkers. Therefore, this study aimed at identifying the origin of hydrocarbons and distinguishing the petroleum sources in sediment cores of the Northwestern Persian Gulf

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by n-alkanes, PAHs, chemical fingerprinting of petroleum (hopanes and steranes) and their diagnostic ratios. The focus was on determining the composition, concentration and origin of hydrocarbons based on the examination of n-alkanes, isoprenoid alkanes, PAHs, and petroleum biomarkers in sediments cores and oil from oilfields in the Northwestern Persian Gulf using chemical fingerprinting of petroleum.

2. Materials and Methods

2.1. Study site and sampling

The Persian Gulf is a shallow basin with special features, such as the anticlockwise water flow circulation, high temperature, high salinity, and shallow depth and it has been posed to contamination over a long time (Jaafarzadeh Haghighi Fard et al., 2015) with effects on the marine ecosystems (Kazemi et al., 2012; Pejman et al., 2015). The Musa Estuary and a part of Hendijan, Deylam and the surrounding area of the Nowruz oilfield are located in the north-western area of the Persian Gulf. A vast harbor, some docks, and many industrial installations, such as petrochemical plants, are situated on the coasts of the Musa Estuary. In the coastal area of Hendijan, the maintenance zone and the traffic of fishing boats are significant. The surveyed regions are habitats of numerous unique species of marine organisms (Pejman et al., 2015).

In July 2017, core sediment samples were collected using a gravity corer at Imam Hasan Port at a depth of 20 m in the Persian Gulf at the latitude of 29° 58′ 89″ N. and the longitude of 50° 08′ 52″ E. (Fig.1). The core length was 12 cm and their diameter was 90 mm. In the field, the core profile was sectioned into 2 intervals. Immediately after sampling, the samples were stored in a clean aluminum foil, transferred to a laboratory, and kept frozen until being analyzed. Five crude oil samples from Hendijan, Bahregansar, Abuzar, Nowruz, and Soroush were provided by the Research Institute of Petroleum Industry in Iran.



Fig. 1. Map of the Persian Gulf and sampling site

2.2. Extraction and fractionation

In the laboratory, the sediment samples were freeze-dried (72 h) and sieved using 63-µm mesh to eliminate the particle size effect. To extract hydrocarbons, about 5 g of freeze-dried sediment was extracted with a Soxhlet system using 100 ml of dichloromethane (DCM) for 10 h. Then, the sulfur was eliminated by adding active copper to this dilution,

which was stored in a refrigerator (4°C) for 24 h. The volume of the sample was reduced to 5 ml by rotary evaporation and, then, it was passed through a 5% H_2O deactivated silica gel column (1 cm i.d., ×9 cm). All hydrocarbons were eluted with 20 ml of DCM/hexane (1:3, v/v). The DCM/n-hexane eluate was fractionated with fully activated silica gel column chromatography (0.47 cm i.d. ×18 cm) to obtain aliphatic and PAH fractions. The *n*-alkanes, hopanes, and steranes were eluted with 4 ml of hexane and the PAHs were eluted with 14 ml of dichloromethane/hexane (1:3, v/v).

For the quality control of the PAH analyses, 100µL of PAH surrogate internal standard mixture (200 ng g^{-1} of each component, naphthalene-d8, anthracene-d10, perylened12 and chrysene-d12) and 100µL of *n*-alkane surrogate internal standard (5µg g^{-1} of n-dodecane-d26) were added to the sediments before analysis. 17a(H)-22,29,30-trisnorhopane, 17β(H), 21β(H)-hopane, diploptene (17β(H),21β(H)-hop-22(29)-ene), 17α(H), 21β(H)- hopanes, and stigmastane-sterane ($C_{29}H_{52}$) were used as analytical standards for biomarkers. Hydrocarbons were analyzed and fractionated according to Zakaria et al. (2001)'s procedure. 100 µL of p-terphenyl-d14 as PAH internal standard was added immediately prior to being injected into the GC–MS (Riyahi Bakhtiari et al., 2010; Harris et al., 2011; Yunker and Macdonald, 2002).

For the analysis of crude oil samples, roughly 20 mg of crude oil samples were weighed and extracted with 2ml DCM/n-hexane (1:3, v/v). Fractionation and purification of the oil extracts were carried out with the same method for the sediment samples. All the reliable PAH and *n*-alkanes standards were procured from Sigma Aldrich and all the solvents used for analysis were of chromatographic grade from Merck. Average recoveries of 94 ± 18% and 102 ± 16% were calculated using the surrogate compounds for the PAH and n-alkane surrogates, respectively, with more than 91% for hopanes and steranes used for the recovery correction calculations.

All compounds were analyzed for GC–MS using an Agilent 5975C quadrupole mass-spectrometer coupled with an Agilent 7890A gas chromatograph equipped with a fused silica capillary column. The carrier gas in this study was helium. Total organic matter was analyzed with the procedure described by Nelson and Sommers (1996).

2.3. Statistical analysis

The source of *n*-alkane and PAHs was also determined by using diagnostic ratios and principal component analysis (PCA). The undetected values were replaced by a random number between zero and the limit of detection before PCA. All principal components (factors) with eigenvalues above one were extracted and rotated using the Varimax method (Yunker and Macdonald, 2003). Kaiser–Meyer–Olkin (KMO), a method developed to measure sampling adequacy, was used to compare the magnitudes of the correlation coefficients observed versus the magnitudes of the partial correlation coefficients. Large KMO (0–1) values are considered good because correlations between pairs of variables can be explained by other variables. Bartlett's sphericity test was used to test the hypothesis that the correlation matrix was an identity matrix with suitable significance ($p < 0.05$). All the statistical calculations were carried out using Statistical Package for Social Sciences (SPSS) 22 and R (3.4.3) software for windows.

3. Results and Discussion

3.1. PAH concentration and diagnostic ratios

All the 30 PAH compounds were identified in the two sediment cores, though in some slices. The total concentration of PAHs ranged from 110 to 496 ng g^{-1} d.w (Fig. 2). Normally, PAHs enter ecosystems via natural and anthropogenic sources. Volcanic eruptions, forests and grassland fires, synthesis by higher plants and microorganisms, as well as diagenesis are natural sources of PAHs in the environment. Anthropogenic inputs come from both petrogenic and pyrogenic sources. Leakage and discharge of petroleum in the processes of exploitation, transportation, production, industrial effluents, and urban discharges are the main sources of petrogenic PAHs. Pyrogenic PAHs result from biomass fuels (wood and grass), incomplete combustion of fossil fuels (coal and petroleum) and exhaust emissions from motor vehicles and human industrial activities (Zakaria et al., 2002; Wu et al., 2001). Isometric ratios of PAHs are important tools to classify sources of PAHs based on the separate configuration characteristics of PAHs from different sources (Yunker et al., 2002; Wu et al., 2001). Among the various ratios, the MP/P (methyl-phenanthrene/phenanthrene) ratio has effectively been used to recognize the pyrogenic and petrogenic sources of PAHs in numerous studies (Guo et al., 2011; Yunker et al., 2002; Zakaria et al., 2002). The MP/P ratio is the ratio of the sum of four isomers of MP to that of Phe. The MP/P ratios measured in combustion mixtures are usually lower than 10, whereas unburned fossil PAHs mixtures typically display a range of values higher than 10 (Prahl and Carpenter, 1983). The petrogenic in all sediment cores presenting an MP/P ratio of > 10. (Fig. 2). These results reveal that all sampling sites in this study area indicate that sedimentary PAHs have received more petroleum products. High oil spills, fuel smuggling, pollution emissions (caused by burning oil and fumes from gasoline and motor oil used to power boats), liquid waste discharge from petrochemical complexes, and the Persian Gulf tides may be responsible for sinking high concentrations of petrogenic PAHs in these parts of the study area (Bemanikharanagh et al., 2017).

Isometric ratios of Ant/(Ant+Phe) are frequently used due to their relatively stable features (Yunker et al., 2002). A ratio of Ant/(Ant + Phe)<0.1 shows petroleum as originating PAH, while Ant/(Ant + Phe)>0.1 recommends biomass burning (Chen et al., 2017; Peng et al., 2011; Sun et al., 2017) (Fig. 2). Also, the LMW/HMW PAH ratio is another useful ratio to distinguish the sources of PAHs.

Previous studies have indicated that petrogenic sources were more abundant in LMW PAHs, with severe depletion of HMW PAHs (four or more rings), whereas pyrogenic sources were more abundant in HMW PAHs (Mai et al., 2003; Zhi et al., 2015).

Incomplete combustion of carbon, wood, and fossil fuels at high temperature produce pyrogenic PAHs. These complexes are highly mineralized via HMW PAH containing 4–6 benzene rings, but petrogenic PAHs include LMW PAH compounds usually related to crude spills and refined oil (Baumard et al., 1998; Tongo et al., 2017). LMW/HMW > 1 were found in all sediment cores (Fig. 2), indicating the occurrence of petrogenic contamination from refined petroleum products or fuel oil (Soclo et al., 2000). Based on our results, combustion and petrogenic sources have both contributed to the main input of PAHs into the sediment cores in the Persian Gulf.

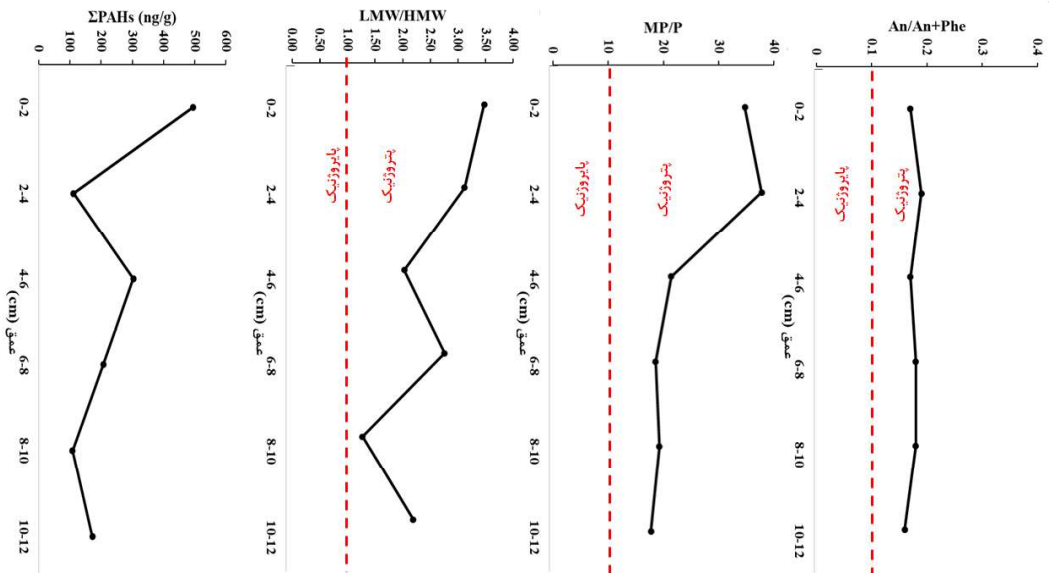


Fig. 2. ∑PAHs, LMW/HMW, MP/P and An/An+Phe distributions versus depth in sediment cores in the Northwestern Persian Gulf

3.2. Aliphatic hydrocarbons and diagnostic ratios

The *n*-Alkanes in the range C_{14}-C_{33} were analyzed in the sample sediments of the Persian Gulf. The chromatogram found in the majority of sediments in the sampling site in the Persian Gulf contained an *n*-alkane distribution with no obvious odd to even predominance with a maximum at *n*-C_{20} and a high UCM (Fig. 3) indicating petroleum input in these sites (Bixiong et al., 2007). Most of the sampling sites were in the area near the hot spots. Oil spills and leakages may happen during oil exploration, exploitation and transportation and contaminate the environment with petroleum-related hydrocarbons (Acosta-González and Marqués, 2016).

The total aliphatic hydrocarbon (TAH) concentrations varied from 350 to 9433 μg g^{-1} in sediment cores of the Persian Gulf (Fig. 4). Little or no contamination is considered to exist when total hydrocarbon concentration is <10 μg g^{-1} dw and the sediments are considered contaminated when the concentration is >100 μg g^{-1} (Readman et al., 2002). The TAH values at all depths were found to be larger than 100 μg g^{-1}. Thus, the hydrocarbon concentration in all cores is considered to be relatively high.

Sources of saturated hydrocarbons in marine environments have become more complex. Some general criteria have been used to determine the possible origins (anthropogenic or natural) of organic compounds (De Souza et al., 2011; Mille et al., 2007). The Carbon Preference Index (CPI) is an important indicator used to determine whether emissions of saturated hydrocarbons come from natural or anthropogenic sources. A CPI value of 1 or close to 1 indicates the presence of n-alkanes from petroleum and anthropogenic activities, whereas CPI values of >2.0 have been recorded for natural inputs (Maciel et al., 2016; Silva et al., 2013; Wang et al., 2018).

The results of this study showed CPI values ranging from 0.76 to 1.01 in the sediments in the Persian Gulf (Fig.4). Generally, based on the above results, CPI values indicated a predominantly petrogenic input of hydrocarbons in the sediment cores (Riyahi Bakhtiari et al., 2010; Resmi et al., 2016). A low CPI value (≤1) in most sediment samples showed an input from petroleum hydrocarbons, recycled

organic matter, and/or microorganisms (Fang et al., 2014). Several studies have confirmed the CPI values of around 1.0 in oil (Kalaitzoglou et al., 2004; Wang and Fingas, 2003; Zheng et al., 2000). Although the mean CPI of the samples in this study was lower than several studies throughout the world (Hu et al., 2009; Maciel et al., 2016; Sojinu et al., 2012; Zheng et al., 2000), it was consistent with a number of studies (Ranjbar Jafarabadi et al., 2017; Zhao et al., 2016), which have stated the domination of petrogenic origins.

The U/R ratio is the ratio between 1.81 to 5.45 sediment cores in the Persian Gulf (Fig. 4). It is used as an indicator of petroleum contamination in the sediment samples (Frysinger et al., 2003). U/R ratio, generally defined as the ratio of unresolved to resolved *n*-alkanes (U/R), is a useful tool to recognize the presence of degraded petroleum hydrocarbons. U/R values of >2 confirm significant contamination by petroleum products (Simoneit, 1986; Lipiatou and Saliot, 1991). According to this index, high petroleum contamination in that area is suggested. The U/R ratio values show important biodegradation of petroleum-related inputs.

Pristane (2,6,10,14-tetramethylpentadecane, C19 isoprenoid) and phytane (2,6,10,14-tetramethylhexadecane, C20 isoprenoid) are among the most abundant isoprenoids in petroleum (Volkman et al., 1992). Phytane is created by petroleum hydrocarbons, but pristane can be generated by biogenic processes in the absence of pollution due to petroleum hydrocarbons (Volkman et al., 1992). The *n*-C_{17}/pristane and *n*-C_{18}/phytane ratios are useful indices of the biodegradation process of crude oil spills in sediments (Gao et al., 2007; Pavlova and Papazova, 2003). Low ratios of *n*-C_{17}/pristane and *n*-C_{18}/phytane (< 1) represent degraded oil while higher ratios (>1) designate an initial phase of biodegradation in petroleum. In the present study, *n*-C_{17}/pristane and n-C_{18}/phytane ratios varied from 1.56 to 1.64 and 1.45 to 1.84 for all sampling sites, respectively (Fig. 4).

Pr/Ph ratios for uncontaminated sediments are typically between 3 and 5, whereas values close to or lower than 1 suggest petrogenic origin (Wu et al., 2001). Low values of Pr/Ph (particularly < 0.6) represent low oxygen sediments with high salinity and oil contamination (Jeng and Huh, 2008; Osuji et al., 2009). The presence of Pr and Ph in all samples and Pr/Ph ratios of <1 in most sites (0.49-0.67) reinforced this origin (Burns et al., 1992) (Fig. 4). This is in agreement with the U/R ratios mentioned above, indicating that the sediments of the wetland have been exposed to weathering, providing evidence of chronic oil contamination in this area.

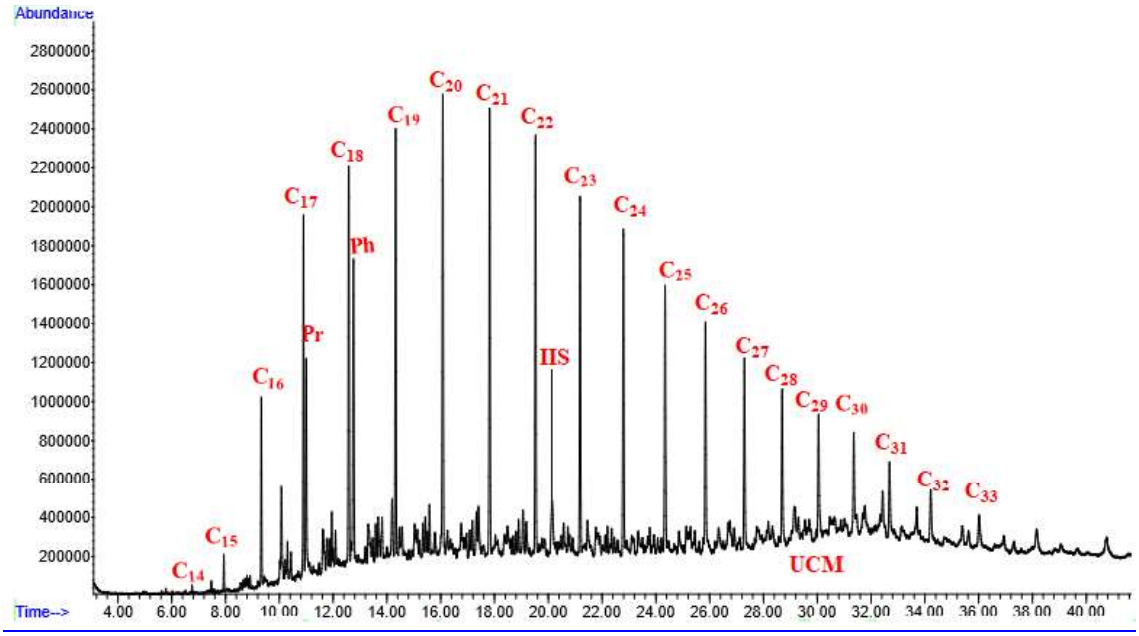


Fig. 3. GC–MS chromatograms of aliphatic hydrocarbons in sediment cores in the Northwestern Persian Gulf. ISS: internal standard, $C_{24}D_{50}$.

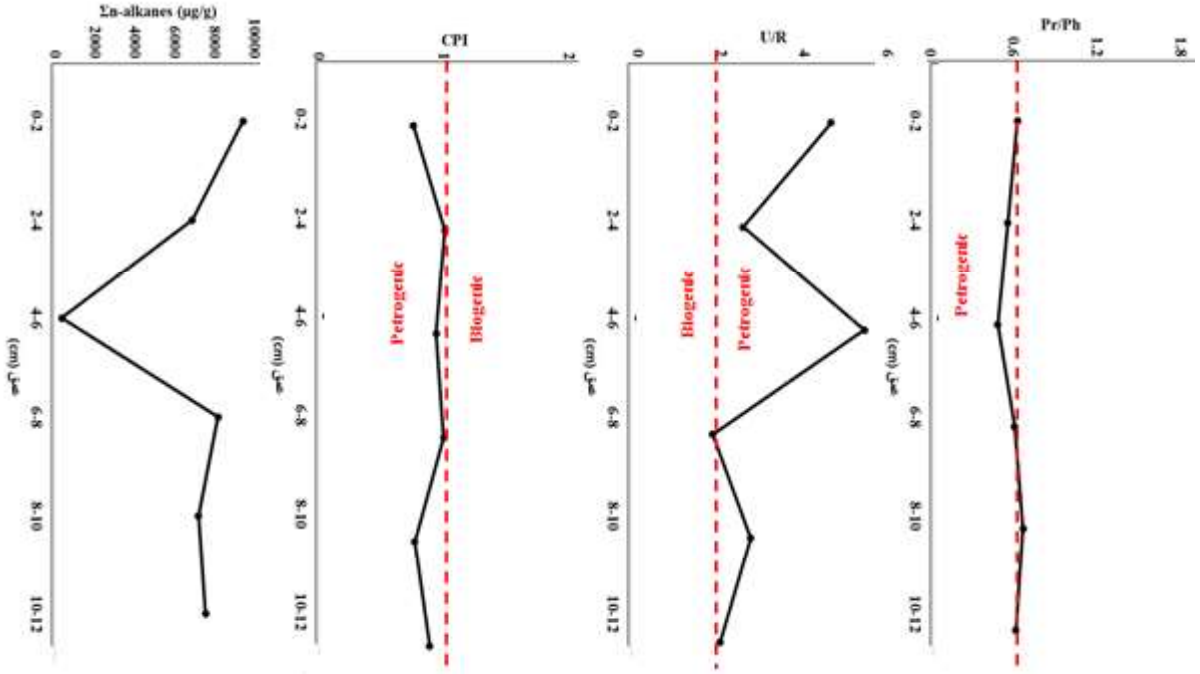


Fig. 4. ∑n-Alkanes, CPI, U/R and Pr/Ph distributions versus depth in sediment cores in the Northwestern Persian Gulf

3.3. Petroleum biomarkers: hopanes and steranes

In order to further substantiate the influence of petroleum at the sampling sites, qualitative analysis of hopanes and steranes was carried out. These compounds are resistant to environmental alteration and have been widely used as molecular markers of oil pollution (Zaghden et al., 2005; Gao et al., 2007). Several geochemical ratios obtained from hopane biomarkers have been used to characterize petroleum inputs. One of these ratios that is evidence of fossil fuel input is determined by the ratio 22S/(22S + 22R) epimers of the homohopanes. This ratio varied between 0.47 and 0.57 in the sediment cores for C31αβ-hopanes, which is very close to the equilibrium value of full maturity at 0.6 (Harris et al., 2011).

The values of the ratio 18α(H)-22, 29, 30-trisnor-hopane (Ts)/sum of Ts + Tm 17α(H)-22, 29, 30-trisnor-hopane varied from 0.48 to 0.75 in the sediment cores. This also confirms the presence of matured petroleum in the sediments. This criterion has been used for characterizing the origin and the degree of maturation of crude oils (Louati et al., 2001). Steranes in fossil fuels are also used as a source and/or maturity indicator for identifying petroleum pollution in urban coastal areas (Albaige's and Cuberes, 1980; Aboul-Kassim and Simoneit, 1996). Here, the sedimentary steranes are derived from the transformation of biological sterol configuration over time. In general, C_{27} and C_{29} steranes are characteristics of algae and higher plant source of organic matter, respectively. So, C_{27}/C_{29}-steranes ratio of >1 suggests an organic matter input from marine algae in the formation of the petroleum, whilst the ratio of < 1 specifies greater input from higher plants (Peters and Moldowan, 1993; Gürgey, 2002).

3.4. Sources of petrogenic inputs

Not only regular spillages from various maritime activities (transport, oil exploitation, harbor operations, etc.), and accidental oil spills are sources of petroleum-derived PAHs in the Persian Gulf. The existence of oilfields in this area is also one of the main sources of petrogenic inputs in the Persian Gulf. So, in order to understand the sources of petrogenic inputs and better distinguish the occurrence of petrogenic hydrocarbons in the Persian Gulf, a PCA was carried out using a diagnostic ratio of n-alkanes, PAHs, hopanes (ratio of 17α-22,29,30-trisnorhopane related to 17α-22,29,30-trisnorhopane + 18α-22,29,30-trisnorhopane)(Ts/Ts + Tm) and ratio ΣTer (sum of all terpanes) to ΣTer plus the main catagenetic hopanes (Tm + C_{29}αβ + C_{30}αβ) (∑Ter/(∑Ter+Tm+C_{29}+C_{30})) and sterane (C_{29} 5a(H) 14a(H) 17a(H))(20S/(20S + 20R)) in oils from Nowruz, Abuzar, Bahregansar, Soroush and Hendijan, and in the sediment samples. The purpose was to identify the source of these samples through a more reliable assessment, using a multi-criteria approach. The biplot between these two components is shown in Fig. 5. It was observed that the Hendijan crude oil was the near source of sediment pollution in the study area and the other crude oils were far away from the petrogenic samples. A possible explanation for this might be that water circulates anti-clockwise, so pollutant moves from east to west. Furthermore, it seems possible that these results are due to oil-related events in the Hendijan oilfield in recent years (oil leakage from the Hendijan oilfield in 2012), which affected sediments with

this pollutant. Moreover, in marine environments, the majority of hydrocarbons in the oil will stay near the spillage point (Rosell-melé et al., 2018). The most interesting aspect of Fig. 5 is that the oil from Nowruz, Abuzar, Bahregansar and Soroush are in one group, away from surface sediment, but the oil from Hendijan is in another group.

Based on the Persian Gulf sedimentation rate that it is almost 1 mm/yr, a layer of 4-6 cm of the deep sediments shows a history of approximately 40 to 60 years. The Bahrengansar oil well is the first Iranian oil well in the Persian Gulf that was discovered in the late 1960s, although the early twentieth century coincided with the start of oil exploration and extraction in Iran (based on the Darcy Oil Contract signed in the year 1901). Also, according to published data, Persian Gulf States, including Saudi Arabia, began to extract oil from the Persian Gulf in 1938. The use of asphalt to cover the street in Iran has begun since 1931, and the first gas station was established in 1931 (Ministry of Oil, 1985), which indicates the existence of petrogenetic resources in recent years.

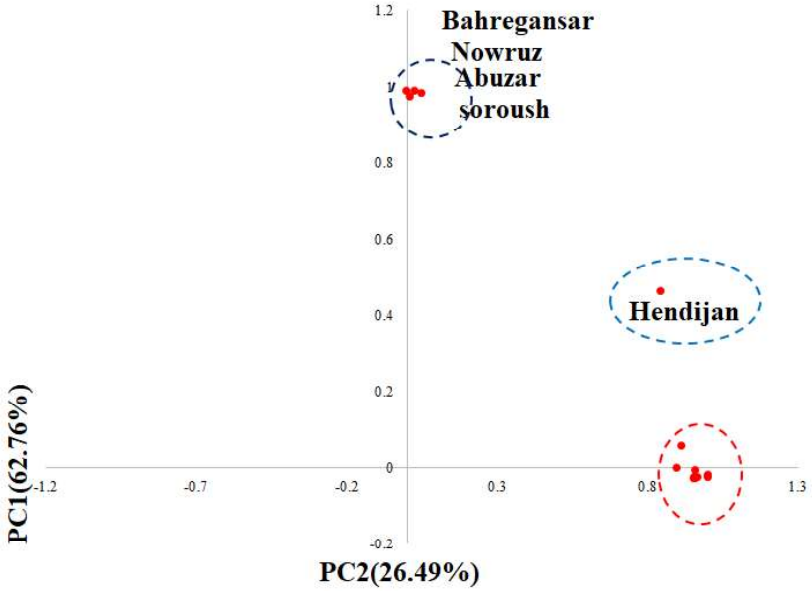


Fig. 5. Principal component analysis (PCA) of n-Alkanes, hopanes, steranes and PAHs diagnostic ratios in sediment cores and oil of the Hendijan, Nowruz, Abuzar, Bahregansar and Soroush oil wells in the Persian Gulf

4. Conclusions

Petrogenic sources were found to be the main sources of hydrocarbons in the sediment cores of the Persian Gulf based on Σ30 PAHs. Also, the presence of UCM, composition patterns, and diagnostic ratios of alkanes in most sampling sites revealed that most of the hydrocarbons were derived mainly from anthropogenic activities such as offshore oil exploration and extraction, along with shipping. Therefore, simultaneous use of *n*-alkanes and PAHs in source identification can be efficient for the precise determination of hydrocarbon sources. As well, the results showed all sediment cores were affected by the Hendijan oilfield using hydrocarbons biomarkers (*n*-alkanes, hopane, sterane and Σ30 PAHs) and chemical fingerprinting of five oil types and sediments. The use of multivariate data analysis also delivered a better empathetic of the differences between the samples, as well as the source of contamination.

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