



Petrogenic and Biogenic Inputs of *n*-alkanes along Shoreline of the Caspian Sea in the Mazandaran Province, North of Iran

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Abstract

The Caspian Sea is the largest lake in the world and is facing an increasing risk of contamination. Sea-based and land-based hydrocarbons inputs are the most critical pollutants of the Caspian Sea. In the present study, *n*-alkanes and related diagnostic ratios were used to identify the sources of hydrocarbon contaminants in surface sediments along the southern coastal area of the Caspian Sea in Mazandaran province. 27 surface sediment samples were collected from a depth of 5 meters under sea level. Contaminant's compositions were extracted by Soxhlet apparatus and analyzed by Gas Chromatography-Mass Spectrometry. According to the results, the total concentration of *n*-alkanes (Σ HC) ranged from 5.2 $\mu\text{g g}^{-1}$ to 690.7 $\mu\text{g g}^{-1}$. The S20 (selected station in Noshahr port) had the highest concentration, and most of the stations have levels in a moderate range. Five diagnostic ratios are used to distinguish petrogenic and biogenic contaminants in shorelines of the Mazandaran province. In all stations, Carbon Preference Index (CPI), LMW/HMW, Pr/*n*-C₁₇, Phy/*n*-C₁₈, Pr/Phy, and U/R values indicated the petrogenic inputs. However, in some stations biogenic inputs were additionally detected. The petrogenic pollutants were almost from sea-based inputs such as oil spills from Turkmenistan and Azerbaijan. On the other hand, biogenic contaminants were almost from rivers and Hyrcania forests.

Keywords: Hydrocarbon; Surface sediment; Pollution; Diagnostic indices; Concentration

Introduction

The Caspian Sea is the world's largest inland body of water and is located among the coun-

tries of Russia, Azerbaijan, Iran, Kazakhstan, and Turkmenistan [1]. In recent years, the Caspian Sea is affected by the high accumulation of

contaminants and oil fields in the south part of the sea that cause oil spills and serious hydrocarbons pollution [2]. From 1986 to 1990, approximately 94,000 to 146,000 tons and from 1988 to 1990, nearly 22,100 tons of oil pollutants have been entered the Caspian Sea through the Volga River and Atrak, Ural, and Kura rivers, respectively [3].

As the major components of petroleum and natural gas, alkanes and polycyclic aromatic hydrocarbons (PAHs) are known to be the main compositions of the contaminants in the Caspian Sea [4–5]. *n*-alkanes are the unique stable compounds of hydrocarbons in the sediments of freshwater, estuarine, and marine environments [4]. PAHs are present in coastal sediments, terrestrial soils and dusts. Their structure is resistant against chemical decomposition and photolysis that make them persistent for a long time [5]. Alkanes and isoprenoids (saturate hydrocarbon fractions of petroleum hydrocarbons) are valuable compounds for fingerprinting oil products, contaminant sources and severe weathering [4]. The main concern exists about these compounds in pollutants because of their poor biodegradability, low water solubility in natural conditions, high persistency, toxicity, bioaccumulation, and biomagnification through the food chain in the aquatic ecosystem [6–7]. Chlorinated or alkyl alkanes are known to be more hazardous. Halogenated alkanes are carcinogenic. Cycloalkanes are more resistant to degradation than alkanes or branched alkanes. Cycloalkanes are more toxic than alkanes or branched alkanes [6–7]. *n*-alkanes enter marine areas and seas with river discharge, sailing activities, sewage disposal, coastal oil production, transportation exhaust, and oil seepage [8]. They also have natural origins such as dry vascular plant waxes, phytoplankton, and marine bacteria [9]. Biogenic sources are generated by biological and terrestrial processes, and petrogenic sources are produced by hydrocarbon inputs in the environment [10]. Resources related to petroleum

are the common origin of these compounds. Measurement of *n*-alkanes are used to fingerprint spilled oils and provide additional information on the source of hydrocarbon contamination and the extent of oil degradation in the environment [2].

Three provinces of Iran have shoreline along the Caspian Sea. Source identification of hydrocarbons along the shorelines of the Caspian Sea is considered the first step in environmental management. The Swimming and fishing activities in this area, and petrogenic hydrocarbons have carcinogenic effects on the food chain and human health [7]. There are ports, factories, and power plants in Mazandaran province that can produce a high amount of wastewater. Oil spills and seepages in other regions of the Caspian Sea can also be entered these areas by waves and storms. The Caspian Hyrcanian Mixed Forests ecoregion, in the temperate broadleaf and mixed forests biome, is an area of lush lowland and montane forests covering about 55,000 square kilometers (21,000 mi²) near the southern shores of the Caspian Sea of Iran and Azerbaijan. More than 130 rivers flow into the Caspian Sea, which passes through the forest of Hyrcani. In recent years, due to the high entry of pollutants to the Caspian Sea, some studies have focused on identification of the source of pollutants in some parts of this area [3, 11–12].

This study aims to identify land- and Sea-based inputs of *n*-alkanes along the Caspian Sea coast in the Mazandaran province and to determine the trends of concentrations from east to west of the province is determined.

Materials and methods

1) Sample collection

Twenty seven stations were selected along the 220 km south shorelines of the Caspian Sea from east to west of the Mazandaran Province in the north of Iran. Location of selected stations are shown in Figure 1. The latitude and longitude coordinates are reported in Table 1. In each

station, 5 surface sediment samples were taken from 5 points (The vertices of a rhombus and its center) using a Veen Grab in January and February 2015. Individual samples were mixed, and finally, 27 composite samples were prepared. Samples were immediately transferred into the aluminum container and stored at -20 °C before analysis. About 200 g of each sample was freeze-dried for 72 h at -60 °C and then homogenized. Samples were powdered by a Chinese pounder and passed through the 63µm sieve.

2) Extraction and fractionation

Five grams of each sample was mixed with 100 mL dichloromethane and placed for 10 h in the soxhlet. The mixture was concentrated to 2 mL by Rotary Evaporator and then was allowed to pass through the 5% H₂O deactivated silica gel column (0.47 cm i.d. × 18 cm). The extracted sample were fractionated by silica gel packed chromatography column. The non-polar fraction (e.g., alkanes, polycyclic aromatic hydrocarbons

(PAHs), alkylbenzene sulfonates, and hopanes) were eluted from the column with 20 mL DCM/ n-hexane (1:3). Samples are concentrated to 1 mL with a rotary evaporator and a gentle flow of nitrogen. Then, n-alkanes were eluted from second column, packed with 5% H₂O activated silica gel, with 4 mL of n-hexane [7, 13]. The quality control of analysis was checked by blank sample. All solvents, glassware, and sample processing hardware was controlled to be free from hydro-carbon interferences during analyses. Monitoring the surrogate internal injection standard (SIIS) was used to quality control for the n-alkanes analyses. External standard sample of known concentration and volume was analyzed separately from the unknown sample under identical conditions. It was used to facilitate the qualitative identification and/or quantitative determination of the sample components. The concentrated n-alkanes were dried under nitrogen flow and then subjected to GC-MS analysis.

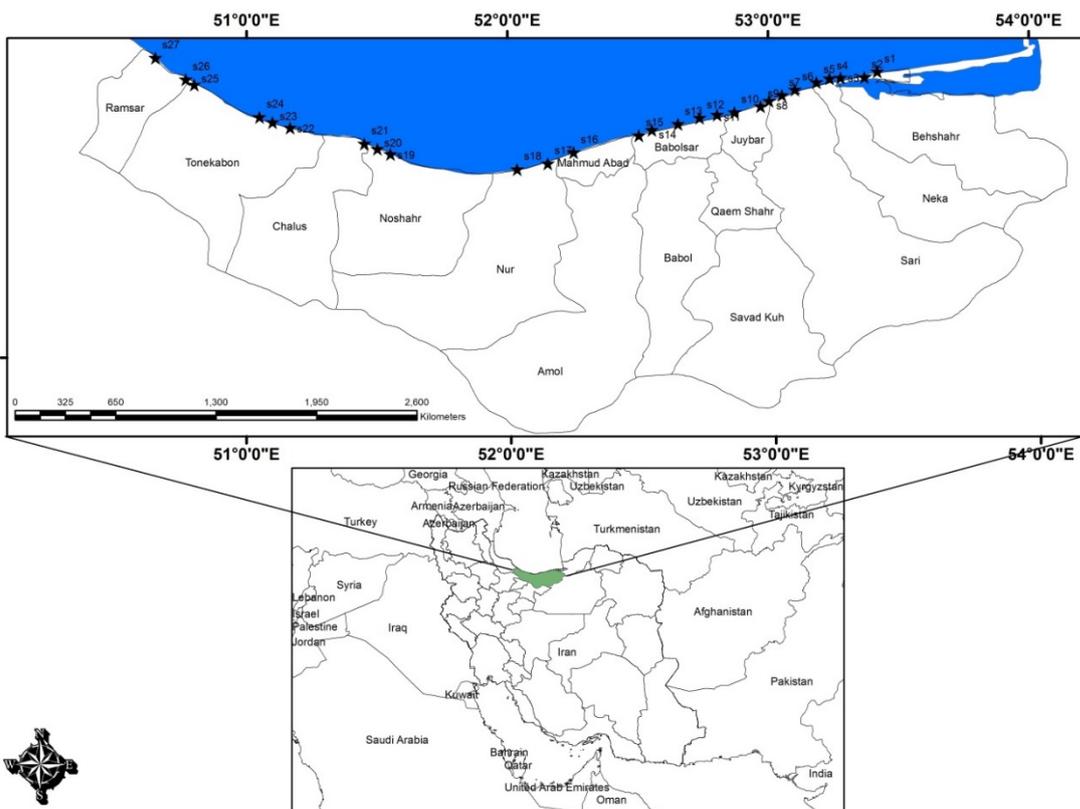


Figure 1 Sampling locations in shoreline of the Caspian Sea from east to west of Mazandaran Province, north of Iran.

Table 1 The latitude and longitude coordinates in shoreline of the Caspian Sea from east to west of Mazandaran Province, north of Iran

No.	Station name	Latitude	Longitude	Sampling point specification
1	Miyankaleh (S ₁)	36° 52' 21"	53° 25' 20"	Near to Miyankaleh Peninsula
2	Amirabad (S ₂)	36° 51' 32"	53° 22' 13"	Near to Amirabad Port
3	Sadra (S ₃)	36° 51' 12"	53° 16' 34"	Near to Sadra shipyard
4	Nirugah (S ₄)	36° 50' 54"	53° 14' 30"	Near to Neka power plant
5	Goharbaran (S ₅)	36° 50' 16"	53° 11' 44"	Tourist beach
6	Farahabad-Tejen (S ₆)	36° 49' 22"	53° 6' 46"	Tourist beach, near to Tejen River
7	Sari 2 (S ₇)	36° 48' 24"	53° 3' 60"	
8	Sari 3 (S ₈)	36° 47' 24"	53° 0' 26"	
9	Larim (S ₉)	36° 46' 53"	52° 58' 9"	Tourist beach, fishing location
10	Chapakrud (S ₁₀)	36° 45' 25"	52° 52' 11"	Tourist beach
11	Naftechal (S ₁₁)	36° 44' 37"	52° 48' 14"	
12	Mirood (S ₁₂)	36° 44' 6"	52° 44' 38"	Fishing Location
13	Babolrud (S ₁₃)	36° 43' 10"	52° 39' 25"	Near to Babolrud River
14	Bandare fereydunkenar (S ₁₄)	36° 42' 17"	52° 33' 45"	Near to Fereydunkenar Port
15	Fereydunkenar 2 (S ₁₅)	36° 41' 54"	52° 30' 40"	Near to river
16	Mahmudabad (S ₁₆)	36° 38' 25"	52° 15' 36"	Tourist beach
17	Izadshar (S ₁₇)	36° 36' 50"	52° 9' 3"	Tourist beach, fishing location
18	Nur (S ₁₈)	36° 35' 14"	52° 2' 27"	Tourist beach
19	Amirrud (S ₁₉)	36° 38' 14"	51° 33' 59"	Near to river
20	Bandar noshahr (S ₂₀)	36° 39' 50"	51° 30' 52"	Tourist beach, near to port, near to forest
21	Chalus (S ₂₁)	36° 40' 20"	51° 27' 47"	Tourist beach
22	Salmanshahr (S ₂₂)	36° 43' 17"	51° 10' 12"	Tourist beach
23	Abbasabad (S ₂₃)	36° 44' 12"	51° 6' 29"	Tourist beach, fishing location, near to forest
24	Nashtarud (S ₂₄)	36° 45' 7"	51° 3' 6"	Tourist beach
25	Shirud (S ₂₅)	36° 51' 40"	50° 48' 10"	Fishing location
26	Chaleekrud (S ₂₆)	36° 52' 48"	50° 46' 10"	Near to river
27	Safarud (S ₂₇)	36° 56' 47"	50° 39' 27"	Tourist beach, near to river

3) Analytical analysis

The GC-MS analysis was carried out by an Agilent Technologies instrument with a gas chromatograph (GC, model 7890A) coupled to a mass spectrometer (MS, 5975C). The carrier gas was nitrogen at the flow rate of 1.5 mL min⁻¹, and the injection volume was 2 µL. The oven temperature was initially set at 60 °C (hold for 2 min) and increased to 300 °C at a rate of 8 °C min⁻¹ (20 min hold). The injector's temperature was 300°C. MS operating conditions were EI ionization, ion source 230°C, electron energy 70 eV, and interface temperature 300°C.

4) Statistical analysis

Clustering analysis was performed with SPSS to classify the stations according to these ratios.

Results and discussion

1) Concentration of total *n*-alkanes

Normal alkanes (*n*-alkanes) from both petrogenic and biogenic origins are found in estuarine, freshwater, and marine sediments and are used to identify the sources of hydrocarbons. *n*-alkanes derived from particular leaf waxes are dominated by long, odd-numbered alkanes within the C24–C35 range [14–15].

Results showed that the concentration of hydrocarbons (ΣHC) in the samples ranges from 5.2 µg g⁻¹ in S₂₇ to 690.7 µg g⁻¹ in the S₂₀ station, as shown in Figure 2a. The average concentration of each detected alkane in the studied stations are indicated in Figure 2b. Noshahr (S₂₀) is an important area for trade with Russia and contains the important port in north of Iran. The

high concentration in S₂₀ confirms the effect of the presence of a port site near the coastal area and the influence of human wastes. Industrialization was significantly slower in this city due to environmental considerations but has an already vibrant economy based on tourism, ship transport, and agriculture. At S₂₇, collected samples were coarse-grained, so organic matter absorption was lower than other stations, and the concentration is low. Ignoring the S₂₀ in Noshahr Port, the concentration of pollution in the east of the province is higher than the west because of more industrial activities in the east parts of Mazandaran Province.

The average concentration of *n*-alkanes throughout the shorelines of Mazandaran Province was 76.8 $\mu\text{g g}^{-1}$ which shows a notable increase compared to previous years. In 2004, the average concentration of *n*-alkanes was around 2 $\mu\text{g g}^{-1}$ in the same areas [2], it was showed that the concentrations had the impressive increases due to entrance of high amount of contaminants annually by ship transportations and industrialization. Also, the studied areas in Mazandaran Province have higher concentration in compare to other areas of the world. In Brazil, the total concentration of *n*-alkanes was found to be about 18 $\mu\text{g g}^{-1}$ [16]. The concentration of *n*-alkanes was about 798.82 $\mu\text{g g}^{-1}$ in the Yellow River in China [17]. In a more recent study, the total

concentration of *n*-alkanes in the southwest of Caspian Sea, Gilan Province, was reported in the range of 249.2 to 3,899.5 $\mu\text{g g}^{-1}$ [18]. As mentioned, several factors such as the presence of many ports and factories in Mazandaran Province as sources of contaminants and human access to the beaches and coastal areas are responsible for variations in the concentration of hydrocarbons in the Caspian Sea.

The total concentration of petrogenic and biogenic hydrocarbons in marine surface sediments which are rich in organic matter, can be up to 100 $\mu\text{g g}^{-1}$ [18]. Samples with higher concentrations indicate the presence of oil products [19]. Areas with sediment samples that have concentrations higher than 500 $\mu\text{g g}^{-1}$ are considered as highly contaminated, between 10–100 $\mu\text{g g}^{-1}$ are moderately contaminated, and the values of less than 10 $\mu\text{g g}^{-1}$ are uncontaminated sites [17, 20]. According to this classification showed in Figure 2, most of the studied stations are moderately contaminated, three stations of S₂, S₈, and S₂₀ are highly contaminated, and S₂₇ is the uncontaminated station. 85.11% of studied area was classified as moderately polluted and 11.11% are highly polluted. The highly polluted areas are port locations in Mazandaran Province and it shows the high effects of transportations, ships, oil tankers and transporting lines in these areas.

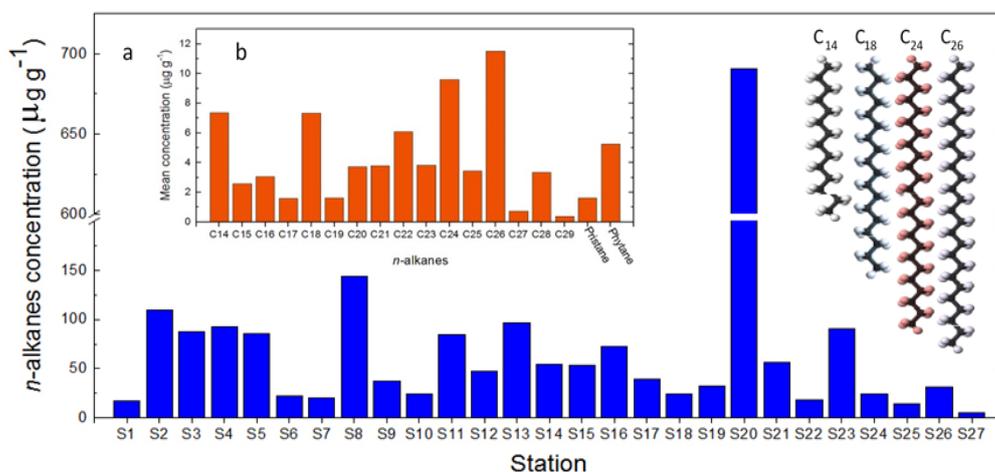


Figure 2 Total concentration of *n*-alkanes in shoreline of the Caspian Sea from east to west of the Mazandaran Province, north of Iran (a) and average concentration of each alkane in the studied area. Scheme: *n*-alkanes with the highest concentrations (b).

Several samples in S₅, S₁₃, S₁₅, S₁₆, S₁₉, and S₂₇ stations were collected from the river's mouth to the Caspian Sea and had a moderate level of concentration because these rivers cross contaminated locations that contains plants residues, human and industrial wastes, and move upstream pollutions to the seashores.

2) Composition of *n*-alkanes

n-alkanes from thermally mature petrogenic sources, such as crude oil and high-rank coal, show the destruction of the odd-carbon number preference with dominance in the C₁₅–C₂₅ range [21–24]. As shown in Table 2, the sediment samples from some stations contain alkanes C₁₄–C₂₅, namely; S₁–S₃, S₅, S₆, S₈, S₁₀–S₁₄, S₁₈,

and S₂₇; and other stations contain alkanes C₁₄–C₃₃; S₄, S₇, S₉, S₁₅, S₁₆, S₁₇, S₁₉–S₂₅ and S₂₆. Hydrocarbons that contain long-chain *n*-alkanes are derived from waxes of higher vascular plants and the lipid debris of conifers. Hydrocarbons that contain short-chain *n*-alkanes are derived from the waxy substances of marine algae [25–27]. The short-chain *n*-alkanes (*n*-C₁₅, *n*-C₁₇, and *n*-C₁₉) are representative of algal material [14]. Long-chain *n*-alkanes (*n*-C₂₇, *n*-C₂₉, and *n*-C₃₁) are representative of land plants. Hydrocarbons composed of a mixture of compounds originating from land plant material show a predominance of odd-numbered carbon chains with CPI~5–10 [28, 23]. Representative TIC chromatographs are shown in Figure 3.

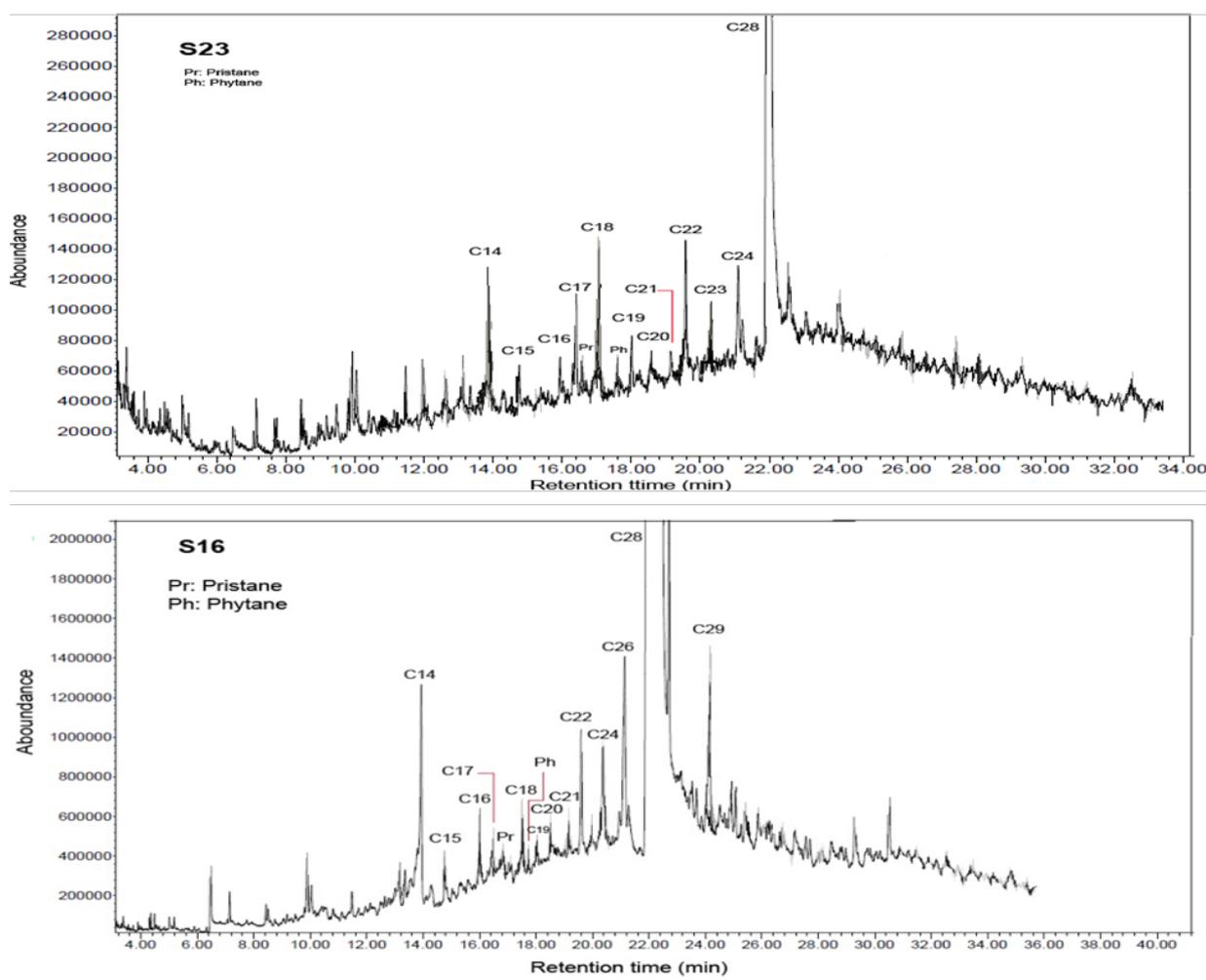


Figure 3 The GC chromatograms of *n*-alkanes detected in S₁₆ and S₂₃ in shorelines of the Caspian Sea from east to west of Mazandaran Province, north of Iran.

Table 2 Concentrations of *n*-alkanes ($\mu\text{g g}^{-1}$) in shorelines of the Caspian Sea from east to west of Mazandaran Province, north of Iran

Station	<i>n</i> -alkanes																Pristane	Phytane
	n-C ₁₄	n-C ₁₅	n-C ₁₆	n-C ₁₇	n-C ₁₈	n-C ₁₉	n-C ₂₀	n-C ₂₁	n-C ₂₂	n-C ₂₃	n-C ₂₄	n-C ₂₅	n-C ₂₆	n-C ₂₇	n-C ₂₈	n-C ₂₉		
S ₁	5.9	1.4	1.8	0.5	2.0	0.1	1.0	0.6	0.5	0.8	0.6	1.1	ND	ND	ND	ND	0.5	1.0
S ₂	10.8	21.0	17.0	5.0	9.7	5.8	6.0	ND	6.8	ND	8.4	18.9						
S ₃	6.3	2.3	ND	1.6	17.4	1.4	3.4	2.4	15.4	3.1	14.5	3.8	ND	ND	ND	ND	1.0	14.9
S ₄	5.7	1.7	2.5	1.7	2.2	1.7	1.0	23.2	7.7	4.1	7.8	7.2	ND	17.0	ND	ND	1.7	6.9
S ₅	7.0	1.5	1.1	0.6	2.3	0.2	0.4	0.2	0.6	0.4	ND	70.0	ND	ND	ND	ND	0.5	0.6
S ₆	9.9	1.7	1.3	0.5	2.4	0.6	0.2	0.7	0.8	1.2	1.7	ND	ND	ND	ND	ND	0.5	1.1
S ₇	9.5	0.9	1.2	0.5	0.7	0.1	0.4	0.5	0.3	0.8	1.9	ND	ND	ND	2.8	ND	0.1	0.3
S ₈	9.2	3.8	11.5	10.9	2.6	8.3	27.9	11.3	10.6	ND	36.0	ND	ND	ND	ND	ND	6.4	5.1
S ₉	2.2	2.6	2.2	0.5	4.0	1.1	4.4	2.1	2.9	3.3	2.3	ND	4.9	ND	ND	ND	1.9	3.2
S ₁₀	6.6	2.2	1.3	0.5	3.6	0.3	0.6	0.3	3.9	0.8	2.3	ND	ND	ND	ND	ND	0.9	0.6
S ₁₁	13.5	2.6	3.7	3.2	4.3	6.2	3.7	2.8	1.4	2.7	15.4	ND	ND	ND	ND	ND	2.1	23.2
S ₁₂	16.0	2.3	2.0	0.7	5.0	0.4	2.7	2.0	5.0	1.8	2.3	3.7	ND	ND	ND	ND	0.3	3.1
S ₁₃	5.2	2.9	4.0	1.5	17.0	0.9	8.0	3.3	5.2	28.2	3.9	ND	ND	ND	ND	ND	3.6	12.9
S ₁₄	7.2	1.0	1.6	1.1	7.9	0.5	1.0	3.2	7.2	1.9	12.4	ND	ND	ND	7.3	ND	0.3	1.5
S ₁₅	7.7	2.6	1.2	0.5	4.4	0.8	1.6	1.2	4.7	1.1	10.1	ND	14.4	ND	ND	ND	0.8	2.1
S ₁₆	8.1	1.8	1.0	0.5	3.7	0.6	1.9	2.6	4.4	2.6	8.8	ND	9.1	ND	12.5	10.4	1.0	3.7
S ₁₇	8.6	1.7	1.7	0.8	4.3	3.0	2.2	1.1	1.0	4.2	1.4	ND	ND	ND	5.3	ND	1.2	2.4
S ₁₈	10.0	2.2	1.3	0.6	3.4	0.2	0.2	0.2	2.9	0.5	1.8	ND	ND	ND	ND	ND	0.2	0.9
S ₁₉	6.7	1.8	1.3	0.6	1.3	0.2	0.3	1.0	0.5	3.2	ND	1.1	ND	2.4	9.7	ND	1.3	0.7
S ₂₀	8.5	3.7	14.6	7.6	70.5	7.7	27.1	32.2	68.3	29.1	107.9	ND	282.4	ND	ND	ND	7.3	23.8
S ₂₁	5.5	2.0	1.5	1.0	6.2	0.8	1.3	3.6	0.8	1.8	9.3	3.7	ND	ND	14.4	ND	0.9	3.6
S ₂₂	4.1	1.2	0.9	0.1	1.0	0.1	0.2	0.3	0.9	0.2	1.6	0.9	ND	ND	6.5	ND	0.1	0.6
S ₂₃	7.9	1.2	3.6	1.3	16.7	1.5	2.9	3.7	9.0	4.2	9.4	ND	ND	ND	21.4	ND	1.3	6.5
S ₂₄	4.9	0.8	1.4	0.1	1.9	0.2	0.2	1.2	2.3	3.1	3.7	ND	ND	ND	3.3	ND	0.4	0.8
S ₂₅	5.5	1.2	1.4	0.5	0.4	0.1	0.1	0.1	0.2	0.1	0.9	ND	ND	ND	2.0	ND	0.6	0.5
S ₂₆	4.1	0.8	0.8	0.4	2.7	0.5	1.8	2.2	0.9	4.0	3.0	1.5	ND	ND	5.3	ND	0.4	2.6
S ₂₇	1.7	0.8	0.4	0.2	0.6	0.1	0.1	0.1	0.1	0.3	0.4	ND	ND	ND	ND	ND	0.3	0.2
LOD	36.0	26.2	25.8	28.7	27.9	25.3	23.5	19.8	24.7	19.2	24.1	25.4	26.3	25.2	23.8	27.5		
LOQ	68.4	46.7	40.8	36.7	34.2	34.7	32.4	29.9	35.1	26.7	31.7	46.2	40.9	45.3	44.2	41.2		

ND: Not detectable

LOD: Limit of Detection, LOQ: Limit of Quantitation

Remark: The concentration of *n*-alkanes with the C numbers of 30-33 was not detected in samples.

3) Diagnostic indices

The five parameters are calculated as shown in Table 3 and used to estimate sources of contamination. Pristane has biogenic sources, and phytane has petroleum and petrogenic sources, so the Pr/Phy values can help us identify the origin of hydrocarbons [29–30]. Thus, high values of Pr/Ph (>3) indicate the biogenic sources, and low values of Pr/Ph (<3) suggest petrogenic sources. All of the Pr/Phy values for studied samples are lower than 3, showing that they all contain petrogenic contaminants. Low values of Ph/n-C₁₈ and Pr/n-C₁₇ (<4) show the petrogenic origins of hydrocarbons, and high values

show the biogenic origin [31]. These two ratios for all stations were lower than 4 and indicated the petrogenic inputs.

LMW/HMW (ratio of low molecular weight hydrocarbons to high molecular weight hydrocarbons) for compounds with values lower than 1 have shows biogenic sources (such as higher plants, marine animals, and sedimentary bacteria) and for compounds with values near and more than 1 have shows petrogenic sources [29, 32]. In this study, the LMW/HMW ratio for most of the samples was higher than 1, indicating the petrogenic source of the hydrocarbons in related stations.

Table 3 Diagnostic ratios for the studied area in shorelines of the Caspian Sea from east to west of Mazandaran Province, north of Iran

Station	Ratios					
	U/R ^f	Pr/Ph ^e	Ph/n-C ₁₈ ^d	Pr/n-C ₁₇ ^c	LMW/HMW ^b	Low CPI ^a
S ₁	0.54	5.75	1.00	0.47	0.56	5.54
S ₂	0.54	82.10	1.66	1.96	0.44	3.34
S ₃	0.23	2.33	0.66	0.86	0.06	0.66
S ₄	1.66	1.31	1.00	3.22	0.25	1.57
S ₅	8.46	0.19	0.77	0.27	0.73	2.32
S ₆	0.6	6.20	1.00	0.43	0.48	3.14
S ₇	0.52	2.54	0.30	0.47	0.47	0.25
S ₈	0.37	0	0.59	2.00	1.25	3.17
S ₉	0.53	2.09	3.84	0.78	0.60	5.08
S ₁₀	0.25	6.22	2.00	0.18	1.38	0.14
S ₁₁	0.57	2.29	0.65	5.55	0.08	3.62
S ₁₂	0.46	4.67	0.50	0.62	0.10	6.34
S ₁₃	0.93	1.49	2.43	0.76	0.27	1.40
S ₁₄	0.24	1.41	0.29	0.19	0.20	0.60
S ₁₅	0.22	0.96	1.63	0.48	0.38	0.61
S ₁₆	0.37	0.57	2.04	1.00	0.28	7.45
S ₁₇	0.92	2.25	1.47	0.56	0.48	0.99
S ₁₈	0.27	9.21	0.32	0.26	0.22	0.29
S ₁₉	1.93	0.82	2.17	0.55	1.83	7.91
S ₂₀	0.27	0.57	0.77	0.33	0.30	8.31
S ₂₁	0.53	0.77	0.84	0.57	0.24	3.30
S ₂₂	0.38	0.95	2.27	0.59	0.24	1.05
S ₂₃	0.27	1.37	1.00	0.39	0.19	8.09
S ₂₄	0.53	1.30	2.77	0.42	0.46	2.12
S ₂₅	0.51	3.09	1.19	1.14	1.4	0.69
S ₂₆	0.89	1.02	1.11	1.00	0.14	3.26
S ₂₇	0.67	5.85	1.51	0.26	1.72	8.93

^aLow CPI=(Σ Odd C₁₅-C₂₃+ Σ Odd C₁₇-C₂₅)/2(Σ Even C₁₆-C₂₄); ^bLMW/HMW= Σ n-C₁₄-22/ Σ n-C₂₃-33

^cPr/n-C₁₇=Pristane/n-C₁₇; ^dPh/n-C₁₈= Phytan/n-C₁₈; ^ePr/Ph=Pristane to phytane ratio

^fU/R= Unresolved complex mixture (UCM)/Resolved complex mixture

The CPI index for petrogenic inputs showed values lower than 1 and for biogenic inputs showed values between 4 and 10. The CPI index below 1 can also be an indication of microbial degradation of hydro-carbons during the long-time existence of them in the environment [28]. Results show that most of the stations had CPI values lower than 1, which implies that hydro-carbons in these stations were affected by microbial activities and occurred a long time ago. In two stations (e.g., 4 and 20), CPI values are approaching 1, indicating early petrogenic contamination. A high value of CPI (8.46) in station 5, shows that this station uncontaminated. However, according to values of other parameters for this station, it may be affected by both petrogenic and biogenic inputs.

Analysis of diagnostic ratios in these 27 stations showed that petrogenic inputs and contaminants were present in all stations due to oil seepages and leaks, tankers, ships, and transportation effects. But in some stations such as S₅, S₈, S₁₅, S₁₆, and S₁₉–S₂₂ biogenic contaminants were also present, which can be caused by the biological process of Hyrcanian forests near the stations. Oil seepages, oil spills during hydrocarbon transportation, factory wastes, ships, and tankers are important sources for the petrogenic entrance and sea-based pollutions. The Hyrcanian forests and rivers that carry some pollutants from upstream sources are the main sources for biogenic entrance to the marine environment.

The Pr/*n*-C₁₇ and Phy/*n*-C₁₈ ratios can also be used for detecting the time of oil contamination by examining the signs of the biodegradation process. Ratios with low values (<1) show recent pollution in the early stage of biodegradation, and the ratios with high values (>1) show degraded oils [28, 32]. In S₁, S₃, S₅, S₆, S₁₄, and S₂₀, there are ports, power plants, and factories around them. Both of the ratios were lower than 1, indicating that contamination in these areas was recent and no considerable biodegradation of contaminants had occurred. Stations S₁₂, S₁₈,

and S₂₃ also had low values of Pr/*n*-C₁₇ and Phy/*n*-C₁₈. However, those stations are not near any port or power plants. Therefore, it can be assumed that the contamination is caused by other human activities that release high amounts of petroleum products in these areas. For other stations (S₂, S₄, S₅, S₇–S₁₁, S₁₃, S₁₅–S₁₇, S₁₉, S₂₁, S₂₂, S₂₄–S₂₇), ratios of Pr/*n*-C₁₇, and Phy/*n*-C₁₈ were higher than 1, which indicates that hydro-carbons in these stations are in moderate and high stages of biodegradation.

Unresolved complex mixture (UCM) was detected in all surface sediment samples of the studied areas as a broad model hump in chromatograms (Figure 3). The presence of UCM in these fractions is an indicator of biodegraded oil in the environment [34–35]. UCM is the composition of branched alkanes that are more resistant to the biodegradation process, so will be appeared in the environment after *n*-alkanes degradation [36]. The ratio of unresolved to the resolved complex mixture (U/R) can be used to confirm the existence of petroleum products with values higher than 2 [37–39]. Calculated U/R values in Table 3 show the effect of petroleum products in more than half stations of the studied areas in S₁, S₂, S₅, S₆, S₈, S₉, S₁₁, S₁₂, S₁₆, S₁₉, S₂₀, S₂₁, S₂₃, S₂₄, S₂₆ and S₂₇ that confirm the above discussions about petrogenic contaminants.

Hierarchical cluster analysis (HCA) was used to identify relatively homogeneous groups of cases (or variables) based on selected characteristics. The results of hierarchical clustering are usually presented in a dendrogram. Samples were clustered based on concentrations and diagnostic ratios. The main method used for clustering analysis was Ward's method of minimum variance, and the distance coefficient between the categories was calculated based on the binary method of the squared Euclidean distance. As shown in the classification of sampling locations in terms of hydrocarbon concentration (Figure 4a), the pattern is divided into two main groups and three sub-

groups. Group I contains samples with concentrations lower than $150 \mu\text{g g}^{-1}$, and it is divided into two subgroups with concentration ranges of $0\text{--}50 \mu\text{g g}^{-1}$ and $50\text{--}150 \mu\text{g g}^{-1}$. Group II contains samples with high concentrations. Also, in the classification of sampling locations in terms of

diagnostic ratios (Figure 4b), the pattern is divided into two groups. The S_2 station is separated from other stations because of its high amount of Pr/Ph ratio. Both parts of the classification show the high similarity between stations to their level of concentration and sources of pollutants.

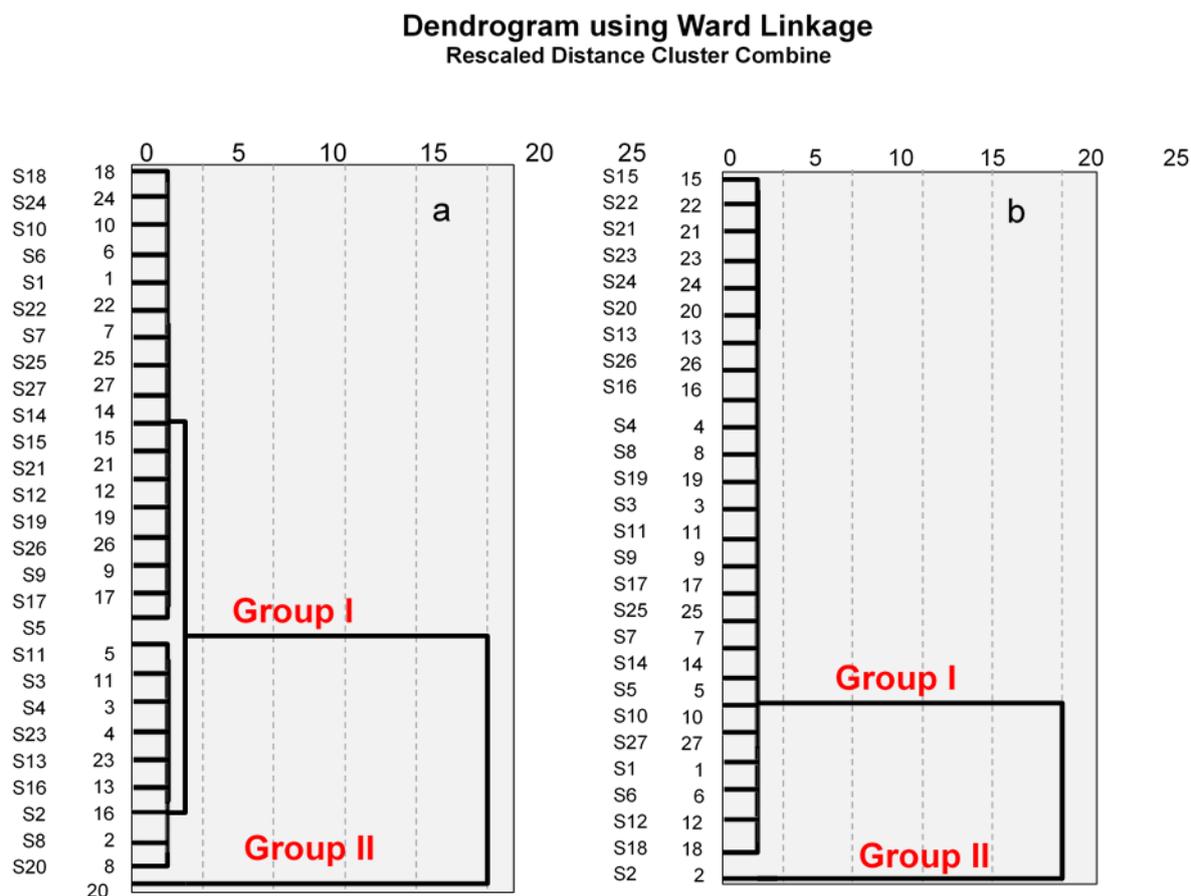


Figure 4 A clustering tree of studied samples in shoreline of the Caspian Sea from east to west of Mazandaran Province, north of Iran, is based on the diagnostic ratio (a) and hydrocarbon concentration (b).

Conclusions

The present study was tried to monitor the dispersion of the hydrocarbon pollution and contaminant inputs based on the total concentration of *n*-alkanes in the coastal sediments along the shorelines of the Caspian Sea throughout coastal areas of Mazandaran Province. The total concentration of *n*-alkanes ranges from 5.2 to $690.7 \mu\text{g g}^{-1}$. The highest concentration ($690.7 \mu\text{g g}^{-1}$) of *n*-alkanes was observed in the S20 station in Nowshahr Port. The average

level of contaminants in studied areas was increased compared to studies in the same areas during the last twenty years because of the high effects of ports, factories, rivers, human activities, and Hyrcania forests. An evaluation of the source diagnostic indices confirmed that surface sediments around the studied area were affected by petrogenic contaminants for all stations, and most of them are sea-based inputs and from oil spills and ships. Also, in some stations, biogenic inputs were detected in

sediment samples. The observed biogenic traces confirmed the effect of Hyrcania forests on the contamination of these areas. The similarities of samples across the stations classified based on the concentrations of hydrocarbons, and diagnostic ratios showed that most of the stations were in the same characteristics in terms of contaminant concentration and source.

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