The Origin of Oil hydrocarbons in Southern Coastal Sediments of the Caspian Sea in the Vicinity of Golestan and Mazandran Provinces

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Introduction
The Caspian Sea as the biggest surrounded water body (lake) in the world is bordered by the states of Azerbaijan, Russia, Iran, Kazakhstan and Turkmenistan. This Sea has long been under pressure environmentally, due to the fact that it is one of the richest oil-and-gas bearing regions which are also surrounded by large domestic, industrial and agricultural areas. Urban development beside increasing industrial and oil production activities (oil refinery and petrochemical plants) in the northern and eastern regions of Caspian Sea in recent years have caused high amount of oily pollutants enter to this sensitive area. In this region, land-based sources, together with offshore oil fields, tanker traffic, and trans-Caspian pipelines have generated large quantities of oil spills which remain trapped within this land-locked system. Despite the high importance of Caspian Sea from ecotourism standpoint, few investigations have been published on the environmental problems arising from offshore oil exploration and production so far. In these studies highly contaminated sediments to oily hydrocarbons in central and south eastern coast of the Caspian Sea in the vicinity of Azerbaijan and Iran western shore have been reported.

Considering different origins of hydrocarbons (biogenic and petrogenic) in marine sediments, distinguishing the origin and the source of the observed hydrocarbons has recently received more attentions. Terrestrial plant waxes, marine phytoplankton, micro and macro marine algae, cyanobacteria and marine animals contribute biogenic source of hydrocarbons, including aliphatic (AHC) and aromatic (AH) hydrocarbons.

Through the analysis of geochemical biomarkers and their physico-chemical properties the source of hydrocarbon contamination and the extent of degradation of the oil spill can be identified.

In the present paper through sampling the surface layer of the bottom sediments in a large area of Golestan and Mazandran provinces shores, southern shelf of the Caspian Sea, spatial distribution and sources of hydrocarbons are investigated.

Sediments are assumed to be the accumulator for hydrocarbon compounds. Considering the low aqueous solubility and hydrophobic properties of hydrocarbons, they tend to associate with particulate matter and fall into the bottom sediment.

Therefore sediments, especially fine sediments, are usually examined for assessment of marine pollution.

Materials and Methods
In the present study, sediment sampling was done using a Van Veen grab and samples were stored in aluminum containers.

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All materials were frozen immediately and kept frozen for transport to the laboratory under USEPA standard method (USEPA-SW-846). Petroleum hydrocarbon and polycyclic aromatic hydrocarbons (PAHs) were measured using gas chromatographic analysis through SW-846 #8015B and SW-846#8100 methods respectively. Data are presented on the content and composition of resolved and unresolved parts of Aliphatic and Aromatic hydrocarbons in the surface sediment matter and were compared with the result of studies performed earlier in the study area.

The main objectives of this paper were to assess the distribution of aliphatic and aromatic hydrocarbons and to determine the origin of hydrocarbons in the study area. In order to differentiate the origins of the hydrocarbons, based on the observed aliphatic parameters, needed evaluation indices have been applied to the sediment samples. \( n-C_{17}/\text{Pristan} \), \( n-C_{18}/\text{Phytan} \), Pristan/Phytan, the low/high molecular weight hydrocarbons (LMW/HMW), \( n-C_{16} \) ratio, major hydrocarbon or n-alkan, Carbon Preference Index (CPI), Even-to-odd ratio (even/odd) and Unresolved Complex Mixture (UCM) concentration indices are the values developed to identify the natural origin of hydrocarbons in the sediment samples.

**Results and Discussion**

The result of sample analysis showed that the aliphatic hydrocarbons (AHC) fraction of the sediments varies in the range of 4.3-39.1 \( \%/\text{kg} \). Resolved components of aliphatic hydrocarbons distribute mostly in central part of the study area in the range of 0.78-12.2 \( \%/\text{kg} \) whereas unresolved complex mixture which attributed to natural organic matter varies in the range of 2.4-27 \( \%/\text{kg} \). The distribution of total aromatic fractions throughout the Caspian Sea sediments also shows variable distribution of absolute concentrations in the range if 3000-15000 \( \%/\text{kg} \) in which the concentrations of resolved and unresolved aromatic hydrocarbon rate from 1200-5600 \( \%/\text{kg} \) and 1800-11000 \( \%/\text{kg} \) respectively. Comparative measurements of the aliphatic and aromatic hydrocarbons in the Caspian Sea show high concentrations of these hydrocarbons in central coast of Iran in comparison to Kazakhstan and Turkmenistan coasts. In the study area the lowest values of aliphatic and aromatic hydrocarbons were recorded in eastern part in the vicinity of Miankale Bay. The concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the study area varies in the range of 150-1600 \( \%/\text{kg} \) that is relatively high in comparison with Black Sea coastlines 7-638 \( \%/\text{kg} \), coastal area of the Adriatic Sea 24-501 \( \%/\text{kg} \), Victoria harbor in Hong Kong 350-450 \( \%/\text{kg} \), Antarctica adjacent to South Orkney Islands 8-280 \( \%/\text{kg} \), Gironde estuary in France 19-252 \( \%/\text{kg} \), Balearic Islands in Mediterranean Sea 30 \( \%/\text{kg} \), Russian coast of Caspian Sea 6-345 \( \%/\text{kg} \) and Kazakhstan coast of Caspian Sea 7-294 \( \%/\text{kg} \).

The developed indices associated with the origin of hydrocarbons also showed the biogenic and nonpetroleum origin of the hydrocarbons in the surface sediments of the study area, whereas the petrogenic origin of the hydrocarbons in the south eastern coast of the Caspian Sea, near the west area of Gilan province, has been previously reported. Major concentrations of C27, C29, C31 and C33 alkanes in the study area show the existence of biogenic hydrocarbon with the origin of vascular land plants.

But not observing C15, C17, C19 and C21 shows the absence of the oily hydrocarbons with the origin of macro and micro marine algae, plankton and cyanobacteria. Low value of LMW/HMW in the range of 0.07-0.3 and low concentrations of unresolved complex mixture in the range of 2.4-27 and also the high measured value of \( n-C_{16} \) (52-147), carbon preference index (3-8), even/odd ratio of chain alkanes (2.7-6.3) and Pristan/Phytan ratio
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(1.6-4.5) are evidences to confirm biogenic origin of hydrocarbon in the central and eastern parts of the Iranian shelf. Sketching the Pristine/ n-C17 and Phytane/ n-C18 ratios which both vary in the range of 0.2-0.94 in the related diagram also shows biogenic origin of hydrocarbon due to terrestrial and marine organic matter in addition to peat-coal materials.

Conclusions

Despite the fact that the absolute concentration of aliphatic, aromatic and polycyclic aromatic hydrocarbons fraction show low concentration of petroleum hydrocarbons in comparison with highly contaminated parts of the Caspian Sea in Azerbaijan coast, they are still in the range of danger which attracts more attention and precaution. The biogenic origin of hydrocarbons in the coastal areas of Mazandran and Golestan provinces also apparently remarks that the oil reduction activities in Azerbaijan do not cause pollution in the far west part of the study area. Finally, the results of the study show good consistency with former studies conducted in the southern part of the Caspian Sea.

Key words

Origin, Hydrocarbon, PAHs, Sediment, Oil pollution, Index, Caspian Sea.