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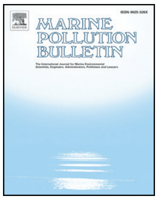

Identifying the source of petroleum pollution in sediment cores of southwest of the Caspian Sea using chemical fingerprinting of aliphatic and alicyclic hydrocarbons

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ABSTRACT

In this study, the concentration and sources of aliphatic and petroleum markers were investigated in 105 samples of Anzali, Rezvanshahr and Astara cores from the southwest of Caspian Sea. Petroleum importation was diagnosed as a main source in most depths of cores by the results of unresolved complex mixture, carbon preference index and hopanes and steranes. From the chemical diagnostic parameters, petroleum inputs in sediment of cores were determined to be different during years and the sources of hydrocarbons in some sections differed than Anzali and Turkmenistan and Azerbaijan oils. Diagenic ratios in most sediments of upper and middle sections in Astara core were determined to be highly similar to those of Azerbaijan oil, while the presence of Turkmenistan and Anzali oils were detected in a few sections of Anzali and Rezvanshahr cores and only five layers of downer section in Anzali core, respectively.

1. Introduction

Marine sediments may provide information on past or on-going environmental processes and components, both natural and human induced (Jeng, 2007).The hydrocarbons in sediment cores have been used to identify source and to reconstruct the historical records of these hydrocarbon inputs for studies on their environmental impact. Of these, the *n*-alkanes are widely used to characterize the organic matter of water, suspended matter and sediments from various environments (Ou et al., 2004; Gao et al., 2007). Several features of *n*-alkanes have been used to identify the sources of organic matter and petrogenic contamination from anthropogenic activity in sediments in the aquatic environment. These features include the ratios of short chain/long chain *n*-alkanes, n-C_{17}/pristane and n-C_{18}/phytane, the unresolved complex mixture (UCM) and a lack of predominance of an even or odd-carbon number for *n*-alkanes (Silva et al., 2012). Moreover, a large number of geochemical markers such as terpane, hopane and sterane can be used as important tools for explaining the origin of the hydrocarbons deposited in a marine system and confirming petroleum contribution (Peters et al., 2005). Also, these components can distinguish between oils and determine their sources, original depositional environment, maturation and the level of biodegradation (Peters and Moldowan, 1993).

Recently, numerous studies were carried out for quantification of *n*-alkanes, hopane and sterane for reconstruction of environmental conditions and past scenarios in the marine and lacustrine environments (e.g. Yunker and Macdonald, 2003; Dongen et al., 2008; Silva et al., 2012).

The Caspian Sea, the biggest enclosed body of water on the Earth bordered by five countries namely Kazakhstan, Azerbaijan, Turkmenistan, Russia and Iran, has attracted the attention of the international oil and gas industry, especially since the break-up of the Soviet Union in 1991 (Effimoff, 2000). Oil fields in Azerbaijan cover the southern part of the Caspian Sea where petroleum exploration and production has been continuing since early 1900s .Also, some potential oil resources exist in Kazakhstan and Turkmenistan of which 30–40% is located offshore (Tolosa et al., 2004). So far, although there has been no exploration from Iran wells (Anzali wells), the natural seeps can be one of the possible sources of the hydrocarbons which needs to be taken into consideration. In addition, due to recent urban development and increasing industrial and oil production activities in the coastal regions of Caspian Sea, considerable amounts of petroleum products are discharged into this marine environment through runoff, industrial and sewerage effluents, storm water drains, shipping activities and spillages (Abessi and Saeedi, 2010).

There are a few studies mostly focused on the distribution of PAH in surface sediment (e.g. Moor et al., 2003; Tolosa et al., 2004; Winkels et al., 1998) and core sediment (Nemati Varnosfaderany et al., 2014). However, for a reliable discrimination between biogenic and anthropogenic origins, determination of their sources, and the influence of the petroleum-related activities, investigating more stable hydrocarbons such as petroleum biomarkers is very useful (Oliveira and Madureira, 2011). Tolosa et al. (2004) reported the only study by using biomarkers

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for determination of origin of hydrocarbons in costal of Caspian Sea limited to two diagenic ratios of hopane in surface sediments of the coastal zone of the Caspian Sea. They showed petrogenic origin in costal of Iran and Baku.

To our knowledge, no report can be found that identified the origin and reconstructed history of oil pollution in sediment cores of southwest coasts of Caspian Sea by using biomarkers. Therefore, this study aimed at identifying the origin of hydrocarbons and distinguishing the petroleum sources in sediment cores of southwest coast of Caspian Sea by anthropogenic hopanes and steranes. The focus was on determination of the composition, concentration and origin of hydrocarbons based on the examination of *n*-alkanes, isoprenoid alkanes and petroleum biomarkers.

2. Materials and methods

2.1. Sample collection

Core sediments were collected using a gravity corer at Rezvanshahr (CR) and Anzali (CA) and Astara shores (CS) at a depth of 20 m on 17 October 2012 (Fig. 1). The core lengths were 120 cm for CR, 115 cm for CA and 62.5 cm for CS with 70 mm in diameter. In the field, the CA and CR were sectioned to 1, 2 and 5 cm intervals immediately after sampling in the upper 10 cm, between 10 and 30 cm and deeper than 30 cm to down of the core, respectively (a total of 75 samples). For CS, sediments were sliced into 1 and 2.5 cm intervals in the upper 30 cm and deeper than 30 cm to down of the core, respectively. Samples were stored in a clean aluminum foil, transferred to the laboratory and kept frozen until analyzed.

Two crude oil samples from Anzali and Turkmenistan were provided by the Research Institute of Petroleum Industry in Iran. An oil sample from Azerbaijan was also included in the analysis.

2.2. Extraction and fractionation

The sediment samples were freeze-dried and extracted by Soxhlet system using 85 ml of dichloromethane for 10 h. The volume of the sample was reduced to 5 ml by rotary evaporation and then passed through a 5% H_2O deactivated silica gel column (1 cm i.d., $\times$9 cm). All hydrocarbons were eluted with 20 ml of DCM/hexane (1:3, v/v) and then the extracts were fractionated into aliphatic and aromatic hydrocarbons using fully activated silica gel column (0.47 cm i.d. $\times$18 cm). The aliphatic hydrocarbon fraction was eluted with 4 ml hexane. PAHs were eluted with 14 ml of dichloromethane/hexane (1:3, v/v) after Alkanes in a separate study. The first fraction was concentrated, transferred to a 1.5 ml glass ampoule and dried under nitrogen gas. The fractionation procedure has been described in detail by Zakaria et al. (2000). Samples were analyzed in 10-sample batches with one blank sample. Procedural blanks demonstrated no hydrocarbon interferences.

Perdeuterated surrogate standard for the alkanes (here $[2H_{26}]$ dodecane) was added to samples prior to extraction. Recoveries of the surrogate standards relative to the recovery standards ranged from 85% to 110% in most of the cases.

Approximately 20 mg of crude oil samples were accurately weighed and extracted with 2 ml DCM/*n*-hexane (1:3, v/v). Fractionation and purification of the oil extracts were performed with the same procedure as for the sediment samples.

2.3. Analytical methods

GC/MS analyses were carried out by an Agilent Technologies (PaloAlto, CA, USA) instrument with a gas chromatograph (GC), model 7890A coupled to a quadrupole mass spectrometer (MS), 5975C. The carrier gas was Helium in this study. The sample peaks were identified by comparison of retention time of the authentic standard run on the same day confirmed by GC–MS.

The biogenic hopanes and the diagenetically modified tri- and tetracyclic terpanes, hopanes, steranes were quantified in the alkane fraction of samples. Petroleum biomarkers were detected using single ion monitoring (SIM) mode: *m*/*z* 191 for tri-and tetracyclic terpane and hopane, *m*/*z* 217 for ααα-steranes and *m*/*z* 218 for αββ-steranes (Ourisson et al., 1987; Volkman et al., 1992; Peters and Moldowan, 1993).

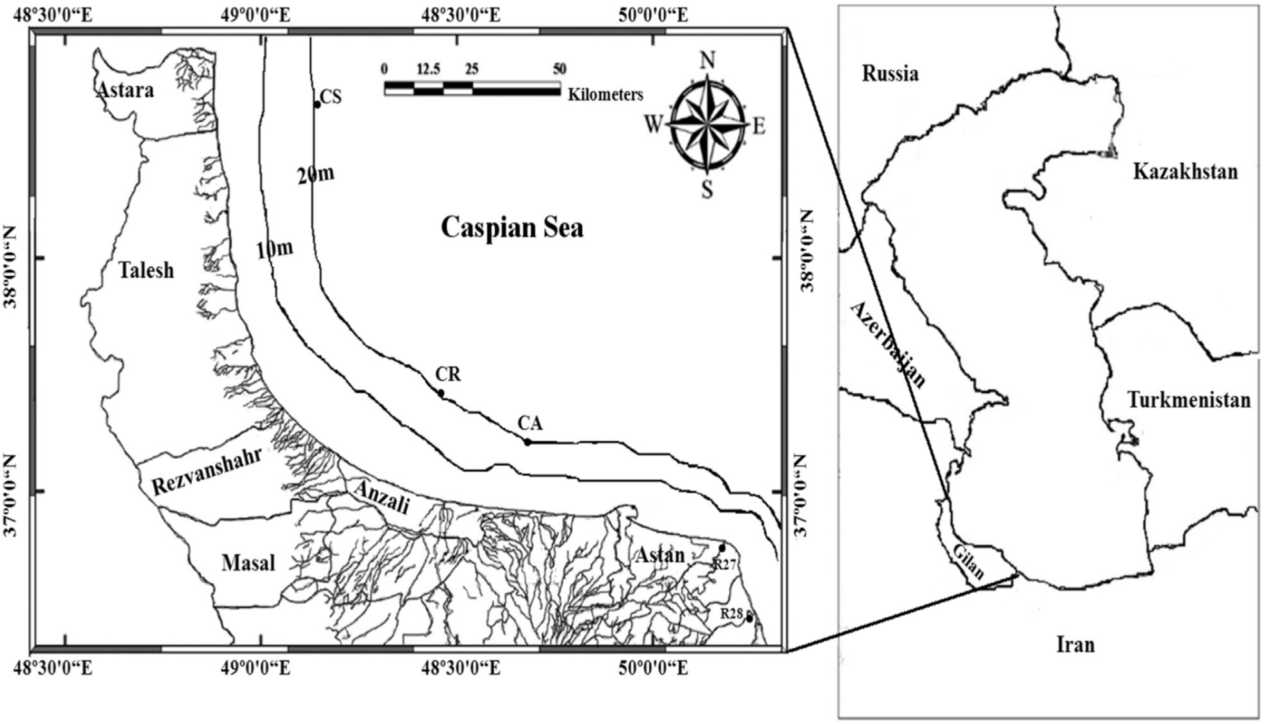

Fig. 1. The sampling stations of core sediment samples in the Southwest coast of Caspian Sea.

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