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Identification of sources of tar balls deposited along the Southwest Caspian Coast, Iran using fingerprinting techniques

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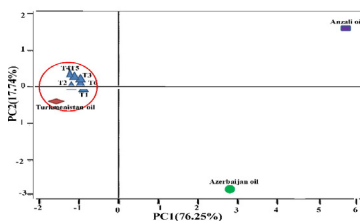
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HIGHLIGHTS

- Multi-marker approach efficiently distinguished the source of tar balls.
- Turkmenistan oil was identified as the most probable source of the tar balls.
- Photo-oxidation, biodegradation and evaporation occurred in tar balls.

GRAPHICAL ABSTRACT



Results of PCA of the 8 source-specific biomarker parameters versus oil samples from Turkmenistan, Azerbaijan and Anzali and 6 tar ball samples.

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ABSTRACT

In 2012, a significant number of tar balls occurred along the Southwest coasts of the Caspian Sea (Iran). Several oil fields of Turkmenistan, Azerbaijan and Iran might be sources of oil spills and lead to the formation of these tar balls. For source identification, 6 tar ball samples were collected from the Southwest beaches of the Caspian Sea and subjected to fingerprint analysis based on the distribution of the source-specific biomarkers of pentacyclic tri-terpanes and steranes. Comparing the diagenic ratios revealed that the tar balls were chemically similar and originated from the same source. Results of double ratio plots (e.g., C_{29}/C_{30} versus $\sum C_{31}-C_{35}/C_{30}$ and $C_{28} \alpha\beta\beta/(C_{27} \alpha\beta\beta + C_{29} \alpha\beta\beta)$ versus $C_{29} \alpha\beta\beta/(C_{27} \alpha\beta\beta + C_{28} \alpha\beta\beta)$) in the tar balls and oils from Iran, Turkmenistan and Azerbaijan indicated that the tar balls might be the result of spills from Turkmenistan oil. Moreover, principle component analysis (PCA) using biomarker ratios on the tar balls and 20 crude oil samples from different wells of Azerbaijan, Iran and Turkmenistan oils showed that the tar balls collected at the Southwest beaches are highly similar to the Turkmenistan oil but one of the Azerbaijan oils (from Bahar field oils) was found to be also slightly close to the tar balls. The weathering characterizations based on the presence of UCM (unresolved complex mixture) and low/high molecular weight ratios (L/H) of alkanes and PAHs indicated the tar ball samples have been significantly influenced by natural weathering processes such as evaporation, photo-degradation and biodegradation. This is the first study of its kind in Iran to use fingerprinting for source identification of tar balls.

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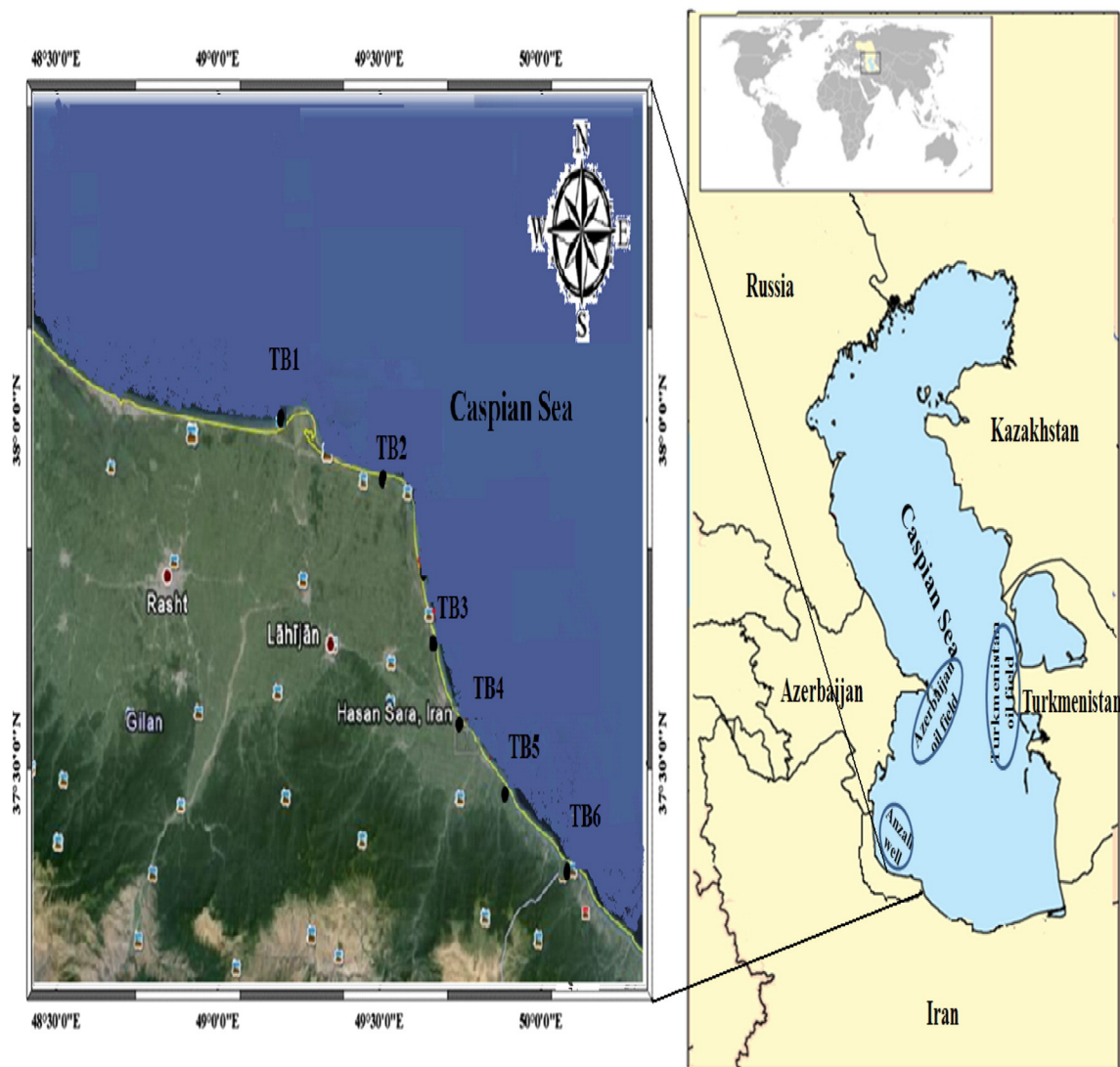


Fig. 1. Locations of Turkmenistan, Azerbaijan oil field, Anzali well and the sampling sites of tar balls collected from the Southwest coast of Caspian Sea.

1. Introduction

The Southwest coast of the Caspian Sea is under the threat of petroleum pollution. In 2009 and 2012, this coast received about 14 and 3 tones of tar balls, respectively. Deposition of tar balls attracts a huge concern for the residents living in this region. Since these tar balls affect the health of the coastal waters and threaten the marine life, Iran’s Environmental Protection Organization has a major concern about this environmental problem. Therefore, tracing of the sources of tar balls is an important environmental management problem.

Tar balls may originate from many petroleum sources. They can be formed during the weathering of oil films in the sea mostly derived from tanker washing and routine shipping operations (Clark, 2002). Operational losses of fossil fuel hydrocarbons from drilling, petroleum platforms and tanker derived oil spills are also the main contributors in tar ball generation (Asuquo, 1991).

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). The nearest possible spill sources to Iran coast in the Caspian Sea are offshore oil fields located off Azerbaijan and Turkmenistan. The Southwest coast of the Caspian Sea is covered by the majority of oil fields in Azerbaijan where petroleum exploration and

production has been continuing since the early 1900s. Guneshli-Chirag-Azeri (GCA), Bahar, and Gum Adasi fields are the most important oil fields in Azerbaijan. Currently, proved reserves of these oil fields are estimated at 18–35 billion barrels. This significant production and exploration could cause the Southwest beaches in Iran to be highly susceptible for stranding of tar balls originating from Azerbaijan. Also there are potential oil resources in Turkmenistan, 30–40% of which are located offshore (Tolosa et al., 2004). Petroleum activities from these areas could have caused some spills which led to the formation of tar balls. Another possible source of tar balls in the Southwest coasts of the Caspian Sea can be Anzali oil well located 30 km away from Northwest of Anzali Port (Fig. 1). This well is an offshore well drilled and completed in April 1991 in Southwest region of Caspian Sea. In spite of existence of

Table 1
Positions and sampling date and codes of tar balls collected from the Southwest coast of Caspian Sea.

Station	Location	Latitude (N)	Longitude (E)	Sand content (%)
TB1	Kiashahr City	37°28'35.74"	49°56'20.40"	5
TB2	Asgarabad City	37°24'43.58"	50°3'58.38"	7
TB3	Chaf City	37°21'30.05"	50°13'42.49"	8
TB4	Chamkhaleh City	37°15'54.06"	50°15'9.03"	6
TB5	Hasansara City	37°8'32.69"	50°19'9.70"	9
TB6	Kalachy City	37°4'21.56"	50°26'5.46"	5

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