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Baseline

Seasonal variation of polycyclic aromatic hydrocarbons in the surface sediments of the southern Caspian Sea

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ABSTRACT

The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in sediments from the southern Caspian Sea in fall 2015 and winter 2016. The sum of 16 PAH (Σ PAH) concentrations varied from 17.3 ± 3.05 to 926.7 ± 157.37 ng g⁻¹ dry weight and 14.3 ± 0.58 to 85.8 ± 4.41 ng g⁻¹ dry weight in fall and winter, respectively. There was no significant correlation between PAH and total organic carbon contents ($p > 0.05$). PAH source identification showed that the PAHs in the sediments originated from petroleum and petroleum combustion. When classified according to the pollution levels, sediments from the southern Caspian Sea could be considered to be low to moderately polluted with PAHs.

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Of all contaminants, oil and petroleum hydrocarbons are of specific international importance from political, economical, and scientific aspects. Since millions of years, there have been oil leaks from deep sources in the oceans into the ocean water. The existence of oil in water severely damages the aquatic environment and harms human life. Petroleum includes a variety of hydrocarbon combinations and variable amounts of sulfur, nitrogen, and oxygen compounds in addition to some metals. Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds constituted from hydrogen and carbon atoms arranged in the form of two or more benzene rings. According to their molecular weight, these compounds are divided in two groups: high-molecular-weight compounds with 4–6 benzene rings and low-molecular-weight compounds with 2 or 3 benzene rings (Neff, 1979; Tolosa et al., 2005). Oil and other fossil fuels are the main sources of PAH entrance into the nature, and 0.2%–7% of petroleum weight belongs to these pollutants. When these hydrocarbons are released into the water or air, they are absorbed by the particles in these environments; thus, these hydrocarbons are retained in marine sediments for a long time at high concentrations. Moreover, PAHs are considered as persistent organic pollutants because of their stable chemical structure and inherent resistance to the biotic and abiotic decomposition. In general, PAHs originate from natural and anthropogenic processes (Md

Suhaimi et al., 2007). Oil contamination, fuel combustion, sewage water (Tam et al., 2001; Valavanidis et al., 2008), industrial processes, transportation, and combustion of wastes introduce considerable amounts of these compounds into the aquatic environment. In addition, oil drilling and industries play a key role in the entrance of these compounds in large amounts into the environment. Overall, there are two main anthropogenic sources that drain pollutants into the aquatic environment: pyrolytic and petrogenic sources. Pyrolytic sources consist of PAHs that are derived from fossil fuel combustion, and petrogenic sources are those in which PAHs originate from petroleum (Neff, 1979; Tolosa et al., 2004; Md Suhaimi et al., 2007). Petrogenic sources often release low-molecular-weight PAHs containing 2–3 benzene rings, whereas pyrolytic sources dominantly releases high-molecular-weight PAHs containing 4–6 benzene rings (Neff, 1979; Beliaeff et al., 2002).

The Caspian Sea, as the largest lake in the world, receives a vast amount of pollutants from the five surrounding countries. In particular, with the extended oil extraction from this water body, the problem of pollution is rapidly growing in recent years. Of these five countries, Iran does not extract any oil from the Caspian Sea. However, other countries such as Azerbaijan, Turkmenistan, and Kazakhstan have oil wells wherein the oil is extracted from the sea and offshore. Taking into consideration the importance of such a unique ecosystem, this study aimed to (1) consider the spatial distribution of PAHs in surface sediments of the southern Caspian Sea in fall and winter seasons and (2) determine the relationship between PAHs in the sediments and sediment characteristics and determine their toxic biological effects on aquatic

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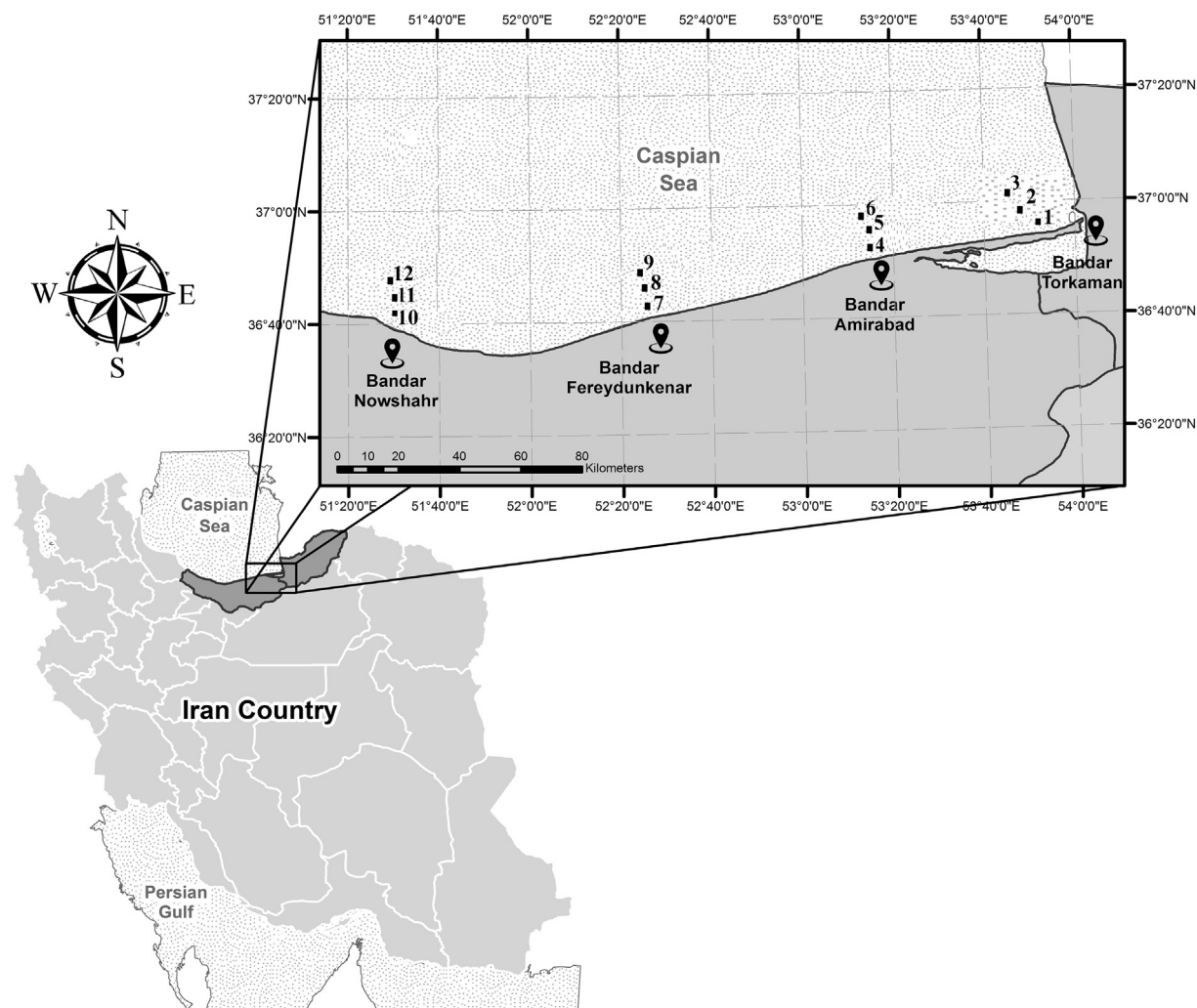


Fig. 1. The locations of the sampling sites in the southern Caspian Sea.

organisms following the sediment quality guidelines, which are widely adopted.

To investigate the PAH compounds in sediments, 12 stations were selected on the Caspian Sea coast from two Mazandaran and Golestan provinces. Sediment samples were collected at each station by a grab sampler in two seasons, i.e., fall and winter 2015 (Fig. 1). The samples from each station were placed in aluminum containers, transferred to the laboratory, and stored at -20°C until further analysis. To measure the PAH contamination levels in the sediments, the standard MOOPAM (Manual of Oceanographic Observations and Pollutant Analyses Methods) (1999) method was used. The organic matter from the samples was extracted using Soxhlet apparatus for 8 h with 320 ml dichloromethane solution and 10 g dry weight of sample (Zakaria et al., 2002; Riyahi Bakhtiari et al., 2009). For recovery, 100 μl of Sarogit was added to the sample, which consisted of four PAH dotrit combinations, namely perylene- d_{12} , chrysene- d_{12} , anthracene- d_{10} , and naphthalene- d_8 . In addition, to remove sulfur from the samples, which interrupts the chromatography peak, a piece of activated copper was added to the samples. These sample solutions were allowed to stand for 24 h in the refrigerator. Then, they were placed in a rotary evaporator until their volume reduced to 2 ml. Thereafter, the samples were applied onto a chromatography column for the first elution using 5% deactivated silica gel as the stationary phase and 20 ml of hexane:dichloromethane solution (3:1) as the mobile phase. The internal diameter of the column was

9 cm, and silica gel was added up to 9 cm into the column. After the removal of the samples from the first run, they were re-evaporated until their volume was reduced to 1 ml and then applied onto the chromatography column for the second elution. In this elution, fully activated silica gel was used as the stationary phase and 14 ml hexane:dichloromethane solution (3:1) was used as the mobile phase. The internal diameter of the column was 0.47 cm, and the silica gel was poured up to 18 cm into the column. Subsequently, the samples were eluted off the column. Their volume was again reduced by evaporation, and the samples were then transferred to the vials. The samples were dried using a gentle flow of 99.99% nitrogen gas. After adding an inner standard, *P*-terphenyl- d_{14} (100 μl), they were injected onto the gas chromatography–mass spectrometry column (Zakaria et al., 2002; Riyahi Bakhtiari et al., 2009).

The abbreviations used for the 16 PAHs are as follows: naphthalene, N; acenaphthylene, AC; acenaphthene, ACE; fluorene, F; phenanthrene, Ph; anthracene, A; fluoranthene, Fl; pyrene, Py; benzo (a)anthracene, B(a)A; chrysene, Ch; benzo(b)fluoranthene, B(b)Fl; benzo(k)fluoranthene, B(k)Fl; benzo(a)pyrene, B(a)Py; indeno(1,2,3-c,d)pyrene, IPy; dibenz(a,h)anthracene, DB(ah)A; benzo(ghi)perylene, B(ghi)Pe.

For grading sediments according to grain size, a particle analyzer (HORIBA-LA950, France & Japan) was used, and the percentage of sand, silt, and clay were specified. Total organic carbon (TOC) content was analyzed using a TOC Analyzer (SGE, ANATOC Seri II Australia).

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