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Spatio-temporal variability, distribution and sources of *n*-alkanes and polycyclic aromatic hydrocarbons in reef surface sediments of Kharg and Lark coral reefs, Persian Gulf, Iran

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ABSTRACT

Environmental pollution, particularly oil pollution, has been a long-standing problem in marine areas. With the aim to assess the pollution status in the Persian Gulf, Iran, herein surface sediments were collected from Kharg and Lark coral reefs, in summer (dry season) and winter (wet season), to evaluate the spatio-temporal variations of *n*-alkanes and PAHs. The mean total organic carbon (TOC) contents of sediments showed a significantly dramatic variation ($p < 0.05$) in both seasons at both Islands, with high values recorded at sites located near pollutant inputs. The total mean percent of clay grain-sized sediments at Kharg were 26.57% and 28.86% in dry and wet seasons, respectively, while in Lark were 26.73% in summer and 24.57% in winter. Additionally, at Kharg the mean Σ25*n*-alkanes and Σ30PAHs ranged from 81.35 to 573 $\mu g\, g^{-1}$ dw and 60.25–491 $ng\, g^{-1}$ dw in dry season, and 171–754 $\mu g\, g^{-1}$ dw and 41.61–693 $ng\, g^{-1}$ dw in winter, respectively. At Lark, the average Σ25*n*-alkanes and Σ30PAHs varied from 31.18 to 272 $\mu g\, g^{-1}$ dw and 41.25–196 $ng\, g^{-1}$ dw in summer, whilst oscillated from 57.99 to 332 $\mu g\, g^{-1}$ dw and 16.56–487 $ng\, g^{-1}$ dw in wet season, respectively. The lowest mean level of the examined pollutants were spanned in offshore sites, while the highest average concentrations indicated that contaminated sediments were at onshore stations at both Islands in both seasons. Significant seasonal variations ($p < 0.05$) were observed at most sampling sites for all pollutants. Molecular Diagnostic Ratio (MDR) and Principal Component Analysis (PCA) indicated that *n*-alkanes and PAHs had mostly a petrogenic source. The compositional profile of PAHs showed that 2 and 3-ring PAHs were abundant at both sampling sites. Significant positive correlation ($r > 0.76$) was observed between Σ25*n*-alkanes and Σ30PAHs at Kharg and Lark sediments with TOC content, especially for the sites with high total pollutant concentrations. Based on the potential impact and ecological risk of *n*-alkanes and PAHs in surface sediments, it is, therefore, necessary in future studies to focus on their effects on corals and other marine organisms within this ecosystem.

1. Introduction

Coral reefs are one of the most productive and varied ecosystems in the world, which are being threatened and destroyed at a global scale by a long list of anthropogenic factors (Gold-Bouchot et al., 2017; Ranjbar Jafarabadi et al., 2017a, 2017b, 2017c, 2018a, 2018b). The values of goods and services offered at coral Islands approximately range from \$172 billion to \$375 billion per year (Fischlin et al., 2007), and include tourism, recreational activities, and fisheries (NOAA, 2011). Coral reefs are in danger of extinction (Hughes et al., 2003), as ten percent of the world's reefs are already seriously damaged (Ranjbar Jafarabadi et al., 2017a; Saha et al., 2016), and sixty percent are predicted to be damaged seriously within the next 20–40 years, likely due to natural and anthropogenic stressors (Gold-Bouchot et al., 2017; Goreau et al., 2000).

Normal alkanes (*n*-alkanes) and polycyclic aromatic hydrocarbons (PAHs) are a major concern for scientists. These pollutants may be found at dangerous levels in marine organisms because of bio-accumulation processes, long biological half-lives and ecological risks. Among these compounds, the aliphatic hydrocarbons (AHs) and PAHs

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are widely used as chemical markers to ascertain potential sources of environmental pollution caused by crude oil, gasoline, and diesel (D'Agata et al., 2014; Froehner et al., 2012; Liu et al., 2008; Maisano et al., 2017). The *n*-alkanes belong to the AHs, which are among the most abundant pollutants found in sediments after petroleum contamination (Barbosa et al., 2016; Vaezzadeh et al., 2015). Natural sources of *n*-alkanes of continental origin are mainly predominant in plants, such as biosynthesis of higher plants and cuticular wax derivatives of vascular plants (i.e. mangroves), while anthropogenic sources are mainly associated with industrial processes, municipal and industrial discharges along with riverine inputs, marine oil and gas exploration, pyrolysis of fossil fuels, oil spills and derivatives (Sanches Filho et al., 2016; Yu et al., 2016). The availability of these lipophilic compounds could be associated with high organic matter in sediments and sediment particle size (specially small size) (Cavalcante et al., 2009; Rau et al., 2013). Besides, AHs can easily spread in the environment and take part in processes such as oxidation, reduction, resuspension, vaporization, as well as biological processes like biodegradation and bioaccumulation that contribute to their transformation because of their specific physico-chemical features (Bigus et al., 2014). The use of AHs as geochemical markers has extensively been used for the evaluation of sediments polluted by domestic wastewater and/or petroleum products (Kucuksezgin et al., 2012; Medeiros and Bıcego, 2004).

PAHs, categorized as persistent organic pollutants (POPs) under the Convention of the United Nations Economic Commission for Europe (UNECE), with fused aromatic rings plus complex mixtures, are ubiquitous in the environment as widely found in terrestrial and marine ecosystems (Ranjbar Jafarabadi et al., 2017a, 2017b; Maisano et al., 2017; Shirneshan et al., 2016; Vaezzadeh et al., 2015). PAHs are of great concern due to their toxicity, mutagenicity, carcinogenicity, and persistency (Tuikka et al., 2016; Yan et al., 2016), as well as high potential to be metabolized in aquatic fauna having active and potent carcinogenic forms (Bonner et al., 2005; Boström et al., 2002; Fasulo et al., 2012). It is reported that the major source of PAHs in the environment is generally of anthropogenic origin (Liu et al., 2016; Rabodonirina et al., 2015). Emitters of PAHs include diverse sources such as combustion of fossil fuels (Christensen and Bzdusek, 2005; Moon et al., 2006), industrial incinerations, transportation and uncontrolled spills (Liu et al., 2016; Nácher-Mestre et al., 2010), wood and coal burning (Cristale et al., 2012; Yan et al., 2016), and metal smelting. In addition, urbanization (Van der Oost et al., 2003) along with atmospheric deposition and shipping (Albuquerque et al., 2016; de Souza Pereira et al., 2007) are other sources of PAHs.

The Persian Gulf, a Mediterranean Sea in western Asia, is an extension of the Oman Gulf through the Strait of Hormuz, which lies between Iran to the northeast and Arabian Peninsula to the southwest (Gammeltoft et al., 2015; Ranjbar Jafarabadi et al., 2017a, 2017b). This area is connected to international waters by the Strait of Hormuz (Banat et al., 1998). The replacement time of water in this area is between 3 and 5 years, which shows that pollutants remain for a considerable time in the Persian Gulf (Sheppard, 1993). Besides various environmental incidents mainly related to occasional oil spills and to the “Persian Gulf War” in 1991 (NOAA, 1992), this area is subjected to intense shipping traffic, transportation and oil pollution, as well as oil spillage. It is known that about 30% of total world oil shipping takes place in the Persian Gulf (Pourang et al., 2005). Among the coral Islands of the Gulf, Kharg and Lark are the most important for the biodiversity of coral species (Ranjbar Jafarabadi et al., 2017a, 2017b, 2017c, 2018a, 2018b), with Kharg comprising of reef-building corals, while Lark contains both reef-building and non-reef-building corals. Both Islands host some of the most magnificent marine species, from corals, fish, turtles to dugongs, which are directly or indirectly dependent on coral reef for their survival, and some of them are on the verge of extinction or considered as endangered species (Marsh and Sobtzick, 2015), due also to a drastic decline in coral population (Bauman et al., 2013; Bento et al., 2016; Ranjbar Jafarabadi et al., 2018a, 2018b).

The main causes of local pollution in the Persian Gulf are attributable to the rapidly growing industrialization, oil extraction from platforms and heavy ships, transportation traffic along with oil spills, while land generated pollution counts as the second most common source of pollution in these areas, with consequent release of contaminants ranging from mercury to acidic or basic toxins and other organic compounds, such as *n*-alkanes and PAHs. To date, there are few systematic investigations on the aliphatic and aromatic hydrocarbon levels in the reef sediments of the Persian Gulf. Therefore, this study was designed with the aim to assess environmental quality status of this area by monitoring reef sediments of Kharg and Lark coral Islands. Hereupon, the objectives of the current study were as follows: (1) to investigate seasonal concentrations along with spatial and temporal distribution of *n*-alkanes and PAHs in reef sediments; (2) to recognize plausible sources of *n*-alkanes and PAHs by using diagnostic ratios and multivariate statistical analysis; and (3) explore the relationship between grain size and organic matter (OM) with concentration of examined compounds.

2. Methods and materials

2.1. Study area

Kharg Island (29.23°N 50.31°E) is located 25 km off the coast of Iran and 483 km northwest of the Strait of Hormuz (Fig. 1). Kharg provides a sea port for oil export and extends Iranian territorial sea claims into the Persian Gulf oil fields. Once Kharg was the world's largest offshore crude oil terminal and the main sea terminal for Iranian oil. Today, it is located in a heavy transportation area and serves as the main transit point for most of the goods (e.g. crude oil, finished products and raw materials) to and from Iran. Lark coral Island (26°51'12" N 56°21'20" E) is 30 km off the coast of Iran, and the narrowest part of the Strait of Hormuz lies between Hormuz and Qeshm Islands (Fig. 1). Lark has been one of Iran's major oil export points since 1987. Moreover, the waters around Lark Island host the most diverse coral reef areas within the Persian Gulf (Ranjbar Jafarabadi et al., 2017a, 2018a, 2018b).

2.2. Sediment sample collection

Reef sediment samples were collected from 16 sampling sites around both Kharg and Lark coral Islands (Fig. 1) in July 2014 (summer, dry season) and January 2015 (winter, wet season). Specifically, among the 16 sampling stations selected at both Islands, some sites are located onshore, namely at a distance within 1 km from the shore in which the main anthropogenic activities are present (i.e. KH.ST_1 to KH.ST_8 and LA.ST_1 to LA.ST_8), while the other sites are situated offshore, at a distance greater than 1 km from the shore (i.e. KH.ST_{10} to KH.ST_{16} and LA.ST_{10} to LA.ST_{16}). At each sampling station, 3 surface sediment samples were collected using a Van Veen grab sampler and then transferred into stainless steel containers and transported at 4 °C to the laboratory, where samples were stored in a cold room (− 20 °C), until further analysis. Overlying water was siphoned off prior to sub-sampling. Large pieces of debris such as rocks, sticks, and leaves were not retained for analysis. Reef sediments were analyzed for *n*-alkanes, PAHs, total organic carbon (TOC) and grain size.

2.3. Chemical analytical techniques

Authentic *n*-alkanes and PAHs standards were purchased from Sigma. The samples were purified and fractionated by a method described elsewhere (Bakhtiari et al., 2009a; Zakaria et al., 2002). The Surrogate Internal Injection Standard (SIIS) mixture was added for quality control of *n*-alkanes and PAHs analyses. The eluate was purified and fractionated using two-step silica gel column chromatography. Normal alkanes and PAHs analyses were done using Agilent