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Baseline

Baseline concentrations and distributions of Polycyclic Aromatic Hydrocarbons in surface sediments from the Qatar marine environment

Hassan Mustafa Hassan*, Azenith B. Castillo, Oguz Yigiterhan, Elnaiem Ali Elobaid, Abdulrahman Al-Obaidly, Ebrahim Al-Ansari, Jeffrey Philip Obbard

Environmental Science Center (ESC), Qatar University, Doha, Qatar

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ABSTRACT

Coastal sediments in marine waters of Qatar have the potential of being contaminated by Polycyclic Aromatic Hydrocarbons (PAHs) due to extensive petroleum exploration and transportation activities within Qatar's Marine Exclusive Economic Zone. In this study, the concentration and distribution of sixteen PAHs classed as USEPA priority pollutants were measured in sediments from the eastern Qatari coast. PAHs were recovered from sediments via accelerated solvent extraction and then analyzed using Gas Chromatography–Mass Spectrometry. Total concentrations of the PAHs were in the range of 3.15–14.35 μg/kg, and the spatial distribution of PAHs is evaluated in the context of sediment total organic content, depth and the grain size together with and the proximity of petroleum exploration and transportation activities. The data show that the concentrations of PAHs within the study area were in the low-range, suggesting a low risk to marine organisms and limited transfer of PAHs into the food web.

Polyaromatic hydrocarbons (PAHs) can occur naturally in the environment as a result of volcanic activity or the result of forest fires (Xu et al., 2006; Baek et al., 1991), as a consequence of anthropogenic activities such as biomass burning, petroleum combustion and spillage, and metal works (Zhang et al., 2008; Baek et al., 1991).

Numerous studies on the carcinogenic, mutagenic and persistent properties of PAHs in the environment have been conducted (Barakat et al., 2011; Li et al., 2012; Magi et al., 2002; Mastrangelo et al., 1996; Tsapakis et al., 2010). Due to their environmental persistence and potential ecotoxicological effects, an evaluation of PAH concentrations and distribution within the marine environment of a country is necessary to evaluate potential impacts on associated ecosystems (Chen et al., 2012; Soclo et al., 2000). The bioavailability and type of PAH compounds present in marine sediments depend on their source (Yunker et al., 2012), where it is generally accepted that PAHs are either petrogenic or pyrogenic in origin (Wang et al., 2014). In coastal marine ecosystems, PAHs originate principally from petrochemical spills, urban runoff and atmospheric deposition (Fathallah et al., 2012).

PAHs are hydrophobic in seawater and predominantly associated with the solid-phase particulate matter which becomes deposited into marine sediments (Vane et al., 2007; Wang et al., 2011; Zhang et al., 2011). A high affinity of PAHs to sediment particles can result in their low bioavailability, slow degradation and long-term persistence in the marine environment. Levels of PAH within sediments are influenced by sediment organic matter content and grain size that affect the sorption of these pollutants onto the solid-phase (Chiou et al., 1998; Wang et al., 2001; Xia and Ball, 1999). In particular, Johnson et al. (2001) demonstrated that a sediment organic carbon content exceeding 0.1% is sufficient to significantly enhance PAH sorption onto marine sediments. Sediment PAH concentrations may also be affected by the type of organic matter present (Chen et al., 2012). For example, Cornelissen et al. (2006) reported that Norwegian marine sediments with a high organic carbon content had a high PAH sorption proficiency.

The role of sediment grain size in PAH sorption is not fully understood. Rockne et al. (2002) reported that higher levels of PAH occur in the larger grain size fraction of sediments (> 500 μm), while Kim et al. (1999) reported the opposite i.e. higher levels of PAH are associated with smaller grain size (c. < 500 μm). Yang et al. (2008) suggested that PAHs are associated with the low-density fraction of sediments derived from plant and coal particulates. In contrast, Mostafa et al. (2009) reported that the levels and distribution of PAHs within sediments is more strongly related to the source of contamination, rather than sediment type.

Qatar's Marine Exclusive Economic Zone (EEZ) is a sub-component of the wider Arabian Gulf, and integral to the country's oil and gas exploration and production infrastructure and includes major international shipping lanes. Although extreme precautions are in place to avoid petroleum leakage and spillages, these do occur (Al-Ghadban

* *Corresponding author.
E-mail address: hassan.hassan@qu.edu.qa (H.M. Hassan).

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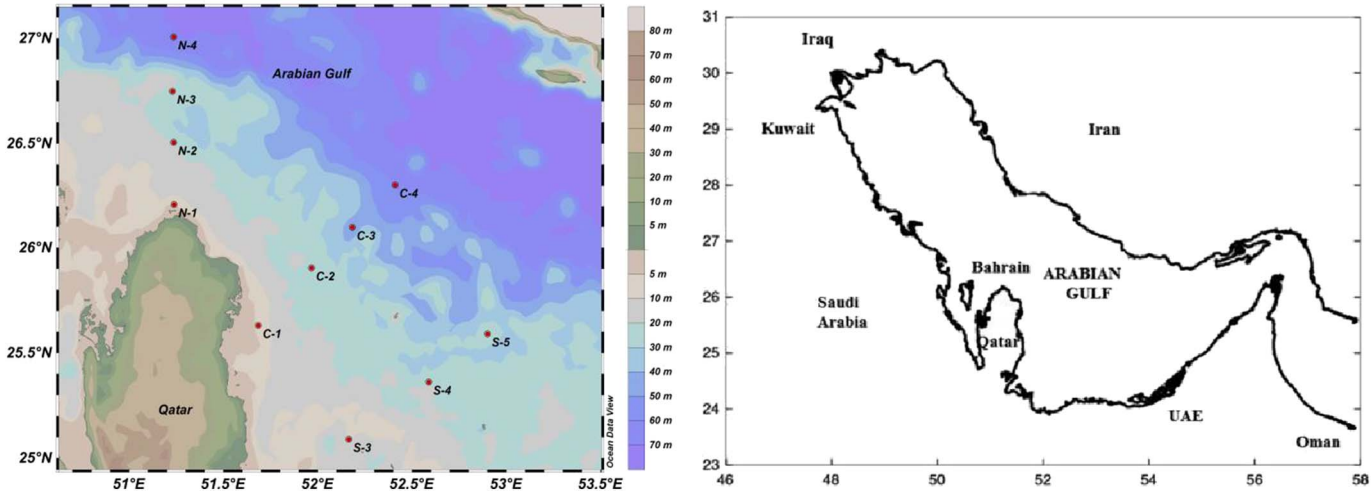

Fig. 1. Sediment sampling point's locations and Qatar geographical location.

et al., 2002)) and thus have the potential to adversely impact the marine environment (Brooks et al., 1986; Overton et al., 2004). In addition, the legacy of the 1991 Gulf War, and the rapid industrialization of countries surrounding the Arabian Gulf have combined to exert additional pressures on the marine ecosystem, which is naturally subject to extreme high-temperatures and atmospheric fallout from dust storms. These factors contribute to the potential exposure of the ecosystem to various pollutants, including PAHs (Massoud et al., 1998; Al-Sarawi et al., 2002.; Al-Ghadban and El-Sammak, 2005).

Limited data are available on the concentration and spatial distribution of PAHs in the areas surrounding Qatar. Therefore, the objective of this paper was to assess the concentration and distribution of PAHs, total organic carbon and grain size in the marine sediments from the northern and eastern regions of Qatar coastal zones (Fig. 1).

Surface sediment samples, at water depths varying from 18 to 67 m, were collected during September 2016 using a van Veen grab that was deployed from Qatar University's research vessel, the Janan. Upon retrieval, each sample was homogenized using a Teflon scoop, and then placed in an acid cleaned 250 ml sample glass vessel, and stored in a freezer at − 20 °C. Sediment particle size distribution was measured by laser diffraction using a Mastersizer 3000 (Malvern) fitted with a Hydro EV. Total organic carbon (TOC). Sixteen PAHs compounds, listed as priority pollutants by the US EPA were analyzed in the sediment samples, including: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a) anthracene, Chrysene, Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, Indeno(1,2,3-cd) pyrene, Dibenzo(a,h) anthracene, and Benzo(ghi) perylene. PAHs were extracted from sediments using a Dionex 350 Accelerated Solvent Extractor (ASE) as per US-EPA method 8015 and analyzed using an Agilent 7890B gas chromatograph coupled to a 5975C triple–axis mass spectrometer (GCMS).

Statistical analyses of data were carried out using Multivariate Analysis of Variance (MANOVA) with Tukey HSD post hoc analysis to delineate differences between stations. P-values equal to or < 0.05 were considered statistically significant. Parameters were correlated using a two-tailed Pearson Correlation Coefficient (R^2) at P values equal to or < 0.01.

Sediment collection depth, TOC, ΣPAH, and grain size data are shown in Table 1. TOC values give indications on the potential for accumulation and release of sediment PAHs, where Karichknoff et al. (1979) reported that the levels of TOC within marine sediments are inversely proportional to grain size. Available data on levels of TOC within sediments from the Arabian Gulf are sparse; where the earliest data was by Evans (1966) reported levels of TOC in the range of 0.83%–1.51%. Hartmann et al. (1971) reported that marine sediment in the Arabian Gulf contains a maximum of 2% TOC. Later, in 1992, other researchers reported that the level of TOC within the marine sediments of Kuwait ranged from 0.5%–0.8% and more recently Al-Timari et al. (2014) reported a TOC range of 0.32%–0.85% within sediments collected from the Shatt Al-Arab River and North-West Arabian Gulf.

In this study, TOC levels in marine sediments from the Qatar EEZ ranged from 0.16% ± 0.02(S4) to 0.73% ± 0.07 (C4) (Table 1). The TOC results are therefore comparable to data from earlier reports for the Arabian Gulf. However, the only available data pertaining to TOC levels in the Qatar EEZ itself were published by de Mora et al. (2010), who reported a range of 0.5% and 2.34% TOC - a higher range compared to our results. It is noted that de Mora et al.'s data were derived from sediments sampled closer to the coastline of Qatar than this study, and this may account for the discrepancy, where land-based sources of TOC may increase nearshore sediment TOC levels via atmospheric deposition and/or terrestrial runoff.

TOC = total organic carbon, PAH = polyaromatic hydrocarbons, SD = standard deviation.

The USEPA (2002) recommends the following assessment categories for TOC in sediments that correspond to major shifts in the benthic data or species richness: low impact: ≤ 1%, intermediate impact: 1 to 3% and high impact: > 3%. Based on these criteria, TOC levels in the sediments from Qatar's EEZ indicate a range of TOC levels associated with a low impact on the marine environment. Our study also shows that sediment TOC content positively correlated with increased depth ($P < 0.01$, $R^2 = 0.82$). Moreover, the relationship between TOC and finer sediment grain size fractions (clay and/or silt) has been previously investigated (Buchanan and Longbottom, 1970; Mayer, 1994; Tyson, 1995). Bergamaschi et al. (1997) showed a linear positive relationship between TOC and grain size, although a later study by Magni et al. (2008) concluded that this relationship is exponential. Finer grain sizes deter the diffusion of oxygen into sediments, thus allowing for the conservation of organic matter, which in turn promotes the adsorption of contaminants onto the charged mineral surfaces. The enhanced surface area of smaller grain sizes also serves to enhance prevailing TOC concentrations in sediments.

Sediment PAH measurements show that the total PAHs (ΣPAH) concentration ranged from 3.146 μg/kg (C1) to 14.350 μg/kg (C4) (see Table 1) and is found to be significantly different between sampling quadrants (Fig. 2, $P < 0.05$). Concentrations of ΣPAHs within the Arabian Gulf have been previously reported by other authors, especially after the 1991 Gulf War, when widespread oil contamination of the Arabian Gulf occurred. Fowler et al. (1993) measured the petroleum hydrocarbons in nearshore Gulf sediments before and after the war, and concluded that regardless of the war-related oil spills and fires, the