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Baseline

Sediment-associated polycyclic aromatic hydrocarbons and potential eco-hazards in Chabahar Bay, Iran

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ABSTRACT

The surface sediments (0–4 cm, $n = 6$) from Chabahar Bay were analyzed to assess the concentrations, composition, and potential eco-hazards of associated PAHs. The range of $\Sigma 16$ PAHs' concentration was 25.75–312.38 ng g^{-1} dw, with mean and median levels of 126.7 and 55.12 ng g^{-1} dw, respectively. The bay was classified as a region with low to moderate PAH pollution. The sources of PAHs varied, and 2–3-ring compounds were dominant (37–90%). There was no significant correlation between TOC/grain size and levels of PAHs. Total carcinogenic PAHs ranged from 0.21 to 79.68 ng g^{-1} dw, and benzo(a)pyrene was the main constituent of calculated toxic equivalencies. The bay sediments were rarely hazardous and could not address narcotic hazards for the benthic community. Biota-sediment accumulation was not predicted for the examined coral *Acropora valida*. In equilibrium conditions, release of $\Sigma 16$ PAHs from the bay sediments was estimated to be 0.536 $\mu\text{g L}^{-1}$ at its maximum.

Although the seas as a whole are pollution-free regions, their coastal zones, especially semi-enclosed parts, are significantly affected by eco-pollutants (Mehdinia et al., 2015). Chabahar Bay is a small and semi-circle basin located on the northeastern coasts of the Oman Sea, Iran (Fig. 1). The estimated surface area (290 km^2) and average depth (12 m, range 4–22 m) of the bay highlight its ability to handle standard oceanic cargo ships. There are no extensive industrial and agricultural activities around the Chabahar Bay, and the major importance of the region is the mentioned ability. The development of the bay, which began in 1973, was delayed since 1979 (Vatanaka, 2015). Presently, the country has decided to develop the area as a free trade zone and a hub for dealing with central Asia. To do so, the construction and development of the Shahid Beheshti port is currently underway in the south-eastern part of the bay (Fig. 1), which serves as the country's only oceanic port. Moreover, this sub-tropical water basin has a high biological production, providing an ideal breeding and nursery ground for economically important fish and shellfish (Fazeli et al., 2010). Furthermore, patches of coral reefs are dispersed in the bay wherever the conditions meet the needs of corals. Presence of coral-growing zones and breeding and nursery grounds makes the bay ecosystem especially vulnerable to the development plans and related pollutant flux (Ajdari et al., 2013; Fazeli et al., 2010). Human activities routinely produce, release, and disperse eco-pollutants in the levels higher than the carrying capacity of the coastal zones. Polycyclic aromatic hydrocarbons (PAHs) are a typical case of such chemicals that are widely released into

marine ecosystems (Aghadadashi et al., 2016; Charles et al., 2012). The compounds meet some criteria that nominate them as persistent organic eco-pollutants under the Aarhus Protocol, and the Environmental Protection Agency (EPA) classifies 16 of them as priority pollutants (Lohmann et al., 2007; UNECE, 1998). A notable part of these eco-pollutants moves toward the marine sediments and sequesters in there for decades (Chen and Chen, 2011; Wang et al., 2001). However, the sediments are occasionally disturbed and re-introduce the trapped fractions into the active compartments of the marine ecosystems. Thus, the marine sediments are an ideal matrix for the establishment of the environmental policies in order to keep the ecosystems' totality.

Because of the importance of the studied region, obtaining baseline data is of major importance. However, the lack of valid and basic information makes it difficult to have a proper view about rapidly occurring changes and consequent eco-hazards in the region. In a study, the PAH levels ranged between undetectable levels to 92.8 ng g^{-1} dry weight (dw) in sediments from the bay (Agah et al., 2017). Thus, our findings about the samples gathered in 2006 would provide baseline information to compare with the present conditions in the bay. In doing so, the concentrations of sediment-associated PAHs, composition of detected polyarenes, their bioavailability and biologically possible effects, organic carbon levels, and particle size distribution of the sediments would be reported in the following sections.

Six stations were selected in the bay for the study, and sediments (0–4 cm) were collected in three replicates using a clean van Veen grab

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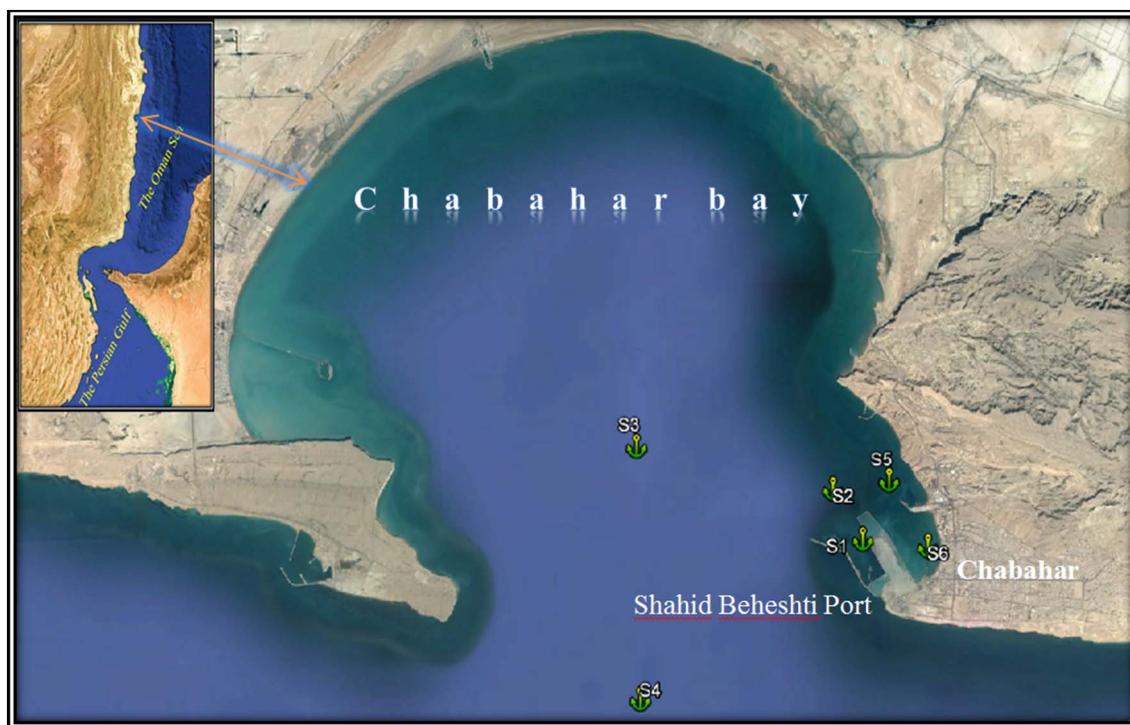


Fig. 1. Study area and sampling sites in the Chabahar Bay.

in December 2006 (Fig. 1). Geographic coordinates were recorded using a GPS-60CSX (Garmin, the USA). The samples were placed in clean aluminum containers and kept in the freezer ($-20\text{ }^{\circ}\text{C}$) until chemical analysis.

In the laboratory, the sediment samples were freeze-dried (OPR-FDB-5503, Korea) at $-40\text{ }^{\circ}\text{C}$ for 24 h to a constant weight. Then, 2 g of freeze-dried and homogenized sediments ($< 250\text{ }\mu\text{m}$) were Soxhlet extracted for 24 h into 150 mL organic solvents (DCM:Acetone,1:1). The extracts were concentrated down to approximately 15 mL using a rotary vacuum evaporator (BÜCHI R-250, Germany). Before column chromatography, the extracts were concentrated, and the solvent was changed to approximately 2 mL of cyclohexane under a gentle flow of clean nitrogen gas (N-EVAP 112, USA). To clean the extracts, chromatography columns ($d = 1\text{ cm}$, $h = 40\text{ cm}$) were evenly filled with slurry packing of 10 g silica gel (dried at $160\text{ }^{\circ}\text{C}$ for 16 h) in 50 mL DCM. The top of the columns was covered with 1 g anhydrous sodium sulfate (dried at $400\text{ }^{\circ}\text{C}$, 4 h). Then, the columns were conditioned by passing 40 mL of pentane through them. The extracts were loaded on the top of the columns using clean Pasteur pipettes and allowed to pass through the columns. Each column was washed by 25 mL pentane, and the resulted fraction was thrown away properly in a waste container. Finally, PAHs were collected by elution with 25 mL DCM-pentane (v/v, 2:3, 2 mL min^{-1}). This fraction was concentrated to a volume of approximately 5 mL, and the solvent changed to acetonitrile after blowing down with a gentle stream of clean nitrogen (USEPA (United States Environmental Protection Agency), 1996). The final volume of the extracts was carefully set at 1 mL. In addition, the dead parts of a coral sample (*Acropora valida*) were ground to powder using a mortar and pestle, and the PAH extraction was performed following the same procedure previously described for the sediments.

The EPA 16 priority PAH concentrations were measured in the surface sediments of the Chabahar Bay. Naphthalene, (Na); Acenaphthylene, (Acy); Acenaphthene, (Ace); Fluorene, (Fl); Phenanthrene, (Ph); Anthracene, (An); Fluoranthene, (Flur); Pyrene, (Py); Benz(a)Anthracene, B(a)A; Chrysene, (Ch); Benzo(b) Fluoranthene, B(b)F; Benzo(k)Fluoranthene, B(k)F; Benzo(a)Pyrene, B(a)P; Indeno(1,2,3-cd)Pyrene, Indeno; Dibenz(a,h) Anthracene, D

(a,h)A; and Benzo(ghi)Perylene, B(ghi)P were the analyzed compounds (Table 1). An Agilent/HP 1100 series HPLC system equipped with UV and Fluorescence detectors was used for instrumental analysis. The initial mobile phase was 50% acetonitrile and 50% Milli Q-water with a flow rate of 1 mL min^{-1} , which changed to 100% acetonitrile in 10 min. The injection volume was $20\text{ }\mu\text{L}$. Replicate samples, certified reference materials (IAEA-417), and procedural blanks were used as quality control programs. Reproducibility and recovery of the analytical procedure were acceptable (Table 1). Quantitative analysis was performed by constructing 6-point external calibration curves using PAH standard solutions. Satisfactory linearity was obtained with R square values above 0.99.

PAH standard solutions (16 USEPA PAHs) were purchased from Sigma-Aldrich, USA. The aforementioned neutral silica gel (ASTM, 70–230 mesh) and anhydrous sodium sulfate were purchased from Merck (Germany). All consumed solvents were HPLC grade (CALEDON, Canada).

Sediment analysis was performed to evaluate the organic matter levels and grain size distribution (Table 1). Total organic matter (TOM) was measured by further weighting approximately 1.5–2 g of dried sediments ($< 250\text{ }\mu\text{m}$) after placing the samples in a furnace (NABERTHERM, P330, Germany) at $550\text{ }^{\circ}\text{C}$ for 4 h. Total organic carbon (TOC) contents were assumed to be approximately half of the calculated TOM levels (Wang et al., 2011; Gaspare et al., 2009).

Sub-samples of sediments (1 g) were soaked with 20 mL of 3% tetra-sodium diphosphate decahydrate (Merck, Germany) to perform granulometric analyses. The soaked sediments were stirred using magnet bars for 12 h to disintegrate the colloidal particles (Aghadadashi et al., 2016). Finally, the slurries were added into a laser-scattering particle size distribution analyzer (HORIBA LA-950, Germany), and the size distribution of the examined sediments was determined. Statistical analyses including mean and median levels, coefficient of variation (CV) values, and skewness and correlation analysis of the resultant dataset were performed using SPSS 19.0 software package.

It is worth noting that in aquatic environments, the levels of hydrophobic eco-pollutants are closely related to the rate of release and

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