Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Polycyclic aromatic hydrocarbons (PAHs) in sediment and sea urchin (*Echinometra mathaei*) from the intertidal ecosystem of the northern Persian Gulf: Distribution, sources, and bioavailability

Mehrzad Keshavarzifard*, Farid Moore, Behnam Keshavarzi, Reza Sharifi

Medical Geology Research Center, Department of Earth Sciences, Faculty of Sciences, Shiraz University, Shiraz, Iran

ARTICLE INFO

Keywords:
Polycyclic aromatic hydrocarbons (PAHs)
Sediment
Sea urchin (*Echinometra mathaei*)
Bioavailability
Intertidal zone
Persian gulf

ABSTRACT

The distribution, sources and bioavailability of polycyclic aromatic hydrocarbons (PAHs) in sediment and sea urchin (*Echinometra mathaei*) from the intertidal zone of the northern Persian Gulf were investigated. Total PAH concentrations varied from 12.8 to 81.25 and from 16.7 to 35 μg Kg^{-1} dry weight in sediment and *Echinometra mathaei*, respectively. The PAH concentrations can be classified as low. Source identification and apportionment using diagnostic ratios and principal component analysis demonstrate that the combustion of fossil fuels, road traffic, combustion of natural gas and biomass, and oil spill could be considered as the main sources of PAH contamination. The first PAH biota-sediment accumulation factors (BSAF) data from sediment to *Echinometra mathaei* in the intertidal zone of the northern Persian Gulf were calculated, indicating accumulation of both lower and higher molecular weight PAHs, with a preferential accumulation of lower molecular weight PAHs.

The Persian Gulf has approximately 60% of the world's proven oil reserves and is visited by two-thirds of the world's marine petroleum traffic, while it just covers < 0.1% of the marine surface of the world (Khan et al., 2002). The Persian Gulf is a unique habitat for many biota species including birds, fishes, bivalves, etc. In addition, to ecological richness, there is also evidence of incomplete combustion of fossil fuels, urban runoff, petrol and oil spills, petroleum refinery and industrial discharges from riparian states (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, and the United Arab Emirates), which are the most likely sources of environmental degradation in the area (Delshab et al., 2017; Nozar et al., 2014). These eight riparian states include economically developing countries. Rapid agricultural, industrial, and urban development in the region has also resulted in environmental contamination.

The rapid growth of the Persian Gulf region poses increasing risks to the neighboring aquatic ecosystem. One of the main concerns is the direct input, and long- and short-range atmospheric transport of polycyclic aromatic hydrocarbons (PAHs). PAHs are an important class of persistent organic contaminants with two or more benzene rings in various arrangements (Neff, 1979). These contaminants are persistent in the environment, hydrophobic, bioaccumulative and toxic. PAHs also have mutagenic, hepatotoxic, teratogenic and carcinogenic effects. The PAH compounds originate from petroleum and petroleum products (petrogenic origin) are typically characterized by low molecular weight (LMW) PAHs with two- and three-ring, while PAH compounds originate from fossil fuels and biomass incomplete combustion at high temperature (pyrogenic PAHs) are generally characterized by high molecular weight (HMW) PAHs with four- to six-ring (Dhammapala et al., 2007; Ergut et al., 2006). PAHs in the atmospheric environment are deposited in soil and sediment via dry and wet deposition. PAHs that reach the aquatic ecosystem can easily combine with suspended particles and be deposited in the sediment (Keshavarzifard et al., 2016; Keshavarzifard et al., 2014). In the literature, it is pointed out that sediment is an important reservoir for organic pollutants, reflecting concentrations and spatial distribution of pollutants (Bakhtiari et al., 2009; Keshavarzifard et al., 2017a; Keshavarzifard and Zakaria, 2015).

The monitoring of organic contamination in the aquatic ecosystems has been accomplished in different areas of the world (Alkhadher et al., 2015; Alkhadher et al., 2016; Ebrahimi-Sirizi and Riyahi-Bakhtiyari, 2013). PAH compounds released into aquatic ecosystems can be accessible and available to aquatic living organisms via different uptake pathways. Benthic organisms can come in contact with sediment as an enriched source of PAHs, therefore can accumulate PAH compounds and transport them in the food chain (Keshavarzifard et al., 2017b; Keshavarzifard et al., 2017c). The portion of pollutants, which could be accumulated (through pore water, soil and food) or transformed by organisms, is normally called available or bioavailable pollutants. Among benthic organisms, invertebrates have a higher capability of

* Corresponding author.
E-mail address: mehrzad17@shirazu.ac.ir (M. Keshavarzifard).

http://dx.doi.org/10.1016/j.marpolbul.2017.09.008
Received 17 April 2017; Received in revised form 25 August 2017; Accepted 6 September 2017

accumulating contaminants compared to vertebrates, therefore they are widely used to evaluate the bioavailability of contaminants in aquatic ecosystems (Baumard et al., 1999; Keshavarzifard et al., 2017c; Mirsadeghi et al., 2013). Due to the lipophilic characteristics of PAH compounds, they can be absorbed and accumulated in fatty and lipid-rich organs and tissues. Therefore, the monitoring of different species of PAHs in different environmental matrices such as biota and sediment is crucial to ensure the required quality standards and assess the bioavailable portion of PAH compounds. Furthermore, benthic organisms have been widely used as sentinel indicators of aquatic pollution.

The intertidal zone or littoral zone is the area of foreshore and seabed of the marine and ocean aquatic environment, which is between the low point and the high point of the tide. Living organisms (including cnidaria (stinging animals), arthropod, mollusks, echinoderms and fish) in the intertidal zone are small and mostly are uncomplicated. One type of benthic organisms living in the intertidal zone of Persian Gulf is sea urchin (*Echinometra mathaei*). This organism plays a key role in benthic communities of coastal waters and can be used as an indicator for contaminants in aquatic ecosystems.

In addition, there are still limited systematic investigations on PAHs in marine organisms and in sediment matrices as well as assessment of their effects on ecological security and human health in the Persian Gulf. In this study, the concentrations of sixteen United States Environmental Protection Agency (USEPA) PAHs in sea urchin tissues were normalized to their concentrations in sediment samples to assess the biota–sediment accumulation factor (BSAF). To date, the concentrations and bioavailability of PAH compounds to sea urchin from sediment in the intertidal zone of the Persian Gulf have not been well documented. Therefore, this research addresses this gap by determining the composition, distribution, and sources of parental PAHs in sediment and *Echinometra mathaei* (*E. mathaei*) in the intertidal zone of the northern part of the Persian Gulf and also evaluates that which compounds of PAHs are more available to be accumulated by *E. mathaei*.

In September 2016, *E. mathaei* and surface sediment samples were collected at five stations from the intertidal zone of the northern part of the Persian Gulf (Fig. 1 and Table 1). Twenty-five individual *E. mathaei* of approximately the same size were collected from each station. The samples were immediately placed in a cooler box containing dry ice and rapidly transported to the laboratory to be kept in deep freeze condition. All samples were freeze dried using a vacuum freeze-drier and stored at − 20 °C until further analysis (Magam et al., 2015).

In brief, each sample (2 g) was spiked with surrogate standards (naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12}), mixed with 100 mL of dichloromethane, and then extracted with soxhlet apparatus. After that, the extract was concentrated using a rotary evaporator to 1 mL and then transferred to an auto-sampler vial. The sixteen USEPA priority PAHs with 2 rings (naphthalene (Nap)); 3 rings (acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant)); 4 rings (fluoranthene (Fluo), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Chr)); 5 rings (benzo[*e*]Pyrene (BeP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP)); and 6 rings (indeno[1,2,3-*cd*]pyrene (InP), dibenzo[*a*, *h*]anthracene (DBA), and benzo[*ghi*]perylene (BgP)) were identified and quantified in surface sediment and sea urchin samples in the laboratory of Isfahan using High-Performance Liquid Chromatograph (HPLC) with Fluorescence Detector (column; 4.6 × 50 mm, 1.8-μm). The flow rate was 0.8 mL/min and the temperature was set at 35 °C.

The carbonate of each sediment sample was removed by adding 1 mL HCl (1 M) to 1 g of freeze-dried and grounded sediment sample (Nelson and Sommers, 1996). The sample was dried at 100 °C in an oven, after which the TOC percentage was measured with a LECO CR-412 Carbon Analyzer (with a furnace temperature of 1350 °C; O_2 boost time of 1 min). A multi-wavelength particle size analyzer (model LS 13320) was used to determine the sediment grain size.

The bioavailability of PAHs in the environment can be assessed by comparing the concentrations of individual PAHs in benthic organism to those in sediment, expressed as the biota-sediment accumulation factor (BSAF) model. BSAF (Eq. (1)) is the ratio of PAH concentration in the biota (C_b) to that in sediment (C_s) (Cortazar et al., 2008; Keshavarzifard et al., 2017c).

$$\mathrm{BSAF} = \frac{C_b}{C_s} \tag{1}$$

The relative biota-sediment accumulation factor (Eq. (2)) (Baumard et al., 1999) is used to evaluate the difference between sampling stations, where RBSAF is the relative bio-concentration factors (%); BSAF is the biota–sediment accumulation factor for each PAH compound; and ΣBSAF is the sum of 16 individual BSAFs for 16 USEPA PAHs.

$$\mathrm{RBSAF} = \frac{\mathrm{BSAF}}{\sum \mathrm{BSAF}} \times 100 \tag{2}$$

This model is used to predict PAHs transfer and accumulation from sediments to benthic organisms based on equilibrium partitioning for establishing sediment quality criteria. PAH concentrations in benthic organisms may be predicted from partitioning between organism lipid fraction and sediment organic carbon. The PAH concentrations in benthic organisms were calculated as per Eq. (3) (USEPA, 1998).

$$\mathrm{Cp} = \frac{C_s \times f_{\mathrm{lipid}} \times \mathrm{BSAF}}{\mathrm{TOC}} \tag{3}$$

Where Cp is the predicted concentration of each individual PAH compound in benthic organisms, C_S is the concentration of each

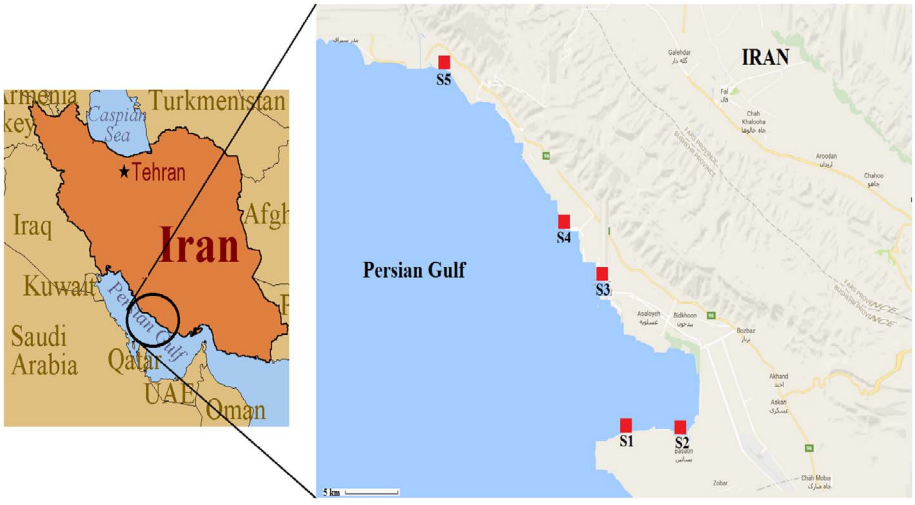

Fig. 1. Sampling stations.