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FULL LENGTH ARTICLE

Distribution and sources of *n*-alkanes and polycyclic aromatic hydrocarbons in shellfish of the Egyptian Red Sea coast

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Abstract Aromatic hydrocarbons and *n*-alkanes were analyzed in shellfish collected from 13 different sites along the Egyptian Red Sea coast. All samples were analyzed for *n*-alkanes (C_8–C_{40}) and polycyclic aromatic hydrocarbons (EPA list of PAHs). *n*-Alkanes in shellfish samples from 13 locations were found to be in the range of 71.0–701.1 ng/g with a mean value of 242.2 ± 192.1 ng/g dry wt. Different indices were calculated for the *n*-alkanes to assess their sources. These were carbon preference index (CPI), average chain length (ACL), terrigenous/aquatic ratio (TAR), natural *n*-alkane ratio (NAR) and proxy ratio (P_{aq}). Most of the *collected samples of n*-alkanes were discovered to be from natural sources. Aromatic hydrocarbons (16 PAHs) from 13 sites varied between 1.3 and 160.9 ng/g with an average of 47.9 ± 45.5 ng/g dry wt. Benzo(a)pyrine (BaP), a cancer risk assessment, was calculated for the PAHs and resulted in ranges between 0.08 and 4.47 with an average of 1.25 ng/g dry wt.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes are marine environment chronic constituents and their concentrations have considerably increased due to anthropogenic activities. This caused undesirable effects, especially in coastal areas adjacent to highly populated urban zones. *n*-Alkanes consist of saturated and straight carbon chains of C_6–C_{40} which contain even and odd carbon numbers that indicate anthropogenic and natural sources of hydrocarbon. The United Nation Environmental Program (UNEP) gave guidelines to identify the levels of harmless (< 10 μg/g) and harmful (> 10 μg/g) *n*-alkanes in marine sediment.

PAHs are organic compounds that result from the partial combustion of organic matter (pyrolytic), and oil and its derivative (petrogenic) sources. Pyrogenic PAHs are characterized by the occurrence of PAHs that carry a heavy set of molecular weights, while petroleum hydrocarbons are dominated by PAHs of the lowest molecular weight (Neff, 1979). They are widely dispersed in the marine environment, particularly in harbors, dockyards, marinas, estuaries and other shallow coastal areas with anthropogenic inputs (El Nemr, 2005,

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2008, 2011). PAHs have been subjected to remediation studies and risk assessment, due to their mutagenic and carcinogenic effects. Therefore, PAHs tend to swiftly be absorbed into the particles and fat tissues of filtrating organisms like mussels and oysters (Zemanek et al., 1997). PAHs are easily absorbed by living beings Due to their high octanol/water partition coefficient (K_{ow}). PAHs can be metabolized into compounds that are detectable in fluids and can be used as biomarkers of the exposure to the PAHs (Nudi et al., 2010). The evaluation and comparison levels of PAHs and their temporal changes in a marine coastal region are very important from an environmental point of view (El Sikaily et al., 2003; Salem et al., 2014). Mussels have been widely used for the monitoring of toxic pollutant levels in coastal environment (Saad et al., 2015).

The aim of the present work is to investigate the precedence of *n*-alkanes and PAHs in the collected shellfish from the Red Sea coast (Egypt) and also, to determine the most polluted regions, diagnose the sources of these pollutants and calculate the cancer risk assessment of these compounds to draw a complete picture of the pollution in these regions and then try to find the best way for treatment.

Materials and methods

The sampling cruise took place in August 2011, that covered about 1700 km (Fig. 1). 13 sampling locations were selected to coverage the studied area. The collected shellfish species and their lipid and water contents are listed (Table 1). There was a wide variation of collected species due to the diversity of the environmental conditions and the biodiversity of the sampling locations. Flesh of the shellfish samples of similar species in each site was scraped out of the shell and dissected. All the soft tissues of the 30–40 individual shellfish were mixed well into a composed sample and then dried in an open oven at 50 °C. The dried sample (5 g) was extracted in methanol (200 ml) for 8 h with Soxhlet extractor. 0.8 M KOH (15 ml) and distilled water (25 ml) were added to the extraction. Then the reflux continued for two more hours to saponify the lipids. The mixture obtained was extracted three times with *n*-hexane (50 ml, each) in a separatory funnel. The *n*-hexane was then combined and sodium sulfate anhydrous was added, filtered and finally concentrated under vacuum down to about 10 ml at 40 °C, followed by a concentration using nitrogen gas streaming 1 ml volume. A column chromatography was prepared using silica gel (10 g), followed by aluminum oxide (10 g) and finally 1 g of sodium sulfate anhydrous (Kelly et al., 2000; El Nemr et al., 2004, 2012).

The concentrated extract (1 ml) was sequentially eluted with 25 ml of *n*-hexane belonging to the fraction of *n*-alkaines (F1), then 50 ml of dichloromethane-*n*-hexane (1:9) belonging to the PAHs fraction (F2). The two fractions (F1 and F2) were concentrated to 1 ml each for the GC–MS analysis.

The blanks of 500 ml of solvent that were used were concentrated to 1 ml and then analyzed by gas chromatography as previous reported by El Nemr et al., 2014. Gas chromatography Shimadzu Class LC-10 equipped with Shimadzu Autoinjector, split/splitless injector and a fused silica capillary B-5 (30 m, 0.32 mm, 0.17 μm) 100% dimethylpolysiloxane. The temperature was programed from 60 to 300 °C with a rate of 5 °C min^{-1} and was then maintained at 300 °C for 25 min.

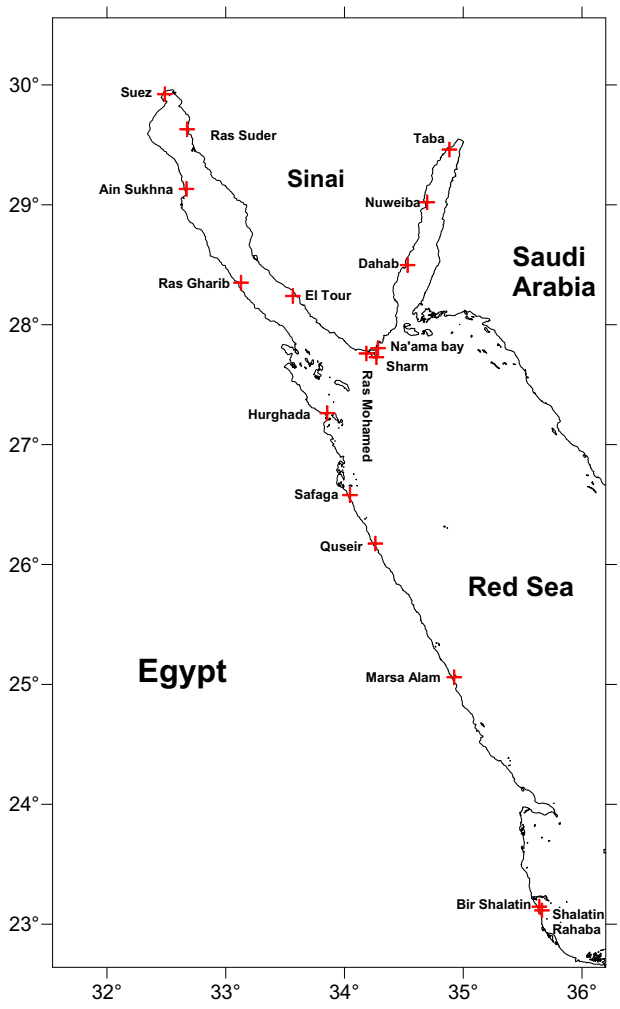

Figure 1 Map of the samples location along the Suez Gulf, the Aqaba Gulf and the Red Sea proper.

The injector and detector temperatures were set at 280 and 300 °C, respectively. Helium was used as the carrier (1.5 ml min^{-1}) and nitrogen as the make-up (60 ml min^{-1}) gas. 2 μL volume of each sample was injected in the split mode (10:1) and the purge time was one minute. Identification and quantification of 16 PAH compounds were based on matching their retention time with a mixture of PAH standards. Compound identification was confirmed by GC coupled to mass spectrometry (Trace DSQ II Ms. with capillary column: Thermo TR-35 MS Mass Selective Detector).

To validate the analytical method used in this study and the accuracy of the results, 6 analyses were made on the PAH compounds in the reference materials, IAEA – 406 (organochlorine compounds, petroleum hydrocarbons in tuna homogenate sample). The recovery efficiencies ranged from 95.22% to 98.93% for IAEA – 406 (Table 2).

Results and discussions

Distribution and sources of ***n****-alkanes*

The sampling locations for the shellfish and their types are listed in Table 1 and the concentrations of *n*-alkanes are