

Assessment of the Sources of Polycyclic Aromatic Hydrocarbons in Mousa Inlet by Molecular Ratios

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are globally distributed environmental contaminants which attract considerable attention because of their known toxic and bioaccumulative effects on animals. They are among the most carcinogenic, mutagenic and toxic contaminants found in most coastal areas of the world. PAHs with two rings are more soluble in water and more volatile than PAHs with three rings or more, which have low solubility in water and a low vapor pressure. As molecular weight increases, the solubility and vapor pressure of PAHs decrease, while the carcinogenicity increases. Thus, heavier PAHs become more toxic and lipophilic. Sixteen individual PAH compounds have been identified as high-priority pollutants by the United States Environmental Protection Agency (USEPA) due to their toxic, mutagenic and carcinogenic properties. Although PAHs in the environment come from both natural and anthropogenic sources, the major sources of PAHs are anthropogenic. PAHs may be generated by three main processes: combustion of organic matter at very high temperature; release of petroleum; and diagenetic processes (degradation of organic matter). Only pyrolytic and petrogenic PAHs have quantitative importance in marine ecosystems and are the only ones addressed here. Incomplete combustion of organic matter at high temperature will release PAHs to environment as airborne particulates, or as solid or liquid byproducts of pyrolytic processes. This usually produces high molecular weighted PAHs. Low molecular weighted PAHs come into aquatic system through accidental leakage of oil spills or natural seepage. Several methods have been used to identify the sources of PAHs in marine ecosystems, one of which includes paired isomeric ratios.

The objective of this study is to determine the sources of PAHs through the ratios of Low Molecular Weight/High Molecular Weight, Phenanthrene/Anthracene, Fluoranthene/pyrene and Benzo(a)anthracene/Chrysene.

Materials and Methods

Mousa Inlet is located in the northwest of the Persian Gulf. In October 2009, 3 locations were selected in Mousa Inlet, namely, Jafari (S1), Ghanam (S2) and Ahmadi (S3). Sampling of subsurface sea water, phytoplanktons, zooplanktons, and two types of fish, mullet (*Liza abu*), and sea bream (*Acanthopagrus latus*) were carried out in each station.

Water samples were collected from each site using prewashed dark glass bottles. Samples were immediately refrigerated, avoiding exposure to light, and rapidly transported to the laboratory to be kept refrigerated until the extraction procedure begins.

Phytoplankton samples were collected using plankton net with 55 mm mesh. Zooplankton samples were collected using plankton net with 100 mm mesh.

The plankton samples were retrieved frozen (-20°C) in prewashed glass jars, and transported to the laboratory. The fish were collected by trawling (fish trawl net). Immediately after capturing, the fish were put in aluminum foils, labeled, kept in ice boxes and brought to the laboratory for chemical analysis. In laboratory, the fish samples were stored at -20°C before analysis.

About 2 grams of each organism samples were submitted to saponification with 10 ml of 1 M KOH in an ethanol solution for 3 hours at 80°C. Then, 20 ml of cyclohexane was added. Samples were mixed by a shaker for 20 minutes and stabled for 10 minutes. The hexanic phase was recovered and the polar mixture was rinsed twice with two aliquots of cyclohexane. The extracts were filtered through filter paper, filled with sodium sulphate anhydrous and run on a column filled with Florisil. The eluates were dried under a flow of air and dissolved in 1 ml of acetonitrile before the analysis. The sea water samples were filtered through filter paper. Afterwards, 10 ml of cyclohexane was added to 20 ml of each sample. Other phases of extraction were the same as other samples. Quantitative analysis of PAHs was carried out using HPLC equipped with UV detector. The software used was Chromgate, version 3.17. PAHs were separated at ambient temperature using a 25 cm long C18 inverse column and a gradient elution program with a flow rate of 2 ml/min. At the beginning of the mobile phase, water was 60% and acetonitrile was 40% in HPLC. Acetonitrile was then gradually changed to 100% in 20 min, held at 100% for 27 min, and then decreased to the initial phase in 30 min.

Statistical data analysis was performed with Excel and SPSS (ver. 16). Normality of data was assessed by means of Kolmogorov-Smirnov test.

Discussion of results

The PAH concentrations of samples for 3 stations were obtained. In this study, the ratios of low molecular weight/high molecular weight (LMW/HMW), phenanthrene/anthracene (Phe/Ant), fluoranthene/pyrene (Fla/Pyr) and chrysene/benzo(a)anthracene (Chr/BaA) were assessed.

Petrogenic sources are characterized by the dominance of low molecular weight aromatic compounds. High molecular weighted PAHs are mostly from pyrolytic origins. Phenanthrene is a more thermodynamically stable tricycle aromatic isomer than anthracene. Petroleum contains more Phenanthrene than anthracene. Thus, petrogenic PAHs are generally characterized by high Phe/Ant ratio. On the contrary, high temperature processes can result in low Phe/Ant ratio. Therefore, the ratios of LMW/HMW < 1, Phe/Ant < 10, Fla/Pyr > 1, Chr/BaA < 1 tend to indicate that the PAH contamination has pyrolytic origin and is from combustion processes and LMW/HMW > 1, Phe/Ant > 10, Fla/Pyr < 1, Chr/BaA > 1 indicate petrogenic originated pollution.

The results showed that for all samples, values of LMW/HMW lower than 1 (between 0.05 and 0.67) except water sample of S2 (1.20), indicated pyrolytic originated pollution.

In order to better characterization of PAH distribution, other molecular indices were used. For all samples, values of Phe/Ant were lower than 10 (between 0.18 and 7.95). This indicates pyrolytic originated pollution. Ratio of Fla/Pyr (between 0 and 1.44) indicates that these 3 stations were contaminated by both petrogenic and pyrolytic PAHs. Finally, the results showed that for the majority of samples (except for 2 samples), values of Chr/BaA lower than 1, indicate pyrolytic originated pollution.

Therefore, PAHs in these 3 locations originated from both pyrolytic and petrogenic inputs, predominantly from pyrolytic origin. Mousa Inlet is highly industrialized and includes Imam Khomeini and Razi petrochemical organizations. Local sources rather than long-range air transportation were responsible for PAH contamination. This would originate from fossil fuel combustion particulates emitted by commercial ships. Combustion-derived PAHs in the atmosphere can enter the water column directly by gaseous exchange across the air-water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall, and indirectly by urban runoff. Domestic and industrial wastewater and sewage are other sources of PAHs in this area. Accidental spills of crude oil and its refined products can result in petrogenic PAHs which were more observed in water and plankton samples, because PAHs with low molecular weight are more water soluble.

Conclusion

The ratios of low molecular weight/high molecular weight (LMW/HMW), phenanthrene/anthracene (Phe/Ant), fluoranthene/pyrene (Fla/Pyr) and chrysene/benzo(a)anthracene (Chr/BaA) showed that PAHs in Mousa Inlet originated from both pyrolytic and petrogenic origins while pyrolytic sources are dominated.

Key words

Polycyclic Aromatic Hydrocarbons, Molecular Ratios, Source, Mousa Inlet

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