

Source Identification of Hydrocarbons in Surface Sediments of Mangrove Forests of Khoran Strait, Persian Gulf

Zohreh Ebrahimi Sirizi¹, Alireza Riyahi Bakhtiyari^{2*}, Sanaz Ghaffari³

1. MSc, Department of Environment, School of Natural Resources, Tarbiat Modares University, Iran (zohrehebrahimi12@yahoo.com)

2. Assistant Professor, Department of Environment, School of Natural Resources, Tarbiat Modares University, Iran

3. PhD Candidate, Department of Environment, School of Natural Resources, Tarbiat Modares University, Iran (sanaz.gh64@yahoo.com)

Received: Nov., 2013

Accepted: Aug., 2014

Expanded Abstract

Introduction

Persian Gulf is one of the most important water pathways in the world. It has been heavily developed for crude oil production, transportation and export. It is clear that such activities result in contamination of the marine environment by petroleum and petroleum production industries. The Persian Gulf represents a highly stressful environment due to prevailing natural conditions and development pressures along its coastline. It has approximately two-thirds of the world's proven oil reserves and currently account for approximately one-fourth of the world oil production. The Persian Gulf is greatly intensified by oil spills with accidental discharges of various magnitudes.

One of the most valuable ecosystems of Persian Gulf is mangrove forests. Mangroves are perhaps the dominant and the most important intertidal habitat along tropical and subtropical coastlines and estuaries. These rich ecosystems are located in the areas of high risk in acute or chronic petroleum pollution. Furthermore, high levels of hydrocarbons may be expected to remain in mangrove sediments after occurrence of petroleum contamination because these environments are not favorable for hydrocarbon depletion by sediment transport or degradation by bacteria. These zones are critical areas in which valuable biological resources and rich biodiversity are threatened. These regions are continually exposed to anthropogenic contamination of hydrocarbons from different sources. Unique features of mangrove such as high productivity, abundant detritus and rich organic carbon may make it an advantageous site for uptake and preservation of hydrocarbons.

The studies about distribution and concentration of hydrocarbons were mainly performed in marine water and sediments. There are scarce studies carried out to assess the distribution and source of hydrocarbons in mangrove ecosystems. Straight chain alkanes (*n*-alkanes) and polycyclic aromatic hydrocarbons (PAHs) are common biomarkers that have been applied to assess the petroleum pollution in the marine environment. Therefore, the primary objective of this study is to investigate hydrocarbons in the mangrove forests of Khoran Strait (Persian Gulf) as well as to identify possible hydrocarbon sources in the area.

Materials and Methods

In order to determine the source and concentration identification of hydrocarbons in the Khoran Strait, 17 surface sediments were collected from mangrove forest of this strait. They were then analyzed for *n*-alkane and PAH compounds.

Sampling was conducted during low tide and any water was not overlying the sediments. Surface sediment samples were collected by using stainless spoon and then transferred into a stainless steel container to reduce any contamination. The containers were labeled and placed in icebox at 4°C then transportation to the laboratory for further analysis. The samples were stored in the Cold Room (-20°C) until further analysis.

The collected sediment samples were freeze dried for 3 days to get rid of any water contained in the samples. After the samples were freeze dried they were then stored frozen before proceeding with the analysis of the hydrocarbons.

About 10 g of each sample (dry weight) was used for extraction of hydrocarbons. The samples were extracted

* Corresponding Author: Tel: +98 9126798768

E-mail: ariyahi@gmail.com

with a soxhlet extractor using 320ml dichloromethane (DCM) for 8 hours. In order to eliminate any sulfur in the samples, a few of copper chips were added into the samples and left overnight.

Volume of the solvents was reduced using rotary-evaporator to approximately 1 ml. The extracts were transferred onto the top of a 5% H₂O-deactivated silica gel column. The column was rinsed with 20ml dichloromethane/hexane (1:3, v/v). In this step, most of the organic pollutants including *n*-alkanes, PCBs, LABs and PAHs were separated from other polar compounds. The eluted sample was reduced in volume by rotary evaporator for the second step of column chromatography. Fully activated silica gel was used in the 2nd step column chromatography. The concentrated sample from the first column was added to the second column and charged with 4ml of hexane to get alkane fraction. To get PAHs fraction 14ml dichloromethane/hexane (1:3, v/v) was used. All fractions were evaporated to approximately 1ml and then transferred to glass ampoule and evaporated to dryness under gentle stream of nitrogen and alkane samples. They were re-dissolved into 100 μ l iso-octane and PAHs samples were re-dissolved into 100 μ l *p*-terphenyl-d₁₄ as an IIS (Internal Injection Standard) for PAHs.

Samples were analyzed by Gas Chromatography – Mass Spectrometry (GC – MS) using an Agilent Technologies 5975C quadrupole mass spectrometer coupled with an Agilent 7890A gas chromatograph. A 30m fused silica capillary column with 0.25 of internal diameter and 0.25 μ m film thickness, helium was used as carrier gas in the analysis.

Results and Discussion

In this study, *n*-alkanes in range of *n*-C₁₄-*n*C₃₃ and twenty-three compounds of PAHs were investigated. Total concentration of *n*-alkanes (mean \pm SE) was 2802 \pm 334 μ g/g and for PAHs was 1.918 \pm 0.267 μ g/g (dry weight).

The diagnostic hydrocarbonic ratios were used for source identification of hydrocarbon in this regain. The sources of PAHs, whether from pyrolytic or from petrogenic origins, may be determined by ratios of individual PAH compounds based on properties in PAH composition and distribution pattern as a function of the emission source. The molecular patterns produced by each source, however, are like fingerprints, which make it possible to hypothesize which processes produce PAHs. For source identification of PAHs, ratio values of phenanthrene/anthracene (Phe/Ant) are widely employed. Pyrogenic source of PAHs are usually characterized with low amount of this ratio. Generally Phe/Ant ratios >10 and Phe/Ant ratios <10 demonstrated petrogenic and pyrogenic source, respectively. In the present study, mean value of this ratio was 19 and this indicates that the major source of PAHs in this region is petrogenic.

Ratio of Fluoranthene/Pyrene is one of the ratios that widely employed as characteristic tools. Similarly, Flr/Pyr ratios >1 and <1 indicate pyrogenic and petrogenic sources, respectively. The mean value of this ratio was 0.48. This suggests strong petrogenic input.

The benzo (a) anthracene/chrysene (BaA/Chr) ratio has also been suggested to identify PAH origins. This ratio tended to increase as petrogenic contribution decreased. In the present study, the mean value of this ratio was 0.22 and PAHs of molecular mass 178 and 202 are widely used to distinguish between petrogenic and pyrogenic sources. For mass 178, ratio of anthracene to anthracene plus phenanthrene (An/ An+Ph) are employed. Ratio < 0.10 and >0.10 indicate petrogenic and pyrogenic sources, respectively. In this study, the value of this ratio was 0.05 and the major source of PAHs in this region is petrogenic.

For mass 202, ratio of fluoranthene to fluoranthene plus pyrene (Fl/Fl+Py) has been suggested to characterize the source of PAHs. The value 0.40 for this ratio specified the petrogenic/pyrogenic transition point. Most of the petroleum samples have (Fl/Fl+Pyr) ratio below 0.40 while those with most combustion produced in PAHs are above 0.40. In this investigation, the mean value of this ratio was 0.35 and this indicates petrogenic source.

Among PAHs with molecular mass of 228, the ratio of benzo (a) anthracene to the sum of the benzo(a)anthracene and chrysene, BaA/BaA+Chr is also declarative of the PAHs sources. Values lower than 0.20 for this ratio suggests a petrogenic source, whereas values from 0.20 to 0.35 indicates a petroleum or combustion source, and any values higher than 0.35 signify a combustion source. For the present study the mean value of this ratio was 0.16. Accordingly, petrogenic sources may be identified by a ratio of indeno (1,2,3-cd) pyrene to the sum of indeno (1,2,3-cd) pyrene and benzo [g,h,i] perylene, IP/(IP+Bghi), lower than 0.20. A ratio between 0.20 and 0.50 may suggest liquid fossil fuel combustion, and a ratio higher than 0.50 indicates biomass and coal combustion. In this study, the mean value of this ratio was 0.17.

The samples were also calculated using methylphenanthrene/phenanthrene (MP/P) ratio to determine the source of PAHs. The value of less than 1 is from the combustion sources and more than 1 is consisted of petroleum sources. In the present study, the mean value of this ratio was 2.

The ratio of LMW/HMW is also employed for identification of PAHs source. The high amount of this ratio strongly indicated petrogenic source. The mean value of this ratio was 19.78, this amount is rather high.

We employed some ratios for source identification of *n*-alkanes in Khuran strait. Wide range of CPI, TAR and U/R for sediment samples of Khuran strait indicated that there are combined sources (biogenic and

petrogenic sources) for organic matter of surface sediments. Therefore, predominate petrogenic source in some of the Middle part stations and biogenic in some others could be explained for these reasons. Pr/Ph, Pr/ n -C₁₇ and Ph/ n -C₁₈ ratios are close to 1 and indicate background petrogenic source in surface sediments of Persian Gulf mangrove forests. In summary, the results showed that the main source of hydrocarbons in this region is mixed source of biogenic and petrogenic origins.

Keywords: hydrocarbon, Khoran Strait, mangrove forests, n -alkanes, PAHs.

Archive of SID