Polycyclic aromatic hydrocarbons in surface sediments of the open Aegean Sea: Contribution of maritime traffic

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were investigated in surficial sediments collected from 39 stations in the open Aegean Sea, in order to assess their occurrence, distribution and major sources. Total PAH concentrations were generally low, comparable to those reported in relatively unpolluted marine areas. The highest values were recorded in the northern part Aegean Sea, which apparently receives more anthropogenic inputs both from continental runoff and atmospheric deposition. Several diagnostic criteria were used to investigate PAHs' origin. Their molecular profile reveals contributions from both pyrolytic and petrogenic sources, with their relative importance displaying significant regional variability. Phenanthrenes, which are known to mostly originate from unburned fossil fuels were found in percentages higher than 50% in the Central part of Aegean Sea and their occurrence was correlated with the marine traffic in the area. The PAH concentrations are significantly correlated with the total organic carbon content of sediments, which indicates that the latter exerts an important control on their transport and ultimate accumulation in sediments.

Keywords: PAH, priority pollutants, sediments, open Aegean Sea

1. Introduction

PAHs are widespread components in marine systems and have been classified as priority pollutants by international environmental agencies (EPA-US, EEA-EU). Their formation and release in the environment is mainly related to various anthropogenic activities including pyrolysis/combustion of organic material (biomass burning and incomplete combustion of fossil fuels) and release of petroleum products, although PAHs of biogenic origin may also occur in environmental samples. Due to their hydrophobic nature, PAHs in the marine realm tend to associate with particles and this is considered as the major mechanism of their downward transport through the water column and subsequent accumulation in sediments (reviewed by Farrington and Takada, 2014).

The Aegean Sea is an active area with unique physiographic and hydrodynamical characteristics. Open marine sites of the Aegean Sea, receives substantial amounts of petroleum discharges, mainly along shipping routes, as a result of merchant shipping and oil transportation, while aeolian transport is also of major importance for the delivery of anthropogenic PAHs (Castro-Jimenez et al., 2012).

2. Sampling and Chemical Analysis

Surface sediments (top 1-cm) were collected from 39 stations in the open Aegean Sea during various oceanographic cruises conducted between 1996 and 2014. For the analysis, freeze-dried sediments were initially spiked with a mixture of perdeuterated internal standards ([$^2H_{10}$]phenanthrene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]perylene and [$^2H_{12}$]benzo[*ghi*]perylene), solvent extracted three times by sonication and combined extracts were fractionated on a silica column. Instrumental analysis was carried out by GC/MS on an Agilent 7890 GC, equipped with an HP-5MS capillary column, coupled to an Agilent 5975C MSD (described in detail by Botsou and Hatzianestis, 2012). In total 18 PAH compounds/ groups, including 15 parent (unsubstitued) priority PAHs along with alkylated homologues of phenanthrene and dibenzothiophene where determined ($\sum PAH_{18}$).

3. Results and Discussion

$\sum PAH_{18}$ concentrations were generally low ranging from 8.98 to 113 ng g^{-1}. Normalized to organic carbon content $\sum PAH_{18}$ concentrations ranged from 3.05 to 17.3 μg g^{-1} OC. Higher concentrations were recorded in the north Aegean Sea (maximum 108 ng g^{-1}, average 67 ng g^{-1}) which likely reflects anthropogenic inputs from major rivers outflowing in the area. The lower concentrations recorded in south Aegean Sea (maximum 90.2 ng g^{-1}, average 46.9 ng g^{-1}) are probably related to the absence of fluvial inputs and the oligotrophic character of the area, which results in lower accumulation of sedimentary organic matter and associated pollutants (Figure 1). Total sedimentary PAH concentrations reported in the study area are significantly lower than those reported for surface sediments in coastal/estuarine areas in the Mediterranean Sea and worldwide receiving enhanced anthropogenic inputs. They are also lower than concentrations found in deep-sea settings such as the Black Sea, while they rather fall within the range found in the open Cretan Sea, deep-sea settings in the northwestern Mediterranean Sea and the open Ionian/NW Levantine Sea (outlined by Parinos et al., 2013).

Three types of PAHs are commonly found in marine sediments: pyrolytic PAHs deriving from the combustion/ pyrolysis of organic materials, petrogenic PAHs which are contained in petroleum and its products and biogenic PAHs from natural, terrestrial or marine, sources. In the sediments examined herein a mixed origin for PAHs both pyrolytic and petrogenic is evident. In most cases pyrolytic PAHs (compounds with ≥ 4 aromatic rings) were dominant, especially in deep stations. Their molecular profile was dominated by benzofluoranthenes, indeno[1,2,3-cd]pyrene and, to a lesser degree by fluoranthene and chrysene. Phenanthrene and its alkylated homologues, which are known to originate from unburned fossil fuels, were less abundant in all areas except the Central part of the Aegean sea, where they were found in percentages higher than 50% of ∑PAH18 and their occurrence was correlated with the marine traffic in this area. Relatively high concentrations of biogenic PAHs (perylene) were recorded close to the northern coastal zone, indicating the transportation of terrigenous material through the rivers.

Similar patterns have been reported in many marine sediment studies. This is attributed to the fact that PAHs deriving from pyrolytic/combustion sources are strongly associated to fine combustion particles (soot and/or char black carbon), resulting in higher resistance of these compounds towards biodegradation and photo-oxidation leading to a preferential accumulation of pyrolytic compounds in marine sediments, in contrast to the selective degradation of low-MW labile compounds such as phenanthrene and its methyl derivatives in the marine environment. The use of several molecular indices based on ratios of selected PAH concentrations also confirms the mixed origin of determined PAHs, probably reflecting differences in the relative importance of sources (Yunker at al., 2002).

PAH concentrations determined in this study show significant correlation with organic carbon (OC), indicating that organic carbon exerts an important control on their transport, fate and ultimate accumulation in the study area, likely attributed to the high affinity of hydrophobic PAHs to organic matter.

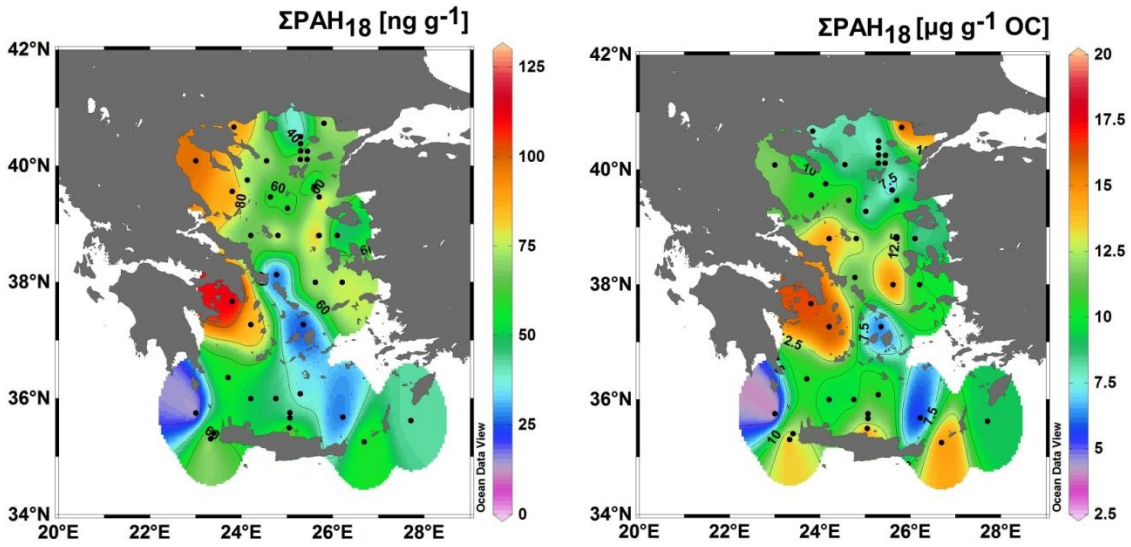

Figure 1. Spatial contour maps of ∑PAH_{18} absolute and OC normalized concentrations respectively in open Aegean Sea surface sediments.

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