POLYCYCLIC AROMATIC HYDROCARBONS IN THE OPEN/DEEP EASTERN MEDITERRANEAN SEA: TOWARDS THE IMPLEMENTATION OF MSFD D8

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Abstract
In this study, we report reference information on polycyclic aromatic hydrocarbons (PAHs) inventories in surface sediments, top-bottom profiles of suspended particles and sediment trap material collected in the open Eastern Mediterranean Sea (Ionian and NW Levantine basins; up to 4300 m depth), essential for the implementation of the MSFD Descriptor 8 in the area. The concentrations of total determined PAHs in all matrices were comparable to those reported for unpolluted open/deep-sea settings, while their molecular profiles reveal contributions from both fossil and pyrolytic sources and chronic petrogenic pollution in the study area. Biogeochemical processes and sub-basin variability of water masses overall control the regional patterns of PAH occurrence, vertical distribution and final accumulation in deep sea sediments.

Keywords: Pah, Pollution, Open sea, Deep sea basins, Mediterranean Sea

PAHs are a widespread class of persistent organic pollutants abundant in the marine domain. Mostly originating from various anthropogenic activities, PAHs are included in lists of priority pollutants since certain compounds present carcinogenic/mutagenic properties. The Eastern Mediterranean Sea (EMS) is a marine setting under anthropogenic pressure that has been receiving major concern regarding the monitoring of chemical pollutants. The Marine Strategy Framework Directive (2008/56/EC; MSFD) aims to achieve GES in European marine waters by 2020. However, there is a lack of data regarding the occurrence of chemical contaminants in deep/open settings of the European Seas [1]. In order to fill this gap, PAHs were investigated in surface sediments, top-bottom profiles of suspended particles and sediment trap material collected in the open EMS (Fig. 1). Our main goal was to assess their major sources, provide reference concentration values of their inventories and shed light on the factors which control their occurrence and fate in open/deep EMS waters/basins in order to provide essential data for the implementation of the MSFD Descriptor 8 in the area.

Undisturbed surface sediments (top 1-cm) were collected at 21 stations in deep basins (1018-4087 m depth) of the open EMS during four oceanographic cruises between 2007-2012. Suspended particulate matter was collected close to the sea surface, within the maximum of chlorophyll fluorescence, the base of the euphotic zone, mesopelagic and bathypelagic layers at 9 stations across the open EMS (1008-4087 m water depth) in January 2007. Sediment trap material was collected at 700 m and 4300 m water depth in the SE Ionian Sea on a two-week basis from May 2007 to October 2008. All collected samples were analyzed by GC-MS for 14 parent (unsubstituted) priority PAHs (EEA-EU, EPA-US), including 7 priority substances identified by the European Water Framework Directive (WFD; 2013/39/EC), along with methyl- and dimethyl-homologues of phenanthrene which are widely considered in marine pollution studies. $TPAH_{16}$ and $TPAH_{WFD}$ refer to hereafter to the total sum of monitored compounds and the sum of the seven WFD priority compounds, respectively.

Sedimentary PAH concentrations ranged between 8.95-154 ng g^{-1} for $TPAH_{16}$ and 3.47-78.1 ng g^{-1} for $TPAH_{WFD}$, while regarding suspended particle-associated PAHs, $TPAH_{16}$ concentrations ranged between 90.6-918 pg L^{-1} and $TPAH_{WFD}$ from 14.8-381 pg L^{-1}. These values are low, comparable to those reported for unpolluted open/deep-sea settings in the Mediterranean Sea and worldwide [2, 3, 4]. Settling fluxes of the studied PAHs ranged between 18.7 and 13.7 μg m^{-2} y^{-1} for $TPAH_{16}$ and 4.75 to 3.39 μg m^{-2} y^{-1} for $TPAH_{WFD}$, at 700 m and 4300 m depth respectively, for the study period.

The occurrence of PAHs in all martices is attributed to a mixed contribution from both fossil (atmospheric inputs and maritime activities) and pyrolytic (atmospheric inputs) sources, as inferred from their molecular profile and source-specific indices, while results are indicative of chronic petrogenic pollution in the study area, with a prominent fossil PAHs signal in deep waters. On the contrary, in deep sediments pyrolytic PAHs predominated, probably due to the degradation of the labile fossil compounds into the sediment-water interface, as a result of their long residence time in this marine site.

The vertical and spatial distribution patterns of PAH mixtures displayed significant variability amongst the study sites, with their overall occurrence and fate being controlled by both biogeochemical processes and water mass circulation patterns. The concentrations of suspended particle-associated PAHs were fairly comparable for particles in mesopelagic/bathypelagic waters and those measured in surface particulate matter, while sedimentary PAH concentrations were positively correlated to water column depth. The above imply that deep EMS waters/basins constitute a pollutant depository.

A substantial standing-stock of PAHs in deep EMS waters (in the order of 970 t for $TPAH_{16}$ and 272 t for $TPAH_{WFD}$) with a residence time in the water column of ~30 y for $TPAH_{16}$ and ~24 y for $TPAH_{WFD}$ (considering only particle settling), can be attributed to 1) the continuous delivery of these compounds from their anthropogenic sources and 2) the water mass circulation patterns resulting into lateral/advective inputs at mesopelagic and bathypelagic waters [3,5]. Our results imply a transport of petrogenic PAHs from the central Aegean Sea towards the EMS through the western Cretan-Antikythera straits canyons, the latter acting as a sink of PAHs [4].

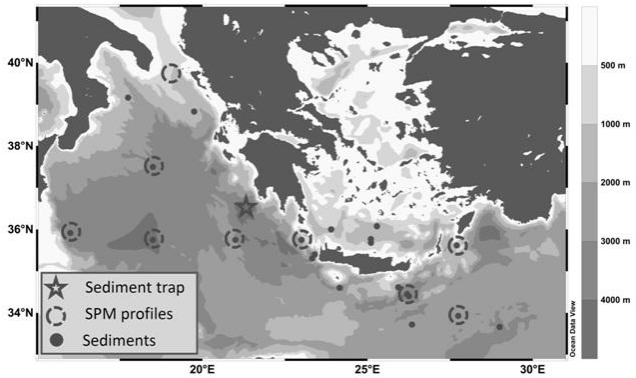

Fig. 1. Location of sampling sites across the open Eastern Mediterranean Sea

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