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Marine organic geochemistry of the Eastern Mediterranean: Polycyclic aromatic hydrocarbons in Aegean and Ionian Sea surface sediments

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Polycyclic aromatic hydrocarbons (PAH) are known hazardous environmental chemicals and are included in the priority pollutant lists. They enter into the marine environment by both aquatic and atmospheric pathways, whereas except the anthropogenic sources they have also several natural ones such as biomass combustion and diagenetic transformation of biogenic precursors. As a result of the variety of their sources, PAHs occur as complex mixtures in environmental samples. Twenty-five individual PAHs, comprising two- to six-ring unsubstituted compounds along with several alkyl-substituted homologues were determined in 157 sediment samples collected form both open sea and coastal marine areas in Aegean and Ionian Seas in Greece. The assessment of the various biogenic and anthropogenic sources of PAHs, and as well as of their relative importance, was achieved by using a molecular marker approach, characteristic compositional patterns and several diagnostic criteria and indices. Several marine areas directly influenced from industrial units operating in the coastal zone were identified as the most contaminated with total PAH concentrations well above 1000 ng/g. In the six major estuarine systems studied, the PAH concentrations were generally only slightly elevated and clearly lower than those reported in other European estuaries. Evros river in Northern Greece was found to be the major PAH supplier into the marine environment, followed by Strymon river located also in Northern Greece. Open sea sediments were generally uncontaminated, with PAH concentrations below 200 ng/g. Based on the characteristics of both the parent compound and the alkyl homologue distributions, the potential sources of PAHs were identified, whereas special isomeric compound ratios were calculated to evaluate the relative importance of different origins and the PAH transport pathways. In the highly contaminated areas a clear predominance of the pyrolytic PAHs, produced during various combustion processes of organic materials, was recorded. Phenathrenes originated from petrogenic sources were present in much lower concentrations and biogenic PAHs were almost negligible. In the sediments collected from the deltaic and estuarine systems a mixed origin for PAHs pyrolytic, petrogenic and biogenic was demonstrated. Pyrolytic PAHs were again present in higher concentrations in most cases, but the petrogenic ones possessed also an important fraction of the PAH mixtures. Retene and perylene deriving mainly from land related biogenic processes were also detected in high concentrations in most deltaic samples, evidencing the important role of the rivers in transferring significant quantities of terrigenous organic material into the sea. In open sea sediments pyrolytic PAHs accounted for more than 60% of the total PAHs, whereas their relative abundance was slightly elevated at the deep sampling sites compared to the shallow ones. This trend suggests that atmospheric deposition could be a potential source of pyrolytic PAHs in deep open sea waters. Petrogenic PAHs coming from unburned fossil fuels accounted for less than 25% of the total PAHs, but their spatial distribution was identical with this of pyrolytic ones suggesting similar input patterns and transport pathways. Relatively high concentrations of terrestrial biogenic PAHs (retene and perylene) were found only in Northern Aegean sea sediments indicating again the influence of the rivers in this marine area.