



Marine organic geochemistry in industrially affected coastal areas in Greece: Hydrocarbons in surface sediments

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Hydrocarbons are abundant components of the organic material in coastal zones. Their sources are mainly anthropogenic, but several natural ones have also been recognized. Among hydrocarbons, the polycyclic aromatic ones (PAHs) have received special attention since they are considered as hazardous environmental chemicals and are included in priority pollutant lists. The purpose of this study was to investigate the distribution, sources and transport pathways of hydrocarbons in marine areas in Greece directly influenced from the operation of major industrial units in the coastal zone by using a molecular marker approach, characteristic compositional patterns and related indices and also to evaluate their potential toxicity.

Thirty two surface sediment samples were collected from three marine areas: a) Antikyra bay in Korinthiakos gulf, affected from the operation of an alumina and production plant b) Larymna bay in North Evoikos, affected from the operation of a nickel production plant and c) Aliveri bay in South Evoikos Gulf, affected from a cement production plant. In all the studied areas aquaculture and fishing activities have been also developed in the coastal zone.

High aliphatic hydrocarbon (AHC) concentrations ($\sim 500 \mu\text{g/g}$), indicating significant petroleum related inputs, were measured only in Antikyra bay. In all the other samples, AHC values were below $100 \mu\text{g/g}$. N-alkanes were the most prominent resolved components (R) with an elevated odd to even carbon number preference, revealing the high importance of terrestrial inputs in the study areas. The unresolved complex mixture (UCM) was the major component of the aliphatic fraction ($\text{UCM/R} > 4$), indicating a chronic oil pollution. A series of hopanes were also identified, with patterns characteristic of oil-derived hydrocarbons, further confirming the presence of pollutant inputs from fossil fuel products.

Extremely high PAH concentrations ($> 100,000 \text{ ng/g}$) were found in the close vicinity of the alumina production plant in Antikyra bay. High levels of PAHs up to $22,000 \text{ ng/g}$ were also found in Aliveri bay, whereas lower values up to 7500 ng/g , but still indicating significant pollution, were measured close to the nickel production plant in Larymna bay. The examination of PAH molecular indices revealed that in Antikyra and Larymna bays more than 80% of the PAHs have pyrolytic origin coming from various combustion sources. On the contrary, in Aliveri bay about 60% of the PAHs are related to petrogenic/petroleum inputs.

With respect to ecotoxicological effects, mean quotient Effect-Range Median (m-ERM) values, higher than 1.5, were calculated in Antikyra bay, indicating a high probability (76%) of toxicity. In Aliveri and Larymna bays the m-ERM values were between 0.11 and 0.5 bay suggesting a lower probability (21%) of toxicity.

Overall, the results of our study reveal that high quantities of PAHs produced from land point sources such as the industrial units can enter into small coastal marine areas supporting activities such as aquaculture and fishing. Thus, desirable and permitted uses must be well defined and regulatory frameworks must be established.