



The role of rivers in transporting organic contaminants in the marine environment of Greece

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The study of trace organic contaminants in coastal marine environments and especially in estuarine systems is of great importance, since these areas, being biologically productive and receiving considerable pollutant inputs from land-based sources via river runoff, act as a transit zone in which contaminants are transported to the sea. The aim of this work is to identify the significance of estuarine export of organic pollution in the marine environment of Greece. For this reason, the distribution, composition and sources of hydrocarbon mixtures were investigated in sediments collected from eight major Greek estuarine systems, by using a molecular marker approach and several diagnostic criteria and indices. Surface sediment samples were collected from the estuaries of five rivers in Northern Greece flowing into Aegean sea (Axios, Aliakmonas, Strymon, Nestos, Evros), one river in Central Greece (Asopos) also flowing into Aegean Sea and two rivers in Western Greece flowing into Ionian sea (Acheloos, Acherontas).

The highest aliphatic hydrocarbon concentrations ($>100 \mu\text{g/g}$), indicative of petroleum pollution, were recorded in Asopos estuaries, followed by Aliakmonas, Axios, Strymon and Evros estuaries ($50-100 \mu\text{g/g}$). On the contrary, in Nestos delta, as well as in Acheloos and Acherontas estuaries, hydrocarbon values were found low and similar to those measured in open sea ($< 25 \mu\text{g/g}$), indicating that these rivers are not major hydrocarbon suppliers in the marine environment. The unresolved complex mixture (UCM) was the main component of the aliphatic fraction in most cases demonstrating some petroleum inputs in all areas, but high values of the ratio unresolved to resolved compounds (U/R), which are clearly indicative of petroleum residues, were measured only in Asopos, Axios and Evros estuary (U/R: 5.1-10.4). The n-alkane distribution was generally similar with that of total aliphatics. The high molecular weight n-alkanes ($>\text{C}23$) predominated in most cases, showing an important odd/even carbon number preference (mean CPI values above 5) which is characteristic of terrestrial higher plant origin. Low CPI values (1.6-3.4) were recorded only in Acheloos river, where very low n-alkane concentrations were also found, suggesting transport of limited amounts of terrigenous organic material in this case.

The highest PAH concentrations were again measured in Asopos and Evros estuary (800-1200 ng/g), followed by Axios, Aliakmonas, Strymon, Acheloos and Acherontas (220 - 650 ng/g), whereas very low values were found in Nestos delta (196.6 ng/g). The study of the compositional patterns of PAH mixtures and the examination of specific isomeric PAH ratios provide useful information regarding their sources and transport pathways. In the Aegean sea estuaries the PAHs of pyrolytic origin, mostly coming from grass, wood or coal combustion were dominant. On the contrary, in Acheloos and Acherontas phenanthrene compounds predominated evidencing an influence of petrogenic sources. High amounts of biogenic compounds (retene and perylene), that are usually considered as indicators of terrestrial influence, were determined only in Strymon, Evros and Acherontas.