Pollution of Aegean Sea by petroleum aromatic hydrocarbons

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The increasing use of crude oil as an energy source as well as a petrochemical feed-stock has created an increased world concern regarding the environmental pollution due to petroleum hydrocarbons.

The aromatic hydrocarbons (PAH) are of particular interest because the toxicities of various oils have been associated to their aromatic content. This class of compounds are generally more soluble (1ppb-30ppm) than paraffins, with a low vapour pressure, while a considerable percentage of them, 5-20%, is considered to be carcinogenic.

Conventional Fluorescence Spectroscopy is a useful technique for the analysis of aromatic hydrocarbons due to its greater sensitivity and selectivity for this class of compounds (SAWICKI, 1964). However, the usefulness of this technique is limited by the complex nature of aromatic mixtures in petroleum and the overlapping of fluorescence patterns. LLOYD, 1971 has considerably improved this technique by varying simultanously both $\lambda^{exc.}$ and $\lambda^{em.}$ while keeping a constant wavelength interval $\Delta\lambda$ between them. This technique of synchronous scanning has been proved very successful in multicomponent analysis, as it offers several advantages including narrowing of spectral bands, enhancement in selectivity by spectral simplification and decrease of measurement time.

In addition, the spectra maxima can be related to the number of the fused rings of the PAH. The spectrum of a higher ring number PAH occurs generally at a longer wave-length than a lower ring number compound (Fig. 1).

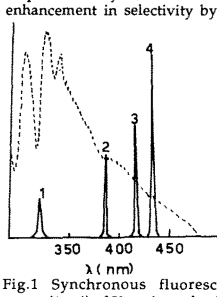

Fig.1 Synchronous fluorescence spectra ($\Delta\lambda$=4) of Kuweit crude oil (--) and a mixture of naphtalene (1), anthracene (2), benzo (a)pyrene (3) and pelylene

Therefore, we have applied the above technique for the analysis of surface marine sediments from the Aegean Sea, for the estimation of Pollution levels by petroleum hydro-carbons as well as to obtain a rough of a mlxture of idea of the relative importance of the PAH sources.

Surface sediments were collected during November 1991 and the sampling sites are shown in Figure 2. PAH content was determined fluorimetrically according to the standard methods of IOC (UNESCO, 1984) and the calculated values varied from 0.5 to 1.6 μg/g (in chrysene equivalents).

The obtained synchronous fluorescence spectra ($\Delta\lambda$=4 nm) implies the presence of naphthalenes (300-340 nm), aromatic compounds with three to four fused rings (340-400 nm) and highly condensed aromatics (400-500 nm) in considerably higher amounts. However such a wide range of aromatic compounds but with much more less amounts of multiringed aromatic compounds is typical of petroleums composition (Fig. 1). The predominance of aromatic hydrocarbons containing five and more rings indicates that these compounds are coming primarily from atmospheric dustfall and in most cases they have pyrogenic origin (products of incomplete combustion of fossil fuels) .

Fig.2. Sampling sites and values of PAHs in sediments of Aegean sea (μg/g in chrysene equivalents)

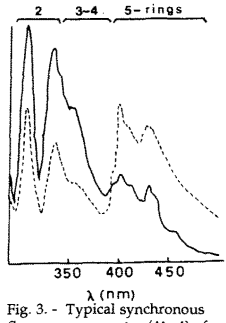

Fig. 3. - Typical synchronous fluorescence spectra ($\Delta\lambda$=4) of PAHs extract in hexane from Saronikos gulf (-) and from Aegean sea (- -) sediments.

Moreover, it is interesting to note the very intense large doublet centered at about 440nm, in all examined samples, which is indicative of the presence of perylene, a biogenic compound formed in marine sediments by reduction of land-derived nonhydrocarbon compounds, such as hydroquinones.

Finally, the spectra of sediments from Aegean Sea are compared to the corresponding typical synchronous spectrum obtained from sediments of Saronikos Gulf (Fig. 3). Saronikos is a semi-closed gulf of Greece which receives a great amount of sewage from the urban activity as well as from the industries located at the northern part of the gulf. This comparison clearly shows the higher content of two, three and four ring compounds (300-400 nm) in the case of Saronikos gulf, indicative of the petroleum origin of PAHs.

In conclusion, the results obtained in this study show that in the Aegean sea the contribution of PAHs of pyrolytic and eventually biogenic origin is the most important.

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