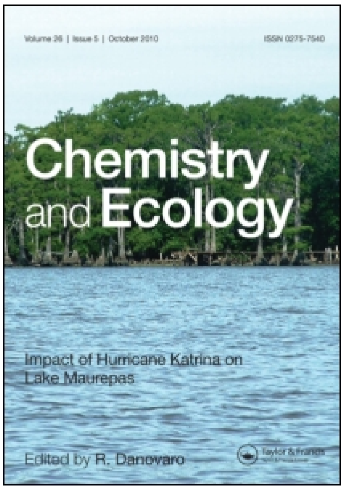

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Application of Synchronous Fluorescence Spectroscopy for Characterization of the Aromatic Hydrocarbons in Sediments of the Middle Adriatic

Josip Dujmov[a]; Perica Sučcevlča[a]
[a] Institute of Oceanography and Fisheries, Yugoslavia

To cite this Article Dujmov, Josip and Sučcevlča, Perica(1990) 'Application of Synchronous Fluorescence Spectroscopy for Characterization of the Aromatic Hydrocarbons in Sediments of the Middle Adriatic', Chemistry and Ecology, 4: 4, 189 — 195

To link to this Article: DOI: 10.1080/02757549008035233

URL: http://dx.doi.org/10.1080/02757549008035233

Chemistry and Ecology, 1990, Vol. 4, pp. 189–195

APPLICATION OF SYNCHRONOUS FLUORESCENCE SPECTROSCOPY FOR CHARACTERIZATION OF THE AROMATIC HYDROCARBONS IN SEDIMENTS OF THE MIDDLE ADRIATIC

JOSIP DUJMOV and PERICA SUČEVIĆ

Institute of Oceanography and Fisheries, 58001 Split, P.O. Box 114, Yugoslavia

(Received 9 January 1990)

UV-fluorescence spectroscopy method with synchronous mode of scanning was used to characterize the types of aromatic hydrocarbons in surface sediments. The sampling stations were located on two transverses between Yugoslavian and the Italian coasts in the middle of the Adriatic Sea. The preparation of sediment samples was made according to IOC/UNESCO (1982). Synchronous excitation/emission scanning were done at wavelengths from 236/260 to 516/540 nm. Since the wavelength of maximum emission is a function of fused aromatic rings in a molecule, the fluorescence spectra of each sample were divided into three intervals: 300–340, 340–400, over 400 nm, corresponding to compounds with 2, 3 and 4, 5 and more rings respectively.

Large qualitative differences were established between sediment samples. PAH with 5 and more rings are more prevalent near the Italian coast.

INTRODUCTION

From the ecological point of view polycyclic aromatic hydrocarbons (PAH) are the most interesting components of petroleum products. Several compounds have carcinogenic and mutagenic properties as well as great stability in the environment. Concentrations of petroleum products in range 1–100 mg dm^{-3} can be lethal to adult stages of aquatic organisms. Even concentrations as low as 0.001 mg dm^{-3} may lead to sublethal effects on behaviour and reproduction of some marine organisms (Hyland and Schneider, 1976).

In sea water organic matter and aromatic hydrocarbons are adsorbed to the surface of clay particles, and transported by currents and settle on marine bottom (Murphy *et al.*, 1988). Determination of qualitative–quantitative PAH composition in sediments can give an integrated picture of the flow of contaminants as well as their sources (Albaiges *et al.*, 1983).

UV-fluorescence spectroscopy method is the simplest method of monitoring these pollutants in the marine ecosystem. There are two measurement modes of fluorescence intensity; one at fixed excitation and emission wavelengths and another with synchronous changing of the excitation and emission wavelengths. The synchronous manner of scanning was employed by Lloyd (1971a). He demonstrated that the wavelength of maximum emission is a function of fused aromatic rings. At fixed excitation wavelength many of fluorescing polynuclear aromatic hydrocarbons are masked. So if the analysed sample is a complex mixture of fluorescing aromatic molecules, this mode gives a clearer structure. Lloyd and Evett (1977) have also shown that considerable improvement may be made by varying the excitation and emission wavelength maintained 20–30 nm less than the emission wavelength.

The synchronous mode of fluorescence analysis of complex mixture of aromatic hydrocarbons in sea water was made by Keizer and Gordon (1973), Gabrielides and Hadjigeorgiou (1986); in sea water, clams and sediment by Smith *et al.* (1987); in mussels by Farrington *et al.* (1980) and in oils and in related materials by Lloyd (1971a, b, c, d; 1975) and John and Soutar (1976).

Because the composition and behaviour of aromatic hydrocarbons in the sea are diverse and not clearly understood, in this paper we try to evaluate the type of aromatics in surface sediments from the open part of the Adriatic Sea.

The Adriatic is a semi-enclosed type of sea and is the most affected part of the Mediterranean region because of its growing human population and its activities (industry, tourism, marine traffic). Many pollutants, among them aromatic hydrocarbons, could present a real danger for the Adriatic (Kurelec, 1985). Although this sea has been intensely investigated through various monitoring pollution programmes, there is no information on the occurrence of PAH in sediments obtained with the synchronous method, but it is well documented for the world oceans (Wakeham, 1977; Law, 1981; Mille *et al.*, 1982; Aboul-Dahab and Halim, 1986; Smith *et al.*, 1987).

Samples of surface sediments were collected in the offshore part of the middle

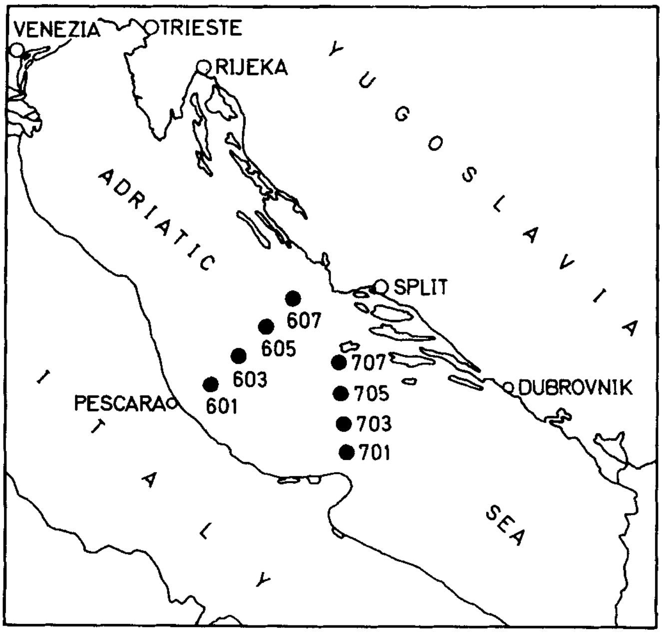

Figure 1 The sampling transects and stations.

Adriatic Sea. Two fixed transects were chosen between Yugoslavia and Italy with the eight sampled stations (transect 6-601, 603, 605, 607 and transect 7–701, 703, 705, 707) (Figure 1). These investigations were carried out as a part of the Yugoslav–Italian project for the protection of the Adriatic Sea.

MATERIALS AND METHODS

The surface sediments (0–5 cm) were sampled with a gravity corer (Meischner and Rumohr, 1974), frozen at −20°C, then freeze dried, homogenized and analysed. UV-fluorescence spectroscopy technique with the synchronous excitation/emission mode of scanning was used for the qualitative determination of aromatic compounds (the number of fused rings) (IOC/UNESCO, 1982). The wavelength interval was 24 nm. A detailed description of methods (saponification,

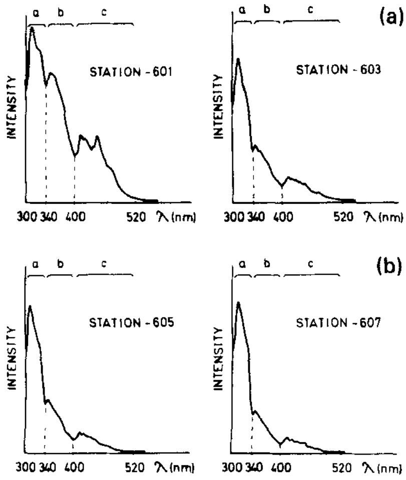

Figure 2 Synchronous spectra of the sediment extracts at transect 6. Wavelength interval 24 nm. (λ—emission wavelength; a-aromatics with 2 fused rings; b—aromatics with 3 and 4; c—aromatics with 5 and more fused rings).

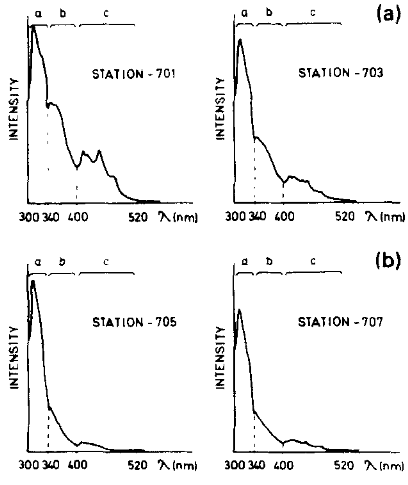

Figure 3 Sychronous spectra of sediment extracts at transect 7. Wavelength interval 24 nm. (λ—emission wavelength; a—aromatics with 2 fused rings; b—aromatics with 3 and 4 fused rings; c—aromatics with 5 and more fused rings).

extraction and separation) was reported previously (Dujmov and Sučević, 1989). The estimation was done from the spectral line shapes obtained in the II aromatic fraction, because the most aromatic compounds are eluated in this fraction.

The regions of spectrum with maximum fluorescence intensity were chosen. These are from 300-340 nm, 340-400 nm and more than 400 nm, representing the aromatics with 2, 3 and 4 (both belonging to aromatics of petroleum origin), 5 and more rings (benzopyrene and perylene types) respectively (Figures 2 and 3). The areas under the spectral line of each region were integrated and the values are given in relation to the area obtained by integration under whole spectral line. The results are expressed as a percentage or as a ratio. The area under the blank line (hexane) was subtracted from the value of the whole integrated area.

RESULTS AND DISCUSSION

The results of the content of polycyclic aromatic hydrocarbons (PAH) obtained with the synchronous technique are given in Table 1. One series of results represents the integrated value of each area in relation to the total integrated area expressed as a percentage (column A) or only as a ratio (column B).

As it can be seen from the same table, all types of aromatic compounds with 2, 3, & 4, 5 and more rings are almost equally present the samples from stations located nearer Italian coast (601, 701). These ratios between aromatics are 0.3:0.4:0.3 at station 601 and 0.4:0.3:0.3 at station 701. This means that the sediments on the west part of the middle Adriatic Sea contain aromatic compounds originating from petroleum, pyrolitic and diagenetic sources. It can also be concluded that the sources of these pollutants are more complex and heterogeneous, and are the consequence of larger human activity.

In Figure 4, histograms of the contents of each aromatic compound group obtained with this technique are shown. As it can be seen from the figure, the presence of aromatics with two rings become more marked going from west to east across the transects, while the gradients of 3, 4, 5 and more rings is decreasing, and at the last stations they are present at very low levels. It is evident that a regular pattern in PAH occurs across the transects.

The proportions change from 0.3:0.4:0.3 (station 601), 0.4:0.3:0.3 (station 603), 0.5:0.3:0.2 (station 605) to 0.6:0.2:0.2 (station 607) at transect 6 and from 0.4:0.3:0.3 (station 701), 0.5:0.3:0.2 (station 703), 0.7:0.2:0.1 (station 705) to 0.6:0.2:0.2 (station 707). From these results we can conclude that in the eastern Adriatic area there is no PAH of pyrolitic or diagenetic origin, only petrochemical, reflecting much less human activity. The aromatic compounds from petrochemical sources could be explained as a consequence of marine traffic activity. Although the samples of sediments of this area consist of the petrochemical types of PAH, the total PAH content value is much lower than that on the west part of the Adriatic.

It must be pointed out that the results of total PAH content obtained with conventional fluorimetry at fixed excitation wavelength are also presented in Table 1. As it can be seen the values of total PAH content are higher at the stations located nearer to the Italian coast (601, 701) and decrease toward the eastern part of the Adriatic (Dujmov and Sučević, 1990).

Table 1 Distribution of various types of aromatic compounds in surface sediments obtained from synchronous emission spectra.

Station	601		603		605		607		701		703		705		707	
Aromatics	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
2 rings	30.1	0.3	43.9	0.4	49.8	0.5	62.4	0.6	36.9	0.4	44.5	0.5	70.9	0.7	57.2	0.6
3&4 rings	38.5	0.4	30.8	0.3	29.7	0.3	17.8	0.2	33.8	0.3	31.5	0.3	18.4	0.2	23.5	0.2
5 and more rings	31.4	0.3	25.3	0.3	20.5	0.2	19.8	0.2	29.3	0.3	24.0	0.2	10.7	0.1	19.3	0.2
Total PAH content*	1.50		0.75		0.72		0.48		1.10		0.89		0.60		0.60	

A—Percent of integrated area for each aromatic type (%)
B—Ratio of the value of the integrated area of each region and the value of total integrated area.
*—μg chrysene equivalents/g dry weight of sediments (Dujmov and Sučević, 1990).

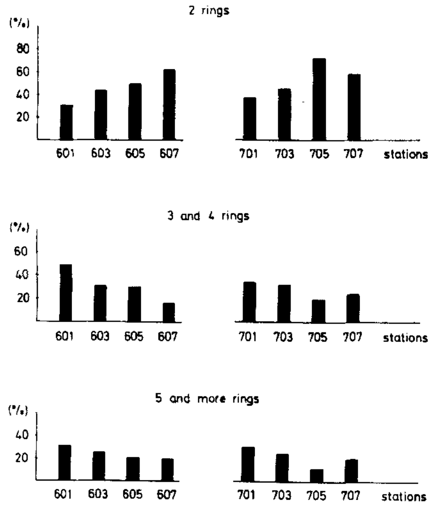

Figure 4 Distribution of percentages of each group of aromatic compounds across transects.

From the sychronous spectra of sediment, it is possible to identify good separation between each group of aromatics through characteristic peaks (Figures 2 and 3), confirming the existing theory established by Lloyd (1971c) about maximum emission of aromatic compounds.

Although some other techniques for determination of aromatic compound give more detailed information in PAH composition, such as gas chromatography and mass spectrometry, this technique (UV-fluorescence spectroscopy with synchronous mode of scanning) can be recommended for monitoring oil in marine sediments. Its advantage is quick evaluation of the type of aromatic compounds and rapid identification of PAH sources.

CONCLUSIONS

On the sampled transects located in the middle Adriatic Sea between Yugoslavia and Italy, it was established that large qualitative and quantitative PAH differences occur between sediment samples. On the west, they originate from petroleum, pyrolitic and diagenetic sources reflecting the much more heterogeneous sources of these pollutants and greater diversity of human activity.

In the sediments sampled nearer the Yugoslav coast, petroleum sources of PAH are more marked in contrast to those associated with pyrolitic and diagenetic sources which scarcely exist.

A regular pattern in PAH is evident across the transects obtained from qualitative synchronous spectra.

It is concluded that this technique is applicable for PAH characterization in sediment samples as well as for monitoring of the same compounds.

References

Aboul-Dahab, O. and Halim, Y. (1986). Petroleum hydrocarbons in Alexandria coastal sediments as assessed by emission and synchronous fluorescence spectra. *Rapports et proces-verbaux des réunions*, **30**, 2, 124.

Albaiges, J., Algaba, J. and Bayrona, J. M. (1983). New perspectives in the evaluation of anthropogenic inputs of hydrocarbons in the western Mediterranean coast. *VI^{es} Journées d'études sur les pollutions marines en Méditerranée*, Cannes, 199–206.

Dujmov, J. and Sučević, P. (1989). Contents of polycyclic aromatic hydrocarbons in the Adriatic sea determined by UV-fluorescence spectroscopy. *Marine Pollution Bulletin*, **20,** 8, 405–409.

Dujmov, J. and Sučević, P. (1990). Distribution of polycyclic aromatic hydrocarbons (PAH) in recent sediments of two transversal transects in the middle part of the Adriatic sea. *Oil & Chemical Pollution* (in press).

Farrington, J. W., Albaiges, J., Burns, K. A., Dunn, B. P., Eaton, P., Laseter, J., Parker, P.L. and Wise, S. (1980). Fossil fuels. In: *The International Mussel Watch*. National Academy of Sciences, Washington, D.C., pp. 1–77.

Gabrielides, G. P. and Hadjigeorgiou, E. (1980). Biochemical studies of selected pollutants in the open waters of the Mediterranean (Med Pol VIII). Greek oceanographic cruise 1980. *MAP Technical Report Series*, **8,** Addendum, pp. 29–34.

Hyland, J. L. and Schneider, E. D. (1976). Petroleum hydrocarbons and their effects on marine organisms, populations, communities and ecosystems. In: *Sources, effects and sinks of hydrocarbons in the aquatic environment*. American Institute of Biological Science, Washington, D.C., pp. 463.

IOC/UNESCO. (1982). The determination of petroleum hydrocarbons in sediments. *Manuals and Guides*, **11,** 1–38.

John, P. and Soutar, I. (1976). Identification of crude oils by synchronous excitation spectrofluorimetry. *Analytical Chemistry*, **48,** 3, 520–523.

Keiser, P. D. and Gordon, D. C. (1973). Detection of trace amounts of oil in seawater by fluorescence spectroscopy. *Journal of the Fisheries Research Board of Canada*, **30,** 1039–1046.

Kurelec, B. (1985) Biološki efekti organskih zagađivala. In: *Problematika procjene opasnosti od štetnih tvari u Jadranu*, JAZU, Zagreb, pp. 115–131.

Law, R. J. (1981). Hydrocarbon concentration in water and sediments from UK Marine waters, determined by fluorescence spectroscopy. *Marine Pollution Bulletin*, **12,** 5, 153–157.

Lloyd, J. B. F. (1971a). The nature and evidential value of the luminescence of automobile engine oils and related materials. Part I. Sychronous excitation of fluorescence emission. *Journal of Forensic Science Society*, **11,** 83–94.

Lloyd, J. B. F. (1971b). See in text.

Lloyd, J. B. F. (1971c). The nature and evidential value of the luminescence of automobile engine oils and related materials. Part III Separated luminescence. *Journal of Forensic Science Society*, **11,** 235–253.

Lloyd, J. B. F. (1971d). Sychronized excitation of fluorescence emission spectra. *Nature Physical Science*, **231,** 20, 64–65.

Lloyd, J. B. F. (1975). Characterisation of rubbers, rubber contact traces and tyre prints by fluorescence spectroscopy. *Analyst*, **100,** 82–95.

Lloyd, J. B. F. and Evett, I. W. (1977). Prediction of peak wavelengths and intensities in synchronous excited fluorescence emission spectra. *Analytical Chemistry*, **49,** 12, 1710–1715.

Meischner, D. and Rumohr, J. (1974). A light-weight momentum gravity corer for subaqueous sediments. *Senkenbergiana maritima*, **6,** 105–107.

Mille, G., Chen, Y. Y. and Dou, H. (1982). Hydrocarbures présents dans des sédiments superficiels méditerranéens (Zone côtière Fos /mer-Monaco). VI^{es} *Journées d'études sur les pollutions marines en Mediterranée*, Cannes, 191–198.

Murphy, P. O., Bates, S. T., Curl, H. C. Jr., Teel, R. A. and Burger, R. S. (1988). The transport and fate of particulate hydrocarbons in an urban fjord-like estuary. *Estuarine and Coastal Shelf Science*, **27,** 461–482.

Smith, J. D., Bagg, J. and Sin, J. O. (1987). Aromatic hydrocarbons in seawater, sediments and clams from Green Island, Great Barrier Reef, Australia. *Australian Journal of Marine and Freshwater Research*, **38,** 501–510.

Wakeham, S. G. (1977). Synchronous fluorescence spectroscopy and its application to indigenous and petroleum-derived hydrocarbons in lacustrine sediments. *Environmental Science and Technology*, **3,** 272–276.