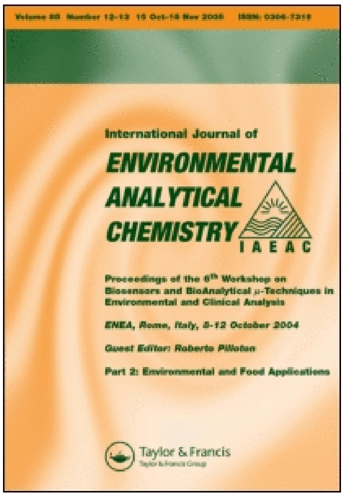

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Polycyclic Aromatic Hydrocarbons in Mediterranean Coastal Sediments†

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Several Mediterranean coastal sediment samples from polluted and non polluted areas of the French coast have been analysed for polycyclic aromatic hydrocarbons. The amounts of selected PAH have been determined in order to identify possible sources of these compounds. Seasonal variations have been observed and are discussed.

KEY WORDS: PAH, Mediterranean sediments.

INTRODUCTION

The polycyclic aromatic hydrocarbons are the largest class of chemical carcinogens known today and they are found at various concentration levels throughout the environment. No data are available for polycyclic aromatic hydrocarbons in Mediterranean coastal sediments. Following studies on the whole hydrocarbon content of Mediterranean sediments,[1] we have undertaken more detailed analysis focusing on the polycyclic aromatic hydrocarbon fraction in order to:

1) determine the amount and the structures of the major components, the carcinogenic activity of which is directly linked to their structures.

2) know the possible sources of these compounds.

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†Presented at the workshop on the chemistry and analysis of hydrocarbons in the environment. Barcelona, November 1981.

EXPERIMENTAL

Sampling sites: The location of the sampling stations are given in Figure 1.

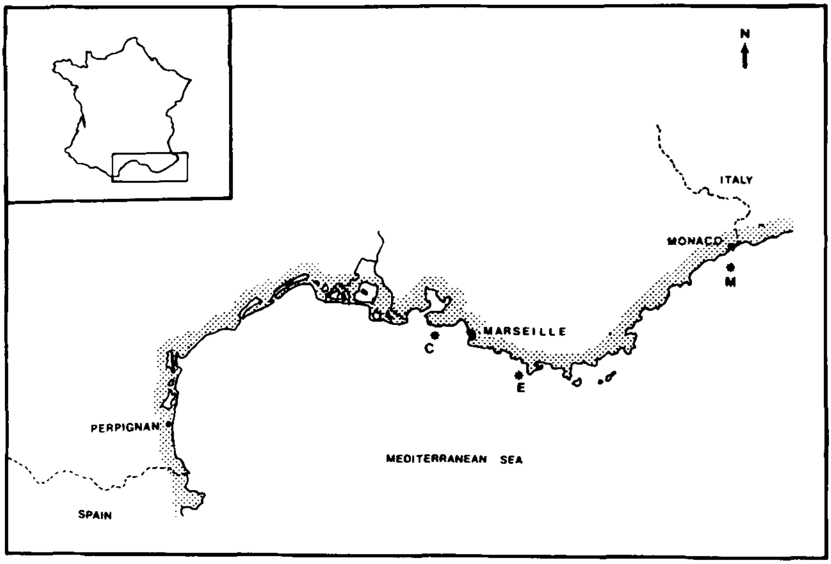

FIGURE 1 Station locations for studies of PAH in sediments.

All the samples were taken between 3 and 10 metres deep. They were taken by divers and are representative of the upper 0–5 cm of surface sediments. Samples taken include:

— Zone C (Côte Bleue): This zone is located between Marseille and the Rhone Delta. Several samples were taken at different places, representing non-polluted areas (H-4, H-5) and possibly polluted areas near a refinery (L). Several samples were also taken at Station 4, one at each season during 1979.

— Zone E (Les Embiez): This zone is located 50 km east from Marseille. It is a big resort area densely populated in summer with an important coastal navigation and boating activities (1l, 1n).

— Zone M (Monaco): This non-polluted area also supports substantial coastal navigation in summer. (F, G).

Extraction and analysis

Hydrocarbons were extracted from wet sediments (~50 g) by direct saponification via alkaline hydrolysis. Samples were heated under reflux for 4 hr in a mixture of 0.5 N KOH in 95% methanol/toluene 2/1 and then elemental sulfur was removed from the extract by percolating through a column of activated Cu/Al_2O_3. Fractions containing hydrocarbons were isolated from column chromatography on a silica gel (5% deactivated with H_2O) column.[2]

PAH analysis was performed by synchronous UV fluorescence spectroscopy, capillary gas chromatography and combined capillary gas chromatography/mass spectrometry.[3]

RESULTS AND DISCUSSION

The gravimetric results of the hydrocarbon analysis of the Mediterranean coastal sediments are listed in Table I and concentrations of some selected PAH are given in Table II. Gas chromatograms of aromatic fractions for Stations H4 (Côte Bleue) and F (Monaco) are presented in Figures 2 and 3.

TABLE I

Hydrocarbon concentrations in Mediterranean coastal sediments (μg/g dry weight)

	Côte Bleue(C)			Les Embiez (E)		Monaco (M)	
	H4	H5	L	11	In	F	G
Total extract	141	134	1610	900	990	203	70
Aliphatic hydrocarbons	12	16	720	78	56	65	46
Aromatic hydrocarbons	1.2	1.3	232	15	13	12.1	5.2
%(aromatic/aliph.)	10	8	31	19	23	19	11
%(aromatic/hydroc)	9	7.5	24	16	19	16	10

Seasonal variations of the PAH content for sediment from Station 4 are indicated by the ratios of concentrations of some selected PAH (Table III) and by the UV fluorescence spectra (Figure 5).

The amounts of hydrocarbons found in Mediterranean coastal sediments are generally low (< 100 μg/g dry weight) except for Station L (952 μg/g) which is located near an oil refinery. The aromatic fraction represents from 7 to 23% of the total hydrocarbons except for the more contaminated station L which was 31%. The values found (1–33 μg/g and 232 μg/g for station L) are close to those found in North Atlantic,[4] lake or river sediments.[5, 6]

The relative concentrations of selected PAH are not the same for all sediments (Table II) and two different patterns can be seen (Figure 4)

TABLE II

Selected aromatic hydrocarbon concentrations in Mediterranean coastal sediments (ng/g dry weight).

Peak number	m/e	Compounds	Côte Bleue (C)			Monaco (M)		Les Embiez (E)	
			H4	H5	L	F	G	11	1n
4	178	Phenanthrene	37.5	11.6	120	8.6	3.8	4.2	5.2
5	178	Anthracene	2	0.8	15	—	—	—	—
6	192	C_1 Phenanthrenes	20	10.7	280	7	5	7.1	12
11	206	C_2 Phenanthrenes	12	10.9	451	3.5	3	6.4	10.6
12	202	Fluoranthene	46	26.9	318	46.5	15	8	13
13	202	Pyrene	28.5	16.8	273	50.4	7.2	6	10
15	216	C_1 Fluoranthene or pyrene	26	15	N.D.	15	4	N.D.	N.D.
	PAH $C_{18}H_{12}$		48	21.5	N.D.	32	21.3	N.D.	N.D.
16	228	Benz(a)anthracene	12.5	5	N.D.	16.3	8.1	N.D.	N.D.
17	228	Chrysene	22	11	N.D.	14.7	9.2	N.D.	N.D.
	PAH $C_{20}H_{12}$		52.5	33.5	N.D.	45	19.6	N.D.	N.D.
18	252	Benzofluoranthenes	20	14	N.D.	20	5.2	N.D.	N.D.
19	252	Benz(e)pyrene	8	4	N.D.	10.5	4.3	N.D.	N.D.
20	252	Benz(a)pyrene	9	5	N.D.			N.D.	N.D.
21	252	Perylene	3	2	N.D.	12	7	N.D.	N.D.
22	278	Dibenzanthracene	—	—	N.D.	6	—	N.D.	N.D.
23	276	Benzo(g, h, i)perylene	—	—	N.D.	7.5	—	N.D.	N.D.

N.D. = Not Determined.

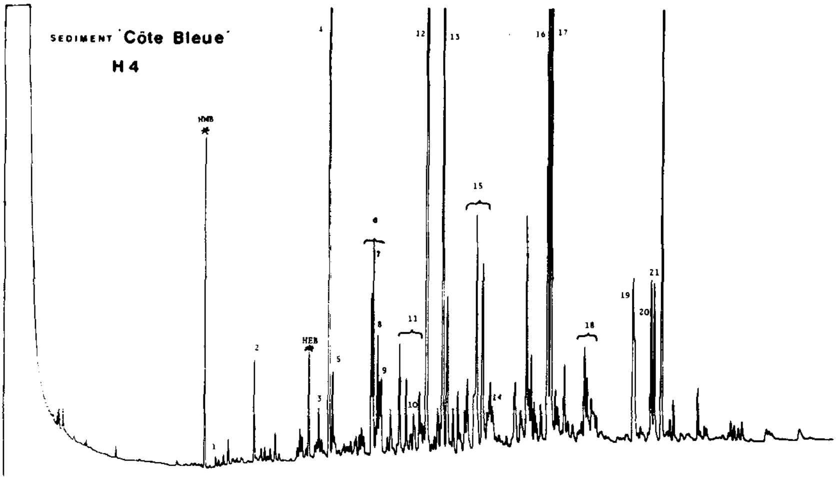

FIGURE 2 Glass capillary gas chromatogram of aromatic hydrocarbons in Mediterranean surface sediments Côte Bleue station H4. S.E. 52 column (15 m × 0.32 mm) installed on a Carlo Arba Model 2150 gas chromatograph equipped with split/splitless injection; Helium carrier gas at 0.55 kg/cm^2. Program 70—270°C at 3°C/mn.

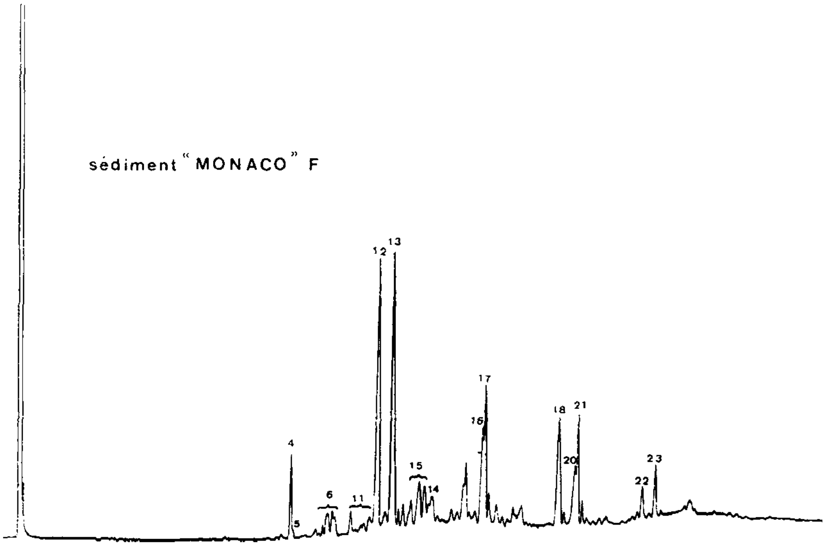

FIGURE 3 Glass capillary gas chromatogram of aromatic hydrocarbons in Mediterranean surface sediments Monaco. Station F. S.E. 52 column (25 m × 0.32 mm) installed in a Carlo Erba Model 4160 gas chromatograph equipped with on column injection. Helium gas carrier gas at 0.55 kg/cm^2. Program 70—300°C at 5°C/mn.

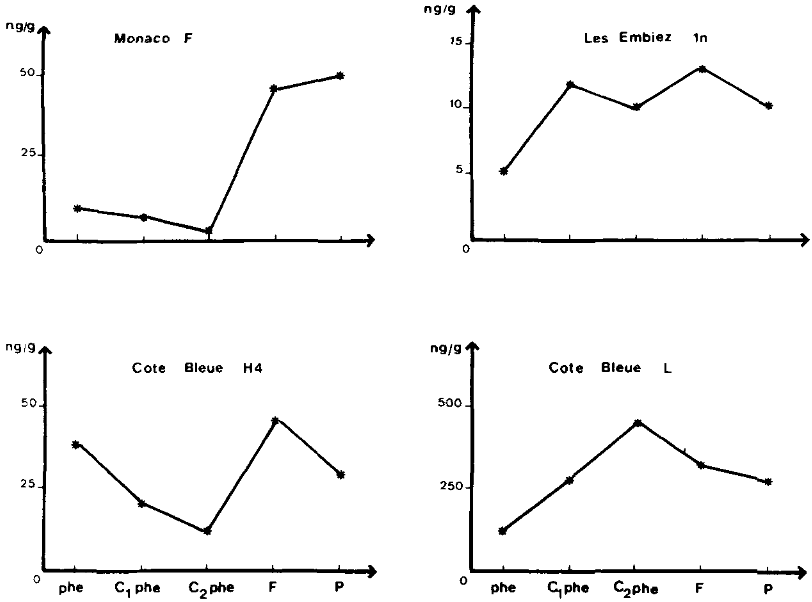

FIGURE 4 Distributions of some selected PAH in Mediterranean coastal sediments.

which indicate different possible sources for polycyclic aromatic hydrocarbons in surface sediments. These sources of polycyclic aromatic hydrocarbons in the marine environment are numerous and are discussed in detail by Giger and Blumer,[7] Youngblood and Blumer,[8] Laflamme and Hites,[9] Hites *et al.*[10] To summarize these discussions, polycyclic aromatic hydrocarbons found in the environment may be derived from:

— Direct deposition of petroleum (ballasting/deballasting operations of tankers, discharge of oily bilge-water, tank washing, refiner effluents, discarded lubricants and other oils, accidents, natural seepage...). In this case PAH are generally present as complex mixtures containing both alkylated and non-alkylated species but there is a deficiency in the unsubstituted compounds.

— Combustion is often an important source of PAH. Natural combustion (forest fire, burning land plants) and anthropogenic combustion (fossil fuels) leads to a mixture of PAH characterized by homologous series which contain a decreasing amount of alkyl substitution as the temperature of combustion increases.

— Early diagenesis in recent sediments may be responsible for the aromatization of some naturally occurring cyclic compounds (e.g. steroids,

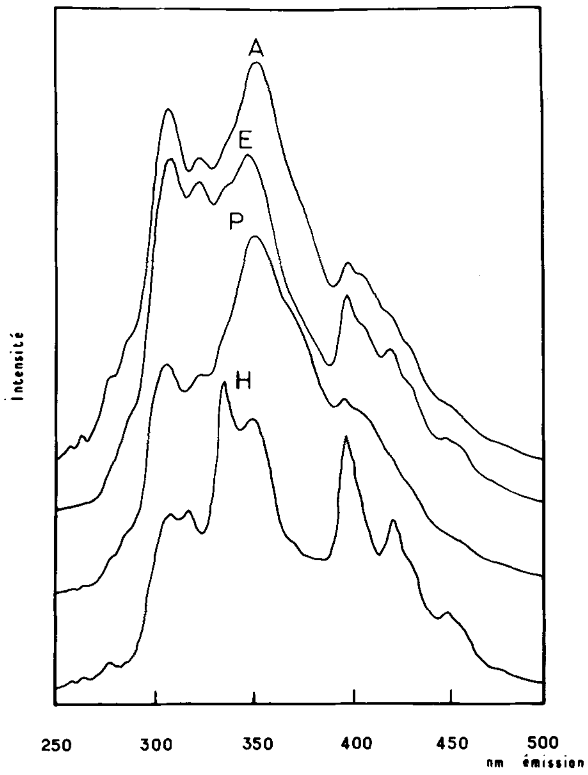

FIGURE 5 Synchronous fluorescence spectra ($\Delta\lambda = 23$ nm) of aromatic hydrocarbons (Côte Bleue, station 4) showing seasonal variations. (A: autumn; H: winter; P: spring; E: summer).

TABLE III

Seasonal variations of the concentration ratios of some selected PAH. (Côte Bleue—Station 4).

	Autumn	Winter	Spring	Summer
Phenanthrene/-1 methyl Phe.	0.06	6.8	0.06	0.06
Phenanthrene/C_1Phe	0.03	1.8	0.03	0.04
Phenanthrene/C_2Phe	0.09	3.1	0.1	0.12
Phenanthrene/Fluoranthene	0.43	0.8	1.5	0.66
Phenanthrene/Pyrene	0.6	1.3	1.5	1
Fluoranthene/C_1Phe	0.07	8.3	0.02	0.06
Pyrene/C_1Phe	0.05	5.2	0.02	0.04
Pyrene/Fluoranthene	0.71	0.62	1	0.66

triterpenoids,[11]) with one or two specific compounds which are directly related to the skeletal structures of the precursors.

For these three sources, relative distribution patterns are different and quantitative measurements of various alkylated and non-alkylated PAH can be useful in the identification of the possible source of PAH, except for the fact that the ability to distinguish between natural and anthropogenic combustion is limited.[8]

— *Zone C* (Côte Bleue): absolute concentrations of selected PAH are the highest for samples taken at Station L and the lowest for samples taken at Station 5 (Table II). Samples H4 and H5 show the same PAH pattern which is different from those of PAH found at Station L. In the case of Stations H-4 and H-5 the PAH mixtures are characterized by the predominence of unsubstituted species (phenanthrene, fluoranthene, pyrene, $C_{18}H_{12}$ and $C_{20}H_{12}$ compounds) over the alkylated species and the relative distribution of the PAH is indicative of combustion (ratios of the phenanthrene to the C_1 or C_2 phenanthrenes, ratio of $C_{16}H_{10}$ isomers: fluoranthene and pyrene to their mono-alkyl homologs, are always $>$to 1).

For Station L the PAH mixture shows both alkylated and non alkylated species and its origin may be direct deposition of non-combusted petroleum (e.g. refinery effluents). The ratios of phenanthrene to the C_1 or C_2 phenanthrenes is less than one which is the case when the source is direct fossil fuel contamination.

For Station 4, several samples were taken at each season of 1979. Samples exhibited lower hydrocarbon concentrations in summer, winter and spring than in autumn.[1] Gas chromatograms and UV fluorescence spectra (Figure 5) show that the composition of the aromatic fraction is not the same for each season. The major difference in the aromatic fraction compositions between winter and the other seasons is seen in the phenanthrene series concentrations. This fact has previously been noticed by Boehm *et al.*[12] in the study of hydrocarbon pollutants in the Georges bank region.

In winter, a combustion source for the PAH seems to be possible whereas for the other seasons a direct fossil fuel contamination seems to be evident. Why do such seasonal variations take place?

Until now we could only make some hypothesis to explain the experimental data including:

a) Combustion source for the PAH in winter and (b) petroleum origin of these PAH during the other seasons (as seen by a deficiency of unsubstituted species, especially phenanthrene). It seems reasonable to assume that natural mechanisms exist that can modify a PAH homolog distribution after the mixture has been deposited in the sediment. Such mechanisms could include differential water solubility of the higher alkyl homologs V/S the unsubstituted species; preferential bioaccumulation of higher homologs, preferential biodegradation of lower homologs, preferential vaporization of lower homologs or preferential accumulation of some specific compounds by organisms.

All these PAH homologs distribution modification mechanisms have yet to be demonstrated. Studies on the seasonal hydrocarbon (PAH) variations will be of great interest on a longer time scale.

— *Zone M* (Monaco F and G): The PAH distribution is similar to the one found for Station H4 and H5 (Zone C) (Figure 3 and 4) with lower amounts of phenanthrene and C_1 C_2 phenanthrenes. A pyrolytic source for this PAH seems to be justified (Fluoranthene/C_1 Fluor. >3) Fluoranthene, Pyrene and Perylene concentrations (sample F) are higher than those found for sample H4.

We analysed a core (15cm length) from Station F and we did not find increasing concentrations of perylene, phenanthrene, fluoranthene, pyrene or chrysene with increasing depth in the core. Based on this it would seem that these PAH cannot result from an in situ diagenesis.

— *Zone E*: We only have determined concentrations of five PAH. Phenanthrene series, fluoranthrene and pyrene and low values (4–10 ng/g) have been found for the concentrations of these compounds. Their relative distribution, ratio of phenanthrene to the C_1 or C_2 phenanthrenes less than one, seems to indicate a petroleum source (Figure 4) for them.

For this station we have begun seasonal samplings in order to know if the composition of the aromatic fraction is the same for each season.

CONCLUSION

Two main sources of polycyclic aromatic hydrocarbons in Mediterranean coastal sediments have been found: combustion source and petroleum source.

Seasonal variations seem to be important and can lead to very different patterns in the distribution of polycyclic aromatic hydrocarbons. The exact reasons for these modifications remain unexplained and further research will be necessary.

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