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Origin of Polycyclic Aromatic Hydrocarbons (PAH) in Recent Sediments from the Continental Shelf of the "Golfe de Gascogne" (Atlantic Ocean) and in the Gironde Estuary[†]

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Several aromatic series have been analysed on sediment extracts by high performance liquid chromatography coupled (HPLC) and by high resolution Shpol'skii spectroscopy. HPLC coupled to a programmable spectrofluorometer as detector has been used for the detection of the sixteen PAH priority pollutants recommended by the US Environmental Protection Agency. Relative distribution in methylated phenanthrene, chrysene, and pyrene series have been examined by high resolution spectrofluorometry in Shpol'skii matrices for the determination of the sources of aromatic matter in the sediments. These complementary studies would provide useful information on the origin of PAH in marine sediments.

KEY WORDS: Polycyclic aromatic hydrocarbons (PAH), high performance liquid chromatography, Shpol'skii effect, estuarine and marine sediments, sixteen PAH priority pollutants, methylphenanthrenes, methylchrysenes, methylpyrenes, quantitative analysis.

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INTRODUCTION

The polycyclic aromatic hydrocarbons (PAH) are mainly formed on the continent by the combustion of organic matter, especially the fossil fuels. Most of these compounds are carcinogenic or mutagenic. They are transported in the aquatic environment through aerial pathways, far away from their sources and then transferred to the sediment through the water column. Numerous recent studies¹⁻⁴ have reported the presence of complex mixtures of PAH in sediments and soils.

The presented studies deal with the detection of selected PAH series in several superficial sediments (0–10 cm) cored in the Gironde estuary and the continental shelf of the “Golfe de Gascogne”. The researched PAH are: the sixteen PAH priority pollutants defined by the US Environmental Protection Agency (EPA)⁵ (see Figure 1). Analyses of PAH have been made on the total organic extracts of the sediments by liquid chromatography on reverse phase with a multi-wavelength microprocessing spectrofluorometer as detector; several series of monomethylated aromatic compounds (phenanthrene, pyrene, chrysene series, see Figure 2). Characteristic concentration ratios between the isomers and their respective parent compounds are generally considered as an indicator of the evolution and the sources of the aromatic sedimentary matter.^{1,6-8} The determination of relative distribution of isomers has been made by high resolution Shpol'skii spectroscopy which has proven previously to be a very selective and sensitive method for the analysis of isomeric PAH.^{9,10}

EXPERIMENTAL

The complete analytical procedure of the studied PAH series is presented in Figure 3.

Sample collection

The sediment cores (0–10 cm) were collected from locations along the “Golfe de Gascogne” continental shelf and in the Gironde estuary (see Figure 4) using a Shipeck grab aboard the O/V “Ebalia” and/or

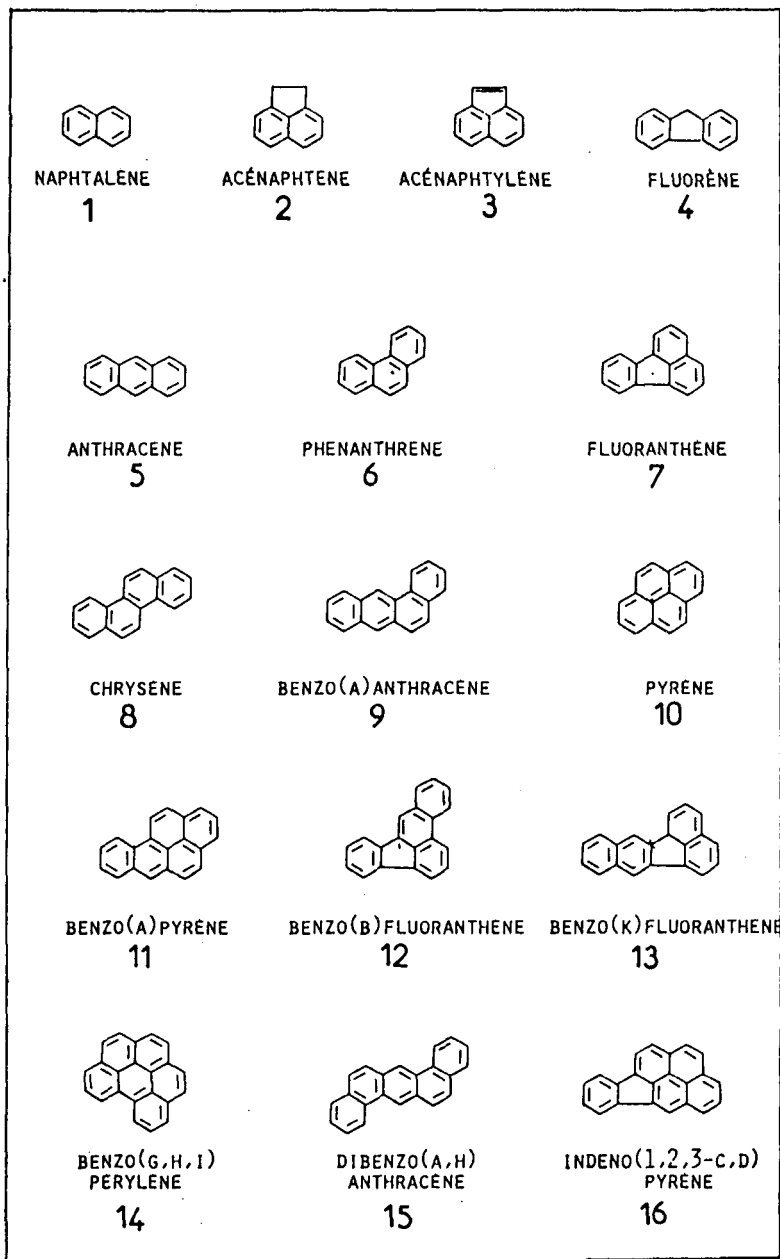


FIGURE 1 The sixteen PAH priority pollutants recommended by the U.S. Environmental Protection Agency (Ref. 5).

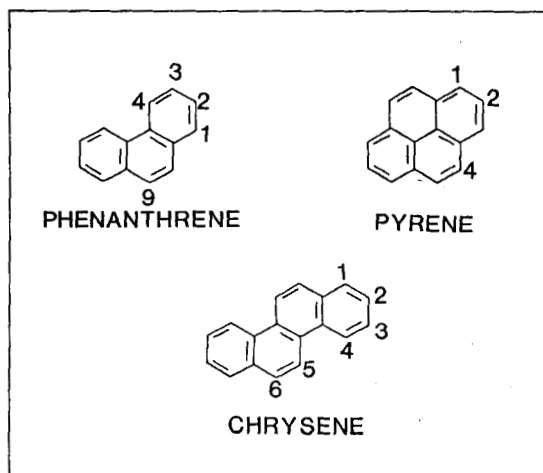


FIGURE 2 Methylated aromatic series studied in this work.

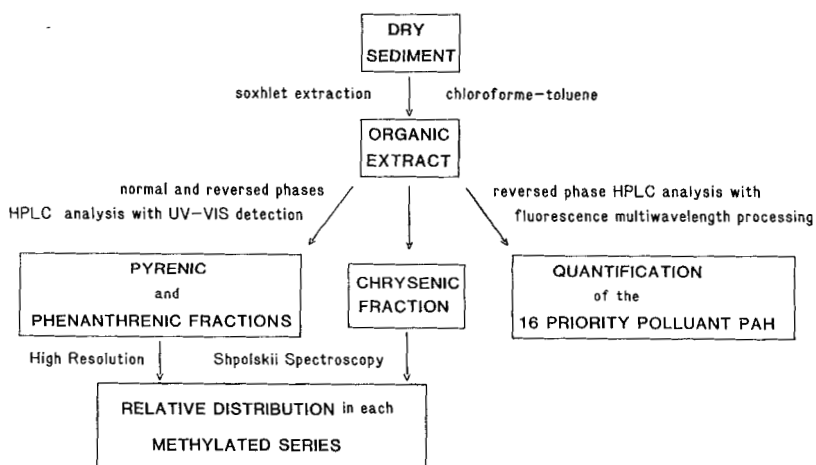


FIGURE 3 Analytical procedure for the extraction and the analysis of PAH in the sediments.

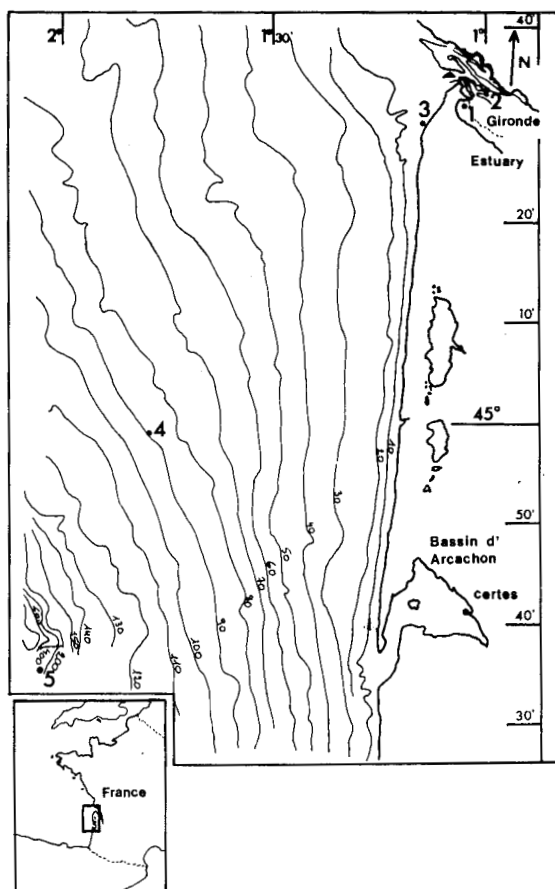


FIGURE 4 Sediment locations on the continental shelf and in the Gironde estuary.

“Côte d’Aquitaine”. The cores were frozen on board and stored until their extraction and analysis.

Aromatic hydrocarbon extraction

The samples are freeze-dried and extracted as indicated by Reference 11. The total organic extract is collected after continuous agitation of the sediment in a mixture of chloroform/toluene (2:1) maintained

at 45°C for 45 min. This process was repeated four times and the solvent volume is gently evaporated under vacuum to a volume of 1–2 ml. This extract is percolated through a Florisil microcolumn (SEP-PAK, Waters–Millipore) to eliminate very polar compounds. The pentane extract is then concentrated to a minimum volume (500 μ l).

Liquid chromatography

The sixteen PAH priority pollutants were quantitatively analysed using a reverse phase column (Vydac 201 TP, L=25 cm) coupled to a LDC-Milton Roy pump. Several acetonitrile/water mixtures were used isocratically for the separation and the quantification of PAH presented in Figure 1.¹² The fluorometric detection is performed by a multi-wavelength microprocessing spectrofluorometer (LS 5, Perkin-Elmer). The selectivity is enhanced by changing the fluorescence excitation and emission wavelengths during the chromatographic separation in order to optimize the detection of each PAH.^{12,13} Perdeuterated PAH (phenanthrene-d₈, pyrene-d₁₀) were added as internal standard in each sample as recently proposed.¹⁴

For the analysis of methylated aromatic series, a sequential HPLC procedure has been used as previously reported elsewhere:^{8,12} a normal phase HPLC isolates compounds according to the degree of aromaticity and a reverse phase HPLC separates parent compounds according to the degree of alkylation. The chromatographic fractions suspected of containing methylated tri- and tetra-aromatic compounds were analysed by Shpol'skii spectroscopy.

Low temperature spectrofluorometry

Low temperature luminescence experiments in Shpol'skii matrices at $T=15$ K were performed with a home made spectrofluorometer previously described using a lamp (Xenon, 450 W) as excitation source.⁸

RESULTS AND DISCUSSION

Reverse phase HPLC analysis

The HPLC chromatograms of PAH in the studied samples are similar

to those presented in Figure 5. We can note the unambiguous identification of each researched aromatic compound in the total organic extract without hydrocarbon class separation due to the selectivity of the detection provided by the spectrofluorometer. Evaporation steps of the solvents during the extraction procedure could change the pattern of the aromatic content of a sample, specially for the compounds having one or two aromatic rings. We have focused our analyses on PAH containing three aromatic rings and more, but some values obtained for low molecular weight PAH have also been mentioned.

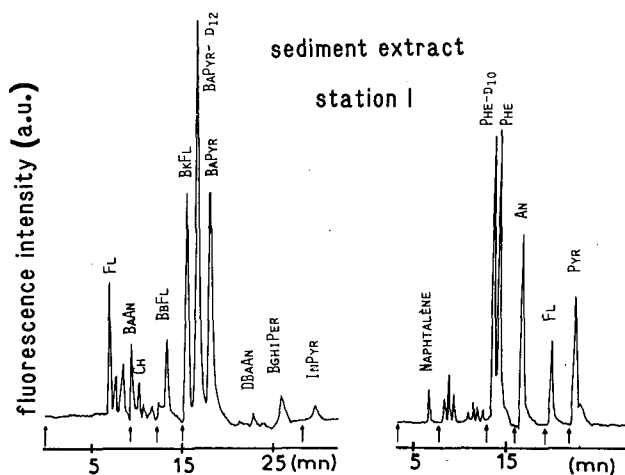


FIGURE 5 Partial HPLC chromatogram on reverse phase HPLC of the total organic extract. Experimental conditions in Ref. 13. Arrows indicate a change in the excitation/emission wavelengths. Perdeuterated phenanthrene and benzo(a)pyrene have been used as internal standards.

The results obtained on three sediment samples are presented in Table I and are compared with those obtained in previous studies on estuarine environments. The PAH concentrations determined in the studied samples are weaker than those reported in two previous studies (Table I). It could be due to the lack of important industrial plant in the Gironde estuary area. Two sediments (Station 2 and Station 3) exhibit a very low level of PAH, partially due to the lithology of the sediments (sand) which does not permit an efficient trap of the organic matter as in muddy sediments (Station 1).

TABLE I

PAH levels in ng/g of dried sediment in the studied samples and in estuarine sediments analysed in previous publications.

A: Ref. 18; B: Ref. 19.

	Station 1	Station 2	Station 3	Severn Estuary (A)	Saudafjord (B)
Naphtalene	43	—	—	—	480
Acenaphthylene	—	—	—	—	—
Acenaphthene	1	—	—	—	32
Fluorene	15	—	—	—	36
Phenanthrene	74	0.8	0.5	—	2175
Anthracene	18	0.2	0.1	300	728
Fluoranthene	100	1	1	1300	2135
Pyrene	102	1	0.5	800	1517
Benzo(a)anthracene	68	1.5	0.2	—	2159
Chrysene	46	5.0	0.2	2300	—
Benzo(e)pyrene	103	—	—	—	6974
Benzo(b)fluoranthene	79	1.2	0.2	—	5587
Pérylene	52	2	—	—	1658
Benzo(k)fluoranthene	24	0.5	<0.1	—	2540
Benzo(a)pyrene	52	0.5	<0.1	700	6313
Dibenzo(a, h)anthracene	12	0.5	—	600	—
Benzo(g, h, i)perylene	72	1	—	400	1969
Indeno(1,2,3, c-d)pyrene	61	—	—	—	—

Analysis of methylated aromatic series

Isomeric forms of methylated derivatives could be distinguished by Shpol'skii spectroscopy.⁸ This technique allows the determination of the relative distribution in each series, as presented in Figure 5 for phenanthrene compounds observed in the Station 1 extract. In this PAH series, the ratio MP/P (i.e. ratio of the total concentration of monomethylphenanthrenes to the concentration of the parent compound) has often been measured in natural samples to distinguish the sources of aromatic compounds.^{1,6} We have also constructed another ratio MPI_2 where the total concentration of the most thermodynamically stable isomers^{15,16} (2MP + 3MP) is divided by the total concentration of the less thermodynamic ones (1MP + 9MP + 4MP). Similar ratios have been also defined in the other PAH series (Table III) and are presented in Table II. The values of these

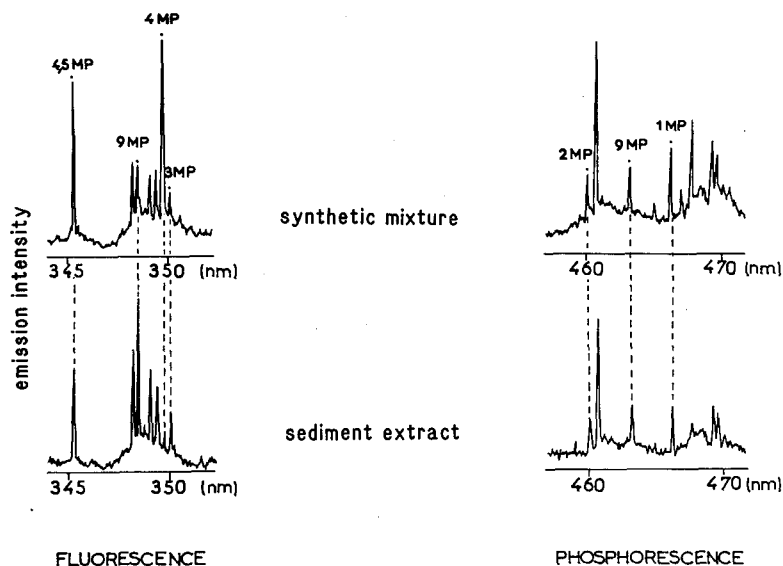


FIGURE 6 High resolution fluorescence and phosphorescence spectra of phenanthrene compounds in *n*-hexane at $T=15$ K. Excitation at 299 nm for fluorescence and at 297 nm for phosphorescence. $C=2 \times 10^{-7}$ M for each compound in the synthetic mixture. Note the presence of the 4,5-methylene phenanthrene (4,5-MP).

TABLE II

Definition of different concentration ratios in phenanthrene, chrysene and pyrene series.

$\frac{MP}{P} = \frac{1MP + 2MP + 3MP + 4MP + 9MP}{P}$	
$MPI_2 = \frac{2MP + 3MP}{1MP + 4MP + 9MP}$	
$\frac{MC}{C} = \frac{1MC + 2MC + 3MC + 4MC + 5MC + 6MC}{C}$	
$MCI_2 = \frac{2MC + 3MC}{1MC + 4MC + 5MC + 6MC}$	
$\frac{MPy}{Py} = \frac{1MPy + 2MPy + 4MPy}{Py}$	
$MPy_2 = \frac{2 \times 2MPy}{1MPy + 4MPy}$	

TABLE III

Phenanthrene, chrysene and pyrene ratios determined in the sediment extracts.

Samples	Phenanthrene ratios			Pyrene ratios		Chrysene ratios	
	MP/P	MPI ₂	% 4,5 MP	MPy/Py	MPyI ₂	MC/C	MCI ₂
Le Verdon (Harbour)	0.94	1.32	9.3	0.39	0.64	0.52	1.22
Crude oil (Indonesia)	3.06	1.10	0	—	—	2.25	0.77
Station 1	1.17	1.03	10.25	—	—	0.37	1.36
Station 4	1.57	1.36	6.20	0.23	0.54	0.81	1.22
Station 5	1.26	1.32	2.40	0.22	0.69	0.94	1.44

ratios reject a recent petroleum contamination of the studied samples since the values observed for a crude oil are completely different. The high values of the MPI₂, MPyI₂ and MCI₂ ratios suggests high temperature combustion processes as sources of aromatics in the sediments, since in such processes, the production of the most thermodynamically stable isomers is favored. These values are comparable with those obtained on air particulate matter.⁸ The presence of the 4,5-methylene phenanthrene, which is typical of pyrolytic origin confirms the origin of the aromatic organic matter in the superficial sediments studied here. We can also mention the lack of steric hindered compounds such as 4 MP, 4 MC and 5 MC in these sediments, whereas some small amounts have been detected in other recent sediments¹⁷ and in crude oils.⁷

CONCLUSION

Present results on the series of the sixteen PAH show a relatively low contamination of the studied sediments in regard with measurements performed on sediments from more polluted European estuaries.

Isomer ratios may be useful to distinguish among petroleum and combustion sources by comparing the values obtained for sediment

extracts and the values observed on materials representative of these sources. More works should be done to investigate other methylated aromatic series (such as alkylated dibenzothiophenes) and also to extend the studies to various representative sources for a true discrimination and a calibration of PAH sources in the sediments.

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Bibliography

1. W. W. Youngblood and M. Blumer, *Geochim. Cosmochim. Acta* **39**, 1303 (1975).
2. W. Giger and C. Schaffner, *Anal. Chem.* **50**, 243 (1978).
3. R. E. Laflamme and R. A. Hites, *Geochim. Cosmochim. Acta* **42**, 289 (1978).
4. S. G. Wakeham, C. Schaffner and W. Giger, *Geochim. Cosmochim. Acta* **44**, 415 (1980).
5. U.S. EPA. Effluents Guidelines Division, Washington, 1977.
6. S. Sporstøl, N. Gjøs, R. G. Lichtenthaler, K. O. Gustavsen, K. Urdal, F. Oreld and J. Skel, *Environ. Sc. Technol.* **17**, 282 (1983).
7. P. Garrigues, R. de Sury, M. L. Angelin, M. Ewald, J. L. Oudin and J. Connan, *Org. Geochem.* **6**, 759 (1984).
8. P. Garrigues, R. de Sury, J. Bellocq and M. Ewald, *Int. J. Environ. Anal. Chem.* **21**, 185 (1985).
9. P. Garrigues and M. Ewald, *Anal. Chem.* **55**, 2155 (1983).
10. P. Garrigues, G. Bourgeois, A. Veyres, J. Rima, M. Lamotte and M. Ewald, *Anal. Chem.* **57**, 1068 (1985).
11. J. C. Monin, R. Pelet and A. Fevrier, *Rev. Inst. Fr. Petr.* **33**, 223 (1978).
12. W. E. May and S. A. Wise, *Anal. Chem.* **56**, 255 (1984).
13. H. H. Soclo, P. Garrigues and M. Ewald, *Analusis* **14**, 344 (1986).
14. W. F. Kline, S. A. Wise and W. E. May, *J. Liq. Chromatog.* **8**, 223 (1985).
15. J. M. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3357 (1952).
16. M. Radke, D. H. Welte and H. Willsch, *Geochim. Cosmochim. Acta* **46**, 1 (1982).
17. P. Garrigues and M. Ewald, *Org. Geochem.* **2**, 52 (1983).
18. E. D. John, M. Cooke and G. Nickless, *Bull. Environ. Contam. Toxicol.* **22**, 653 (1979).
19. A. Bjorseth, J. Knutzen and J. Skel, *Sci. Tot. Environ.* **13**, 71 (1979).