

# Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH)

Anthropogenic/natural inputs  
Estuary  
Hydrocarbons  
Mediterranean  
Sediments

Apports anthropogéniques/naturels  
Estuaire  
Hydrocarbures  
Méditerranée  
Sédiments

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## ABSTRACT

Surface sediments were collected in the Rhone delta, NW Mediterranean, at two seasons and analyzed for composition of non-aromatic hydrocarbons (NAH), long-chain linear alkylbenzenes (LAB) and polycyclic aromatic hydrocarbons (PAH) by GC and GC/MS following fractionation by normal phase HPLC. Concentrations varied from 21.2 to 166.7  $\mu\text{g/g}$  for NAH, from 2097.9 to 9324.2  $\text{ng/g}$  for total PAH and from 342.5 to 2713.0  $\text{ng/g}$  for LAB. These levels are comparable to those reported for other coastal areas worldwide in the vicinity of important urban and industrial activities. Detailed analysis permitted identification of several contributions to the bulk sedimentary hydrocarbon mixture from fossil fuel related sources, pyrolytic processes, domestic wastes as well as from natural precursors. The various hydrocarbon inputs showed distinct variations at the two seasons. Thus, pyrolytic inputs were significantly higher in winter, whereas other hydrocarbon inputs (fossil and natural) showed a slight increase in late summer. Distributions in the deltaic area, from the river mouth as far as the limit of the continental shelf, evidenced that hydrocarbons followed dissimilar dispersal modes depending on their origin, which indicated specific, non identical particle associations. Fossil and naturally-derived hydrocarbons displayed a regular decreasing trend seawards which was highly correlated to the decrease of the organic carbon content of sediments. Compounds derived from domestic wastes (LAB) showed a very sharp decrease offshore, suggesting their association with very rapidly settling particles. Hydrocarbons derived from pyrolytic sources were not significantly correlated with the organic carbon and also showed some accumulation trends in specific areas. Our data indicate that simultaneous analysis of multiple hydrocarbon classes constitutes a powerful and indispensable approach in estuarine and coastal regions for the comprehensive assessment of various inputs, both anthropogenic and natural, as well as for the determination of their environmental behaviour.

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## RÉSUMÉ

Étude des apports organiques naturels et anthropogéniques aux sédiments estuariens par les traceurs hydrocarbures (HNA, ABL, HAP)

Des sédiments superficiels collectés dans le delta du Rhône (Méditerranée nord-occidentale) à deux saisons ont été analysés pour leur composition en hydrocar-

bures non-aromatiques (HNA), alkylbenzènes linéaires à longue chaîne (ABL) et hydrocarbures aromatiques polycycliques (HAP), en chromatographie gazeuse et par couplage chromatographie gazeuse-spectrométrie de masse après fractionnement en chromatographie liquide haute performance. Les concentrations mesurées varient de 21,2 à 166,7 µg/g pour les HNA, de 2097,9 à 9324,2 ng/g pour les HAP totaux et de 342,5 à 2713,0 ng/g pour les ABL. Ces teneurs sont comparables à celles rapportées dans la littérature pour des zones côtières à proximité d'activités industrielles et urbaines importantes. L'analyse détaillée met en évidence des contributions de diverses sources associées à des produits pétroliers, aux processus de pyrolyse/combustion, à des déchets urbains ainsi qu'aux processus naturels. Les teneurs en différentes classes d'hydrocarbures montrent des variations distinctes d'une saison à l'autre qui reflètent les fluctuations des divers apports. Ainsi les apports pyrolytiques sont sensiblement plus élevés en hiver tandis que les apports fossiles et naturels montrent une légère croissance en fin d'été. Les distributions dans la zone deltaïque, à partir de l'embouchure et jusqu'à la limite du plateau continental, révèlent que les hydrocarbures suivent des modes de dispersion différents selon leur source, ce qui implique des associations spécifiques avec les particules. Les teneurs en hydrocarbures d'origine fossile et naturelle montrent une décroissance régulière vers le large, bien corrélée avec celle du contenu en carbone organique des sédiments. Les apports liés aux déchets urbains (ABL) sont caractérisés par une très forte décroissance, qui indique leur association avec des particules à sédimentation rapide. Les teneurs en hydrocarbures d'origine pyrolytique ne montrent pas de relation significative avec le carbone organique. Nos résultats mettent en évidence que l'analyse simultanée des diverses classes d'hydrocarbures constitue une approche puissante et nécessaire en milieux estuarien et côtier pour la détermination des divers apports anthropogéniques et naturels, ainsi que pour la compréhension de leur comportement environnemental.

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## INTRODUCTION

Coastal sediments act as a temporary or long-term sink of materials derived from land-based sources. Areas adjacent to major rivers receive large inputs of detrital organic matter from riverine discharge which may include natural components as well as varying levels of anthropogenic compounds. Hydrocarbons are commonly important components of the land-derived organic inputs transported by rivers towards coastal areas. The chemical composition of sedimentary hydrocarbon mixtures reflects the relative contributions of various natural and anthropogenic sources. The latter include mainly compounds related to fossil fuels and to their combustion and are often prominent in the vicinity of highly populated and industrialized areas.

Polycyclic aromatic hydrocarbons (PAH) have received special attention as they have long been recognized as hazardous environmental chemicals (NAS, 1983). They mainly derive from unburned fossil fuels and from their pyrolysis/combustion (Neff, 1979). They enter the marine environment through industrial discharges, petroleum spills and non-point sources such as urban runoff and atmospheric fallout (Neff, 1979; Eganhouse and Kaplan, 1982; Hoffman *et al.*, 1984; McVeety and Hites, 1988). The ubiquity of PAH residues in sediments has been well established on a global basis (Laflamme and Hites, 1978; Hites *et al.*, 1980; Tan and Heit, 1981; Boehm and Farrington, 1984; Johnson *et al.*, 1985). The determination

of their detailed molecular composition has been shown as a useful tool for ascertaining their specific sources and environmental fate (*e. g.*, Lee *et al.*, 1977; Laflamme and Hites, 1978; Wakeham *et al.*, 1980; Gschwend and Hites, 1981; Prahl and Carpenter, 1983; Readman *et al.*, 1986; Colombo *et al.*, 1989) and thus for identifying and tracing anthropogenic inputs.

In recent years, the occurrence of long-chain linear alkylbenzenes (LAB) in coastal areas has been recognized (Eganhouse *et al.*, 1983; Takada and Ishiwatari, 1987; Albaiges *et al.*, 1987). These compounds are used as raw material for synthesizing linear alkylbenzenesulfonates (LAS), which are commonly used anionic surfactants in synthetic detergents. The occurrence of LAB in the aquatic environment results from their incomplete sulfonation during the synthesis of LAS-detergents and their subsequent discharge to the aquatic environment by the use of such detergents. LAB are resistant to microbial degradation relatively to LAS (Takada and Ishiwatari, 1990) and they have been proposed as promising molecular indicators of domestic wastes.

The study of sedimentary non-aromatic hydrocarbons (NAH) has been frequently focused on the determination of natural inputs, since a large fraction of these compounds derives from terrestrial and marine biological sources such as vascular plants, animals, bacteria, macroalgae and microalgae (Saliot, 1981). Certain hydrocarbons are also produced from bacterial and chemical

degradation of naturally occurring lipids. However, petroleum-related sources also contribute to significant, and sometimes major, non-aromatic hydrocarbon inputs (NRC, 1985). Considerable amounts of petroleum are discharged into the marine environment through runoff, industrial and sewage effluents, storm-water drainage, shipping activities, spillages... (Eganhouse and Kaplan, 1982; Burns and Saliot, 1986). Several criteria based on characteristic compositional profiles and on the occurrence of specific components have been used for distinguishing such anthropogenic inputs (Dastillung and Albrecht, 1976; Mazurek and Simoneit, 1984; Readman *et al.*, 1986).

Studies on hydrocarbons in the aquatic environment can be based on the analysis of either the water column or sediments. Although analysis of hydrocarbons in the water column can provide insight into both short-term qualitative/quantitative variations of pollutant discharges and aspects of their transport mechanisms and fate prior to deposition (Bouloubassi and Saliot, 1991 *b*), sedimentary hydrocarbons have received special attention, since the application of the concept that aquatic sediments act as pollutant sinks may provide an integrated picture of the events taking place in the water column. Nevertheless, most studies have involved evaluations on a single sedimentary hydrocarbon class. A few studies have combined information provided from non-aromatic and polycyclic aromatic hydrocarbons (Farran *et al.*, 1987; Colombo *et al.*, 1989; Lipiatou and Saliot, 1991). Because hydrocarbons are commonly found in the environment as complex mixtures deriving from multiple sources, the confident discrimination between biogenic and anthropogenic origin, as well as the further recognition of inputs from petrogenic, pyrogenic and domestic wastes sources requires a multi-marker approach. This approach is also needed because various hydrocarbon classes show differences in their residence time, stability, transport mechanisms and fate, depending on their physical-chemical properties and sources.

In this respect, the present paper focuses on the determination of levels, sources and transport pathways of three sedimentary hydrocarbon classes: non-aromatic hydrocarbons (NAH), polycyclic aromatic hydrocarbons (PAH) and linear alkylbenzenes (LAB). As a case study we have chosen an area of high environmental interest, the Rhone delta, in the Northwestern Mediterranean Sea. This area receives major discharges of anthropogenic inputs derived from the Rhone river which has a highly urbanized and industrialized drainage basin, as well as from the adjacent industrialized area of the Gulf of Fos. In addition to anthropogenic inputs, the Rhone river also carries important detrital organic inputs of natural origin. Detailed information on the molecular composition of hydrocarbons was obtained by capillary gas chromatography (GC) and by gas chromatography combined with mass spectrometry (GC/MS), following fractionation by normal phase HPLC. Major sources are investigated using several diagnostic indexes and characteristic compositional trends.

Table 1

*Annual mean flows and drainage areas of the principal rivers entering the Mediterranean Sea. From UNEP et al. (1984).*

*\* Present flow. Before the construction of the Aswan Dam the flow was 2800 m<sup>3</sup> at Cairo. After Aswan, the flow was reduced to 1500 m<sup>3</sup>. Downstream irrigation further reduces the flow into the Mediterranean Sea (UNEP, 1989).*

*Débits moyens annuels et superficies des bassins versants des principaux fleuves se jetant en Mer Méditerranée. D'après UNEP et al. (1984).*

*\* débit actuel. Avant la construction du barrage d'Assouan, le débit était de 2800 m<sup>3</sup>/s au Caire. Après la construction, le débit a été réduit jusqu'à 1500 m<sup>3</sup>/s. La décroissance ultérieure de l'apport à la Méditerranée est due à l'irrigation (UNEP, 1989).*

River	Flow (m <sup>3</sup> s <sup>-1</sup> )	Drainage area (10 <sup>3</sup> km <sup>2</sup> )
Rhone	1712	96
Po	1550	70
Ebro	550	84
Nile	500*	2960

## MATERIALS AND METHODS

### Study area

The Rhone river is the largest freshwater input to the Mediterranean Sea, exceeding even the Nile (Tab. 1), with a mean flow of 1712 m<sup>3</sup>/s and an annual solid discharge of 4-5x10<sup>6</sup> t (Span, 1984). Its drainage basin (96x10<sup>3</sup> km<sup>2</sup>) contains important urban centres, substantial industrial activities as well as much agriculture land. It represents the major supplier of land-derived detrital materials, both natural and anthropogenic, to the deltaic area and the continental shelf of the Gulf of Lions. Additional anthropogenic inputs in this area occur from the adjacent highly industrialized Gulf of Fos. The continental riverborne materials are transported towards the open sea by the surface riverine plume which extends to the southwest under the influence of the dominant winds and also by a benthic nepheloid layer mostly towards the southwest as well. The dominant SW direction of the riverine inputs corresponds to the seaward shift of the front between the coastal waters and the Liguro-Provençal cyclonic gyre, a major forcing function in the Gulf of Lions.

### Sampling

Deltaic sediment samples were obtained from the river outflow up to the limit of the continental shelf (water depth 95m) during two cruises in February 1985, stations E, IC, IP, PL, and in September 1986, stations 5, 7, 8, 10, 19 (Fig. 1). Use of a metallic box-corer permitted sampling of a non-disturbed surface sediment. The first top centimetre was collected and stored frozen (-20°C) until analysis in the laboratory.

### Analysis

The analytical procedure summarized below has been previously described in detail (Bouloubassi and Saliot, 1991 *a*). It involves the extraction of freeze-dried sediments with a

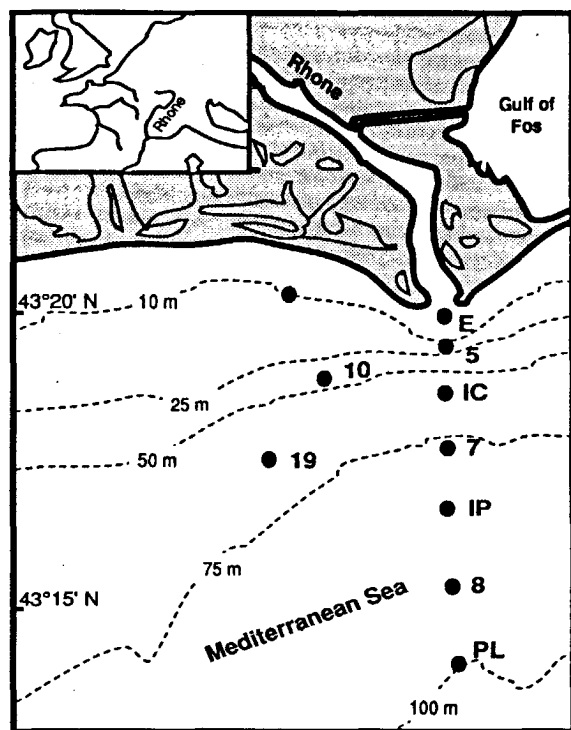


Figure 1

Location of sampling sites in the Rhone delta, France, NW Mediterranean.

Emplacement des stations de prélèvement dans le delta du Rhône, Méditerranée nord-occidentale, France.

$\text{CH}_2\text{Cl}_2/\text{MeOH}$  mixture (2:1 v/v) under reflux during 3 hours. After spiking with perdeuterated internal standards ( $n\text{-C}_{24}\text{D}_{50}$ , phenanthrene- $\text{D}_{10}$ , pyrene- $\text{D}_{10}$ ) the lipid extract was saponified with a  $\text{KOH}/\text{MeOH}$  solution (2M, 20 %  $\text{H}_2\text{O}$ ) and the neutral lipids were subsequently recovered by extraction with hexane-ether mixtures. Normal phase HPLC

with UV detection (254 nm) was used to isolate aliphatic and aromatic hydrocarbons and to further fractionate the latter into different groups according to the number of fused aromatic rings. Amino-bonded silica (Nucleosil,  $5\text{NH}_2$ ) was used as stationary phase and fractions were eluted with n-hexane. Analytical capillary gas chromatography was carried out on a Girdel 3000 instrument fitted with a FID detector and a Ross injector. Hydrocarbon fractions were injected on a fused silica capillary column (30 m x 0.25 mm i. d.) coated with DB-5 phase (J & W Scientific). Temperature was programmed from  $100^\circ$  to  $300^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  for the analysis of non-aromatic hydrocarbons and from  $80^\circ$  to  $300^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  for the analysis of the aromatic fractions. Helium was used as carrier gas at a flow of 2 ml/min. Gas chromatography-mass spectrometry (GC/MS) analyses were performed in the EI mode on a Nermag R1010C quadrupole mass spectrometer interfaced with a Girdel 32 gas chromatograph. Column and temperature programming were the same as for GC analysis. The mass spectrometric data were acquired and processed on a PDP 11/23 Plus-Sidar 111/3 data system. Identification of individual compounds was achieved by comparison of GC retention times with those of standard compounds, as well as by comparison of retention indices with those reported by Lee *et al.* (1979). Further structural confirmation was accomplished by interpretation of mass spectra and/or comparison with data available in the literature. Quantification of individual compounds was based on comparison of peak areas obtained by electronic integration (Vista 401, Varian) with those of internal standards. The average reproducibility of the method was 10 %, evaluated from duplicate analyses. Strict precautions were taken to avoid contamination of the samples during sampling operations and laboratory work up. Solvents were distilled twice; filters and chemicals were solvent extracted; glassware was cleaned by heating at  $450^\circ\text{C}$  for 24 h and rinsed with solvent before use. Blank procedures were systematically carried out, showing no noticeable interference.

Table 2

Selected parameters and analytical data of non-aromatic hydrocarbons in sediments from the Rhone delta. OC: organic carbon content; NAH: total non-aromatic hydrocarbons; n-ALK: n-alkanes; UCM: unresolved complex mixture; CPI: carbon preference index calculated in the 25-35 carbon range;  $C_{\text{max}}$ : carbon number of the most abundant n-alkane; U/R: ratio of unresolved to resolved compounds;  $C_{27}\text{-}C_{31}$ : sum of n-alkanes with 27, 29 and 31 carbon atoms;  $C_{17}/C_{29}$ : ratio of n- $C_{17}$  to n- $C_{29}$  alkane.

Paramètres-clés et résultats de l'analyse des hydrocarbures non aromatiques dans les sédiments du delta du Rhône. OC = teneur en carbone organique; NAH = hydrocarbures non aromatiques totaux; n-ALK = n-alcane; UCM = enveloppe non résolue; CPI = indice de prédominance calculé dans la gamme de carbone 25-35;  $C_{\text{max}}$  = nombre d'atomes du n-alcane le plus abondant; U/R = rapport entre les concentrations des composés non résolus et résolus;  $C_{27}\text{-}C_{31}$  = somme des n-alcane ayant 27, 29 et 31 atomes de carbone;  $C_{17}/C_{29}$  = rapport des n-alcane ayant 17 et 29 atomes de carbone.

	Station 5	Station 10	Station 7	Station 19	Station 8	Station E	Station IC	Station IP	Station PL
Depth (m)	25	43	78	71	90	5	66	85	100
OC (%)	1.58	1.51	1.23	1.27	1.03	2.00	1.34	1.01	0.81
NAH ( $\mu\text{g}/\text{g}$ )	166.7	126.3	82.5	92.3	57.9	153.1	69.2	46.9	21.2
n-ALK ( $\mu\text{g}/\text{g}$ )	8.7	7.7	4.1	5.2	3.7	12.1	4.1	3.1	2.0
UCM ( $\mu\text{g}/\text{g}$ )	145.7	109.7	69.6	78.6	49.9	129.7	59.2	41.1	17.7
CPI (25-35)	2.8	2.9	3.0	2.4	2.3	2.9	3.9	2.7	2.8
$C_{\text{max}}$	$C_{29}$	$C_{29}$	$C_{29}$	$C_{29-31}$	$C_{31}$	$C_{29}$	$C_{29}$	$C_{31-29}$	$C_{31}$
U/R	7.0	6.6	5.4	5.8	6.2	5.7	6.3	7.5	5.4
$C_{27}\text{-}C_{31}$ ( $\mu\text{g}/\text{g}$ )	3.9	3.5	2.5	2.1	1.34	5.4	2.0	1.2	0.6
$C_{17}/C_{29}$	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.3

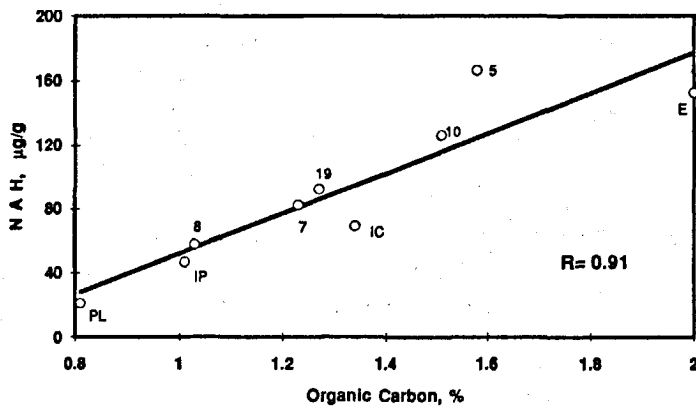


Figure 2

Relationship between non-aromatic hydrocarbons (NAH, in  $\mu\text{g/g}$  of dry sediment) and the organic carbon content of sediments from the Rhone delta.

Relation entre les concentrations en hydrocarbures non aromatiques (NAH) exprimées en  $\mu\text{g/g}$  de sédiment sec, et la teneur en carbone organique pour les sédiments du delta du Rhône.

## RESULTS AND DISCUSSION

### Non-aromatic hydrocarbons (NAH)

#### Distributions and concentrations

Analytical data and selected parameters are given in Table 2. The organic carbon content (OC %) of the deltaic sediments varied in a narrow range, from 2.00 % near the river mouth to 0.81% at the limit of the continental shelf. The slight seaward decrease reflected the sedimentation of terrestrial organic inputs carried by the Rhone river. Total concentrations of non-aromatic hydrocarbons (NAH) showed sharp spatial variations, from 21.2 to 166.7  $\mu\text{g/g}$  of dry sediment. They represent 2.6-10.6 mg of NAH/g of organic carbon. The highest levels were encountered near the river mouth (stations 5, E), whereas a strong decrease was observed with increasing distance offshore. This feature underlined the fact that riverine inputs are the major hydrocarbon supplier to the deltaic sediments. The significant hydrocarbon accumulation in the area in front of the river mouth is consistent with the high deposition rates measured in this area, up to 30 cm/yr (Calmet and Fernandez, 1990). Furthermore the rapid burial of riverborne materials is favored by electrochemi-

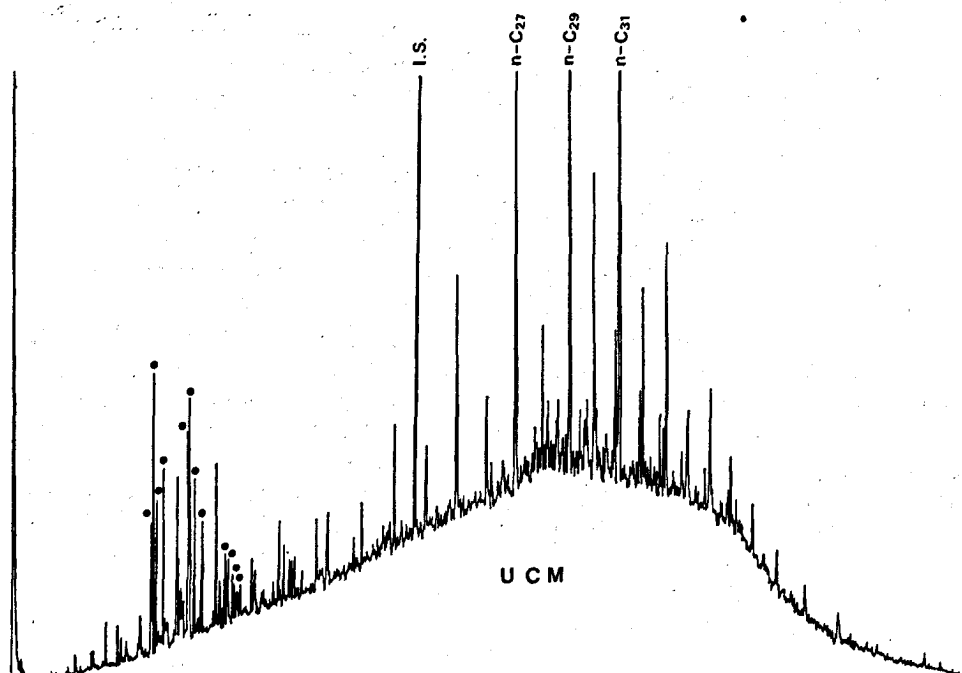
cal flocculation and aggregation phenomena occurring near the river outflow (Aloisi *et al.*, 1982).

The concentrations of total non-aromatic hydrocarbons found in the Rhone delta sediments were significantly higher than those reported in unpolluted intertidal and estuarine sediments. The latter may range from sub- $\mu\text{g/g}$  to  $\approx 10 \mu\text{g/g}$  (*e. g.*, Volkman *et al.*, 1980; Van Vleet *et al.*, 1984; Pillon *et al.*, 1986). Concentrations may be two or three times higher where significant inputs of n-alkanes derived from plant waxes occur. Organic-rich marine sediments may contain up to 100  $\mu\text{g/g}$  total aliphatic hydrocarbons, but concentrations higher than this level are usually due to petroleum inputs. Values up to 1800  $\mu\text{g/g}$  have been reported in petroleum-contaminated surface sediments from the New York bight (Farrington and Tripp, 1977), whereas concentrations from 4 to 350  $\mu\text{g/g}$  were reported in Puget Sound sediments (Barrick *et al.*, 1980). From the existing data it is clear that the concentration of hydrocarbons from biogenic sources may exceed that from pollutant sources where the total concentration is  $< 50 \mu\text{g/g}$ . Inversely, higher concentrations ( $> 100 \mu\text{g/g}$ ) indicate the presence of substantial petroleum contamination. Other authors have used the ratio of non-aromatic hydrocarbons (in  $\mu\text{g/g}$ ) to the organic carbon content of sediments as a

Figure 3

Gas chromatogram of sedimentary non-aromatic hydrocarbons from the Rhone delta (station 5). Main resolved peaks are n-alkanes. I.S.: internal standard; n-C<sub>27</sub>, n-C<sub>29</sub>, n-C<sub>31</sub> refer to n-alkanes with 27, 29 and 31 carbon atoms; UCM: unresolved complex mixture; linear alkylbenzenes are indicated by black circles.

Chromatogramme en phase gazeuse des hydrocarbures non-aromatiques extraits des sédiments du delta du Rhône à la station 5. Les pics résolus majeurs sont les n-alcane. I.S. = standard interne; n-C<sub>27</sub>, n-C<sub>29</sub>, n-C<sub>31</sub> désignent les n-alcane ayant 27, 29 et 31 atomes de carbone; UCM = enveloppe non résolue; les alkybenzènes linéaires sont notés par un cercle noir.



diagnostic tool and proposed that values of this ratio higher than 50 might indicate petroleum pollution (Marchand and Roucache, 1981; Boehm, 1984). Following the criteria reported above, sediments near the outflow of the Rhone river appeared affected by important petroleum pollution.

Variations of NAH concentrations between winter and late summer samples were minor for the near shore sediments, but more significant for the offshore ones (*i. e.* station 8). Nevertheless, sediments from the same area collected in May 1987 showed significantly higher concentrations, especially at the station located at the limit of the continental shelf (Lipiatou and Saliot, 1991). These variations are most likely related to the river flow, since the highest NAH levels offshore were found in periods of higher river flow which expels riverine discharges seawards. The variation of the NAH concentrations was closely related to that of the organic carbon content (OC %) of sediments, as it was evidenced by the significant correlation observed ( $R = 0.91$ ,  $n = 9$ , Fig. 2). Thus, in general terms, the hydrocarbon-laden particles appeared to follow similar dispersal trends as those carrying bulk organic carbon.

#### Composition and sources

##### · Unresolved Complex Mixture (UCM)

Gas chromatographic traces of non-aromatic hydrocarbons (Fig. 3) were characterized by two general features: resolved compounds and an unresolved complex mixture (UCM). The latter appeared in all samples as a broad unimodal hump in the range  $C_{18}$ - $C_{35}$ . The maximum height of UCM usually occurred between  $C_{27}$  and  $C_{31}$ . The UCM is generally considered as a mixture of many structurally complex isomers and homologs of branched and cyclic hydrocarbons that cannot be resolved by capillary columns. However, Gough and Rowland (1990) have shown using chemical degradation techniques that the UCM consists primarily of linear chains connected at branch points giving rise to "T-shaped" molecules. These molecules are resistant to biodegradation and thus accumulate in sediments. In general, the presence of an important UCM in the aliphatic hydrocarbon chromatogram has a well-known linkage to degraded or weathered petroleum residues (Eglinton *et al.*, 1975; Farrington and Tripp, 1977; Alexander *et al.*, 1982). UCM distributions, mainly in the lower molecular weight range, have also been attributed to bacterial degradation of natural organic inputs, such as algal detritus (Venkatesan and Kaplan, 1982; Broman *et al.*, 1987). UCM formation eluting between  $C_{16}$  and  $C_{22}$  has been observed during bacterial reworking of sedimentary organic matter by Grimalt *et al.* (1988). The presence of an UCM can also indicate hydrocarbon inputs derived from the weathering of ancient rocks (Rowland and Maxwell, 1984). Too few data are at present available to quantify the importance of this as a source of geologically old organic matter in marine sediments, but in most sediments the concentrations would be in the low- $\mu\text{g/g}$  range. The absolute UCM concentrations or, alternatively, its relative importance expressed as the ratio of unresolved to resolved compounds (U/R) are commonly used as diagnostic criteria of pollutant inputs (Mazurek and Simoneit, 1984).

In the study area the unresolved complex mixture (UCM) was by far the major component of the total sedimentary non-aromatic hydrocarbons (NAH). UCM concentrations varied from 17.7 to 145.7  $\mu\text{g/g}$  dry weight, which accounted for 84-88 % of the total NAH. The U/R ratio showed values in the range 5.4-7.5 (Tab. 2). The highest ones were recorded in samples near the river outflow, which also showed the highest NAH levels. According to the commonly used criterion ( $U/R > 4$ , Mazurek and Simoneit, 1984), these values evidenced the widespread presence of important petroleum-related residues in the deltaic area. The U/R ratio did not show significant variations with sampling period and rather represents a background chronic contamination. In May 1987 the values of the U/R ratio were lower (3.6-4.7) but still in the range indicative of petroleum contamination (Lipiatou and Saliot, 1991). These lower values resulted from the significant increase of the concentrations of the resolved compounds in this season, mainly n-alkanes, whereas the absolute UCM concentrations were comparable to those found in the present study.

##### · n-alkanes

n-alkane concentrations throughout the n- $C_{15}$  to n- $C_{40}$  ranged from 2.0 to 12.1  $\mu\text{g/g}$  dry weight (Tab. 2). They accounted for 32-57 % of the total GC resolved compounds and for 5-10 % of the total NAH. Significantly higher concentrations (11.8-27.1  $\mu\text{g/g}$ ) were reported for samples collected in early summer 1987 (Lipiatou and Saliot, 1991), which suggested fresher inputs at this season, presumably in relation with the higher river flow. The variations of the n-alkane concentrations were similar to those observed for NAH, which are quantitatively dominated by the UCM (Fig. 4). Several authors have reported differential particle associations for n-alkanes and UCM. The former, and especially the terrigenous components, have been found associated with coarse sediment fractions assimilated to vegetal debris, whereas the anthropogenic UCM has been found in association with fine particles (Thomson and Eglinton, 1978; Brassell and Eglinton, 1980; Boehm, 1984). Nevertheless Pillon *et al.* (1986) have reported that planktonic/microbial material may also be included within fine particles,  $< 5 \mu\text{m}$ . In the case of the Rhone delta sediments, the similarity of the n-alkanes and UCM variations may indicate a rather homogenous dispersal of different particle classes or, alternatively, a rather equal distribution of the two hydrocarbon groups among various particle classes.

The composition of n-alkanes as shown by the GC analysis (Fig. 3) presented a common profile in all samples. Odd carbon-numbered compounds in the range n- $C_{25}$ -n- $C_{33}$  strongly predominated and n- $C_{29}$  or n- $C_{31}$  was the major compound ( $C_{\text{max}}$ ). This distribution pattern is indicative of prominent terrigenous inputs derived from higher plant waxes (Brassell *et al.*, 1978) which possibly dominated n-alkanes derived from petroleum and its derivatives. The latter usually show distribution with no odd/even predominance maximizing in a lower molecular weight range (Brassell *et al.*, 1978; Simoneit, 1984 *b*).

The sum of the three most abundant compounds (n- $C_{27}$ , n- $C_{29}$ , n- $C_{31}$ ) accounted for 31-61 % of the total n-alkane amount, which underlines the high natural terrigenous

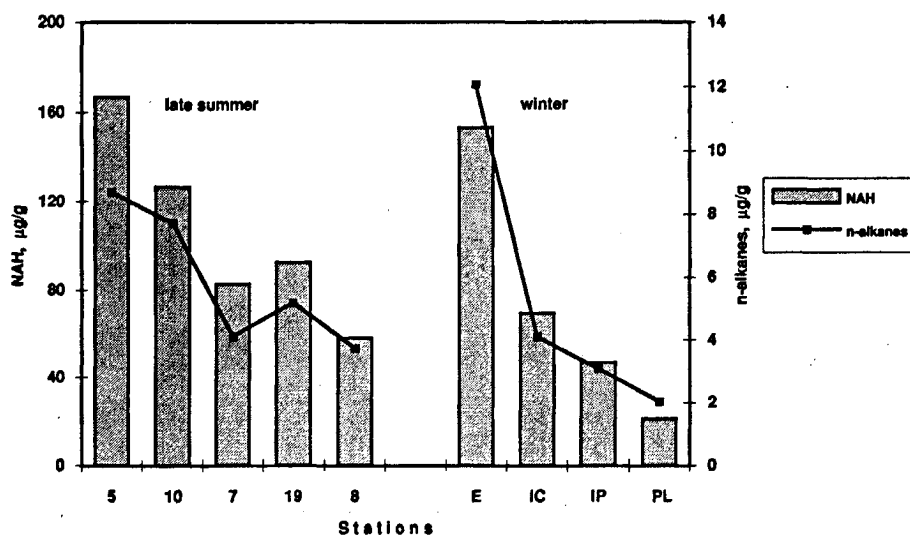


Figure 4

Distributions of non-aromatic hydrocarbons (NAH) and n-alkanes in sediments from the Rhone delta.

Distributions des hydrocarbures non-aromatiques (NAH) et des n-alcane dans les sédiments du delta du Rhône.

inputs in the deltaic area. The odd/even predominance can be quantitatively formulated by specific indexes such as the CPI (Carbon Preference Index) defined as the weighted ratio of odd to even carbon-numbered n-alkanes in the range n-C<sub>25</sub> to n-C<sub>35</sub>. The CPI values in the Rhone delta sediments varied from 2.3 to 3.9 (Tab. 2) and did not show significant spatial or seasonal variations. These values are lower than those typically attributed to high terrigenous inputs (CPI > 4.5). This reflects the admixture of fossil n-alkane series with low odd/even predominance (CPI ≈ 1), as it was suggested by the high abundance of the unresolved compounds and the high values of the U/R ratio. Nevertheless, a contribution from microbial long-chain n-alkanes without odd/even predominance or from microbial alteration of terrestrial n-alkanes giving rise to "smooth" patterns cannot be excluded.

A progressive shift of the C<sub>max</sub> was observed, from C<sub>29</sub> at the stations near the river mouth, to C<sub>31</sub> at the stations located at the limit of the continental shelf. In the intermediate stations, C<sub>29</sub> and C<sub>31</sub> were almost equivalent. Pillon *et al.*, (1986) have reported differences between the C<sub>max</sub> of various granulometric fractions. Higher C<sub>max</sub> were observed in clays and lower ones in sands. Hence, in our samples this could suggest a higher proportion of fine particles in sediments at the limit of the continental shelf relative to those near the river mouth. It is noteworthy that similar shifts were observed in surface water samples (Bouloubassi, 1990).

The n-alkanes in the range n-C<sub>12</sub>-n-C<sub>20</sub> have proved to give good indications of aquatic algal/microbial origins. Among these, n-C<sub>15</sub> and n-C<sub>17</sub> are particularly useful as indicators of planktonic contributions (Saliot, 1981). These alkanes were found only as minor components in the Rhone delta sediments. Other compounds having also a major marine origin, such as linear or acyclic mono- or poly-olefins, were not detected although they have been found in other coastal areas (Barrick *et al.*, 1980; Requejo and Quinn, 1983). This may indicate either very low autochthonous inputs in sediments or low preservation of bulk marine organic matter, at least in its original readily recognized biological form. The second hypothesis seems more plausible, since mono- and poly-olefins were detect-

ed in suspended matter of the overlying water column (Bouloubassi, unpublished data). Moreover, Prahl and Carpenter (1979) showed that aquatic organic matter is preferentially remineralized during sinking and at the sediment-water boundary. This commonly results in an apparent predominance of terrigenous biomarkers in sediments. For this reason the ratio n-C<sub>17</sub>/n-C<sub>29</sub> cannot be confidently used as an indicator of the relative importance of natural marine vs. terrestrial inputs in sediments. However the slight variation of this ratio in our samples indicated a small apparent increase of the relative importance of planktonic inputs in the offshore stations. This can be explained by both the sharp decrease of the terrestrial inputs and the increased surface productivity at the limit of the continental shelf, in the periphery of the riverine plume (Leveau *et al.*, 1990). It is also noteworthy that squalene, a biogenic polyisoprenoid compound, was detected only at the offshore stations 8 and 19 in the late summer samples. In the winter sample set, squalene was found at all stations, which is in all probability linked to the significant mid-water productivity observed at this season through the deltaic area (Bouloubassi, 1990; Denant and Saliot, 1991).

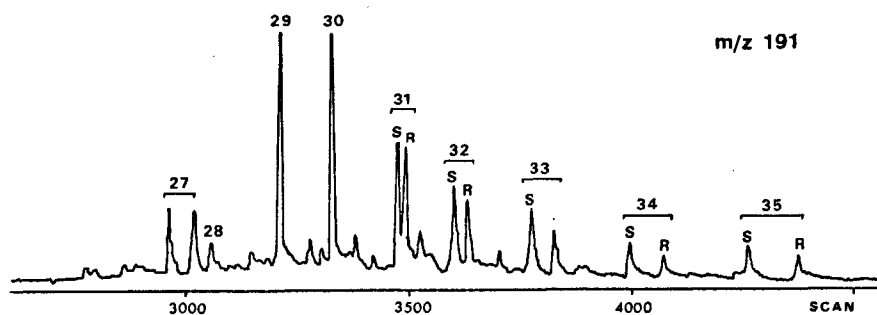
#### • Hopanes

A series of hopanes was detected in all sediment samples. Their recognition was facilitated by GC/MS analysis using the m/z 191 ion as a diagnostic tool, with structural assignments based on full mass spectra. Many of these compounds are ubiquitous in crude oils and, unlike many other hydrocarbons found in oils, are slightly affected by the processes of weathering and bacterial degradation. Their distributions can therefore be used to "fingerprint" oils even after fairly extensive degradation has occurred. Figure 5 shows a characteristic mass fragmentogram for m/z 191 from the GC/MS analysis of the hydrocarbons in the Rhone delta sediments. The major identified components had the thermodynamically stable 17α(H), 21β(H) configuration which, in recent sediments, is indicative of pollution from fossil fuel products. Minor compounds of 17β(H), 21α(H) configuration were also present, while only traces of 17β(H), 21β(H) hopanes of recent microbiological origin were detected. Further confirmation of a dominant fossil origin of the hopanoid triterpanes was provided by the pre-

Figure 5

GC/MS fragmentogram ( $m/z$  191) showing the distribution of  $\alpha$ ,  $\beta$  hopanes at station 5. Numerals refer to carbon number; S and R indicate epimerisation at C-22.

Fragmentogramme obtenu par couplage chromatographie en phase gazeuse/spectrométrie de masse (CG/SM) pour l'appel d'ion 191 ( $m/z$  191), montrant la distribution des hopanes  $\alpha$  et  $\beta$  dans les sédiments du delta du Rhône à la station 5. Les chiffres désignent le nombre d'atomes de carbone ; S et R indiquent les deux épimères en C<sub>22</sub>.



sence of 22S and 22R epimers of the C<sub>31</sub>-C<sub>35</sub> 17 $\alpha$ (H), 21 $\beta$ (H) extended hopanes. The 22S/22S + 22R epimer ratios for C<sub>32</sub> and higher homologs were close to the equilibrium value at maturity (0.6, Mackenzie *et al.*, 1980), which is also indicative of oil pollution (Dastillung and Albrecht, 1976).

### Long-chain linear alkylbenzenes (LAB)

A suite of peaks appearing in GC chromatograms between the C<sub>16</sub> and C<sub>20</sub> n-alkanes (Fig. 3) were identified in GC/MS as being homologous series of linear alkylbenzenes (LAB). They have alkyl side chains ranging from ten to fourteen carbon atoms and each homolog consisted of several phenyl positional isomers (Eganhouse *et al.*, 1983; Takada and Ishiwatari, 1987). Their mass spectra present a characteristic base peak at  $m/z$  91 or  $m/z$  105 as well as a secondary peak indicative of the position of the phenyl group in the alkyl chain. Their detection in the Rhone delta sediments confirmed their widespread occurrence in coastal environments adjacent to urban activities.

Table 3 gives the LAB concentrations in the deltaic sediments. Their sum, referred to here as  $\Sigma$ LAB, range from 0.3 to 2.7  $\mu$ g/g dry weight. These values are similar to those reported in estuarine and offshore sediments from the Tokyo Bay (Takada and Ishiwatari, 1991) and in offshore sediments from the South California coast (Eganhouse *et al.*, 1983), but lower than the levels reported in estuarine sediments from the Spanish Mediterranean coast (Valls *et al.*, 1989). The LAB distribution was dominated by the C<sub>11</sub>- and C<sub>12</sub>-LAB homologs, whereas the C<sub>10</sub>- and C<sub>14</sub>-

LAB were detected at very low levels (Fig. 6). Their isomeric distribution was quite different from that observed in LAS-detergents. In the latter the abundance of each isomer with a given alkyl chain length is almost equal (Takada and Ishiwatari, 1987), whereas in sediment samples the internal isomers (*e. g.*, 5- and 6-C<sub>12</sub>-LAB) dominated over the external ones (*e. g.*, 2-C<sub>12</sub>-LAB; n-C<sub>m</sub>: n indicates the position of the phenyl group in the alkyl chain and m indicates the carbon number of the alkyl chain). The relative depletion of external isomers in sediment samples indicates that LAB are relatively biodegraded since this process affects preferentially the external isomers (Takada and Ishiwatari, 1990; Eganhouse *et al.*, 1983; Bayona *et al.*, 1986). Similar changes in isomer distributions have been reported for the Southern California (Eganhouse *et al.*, 1983), the Tokyo Bay (Takada and Ishiwatari, 1987), the Spanish Mediterranean (Albaiges *et al.*, 1987) and the Australian (Murray *et al.*, 1987) coastal zones.

On the basis of incubation experiments, Takada and Ishiwatari (1990) have demonstrated that the internal/external isomer ratio (I/E) for the C<sub>12</sub> homologs is quantitatively related to the degree of LAB degradation and proposed an index of LAB degradation. As shown in Table 3, I/E ratios in our samples ranged from 1.4 to 1.9 which, according to these authors, correspond to  $\approx$  35 % degradation of LAB in untreated domestic waters. During the late summer 1986 cruise LAB were detected at all stations except for the most remote one, whereas in winter 1985 they occurred only at the station located at the river outflow in relatively lower levels. This feature in all likelihood reflects seasonal variations of source inputs. Moreover the E/I ratio was slightly higher in winter, indi-

Table 3

Concentrations of linear alkylbenzenes (LAB) in sediments from the Rhone delta. C<sub>11</sub>-, C<sub>12</sub>-, C<sub>13</sub>- indicate carbon atom number in the alkyl chain;  $\Sigma$ LAB: sum of detected LAB; I/E: ratio of internal to external isomers of the C<sub>12</sub>-LAB.

Concentrations des sédiments du delta du Rhône en alkylbenzènes linéaires (LAB). C<sub>11</sub>-, C<sub>12</sub>-, C<sub>13</sub>- indiquent le nombre d'atomes de carbone de la chaîne alkylée;  $\Sigma$ LAB : somme des LAB détectés; I/E : rapport isomères internes/isomères externes des C<sub>12</sub>-LAB.

	Station 5	Station 10	Station 7	Station 19	Station 8	Station E	Station IC	Station IP	Station PL
C <sub>11</sub> -LAB (ng/g)	1122.7	401.0	203.8	114.8	n.d.	231.0	n.d.	n.d.	n.d.
C <sub>12</sub> -LAB (ng/g)	1101.4	386.1	227.9	136.1	n.d.	252.8	n.d.	n.d.	n.d.
C <sub>13</sub> -LAB (ng/g)	488.9	232.8	167.3	91.6	n.d.	237.8	n.d.	n.d.	n.d.
$\Sigma$ -LAB (ng/g)	2713.0	1019.8	599.1	342.5	n.d.	721.6	n.d.	n.d.	n.d.
I/E	1.5	1.4	1.4	1.5	-	1.9	-	-	-



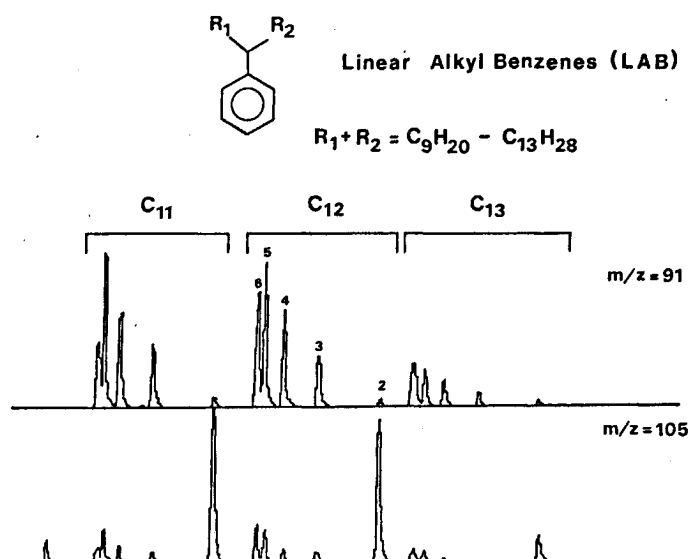


Figure 6

GC/MS fragmentogram ( $m/z$  91, 105) showing the distribution of sedimentary long-chain linear alkylbenzenes (LAB) in the Rhone delta (station 5).  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$  indicate the alkyl chain length. 2, 3, 4, 5, 6 refer to the position of the phenyl group on the alkyl chain.

Fragmentogramme obtenu en CG/SM pour l'appel des ions 91 et 105, montrant la distribution des alkylbenzènes à longue chaîne linéaire (LAB) dans les sédiments du delta du Rhône à la station 5.  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$  précisent la longueur de la chaîne alkylée. 2, 3, 4, 5, 6 indiquent la position du groupe phényle sur la chaîne alkylée.

cating more biodegraded inputs. Highest levels were found near the river mouth. With increasing distance from the shore, the LAB concentrations rapidly decreased. This trend was much more pronounced than those observed for the other hydrocarbon classes. Such drastic decreasing trends were also observed in the South California (Eganhouse *et al.*, 1983), where they have been interpreted as implying a considerable degradation of LAB in coastal areas. However, this was not the case in the Tokyo Bay (Takada and Ishiwatari, 1991). These discrepancies may be interpreted in terms of different physical-chemical conditions in various depositional environments as well as in terms of removal process occurring in the water column prior to deposition. In the case of the Rhone delta, the sharp seaward decrease is rather explained by enhanced scavenging of LAB from the water column, indicating their association with rapidly sinking particles. Biodegradation does not appear to account significantly for the decrease of concentrations seawards, since the E/I ratio did not exhibit noticeable variations.

### Polycyclic aromatic hydrocarbons (PAH)

The combined use of normal phase HPLC and GC, GC/MS in the present study provided a powerful tool to isolate and further resolve the complex, sedimentary PAH assemblages into simpler fractions. Thus, more than 80 compounds were identified and quantified. They comprise unsubstituted three- to six-ring PAH (*i. e.*, parent PAH), several alkyl-substituted homologs as well as sulfur-heterocyclics (benzothiophenes, benzonaphthothiophenes and their alkylated homologs). The concentrations of individual PAH in the

Rhone delta sediments ranged from tens to hundreds of nanograms per gram dry weight (Tab. 4). In many environmental studies dealing with PAH, the concentrations have been reported as the sum of three to five- (or six-) ring parent compounds, *i. e.* PAH with molecular weight 178, 202, 228, 252 (and 276). Although this can facilitate comparisons, it may also underestimate, sometimes severely, the bulk amount of PAH occurring in environmental samples (Bouloubassi and Saliot, 1991 *a*). Moreover, from the qualitative point of view, this parameter does not take into account PAH mainly deriving from fossil sources, since the latter are characterized by high abundances of alkylated homologs and sulfur-heterocyclics as it will be discussed below. For this reason we preferred to use in this study the sum of all PAH compounds identified and quantified (TPAH), as summarized in Table 4. These constituents derive from anthropogenic sources with the exception of three minor compounds, retene (RET) and two tetrahydrochrysenes ( $\alpha$ THC,  $\beta$ THC) which have natural terrestrial precursors. Their occurrence and geochemical significance have been discussed in detail elsewhere (Bouloubassi and Saliot, 1993 *a*).

Concentrations of PAH in the range 1225-2427 ng/g were reported by Lipiatou and Saliot (1991) in sediment samples from the Rhone deltaic area collected in early summer 1987. These levels correspond to the sum of three- to six-ring parent PAH compounds. The same summation applied to our samples gave comparable values for the late summer 1986 cruise (1070-2073 ng/g) but much higher ones for the samples collected in winter 1985 (2399-6364 ng/g). The latter values are comparable to those found in the Ebro delta (Albaiges *et al.*, 1982) and slightly higher than those found off the Spanish coast (Grimalt *et al.*, 1984). Moreover they are much higher than those recorded in other Mediterranean coastal and shelf areas such as the Ligurian Sea off Monaco (Burns and Villeneuve, 1983), the Adriatic Sea (Marcomini *et al.*, 1986), the coast between Monaco and the Rhone delta (Mille *et al.*, 1982).

TPAH concentrations varied from 2097.9 to 9324.2 ng/g dry sediment (Tab. 5). Highest TPAH levels were found in winter, indicating enhanced PAH discharges during this season. Study of suspended matter in surface waters (Bouloubassi and Saliot, 1991 *b*) confirmed that particles were considerably enriched in PAH, mainly of pyrolytic origin, in winter which is probably linked to the more intensive combustion/pyrolysis of fossil fuels during this season. The variations of sedimentary PAH concentrations showed that fluctuations of PAH discharges can be rapidly recorded in superficial deltaic sediments which, therefore, may be used for monitoring pollution. An interesting feature is that such variations between winter and late summer samples were not observed for NAH. Although important contributions from anthropic sources were recognized in the NAH composition previously discussed, this dissimilarity between NAH and TPAH underlined that NAH should be considered as having mixed origins, natural and anthropic, whereas, on the other hand, PAH are essentially representative of the latter. However, even if we consider the variations of the UCM levels, which is mainly attributed to

Table 4

Concentrations (ng/g) of individual polycyclic aromatic hydrocarbons (PAH) in sediments from the Rhone delta. C<sub>1</sub>-, C<sub>2</sub>-, C<sub>3</sub>-: mono-, di- and tri-methyl PAH; DBT: dibenzothiophene; PHE: phenanthrene; A: anthracene; 4,5 MePHE: 4,5-methylenePHE; RET: retene;  $\alpha$ THC and  $\beta$ THC: 3,4,7- and 3,3,7-trimethyl-tetrahydrochrysenes; FLTH: fluoranthene; ACE: acephenanthrylene; PYR: pyrene; cpPYR: cyclopenta[cd]PYR; BghiPYR: benzo[ghi]pyrene; BcPHE: benzo[c]PHE; BNT[2,1]: benzonaphtho[2,1]thiophene; BNT[1,2]: benzonaphtho[1,2]thiophene; BNT[2,3]: benzonaphtho[2,3]thiophene; BaA: benz[a]anthracene; CHR/TRI: chrysenel triphenylene; NATH: naphthacene; cpCHR/TRI: cyclopenta[cd]CHR; B[b + j]FLTH: benzo[b + j]fluoranthene; B[k]FLTH: benzo[k]fluoranthene; BePYR: benzo[e]pyrene; BaPYR: benzo[a]pyrene; PER: perylene; IndPYR: indeno[1,2,3-cd]pyrene; B[ghi]PER: benzo[ghi]perylene; ANTH: anthanthrene.

Concentrations (ng/g) des sédiments du delta du Rhône en hydrocarbures aromatiques polycycliques individuels (PAH). C<sub>1</sub>-, C<sub>2</sub>-, C<sub>3</sub>-: mono-, di- et triméthylPAH; DBT: dibenzothiophène; PHE: phénanthrène; A: anthracène; 4,5 MePHE: 4,5-méthylènePHE; RET: rétène;  $\alpha$ THC et  $\beta$ THC: 3, 4, 7- et 3, 3, 7-triméthyl-tétrahydrochrysenes; FLTH: fluoranthène; ACE: acéphénanthrylène; PYR: pyrène; cpPYR: cyclopenta[cd]PYR; BghiPYR: benzo[ghi]pyrène; BcPHE: benzo[c]PHE; BNT[2, 1]: benzonaphto[2, 1]thiophène; BNT[1, 2]: benzonaphto[1, 2]-thiophène; BNT[2, 3]: benzonaphto[2, 3]thiophène; BaA: benz[a]anthracène; CHR/TRI: chrysène/triphénylène; NATH: naphthacène; cpCHR/TRI: cyclopenta[cd]CHR; B[b + j]FLTH: benzo[b + j]fluoranthène; B[k]FLTH: benzo[k]fluoranthène; BePYR: benzo[e]pyrène; BaPYR: benzo[a]pyrène; PER: perylène; IndPYR: indéno[1, 2, 3-cd]pyrène; B[ghi]PER: benzo[ghi]pérylène; ANTH: anthanthrène.

Compound	Station 5	Station 10	Station 7	Station 19	Station 8	Station E	Station IC	Station IP	Station PL
DBT	9.6	6.8	10.5	17.2	17.1	41.2	21.7	22.2	11.8
C1-DBT	49.1	62.3	33.	37.60	30.8	89.8	43.7	38.1	26.5
C2-DBT	97.5	86.8	69.8	74.4	83.5	182.0	58.1	44.9	28.0
C3-DBT	72.60	87.70	41.10	46.40	46.4	109.0	97.3	66.8	51.7
PHE	193.1	186.2	149.5	172.1	175.7	360.5	237.9	225.8	108.5
A	29.4	25.9	21.4	27.8	31.1	61.0	38.1	32.8	15.3
C1-PHE	165.1	204.3	121.8	132.7	134.9	270.4	196.8	149.9	97.0
4,5 MePHE	26.0	26.2	13.0	19.9	17.5	76.4	33.4	30.0	15.1
C2-PHE	261.5	269.3	214.7	193.3	187.6	320.8	264.0	198.4	120.1
C3-PHE	154.4	105.2	119.0	110.8	88.3	169.8	129.5	94.5	59.5
RET	67.7	52.9	46.8	20.1	16.1	35.5	27.1	13.0	12.9
$\alpha$ THC	31.5	25.7	15.3	15.0	9.8	n.d.	10.2	11.0	n.d.
$\beta$ THC	66.8	49.0	29.2	33.5	16.8	63.5	43.4	14.5	5.2
FLTH	274.4	314.2	207.7	262.9	226.6	968.1	300.4	697.1	390.8
ACE	4.5	8.6	8.8	8.5	13.5	16.2	8.1	9.1	7.5
PYR	219.8	263.6	165.9	210.1	176.1	763.7	230.4	583.9	400.9
C1-PYR	72.1	78.9	53.5	70.6	51.5	228.8	74.8	169.3	109.7
C2-PYR	44.6	91.4	39.3	69.0	77.7	126.0	72.1	162.7	113.3
cpPYR	11.8	9.6	10.2	10.1	18.7	8.3	5.4	16.1	5.3
BghiFLTH	20.6	26.7	18.4	23.6	21.8	77.0	29.8	57.6	35.8
BcPhe	23.1	25.4	16.7	19.7	13.5	67.3	18.5	47.3	30.8
BNT[2, 1]	38.6	43.7	27.5	33.2	20.5	147.9	45.2	112.0	67.9
BNT[1, 2]	12.3	19.1	10.2	9.4	n.d.	43.1	20.3	61.2	15.5
BNT[2, 3]	8.2	8.7	4.4	3.1	n.d.	33.4	12.9	29.1	12.2
C1-BNT	4.2	10.0	4.1	7.6	9.2	n.d.	11.5	n.d.	22.7
C2-BNT	15.2	23.7	18.2	36.8	40.8	68.8	35.7	43.4	n.d.
BaA	119.2	129.6	75.9	88.1	45.3	457.6	125.4	349.4	163.6
CHR/TRI	186.3	219.6	152.9	177.3	107.2	680.2	242.1	613.5	298.0
NATH	24.1	31.7	16.6	19.8	10.6	99.3	26.9	60.7	33.6
C1-CHR/TRI	123.1	135.5	80.1	127.2	59.7	453.2	127.3	297.1	195.5
cpCHR/TRI	20.9	23.6	13.8	18.1	14.0	56.9	17.7	48.5	29.9
C2-CHR/TRI	4.6	25.5	13.8	24.7	27.3	78.0	26.2	n.d.	9.7
B[b + j]FLTH	274.5	333.2	196.4	191.0	108.9	1038.2	307.5	903.9	361.3
B[k]FLTH	23.6	38.4	16.7	20.3	15.5	144.0	34.5	99.4	40.3
B[e]PYR	129.5	163.6	99.4	107.0	83.3	462.1	126.7	390.1	159.0
B[a]PYR	118.9	128.2	69.8	73.1	29.0	478.3	106.2	360.9	136.5
PER	64.4	77.5	28.9	35.1	20.6	197.0	56.0	254.0	74.1
IndPYR	75.2	93.9	52.0	66.2	26.8	343.6	76.5	281.1	96.9
B[ghi]PER	79.4	108.2	62.8	75.4	24.2	376.2	78.4	307.5	100.8
ANTH	24.1	37.0	17.0	27.0	n.d.	130.9	19.7	79.6	19.4

pollutant sources, there is no covariation with the PAH levels which indicates that these hydrocarbon groups do not show similar input rates.

TPAH concentrations did not show any significant correlation with the organic carbon content of sediments. Several authors have, however, reported preferential association of PAH with organic rich particles, mainly

silt/clays, which normally gives rise to high correlations between PAH and organic carbon (Boehm and Farrington, 1984). The close relationship between PAH and the organic carbon has been commonly interpreted in terms of the lipophilic properties of PAH which favour their partition into organic matrices. Deviations from the linear regression equation have been proposed as indica-

Table 5

Selected parameters of polycyclic aromatic hydrocarbons (PAH) in sediments from the Rhone delta. TPAH: total PAH;  $\Sigma$ COMB: combustion PAH as the sum of parent compounds with MW 202, 228, 252, 276;  $\Sigma$ Phe: sum of phenanthrene and its alkylated homologs;  $\Sigma$ DBT: sum of dibenzothiophene and its alkylated homologs.

Paramètres caractéristiques des hydrocarbures aromatiques polycycliques (PAH) des sédiments du delta du Rhône. TPAH : PAH totaux ;  $\Sigma$ COMB : PAH issus de processus de combustion représentés par les composés parents de poids moléculaire 202, 228, 252 et 276 ;  $\Sigma$ PHE : somme du phénanthrène et de ses homologues alkylés ;  $\Sigma$ DBT : somme du dibenzothiophène et de ses homologues alkylés.

	Station 5	Station 10	Station 7	Station 19	Station 8	Station E	Station IC	Station IP	Station PL
TPAH (ng/g)	3241.5	3657.4	2366.9	2715.7	2097.9	9324.2	3437.4	6976.4	3482.6
$\Sigma$ COMB (ng/g)	1525.0	2051.3	1133.1	1318.3	853.5	5924.2	1674.7	4727.0	2275.3
$\Sigma$ COMB/TPAH (%)	45.5	54.0	45.8	46.7	38.9	62.3	64.7	66.8	65.4
$\Sigma$ Phe (ng/g)	800.1	791.2	618.0	628.8	604.0	1197.9	861.6	698.6	400.2
$\Sigma$ DBT (ng/g)	228.8	243.6	155.2	175.6	177.8	422.2	220.8	172.0	118.0

tive of pollution. In our samples the lack of a significant correlation resulted mainly from the fact that sediments collected in winter were highly enriched in PAH, whereas their organic carbon content did not show any noticeable variation. However, the association of PAH with particles still remains controversial. Prahl and Carpenter (1983) have shown that low density sand-sized materials, although they may comprise a small percentage of the total sediment weight, contain high levels of PAH. These authors have suggested specific PAH-particle associations which are dependent on the respective sources of these hydrocarbons and possibly represent the original physical structure of PAH initially introduced into the environment upon formation. This particle selectivity influences the dispersal and distribution of PAH in the environment, and may also affect their availability to organisms and ultimate biological fate. The phase associations between PAH and natural particles points to a reevaluation of the use of simple equilibrium sorption/desorption models in assessing the fate and effects of PAH in aquatic systems. In the studied area, significant deviations from this equilibrium were observed in water samples (Bouloubassi and Salot, 1993 b), which suggested that PAH may show specific associations with particles (e.g. sequestration, occlusion...) upon their formation which may render them unavailable for partition, as proposed by Readman *et al.* (1984).

The lack of TPAH/OC correlation further confirmed the discrimination between PAH and NAH since the latter showed a strong correlation as discussed earlier. Thus, it clearly appears that, in addition to their different input patterns, NAH and PAH also display significant dissimilarities in their dispersal modes. Consequently, their simultaneous analysis appears necessary for a comprehensive assessment of levels, sources and fate of pollutant inputs.

The spatial variations of TPAH concentrations were characterized by high levels near the riverine-end with subsequent dilution by less polluted sediments, resulting in a seaward trend of decreasing concentrations (Fig. 7). However some accumulation trends were observed at stations 10 and IP which are probably linked to sedimentological parameters. This pattern again discriminates between PAH and the other hydrocarbon classes confirming different particle associations.

#### Composition and sources

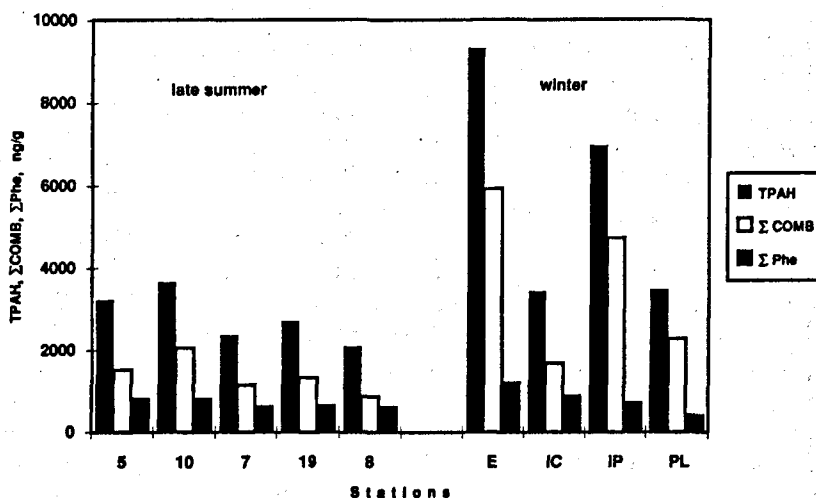
##### Unsubstituted (parent) PAH

Unsubstituted compounds were the major PAH components in all sediments. Among them, five-ring (benzofluoranthenes and benzopyrenes, MW 252) and four-ring PAH (fluoranthene and pyrene, MW 202) dominated the distributions (Fig. 8). Such patterns are characteristic of PAH mixtures generated by pyrolysis/combustion of fuels

Figure 7

Distributions of total PAH (TPAH), combustion PAH ( $\Sigma$ COMB), and sum of phenanthrene compounds ( $\Sigma$ Phe) in sediments from the Rhone delta.

Distributions des hydrocarbures aromatiques polycycliques totaux (TPAH), des hydrocarbures issus de processus de combustion ( $\Sigma$ COMB) et de la somme des composés phénanthréniques ( $\Sigma$ PHE) dans les sédiments du delta du Rhône.



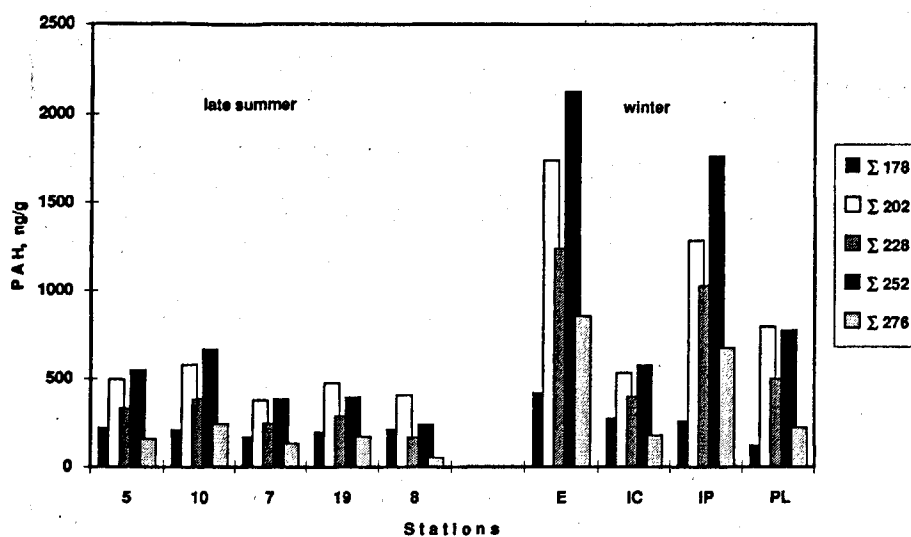


Figure 8

Composition of unsubstituted PAH with molecular weight 178, 202, 228, 252, 276 in sediments from the Rhone delta. Identification of each group is given in the text.

Composition des hydrocarbures aromatiques polycycliques non substitués de poids moléculaire 178, 202, 228, 252 et 276 dans les sédiments du delta du Rhône. L'identification de chaque groupe est précisée dans le texte.

regardless of the fuel burned (Lee *et al.*, 1977). Furthermore, the dominant presence of five-membered alicyclic rings (*e. g.*, fluoranthene, benzofluoranthenes) which, once formed, do not easily revert to pericondensed aromatic PAH, indicated inputs derived from high temperature pyrolytic processes (Simoneit, 1984 *a*). In the studied area, similar PAH compositional features, *i. e.* the prominence of the four- and five-ring parent PAH, have been observed in suspended particles from surface waters under direct influence of riverine discharges (Bouloubassi and Saliot, 1991 *b*). Other authors have also reported such profiles in aerosols collected over the NW Mediterranean (Sicre *et al.*, 1987). Although the main trends of the PAH compositional profiles were similar at all stations in both seasons, the relative abundance of PAH with MW 202 and 252 showed slight spatial trends. Whereas at stations near the river outflow the dominant group was that of five-ring PAH (MW 252) the relative importance of four-ring PAH (MW 202) increased seawards; this group was predominant at the most remote stations. The extent to which particle size distribution controls this trend of change in the PAH distribution pattern, as it has been proposed by Readman *et al.* (1984), requires further investigation.

The dominant PAH composition profile in the Rhone delta sediments has been commonly found in various sedimentary environments. Because of the similarity of these profiles with those derived from combustion, combustion/pyrolysis PAH are expressed in Table 5 as  $\Sigma$ COMB. This parameter is defined as the sum of fluoranthene (Flth), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene/triphenylene (Chr), benzofluoranthenes (BFlth), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), indeno[1, 2, 3-*c, d*]pyrene (IndP) and benzo[*ghi*]perylene (BPer) (Prahl and Carpenter, 1983; Barrick and Prahl, 1987). Phenanthrene (Phe) is not comprised in the  $\Sigma$ COMB term because it may derive from both combustion and fossil sources, as will be discussed in the next section. Although other PAH result from pyrolysis processes, the compounds mentioned represent the most abundant PAH produced. Therefore, the term  $\Sigma$ COMB is considered to be quantitatively representative of the level of combustion PAH. The use of  $\Sigma$ COMB as an indicator of only PAH from combustion would certainly be questionable

in regions where significant inputs from petroleum have occurred.  $\Sigma$ COMB concentrations varied in the range 853.5 to 5942.2 ng/g dry weight and represented 40-67 % of the TPAH. Spatial and seasonal variation trends for  $\Sigma$ COMB were similar to those observed for TPAH (Fig. 7). However, their relative importance with respect to TPAH showed interesting variations. The combustion PAH accounted for 40-54 % of the TPAH in the late summer samples, whereas in winter their percentage was higher, 62-67 %. This confirms that the PAH enrichment of winter samples is mainly due to the increase of pyrolytic inputs. For example, at the river mouth, TPAH concentrations were three-fold higher in winter, whereas pyrolytic inputs, expressed by  $\Sigma$ COMB, were fourfold higher.

#### Phenanthrene compounds

In many cases fossil imprints are less readily recognizable in environmental PAH mixtures than pyrolytic ones, unless important petroleum inputs have occurred. Low MW, mono-, bi- and tri-cyclic aromatics are generally the most abundant constituents of unburned fossil fuels with only minor relative amounts of tetracyclic and larger PAH (Neff, 1979; and references therein). In contrast, combustion PAH mixtures are dominated by compounds of three or more condensed rings. The low MW PAH of primarily fossil origin are known to degrade more severely than the larger PAH through physical-chemical and microbial processes (Lee *et al.*, 1978). Jones *et al.* (1986) reported preferential biodegradation of oil-derived PAH with respect to pyrolytic ones. They suggested that the latter show specific associations with particles (sequestration, occlusion) which render them relatively inaccessible to bacterial action, while oil-derived PAH are mainly introduced in the aquatic environment as emulsions presenting a large surface area to the degrading organisms. Hence, the commonly observed apparent predominance of pyrolytic PAH in environmental samples may result from both high contributions of related sources and better preservation of these imprints.

Overlap of fossil and combustion-derived PAH mainly occurs within the phenanthrene compounds. A criterion commonly used to differentiate them is based upon the relationship between the parent compound (Phe) and its

alkylated homologs. Under conditions of relatively low temperature and slow heating, such as in petroleum formation, the alkylated homologs are formed in the greatest abundance. The distribution shows a maximum for the di- or tri-methyl phenanthrenes (C2-, C3-Phe). Under conditions of higher temperature and more rapid heating, such as during combustion, the alkylated homologs undergo thermal cracking, resulting in a greater abundance of the unsubstituted compounds (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Hites *et al.*, 1980; Sporstol *et al.*, 1983). The above relationships are usually expressed by the ratio of monomethyl-phenanthrenes to phenanthrene (MP/P). Values of MP/P range from 2 to greater than 6 in petroleum, whereas typical values measured in combustion PAH mixtures are significantly lower and generally range between 0.5 and 1.0 (Lee *et al.*, 1977; Prahl and Carpenter, 1983). The underlying assumption in using this diagnostic tool for distinguishing fossil from pyrolytic sources is that the trends in distributions of the alkylated homologs are not significantly altered by weathering or degradation processes. While this tool is widely used (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Lake *et al.*, 1979; Wakeham *et al.*, 1980; Sporstol *et al.*, 1983), the degree to which these compounds are altered in the environment is not clearly understood. Lake *et al.* (1979) and Sporstol *et al.* (1983) have argued that members of an homologous series are weathered at approximately the same rate and that, while the abundance of all compounds of one series may decrease relative to other PAH series, the alkyl homologs distribution is not significantly altered. Nevertheless, differential water solubility of alkylated homologs has been demonstrated (Boehm and Quinn, 1973; Eganhouse and Calder, 1976). If these modification mechanisms are small, the measured distribution patterns would give a clear indication of PAH source material. However until these mechanisms are more clearly understood, we can only use this type of criteria to indirectly infer PAH sources.

Figure 9 illustrates the distribution of phenanthrene and its alkylated homologs in the Rhone delta sediments. The dominant compounds were the phenanthrene (Phe) and the

dimethyl-phenanthrenes (C2-Phe). This profile is not typical of one source but results from the admixture of fossil and combustion-derived phenanthrenes without a net predominance of one source. In most cases methyl-phenanthrenes were more abundant than the parent compound, which gave rise to values of MP/P varying from 0.66 to 1.45. Hence, according to the MP/P criterion, a dominant pyrolytic origin for the phenanthrenes can be postulated. The MP/P values were in general lower in the winter samples (0.7-1.1) than in late summer samples (1.0-1.5). This is consistent with higher pyrolytic inputs in winter in agreement with our previous conclusions. In our samples, however, the use of the MP/P ratio probably leads to an underestimation of the fossil contribution. This is because the fossil signature is rather discernable in the relative abundance of C2-Phe and not in that of C1-Phe. In most samples the maximum of the distribution was, in fact, observed on the dimethyl-phenanthrenes, which suggested that fossil phenanthrenes generally prevailed over the pyrolytic ones. This conflicts with the indications given by the MP/P ratio. Furthermore, the relative abundance of the unsubstituted compound with respect to the C2-Phe was higher in the winter samples in accordance with the variations of the MP/P values. Although contradictory, these observations show the limitations of the use of the MP/P ratio as a diagnostic tool for distinguishing fossil and pyrolytic inputs in the phenanthrene series. In the case of mixed inputs without a clear predominance of one source, the MP/P ratio may overlook fossil inputs. We propose that in such cases the relative abundance of di- and/or tri-methyl-phenanthrenes should also be considered. Among the phenanthrene homologs, 4,5 methylene-phenanthrene (4,5 MP, MW 190) is formed at high temperatures while it is absent in unburned fuels. It, thus, constitutes a specific marker of the combustion derived phenanthrenes. Depending on chromatographic conditions and column this compound may coelute with the monomethyl-phenanthrenes (MP) which may lead to errors in the estimation of the MP/P ratio. In our study 4,5 MP was resolved and quantified. Its relative abundance with respect to the MP (4,5 MP/MP) may also give an indication of the pyrolytic contributions. This ratio took values from 0.11 to 0.16 in the late summer

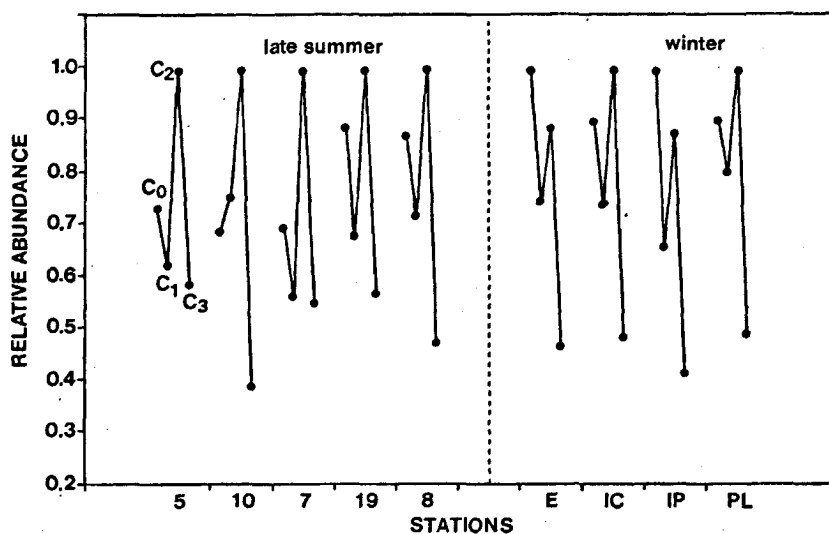


Figure 9

Relative abundance of phenanthrene and its alkylated homologs in sediments from the Rhone Delta. C0: unsubstituted phenanthrene; C1, C2, C3: mono-, di- and tri-methylphenanthrenes. Distributions are normalized to the most abundant species.

Abondance relative du phénanthrène et de ses dérivés alkylés dans les sédiments du delta du Rhône. C<sub>0</sub> = phénanthrène non substitué ; C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> = mono-, di- et tri-méthylphénanthrènes. Les distributions sont normalisées par rapport au composé le plus abondant.

samples and from 0.15 to 0.28 in the winter ones. This, again argued for the occurrence of higher pyrolytic inputs in winter.

The peculiar character of phenanthrenes was also indicated by the variation of the PAH composition as shown in Figure 8. Whereas the typical pyrolytic PAH (MW 202, 228, 252) exhibited large variations, the concentrations of phenanthrene and anthracene (MW 178) remained quite similar. This is more striking when we compare the variation of the sum of phenanthrene compounds ( $\Sigma$ PHE) which includes phenanthrene and its alkylated homologs, with the variations of  $\Sigma$ COMB and TPAH (Fig. 7). The observed correlation between  $\Sigma$ COMB and phenanthrene was not significant ( $R = 0.74$ ) and even less significant if we considered the sum of phenanthrene compounds, *i. e.* phenanthrene and its alkylated homologs ( $R = 0.60$ ). Moreover, the sum of phenanthrene compounds exhibited a high correlation with the organic carbon content of sediments ( $R = 0.92$ ), which contrasts remarkably with the pyrolytic PAH. These observations clearly demonstrate that phenanthrene compounds of mainly fossil origin display different input and dispersal trends from those of pyrolytic ones, which implies different particle associations of PAH depending on their sources. Additionally, the distributions of phenanthrene compounds resemble those of non-aromatic hydrocarbons (NAH). Since the latter is quantitatively dominated by the UCM, it clearly appears that fossil inputs (UCM,  $\Sigma$ Phe) follow similar dispersal trends.

#### • Sulfur-containing PAH

Among the sulfur-heterocyclics detected in our samples, dibenzothiophene (DBT) and its alkylated homologs (C1-, C2- and C3-DBT) were the most abundant. The sum of their concentrations ( $\Sigma$ DBT) varied from 118 to 422 ng/g dry weight (Tab. 5). These compounds may occur in both fossil fuels and various pyrolytic emissions (Grimmer *et al.*, 1983). In contrast with phenanthrene, their alkyl homolog distributions cannot discriminate between fossil and pyrolytic sources (Sporstol *et al.*, 1983). In the Rhone delta sediments this distribution was similar in almost all samples, characterized by the predominance of the di- and tri-methyl DBT. In order to decipher the origin of these compounds we compared their variations with those of other relevant PAH groups.  $\Sigma$ DBT showed poor correlation with the pyrolytic PAH, namely  $\Sigma$ COMB, ( $R = 0.63$ ) whereas they were significantly correlated with the sum of phenanthrene compounds ( $R = 0.96$ ). This strongly suggested common origin and dispersal trends for  $\Sigma$ DBT and  $\Sigma$ Phe.

## CONCLUSION

The study of three hydrocarbon classes (NAH, LAB, PAH) in sediments from the microtidal deltaic system of the Rhone river, NW Mediterranean Sea, provided useful insight into both environmental and geochemical aspects of these compounds.

• High NAH levels were found, comparable to those reported in industrialized and/or urbanized coastal areas world-

wide. The absolute NAH concentrations as well as their compositional features indicated a major contribution of fossil inputs along with significant natural land-derived inputs, whereas marine imprints were less important.

• A series of LAB deriving from domestic wastes (detergents) was detected, confirming their widespread occurrence in coastal areas adjacent to urban centers. Their concentrations were similar to those recently reported for other coastal areas.

• Total PAH concentrations were higher than those found in other coastal sites in the NW Mediterranean. These levels were comparable to those reported for coastal areas worldwide receiving important pollutant inputs. Pyrolytic and fossil contributions were identified within this hydrocarbon class, the former being in general prominent.

The various contributions to the bulk sedimentary hydrocarbons exhibited different variations between the winter and late summer situations:

• Fossil inputs, evidenced by the abundance of phenanthrene compounds as well as by the absolute levels of UCM and the ratio U/R, showed similar concentrations in both seasons.

• Natural inputs in the NAH group also showed no noticeable variations between the two seasons. Bouloubassi and Saliot (1993 *a*) reported similar behaviour for the naturally-derived PAH.

• Inputs related to domestic wastes (LAB) were higher in late summer whereas in winter they were detected only at the river mouth.

• Pyrolytic inputs, evidenced within the PAH group, were significantly higher in winter. This also revealed the potential of superficial deltaic sediments to rapidly record short-term quantitative and qualitative fluctuations of inputs.

Furthermore, the hydrocarbon classes considered in this study were also characterized by distinct dispersal modes, which can be interpreted in terms of specific particle class associations. All hydrocarbon groups were highly enriched in sediments close to the river mouth, indicating that riverine inputs are the major hydrocarbon supplier to the sediments. This accumulation is favoured by the high sedimentation rates occurring in this area. However, the trends of change of their distributions seawards showed significant dissimilarities which discriminate between the various origins:

• NAH, which are quantitatively dominated by the fossil UCM, displayed a regular decreasing trend seawards which was highly correlated with the distribution of the organic carbon.

• LAB (domestic wastes) showed a very sharp decrease seawards, which indicates their association with very rapidly settling particles.

• Total PAH (TPAH) as well as the pyrolytic components,  $\Sigma$ COMB, did not show significant correlation with the organic carbon. This mainly resulted from their high enrichment in winter. Moreover they exhibited distinct accumulation trends.

• Fossil inputs in the PAH family ( $\Sigma$ Phe,  $\Sigma$ DBT) showed spatial distributions similar to those observed for the NAH

(mainly dominated by the fossil UCM). Furthermore, like NAH, they were well correlated with the organic carbon content.

• Natural inputs in the NAH group followed dispersal trends comparable to those of fossil inputs, which indicates similar particle associations. Natural inputs in the PAH group, discussed in detail by Bouloubassi and Saliot (1993 *a*), also exhibited different dispersal trends from those of pyrolytic PAH but similar to those of natural aliphatic hydrocarbons of terrestrial origin.

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