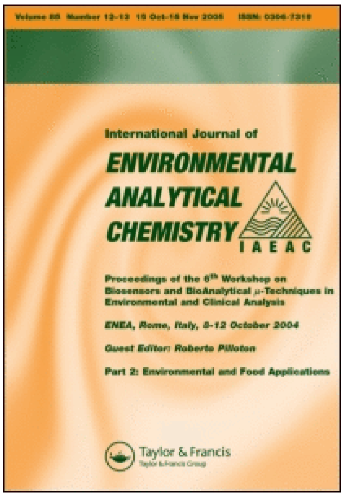

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Dissolved and Particulate Hydrocarbons in the Loire Estuary, from the Riverine Zone to the External Estuary: Budget at Different Seasons†

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In order to investigate the fate and transport processes of hydrocarbons in estuarine and coastal environments, we have undertaken a study of different hydrocarbon species in both dissolved and particulate forms. This two years study has been conducted in the Loire estuary at different reference stations (riverine, injection of sewage effluents, maximum turbidity zone, open sea) and at different seasons corresponding to various hydrological (high and low water) and biological conditions.

Quantitative and qualitative analysis of hydrocarbons has been carried out by GC, GC/MS, focusing on *n*-alkanes and *n*-alkenes.

Overall dissolved *n*-alkane concentrations vary in a narrow range, from 0.1 to 1.2 $\mu g\,l^{-1}$. Dissolved *n*-alkanes show fairly constant distribution patterns, with a slight odd/even carbon chain predominance, extending from n-C_{16} up to n-C_{42}, maximizing

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at n-C_{27}, n-C_{29} and n-C_{31}. CPI values are low (1–1.7) and may indicate the predominance of two sources, petroleum products and microbial and algal production superimposed on higher plant waxes.

The pathway of particulate hydrocarbons is completely different and depends on hydrological conditions. Detritic terrigenous compounds are accumulated in the maximum turbidity zone (n-alkane concentrations can reach $20\,\mu g\,l^{-1}$). This zone appears as an efficient filter between the internal estuary and the open coastal sea, where n-alkanes show concentrations not exceeding $1\,\mu g\,l^{-1}$, and low CPI values. This zone is also characterized by a remarkable microbial degradation and/or removal of the most labile compounds such as biogenic n-alkenes and phytadienes.

KEY WORDS: Estuary, hydrocarbon, *n*-alkane, organic matter, transport.

INTRODUCTION

Estuaries are characterized by an intense mixing of large quantities of organic matter produced by the autochtonous biological productivity, compounds issued from the land drainage and products of anthropic origin. Transport, degradation and recycling processes of mineral and organic chemical species are conditioned by complex hydrological and biological systems, and by the existence of four interfaces: water–air, water–sediment, water–particles and freshwater–sea water. The budget of the mixing processes is partially known; to appreciate the quality of the waters of coastal zones in terms of large-scale geochemical cycling, it would be necessary to evaluate the capacity of estuaries for degrading and stocking the anthropic inputs. A few studies have been conducted on the fate of hydrocarbons present in water and suspended particles in rivers and estuarine or deltaic systems, as for example by Peake *et al.*[1] in the Mackenzie river, Beaufort Sea; Boussuge *et al.*[2] off the Amazon delta; Burns and Villeneuve[3] on the Var estuary, Mediterranean Sea; Albaiges *et al.*[4] off the Ebro delta, Mediterranean Sea; and Saliot and Gonzalez[5] off the Mahakam delta, Borneo.

To investigate the fate and transport processes of hydrocarbons in a macrotidal estuary, we have undertaken a seasonal study of different hydrocarbon species (*n*-alkanes, *n*-alkenes) in both dissolved and particulate forms in the Loire estuary, which has been conducted at the same time for an extensive biogeochemical study of the organic matter.[6,7] This two years study has been carried out at different reference stations (riverine, injection of sewage effluents of Nantes city, maximum turbidity zone, open sea) and at different seasons, corresponding to various hydrological (high and low river flow, high and low tidal coefficient) and biological conditions from June 1982 up to January 1984.

EXPERIMENTAL

Water samples have been collected at different stations, chosen along the Loire estuary from the riverine zone, Montjean (MJ) or Ancenis (AN), up to the open sea (Figure 1).

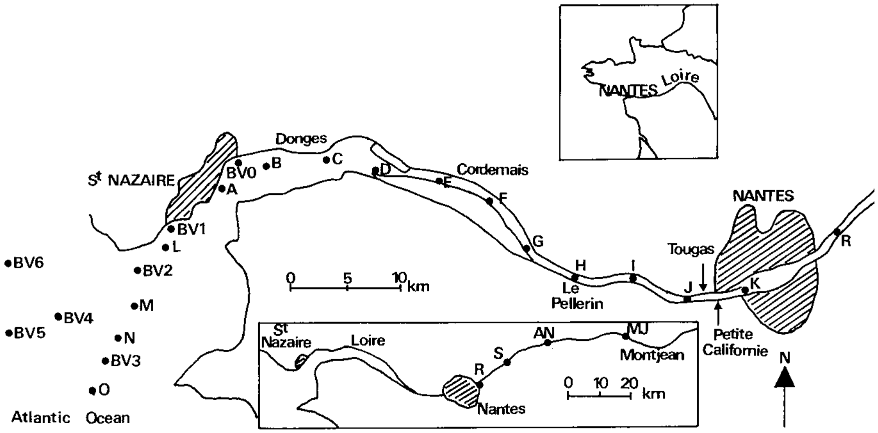

FIGURE 1 Sampling sites. Tougas and Petite Californie are the two sewage water treatment plants of Nantes city.

Five sampling cruises have been conducted for hydrocarbon studies, whose characteristics are reported in Table I. The physico-chemical and biological structures of the estuary for each sampling time have been reported in detail by Saliot *et al.*[6] and Billen *et al.*[7]

Sampling and filtration

Water samples (3–20 litres) were collected 1 m below the surface from the Research Vessel Côtes d'Aquitaine in glass carboys set on a metallic rack with other glass bottles for organic matter analysis,

TABLE I

Characteristics of the sampling cruises and sites

Cruises	Tidal coefficient	River flow (m^3/s)	Stations[a]	Comments
8 to 11/6/1982	60 to 76	300	MJ, D–E, M	Low water Low tidal coefficient
28/2 to 2/3/1983	105 to 108	2700 ± 100	MJ, J, B, O	High flow High tidal coefficient
22 to 24/5/1983	66 to 86	3500 ± 500	AN, BV1, BV6	Spring flow
20 to 22/1/1984	92 to 99	1700	AN, B, J, O	High water of winter

[a] Stations correspond to reference riverine site, Nantes city, maximum turbidity, open sea. See sampling sites, Figure 1.

such as total suspended matter, pigments, dissolved organic carbon, particulate organic carbon. The samples were transferred within 6 hours to the land-based laboratory and filtered under reduced pressure on glass fibre filter Whatman GF/F, 0.7 μm pore size, 15 mm diameter. The filters were kept in the dark in a freezer ($t < -20°C$) until laboratory analysis.

Isolation of dissolved and particulate hydrocarbons

Dissolved lipids were extracted three times with doubly distilled chloroform (twice at pH 8, once at pH 2). Chloroform extracts were combined, dried over $CaCl_2$, and evaporated in a Büchi evaporator under vacuum ($t < 40°C$), dried under a pure nitrogen stream and stored in a freezer until analysis.

Filters containing the suspended materials were extracted in a soxhlet apparatus using a 1:2.4 mixture of toluene and methanol. The extract was dried over $CaCl_2$, evaporated under vacuum, dried under a pure nitrogen stream and then stored frozen until analysis.

Column chromatography of total lipids

Each extract was spiked with a known amount of n-C_{22} as internal standard, in order to evaluate the efficiency of the following analytical steps. The extract was saponified under argon in a Sovirel tube SVL, with MeOH—KOH 2 N during 2 hours. After acidification to pH 2, the unsaponifiable fraction and the fatty acids were extracted by a 9:1 mixture of hexane and ether (3×1 ml). Extracts were evaporated to dryness under a nitrogen stream and separated by adsorption chromatography on a micro-column 4 mm internal diameter (i.d.), filled with SiO_2 (2 g). The first fraction eluted (6 ml hexane) contained alkanes and alkenes. The second fraction containing aromatic hydrocarbons >3 cycles was eluted successively by 3 ml of hexane + 60 μl of ethyl acetate, 3 ml of hexane + 15 μl of ethyl acetate and 2 ml of hexane. Finally, the third fraction eluted by 20 ml of ethyl acetate contained fatty acids. Analysis of aromatic hydrocarbons and fatty acids will be reported elsewhere.

Analysis of non-aromatic hydrocarbons by capillary gas-chromatography

The fraction containing saturated and olefinic hydrocarbons was analysed using a Girdel 3000 gas chromatograph with flame ionisation detector and Ross injector. The column employed was fused silica capillary, 25 m long, 0.32 mm i.d., coated with CP Sil 5 phase (Chrompack). The gas chromatograph was operated from 100°C to 300°C at a rate of $2°C\,min^{-1}$. The injector and detector temperatures were held at 250°C and 320°C respectively. Quantitation was based on calibrated flame ionisation response to internal standard (n-C_{22}).

Capillary gas chromatography–mass spectrometry

GC–MS analyses were performed on a R 10–10C Nermag quadrupole mass spectrometer coupled with a Girdel 32 gas chromatograph, using the conditions previously described. The mass spectrometer was scanned repetitively from 31 up to 550 amu with one scan per second. Electron energy was 70 eV; MS data were acquired and processed using on-line PDP 11/23 PLUS computer with SIDAR 111 data system. The mass spectra were compared with those of standards and data reported in the literature.

Blanks, limits of detection

Blanks were carried out daily, and care was taken for entire analytical procedure (all solvents were distilled, glass ware was kept in sulfo-chromic bath for 24 hours and rinsed with distilled water and organic solvents). Total analytical precision for individual hydrocarbon was measured in two particulate samples, collected in duplicate in the field. Overall precision was good for *n*-alkane measurements, with an average percentage deviation (% dev.) ± 6%. The limit of the chromatographic detection was 0.4 ng for individual *n*-alkane.

RESULTS AND DISCUSSION

We will consider successively data relative to dissolved hydrocarbons and to hydrocarbons associated with suspended matter, as their nature and fate during mixing and transport processes are different and merit detailed attention as previously discussed by Marchand *et al.*[8] for the first observations obtained in June 1982 in the Loire estuary.

Dissolved hydrocarbons

The data collected from the five sampling cruises in June 1982, February–March 1983, May 1983, September 1983 and January 1984 are listed in Table II for the concentrations in dissolved organic carbon (DOC) and *n*-alkanes. The data relative to DOC and *n*-alkanes are plotted in Figure 2.

N-alkane concentrations are low (less than 1 $\mu g\,l^{-1}$) with two exceptions for one sample collected in the riverine zone in May 1983 (16.4 $\mu g\,l^{-1}$) and another in the open sea area in January 1984 (4.3 $\mu g\,l^{-1}$). These two water samples whose DOC values are not high (5.45 $mg\,l^{-1}$ for the riverine station, and 1.4 $mg\,l^{-1}$ for the marine station) are probably polluted. *N*-alkane concentrations are in the same range in the riverine and the maximum turbidity zones (0.5 $\mu g\,l^{-1}$), whereas we observe lower concentrations in the open sea area (0.1–0.3 $\mu g\,l^{-1}$). These variations suggest a low reactivity behaviour for non-aromatic dissolved hydrocarbons throughout the

TABLE II

Dissolved organic carbon (mg·l^{-1}), and dissolved *n*-alkanes (μg·l^{-1}) concentration and characteristics

Sample cruise	Stations River	 Nantes	 Maximum turbidity	 Ocean
June 1982				
DOC	4.00		2.80	0.86
N-alkanes	0.623		0.283	0.105
N-alkanes/DOC %	0.016		0.010	0.012
CPI[a]	1.26		1.48	1.25
Characteristics[b, c]	II		II	II
	17, 27, *29*		17, 26, 29, 31	17, *20*, 29
February–March 1983				
DOC	5.85	5.80	4.05	1.35
N-alkanes	1.177	0.357	0.277	0.141
N-alkanes/DOC %	0.020	0.006	0.006	0.010
CPI[a]	1.68	3.44	1.36	1.42
Characteristics[b, c]	II	II[d]	II	II
	29, *31*, 33	*29*, 31	*29*, 31	27, 31
May 1983				
DOC	5.45		5.40	1.70
N-alkanes	16.39		1.048	0.372
N-alkanes/DOC %	0.300		0.019	0.022
CPI[a]	1.00		1.04	1.11
Characteristics[b, c]	I		I	I
	29, *30*, 31		*29*, 30, 31	17, *29*, 31
September 1983				
DOC		3.80 –4.00	4.20	1.30
N-alkanes		0.439–0.127	0.228	0.129
N-alkanes/DOC %		0.012–0.003	0.005	0.010
CPI[a]		1.14 –1.92	1.13	1.15
Characteristics[b, c]		II	II	I
		17, *29*, 31	28, *29*, 31	27, *28*, 29
January 1984				
DOC	5.40		6.10	1.40
N-alkanes	0.350		0.493	4.295
N-alkanes/DOC %	0.006		0.008	0.31
CPI[a]	3.14		1.52	0.99
Characteristics[b, c]	II[d]		II	I
	27, *29*, 31		27, *29*, 31	27, 28, 31

[a] C_{22} to C_{39}.

[b] Type of chromatogram described in text.

[c] Number of carbons of major *n*-alkanes—maximum italicised.

[d] Petroleum/natural background of regularly distributed *n*-alkanes very low.

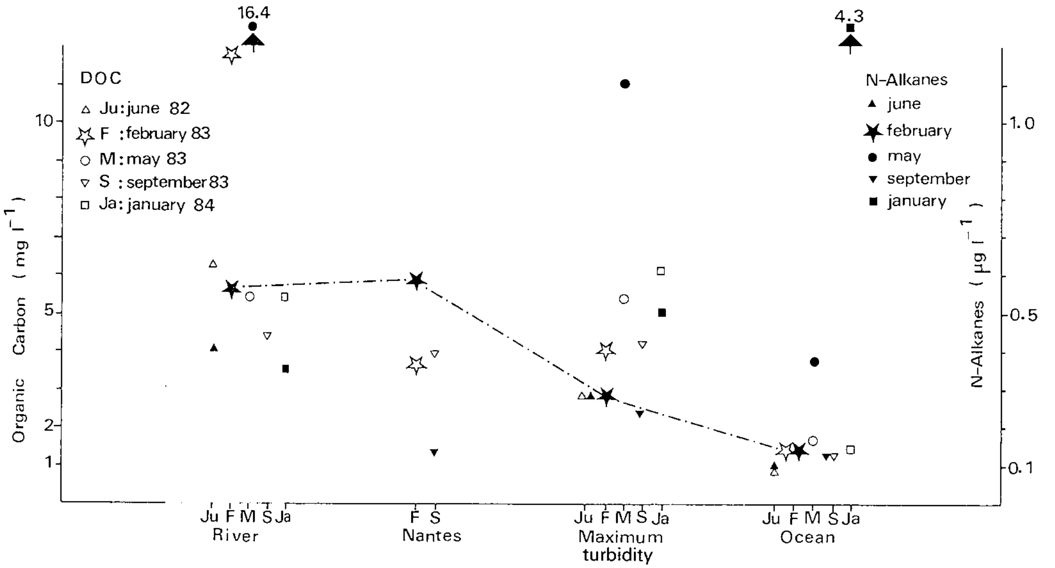

FIGURE 2 Dissolved organic carbon (DOC) and dissolved *n*-alkane concentrations found in the Loire estuary during five different sampling cruises, June 1982, February–March 1983, May 1983, September 1983 and January 1984.

estuarine system which could be referred to the conservative pathway of the dissolved organic carbon as described for the same profiles by Billen *et al.*[7] The distribution patterns of dissolved *n*-alkanes as a function of carbon number are characteristic and would allow to discuss the origins of hydrocarbons.

Two types of *n*-alkane distribution patterns are clearly identified.

Type 1 *N*-alkanes show a uniform distribution pattern without predominance of odd or even carbon chain compounds maximizing at *n*-C_{27}–*n*-C_{29}. This type 1 is illustrated for a sample collected in January 1984 at the marine station in Figure 3, which shows the GC trace of non-aromatic hydrocarbons with both resolved compounds and unresolved complex mixture of hydrocarbons assigned to branched and cyclic naphthene series and the histogram of *n*-alkanes expressed in $\mu g\, l^{-1}$ as a function of carbon number. Noteworthy is the absence of large amounts of *n*-alkanes in the carbon range C15–

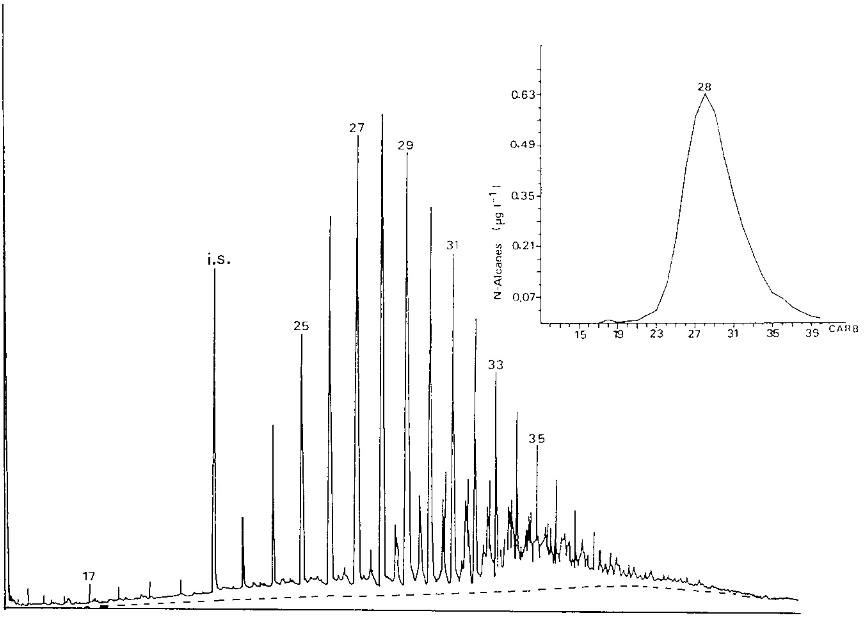

FIGURE 3 Gas chromatogram (type 1) of non-aromatic hydrocarbons and distribution pattern (type 1) of *n*-alkanes present in the water collected in January 1984 at the open sea station. Concentrations of *n*-alkanes expressed in $\mu g\, l^{-1}$ are plotted as a function of carbon number.

C20. The value of the carbon preference index (CPI), calculated in the carbon range C22–C39, is close to 1.

This type 1 could be associated with two source inputs: a mixture of petroleum products, incomplete combustion derivatives from fossil materials, and/or the result of various autochthonous natural inputs by water (fresh or marine) organisms: vegetals, micro-organisms as discussed by Saliot.[9]

Type 2 One characteristic is common to the preceding type—the large distribution of *n*-alkanes: but, in the >C21 carbon range we observe a predominance of odd carbon number *n*-alkanes maximizing at *n*-C_{31}. This type 2 is illustrated in Figure 4, which shows the GC trace of non-aromatic hydrocarbons present in the water collected at the riverine station in February–March 1983 and the histogram of *n*-alkanes.

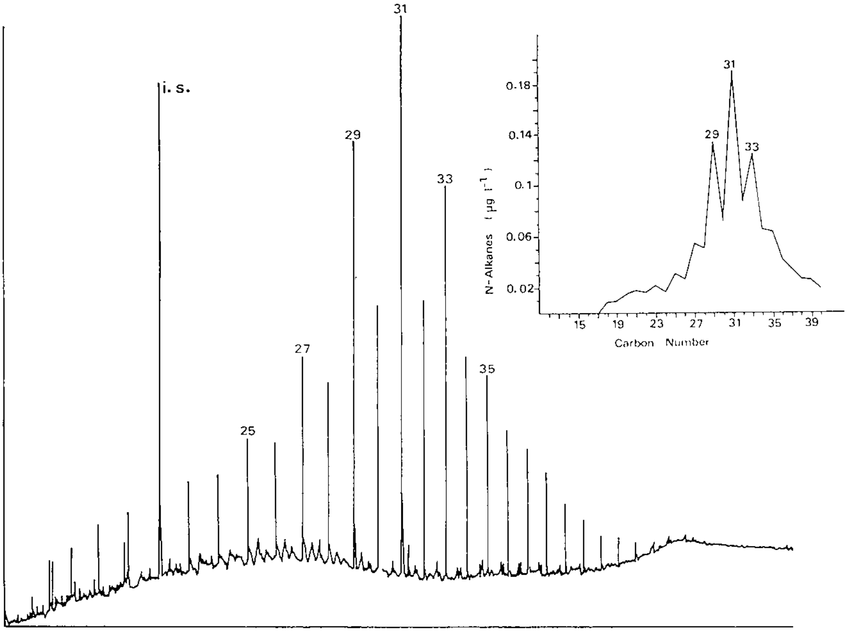

FIGURE 4 Gas chromatogram (type 2) of non-aromatic hydrocarbons and distribution pattern (type 2) of *n*-alkanes present in the water collected at the riverine station (Montjean) in February–March 1983. Concentrations of *n*-alkanes expressed in $\mu g\,l^{-1}$ are plotted as a function of carbon number.

In this case, we have evidence of another contribution by terrestrial higher plants such as shown by different authors,[10,11] which is superimposed on the mixed petroleum/natural background or regularly distributed *n*-alkanes.

The type of *n*-alkane distribution pattern, 1 or 2, is indicated in Table II for the different samples. Type 2 is characteristic for the riverine zone up to the maximum turbidity zone and for the open sea area at two occasions (June 1982 and February–March 1983). However, higher values of the CPI (3.1 and 3.4) were encountered for two samples: the riverine zone in January 1984 and at Station 5, just downstream from the city of Nantes in February–March 1983. Type 1 is identified essentially in sea waters.

Thus the terrigenous influence identified in the dissolved matter present in waters off the estuary appears to vary with the season.

Particulate hydrocarbons

Data relative to particulate matter, particulate organic carbon (POC) and *n*-alkanes are listed in Table III and illustrated in Figure 5.

Figure 5 shows the non-conservative pathway of the particulate organic matter, the accumulation of both particulate organic carbon and *n*-alkanes in the zone of maximum turbidity and the efficiency of this zone for temporary retaining particulates. Effectively, the *n*-alkane concentrations encountered in the open sea off the estuary are very low, less than $1\,\mu g\,l^{-1}$; they vary in the range 10–$20\,\mu g\,l^{-1}$ in the maximum turbidity zone.

All *n*-alkane distribution patterns belong to type 2, with variable contributions of natural/petroleum background of regularly distributed *n*-alkanes, and reflect the presence of higher plant debris along the estuary as shown in Figures 6–8, from the September 1983 cruise. The terrigenous influence decreases from the riverine zone characterized by high CPI values in the range 1.2–4.7, to open sea waters for which CPI values are in the range 1.2–1.9. The CPI values are also high in the maximum turbidity zone (2.3–5.8). Some samples have a high n-C_{17} (Figure 6, for example). This compound is probably derived from freshwater plankton; it is not predominant here for marine waters although n-C_{17} is one of the major hydrocarbons from phytoplankton and benthic algae as described by Blumer *et al.*[12] and Youngblood *et al.*[13]

TABLE III

Particulate organic carbon (mg·l^{-1}) and *n*-alkanes (μg·l^{-1}) associated with particles (SM, mg·l^{-1}) concentration and characteristics

Sample cruise	Stations			
	River	Nantes	Maximum turbidity	Ocean
June 1983				
SM	39.4		908.0	6.2
POC	6.10		11.00	0.76
N-alkanes	7.22		14.010	0.223
N-alkanes/POC %	0.118		0.130	0.029
CPI[a]	1.24		3.55	1.45
Characteristics[b,c]	II		II[d]	II
	27, 28, *29*		27, 29, *31*	20, *29*, 31
February–March 1984				
SM	66.0		866.0	37.0
POC	3.49		33.26	1.32
N-alkanes	3.592		12.967	0.230
N-alkanes/POC %	0.103		0.039	0.017
CPI[a]	3.30		5.78	1.90
Characteristics[b,c]	II[d]		II[d]	II
	27, *29*, 31		27, *29*, 31	20, *29*, 31
May 1983				
SM	70.0		477.0	4.28
POC	2.35		14.98	0.78
N-alkanes	2.438		8.774	0.763
N-alkanes/POC %	0.104		0.049	0.098
CPI[a]	2.53		4.14	1.37
Characteristics[b,c]	II		II[d]	II
	20, *29*, 31		*29*, 31	20, *21*, 29
September 1983				
SM	52.5	40.2 –36.8	926.0	9.8
POC	6.50	4.66 – 4.14	29.20	0.47
N-alkanes	4.261	2.508– 1.892	9.660	0.780
N-alkanes/POC %	0.066	0.054– 0.046	0.033	0.166
CPI[a]	2.86	3.69 – 2.70	2.33	1.45
Characteristics[b,c]	II	II	II[d]	II
	17, 29		18, *29*, 31	25, *29*, 31
January 1984				
SM	84.0	73.9	574.0	11.9
POC	3.68	3.55	17.70	0.37
N-alkanes	4.378	3.463	16.701	0.922
N-alkanes/POC %	0.119	0.098	0.094	0.249
CPI[a]	4.65	3.44	3.72	1.23
Characteristics[b,c]	II[d]	II	II[d]	II
	27, *29*, 31		27, *29*, 31	27, *29*, 31

[a] C_{22} to C_{39}.

[b] Type of chromatogram described in text.

[c] Number of carbons of major *n*-alkanes—maximum italicised.

[d] Petroleum/natural background of regularly distributed *n*-alkanes very low.

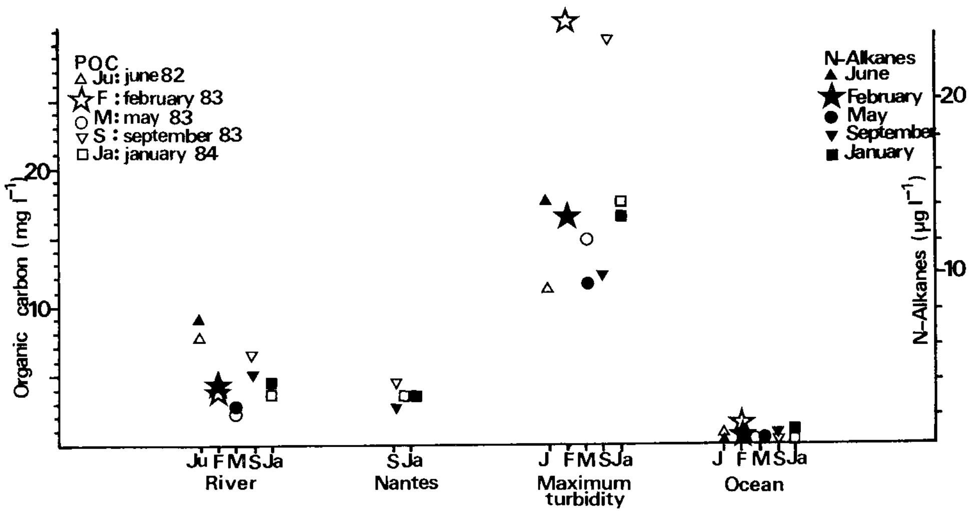

FIGURE 5 Particulate organic carbon (POC) and particulate *n*-alkane concentrations found in the Loire estuary during five sampling cruises, June 1982, February–March 1983, May 1983, September 1983 and January 1984.

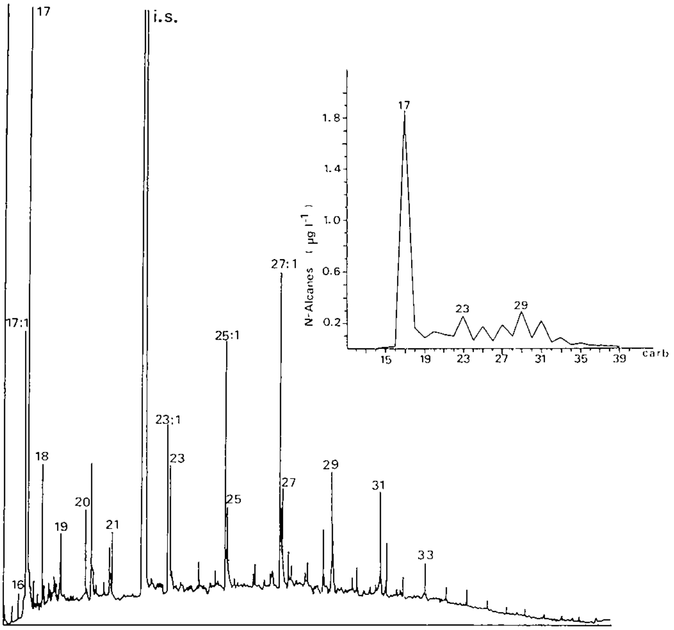

FIGURE 6 Gas chromatogram of non-aromatic hydrocarbons and distribution pattern of *n*-alkanes associated with particles collected in September 1983 at the riverine station.

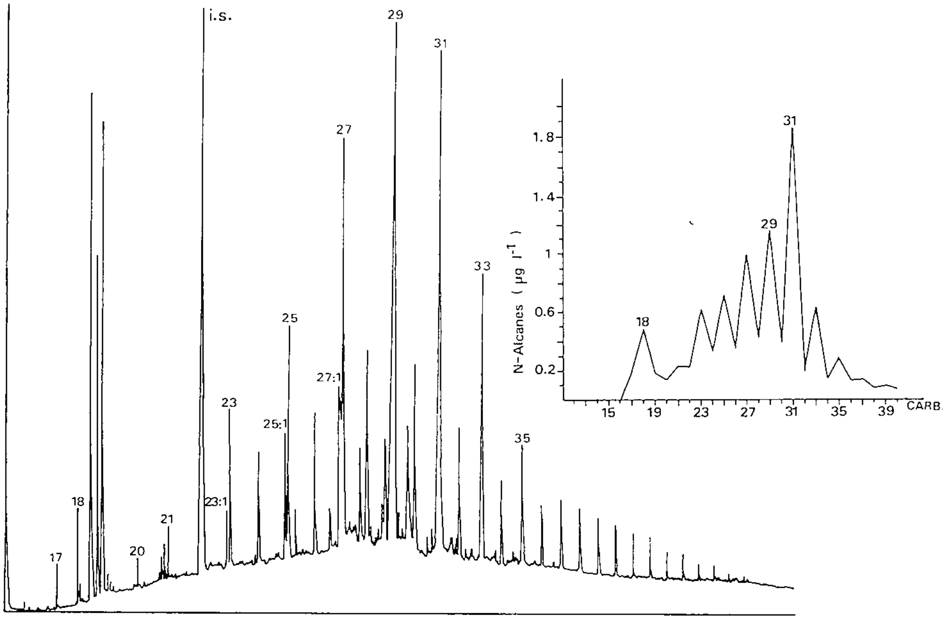

FIGURE 7 Gas chromatogram of non-aromatic hydrocarbons and distribution pattern of *n*-alkanes associated with particles collected in September 1983 at the maximum turbidity zone station.

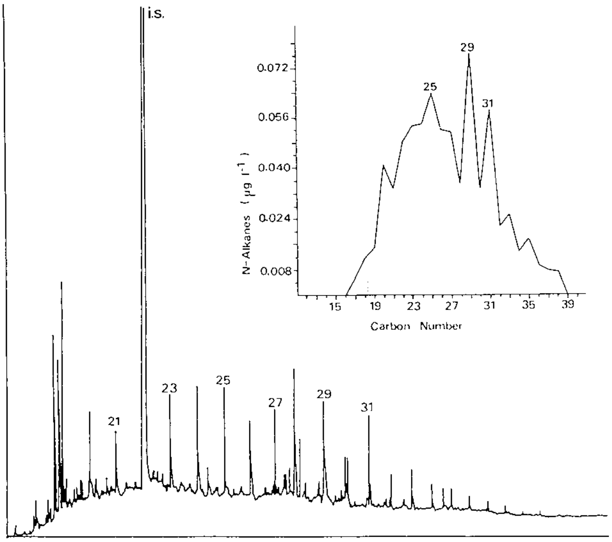

FIGURE 8 Gas chromatogram of non-aromatic hydrocarbons and distribution pattern of *n*-alkanes associated with particles collected in September 1983 at the open sea station.

The evolution of *n*-alkane distribution patterns between the maximum turbidity zone and the open sea stations is illustrated for three samples (BV0, BV1 and BV4, see Figure 1) collected in May 1983 within high tidal coefficient and high river flow values leading to an intense extension of the maximum turbidity zone in the external estuary. These samples are characterized by the following conditions: BV0: S $S = 0.34‰$, total suspended matter $SM = 477\,mg\,l^{-1}$, *n*-alkane pattern, Figure 9; BV1: $S = 3.8‰$, $SM = 58\,mg\,l^{-1}$, *n*-alkane pattern, figure 10; and BV4: $S = 23.6‰$, $SM = 17.9\,mg\,l^{-1}$, *n*-alkane pattern, Figure 11.

Figures 9 and 10 suggest a strong predominance of continentally-derived inputs from higher plants with high CPI values: 4.1; the extent of this continental influence is limited off the external estuary: effectively Figure 11 shows a uniform distribution pattern for *n*-alkanes derived from both petroleum products and autochthonous inputs.

The analysis of particulate non-aromatic hydrocarbons indicates that in addition to the *n*-alkane distribution patterns belonging to

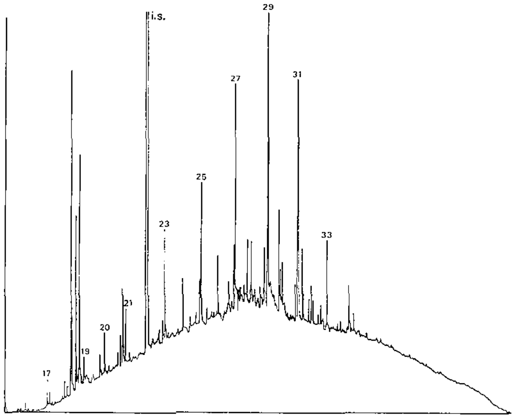

FIGURE 9 Gas chromatogram of non-aromatic hydrocarbons associated with particles collected in May 1983 in the maximum turbidity zone (Station BVO, Figure 1).

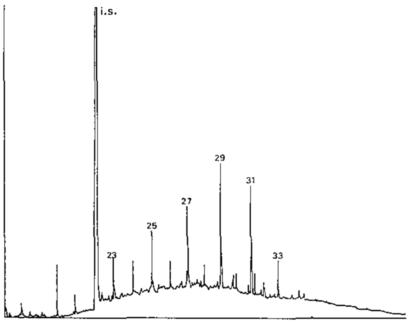

FIGURE 10 Gas chromatogram of non-aromatic hydrocarbons associated with particles collected in May 1983 in the external estuary (Station BV1, Figure 1).

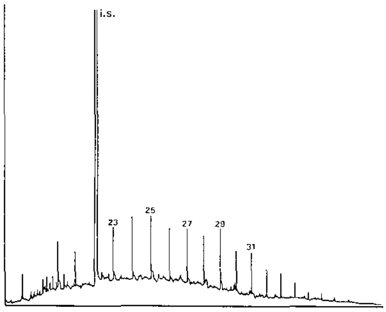

FIGURE 11 Gas chromatogram of non-aromatic hydrocarbons associated with particles collected in May 1983 in the external estuary (Station BV4, Figure 1).

type 2 described precedingly, predominant components in the riverine zone are *n*-alkenes. The presence of these *n*-alkenes, *n*-C_{17}:1, *n*-C_{23}:1, *n*-C_{25}:1 and *n*-C_{27}:1, whose structure has been definitively confirmed by GC/MS, has already been recognized in other riverine systems[4] and is illustrated for the riverine station in Figure 6.

These *n*-alkenes derive drom different potential sources such as higher plants,[14,15] freshwater or marine plankton.[12,16] They are also present at the same time in the maximum turbidity zone, but in lower levels; the corresponding *n*-alkene/*n*-alkane ratios are less than 1, as shown in Figure 7. We could interpret this concentration decrease as issued from degradation processes, both physico-chemical and biological, occurring in the maximum turbidity zone, so far as these compounds are totally absent or present at trace levels in open sea waters off the estuary. As an example, the GC trace of non-aromatic hydrocarbons present in the particulates at the marine station for the same sampling cruise shows a regular distribution of *n*-alkanes and only traces of *n*-alkenes (Figure 8).

In the GC traces of samples collected in the maximum turbidity zone a series of compounds in the *n*-C_{17} retention time region appear to be present in large amounts. A preliminary study by GC/MS has permitted the identification as phytadiene-type compounds. They are absent in open sea waters and present at high levels in the maximum turbidity zone; thus, their presence could be explained by degradation processes from chlorophyll pigments,[17] biologically mediated in the maximum turbidity zone, so far as the microbial activity has been shown to be intense at this period.[7]

CONCLUSIONS

The variations in dissolved *n*-alkane concentrations along the estuary (same range in the riverine and the maximum turbidity zones, 0.5 $\mu g\,l^{-1}$, lower values in the open sea waters, 0.1–0.3 $\mu g\,l^{-1}$) suggest a low reactivity behaviour for non-aromatic hydrocarbons throughout the estuarine system, which could be referred to the conservative pathway of dissolved organic carbon. A few exceptions characterized by high concentrations indicate punctual pollution inputs. *N*-alkane distribution patterns show several origins for the hydrocarbons:

various autochthonous natural inputs, contribution of continental higher plants superimposed on a mixture of petroleum products.

The pathway of particulate hydrocarbons is different, marked by an intense accumulation in the maximum turbidity zone and the degradation of the most labile compounds such as biogenic *n*-alkenes, n-C_{17}:1, n-C_{23}:1, n-C_{25}:1 and n-C_{27}:1.

A series of phytadiene-type compounds, derived probably from chlorophyll pigments, is identified only in the maximum turbidity zone. Their presence could be associated with the intense bacterial activity of this zone, which could be considered as an effective filter between the river and the open ocean.

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