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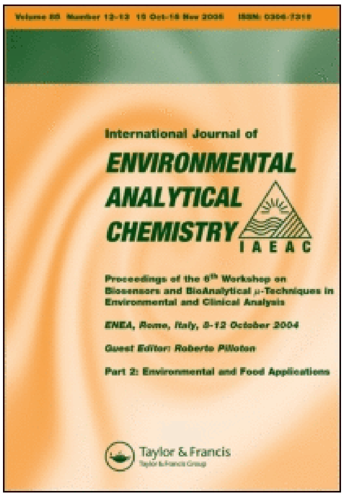

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Hydrocarbons in the Mediterranean Sea: Their Occurrence and Fate in the Sediment and in the Water Column, as Dissolved and Associated with Small and Large Size Particulates†

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Transfer and transformation processes of hydrocarbons between the surficial water and the sediment have been studied in the open Western Mediterranean Sea, by determining concentrations and distributions of non-volatile *n*-alkanes, isoprenoids, non-aromatic and aromatic hydrocarbons in the surficial sediment and in three fractions of the water column: dissolved matter, small-size and large-size particulates ($>63\,\mu$m).

Hydrocarbons have been analysed by capillary gas liquid chromatography and HPLC/UV spectrophotometry.

Hydrocarbons are present essentially in a dissolved form in the water column (for more than 90% for samples collected below 1,000 m) and associated with small-size particles. The stock of hydrocarbons present in large-size, rapidly sinking particles accounts for less than 0.3%.

Concentrations found in the water column are low, except for the surficial water in the Ligurian Sea ($>20\,\mu g\,l^{-1}$). They decrease with depth to reach values less than

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0.2 μg l^{-1} below 1,000 m. The sediments are characterized by low concentrations (3.9–7.1 μg g^{-1}).

The nature of hydrocarbons is very different with respect to each pool: essentially petrogenic for the water column, derived from marine productivity and terrestrial higher plants waxes for large-size particles and sediments. Estimations of vertical flux of hydrocarbons are discussed in terms of mode of settling of hydrocarbons from the sea surface.

KEY WORDS: Hydrocarbons, Mediterranean Sea, particles, sediment, vertical flux, capillary gas liquid chromatography, HPLC/UV spectrometry.

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INTRODUCTION

The organic matter involved in sedimentation processes in the sea is essentially derived from the productivity in the superficial waters.[1,2] Within this internal source, organic matter of continental origin, both natural and anthropic, is introduced into the sea by two major transport processes: rivers and streams[3,4] and eolian aerosols and dusts.[5]

The nature of organic compounds such as hydrocarbons that reach the sediment is not only related to the biogenic production of the upper water layers and the superficial inputs by wet and dry deposition from the atmosphere, river runoff, ship traffic, coastal industrial activities such as refineries, but also to the transformations that take place before and during sedimentation. Recent investigations[6-11] have shown that most of the vertical flux of organic matter can be attributed to rapidly sinking, large-size ($>50\,\mu$m) particles. Different mineral and organic species, living and dead organisms, faecal pellets and faecal material, macroscopic aggregates can be associated with these large particles. Transfer and transformation processes, both physico–chemical and biological, involving sinking suspended matter can be elucidated by determining distribution patterns of specific organic compounds associated within these particles, such as hydrocarbons, as demonstrated by Prahl and Carpenter,[12] Wakeham *et al.*,[13] Saliot *et al.*,[14,15] Burns and Villeneuve,[16] Lee *et al.*,[17] Albaiges *et al.*,[18] among others.

From MERL experiments, Gearing and Gearing[19] suggested that hydrocarbon sedimentation was carried out more effectively by living and detrital particles in the water column than by resuspended sediment particles from the bottom. From the studies achieved by

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either *in situ*[12,14] or either *in vitro* in microcosm experiments, it appears that a non-negligible part of hydrocarbons introduced in the superficial ocean can be incorporated into large-size, rapidly settling particles.

Nevertheless, in terms of vertical transport of organic matter, active interactions exist between the different stocks: dissolved material in water, small-size particles, large-size particles and sediment, as suggested by Saliot *et al.*[14,15] Thus, in order to elucidate the pathway of hydrocarbons in the water column, it is useful to analyse these different pools.

We present here data obtained at three open sea stations of the Western Mediterranean Sea. Water, particulates ($>0.7\,\mu$m and $>63\,\mu$m), faecal pellets collected *in situ* and sediments have been simultaneously sampled and analysed for their organic carbon content, *n*-alkanes and aromatic hydrocarbons in order to discuss these questions:

1) What are the respective stocks of hydrocarbons for water and particulates at different depths down to the bottom water?

2) Is there a relationship between the hydrocarbons present in different phases, at different depths?

3) Is there a close relationship between the hydrocarbons present in the surface sediment, and in the faecal material or in the rapidly settling or slowly settling particles?

4) Is there a relationship between the material collected in the water column and the sediment and the aerosols sampled during the same cruise?

5) What estimations of the flux of hydrocarbons can be proposed for the Western Mediterranean Sea at the time of the cruises, April and May 1981?

EXPERIMENTAL

Sampling sites and techniques

Three stations were selected for this paper: GYL in the Ligurian Sea (43° 05′ 4N; 08° 00′ 5E) and ETR2 off the Rhône delta (42° 02′ 3N; 05° 05′ 4E) occupied during the PHYCEMED I cruise of the R/V

"Le Suroit" in April 1981; P81, 25 miles off Villefranche sur mer on the transect Nice–Calvi occupied during the MEDPAR 81 cruise of the R/V "Korotneff" and "Alciope" in May 1981 (Figure 1).

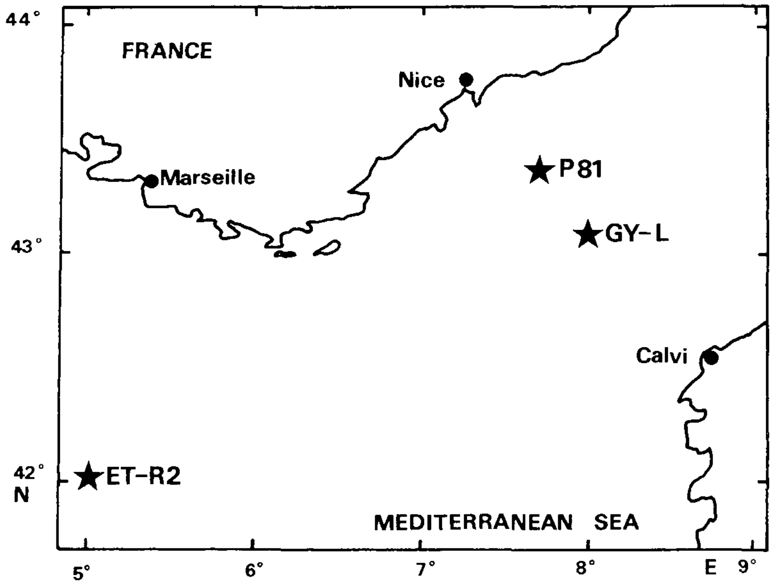

FIGURE 1 Sampling sites; GYL and ETR2 stations were occupied during the PHYCEMED I cruise, in April 1981. P81 station was occupied during the MEDPAR 81 cruise, in May 1981.

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Sea water was collected from a zodiac discarded 1 mile upwind from the main ship by immersing a glass carboy 0.2 m below the surface, and at different depths throughout the water column up to the bottom by closing a Brès metallic 200 l bottle equipped with an ultrasonic pinger.

Small-size particles ($>0.7\,\mu$m) were obtained by filtering 50 l of sea water on a 15 cm diameter Whatman GF/F glass fibre filter.

Surface large-size particles were collected at the P81 station using three plankton nets, of mesh size 63 μm, 120 μm and 210 μm, equipped with stainless steel collectors. The resulting material was concentrated by filtering the collector contents on a Whatman GF/F filter.

Faecal material was obtained using a zooplankton faecal matter collector adapted from La Rosa,[20] but entirely made in stainless steel, consisting in a large (150 l) collector equipped at the base with a metallic screen, of mesh size 170 μm. The zooplankton was captured using an Omori net and placed in the collector filled with filtered sea water (1.2 μm). The faecal matter passing through the screen was collected during two experiments at the P81 station: Sample 1; collection time, 7 h 20 min during night, and Sample 3; collection time, 4 h 45 min during day.

Deep large-size particles were collected by towing a plankton net, 63 μm in the mesh size, equipped with a metallic collector, either horizontally at a desired depth or vertically, opened at about 100 m above the sediment, then operated very slowly (0.5 m sec^{-1}) and closed at about 1,000 m from the surface to avoid the collection of surficial living planktonic organisms.

The content of the collector was collected on a Whatman GF/F glass fibre filter.

The sediment was sampled with an Usnel type box corer. The first top centimetre was analysed and the level 5–8 cm for the GYL station.

Filters with their particulate material and sediments were kept frozen until extraction in the land-based laboratory.

Dissolved lipids were extracted on board from 20 l of filtered water by liquid–liquid extraction with cloroform, 2 times at pH 8, the third one at pH 2. The chloroform extracts were dried over $CaCl_2$ and evaporated to dryness using a rotary evaporator, at low temperature ($t < 40°C$).

Before the cruise, all the fibreglass collection filters were precleaned by extraction with doubly distilled chloroform in a Soxhlet during 24 hours, and kept in solvent-rinsed aluminium foil.

Isolation and analysis of hydrocarbons

The analytical procedure scheme has been described in detail elsewhere.[21] Briefly, lipids were extracted with a solvent ($CHCl_3$ or toluene/methanol, 1:1) and separated into three fractions by microcolumn chromatography: saturated and unsaturated hydrocarbons, aromatic hydrocarbons (with other compounds such as ketones) and more polar compounds such as fatty acids and fatty alcohols.

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Analysis was performed by capillary gas chromatography (non-aromatic hydrocarbons) and high pressure liquid chromatography/UV spectrophotometry, HPLC/UV spectrophotometry (aromatic hydrocarbons).

The fraction containing saturated and unsaturated hydrocarbons was analysed using a Girdel 3000 gas chromatograph with flame ionisation detector and a Ross injector. The column employed was glass capillary, 25 m long, 0.25 mm internal diameter (i.d.), wall coated with SE 52. Helium was used as carrier gas. Temperature was programmed from 120°C to 270°C at a rate of $4°C\,min^{-1}$. Peak areas were determined using a Varian Vista 401 integrator. *N*-alkanes and isoprenoid compounds were identified by comparison of their retention times with those of known standards injected under the same conditions, and quantified with respect to the internal standard, *n*-C22. The same calibration factor was used for the unresolved components, appearing as a hump in the gas chromatograms.

Aromatic hydrocarbons were analysed by HPLC/UV spectrophotometry.[21,22] This method produced HPLC fingerprints corresponding to the separation of aromatic hydrocarbons by increasing degree of aromaticity. Aromatic hydrocarbons were fractionated on an analytical column 20 cm long, 4.7 mm i.d., filled with $5\,\mu m$ SiO_2 bonded NH_2 stationary phase. The solvent used was hexane. Sample injection was realized using a Rheodyne valve, with an injection loop of $20\,\mu l$. The pump, Chromatem Altex 380, was used with a pulsation damper at a flow of $1.8\,ml\,min^{-1}$. Aromatic hydrocarbons were detected by ultraviolet absorption at 254 nm, with a Schoeffel spectromonitor. Within these conditions, aromatic hydrocarbons were separated essentially by degree of aromaticity, with little effect of substitution.

On the HPLC chromatograms obtained, retention times of authentic standards from benzene (Be) to perylene (Pe) were indicated. Peaks emerging from the hump corresponded to mono- to penta-aromatic series.

Great care was taken to avoid contamination during on board and laboratory work up. Solvents were distilled before the cruise and a second time on board just before use. Filters, Na_2SO_4, $CaCl_2$ were extracted in a Soxhlet with distilled chloroform. Procedural blanks showed that only traces of interfering compounds were present in our samples.

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Data were corrected for losses during laboratory work-up, using recovery of the internal standard, *n*-C22 alkane. Although drastic precautions were taken during evaporation steps, losses of the more volatile compounds occurred. Consequently, data given for <C16 alkanes and <3 rings aromatic compounds are only semi-quantitative.

The corresponding limits of detection were as follows: 5 ng l^{-1} for individual *n*-alkanes, and 1 ng l^{-1} for aromatic fractions for dissolved and small-size particulate species; 0.1×10^{-3} ng l^{-1} for *n*-alkanes and aromatic fractions for large-size particles; 5 ng g^{-1} dry weight for *n*-alkanes and aromatic fractions for sediments.

RESULTS AND DISCUSSION

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We will consider successively the budget of hydrocarbons in the water column and in the surficial sediments and discuss both for concentrations and nature. The nature of hydrocarbons can be elucidated by examining several criteria that have been developed for distinguishing the potential origins of hydrocarbons.

N-alkanes enter the marine environment both by anthropic, transport and use of petroleum products, and natural sources, soil, continental vegetation and marine production. The distribution of *n*-alkanes and the isoprenoids, pristane and phytane, permits one to distinguish between different sources, natural and anthropic.[23–30] Different diagnostic tools have been proposed:

1) Carbon preference index (CPI) values: a high CPI (>4) indicates the major incorporation of recent biological constituents into the sample. The addition of contaminants reduces the CPI such that values of about 1 reflect a significant input of anthropic compounds. Nevertheless, it has been reported in the literature[26] that planktonic material showed a regular distribution pattern of *n*-alkanes without predominance of odd over even carbon chains. Thus the use of this first simple criterion must be crossed with others.

2) Cmax: a Cmax>27 for *n*-alkanes reflects the significant incorporation of higher plant waxes, whereas maxima at lower carbon numbers may indicate the major input by microbial or petroliferous sources.[30]

3) Ratio of unresolved to resolved hydrocarbon components (U/R) or ratio of unresolved components to *n*-alkanes or percentage

of *n*-alkanes to total hydrocarbons. Contaminated samples contain the largest ratio of unresolved components which belong to branched-cyclic napthene series.

Polycyclic aromatic hydrocarbons (PAH) are introduced into the sea essentially by petroleum activities and combustion processes.[31–38] A distribution of alkylated components dominated by the parent compound suggests strongly a fossil fuel combustion origin. On the other hand, a distribution of alkylated homologues maximizing at C3–C4 species suggests a non-combusted petroleum-like material.[39] Natural inputs can also be recognized through the identification of specific compounds such as perylene for continental inputs[40] or chrysenic compounds which derive from either marine or bacterial biomasses.[41]

By coupling the CPI, Cmax, U/R, *n*-alkanes/non-aromatic compounds, distribution of alkylated homologues in the polycyclic aromatic hydrocarbon series, HPLC/UV spectrophotometry fingerprints and combining this information with the individual fraction quantifications, it is possible to compile a reasonably discriminating description of the amount and probable sources of marine hydrocarbons.

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WATER COLUMN

Dissolved and small-size particulate hydrocarbons

Concentrations of hydrocarbons (*n*-alkanes, total non-aromatic and aromatic compounds) are listed in Table I for various reservoirs at different levels from the surface down to the bottom layer collected at a few metres from the sediment. Concentrations are expressed in $\mathrm{ng\,l^{-1}}$ and given for the water itself ("dissolved" hydrocarbons which are more precisely hydrocarbons passing through a $0.7\,\mu\mathrm{m}$ pore size filter), and the particulate material ($>0.7\,\mu\mathrm{m}$). As it has been precedingly noted by Hô *et al.*,[21] surface concentrations are higher for the GYL station than for the station located off the Rhône delta (ETR2). During the PHYCEMED cruise concentrations encountered below 100 metres are relatively constant at low levels, less than $200\,\mathrm{ng\,l^{-1}}$ for dissolved *n*-alkanes, $20\,\mathrm{ng\,l^{-1}}$ for particulate *n*-alkanes. The fractionation of hydrocarbons between the dissolved form and

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particulates depends on different physico-chemical properties: solubility, presence of organic complexes such as humic or fulvic acids, adsorption capacities of particulates. But here non-aromatic hydrocarbons are essentially in the dissolved fraction, even when concentrations are higher than solubilities of pure hydrocarbon compounds. As for example, the respective solubilities at 25°C of *n*-C20, *n*-C22 and *n*-C26 are 800, 700 and 100 ng l^{-1}.[42] As a function of depth we note a decrease of non-aromatic hydrocarbon concentrations both for the *n*-alkanes and the unresolved compounds in the branched-cyclic napthene series. The depth profiles of dissolved and particulate organic carbon, dissolved and particulate *n*-alkanes, dissolved and particulate total non-aromatic hydrocarbons for station GYL are given in Figure 2.

Considering *n*-alkanes, if the concentrations are in the same range for particulate components as those encountered by Albaiges *et al.*[18] off the Ebro delta (10–60 ng l^{-1}), they are much higher for dissolved compounds, up to 20 μg l^{-1} (off the Ebro delta: 20–50 ng l^{-1}).

Hydrocarbons are essentially non-aromatic in nature which indicates that the pollution of the open sea waters by pyrolytic-like products is low. The distribution of dissolved and small-size particulate *n*-alkanes identified as a function of carbon number and for several depths at station GYL is shown in Figure 3. These distribution patterns (regular without predominance of any individual compound such as the biogenic *n*-C15, *n*-C17 or *n*-C19) suggest that they are partially issued from petroleum. Nevertheless we cannot exclude a natural contribution by different algal or microbial sources which could lead to regular distributions of *n*-alkanes as previously described by Clark and Blumer,[43] reviewed by Saliot[26] and clearly identified here for the biologic superficial material and the faecal pellets from zooplankton (Figure 5). Of note is the absence of typical compounds of planktonic origin found in productive surface waters such as the *n*-C15, *n*-C17 or pristane.[44] Traces of biological imprints can be detected as for example for the dissolved *n*-alkanes present at 1,000 m, marked by a predominance of *n*-C27, *n*-C29 and *n*-C31, originating from terrestrial higher plants cuticular waves.[45–47]

Surface large-size particulates

To investigate the nature of hydrocarbons occurring in surface

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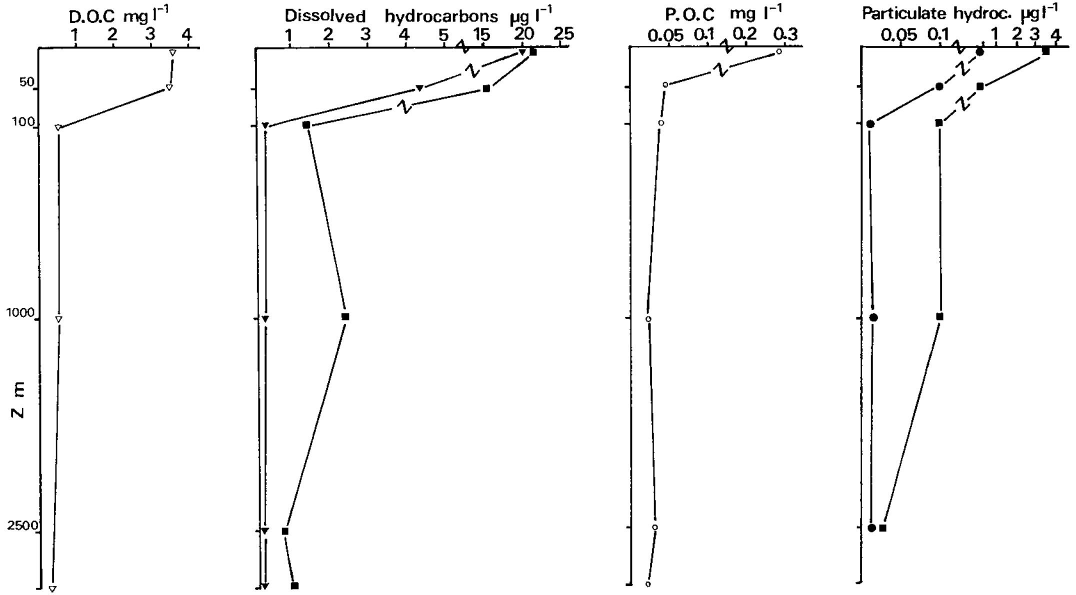

FIGURE 2 Depth profiles of dissolved organic carbon, D.O.C. ($mg\,l^{-1}$), dissolved hydrocarbons for both ▼ *n*-alkanes and ■ non-aromatic hydrocarbons ($\mu g\,l^{-1}$), particulate organic carbon, P.O.C. ($mg\,l^{-1}$), and particulate hydrocarbons for both ● *n*-alkanes and ■ non-aromatic hydrocarbons ($\mu g\,l^{-1}$).

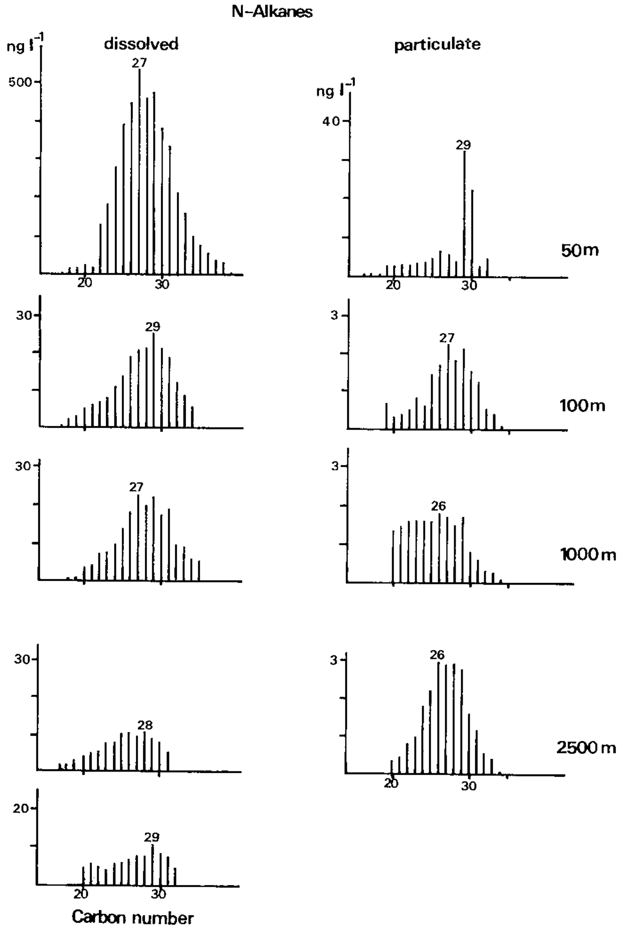

FIGURE 3 PHYCEMED I cruise, April 1981; Western Mediterranean Sea: distribution patterns of dissolved and particulate *n*-alkanes as a function of carbon number for various depth samples collected in the Ligurian Sea (station GYL).

waters, two types of material have been sampled: surface plankton and faecal pellets. A three-fold net tow has been accomplished at P 81 station throughout large clouds of salps. After discarding these organisms, three particle size fractions have been obtained, composed essentially of zooplankton and gelatinous aggregates and very small quantities of phytoplankton. The amount of material

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collected in the 63–170 μm fraction for the same volume of sea water is about three times more abundant than those corresponding to fractions 120–170 μm and 210–800 μm. The characteristics of the three fractions (63–120 μm, 120–170 μm and 210–800 μm) have some common features as for example the value of the ratio *n*-alkanes/non-aromatic hydrocarbons ranging from 20 to 30%. The distributions of *n*-alkanes as a function of carbon number are very different, maximizing at about *n*-C20-*n*-C21 for the smallest fraction, *n*-C27 for the 120–170 μm fraction and presenting the two modes (*n*-C21 and *n*-C26-*n*-C27) in the 210–800 μm fraction (Figure 4).

So far as the abundance of *n*-alkanes in the low molecular range can be attributed to microorganisms,[30] Figure 4 suggests an important bacterial biomass associated with large-size particulates. Another point merits attention; these regular distribution patterns of *n*-alkanes support a biologic origin for these compounds which are also encountered in petroleum products. We cannot exclude the explanation consisting to interpret these distribution patterns as an evidence of the efficiency of zooplankton for concentrating petroleum hydrocarbons occurring in their food or in particulates in their faecal pellets.

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N-alkane distribution patterns of faecal material produced by natural *Calanus Helgolandicus* are shown in Figure 5. They belong also to a very regular type of pattern; of note is the difference in Cmax, *n*-C25 for the material obtained during day and *n*-C29 for the pellets collected during night. The pellets are not enriched in compounds from the zooplankton itself such as the pristane, an observation corroborating the data of Andrie[48] and Prahl *et al.*[49]

Deep large-size particulates (> 63 μm)

Total non-aromatic hydrocarbon concentrations are 1.22 ng l^{-1} for station GYL and 2.15 ng l^{-1} for station ETR2. They are much higher than those found by Saliot *et al.*[14] in the productive waters of the Arabian Sea, which ranged from 0.002 to 0.005 ng l^{-1} and in the Ligurian Sea, off Villefranche Bay, which ranged from 0.015 up to 0.83 ng l^{-1}.[48] Concentrations found in large-size particles represent a minute percentage of the total hydrocarbon stock present in deep waters as illustrated on Figure 6 for non-aromatic compounds.

Deep large-size particles are completely different in nature

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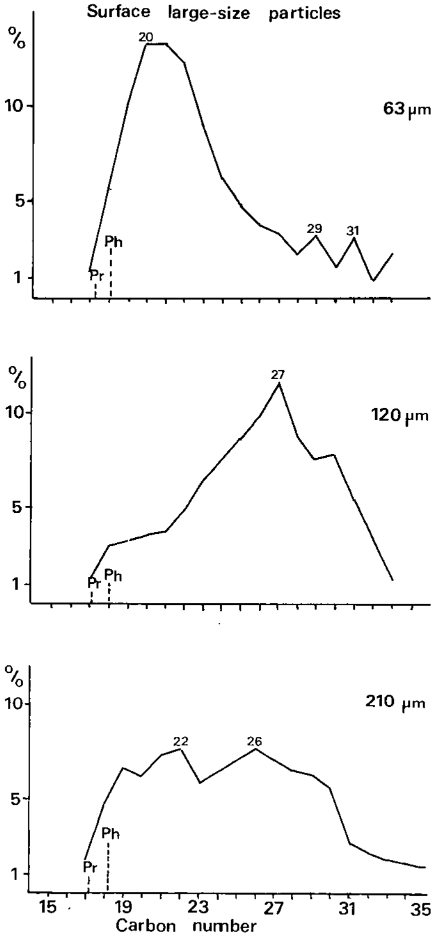

FIGURE 4 PHYCEMED I cruise, April 1981, Western Mediterranean Sea: carbon number distribution patterns of *n*-alkanes associated with surface particles (0–200 m) collected with three plankton nets: 63, 120 and 210 μm; Pr = pristane; Ph = phytane.

compared with small-size material (Figure 7). A microscopic examination of the content of the collector has shown the quasi-absence of living organisms and large amounts of carcasses of copepods and nauplii, eggs of fish, faecal pellets and aggregates. This explains the predominance of pristane, a compound originating from zooplankton[50] among the non-aromatic resolved compounds in GC

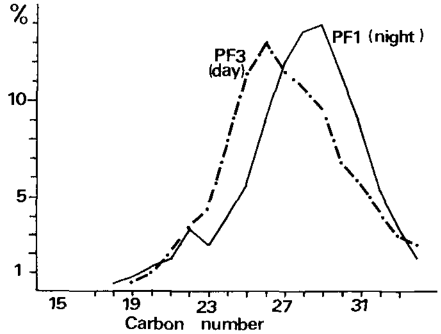

FIGURE 5 MEDPAR 81 cruise, May 1981, Western Mediterranean Sea, station P81: carbon number distribution patterns of *n*-alkanes from faecal matter collected during night (PF1) and day (PF3) from zooplankton captured with an OMORI net.

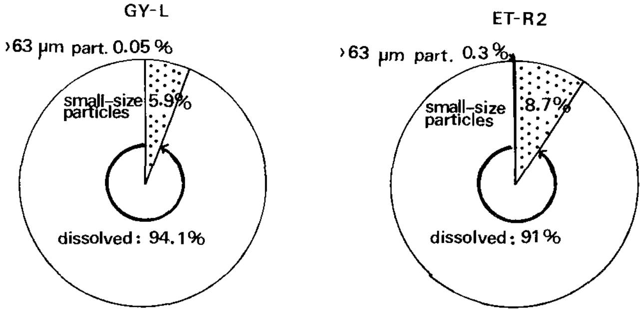

FIGURE 6 PHYCEMED I cruise, April 1981, Western Mediterranean Sea, stations GYL and ETR2: relative importances (%) of the hydrocarbon stocks present in the water column at 1,000 m in three forms: dissolved in the water, associated with small-size particles and associated with large-size (> 63 μm) particles.

runs. Other characteristics are the presence of a first group of *n*-alkanes centered around the *n*-C20 probably of microbiologic origin and, only for station GYL, of the common group of high molecular weight *n*-alkanes maximizing at *n*-C27, *n*-C29 and *n*-C31, indicating continentally-derived inputs which can be attributed here to eolian contributions.[51] To summarize, large-size particles are essentially naturally-deriving both from micro-organisms, marine plankton and terrestrial inputs for station GYL. The values of the ratio *n*-alkanes/unresolved compounds, 3.9 and 3.2 for the GYL and ETR2 stations reflects microbial imprints and a large contribution of napthenic petroleum-derived compounds.

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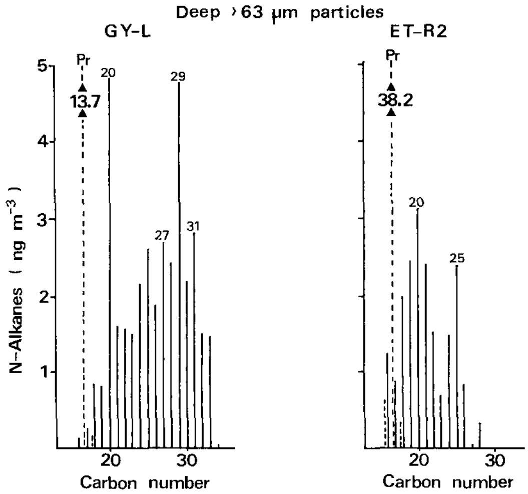

FIGURE 7 PHYCEMED I cruise, April 1981, Western Mediterranean Sea, stations GYL and ETR2: carbon number distribution patterns of *n*-alkanes associated with deep > 63 μm particles.

SEDIMENT

Hydrocarbon concentrations for the surficial sediment cored at station GYL and ETR2 are given in Table I. There are a few data on hydrocarbon contents of open sea Medditerranean sediments: Burns and Villeneuve[16] reported hydrocarbon concentrations for the first cm of sediments cored at a 250 m water column station off Monaco: total hydrocarbons 6.7–14.6 $\mu g\,g^{-1}$; 5.1–11.6 $\mu g\,g^{-1}$ for GC unresolved compounds and 0.6–0.73 $\mu g\,g^{-1}$ for PAH. These concentrations are close to ours which are lower than values reported for Mediterranean coastal sediments by Mille *et al.*[52] and Albaiges *et al.*[3], 12–720 $\mu g\,g^{-1}$ and 2–62 $\mu g\,g^{-1}$ for aliphatic hydrocarbons, 1.2–232 $\mu g\,g^{-1}$ and 1–66 $\mu g\,g^{-1}$ for aromatic hydrocarbons respectively. The distribution of sedimentary *n*-alkanes and present isoprenoid compounds is shown in Figure 8 for samples collected at the two stations GYL and ETR2. They indicate undoubtedly the predominance of terrigenous inputs (*n*-C27, *n*-C29 and *n*-C31 predominant) which is encountered for most of open sea sediments.[24] The abundance of perylene in the aromatic fraction (Figure 9) con-

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TABLE I

N-alkane, non-aromatic and aromatic hydrocarbon concentrations in different reservoirs: water column for dissolved and small size particulates pools (ng l^{-1}), deep large-size particulates captured below 1,000 m (ng l^{-1}) and surficial sediments (μg g^{-1}).

Water column (depth and material)		*N*-alkanes			Non-aromatic hydrocarbons			Aromatic hydrocarbons	
		GYL	ETR2	P 81	GYL	ETR2	P 81	GYL	ETR2
0.2 m	Water	20,570	50		22,160			111	46
	particulates	520	180		3,550	1,610		81	28
50 m	Water	4,330	140	131	15,800	1,070	365		
	particulates	100	32	9.7	520	350	15		
100 m	Water	200	80		1,650	400			
	particulates	20	12		120	220			
1,000 m	Water	190	60		2,400	630			
	particulates	20	8		150	60			
2,500 m	Water	100	175		960	—[a]	2,500		
	particulates	20	5.3		30		12		
Bottom	Water	90	—[b]		1,120	—[b]			
	particulates	—[a]	10		—[a]	125			
Deep large-size particulates					1.22	2.15	0.1–0.4	0.021	0.032
Sediment									
Level: 0–1 cm		0.66	1.18		3.3	6.4		0.62	0.75
5–8 cm		0.58			1.97			—[b]	

[a] Non-determined.

[b] Below the detection limit.

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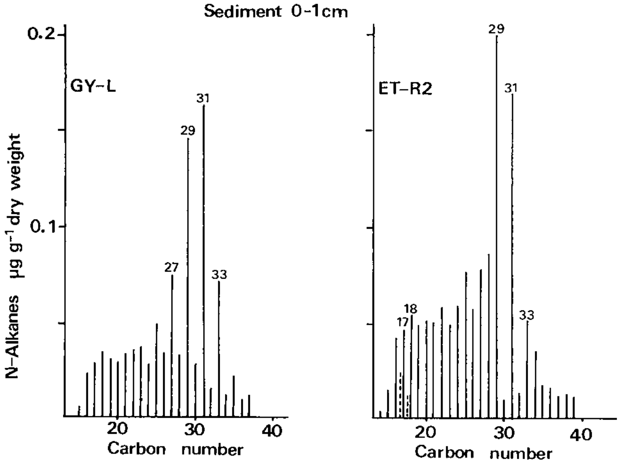

FIGURE 8 PHYCEMED I cruise, April 1981, Western Mediterranean Sea, stations GYL and ETR2: carbon number *n*-alkane distribution patterns for surficial sediment (0–1 cm).

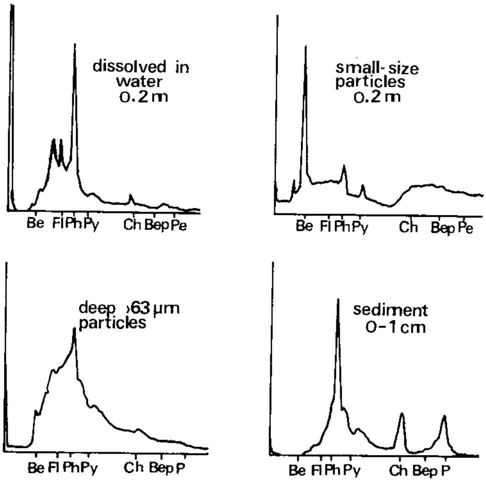

FIGURE 9 PHYCEMED I cruise, April 1981, Western Mediterranean Sea, station GYL: polycyclic aromatic hydrocarbon fingerprints using HPLC/UV spectrophotometry determined for PAH dissolved in the water and associated with small-size particles collected 0.2 m below the surface, PAH associated with deep > 63 μm particles and PAH of surficial sediment (0–1 cm).

Be = benzene; Fl = fluoranthene; Ph = phenanthrene; Py = pyrene; Ch = chrysene; BeP = benzopyrene; P = perylene.

firms also the importance of continentally-derived inputs. For station GYL we note a decrease of *n*-alkane, non-aromatic and aromatic hydrocarbon concentration between the first centimetre level and the level 5–8 cm which could be explained by the consumption and degradation of organic matter during the first steps of diagenesis and/or by changes in the organic burden of sedimentary material during last decades.

RELATIONSHIPS BETWEEN HYDROCARBON POOLS AND FLUXES INVOLVED

Regarding the questions that have been formulated at the beginning of this study, it appears that hydrocarbons identified in large-size rapidly settling particulates constitute an original stock in nature, different from the other hydrocarbon pools (dissolved and associated with small-size particles, see for example Figure 9 where PAH fingerprints show different patterns for the same station. This stock represents a small percentage of the total hydrocarbon pool. This rapidly settling material is more related in nature to the surficial sediment with the importance of continentally-derived imprints (identified in the *n*-alkane distribution patterns and the PAH fingerprints). These imprints encountered in the aerosols sampled during the same cruise are transported with fine dusts, in association with predominant winds.[51]

Semi-quantitative estimations of the vertical fluxes of hydrocarbons have been tentatively made, from the settling model of McCave,[6] *in situ* observations[8,54,55] and *in vitro* estimations of the settling velocity of copepod faecal pellets by Small *et al.*[56] We have chosen a value of 100 m per day as the mean settling velocity. The estimations obtained are listed in Table II.

The first evident comment consists to emphasize the variability of fluxes as a function of the station occupied and the time of sampling; but, this is also evident from previous observations by Deuser and Ross[57] from their total organic carbon determinations in close relationship with the surficial productivity and as shown here from the variability in the production of faecal material (Figure 5). Further semi-quantitative determinations of hydrocarbon nature and production from natural populations of zooplanktonic organisms

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TABLE II

Estimations of hydrocarbon fluxes, expressed in $mg\,m^{-2}\,yr^{-1}$ for three stations in the Western Mediterranean Sea (GYL and ETR2, PHYCEMED I cruise, April 1981; P81, PARMED cruise, May 1981). These estimations have been determined from concentrations of large-size particulates ($>63\,\mu m$ for the PHYCEMED samples; 61–170 μm for the PARMED sample).

Station	GYL	ETR2	P81
Flux of *n*-alkanes	1.79	2.51	0.52–5.56
Flux of non-aromatic hydrocarbons	45.9	78.4	2.6–13.9
Flux of aromatic hydrocarbons	0.76	1.19	
Flux of total hydrocarbons	46.7	79.6	

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must be accomplished. The range encountered for deep fluxes here varies from 0.5 up to $5.5\,mg\,m^{-2}\,yr^{-1}$ for *n*-alkanes and from 2.6 to $78.4\,mg\,m^{-2}\,yr^{-1}$ for non-aromatic hydrocarbons. These values can be compared with those reported at a station off Monaco by Burns and Villeneuve;[16] they reported sediment trap total hydrocarbon 100 m fluxes of about $14–19\,mg\,m^{-2}\,yr^{-1}$. Andrie[48] and Saliot *et al.*[15] reported non-aromatic hydrocarbon sediment trap 50 m fluxes at a station close to the P81 (May 1980) of $4{,}250\,mg\,m^{-2}\,yr^{-1}$. But it is known that a rapid degradation of organic compounds occurs in the first hundred metres of the water column.

With respect to other oceanic areas (Arabian Sea, deep large-size hydrocarbon fluxes: $0.15\,mg\,m^{-2}\,yr^{-1}$;[14] Equatorial Atlantic ocean; 389–5,068 m sediment trap hydrocarbons: $0.25–3.6\,mg\,m^{-2}\,yr^{-1}$),[13] it appears that the Mediterranean is the subject of important fluxes of hydrocarbons throughout the water column which can be explained both by a relatively heavy hydrocarbon pollution by ship traffic and industrialized activities and by the eolian inputs. As an example although annual estimations of dry and wet deposition are speculative from the data obtained during a cruise, Hô *et al.*[51] have estimated the annual hydrocarbon deposition for the transect GYL-ETR2 in the following ranges: $1.9–19.1\,mg\,m^{-2}\,yr^{-1}$ for *n*-alkanes and 2.6–26.1 $\mathrm{mg\,m^{-2}\,yr^{-1}}$ for total hydrocarbons. Thus for the Mediterranean Sea, the eolian inputs are an essential component with the planktonic productivity in deep settling of hydrocarbons.

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