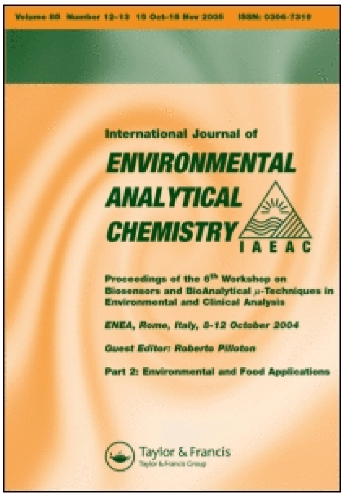

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Hydrocarbons in the Western Mediterranean Sea, 1981†

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Hydrocarbons in the western Mediterranean Sea were analysed for surface microlayer and subsurface waters during April 1981. Three methods were used for determining both concentrations and markers distribution patterns: U.V. spectrofluorimetry, an original HPLC/U.V. spectrophotometry method and capillary gas liquid chromatography.

No systematic relationship was found between concentrations determined by U.V. spectrofluorimetry and HPLC/U.V. spectrophotometry. Concentrations variation ranges are: 0.01–0.20 $\mu g\,l^{-1}$ for dissolved aromatic hydrocarbons; 0.02–0.13 $\mu g\,l^{-1}$ for particulate aromatic hydrocarbons; 0.02–20.57 $\mu g\,l^{-1}$ for dissolved *n*-alkanes; 0.13–0.83 $\mu g\,l^{-1}$ for particulate *n*-alkanes. Surficial waters appear as very slightly polluted with an exception, the Ligurian Sea for which highest concentrations were encountered.

There is a slight enrichment of particulate hydrocarbons in the surface microlayer in the range 1–3. But, dissolved hydrocarbons can be either depleted or enriched up to 270 times in the surface microlayer, indicating the extreme efficiency of sea-air exchange processes.

Aromatic fingerprints and *n*-alkane distribution patterns are discussed both for pollution and fractionation processes indicators at the sea-air interface.

KEY WORDS: Mediterranean Sea, dissolved hydrocarbons, particulate hydrocarbons, sea water, sea-air interface.

INTRODUCTION

The western Mediterranean Sea is exposed to serious pollutions especially by hydrocarbons, due to an increasing ship traffic and the industrialization of coastal states. Annual inputs of petroleum hydrocarbons to the Mediterranean are estimated in the range 0.5–1.0 million tons.[1]

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This context points out a critical situation for the semiclosed Mediterranean Sea owing to geographic and hydrologic characteristics.

Although petroleum monitoring programmes have been developed,[2] there is a lack concerning Mediterranean open sea waters, except a few data by Horn *et al.*,[3] Morris *et al.*[4] and Albaiges *et al.*[5] dealing with surface pelagic tar evaluations, Faraco and Ros,[6] Brown and Huffman[7] and Zsolnay[8] about hydrocarbons in open sea waters. It has appeared necessary to dispose of a new reference state for the open Mediterranean Sea. This has been realised during the PHYCEMED cruise on the R/V *Le Suroit* in April 1981. During this cruise, surficial water (0.2 m depth) and surface microlayer sampled by a metallic screen, have been collected taking all precautions against contamination.

Analyses of hydrocarbons and other geochemical markers have been performed separately on dissolved and particulate matter. Various global and precise techniques have been used. U.V. spectrofluorimetry on sea water hexane extracts gives total aromatic hydrocarbon concentrations. High pressure liquid chromatography coupled to U.V. spectrophotometry enables to obtain a fingerprint of aromatic hydrocarbons separated upon their degree of aromaticity. Finally, gas liquid chromatography on capillary column allows to analyse *n*-alkanes, isoprenoids and saturated unresolved compounds and evaluate respective biogenic and anthropogenic contributions. Data are discussed attempting to correlate aromatic hydrocarbon concentrations obtained through different methods and focusing on the accumulation or depletion of hydrocarbons in the surface microlayer and associated sea-air exchange processes.

EXPERIMENTAL

Sampling sites (Figure 1)

Samples have been collected during the PHYCEMED cruise of the R/V *Le Suroit* in the western Mediterranean Sea, in April 1981. Stations have been chosen corresponding to different hydrologic systems. Dominant characteristics of the five sites are indicated in Table I.

Sampling

Water samples were collected from a rubber Zodiac boat, at about 1–2 km upwind of the main ship. Surface microlayer samples (20 litres) were obtained using a stainless steel screen (1.25 mm square openings in the mesh) collecting a water film approximately 0.44 mm thick. Subsurface water samples (20 litres) were obtained by immersing a 25 litres glass

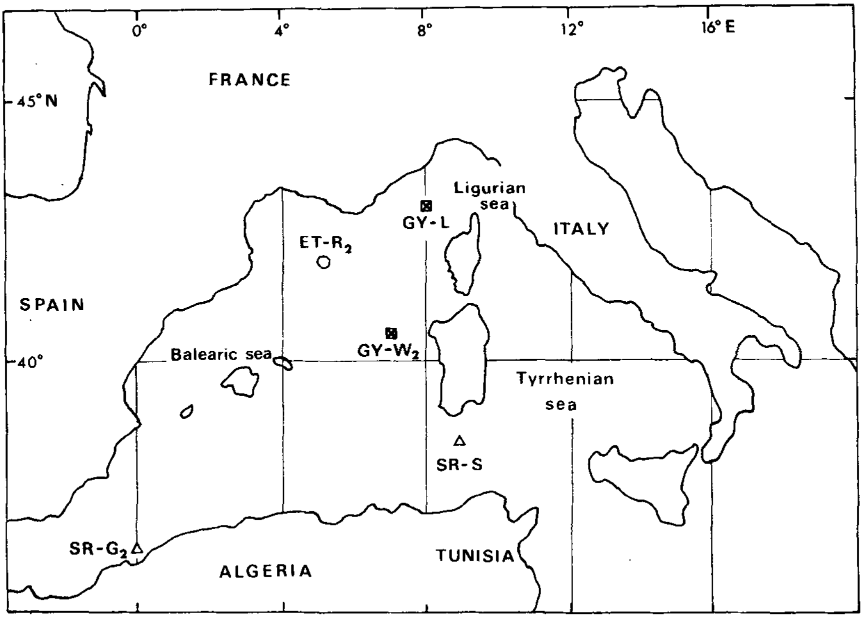


FIGURE 1 Sampling sites, PHYCEMED cruise, April 1981. ○ estuary station: ET-R_2, △ strait stations: SR-G_2 and SR-S, ☒ gyre circulation stations: GY-L and GY-W_2.

bottle about 0.2 m below the water surface. Thus, two samples were collected for each station and treated immediately on board ship.

Treatment and analysis of the samples

The analytical flow diagram is shown in Figure 2.

Analysis of total aromatic hydrocarbons by U.V. spectrofluorimetry On board ship, one litre of sea water was extracted three times with spectro U.V. grade hexane (2×20 ml; 1×10 ml). In the laboratory, the joined extracts were dried over Na_2SO_4 and evaporated under nitrogen. They were stored at -25°C. The extract was dissolved in 5 ml of hexane and then analysed using a Perkin Elmer MPF-3L spectrofluorimeter according to the method of Keizer and Gordon.[9] Measurement conditions were: cell, 1 cm; λ excitation 310 nm, slit width 3 nm; λ emission 320–420 nm, slit width 4 nm; λ measurement 360 nm. Fluorescence response was calibrated with solutions of chrysene in the concentration range comparable to the samples. Results are expressed in $\mu g\ l^{-1}$ of chrysene equivalent. It must be

TABLE I

Stations sampled in the Mediterranean, PHYCEMED cruise, April 1981

Station code number	Type	Date	Lat. °N	Long. °E	Sea conditions
GY-L	Gyre	7 April	43°05,4	08°00,5	rough
ET-R_2(1)	Estuary	10 April	42°02,3	05°05,4	rough
ET-R_2(2)	Estuary	11 April	42°02,3	05°05,4	slight
SR-G_2	Strait	18 April	36°16,9	00°06,3	slight
SR-S	Strait	20 April	38°22,9	09°24,8	smooth
GY-W_2	Gyre	23 April	40°36,6	07°10,7	moderate (rain)

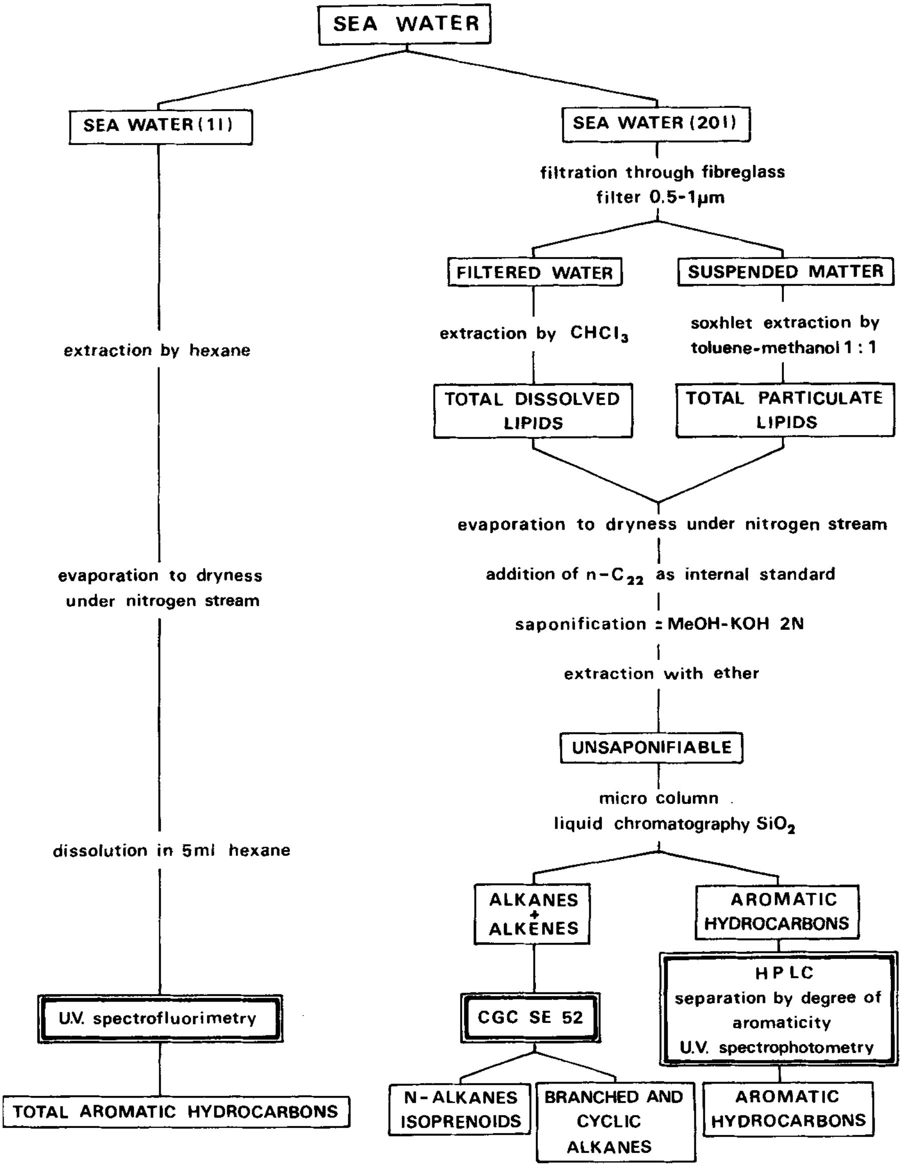


FIGURE 2 Analytical flow diagram.

emphasized that this method is not specific for petroleum hydrocarbons, but detects any fluorescing compounds that are not lost during the evaporation step.

Isolation of dissolved and particulate hydrocarbons Particulate matter was obtained from sea water by filtration under reduced pressure on Whatman GF/F glass fibre filters (15 cm diameter), collecting particles with a diameter greater than 1 μm. Filters were then kept frozen until extraction for 36 hours (solvent being changed after 24 hours) in a soxhlet apparatus using a 1:1 mixture of toluene and methanol. The extract was dried over $CaCl_2$, evaporated under vacuum at reduced temperature ($t < 40°C$), dried under nitrogen stream, then stored frozen until analysis.

Dissolved lipids were extracted on board three times by chloroform (twice at pH 8, once at pH 2). Chloroform extracts were added together, dried over $CaCl_2$ and evaporated in a Büchi rotavapor. They were stored frozen until analysis.

Column chromatography on total lipids Internal standard, $n-C_{22}$ was added to each extract in order to evaluate the efficiency of following analytical steps. The extract was saponified under nitrogen in a Sovirel SVL tube by MeOH-KOH 2N during 2 hours. After acidification to pH 2, the unsaponifiable fraction was extracted by ether (3 × 1 ml). Ether extracts were evaporated to dryness under nitrogen stream and separated by adsorption chromatography on a microcolumn filled with SiO_2. The first fraction eluting (6 ml hexane) contained alkanes and alkenes. The second fraction containing aromatic hydrocarbons 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.

Analysis of saturated hydrocarbons by capillary gas chromatography The fraction containing saturated and olefinic hydrocarbons was analysed using a Girdel 3000 gas chromatograph with flame ionization detector and Ross injector. The column employed was glass capillary 25 m long, 0.25 mm internal diameter, wall coated with SE 52. Helium was used as carrier gas at a flow of $2\,\mathrm{ml\,min^{-1}}$. Temperature was programmed from 120 to 270°C at a rate of $4°\mathrm{C\,min^{-1}}$. Peak areas were determined using a Varian Vista integrator. *N*-alkanes and isoprenoids were identified by comparison of their retention times with those of known standards from n-C_{11} to n-C_{36} injected in the same conditions, and quantified in respect to the internal standard, n-C_{22}. The same calibration factor was used for the unresolved envelope.

Analysis of aromatic hydrocarbons by high pressure liquid chromatography/U.V. spectrophotometry Aromatic hydrocarbons were analysed by HPLC according to the method of Moinet,[10] described in Moinet *et al.*[11] This method allows to obtain a HPLC fingerprint corresponding to the separation of hydrocarbons by increasing degree of aromaticity. Briefly, aromatic hydrocarbons were fractionated on an analytical column 20 cm long, 4·7 mm internal diameter filled with 5 μm SiO_2 bonded-NH_2 stationary phase. Sample injection was realised using a Rheodyne 7120 valve, with an injection loop of 20 μl. 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 ultra violet absorption at 254 nm with a Schoeffel spectromonitor. In these conditions aromatic hydrocarbons are separated essentially by degree of aromaticity, with little effect of alkyl substituents.[12] On HPLC chromatograms presented, retention times of known standards from benzene (Be) to perylene (Pe) are indicated. Peaks emerging from the envelope correspond to mono- to penta-aromatic series.

Blanks, limits of detection Great care was taken against contamination during on board ship 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 and blanks showed that only traces of interfering compounds were present in our samples.

Data were corrected for losses during laboratory work up, using recovery of the internal standard (n-C_{22}). Although drastic precautions have been taken during evaporation steps, losses of the more volatile compounds occur. Consequently, data given for $<C_{14}$ alkanes and <3 rings aromatic hydrocarbons are only semi-quantitative.

The analytical precision, taking into account extraction, chemical steps during sample work up, and gas liquid or high pressure chromatography analysis has been estimated as 25% for saturated and aromatic hydrocarbons. The corresponding limits of detection are as follows: 0.02 μg l^{-1} for total aromatic hydrocarbons (U.V. spectrofluorimetry), 0.005 μg l^{-1} for individual n-alkanes (CGC), and 0.001 μg l^{-1} for aromatic fractions (HPLC/U.V. spectrophotometry).

RESULTS AND DISCUSSION

Concentrations

Aromatic hydrocarbons Concentrations of aromatic hydrocarbons evaluated using U.V. spectrofluorimetry and HPLC/U.V. spectrophotometry are given in Table II.

TABLE II

Western Mediterranean sea; PHYCEMED cruise, April 1981. Concentrations of aromatic hydrocarbons determined by U.V. spectrofluorimetry and HPLC/U.V. spectrophotometry for dissolved and particulate matter, expressed in $\mu g\ l^{-1}$ as chrysene equivalent

Station		Aromatic hydrocarbon concentrations		
			HPLC/U.V. spectrophotometry	
		U.V. spectrofluorimetry	Dissolved	Particulate
GY-L	microlayer	0.35	0.049	0.131
	subsurface	0.47	0.111	0.081
ET-R_2(1)	microlayer	0.26	0.165	0.061
	subsurface	0.84	0.046	0.028
ET-R_2(2)	microlayer	0.28	0.229	0.102
	subsurface	0.49	0.127	0.046
SR-G_2	microlayer	5.15	0.084	0.029
	subsurface	0.20	0.077	0.022
SR-S	microlayer	0.25	0.105	0.077
	subsurface	0.07	0.009	0.026
GY-W_2	microlayer	0.70	0.197	0.122
	subsurface	0.33	0.061	0.039

Concentrations in total aromatic hydrocarbons (U.V. spectrofluorimetry) vary in the range 0.07–5.15 $\mu g l^{-1}$. This concentration range is less than the range reported for coastal waters of the Mediterranean, using also U.V. spectrofluorimetry,[2] indicating that open sea waters are not heavily polluted. It must be mentioned here that after Keizer and Gordon,[9] concentrations in excess of 2 $\mu g l^{-1}$ indicate either the presence of petroleum residues or sample contamination.

Figure 3 shows that there is no relationship between concentrations determined by the two methods: U.V. spectrofluorimetry and HPLC/U.V. spectrophotometry. Some of the values obtained by U.V. spectrofluorimetry are highly overestimated *versus* concentrations by U.V. spectrophotometry, as for example samples SR-G_2 microlayer and ET-R_2(1) subsurface. Such discrepancies have been previously related and can be interpreted by the interference of fluorescing compounds which are not aromatic hydrocarbons. This point underlines difficulties of the interpretation of aromatic hydrocarbon concentrations issued from spectrophotometric methods without a purification step of the initial extract. As a consequence, we have selected HPLC/U.V. spectrophotometry

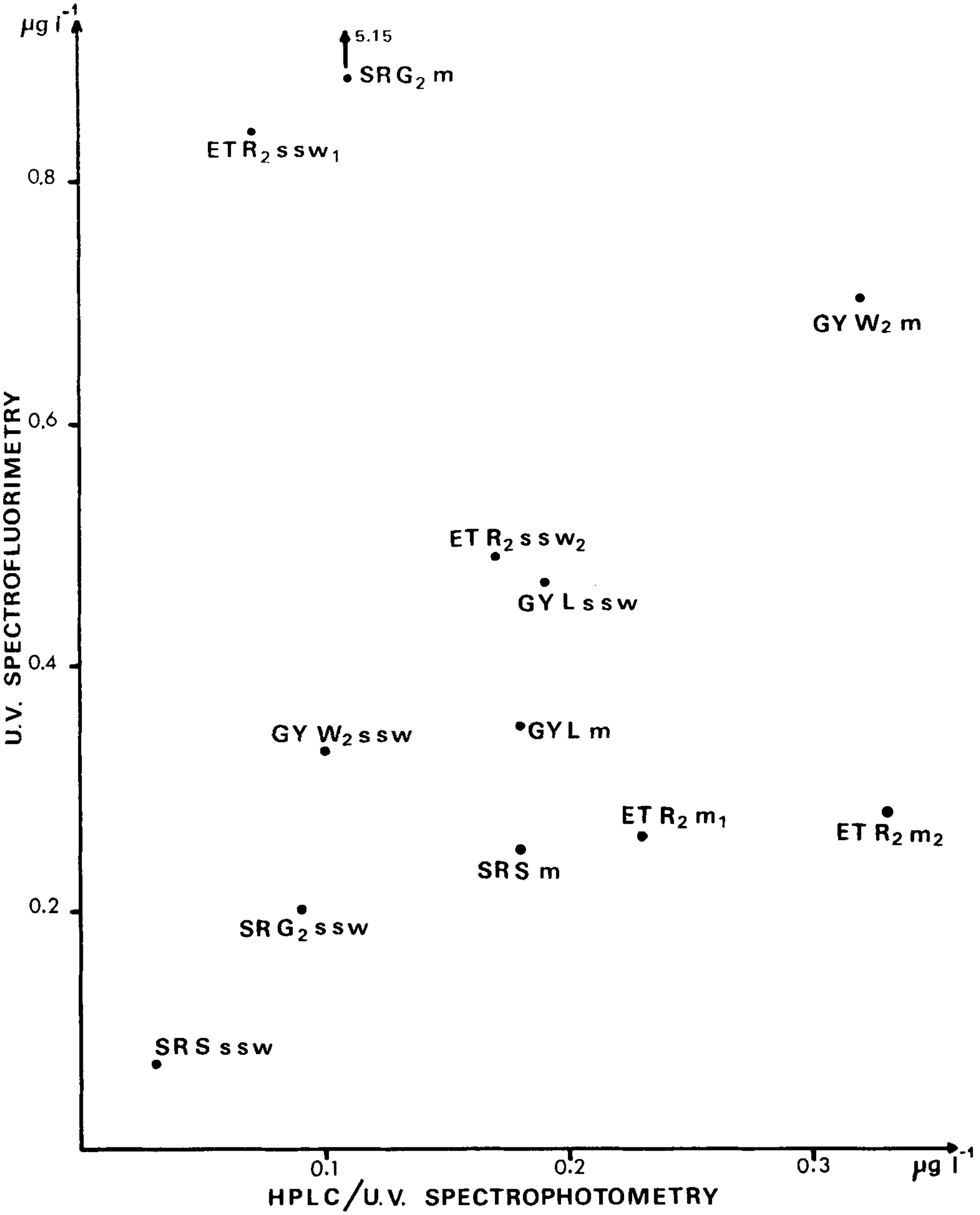


FIGURE 3 Total hydrocarbon concentrations determined by U.V. spectrofluorimetry *versus* dissolved + particulate hydrocarbon concentrations determined by HPLC/U.V. spectrophotometry. m: microlayer, ssw: subsurface water.

concentrations because in this method aromatic hydrocarbons are purified on a SiO_2 microcolumn. This method enables also to distinguish between dissolved and particulate compounds.

Dissolved aromatic hydrocarbon concentrations vary from 0.01 to 0.20 $\mu g\,l^{-1}$, particulate in the range 0.02–0.13 $\mu g\,l^{-1}$. There is about 2 to 3 times less of particulate hydrocarbons in the subsurface water. Particulate hydrocarbons are accumulated in the surface microlayer with an enrichment factor varying from 1 to 3. The enrichment factor (E.F.) is defined as the ratio between the concentration of a compound in microlayer and in subsurface water. Such values have been reported for both coastal and open ocean locations.[13–15]

Slight enrichments of up to 3 or 4 are typical of the microlayer under ambient surface conditions. In areas of high pollution by petroleum, the surface film can be enriched many thousands of times with hydrocarbons as a result of multilayer oil films.[16]

Contrarily drastic changes are observed for dissolved hydrocarbons: depletion for sample GY-L (E.F. = 0.43), high accumulation for sample SR-S (E.F. = 12).

Saturated hydrocarbons Dissolved and particulate *n*-alkane and total saturated hydrocarbon concentrations are listed in Table III.

Concentrations in dissolved *n*-alkanes vary from 0.02 to 20.57 $\mu g\,l^{-1}$. The variation range for particulate *n*-alkanes is 0.13–0.83 $\mu g\,l^{-1}$. The relative importance of *n*-alkanes *versus* total saturated hydrocarbons is highly variable, from 9 to 93% for dissolved hydrocarbons. This percentage is less for hydrocarbons associated with suspended matter: 5–22%. The fractionation of hydrocarbons between the dissolved and particulate states which is the result of various physico-chemical processes is largely dependent on local conditions; the ratio dissolved/particulate vary from 10 times less to 40 times higher.

As for aromatic compounds, if there is a slight but constant enrichment of particulate hydrocarbons in the surface microlayer, an inverse situation characterizes the dissolved pool of hydrocarbons: high depletion for sample GY-L (E.F. = 8×10^{-3}), important accumulation for ET-R2(1) (E.F. = 268). Another observation must be mentioned: the extreme local variability of both dissolved and particulate concentrations as shown for the same station ET-R2 sampled at 24 hours interval; the enrichment factor for dissolved *n*-alkanes decreases from 268 to 2.

Total hydrocarbons In order to compare the PHYCEMED data with those reported earlier, we have listed in Table IV total hydrocarbon concentrations by adding both aromatic (U.V. spectrophotometry) and saturated (CGC), dissolved and particulate concentrations.

TABLE III

Western Mediterranean Sea: PHYCEMED cruise, April 1981. Concentrations of dissolved and particulate *n*-alkanes and saturated hydrocarbons determined by CGC, expressed in $\mu g\, l^{-1}$. a: non determined.

Station		Dissolved hydrocarbons			Particulate hydrocarbons		
		n-alkanes	Total saturated hydrocarbons	*n*-alkanes / Saturated hydrocarbons %	*n*-alkanes	Total saturated hydrocarbons	*n*-alkanes / Saturated hydrocarbons %
GY-L	microlayer	0.17	1.88	9	0.83	7.23	11
	subsurface	20.57	22.16	93	0.52	3.52	15
ET-R_2(1)	microlayer	13.30	34.20	39	0.18	1.37	13
	subsurface	0.05	—[a]	—	0.17	1.61	11
ET-R_2(2)	microlayer	2.59	—	—	0.27	1.27	22
	subsurface	1.22	2.67	46	0.28	2.32	12
SR-G_2	microlayer	—	—	—	0.18	1.45	12
	subsurface	0.15	2.14	7	0.13	2.65	5
SR-S	microlayer	0.09	0.79	12	0.48	—	—
	subsurface	0.02	0.08	34	0.21	0.98	21
GY-W_2	microlayer	0.31	3.52	9	0.38	4.02	9
	subsurface	0.26	2.56	10	0.13	0.79	16

TABLE IV

Western Mediterranean Sea: PHYCEMED cruise, April 1981. Concentrations of total (dissolved + particulate) hydrocarbons

Station		Total D + P hydrocarbons	$\frac{\text{Aromatic hydrocarbons}}{\text{Total hydrocarbons}}$ %
GY-L	microlayer	9.30	1.9
	subsurface	25.87	0.8
ET-R_2(1)	microlayer	35.80	0.6
	subsurface	1.73[a]	4.0
ET-R_2(2)	microlayer	4.18[a]	7.9
	subsurface	5.16	3.3
SR-G_2	microlayer	—	—
	subsurface	4.89	2.0
SR-S	microlayer	1.45[a]	12.4
	subsurface	1.08	2.8
GY-W_2	microlayer	8.05	4.0
	subsurface	3.45	3.0

[a] Non resolved saturated components are not included.

The Mediterranean has been the subject of several investigations for non volatile hydrocarbons as by Horn *et al.*,[3] Morris *et al.*[4] and Albaiges *et al.*[5] for surface pelagic tars; by Monaghan *et al.*,[17] Faraco and Ros,[6] and Zsolnay[8] for hydrocarbons in surficial water. But a few data is available for the western Mediterranean. The Ligurian Sea has been studied between Nice and Calvi in 1972[14] and off Villefranche bay in 1976–1977.[18]

Concentrations reported were in the range 4–40 $\mu g\,l^{-1}$, which indicates in respect with relatively high values encountered in 1981 that the central part of the Ligurian Sea is effectively polluted. This can be correlated with the gyre type superficial water circulation, accumulating different urban run off and refinery wastes.

Algerian coastal waters have been sampled in 1974–1975 and Zsolnay in 1979 reported a mean concentration of 20 $\mu g\,l^{-1}$. In 1981, the concentration found in SR-G2 is about 5 $\mu g\,l^{-1}$.

On a global scale, total concentrations obtained in 1981 vary in the range from a few $\mu g\,l^{-1}$ to 35 $\mu g\,l^{-1}$. Percentages of aromatic vs total hydrocarbons are low, below some per cent. Regarding concentrations, the western Mediterranean appears as non-heavily polluted with an exception for the Ligurian Sea (station GY-L).

Aromatic fingerprints and *n*-alkane distribution patterns; utilization as pollution and fractionation processes indicators at the sea-air interface.

To illustrate the potential use of the precise analysis of hydrocarbons we have selected two stations representative of two opposite conditions: first, SR-S, which could be considered obviously as a reference station with a very low hydrocarbon background level and GY-L which appears to be slightly polluted.

Station SR-S HPLC chromatograms of dissolved and particulate hydrocarbons, both for microlayer and subsurface water are presented in Figure 4.

Two series, triaromatic (phenanthrene) and tetraaromatic (pyrene) predominate in subsurface water. Very different fingerprints are observed for the microlayer. They are characterized by the predominance of triaromatic structures (phenanthrene) for particles and lower aromaticity degree structures for dissolved hydrocarbons.

The high value of the enrichment factor, 12, is related to the accumulation of volatile compounds in the microlayer, a preliminary step before evaporation into the atmosphere. According to this explanation the enrichment factor for $<C_{20}$ *n*-alkanes which are less volatile than phenanthrene has a lower value, 3. Smooth sea conditions encountered at this station (Table I) allows this steady-state accumulation vs evaporation.

Station GY-L The subsurface is characterized by two different types of aromatic fingerprints, with a marked predominance of low aromaticity compounds: monoaromatic (benzene) in the particulate fraction, diaromatic (fluorene) in the dissolved (Figure 5).

Note that the evaluation of these compounds is only semi-quantitative, due to losses during evaporation steps but particularly important in connection with toxicity problems. It is well known that benzene-type monoaromatic hydrocarbons, are highly toxic for the marine life.[19, 20]

Particulate hydrocarbons are accumulated in the surface microlayer (mean E.F. = 2), the monoaromatic fraction being evaporated. In the dissolved pool, the more volatile compounds have disappeared during the microlayer formation.

The examination of *n*-alkane distribution patterns (Figure 6) and saturated hydrocarbon enrichment factors lead to the same figure. Dissolved *n*-alkanes are not accumulated (E.F. $= 8 \times 10^{-3}$). Particulate *n*-alkane distributions suggest that there is a more pronounced biological activity in the surface film than for other samples. This is

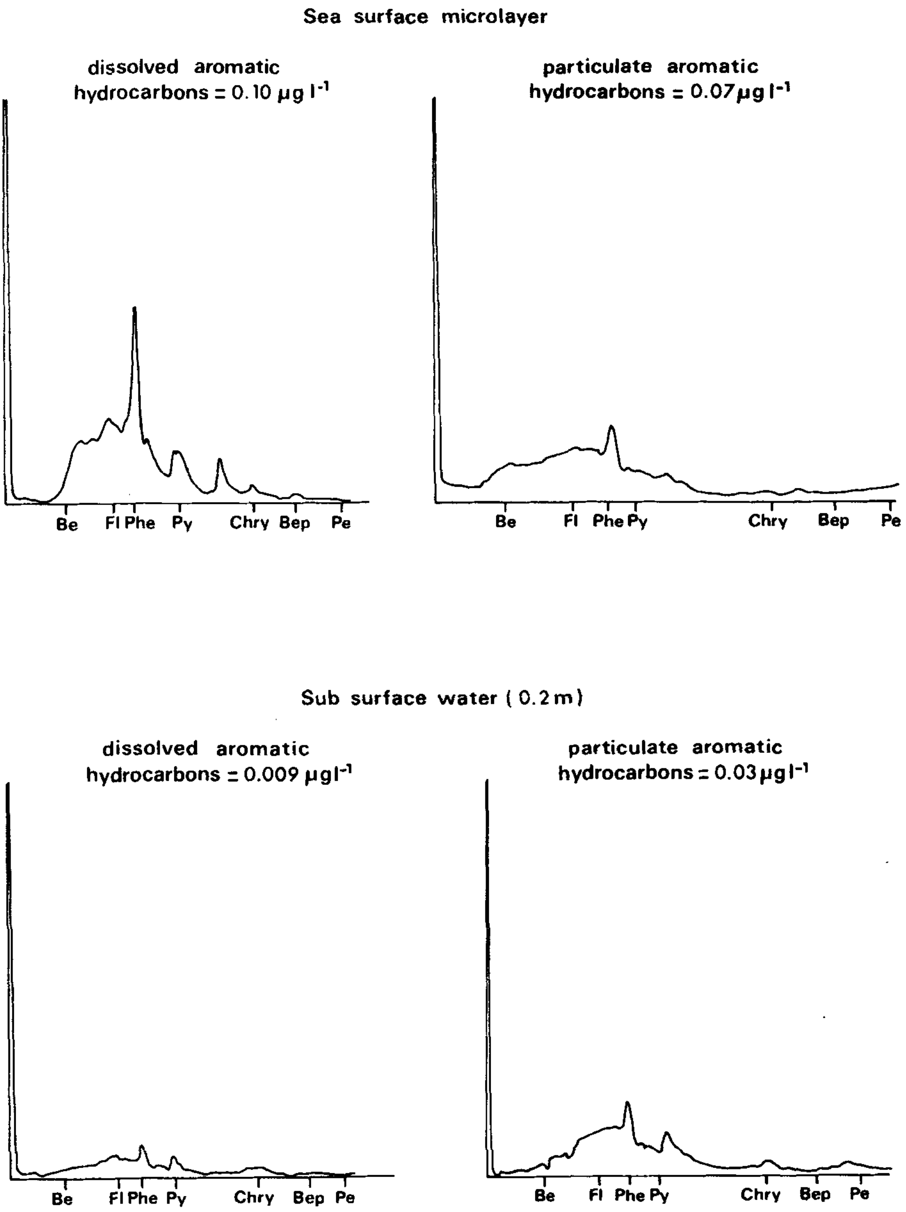
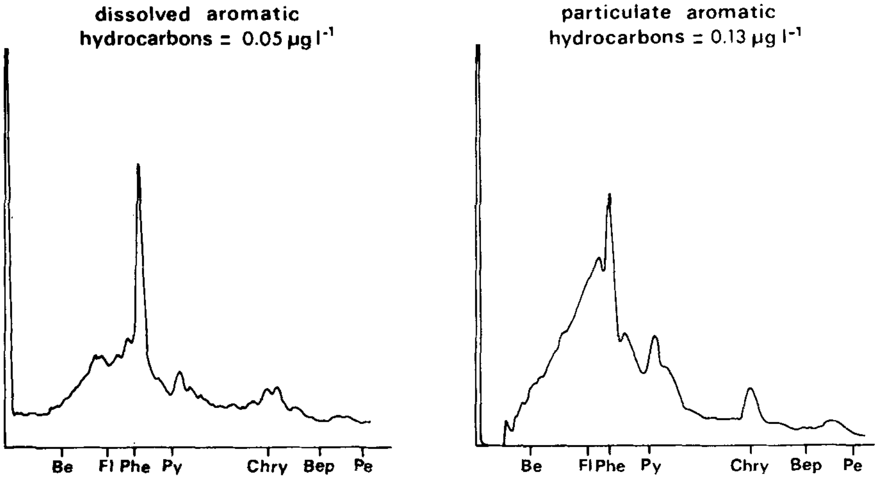


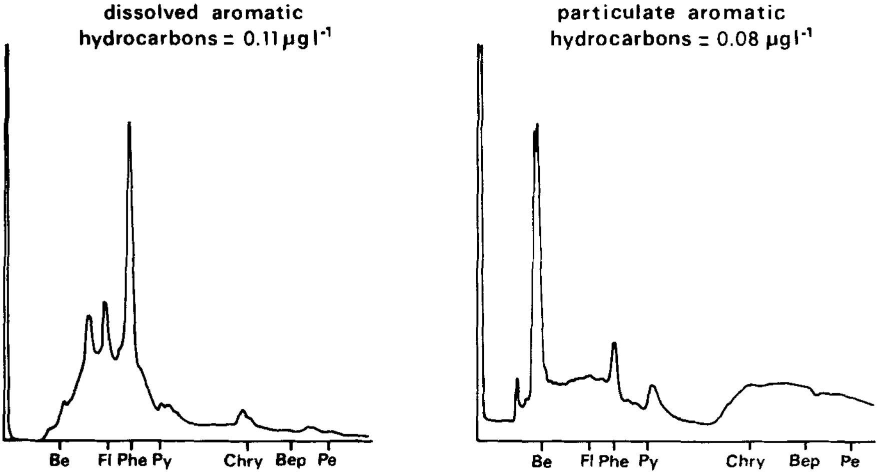
FIGURE 4 Aromatic hydrocarbon fingerprints obtained by HPLC/U.V. spectrophotometry, station SR-S.

Sea surface microlayer


dissolved aromatic hydrocarbons = 0.05 $\mu g\ l^{-1}$

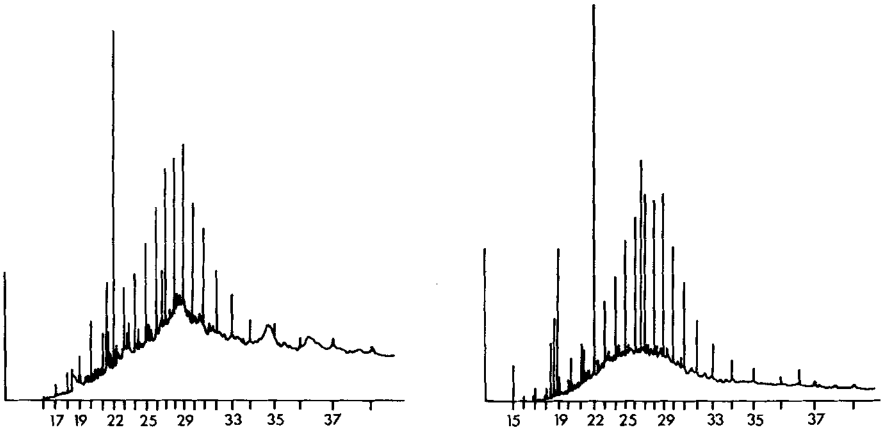
particulate aromatic hydrocarbons = 0.13 $\mu g\ l^{-1}$

Sub surface water (0.2 m)


dissolved aromatic hydrocarbons = 0.11 $\mu g\ l^{-1}$

particulate aromatic hydrocarbons = 0.08 $\mu g\ l^{-1}$

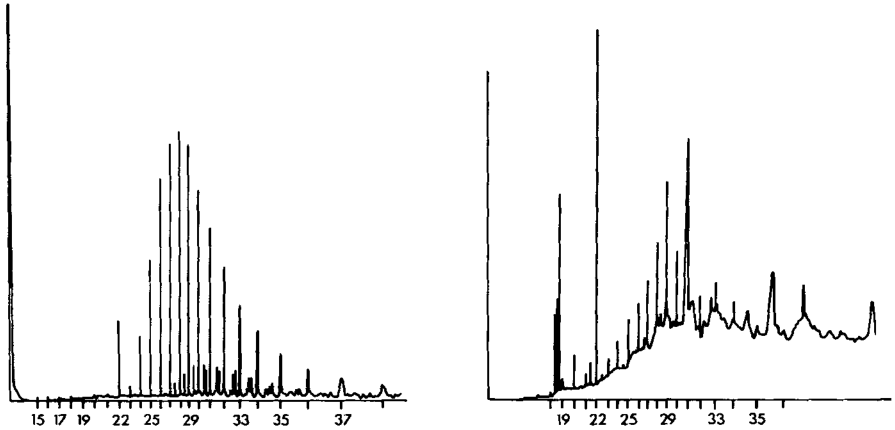
FIGURE 5 Aromatic hydrocarbon fingerprints obtained by HPLC/U.V. spectrophotometry station GY-L.



Sea surface microlayer

dissolved n-alkanes ≃ 0.17 µg l^{-1}

particulate n-alkanes ≃ 0.83 µg l^{-1}



Sub surface water (0.2 m)

dissolved n-alkanes ≃ 20.57 µg l^{-1}

particulate n-alkanes ≃ 0.52 µg l^{-1}

FIGURE 6 Saturated hydrocarbon chromatograms showing *n*-alkane distribution patterns, station GY-L.

indicated by the importance of n-C_{15} and n-C_{17}, associated with planktonic activity.[21] Owing to the more degradability of n-alkanes vs other branched and cyclic compounds, this could explain the decrease of n-alkane importance *versus* total saturated hydrocarbons in the microlayer (9%) in respect to subsurface water (27%).

Of note is a terrestrial contribution in particulates of subsurface water, shown by the predominance of an odd carbon number series in the range C_{25}–C_{31}. This illustrates the decoupling between the two organic matter pools, dissolved and particulate, recently clearly demonstrated by Boehm[22] and Barbier *et al.*[23]

All these observations show that the microlayer is a site of specific biological and physico-chemical processes and active exchanges between the surficial water and the atmosphere. In fact, for polluted stations, the examination of hydrocarbons budget in the microlayer allows to precise the efficiency of the degradation and transfer from the sea to the atmosphere of hydrocarbons, both biogenic and petrogenic.

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