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Aliphatic and Aromatic Hydrocarbons in the Mediterranean Aerosol†

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The atmospheric transport of organic pollutants over long distances and their effect on the biological cycles of the sea are two major questions of concern in environmental chemistry. These processes are of particular importance in the Mediterranean Sea because of its semi-enclosed characteristics, which determine the accumulation of the pollutants entering into the system.

In order to get some insight into these processes a project (PHYCEMED), was developed for the evaluation of the atmospheric budget of organic and inorganic substances in the Western Mediterranean and for the investigation of the exchange mechanisms of these materials across the air/sea interface.

A high volume air sampling system including a cascade impactor was placed on board of the R/V *le Suroit* for collecting the aerosols along several transects parallel to the French, Spanish and North-African coasts, facing areas of different population densities and industrial activities. The cruise was realised on October 1983 and the particulate material was fractionated into the following sizes: 7.2, 3.0, 1.5, 0.96, and 0.03 μm . Quantitative and qualitative analyses of the aliphatic and the aromatic hydrocarbons present in these fractions were performed by high resolution gas chromatography and gas chromatography-mass spectrometry.

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Total non-aromatic hydrocarbon concentrations are in the range 30–57 ng/m³ (10–14 ng/m³ for *n*-alkanes). The distribution of *n*-alkanes indicates that most of the aerosol mass is associated with small particles (<1 μm).

Polycyclic aromatic hydrocarbons are identified from phenanthrene to benzo(ghi)perylene with fluoranthene and pyrene as dominant compounds. Concentrations for individual PAH vary in the range 4.1 pg/m³ for benzo(a)anthracene up to 100 pg/m³ for fluoranthene. The evaluation of different contributions such as land plant waxes or soil sources and various anthropogenic sources is discussed from *n*-alkanes and PAH distribution patterns.

KEY WORDS: Air pollution, aliphatic hydrocarbons, marine aerosol, Mediterranean Sea, polycyclic aromatic hydrocarbons.

I. INTRODUCTION

In order to study the atmospheric part of the cycling of hydrocarbons between continent and ocean, many research programs have been recently developed for measuring concentrations of major hydrocarbon-type compounds present in the marine atmosphere in gas phase or associated within particles. Data have been reported for aliphatic hydrocarbons, essentially *n*-alkanes,^{1–11} and aromatic compounds.^{12–15}

As the atmospheric pathway and fate of organic compounds is closely associated with the size and the nature of the particles involved, it appears that the knowledge of the association of organic components with different types of particulates could help in interpreting and modelling the fate of atmospheric hydrocarbons and their transport to and from the ocean. For example the settling velocity and consequently the dry deposition rate of particles depends within the size and the density of particles.^{16,17}

This paper deals with the study of aerosols separated as a function of particle size from <0.03 μm up to 7.2 μm in diameter, collected over the Mediterranean Sea during an oceanographic cruise in 1983, along two transects off the French and south Spanish coasts.

Qualitative and quantitative analyses are discussed with three major aims:

- i) The estimation of background concentrations of hydrocarbons in the particles over the Mediterranean Sea and the comparison with other remote marine areas.

ii) The identification of organic compounds which may reflect unequivocally specific inputs.

iii) The assessment of the association of the aerosol particle size with the organic composition and its implication in long distance transport of natural and anthropogenic compounds.

II. SAMPLING

A. Sampling methods

Aerosols were collected using a five-stage cascade impactor for large air volumes (Sierra instruments). Air flow was $68 \text{ m}^3 \text{ h}^{-1}$ and collection time about 48 hours. The aerosol collector was located on the bow of the ship at about 8 meters above the sea level. The pump was electrically connected to a wind direction monitor which interrupted all sampling when the wind direction deviated more than a sector of 30° from the ship's route. The pump was not operating when the wind speed was $< 3 \text{ m/s}$ or when the boat was stopped.

Air particles were separated into six size fractions on glass fibre filters according to their equivalent diameter:

1st stage :	$d = 7.2 \mu\text{m}$
2nd stage :	$d = 3.0 \mu\text{m}$
3rd stage :	$d = 1.50 \mu\text{m}$
4th stage :	$d = 0.96 \mu\text{m}$
5th stage :	$d = 0.50 \mu\text{m}$
FF :	$d = 0.03 \mu\text{m}$

After sampling, the filters were frozen until the analysis in the laboratory.

B. Sampling sites

Samples were collected during the PHYCEMED II cruise in September–October 1983, over the Mediterranean Sea. The first air sample, IMP1, was collected along the east Spanish coast and stopped at station SR-GZ, as indicated on Figure 1. The second one was collected over the Alboran Sea and stopped at station SR-G2.

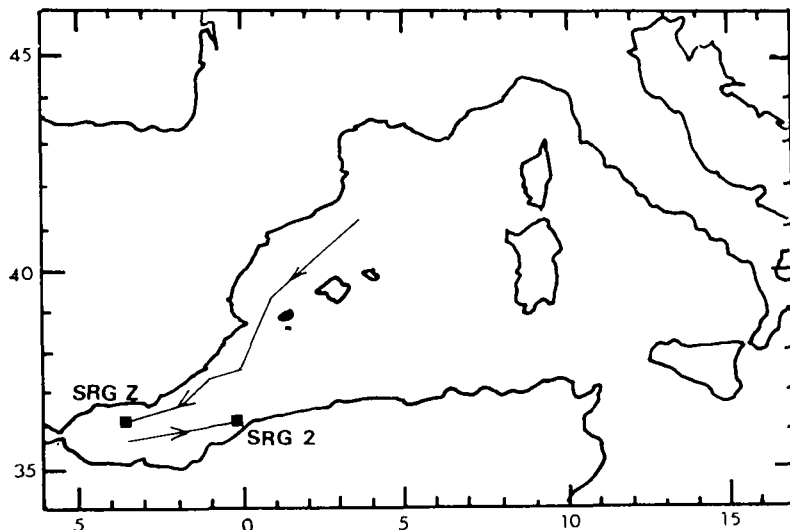


FIGURE 1 Sampling routes for Impactor 1 (IMP1) and Impactor 2 (IMP2) during PHYCEMED II cruise, over the Western Mediterranean Sea. (October 1983).

Sampling conditions for these two aerosols were different. The main wind direction at the beginning of the IMP1 sampling was ESE with a wind speed of about 3.5 m/s; 15 hours later the wind direction turned NE with a wind speed around 10 m/s. For IMP2 the wind direction fluctuated from WNW to SW with a wind speed around 4 m/s; then wind turned NE-ESE with a wind speed of about 5 m/s. The air mass trajectories are reported on Figure 2(a, b).

III. ANALYTICAL METHODS

A. Chemical treatment of the samples

The quantitative and qualitative analyses of the aliphatic hydrocarbons were performed in the "Laboratoire de Physique et Chimie Marines" in Paris.

After sample collection, the filters were spiked with an internal standard (C22 *n*-alkane) for recovery determination, and soxhlet extracted 30 hours with CH_2Cl_2 . The extract was saponified under argon flow during two hours with $\text{CH}_3\text{OH}/\text{KOH}$ 2N. After

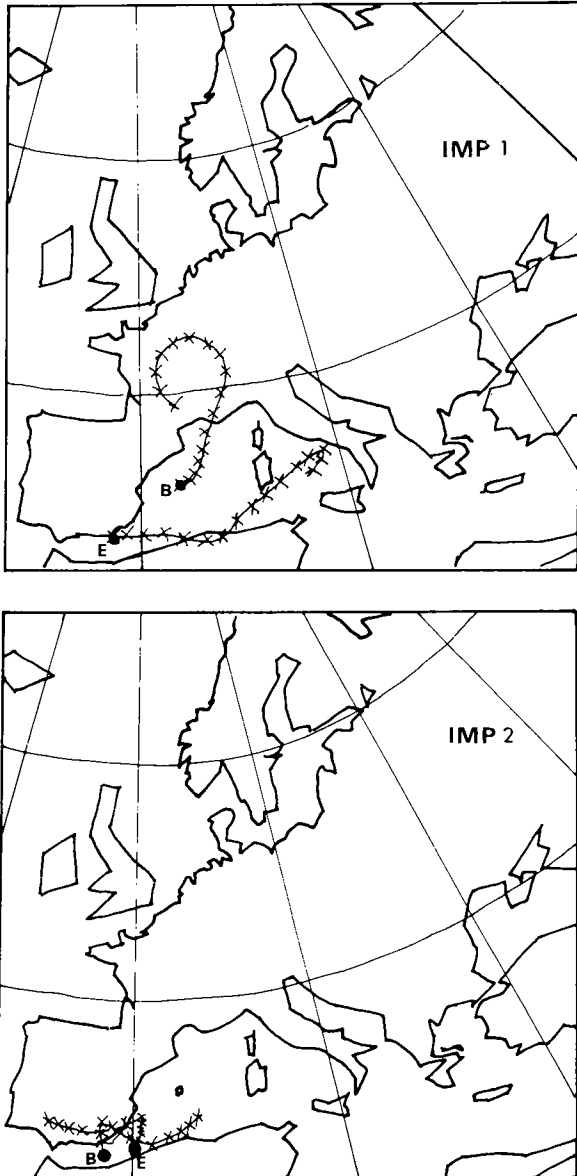


FIGURE 2 Air mass trajectories corresponding to the beginning of sampling (B) and to the end of sampling (E)-a: for IMP1-b: for IMP2.

acidification to pH 2 the unsaponifiable fraction together with the saponified acids were extracted 5 times with 1 ml of a mixture hexane-ether (9:1 v/v) which was then evaporated under nitrogen. The extract was separated into compound classes by adsorption chromatography on precleaned silica MERCK 60 G type, using solvents of increasing polarity; This procedure enables to separate *n*-alkanes (6 ml of hexane), aromatic hydrocarbons (3 ml of 0.2% of ethyl acetate + 3 ml of 0.05% of ethyl acetate in hexane + 2 ml of hexane), fatty acids and alcohols (20 ml of ethyl acetate) and more polar compounds (10 ml of methanol). Fatty acid results will be published elsewhere.

Aliphatic hydrocarbons were analysed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), GC analyses were performed on a fused silica capillary column coated with a non polar phase CP Sil 5 (25 m long and 0.32 mm i.d.) using a Ross injector.

Peak areas were determined on the chromatograms, with a Varian Vista 401 Integrator, and compared to the C₂₂ *n*-alkanes area for quantitation. Compounds were identified by comparison of retention times with those of known standards and by GC/MS. *n*-Alkanes were detected in the range of 20 to 45 carbon atom number. No significant amounts were detected in the range of less than 20 carbon atom number.

Aromatic hydrocarbons were analysed in the Department of Environmental Chemistry in Barcelona, as well as *n*-alkanes for inter-calibration exercise.

The samples were Soxhlet extracted with a mixture of 2:1 (v:v) CH₂Cl₂—CH₃OH during 30 hours; then an internal standard containing perdeuterated *n*-C₂₄, *n*-C₃₂, and anthracene was added to the extract. The mixture was evaporated under vacuum to almost dryness and the residue was saponified during 24 hours with 20 ml of 6% KOH in water. Following this step the neutral lipids were separated by extraction with 5 × 20 ml of *n*-hexane. This organic solution was dried overnight by addition of 1 g of clean anhydrous Na₂SO₄. Then the *n*-alkane solution was decanted, the Na₂SO₄ rinsed with more solvent and the original *n*-hexane plus rinses were evaporated under vacuum to approximately 0.5 ml. This concentrated solution was submitted to chromatographic separation using a

column filled with 800 mg of 5% deactivated silica (bottom) and 800 mg of 5% deactivated alumina (top). The following fractions were collected: (a) saturated hydrocarbons (3 ml of hexane), (b) aromatic hydrocarbons (6 ml of 20% of methylene chloride in hexane), and (c) polar compounds (6 ml of 10% of methanol in methylene chloride).

GC and GC/MS analyses were performed on SE-52 capillary columns, temperature programmes from 60°C to 300°C at 6°C/min. The injection was made in the splitless mode keeping the valve closed for 40 s and the injection port at 260°C.

The *n*-alkane quantitative values were obtained from the gas chromatographic profiles. The calculations were performed by comparison of the peak areas of the *n*-paraffin series present in the samples with those of spiked hydrocarbon standards. In one case the peaks were compared with that of a known amount of docosane and in the other two reference peaks (perdeuterated tetracosane and dotriacontane) were selected, the first for the *n*-paraffins lower than nonacosane and the second for those higher than octacosane.

Concentrations of polycyclic aromatic hydrocarbons were obtained by mass fragmentography from the molecular ions of the compounds present in the samples. Important quantities of the fractions of aromatics had to be injected in each run (i.e. 3 μ l out of 10 μ l) and in consequence an internal standard of perdeuterated anthracene was used to compensate for the lack of reproductibility of the injections. Thus the *m/z* 188 peak area corresponding to the *d*₁₀-anthracene eluting in the current run was compared with that of a known amount of the same compound present in a PAH mixture used for quantitation. This hydrocarbon mixture was at the same time an external standard used to calculate the concentrations of the PAHs in the aerosols. Accordingly the molecular ion peak areas of the samples and standard mixture were compared with the following rules: an anthracene standard was used to calculate the concentrations of anthracene and phenanthrene (*m/z* 178) in the samples; a fluoranthene standard was used for fluoranthene and pyrene (*m/z* 202); a chrysene standard for chrysene plus triphenylene and benzo(a)anthracene (*m/z* 228), benzo(a)pyrene for the quantitation of benzo(a)pyrene, benzo(e)pyrene and several coeluting benzofluoranthenes (*m/z* 252) and finally, benzo(ghi)perylene for benzo(ghi)perylene and indeno(1,2,3-cd)pyrene (*m/z* 276).

B. Blanks

Precautions were taken, in order to avoid any contamination. All the solvents used in the laboratory were distilled. The glass fibre filters used for air sampling were extracted 30 hours with CH_2Cl_2 . Before the analyses, blanks were performed for testing the analytical procedure. No significant amounts of *n*-alkanes or PAH were found above the detection limit. Detection limit for individual *n*-alkanes was about 5 pg/m^3 , and about 0.1 pg/m^3 for PAH.

C. Intercalibration

Table I lists the total *n*-alkane concentrations and CPI values for each particle size obtained by the two research groups.

One aspect of this comparison is to indicate marked differences in concentrations between the two sets of data, one set being more than two times higher than the other. These quantitative differences can be explained by: (i) the loss of compounds in the range of less than 20 carbon atom number due to analytical procedure and especially to the conditions of injection (ii) differences in concentrations observed for compounds with more than 20 carbon atom number. It must be mentioned that deviations between two sets of concentrations corresponding to the same sample but analysed in the different laboratories are constant all over the range of the *n*-alkanes

TABLE I

Concentrations of total *n*-alkanes in pg/m^3 and CPI values calculated from 21 to 36 atom carbon number, for the different stages of impactors. (a) Values obtained by the LPCM in Paris. (b) Values obtained by the Department of Environmental Chemistry in Barcelona.

Stage	1	2	3	4	5	FF
IMP1(a)	705	2444	2261	2428	2840	3234
IMP1(b)	1700	4900	3400	3600	4400	9800
CPI(a)	3.47	2.94	2.30	1.57	1.72	1.55
CPI(b)	1.99	2.94	2.34	1.60	1.74	1.49
IMP2(a)	764	1521	1656	1453	1777	2593
IMP2(b)	1600	3300	2300	3100	3100	5400
CPI(a)	3.53	3.20	1.72	1.44	1.32	1.37
CPI(b)	1.53	2.99	1.75	1.47	1.42	1.31

detected (from 20 to 45 carbon atom number), but are different according to the impactor stage.

In spite of these differences, the very important point is that the two sets of CPI values are very similar except on stage 1, probably due to the heterogeneity in repartition of the largest particles on the whole filter surface. Therefore the geochemical interpretations which can be done from these results are identical: indeed the relative contributions of the different sources to the composition of the aerosol are the same.

IV. RESULTS

N-alkane results for IMP1 and IMP2 are reported in Table II. Resolved components by GC are almost exclusively *n*-alkanes. Total *n*-alkane concentrations are around 14 ng/m³ and 10 ng/m³ for IMP1 and IMP2 respectively. These values are greater than those observed in remote areas: 20–160 pg/m³ for the Tropical North Pacific,⁶ 200–600 pg/m³ for the North Pacific,¹⁰ but comparable with other data: 6–13 ng/m³ for the Equatorial Atlantic,⁸ about 32 ng/m³ for the Tropical North Atlantic.¹⁸ The concentrations of the total *n*-alkanes for these two Mediterranean aerosols are close to that found in the aerosols collected over the Mediterranean Sea during PHYCEMED I cruise in 1981^{19,20} (20 ng/m³).

TABLE II

Concentrations of total *n*-alkanes and non aromatic hydrocarbons (NAH) as a function of particle size for impactor 1 and 2 (pg/m³).

Stage	1	2	3	4	5	F	Total
IMPACTOR 1							
Total							
<i>n</i> -alkanes	705	2444	2261	2428	2840	3234	13912
NAH ^a	3870	8340	9160	7560	5980	22510	57420
IMPACTOR 2							
Total							
<i>n</i> -alkanes	764	1521	1656	1453	1777	2593	9764
NAH ^a	2940	4770	4190	3970	4790	8950	29610

^aNAH: Non aromatic hydrocarbons.

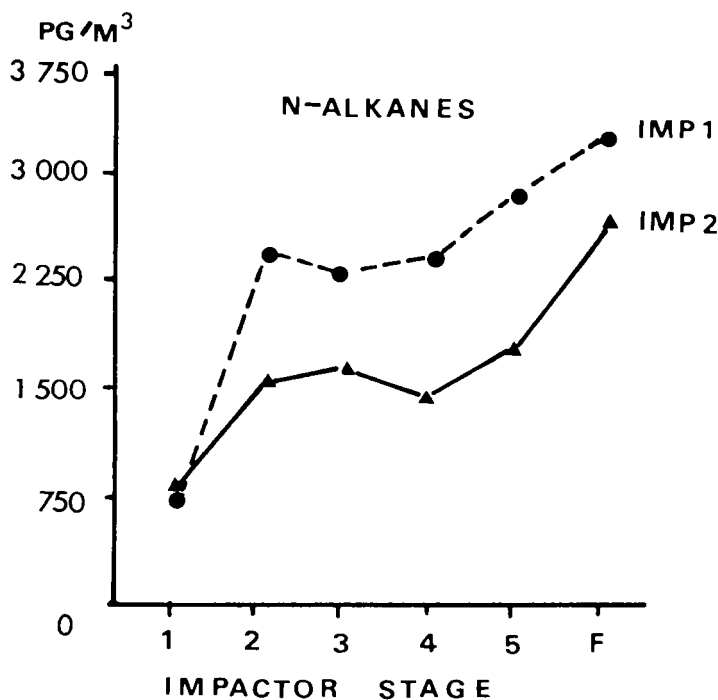


FIGURE 3 Total *n*-alkanes distribution in pg/m^3 as a function of particle size for IMP1 and IMP2.

The comparison between IMP1 and IMP2 samples shows that IMP1 is more concentrated than IMP2 either for total *n*-alkanes, (respectively $13.8 \text{ ng}/\text{m}^3$ and $9.8 \text{ ng}/\text{m}^3$) or for non aromatic hydrocarbons (NAH), (respectively $57.4 \text{ ng}/\text{m}^3$ and $29.6 \text{ ng}/\text{m}^3$). The distribution of *n*-alkanes as a function of particle size, indicates that most of the aerosol mass is associated with small particles, $<1.5 \mu\text{m}$, (about 60% of the total mass is on stages 4, 5, F) (Figure 3).

Table III lists the concentrations of polycyclic aromatic hydrocarbons present in higher amounts in the samples. Here, as for *n*-alkanes, the stages of every impactor were studied separately. Parent compounds range from phenanthrene to benzo(ghi)perylene and the dominant analogs are fluoranthene and pyrene. These hydrocarbon mixtures correspond to a pyrolytic origin,²¹⁻²⁷ as suggested by the

TABLE III
Concentrations of the major PAH identified in IMP1 and IMP2 samples (in $\mu\text{g}/\text{m}^3$).

	I1 E1	I1 E2	I1 E3	I1 E4	I1 E5	I1 F	I1 T	I2 E1	I2 E2	I2 E3	I2 E4	I2 E5	I2 F	I2 T
Phenanthrene	17	15	-	12	11	13	68	3.5	7.0	4.5	5.0	7.0	9.5	36
Anthracene	0.5	0.8	-	0.5	1.0	2.0	5.0	0.3	0.5	0.5	0.6	1.5	2.5	5.9
Fluoranthene	12	21	-	27	27	13	100	2.5	10	8.0	12	14	17	63
Pyrene	9.0	14	-	18	27	11	79	2.5	8.0	5.0	9.5	16	19	60
Benzo(a)anthracene	0.9	1.5	-	2.0	3.5	1.0	9.0	0.3	0.2	0.2	0.4	1.0	2.0	4.1
Chrysene + triphenylene	5.0	8.0	-	15	19	6.5	53	1.5	3.0	3.0	6.0	8.0	11	32
Benzofluoranthenes	3.0	4.5	-	7.5	22	5.5	42	0.4	4.0	3.0	5.5	7.0	8.0	28
Benzo(e)pyrene	2.0	3.0	-	3.5	13	3.0	24	0.3	2.0	2.0	3.0	4.5	6.0	18
Benzo(a)pyrene	0.5	0.8	-	1.0	5.0	1.5	9.0	0.2	0.9	0.7	1.0	2.0	3.0	7.8
Indeno(1,2,3-cd)pyrene	0.4	0.8	-	2.0	3.5	0.6	7.0	<0.1	0.7	0.5	1.0	1.0	1.5	4.7
Benzo(ghi)perylene	1.5	2.5	-	2.5	5.5	1.5	13	<0.1	1.0	0.8	1.5	3.0	2.5	8.8
Total	52	72	-	91	137	59	410	11	37	28	46	67	82	270

presence of five-membered alicyclic ring compounds of catacondensed structure (Fluoranthene is the major analog in most cases) which indicates a high temperature origin for the mixture.^{28, 29}

The main difficulty for the comparison of the quantitative values of Table III with data obtained in other areas is the lack of information on concentration levels of PAHs in marine aerosols sampled elsewhere; only urban or rural aerosols can be compared. As it must be expected, PAHs in aerosols from urban areas are in much higher levels than the concentrations found in the Mediterranean. For example, in Christchurch (New Zealand) Cretney *et al.*³⁰ found individual concentrations ranging from 1 to 200 ng/m³ (i.e. chrysene 2 71 ng/m³; benzo(a)pyrene 1 72 ng/m³; benzo(ghi)perylene 11–213 ng/m³) and Keller and Bidleman³¹ when analysing both the particulate and the vapor phases of air samples in Columbia City (South Carolina, U.S.A.) reported a range of individual concentrations from 0.3 up to 140 ng/m³ for phenanthrene, anthracene, fluoranthene and pyrene, whereas the range of benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and coronene in the particulates was 0.03–5 ng/m³. Furthermore, Van Vaeck and Van Cauwenberghe³² found that the levels of benzofluoranthenes in Wilrijk (Belgium) ranged from 0.1 to 30 ng/m³.

In rural areas lower concentrations have been described, although they are still higher than those found in the present paper for the Mediterranean aerosols. Van Vaeck and Van Cauwenberghe³² reported concentrations of benzofluoranthenes in the range of 0.05–5 ng/m³ for aerosols sampled in Dourbes (Belgium), a rural station situated about 40 kms away from significant industrial activities. Keller and Bidleman,³¹ in several rural sampling stations located in the Savannah River area (South Carolina, U.S.A.), found concentrations of phenanthrene in the order of 10 ng/m³ (particulates plus vapor phase), and fluoranthene and pyrene ranging between 0.4 and 4 ng/m³. In the same paper, it is mentioned a level of 0.02 ng/m³ for benzo(ghi)perylene (particulates only) and less than 0.02 ng/m³ for the concentration of benzo(a)pyrene. In general these results are sensibly higher than those reported by Simoneit²⁷ when analysing urbanized areas of the Western United States and Nigeria or rural air basins with elevated vehicular traffic (Los Angeles, California, U.S.A.). The individual concentrations of parent PAHs ranged from 0.4 pg/m³ up to 500 pg/m³, the more abundant analogs being fluo-

ranthene (5–470 pg/m^3 , and pyrene (4–500 pg/m^3). The minor components were anthracene (1–12 pg/m^3), coronene (1–20 pg/m^3) and benzo(a)pyrene (0.4–25 pg/m^3).

Results of Table III are within the range of concentrations described by Simoneit,²⁷ being closer to the lower limits than to the higher. The values of the two impactors are relatively similar; impactor 1 shows a higher concentration of total PAHs, as already found for the aliphatic hydrocarbon fraction. The highest concentration for an individual polycyclic aromatic hydrocarbon is 100 pg/m^3 (fluoranthene, impactor 1) and the lowest is 4.1 pg/m^3 (benzo(a)anthracene, impactor 2). It can be observed that the detection limit of individual PAHs in the marine aerosols here is higher than that reported by Simoneit²⁷ in urban and rural areas: this is a consequence of the fractionation by size of the aerosol samples in the present study and of the independent analysis of each fraction. The same effect can also explain for the lack of detection of coronene and dibenzoanthracenes, PAHs that are usually present as minor components in samples of pyrolytic origin^{33,34} that have been found in several of the above referenced aerosols.^{27,30,35}

Alkylsubstituted polycyclic aromatic hydrocarbons have also been found as minor PAHs in the aerosols. These are constituted by the alkylphenanthrene series (phenanthrene plus C₁, C₂, C₃ homologs, see Figure 4, the alkylidibenzothiophene series (thiophene plus C₁, C₂, C₃ homologs, see Figure 5 and a small amount of methylated fluoranthenes and pyrenes.

V. DISCUSSION

In Table IV are reported some calculations from *n*-alkane concentrations. The CPI (Carbon Preference Index) is used to evaluate the predominance of *n*-alkanes with an odd number of carbon atom in the range of C₂₁ to C₃₆ carbon atom number in our marine samples. For the different stages values demonstrate that the terrestrial contribution is more important on the large particles collected on stages 1, 2, and 3, and decreases on the small particles.

The value of the ratio U/R (Unresolved compounds/Resolved compounds in GC) can be used as a criterion to follow the evolution of anthropogenic inputs according to the particle size. The mean

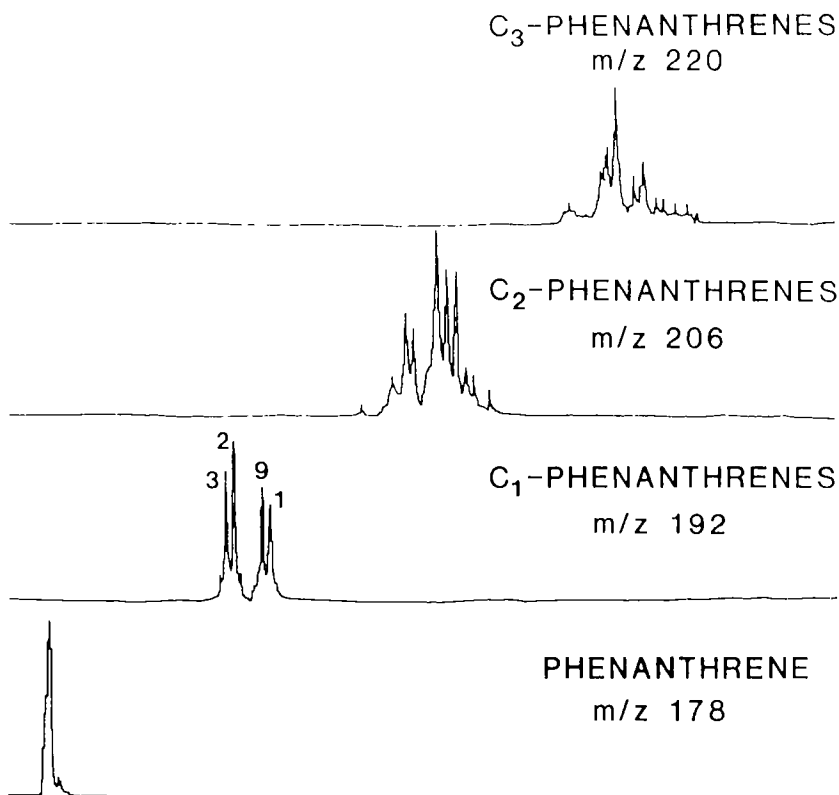


FIGURE 4 Alkyphenanthrenes found in the Mediterranean aerosols.

values calculated over all the particle spectrum indicate that the anthropogenic inputs are stronger in IMP1 aerosol (mean value: 4.2) than in the IMP2 aerosol (mean value 3.0). Such U/R ratio values are representative of an intermediate level of pollution. These data are consistent with previous comments: IMP1 and IMP2 aerosols were collected in different meteorological conditions. As indicated on Figures 2a and 2b, IMP1 sample originates from the European continent; thus we should expect significant inputs from both terrestrial and anthropogenic sources, whereas IMP2 corresponds to a less anthropogenic origin from the south of Spain.

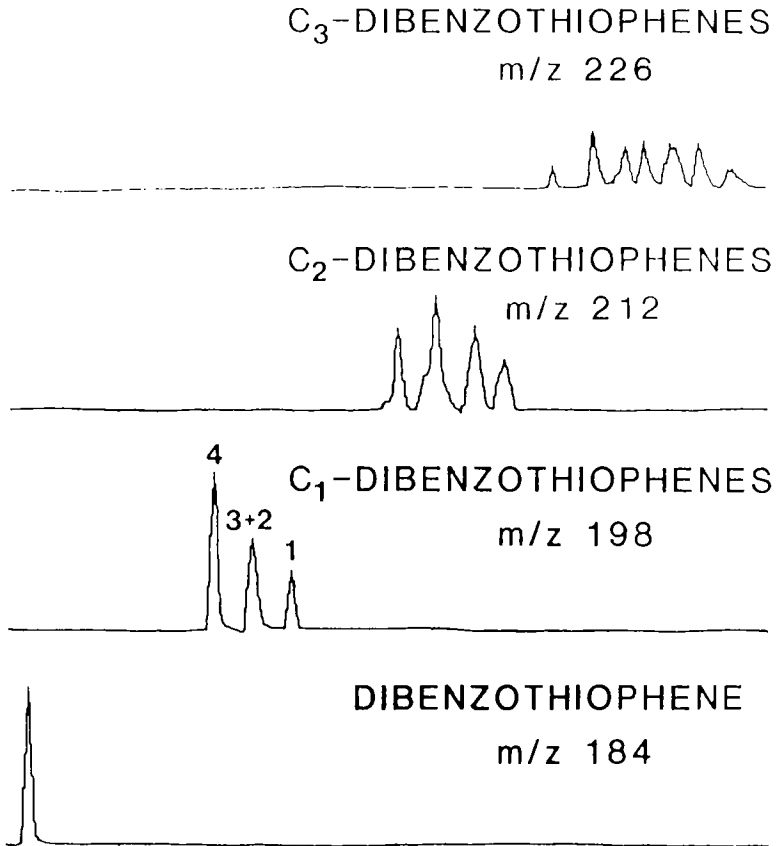


FIGURE 5 Alkyl dibenzothiophenes found in the Mediterranean aerosols.

To evaluate the different contributions, we will use the calculation proposed by Schneider *et al.*¹⁰; assuming *n*-alkanes to be from two origins: land plant waxes or soil sources (with a mean CPI=5) and anthropogenic sources (with a CPI=1) we have used the same CPI mean value for the terrestrial source for comparison with their data, although this mean value may be different for different sampling sets, corresponding to different strength of this source depending on the sampling site and/or the distance from this source. The calculated concentrations of terrestrial and anthropogenic *n*-alkanes for the two

TABLE IV

Calculations: U/R ratio, CPI index, terrestrial *N*-alkanes calculated from 21 to 36 carbon atom number, % of terrestrial *n*-alkanes for Impactor 1 and 2.

Stage	1	2	3	4	5	FF	Total
IMPACTOR 1							
Terrestrial							
<i>n</i> -alkanes	559	1692	1162	652	933	906	5904
%ter.	81%	73%	58%	32%	41%	31%	
U/R ^a	4.48	2.41	3.05	2.11	1.1	5.96	
CPI ^b	3.47	2.94	2.30	1.57	1.72	1.55	
IMPACTOR 2							
Terrestrial							
<i>n</i> -alkanes	623	1075	534	321	286	493	3332
% ter.	81%	77%	40%	27%	20%	23%	
U/R ^a	2.85	2.14	1.53	1.73	1.69	2.45	
CPI ^b	3.53	3.20	1.72	1.44	1.32	1.37	

^aU/R: Unresolved to resolved hydrocarbon components.

^bCPI: Carbon preference index from 21 to 36 carbon atom number.

impactors are plotted as a function of particle size on Figures 6 and 7. The terrestrial contribution seems to be different according to the particle size, being stronger on the large particles, with a maximum in both cases on stage 2 (Figure 6). Inversely, *n*-alkanes from anthropogenic origin are evenly distributed and essentially associated with small particles (Figure 7). This trend is usually attributed to emission of small particles containing *n*-alkanes during fossil fuel combustion processes. The same type of repartition of anthropic versus terrestrial distribution of *n*-alkanes has been found in the aerosols collected over the Atlantic Ocean⁸ and off the coast of Peru.^{36,37}

In Figure 8 the concentrations of the PAHs listed in Table III are represented for each stage of impactor 2. There can be observed that whereas there is an increase in concentration when passing from bigger to smaller aerosol particle size, the qualitative composition remains essentially unaltered. The distribution of the parent compounds for the different stages is quite similar for each impactor. The catacondensed structures are predominant, fluoranthene being in

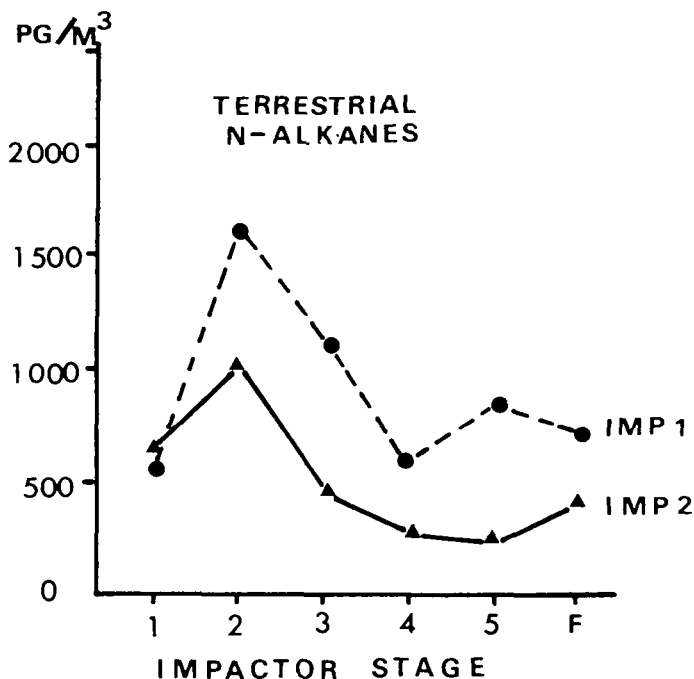


FIGURE 6 Terrestrial *n*-alkanes versus particle size for IMP1 and IMP2.

most cases the major compound which indicates high temperature origin for the mixture.^{28,29} Thus there is a contrast with the conclusions obtained from *n*-alkanes, where different hydrocarbon sources (terrestrial or petrogenic) were contributing differently to distinct aerosol size particles: *n*-alkanes from anthropogenic sources were evenly distributed according to the particle size as found for PAHs whereas the behavior of the terrestrial *n*-alkanes appears very different, probably due to different emission processes or/and different transport pathways.

Other sources have also been detected: among the alkylsubstituted polycyclic aromatics, the alkylphenanthrene series is predominant. This group of hydrocarbons usually constitute an important proportion of the PAH mixtures present in crude oils. However, its occurrence in the environment is associated with low temperature

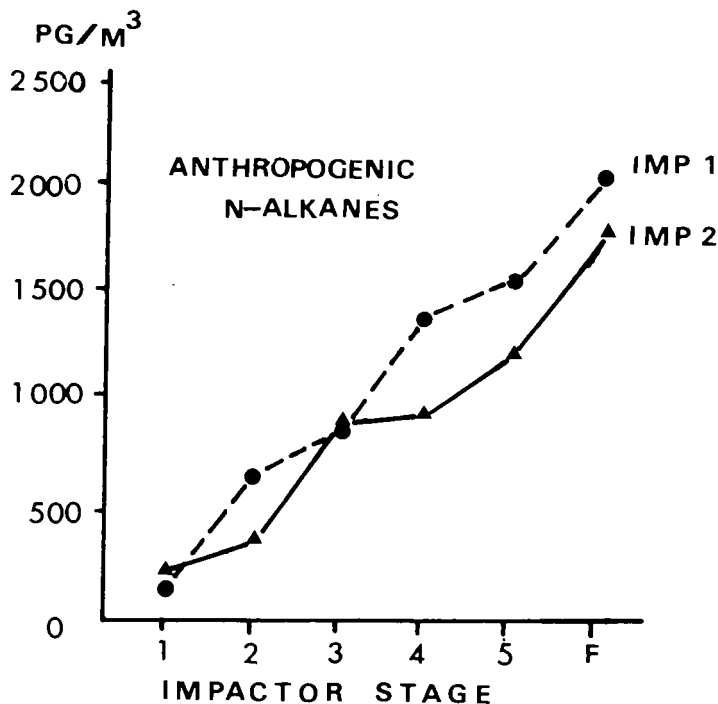


FIGURE 7 Anthropogenic *n*-alkanes versus particle size for IMP1 and IMP2.

pyrolytic processes^{24,38} such as combustion of diesel oil,³⁹ gasoline⁴⁰ or even coal in residential stoves.^{41,42}

In addition the dibenzothiophene series is found in several types of fuels derived from crude oils^{43,44} or coal^{45,46} and it can also be produced in low temperature pyrolytic processes.⁴² Thus the occurrence of these alkylated series in a minor proportion with respect to the major PAHs of the aerosols is consistent with a pyrolytic origin for this aromatic fraction.

Finally, in some cases, compounds present in minor amounts allow to differentiate among various inputs. For example, the benzo(b)naphto(1,2-d)thiophene, which has been found also here, is characteristic of coal combustion^{41,42} but is not present at detectable levels of concentration in exhausts from gasoline engines.⁴⁷

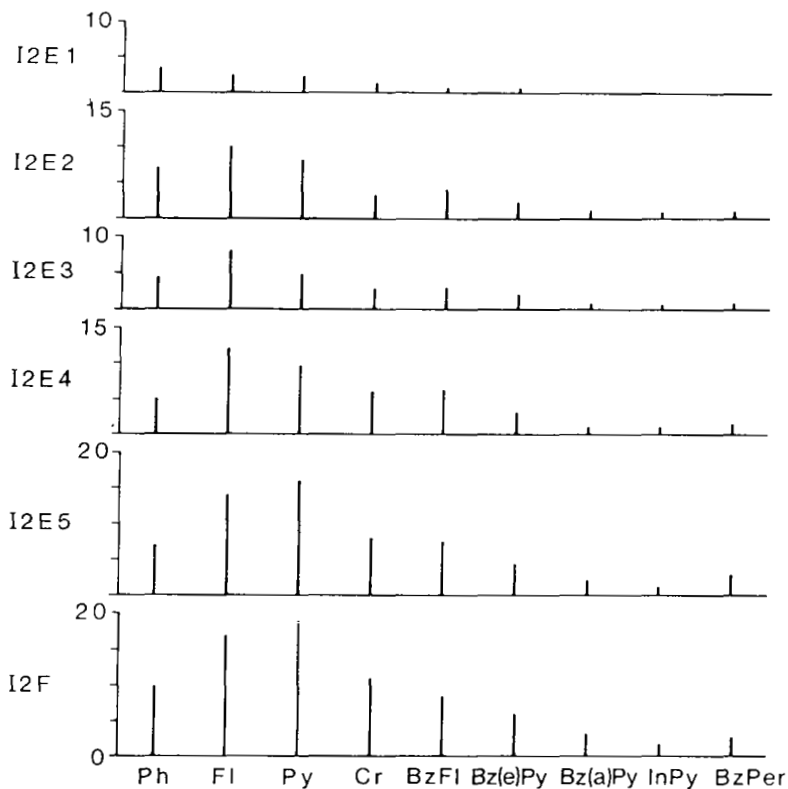


FIGURE 8 Histogram of the concentrations of the major PAH found on every stage of IMP2.

CONCLUSIONS

Sampling of aerosol with low concentrations of organic compounds implies some difficulties due to contaminants, and thus requires ultra clean sampling conditions and precautions during the analytical procedure. Another point is that long time sampling is necessary to collect sufficient amount of material for the analyses, which represents an integration on a relatively large time and space scale of different air masses. The improvement of the sampling techniques

should permit to reduce the collection time and then to access to variations on a time scale of a few hours.

Impactor is an interesting tool to sample and separate air particles into size fractions from very small up to several micrometers particles and thus to obtain information about the specificity of each marker class in terms of sources and transport pathways. On the point of view of environmental consequences, the fact that most of the anthropogenic compounds such as petroleum residues and pyrolytic derived aromatics are carried by small particles in the range of less than $1\ \mu\text{m}$ is essential, as these compounds can be transported over long distances from their sources.

Calculations of dry deposition fluxes of atmospheric particles need to know the concentrations of the compound of concern and the settling velocity which varies according to the particle size. Thus in order to evaluate fluxes more precisely, it is important to take into account the distribution of the organic compounds as a function of particle size. But very few data from remote areas are available especially for PAH for such calculations. The next step should be then to undertake efforts to have more data in order to get a better understanding about long range transport.

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