

Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments

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Abstract

As part of a lipid biogeochemical study, aliphatic and polyaromatic hydrocarbons were determined in surficial sediments from the Cretan Sea (South Aegean Sea) in the Eastern Mediterranean. Total concentrations of both aliphatic (AHC) and polyaromatic (PAH) hydrocarbons were low (562–5697 and 14.6–158.5 ng/g, respectively) with respect to other coastal sediments worldwide and compare with concentrations found in open sea areas. The composition of AHC was dominated by unresolved complex mixture (UCM) indicating the presence of petroleum-related hydrocarbon inputs as confirmed by the detection of specific α,β -hopanes. PAH consisted mainly of pyrolytic four- to five-ring compounds. UCM and PAH amounts revealed that Cretan Sea receives low supply of anthropogenic material compared to NW Mediterranean. The spatial distributions of AHC and PAH indicated that urban run-off and transport from the continental self are the major input pathway of anthropogenic and biogenic hydrocarbons from terrestrial sources in the near shore area, whereas atmospheric transport might be the significant source of hydrocarbons in the deep area. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Marine coastal areas play an important role in the global carbon cycle either as sources of organic matter to the open ocean or as carbon sinks due to accumulation in sediments (Meybeck, 1982; Prahl et al., 1994 and references therein). These areas are characterized by significant continental inputs which

lead to increase of the marine productivity (Berger, 1989). In addition, pollutants are often major components of the land-borne material introduced in coastal areas and have significant impact on coastal ecosystems and public health. Research on coastal environment has been thus recognized as critical for the understanding of the global carbon cycle and for achieving a sustainable management and ecosystem preservation.

Hydrocarbons are abundant components of the organic material in coastal zones and one major class of organic compounds. They enter into the marine

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environment by both aquatic and atmospheric pathways, the latter consisting in dry and wet deposition. The relative importance of the two main input pathways for a given environment depends on the geographical setting of the later (Prahl et al., 1984; Gagosian and Peltzer, 1986; Lipiatou and Albaiges, 1994). Among hydrocarbons, the polycyclic aromatic ones (PAHs) have received special attention since they have long been recognized as hazardous environmental chemicals (NAS, 1975), and are included in priority pollutant lists (e.g., United States Environmental Protection Agency (USEPA) list). Aside from anthropogenic sources, hydrocarbons have also several natural ones, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and diagenetic transformation of biogenic precursors. As a result of the variety of their sources, hydrocarbons occur as complex mixtures in environmental samples.

Their sources and their physical–chemical properties largely control transport and fate of hydrocarbons in the marine environment. Bioavailability/biodegradation rates of PAHs in the marine environment, can differ drastically (Mackay et al., 1992; Schwarzenbach et al., 1993). Association with fast sinking particles (such as fecal pellets and marine snow) is considered as the major mechanism of hydrocarbon transport from the surface to the deep-water column and accumulation in sediments (Prahl and Carpenter, 1979; Baker et al., 1991; Marty et al., 1994; Lipiatou et al., 1997).

While a large body of hydrocarbon data in the Western Mediterranean sediments has been published during the last decade (Albaiges et al., 1984; Grimalt and Albaiges, 1987, 1990; Bouloubassi and Saliot, 1991; Lipiatou and Saliot, 1991, 1992; Bouloubassi and Saliot, 1993b; Tolosa et al., 1996; Bouloubassi et al., 1997; Lipiatou et al., 1997), there is a striking paucity of data for the Eastern Mediterranean. The present study focuses on the determination of aliphatic and polyaromatic hydrocarbons in the sediment of Cretan Sea in Eastern Mediterranean. The assessment of the various biogenic and anthropogenic sources of hydrocarbons in the study area, and as well as of their relative importance, was achieved by using a molecular marker approach, characteristic compositional patterns and related indices (Simoneit and Mazurek, 1982; Simoneit, 1984).

2. Material and methods

2.1. Study area

The Cretan Sea (South Aegean Sea) is part of the Eastern Mediterranean Sea. It communicates with both the Levantine and the Ionian Sea through the eastern and western straits of the Cretan Arc, respectively (Fig. 1A). Its hydrology is influenced by two major gyres, which form a water jet with an on-slope (SE, ESE) flow direction (Theocharis, 1995). The productivity levels in the area are among the lowest encountered in the Eastern Mediterranean Sea (Ignatiades, 1998), which is one of the most oligotrophic marine areas in the world ocean (Azov, 1986).

The study area lies at the southern continental margin of the Cretan basin and extends from the northern coastal zone of the island of Crete to the deeper parts (> 1500 m) of the basin (Fig. 1C). A narrow and steep continental shelf and slope characterize it, with coarse sediments near the coastal zone and progressively finer sediments seaward (Chronis et al., 1996).

The city of Heraclion is the major urban center in the north coast of Crete (ca 200,000 inhabitants) with considerable portuary traffic, while there are no river estuaries and major industrial outflows in the entire area.

2.2. Sampling

Thirteen sampling sites were selected along transects covering an area from the near-shore zone towards the continental shelf (Fig. 1C; Table 1). Sediments were collected with a Multicorer in May and August 1994, with the R/V PHILIA. The undisturbed sediment surface (ca 1 cm) was recovered, wrapped in aluminum foil and stored at -30°C until analysis.

2.3. Lipid isolation and fractionation

The analytical procedure summarized below has been recently described in detail by Gogou et al. (1998) and is a modified and optimized version of the method published by Wünsche et al. (1987). Freeze-dried sediments were Soxhlet-extracted with a

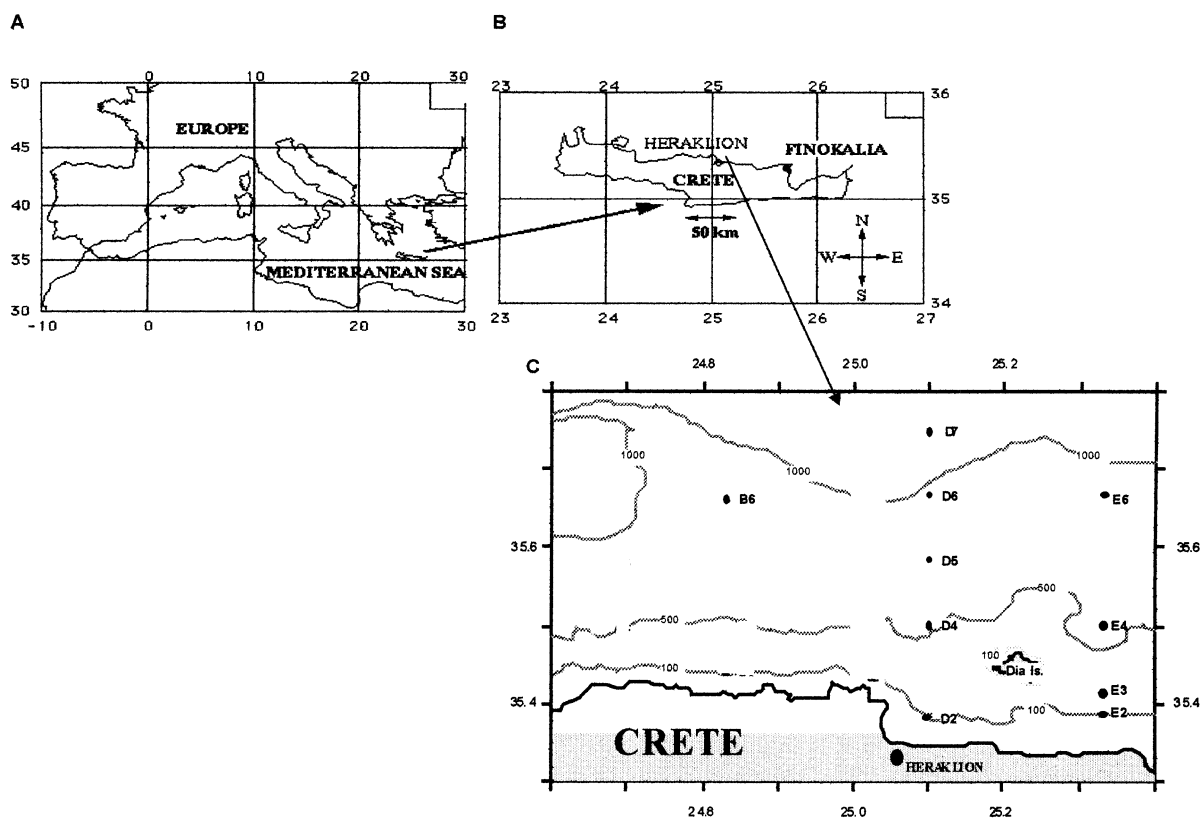


Fig. 1. Location of the sampling area (Cretan Sea) in Eastern Mediterranean.

methanol/methylene chloride mixture for 20 h. The total extract was then fractionated into five individual lipid classes by flash chromatography on silica

gel. Aliphatic and aromatic hydrocarbons were eluted in the first and second fraction with 15 ml *n*-hexane and 15 ml toluene/*n*-hexane, respectively.

Table 1
Cretan Sea sampling area characteristics and sediment samples OC content

Sampling site	Latitude	Longitude	Water column depth (m)	Sampling period	Organic carbon (%) (dry weight)
D2	35°23'	25°06'	100	May 1994	0.82
D4	35°30'	25°06'	540	May 1994	0.51
				August 1994	0.51
D5	35°35'	25°06'	700	May 1994	0.49
				August 1994	0.48
D6	35°40'	25°06'	940	May 1994	0.38
				August 1994	0.39
D7	35°45'	25°06'	1570	August 1994	0.46
E2	35°23'	25°20'	100	May 1994	0.30
E3	35°26'	25°20'	200	May 1994	0.34
E4	35°30'	25°20'	540	May 1994	0.48
E6	35°40'	25°20'	900	May 1994	0.43
B6	35°40'	24°83'	910	May 1994	0.50

2.4. GC and GC–MS analysis

Gas chromatography (GC) was performed using a Hewlett Packard HP-5890 gas chromatograph, equipped with a fused silica capillary column (50 m \times 0.32 mm i.d.; HP-5), on-column injector, and flame ionization detector (FID). Helium was used as carrier gas with a back-pressure of 1 atm. The oven temperature was programmed from 40 (1 min) to 150 at 10°C/min, from 150°C to 290°C at 5°C/min and isothermal at 290°C for 30 min. Data were retrieved with Hewlett Packard Chemsampling site.

Gas chromatography–mass spectrometry (GC–MS) analyses were carried out on a Hewlett Packard Mass Selective Detector. A Hewlett Packard HP-5890 gas chromatograph equipped with a Grob-type split–splitless injector, and a fused silica capillary column (30 \times 0.25 mm, HP-5 MS) was fed directly into the ion source. Helium was used as the carrier gas with a back-pressure of 0.8 atm. The oven temperature was programmed from 70°C (1 min) to 150°C at 10°C/min, from 150 to 290°C at 5°C/min and isothermal at 290°C for 30 min. Samples were injected in the split-less mode, and the hot needle technique. The electron impact ionization mode conditions were: ion energy 70 eV; ion source temperature 195°C; electron multiplier voltage 1700–1800 V. The instrument was operated either in Full Data Acquisition mode (mass range 35–590 m/z) or in Selected Ion Monitoring mode. Data were collected on a Hewlett Packard MS-Chemstation.

Compound identification was performed by GC–MS analysis and co-injection with authentic standard compounds. For quantitative determinations, the individual fractions were spiked with internal standards just before the GC–FID and GC–MS analysis (1-chlorohexadecane for *n*-alkanes (NA) and pristane and phytane, and hexamethylbenzene for PAH). Relative response factors, were calculated for 3–10 standard compounds, representing each compound class. All quantitation details have been described by Gogou et al. (1998).

2.5. Organic carbon analysis

Total carbon was determined on dried samples by combustion in an oxygen atmosphere and the pro-

duced carbon dioxide was quantitatively measured using a Leco C-S 125 analyzer. Organic carbon was determined by the same method after removal of inorganic carbon by treatment with 0.5 N HCl.

3. Results and discussion

3.1. Organic carbon content (OC)

OC contents ranged from 0.30% to 0.82% (Table 1). Higher values have been reported in NW Mediterranean sediments in coastal areas receiving fluvial discharges (up to 4.40%; Bouloubassi et al., 1997). The levels encountered in the study area are comparable to those found in open sea areas in the NW Mediterranean (0.38%–1.47%; Bouloubassi et al., 1997). Sampling site D2, located near the city and harbor of Heraclion exhibited the highest OC content (Fig. 1C; Table 1), suggesting inputs related to anthropogenic sources.

The concentration of organic carbon and of its numerous components in various environmental samples can vary due to fluctuations of bulk and specific organic supply but also because of variation of inorganic materials (dilution effect). Therefore, hereafter we consider in addition to the absolute concentrations (ng/g of dry sediment) the organic carbon normalized concentrations ($\mu\text{g/g}$ or mg/g of OC) for the various hydrocarbon classes (see below).

3.2. Aliphatic hydrocarbons (AHC)

NA and an unresolved complex mixture (UCM) dominated the aliphatic hydrocarbon fraction. Absolute (AHC) and organic carbon-normalized (AHC/OC) concentrations ranged from 562 to 5697 ng/g and from 144 to 1048 $\mu\text{g/g}$, respectively (Table 2). The AHC and AHC/OC concentrations observed in this study were definitely lower than those reported in sediments collected from coastal areas under urban or fluvial influence in the Western Mediterranean (in Ebro delta: 0.67–32.5 $\mu\text{g/g}$, Grimalt and Albaiges, 1990; in Rhone delta: 6.5–348.9 $\mu\text{g/g}$ and 1.7–20.2 mg/g of OC, Lipiatou and Salot, 1991; off the city of Barcelona: mean values

Table 2
Aliphatic hydrocarbons characteristic parameters determined in Cretan Sea sediment samples

Sampling sites	D2	D4	D5		D6		D7	E2	E3	E4	E6	B6	
	May	May	August	May	August	May	August	August	May	May	May	May	
<i>Parameters</i>													
AHC (ng/g)	5696.2	3110.8	5343.0	3017.4	2788.7	588.9	561.9	2829.5	2830.9	2854.9	4464.7	2588.6	2756.0
AHC/OC ($\mu\text{g/g}$)	694.7	610.0	1047.6	615.8	581.0	155.0	144.1	615.1	943.6	839.7	930.1	602.0	551.2
NA (ng/g)	896.2	578.2	790.0	496.7	416.7	80.1	219.3	274.7	335.0	359.0	847.1	243.5	296.3
NA/OC ($\mu\text{g/g}$)	109.3	113.4	154.9	101.4	86.8	21.1	56.2	59.7	111.7	105.6	176.5	56.6	59.3
$\Sigma(\text{C}_{21}\text{--C}_{36})$ (ng/g)	782.9	461.8	628.5	365.4	336.0	65.1	180.2	221.4	255.4	295.4	704.6	210.2	244.0
CPI($\text{C}_{21}\text{--C}_{36}$)	4.2	3.3	3.4	3.1	3.7	2.5	4.4	2.6	2.9	3.0	3.3	2.7	2.1
Ter (ng/g)	416.9	227.6	307.4	183.3	174.8	27.8	103.6	96.1	116.0	132.7	352.8	94.1	106.0
$\Sigma(\text{C}_{15}\text{--C}_{20})$ (ng/g)	42.2	42.0	68.3	44.6	47.9	9.1	15.2	37.6	20.3	23.7	41.2	19.2	29.7
Mar (ng/g)	24.0	19.2	28.6	27.5	23.0	5.4	8.5	15.0	11.1	13.3	20.0	11.0	12.0
$\text{C}_{29}/\text{C}_{31}$	0.6	0.7	0.7	0.7	0.7	1.3	0.8	1.1	0.7	0.8	0.7	1.1	1.0
UCM (ng/g)	4800.5	2532.5	4553.0	2520.7	2372.0	508.8	342.6	2554.8	2495.9	2831.6	3617.6	2345.1	2459.7
UCM/NA	5.4	4.4	5.8	5.1	5.7	6.4	1.6	9.3	7.5	7.9	4.3	9.6	8.3
UCM/OC ($\mu\text{g/g}$)	585.4	496.6	892.7	514.4	494.2	133.9	87.8	555.4	832.0	832.8	753.7	545.4	491.9

AHC: aliphatic hydrocarbon total concentration; NA: *n*-alkanes concentration; $\Sigma(\text{C}_{21}\text{--C}_{36})$: sum of concentrations of NA from heneicosane to hexatriacontane; $\Sigma(\text{C}_{15}\text{--C}_{20})$: sum of concentrations of NA from pentadecane to eicosane; UCM: unresolved complex mixture; OC: organic carbon content; CPI: carbon preference index; Ter: sum of concentration of terrestrial NA heptacosane, nonaneicosane and hentriacontane; Mar: sum of concentration of marine NA pentadecane, heptadecane and nonadecane; $\text{C}_{29}/\text{C}_{31}$: nonaneicosane to hentriacontane concentration ratio.

of 495.7 $\mu\text{g/g}$ and 275.4 mg/g of OC, Tolosa et al., 1996) and in sediments from other coastal areas worldwide, such as the North Atlantic coastal zone (5–3000 mg/g, Farrington and Tripp, 1977), the Black Sea (10–153 $\mu\text{g/g}$ and 3–41 mg/g of OC, Wakeham, 1996) and the coastal area off the city of Alexandria in Southeastern Mediterranean (20.3–1356.3 $\mu\text{g/g}$ and 1.0–34.5 mg/g of OC, Aboul-Kassim and Simoneit, 1995). However, the AHC concentrations observed in our study were within the same range of magnitude with those observed for sediments collected from open marine areas, such as in Western North Atlantic (1.3–7.5 $\mu\text{g/g}$, Farrington and Tripp, 1977), in Southern New England (mean values of 0.7 $\mu\text{g/g}$ and 0.58 mg/g of OC, Venkatesan et al., 1987) and in Western Mediterranean (10.1 to 12.4 mg/g, Tolosa et al., 1996).

3.2.1. *n*-Alkanes (NA)

NA ranged in carbon chain length from C_{15} to C_{40} and were the most prominent resolved components (Fig. 2A and B) with concentrations varying from 80 to 896 ng/g (Table 2). Their compositional profile showed a high predominance of long-chain homologues ($\Sigma(\text{C}_{21}\text{--C}_{36})$) in Table 2 and Figs. 2 and

3A and B) with an elevated odd to even carbon number preference, reflected in high CPI values (CPI($\text{C}_{21}\text{--C}_{36}$), Table 2). These long-chain homologues are known to derive from higher plant waxes (Eglinton and Hamilton, 1967; Tulloch, 1976) and their occurrence reveals the importance of terrestrial inputs in the study area. The sum of the concentration of the three most abundant terrestrial NA (C_{27} , C_{29} , and C_{31}) ranged from 28 to 417 ng/g (Ter, Table 2), which accounts for 35%–47% of the total NA concentration. Much higher concentrations of terrestrial NA were found in coastal areas in the NW Mediterranean receiving riverine discharges, e.g., up to 2.0 $\mu\text{g/g}$ in the Ebro delta and up to 12.9 $\mu\text{g/g}$ in the Rhone delta (Bouloubassi et al., 1997).

Short-chain NA ($\text{C}_{15}\text{--C}_{20}$) were found in low concentration ($\Sigma(\text{C}_{15}\text{--C}_{20})$) in Table 2 and Figs. 2 and 3A and B). The homologues of mainly marine origin (defined as the sum of C_{15} , C_{17} , and C_{19}) were minor constituents (up to 7%) of the total NA (Mar, Table 2). Their low abundance reflects both, the low productivity in the area and the labile character of these compounds. In accordance to our observation, previous studies showed that terrestrial NA generally dominate over the marine-derived in envi-

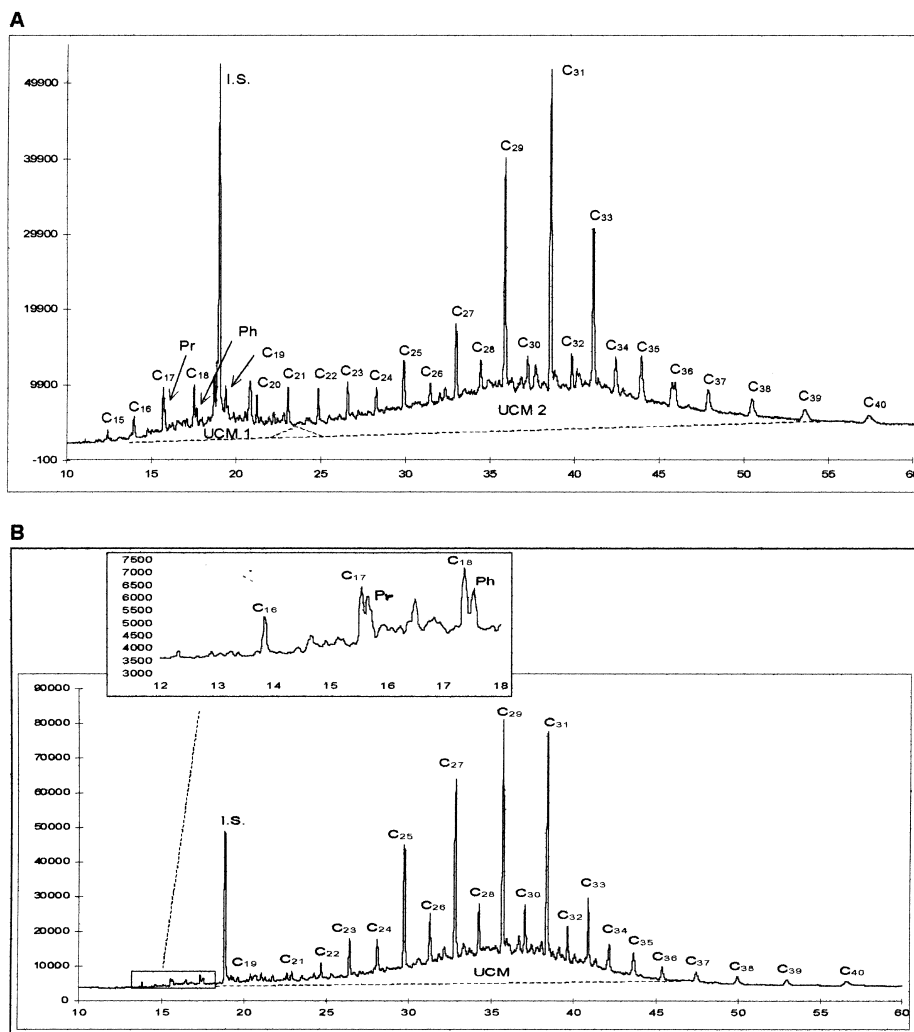


Fig. 2. Characteristic gas chromatograms of Cretan Sea sediment aliphatic fraction. Pr: pristane; Ph: phytane.

ronments close to land, particularly when riverine discharges occur (Prah and Carpenter, 1984; Wakeham, 1996; Bouloubassi et al., 1997). They are also often prominent in open sea areas (Santos et al., 1994; Ohkouchi et al., 1997) where they are mostly introduced by atmospheric transport and well preserved due to their resistant character (Gagosian and Peltzer, 1986; Poynter et al., 1989).

NA distributions similar to the corresponding distributions found in the sediment — with high predominance of terrestrial components — were also found in the aerosols (Fig. 3C and D; Gogou et al.,

1996) of this marine area at the sampling site Finokalia (Fig. 1B).

Terrestrial NA concentrations (both per weight and OC-normalized) showed a negative gradient seawards along the D transect, suggesting that continental run-off is the major input mechanism of terrestrial organic matter to the study area (Fig. 4A and B). Similar to the terrestrial NA spatial distribution, marine NA concentration display a decrease — in accordance to the sharp decrease of primary production rates (Psarra et al., 1996) — from the coastal to the deeper sampling sites (Fig. 4B). These trends are

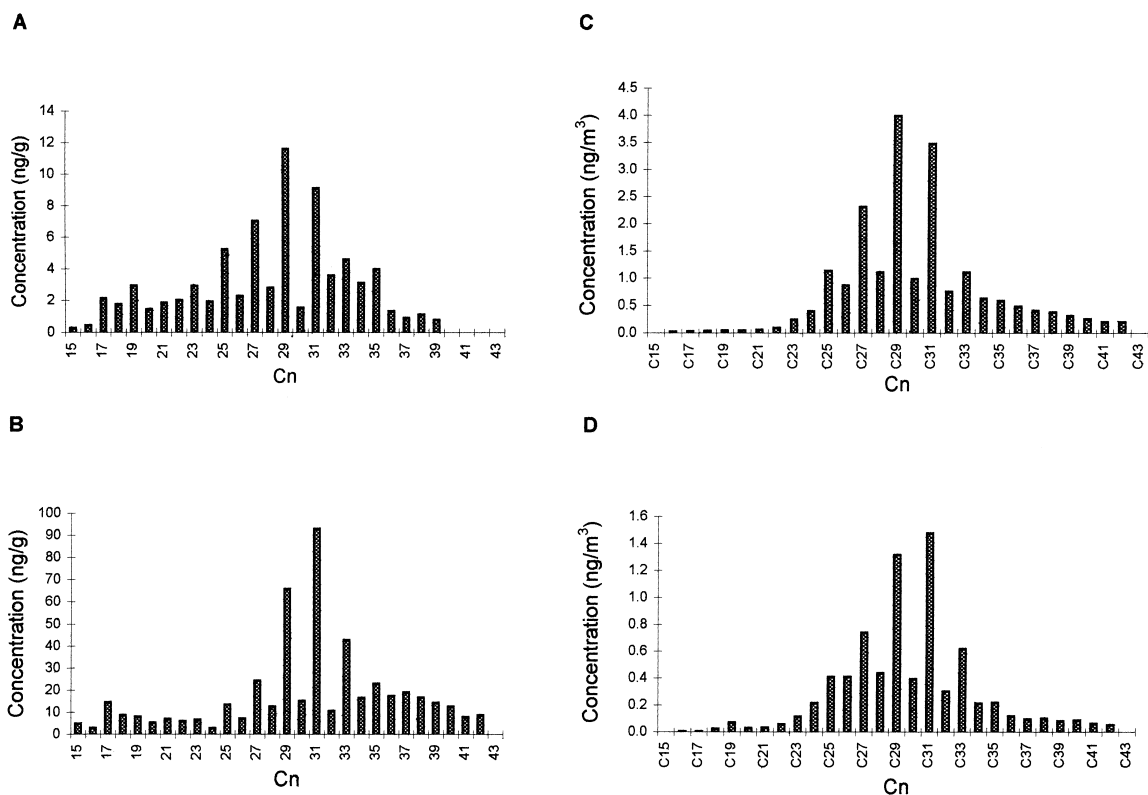


Fig. 3. NA homologues distributions determined in Cretan Sea sediment samples at D6 in May (A) and at D2 in May (B). NA homologues distributions determined in Cretan Sea aerosol samples with N/NW winds and local S/SW winds. NA homologues are assigned with their carbon atoms number. For sample information, see Table 1. For aerosol, see Gogou et al., 1996.

much more pronounced in the D compared to the E transect sampling sites (Fig. 4A), which is located farther from the city of Heraklion (Fig. 1C). A relative increase of terrestrial NA concentration was observed at the sampling sites E4 and D7, compared to the shallower ones of the same transects (E3 and D6, respectively). Sampling sites E4 and D7 are located at the end of continental slopes (Fig. 1C). Chronis et al. (1996) have shown, through a sedimentological study, the occurrence of erosional and resuspension processes at these slopes. These observations could justify the noticed trend of NA, UCM and PAHs (see below and Tables 2 and 4) concentration increase, which also coincides with higher OC accumulation (Table 1), at E4 and D7.

NA profiles exhibited significant differences at off-shore (water column depth > 700 m; Fig. 3A) and on-shore (water column depth < 700 m; Fig. 3B)

sampling sites, as it is revealed by their odd-to-even predominance (OEP; Scalan and Smith, 1970) curves (Fig. 5A and B). Additional supporting evidence for the occurrence of two different pools of NA is provided by the C_{29}/C_{31} ratio. The ratio takes values < 1 at the shallow sampling sites whereas is > 1 in the off-shore area (Table 2). According to the aerosol study (Gogou et al., 1996) performed in the same marine area (Finokalia, Fig. 1B), the terrestrial material transported by N/NW winds (dominant up to 85% in yearly base in the study area) is characterized by C_{29}/C_{31} values > 1, as indicated in Fig. 3C. Conversely, local sources (S/SW winds from the island of Crete) exhibited C_{29}/C_{31} values < 1 (Fig. 3D; Gogou et al., 1996). These trends suggest that continental run-off is the dominant source of terrestrial material in the near-shore zone, whereas atmospheric transport is probably an important source of

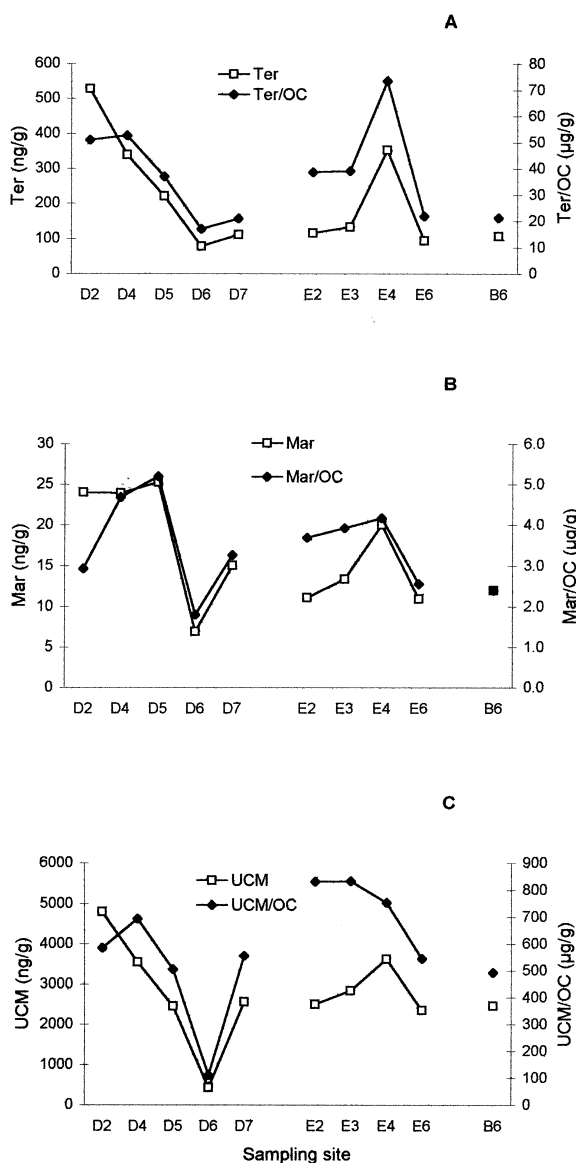


Fig. 4. Spatial distribution of terrestrial (A), marine (B) and unresolved complex mixture (C) determined in Cretan Sea sediment. Ter is the sum of concentration of terrestrial NA, heptacosane, nonaneicosane and hentriacontane and Ter/OC the same normalised with OC. Mar is the sum of concentration of marine NA, pentadecane, heptadecane and nonadecane and Mar/OC the same normalised with OC. UCM is the concentration of unresolved complex mixture and UCM/OC the same normalised with OC.

terrestrial material in the deep study area. The latter may enter the area by direct (in situ) deposition or

they may have been deposited over the South Aegean and transported in the study area by the dominant southward marine currents (Theocharis, 1995). In accordance to this hypothesis, atmospheric transport has been reported as the main pathway for the transfer of terrestrial material and pollutants from land-based sources in open marine areas (Gagosian and Peltzer, 1986; Baker and Eisenreich, 1990; Lipitatu et al., 1997).

3.2.2. UCM, isoprenoid and triterpenoid hydrocarbons

UCM was the major component of the aliphatic hydrocarbon fraction (higher than 80%, Table 2) appearing in the GC trace as a bimodal hump in the range $n\text{-C}_{16}\text{-}n\text{-C}_{40}$ (UCM₁ and UCM₂, Fig. 2A). It consists of a complex mixture of branched alicyclic hydrocarbons (Gough and Rowland, 1990) and has a well-known linkage to biodegraded petroleum residues (Farrington and Quinn, 1973; Brassell and Eglinton, 1980). Venkatesan and Kaplan (1982) and

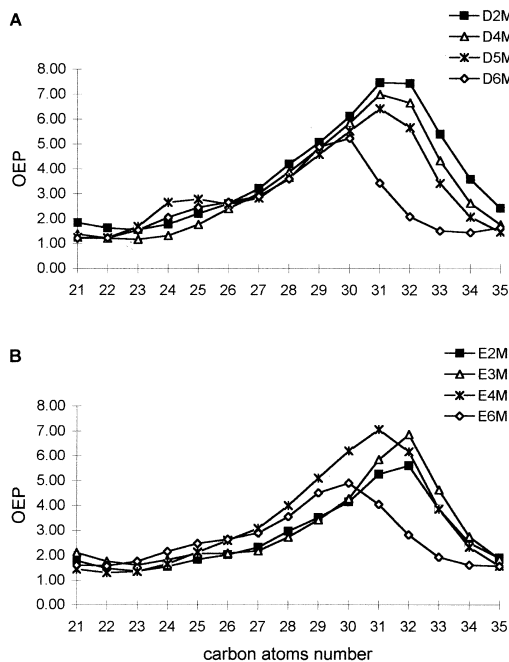


Fig. 5. Odd-to-even predominance curves (OEP) of NA determined in Cretan Sea sediment. $OEP = [(C_n + 6C_{n+2} + C_{n+4}) / (4C_{n+1} + 4C_{n+4})]^{(-1)^{n+1}}$, where n is the number of carbon atoms for each NA homologue (Scalan and Smith, 1970). The samples (Table 1) are assigned accordingly to their site and month of collection (D2, ... and E2, ...; M: May).

Laureillard et al. (1997) suggested that UCM in the lower MW range (UCM₁, Fig. 2A) can result from bacterial reworking of algal material. Nevertheless clear evidence for the latter aspect is lacking in our case.

The high abundance of UCM in all sampling sites (509–4800 ng/g; Table 2) is a positive indication of chronic oil-pollution. Additional evidence is provided by the ratio of UCM to NA (UCM/NA) which at most sampling sites takes values > 4 up to 9.6 (Table 2). This range characterizes hydrocarbon mixtures with significant contribution from degraded petroleum products (Simoneit and Mazurek, 1982; Simoneit, 1984). This is firmly confirmed by the occurrence of specific biomarkers (e.g., hopanes, see below). UCM levels in the Cretan Sea sediments were, however, much lower than those found in coastal areas in the NW Mediterranean near urban centers and major rivers (7–488 μg/g, Tolosa et al., 1996). They were even lower than concentration levels encountered in the open NW Mediterranean (7–13 μg/g, Tolosa et al., 1996).

The spatial distribution of the UCM values, indicates that more pronounced petroleum-related inputs occurred at the near-shore sampling sites, particularly those situated in the vicinity of the city and harbor of Heraclion (Fig. 1C and Fig. 4C). Urban discharges and portuary activities appear to be then the major sources of such inputs in the study area. It is noteworthy, however, that the UCM/NA ratio values are relatively high at sampling sites along the E transect, while lower values of this ratio were calculated for the sampling sites under the direct influence of anthropogenic inputs related to the urban center (D transect). Moreover, OC-normalized concentrations of UCM (UCM/OC, Fig. 4C) at near-shore E sampling sites are even higher than those observed at D sites of similar depth, although OC contents are lower (Table 1). This most likely stems from the preferential preservation of the highly resistant UCM, which results in enhanced UCM enrichment in OC-poorer sediments.

The isoprenoid hydrocarbons pristane and phytane were present in all analyzed samples (Table 2;

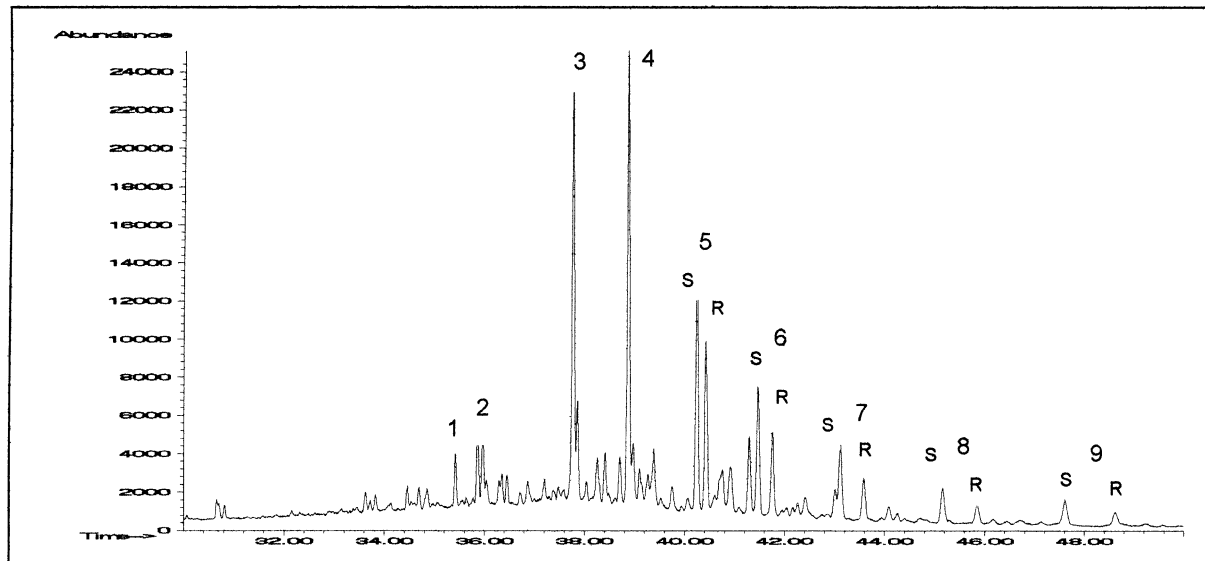


Fig. 6. Ion chromatogram (m/z 191) of hopanes determined in Cretan Sea sediment samples. Hopanes: (1) $18\alpha(H)$ -22,29,30-trisnorhopane (Ts, $C_{27}H_{46}$); (2) $17\alpha(H)$ -22,29,30-trisnorhopane (Tm, $C_{27}H_{46}$); (3) $17\alpha(H)$, $21\beta(H)$ -29-norhopane ($C_{29}H_{50}$); (4) $17\alpha(H)$, $21\beta(H)$ -hopane ($C_{30}H_{52}$); (5) $17\alpha(H)$, $21\beta(H)$ -homohopane ($C_{31}H_{54}$, 22S and 22R); (6) $17\alpha(H)$, $21\beta(H)$ -bishomohopane ($C_{32}H_{56}$, 22S and 22R); (7) $17\alpha(H)$, $21\beta(H)$ -trishomohopane ($C_{33}H_{58}$, 22S and 22R); (8) $17\alpha(H)$, $21\beta(H)$ -tetrakishomohopane ($C_{34}H_{60}$, 22S and 22R); (9) $17\alpha(H)$, $21\beta(H)$ -pentakishomohopane ($C_{35}H_{62}$, 22S and 22R).

Fig. 2B). Their presence also corroborates the impact of petroleum residues in the study area as suggested by previous studies (e.g., Volkman and Maxwell, 1986).

A series of C_{27} – C_{35} pentacyclic triterpanes (hopanes) were identified in all sediment samples on the basis primarily of their mass spectra and GC retention time. Fig. 6 shows their characteristic m/z 191 mass fragmentogram. Homologues with number of carbon atoms $\geq C_{29}$ exhibited the thermodynamically more stable $17\alpha(H)$, $21\beta(H)$ configuration, while the extended α -hopane series (C_{31} – C_{35}) occurred as $22S$ and $22R$ epimers (Fig. 6). These patterns are characteristic of oil-derived hydrocarbons (Philp, 1985). The hopane pattern in the study area further confirms the presence of pollutant inputs from fossil fuel products, as already suggested by the presence of UCM and pristane and phytane.

3.3. Polycyclic aromatic hydrocarbons (PAHs)

Twenty-five individual PAHs were determined comprising three- to six-ring unsubstituted com-

pounds along with several alkyl-substituted homologues. Fig. 7 presents a characteristic gas chromatogram of PAHs determined in a sediment sample of the study area. In Table 3, the concentrations of individual PAH compounds determined in all the samples collected for this study are given. Fig. 8A and B illustrate representative distribution profiles of the PAHs found in the study area.

Total PAH concentrations (TPAH) ranged from 14.7 to 161.5 ng/g (Table 4). With few exceptions the PAHs found in Cretan Sea sediments originated mainly from anthropogenic sources. As in some cases, high concentration levels of naturally derived PAH were observed (mainly 7-isopropyl-1-methylphenanthrene (retene), see Table 3) the term TPAH* (TPAH* is the concentration of TPAH minus the concentration of retene) is used here to account for anthropogenic PAHs. TPAH* varied in the range 14.6–158.5 ng/g d.w. or 3.9–26.6 $\mu\text{g/g}$ of OC when normalized to the OC (Table 4). These values are considerably lower than those reported in NW Mediterranean areas located near the outflow of the

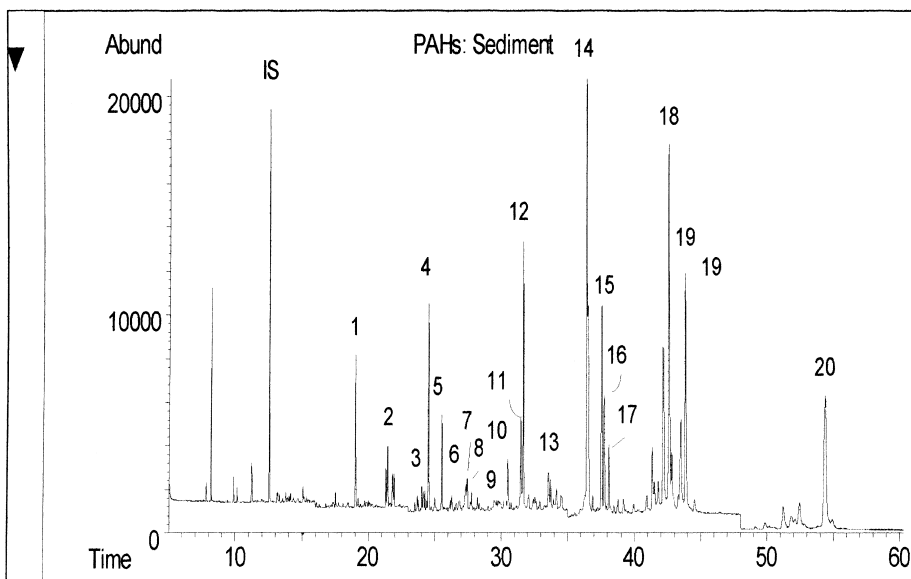


Fig. 7. Characteristic ion chromatogram of PAHs determined in Cretan Sea sediment. (1) Phenanthrene, (2) methyl-phenanthrenes, (3) dimethyl-phenanthrenes, (4) fluoranthene, (5) pyrene, (6) trimethyl-phenanthrenes, (7) methyl-fluoranthenes and -pyrenes, (8) retene, (10) 4(*H*)-cyclo-penta-*cd*-pyrene, (11) benzo[*a*]anthracene, (12) chrysene/triphenylene, (13) methyl-chrysenes, (14) benzo[*b,j,k*]fluoranthene, (15) benzo[*e*]pyrene, (16) benzo[*a*]pyrene, (17) perylene, (18) indeno[1,2,3-*cd*]pyrene, Dibenzo[*a,h*]anthracene (DBA) enzo[*ghi*]perylene, (19) benzo[*ghi*]perylene, (20) coronene. For the molecular ions used for SIM see Table 3.

Table 3
Concentration of polycyclic aromatic hydrocarbons determined in Cretan Sea surficial sediment

Sampling sites PAH compound	MW	D2	D4		D5		D6		D7	E2	E3	E4	E6	B6
		May	May	August	May	August	May	August	August	May	May	May	May	May
Phenanthrene (Phe)	178	4.18	3.39	3.77	1.49	2.15	0.13	0.97	1.23	1.15	0.91	1.78	1.15	0.74
Anthracene (Anth)	178	0.32	0.18	0.18	0.00	0.00	0.01	0.05	0.05	0.08	0.06	0.12	0.05	0.04
Methyl-phenanthrenes (MP)	192	5.07	2.50	3.86	2.43	3.14	0.36	1.07	1.82	1.45	1.32	1.72	1.16	1.31
Dimethyl-phenanthrenes (DMP)	206	6.26	2.95	3.86	3.00	3.19	0.56	1.07	2.04	1.93	2.53	2.04	1.24	1.37
Pimanthrene (Pim)	206	1.65	0.54	1.08	1.21	1.60	0.10	0.28	0.57	0.45	0.46	0.37	0.56	0.46
Trimethyl-phenanthrenes (TMP)	220	3.04	1.01	1.26	0.75	1.97	0.16	0.48	0.76	0.86	0.80	0.68	0.40	0.49
Fluoranthene (Fl)	202	11.10	6.02	5.77	4.69	5.84	1.13	2.04	3.61	3.65	3.14	3.48	1.90	2.36
Acephenanthrylene	202	0.71	0.45	0.62	0.40	0.65	0.08	0.19	0.33	0.25	0.22	0.36	0.19	0.28
Pyrene (Py)	202	6.35	5.86	4.19	3.65	2.85	0.57	1.66	2.04	3.05	2.55	2.77	0.84	0.50
Me-fluoranthenes/-pyrenes and benzofluorenes (MF-P)	216	10.41	3.43	2.86	0.86	6.80	0.77	1.49	2.56	3.25	2.62	2.28	1.10	0.74
Retene (Ret)	234	2.93	1.32	21.17	20.62	51.92	0.16	3.09	7.67	2.51	0.26	0.84	0.34	5.32
4(<i>H</i>)-Cyclo-penta- [<i>cd</i>]-pyrene (CyPy)	226	2.15	1.01	1.36	0.88	0.92	0.20	0.34	0.49	0.75	0.60	0.64	0.30	0.41
Benzo[<i>a</i>]anthracene (BA)	228	4.82	1.63	1.55	1.02	1.72	0.36	0.52	0.86	1.27	1.02	0.90	0.51	0.62
Chrysene/Triphenylene (CT)	228	7.30	4.41	4.11	2.64	4.27	0.97	1.59	2.63	2.26	2.24	3.01	1.60	1.74
Methyl-chrysenes (MC)	242	6.19	2.31	2.47	1.00	2.40	0.51	0.81	1.23	1.41	1.25	1.68	0.76	0.88
Benzo[<i>b,j,k</i>]fluoranthene (BFluo)	252	22.12	14.55	13.92	8.10	13.46	2.93	4.50	8.32	6.47	6.78	10.21	5.19	5.85
Benzo[<i>a</i>]fluoranthene	252	1.27	0.44	0.55	0.23	0.38	0.08	0.14	0.30	0.30	0.22	0.39	0.18	0.17
Benzo[<i>e</i>]pyrene (BeP)	252	8.90	4.41	4.12	2.49	4.01	0.90	1.33	2.61	2.46	2.29	2.96	1.62	1.87
Benzo[<i>a</i>]pyrene (BaP)	252	6.65	2.36	2.21	1.02	2.11	0.54	0.70	1.35	1.94	1.08	1.69	0.96	1.07
Perylene (Per)	252	18.35	2.24	2.30	0.43	1.35	0.29	0.50	0.77	3.12	1.50	1.44	0.55	0.49
Indeno[7,1,2,3- <i>cdef</i>]chrysene (IC)	276	3.97	3.32	3.19	2.02	2.88	0.68	1.02	2.23	1.50	1.42	2.46	1.71	1.87
Indeno[1,2,3- <i>cd</i>]pyrene (IP)	276	9.85	7.22	7.11	4.36	6.06	1.39	2.03	4.49	3.76	3.48	5.42	3.38	3.91
Dibenzo[<i>a,h</i>]anthracene (DBA)	278	2.46	1.84	2.06	1.28	1.65	0.37	0.64	1.37	0.85	0.90	1.10	0.98	1.12
Benzo[<i>ghi</i>]perylene (BgP)	276	8.91	4.25	4.10	2.56	3.34	0.79	1.11	2.51	3.12	2.39	3.50	2.22	2.39
Coronene (Cor)	300	5.92	3.90	4.36	2.39	3.08	0.72	0.93	2.67	2.41	1.54	3.12	2.64	2.90

Rhone and Ebro rivers, where TPAH* concentrations reached values up to 6500 ng/g (Lipiatou and Saliot, 1991; Bouloubassi and Saliot, 1993b; Tolosa et al., 1996). Also in the vicinity of urban centers, e.g., Barcelona, Valencia the TPAH* concentrations were measured in levels up to 2313 ng/g (Grimalt et al., 1984). TPAH* concentration levels in the study area fall in the range of those reported in open sea areas in the Mediterranean, such Adriatic Sea (12–174 ng/g, Marcomini et al., 1986) and NW Mediterranean (100–500 ng/g, Tolosa et al., 1996). The concentration of PAHs measured in this study falls in the same range of corresponding concentration (ca. a few hundred nanograms per gram) measured at open sea worldwide (Boehm and Farrington, 1984; Prahl and Carpenter, 1984; Barrick and Prahl, 1987; Venkatesan et al., 1987; Wakeham, 1996).

3.3.1. Pyrolytic PAHs

Five-ring PAHs (MW 252, e.g., benzo[*b,j,k*]fluoranthenes, benzo[*e*]pyrene and benzo[*a*]pyrene) were the most abundant components, followed by four-ring PAHs (MW 202, e.g., fluoranthene, pyrene) or six-ring PAHs (MW 276, e.g., indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) (Table 3). The compositional pattern of PAH (dominance of parent PAH with MW > 202; Table 3), is characteristic of PAH mixtures formed during high temperature combustion (pyrolysis) of fossil fuels (Laflamme and Hites, 1978; Sporstol et al., 1983). Similar patterns have been reported for a variety of environmental samples worldwide, e.g., atmospheric particles (Simoneit, 1984; Sicre et al., 1987; Gogou et al., 1996), rainwater and lacustrine sediments (Giger and Schaffner, 1978), seawater (Bouloubassi and Saliot, 1993a),

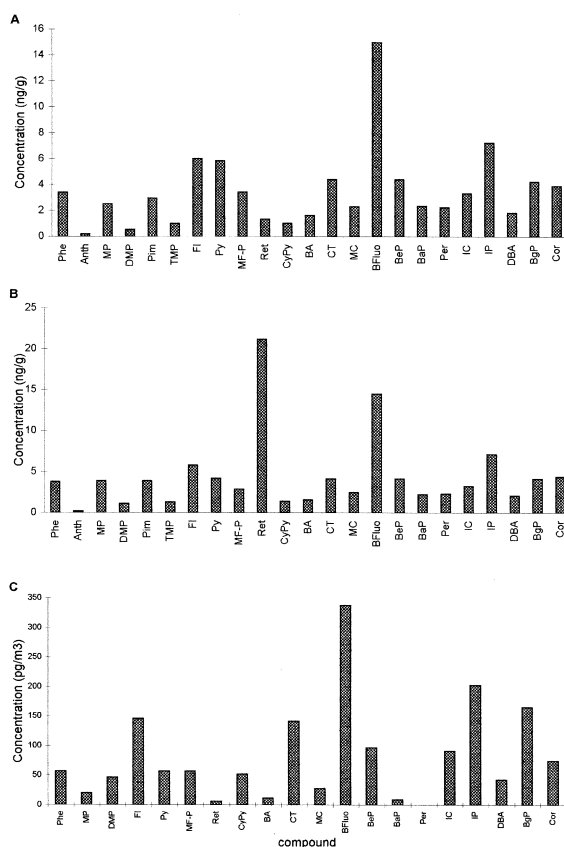


Fig. 8. Polycyclic aromatic hydrocarbon distribution determined in Cretan Sea sediment samples at D4 in May (A) and at D4 in August (B). Polycyclic aromatic hydrocarbon distribution determined in Cretan Sea aerosol. For compound assignments, see Table 3. For sample information, see Table 1. For aerosol, see Gogou et al., 1996.

sinking material (Lipiatou et al., 1993), and marine sediments (Prahl and Carpenter, 1979; Boehm and Farrington, 1984; Baker and Eisenreich, 1990; Grimalt and Albaiges, 1990; Lipiatou and Saliot, 1991, 1992; Bouloubassi and Saliot, 1993b; Yunker et al., 1995).

The sum of parent PAHs with MW 202, 228, 252, 276, 278, 300 is used hereafter to represent pyrolytic PAHs (COMB; Table 4). Phenanthrene and anthracene (MW 178) are not comprised in COMB because they may also derive from fossil (petrogenic) sources. Perylene (MW 252) is also excluded since it may have natural sources (Aizenshtat, 1973). Pyrolytic PAH concentration varied from 11.4 to 99.6 ng/g and accounted for 63–79% of the TPAH*

(COMB/TPAH*, Table 4). Pyrolysis and combustion processes appear as the major sources of PAH encountered in the study area.

The relative abundance of pyrolytic PAH (COMB/TPAH*, Table 4) was slightly elevated at the deep sampling sites compared to the shallow ones (Table 4). Such a trend has been previously observed in several environments. This trend most likely results from: (I) the preferential preservation of PAH released from combustion processes which are known to resist to degradation during atmospheric transport and sedimentation (Behymer and Hites, 1988; Baker et al., 1991; Wakeham, 1996), and (II) the preferential association of pyrolytic PAH with fine particles, which can be transported along long distances from the coast (Boehm and Farrington, 1984; Readman et al., 1984). In accordance to our interpretation for the sources of terrestrial NA, this trend suggests that atmospheric deposition could also be a potential source of pyrolytic PAHs in the study area. This statement is further supported by the PAH distribution profile of aerosols samples, collected in this marine area (Finokalia, Fig. 1B), which is similar to the one observed for the majority of the sediments (Fig. 8C).

Pyrolytic PAH concentration levels showed a steep seaward decrease along the D transect (COMB, Table 4; Fig. 9A). Such a trend was not observed along the E transect (Table 4; Fig. 9A), where pyrolytic PAHs occurred at lower concentrations. These observations suggest that major anthropogenic PAH inputs in the study area are linked to the urban and portuary zone of Heraclion. Differences in COMB levels are much attenuated when COMB concentrations are normalized to OC (Fig. 9A).

Diagnostic ratios between specific PAH have been used to assess the different sources and origins of PAH in aerosols (Simoneit and Mazurek, 1982; Simoneit, 1984; Gogou et al., 1996). Nevertheless, their use in sediments can be significantly biased due to modifications occurring from emission of the PAH to their deposition on sediments. Despite this, characteristic ratios between PAH of the same MW and with different reactivity can still enable recognition of major transport pathways. We used here the concentration ratios of benzo[*a*]anthracene and chrysene/triphenylene (BA/BA + CT) and benzo[*e*]pyrene and benzo[*a*]pyrene (BeP/BeP + BaP)

Table 4

Polycyclic aromatic hydrocarbons characteristic parameters determined in Cretan Sea sediment samples

Sampling sites	D2		D4		D5		D6		D7	E2	E3	E4	E6	B6
	May	May	August	May	August	May	August	August	May	May	May	May	May	May
<i>Parameters</i>														
TPAH (ng/g)	161.5	81.2	101.9	68.1	127.6	14.7	29.7	54.5	50.1	40.4	54.6	31.1	38.9	
TPAH* (ng/g)	158.5	79.8	80.7	47.5	75.6	14.6	26.6	46.8	47.6	40.2	53.8	30.8	33.6	
TPAH/OC ($\mu\text{g/g}$)	19.7	15.9	20.0	13.9	26.6	3.9	7.6	11.8	16.7	11.9	11.4	7.2	7.8	
COMB (ng/g)	99.6	60.2	57.3	36.4	51.7	11.4	18.2	35.0	33.1	29.1	41.0	23.7	26.4	
COMB/TPAH* (%)	62.8	75.4	70.9	76.8	68.3	78.5	68.4	74.7	69.4	72.4	76.2	77.1	78.6	
BA/BA + CT	0.4	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.4	0.3	0.2	0.2	0.3	
BeP/BeP + BaP	0.6	0.7	0.7	0.7	0.7	0.6	0.7	0.7	0.6	0.7	0.6	0.6	0.6	
TPhe (ng/g)	15.5	8.8	11.5	6.9	8.5	1.1	3.1	5.1	4.5	4.8	5.5	3.5	3.4	
Retene/TPAH (%)	1.8	1.6	2.8	30.3	40.7	1.1	10.4	14.1	5.0	0.6	1.5	1.1	13.7	
Perylene/TPAH (%)	11.4	2.8	2.3	0.6	1.1	1.9	1.7	1.4	6.2	3.7	2.6	1.8	1.3	
B[e]P/Per	0.5	2.0	1.8	5.8	3.0	3.1	2.7	3.4	0.8	1.5	2.1	2.9	3.8	

TPAH: Total concentration of polycyclic aromatic hydrocarbons (see Table 3); TPAH*: TPAH except retene; COMB: sum of concentrations of pyrolytic polycyclic aromatic hydrocarbons with MW 202, 228, 252, 276, 278 and 300 except perylene (see Table 3); OC: organic carbon content; TPhe: sum of concentrations of phenanthrene, methyl- and dimethyl-phenanthrene (see Table 3); BA: benzo[*a*]anthracene; CT: chrysene + triphenylene; BeP: benzo[*e*]pyrene; BaP: benzo[*a*]pyrene; Per: perylene.

(Grimmer et al., 1983). The ratio BA/BA + CT varied between 0.24 and 0.40 with highest values at the shallow sampling sites of transect D (see Fig. 1C; Table 4). The ratio BeP/BeP + BaP ranged from 0.56 to 0.71 with lowest values at the shallow sampling sites of transects D and E (see Fig. 1C; Table 4). If we consider that benzo[*a*]anthracene and benzo[*a*]pyrene show a faster decay compared to their isomers chrysene/triphenylene and benzo[*e*]pyrene, respectively (Baker et al., 1991), these trends reveal the occurrence of less «reworked» pyrolytic inputs in the near shore area, which derive from local sources.

3.3.2. Fossil PAHs

Unburned fossil fuels contain mainly low MW PAHs (one to three rings) and their alkylated derivatives as their most abundant constituents (Neff, 1979). These compounds are known to degrade more severely than high-molecular weight, mostly pyrolytic, PAH through physical–chemical and microbial processes (Simo et al., 1997). As a consequence, an apparent predominance of pyrolytic PAHs is commonly observed, unless outstanding petroleum-related inputs have occurred.

Petrogenic PAHs can be recognized within the phenanthrene series by considering the concentration pattern of the phenanthrene and its alkylated homo-

logues, namely methyl- and dimethyl-phenanthrene (Table 3). In this study, at almost all sampling sites, dimethyl-phenanthrene was observed at concentrations higher than the corresponding concentration of phenanthrene and methyl-phenanthrene (Table 3). This observation reveals that petroleum-related products are the dominant source of phenanthrenic compounds (Sporstol et al., 1983; Simoneit, 1984). Accordingly, the sum of phenanthrene and of its homologues methyl- and dimethyl-phenanthrenes (TPhe, Table 4 as calculated in Table 3) is used here to represent petrogenic PAH sources in the study area. TPhe concentrations were low accounting for less than 15% of the TPAH (Table 4). Despite their different sources pyrolytic PAH (COMB) and petrogenic PAH (TPhe) showed identical spatial trends (Fig. 9A and B). This observation suggests similar input patterns and transport pathways for these two compound classes. This contrasts with previous reports indicating significant discrepancies in the distributions and behavior of these two PAH groups (Bouloubassi and Saliot, 1993a,b; Wakeham, 1996).

TPhe concentration levels provide evidence of very low petrogenic inputs, which contrasts with the dominant occurrence of UCM. However, the latter is very resistant and rather reflects chronic oil-pollution, whereas TPhe are much more labile (Bouloubassi and Saliot, 1993a,b).

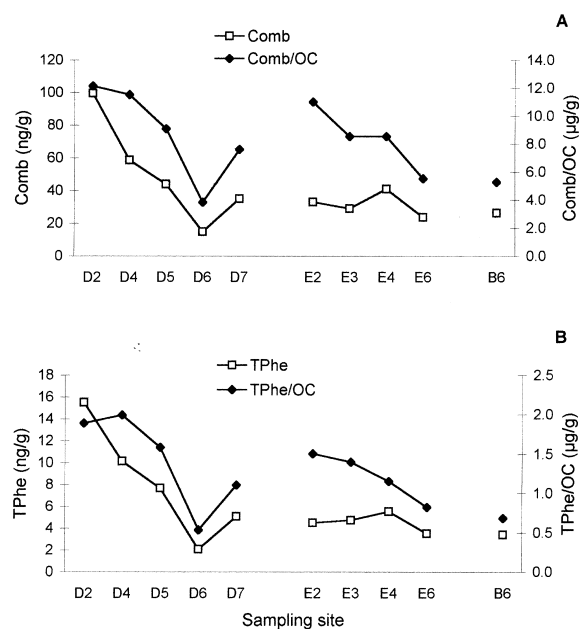


Fig. 9. Spatial distribution of pyrolytic polyaromatic hydrocarbons (A) and petrogenic polyaromatic hydrocarbons (B) determined in Cretan Sea sediment. COMB is the sum of concentrations of pyrolytic polycyclic aromatic hydrocarbons with MW 202, 228, 252, 276, 278 and 300 except perylene (see Table 3) and COMB/OC the same normalised with OC. TPhe is the sum of concentrations of phenanthrene, methyl- and dimethyl-phenanthrene (see Table 3) and TPhe/OC the same normalised with OC.

3.3.3. Biogenic PAHs

Retene was the major naturally derived PAH determined in the study area. It derives from abiatic acid, a common diterpenoid constituent of plant resins, especially conifer resins in temperate climates (Laflamme and Hites, 1978). Retene has been reported in a variety of environmental samples such as sediment (Wakeham et al., 1980; Venkatesan and Kaplan, 1982; Lipiatou and Saliot, 1992; Wakeham, 1996; Bouloubassi et al., 1997 and references therein), water particles (Bouloubassi and Saliot, 1993a) and aerosol (Simoneit and Mazurek, 1982; Sicre et al., 1987; Gogou et al., 1996, 1998).

Retene in the study area reached relatively high concentrations (up to 52 ng/g, Table 3). These concentrations compare to those encountered in the Rhone Delta, in NW Mediterranean, (13–68 ng/g, Bouloubassi et al., 1997) but were higher than measured in the Ebro delta, also in the NW Mediter-

ranean (0.2–3.9 ng/g, Bouloubassi et al., 1997). This comparison underlines the importance of naturally derived PAH in the study area which, unlike those investigated in the western Mediterranean basin, does not receive major fluvial inputs.

Retene concentrations did not show any systematic spatial trend and were not correlated to the terrestrial NA despite their common origin. This observation suggests different input patterns and/or transport mechanisms. The most striking observation is the high retene concentration observed in samples collected in summer, where retene is among the dominant PAH components accounting even for up to 40% of the total PAH (Table 3; Fig. 8B). Rapid formation of retene occurs during combustion of pinewood (Ramdahl, 1983). Intense forest (mainly conifer forests) fires are very frequent in the area around the Aegean Sea during summer months. Indeed retene was present in all aerosol samples collected in the same area in summer and associated with air masses originated from areas in which forest fires occurred (Gogou et al., 1996). We thus propose that these high retene concentrations, observed in samples collected in August, reflect inputs from forest fires transported southwards by the dominant N/NW winds (which are intensified during summer in the Aegean) and/or the dominant southward marine currents (Theocharis, 1995).

Pimanthrene concentration varied from 0.1 to 1.65 ng/g of dry sediment (Table 3). Pimanthrene concentration was correlated with this of retene ($R^2 = 0.855$), except for the sampling sites D2 and E2 (Fig. 1C). For these sampling sites, the higher pimanthrene concentrations may indicate additional sources. The observed decoupling of retene and pimanthrene distribution at the shallower sampling sites (Table 3) provides another evidence for the atmospheric transport of retene in this marine environment. For this reason retene accumulates preferentially to deeper sampling sites.

Perylene, a PAH compound which may also be of natural origin, was determined at concentrations varying from 0.4 to 18 ng/g, which accounted for up to 11% of the total PAH (Table 3). Early studies reported diagenetic formation of perylene from terrestrial precursors in anoxic conditions (Aizenshtat, 1973). However, perylene is also produced during pyrolytic processes (Venkatesan, 1988). The low

relative abundance of perylene in the study area argues for a dominant anthropogenic (pyrolytic) origin (Venkatesan, 1988), as in the case of the Rhone delta (Lipiatou and Saliot, 1992; Bouloubassi and Saliot, 1993b). Nevertheless, at the near shore sampling sites, perylene occurred at higher relative abundance and was among the major PAHs (Table 3). This fact suggests significant diagenetically derived perylene inputs in the shallow area. Compared to benzo[*e*]pyrene, a characteristic pyrolytic PAH of the same MW, perylene showed higher relative abundance at the shallow sampling sites (D2, D4, E2 and E3; see BeP/Per in Table 4) which further supports the assumption of natural perylene inputs in the area close to the land.

3.4. Conclusions

The amounts of anthropogenic tracers, such as UCM and PAHs, determined in this study, revealed that the Cretan Sea receives low supply of anthropogenic material compared to coastal areas from the NW Mediterranean. Compounds deriving from terrestrial sources (higher plants), such as long-chain NA and retene, were the dominant biogenic constituents of the hydrocarbon mixtures. Only minor marine-derived hydrocarbons were present. This observation reflects the extremely low trophic state of the area, along with the labile character of marine hydrocarbons.

A significant correlation observed between COMB and TPhe ($R^2 = 0.9051$; Fig. 10A), which indicates the same transport mechanism for both combustion-derived and the mainly petrogenic PAHs in this sampling area. This was not observed in other coastal areas, receiving important fluvial inputs (Bouloubassi and Saliot, 1993b). Furthermore, the significant correlation between terrestrially derived NA (Ter) with both pyrolytic (COMB) ($R^2 = 0.7042$; Fig. 10B) and petrogenic (TPhe) PAHs ($R^2 = 0.8416$; Fig. 10C), indicates the same mechanism for the introduction of allochthonous material — both biogenic and anthropogenic — in distinct sampling sites. For the transect D, located closer (same longitude) to the city of Heraclion, the transport of material via continental runoffs seems to be the predominant mechanism for sampling sites up to 700 m depth. For the deeper sampling sites and for these located at a greater

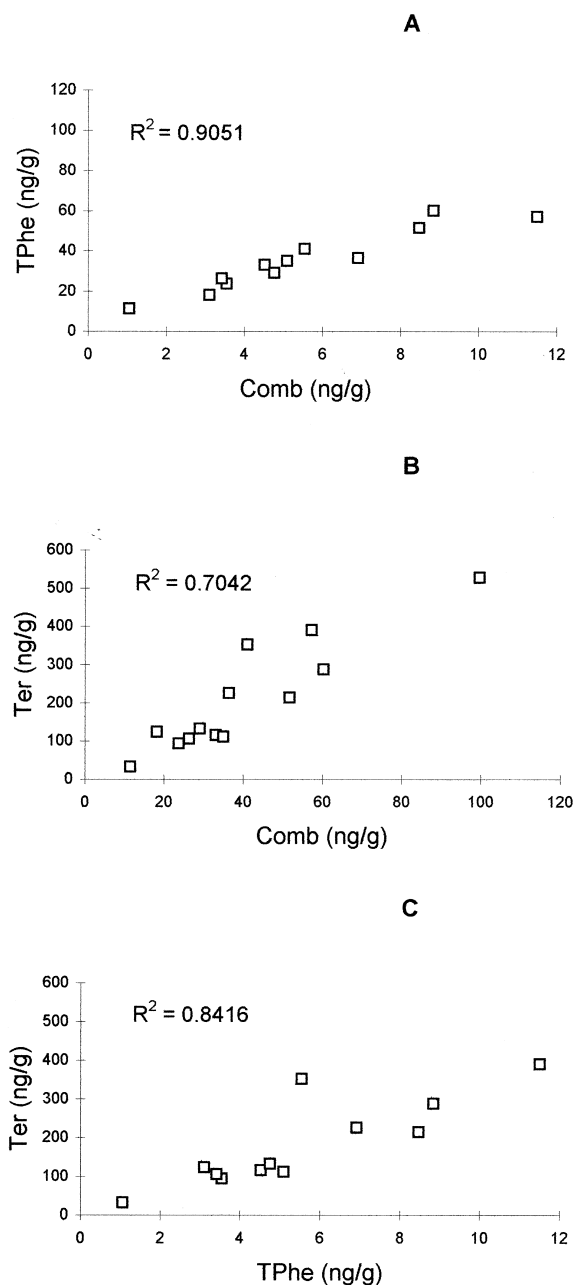


Fig. 10. Correlation between pyrolytic and petrogenic polyaromatic hydrocarbons (A), terrestrial NA and pyrolytic (B) and petrogenic polyaromatic hydrocarbons (C) determined in Cretan Sea sediment. For Ter, see Table 2 and for COMB and TPhe, see Table 4.

distance of the urban influence (E and B sampling sites), atmospheric input could be an important source

of anthropogenic and terrestrially derived hydrocarbons.

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