



# The *Aegean Sea* Oil Spill in the Galicia Coast (NW Spain). I. Distribution and Fate of the Crude Oil and Combustion Products in Subtidal Sediments

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The spatial distribution and fate of petrogenic and pyrogenic hydrocarbons in coastal sediments following the *Aegean Sea* oil spill (Galicia, NW Spain) was investigated through a detailed study of chemical markers. Alkanes and acyclic isoprenoid hydrocarbons were degraded within six months of the accident, but triterpane and sterane distributions were still detectable and were useful in monitoring, respectively, the oil source and weathering. Aromatic steranes were also useful source indicators, and oil degradation was clear from the decrease of certain alkyl dibenzothiophene and phenanthrene isomers. The pyrogenic polycyclic aromatic hydrocarbons produced in the tanker wreck were found more persistent than the petrogenic ones. However, the presence of the oil in the sediments was recognized even one year after the accident and was found particularly preserved in the subsurface layers. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** oil spills; fossil markers; PAHs; coastal sediments; Galicia coast; *Aegean Sea* tanker.

## Introduction

After several days of severe weather conditions, in the early morning of 3 December 1992, the tanker *Aegean Sea* ran aground off La Coruña harbour, on the Galicia coast (NW Spain). The tanker was transporting 79 000 t of the relatively light Brent crude oil (North Sea) from Sullom Voe to La Coruña refinery. First rescue operations were unsuccessful and in a short time the ship broke in two and caught fire. During five days the oil tanker was leaking and burning. However, by the combined effects of severe weather and fire the amount of oil which affected the coastal area was only around 10% of the cargo. The winds and sea currents drove the

spilled oil and the combustion products towards the north-east, rather far from the wreck point (Fig. 1).

The clean-up was confined to mechanical means (skimmers and booms) which succeeded in removing most of the visible oil during the following two months. Although the oil did not enter La Coruña harbour and beaches, about 200 km of coast line were affected and, particularly, the estuaries ('rias') of Ares and El Ferrol, where booms were unable to contain the oil due to the strong winds and rough sea (Nunes, 1993).

As the Galician coast is the most important fishing area in Spain, with salmon farming, crab and lobster industries, as well as an enormous shellfish production (more than 200 kT yr<sup>-1</sup>), major concerns were raised for the contamination of shallow inshore areas affecting the muddy sediments and the associated benthic fauna. Therefore, when cleaning operations came to an end, a survey programme on the mid- and long-term effects of the oil spill on the marine ecosystem was established by the Spanish authorities. This involved, among other objectives, the assessment of the area of impact and the temporal evolution of the oil and combustion products. To this end, the characterization of the spilled oil and its identification in subtidal sediments was the first issue. The system adopted should be able to unambiguously identify the oil, and distinguish it from other possible inputs that could occur in the area during the observation period. Moreover, the occurrence of pyrolytic products and their fate should also be investigated for their harmful effects on biota and the quality of edible products. The extensive use of fossil markers was the applied strategy and the results obtained are reported in this paper.

## Experimental

### *Sample handling*

A crude oil sample from the tanker (0.5 g) was sonicated in *n*-hexane (20 ml) for 10 min. The mixture was left overnight to precipitate asphaltenes and the solution

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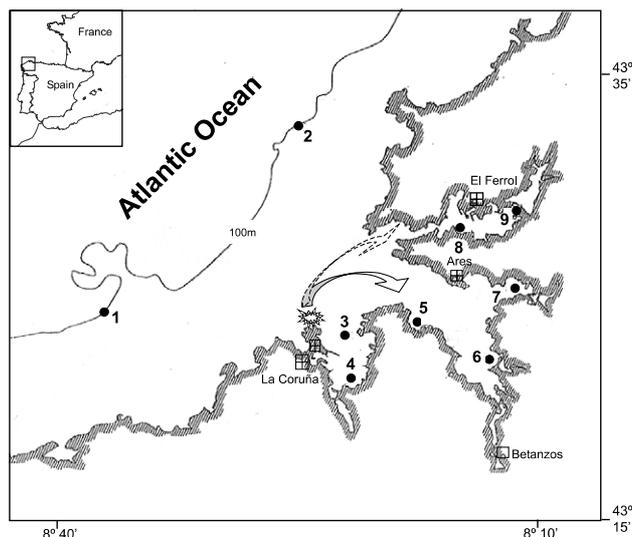


Fig. 1 Map of the area of study showing the grounding site of the *Aegean Sea* (\*), the movements of the oil spill and the pyrolytic material, and the sampling stations for marine sediments.

was separated and vacuum evaporated at 60°C for 6 h to simulate light weathering. The residue (68% of the original oil) was fractionated into aliphatics and aromatics as indicated below.

Surficial sediments were sampled four times in 1993 (April, July, September and November) with a conventional box corer in the stations indicated in Fig. 1. Two layers of 5 cm depth were separated on selected samples. Stations 1 and 2 were considered as reference. Stations 3, 4, 5 and 6 corresponded to areas with aquaculture activities, and stations 5, 7, 8 and 9 were heavily oiled sites. These stations were further surveyed in October 1995, three years after the accident. All samples had a muddy-sandy texture, with 0.5–0.7% organic carbon (OC), except stations 8 and 9 which were very muddy (3.9–6.4% OC).

Samples were placed in glass jars and kept frozen (–20°C) until they were freeze-dried, sieved at 1 mm to remove coarse sands and organic debris and Soxhlet extracted for 12 h with a mixture of *n*-hexane-dichloromethane (4:1). The extract was collected and treated overnight with recently activated copper for elemental sulphur removal. The solution was carefully evaporated to dryness and dissolved with 0.5 ml of *n*-hexane for further fractionation into aliphatic and aromatic hydrocarbons.

#### Chemical analyses

Extracts were fractionated by open column liquid chromatography with 5% water deactivated silica-alumina (Aceves *et al.*, 1988). Aliphatic hydrocarbons (fraction I) were eluted using 20 ml of *n*-hexane, and aromatics (fraction II) using 30 ml of *n*-hexane:dichloromethane (9:1) and 20 ml a mixture (8:2) of the same solvents.

The first fraction was analysed by capillary gas chromatography–flame ionisation detector (GC–FID)

using a Fisons 5000 instrument, equipped with a fused silica 30 m × 0.25 mm ID 5% phenyl-methyl-polysiloxane DB5 column (J&W, Scientific, USA), temperature programmed from 60°C to 100°C at 15°C min<sup>-1</sup> and from 100°C to 300°C at 6°C min<sup>-1</sup>, with a final hold-up time of 10 min. The injector and detector temperatures were 270°C and 310°C, respectively. The carrier gas was helium.

External standards of C14, C22, and C32 *n*-alkanes were used for quantification of the resolved and unresolved compounds of the aliphatic fraction (Soler *et al.*, 1989). All samples were also analysed by gas chromatography coupled to mass spectrometry (GC–MS) using a Fisons 800 GC interfaced to a Fisons MD 800 MS, operating in the electron impact (EI) mode, with the chromatographic conditions reported previously, except the carrier gas was helium.

The second fraction was also analysed by GC–MS with full scan, for fingerprinting chemical markers, and selected ion monitoring (SIM), for quantification of individual polycyclic aromatic hydrocarbons (PAHs) (Solé *et al.*, 1996). A standard mixture containing the following components was used: phenanthrene (Ph), anthracene (A), fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (C), benzo[*b*]fluoranthene (BbF1), benzo[*k*]fluoranthene (BkF1), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IP), dibenz[*ah*]anthracene (DBA) and benzo[*ghi*]perylene (BPe).

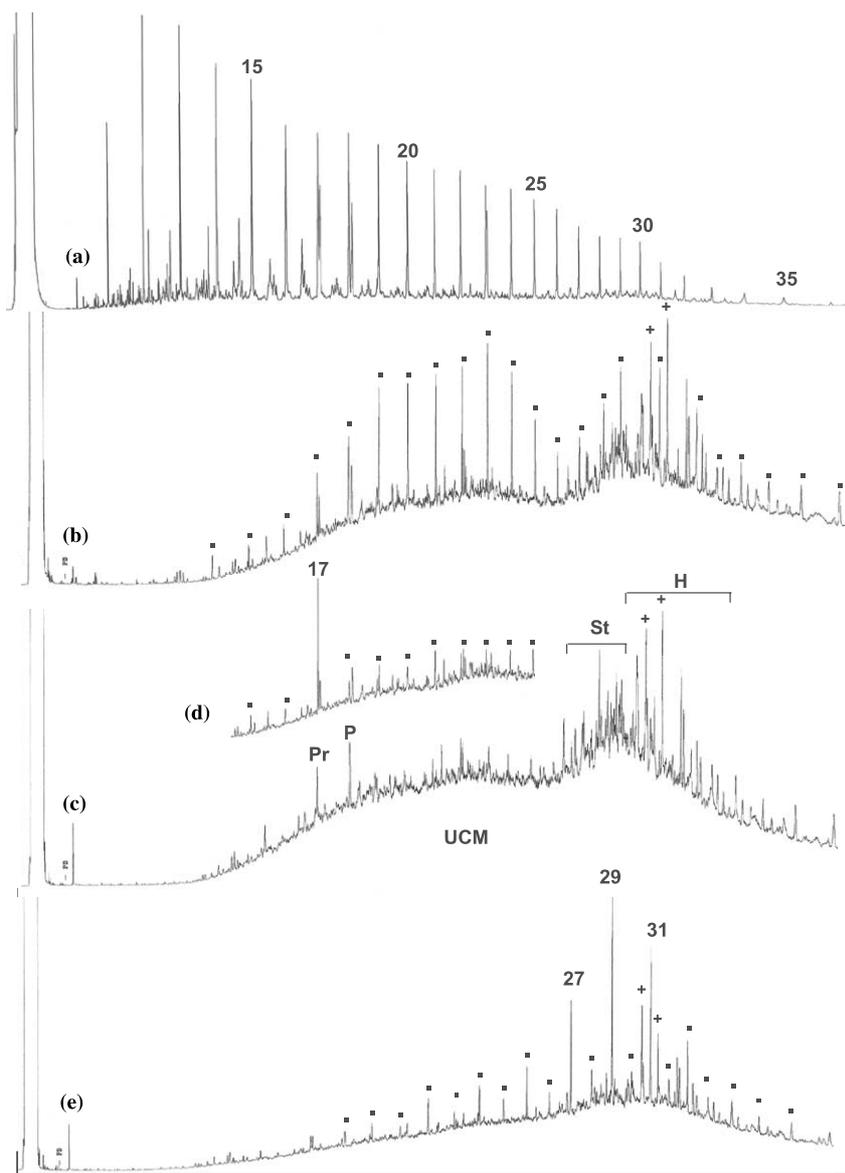
#### Analytical performance

The above-reported methods included the processing of blanks, duplicates and standard mixtures between each group of samples as customary (Tolosa *et al.*, 1996; Porte *et al.*, 2000). The GC injections were performed with an automatic injector to improve reproducibility that was better than 14% for the whole procedure. The whole protocols were validated through the analysis of certified reference materials and the participation in intercalibration exercises (UNEP-IOC-IAEA).

## Results and Discussion

#### Characterization of hydrocarbon sources

The crude oil carried by the tanker was of light Brent type (North Sea) with about 30% of volatiles (C<sub>1</sub>–C<sub>10</sub>), and a residue composed by 62% of aliphatics, 28% of mono- and di-aromatics, 4% of polyaromatics, 3.5% of resins and 2.5% of asphaltenes. The GC profile showed the whole series of *n*-alkanes and the two major acyclic isoprenoids, pristane (Pr) and phytane (P), in a 1.1 ratio (Fig. 2(a)). However, this profile was no longer visible four months after the accident (Fig. 2(b)), due to weathering processes. The result was a GC profile devoided of light components and resolved peaks, and often showing little more than an unresolved complex mixture (UCM) of hydrocarbons.



**Fig. 2** Representative GC profiles of the Aegean Sea crude oil (a) and sediment aliphatic fractions (b) St. 4, April; (c) St. 4, July; (d) St. 4, November; (e) St. 9, November. Numbers indicate the number of carbon atoms of the *n*-alkanes series (●). St: steranes. H: hopanes (+, C<sub>29</sub> and C<sub>30</sub> αβ-hopanes).

Distinctive features for oil source characterization can be found in the UCM, like the geochemical markers, used in organic geochemistry for oil/oil and oil/source rock correlations (Peters and Moldowan, 1993). Particularly valuable are acyclic isoprenoids, steranes and pentacyclic triterpanes, that can be easily monitored by mass fragmentography, using the corresponding diagnostic fragment ions (Albaiges and Albrecht, 1979). This approach has been used in assessing the effects of major oil spills (Page *et al.*, 1988; Sauer *et al.*, 1993; Hostettler and Kvenvolden, 1994; Bence *et al.*, 1996) and the sources of tar balls chronically polluting coastal zones (Albaiges, 1980; Barakat *et al.*, 1999).

Geochemical markers of Brent type oils have been described in the literature (Grantham *et al.*, 1980;

Wardroper *et al.*, 1984; Horstad *et al.*, 1990), and also used in relation with several oil spill accidents in the North Sea (Tibbetts *et al.*, 1983; Grahl-Nielsen and Lygre, 1990; Wolff *et al.*, 1993).

The profile of the pentacyclic triterpanes (*m/z* 191) encompasses, besides the current series of C-29–C-35 17α(H), 21β(H)-hopanes, the two C-27 isomers, namely the 18α(H)-22, 29, 30-trisnorneohopane (*T<sub>s</sub>*) and the 17α(H)-22, 29, 30-trisnorhopane (*T<sub>m</sub>*), the ratio of which is source and maturity dependent, and the rather unusual C-28 member of the series, the 17α(H), 18α(H), 21β(H)-28, 30-bisnorhopane (Grantham *et al.*, 1980).

Steroid hydrocarbons are found in the saturated form and also partially or totally aromatized. The *m/z* 217

mass fragmentogram shows the complex mixture of C-27, C-28 and C-29 normal and rearranged steranes. The relative distribution of the three parent compounds, although of questioned significance, is source dependent and can be used in correlation studies and sample set discrimination. In this respect, it is known that Brent type oils are characterized by a depletion of the C-28 member (Horstad *et al.*, 1990). The presence of the extended C-30 homologues is also discernible in the fragmentogram and may be of interest.

The complexity of the sterane mixture diminishes with aromatization, a process that depends on the thermal history of the oil. The  $m/z$  253 and 231 mass chromatograms show, respectively, the two series of mono and tricyclic aromatic derivatives. Although they are derived from the saturated counterparts, the aromatisation process may introduce changes in the component ratios reflecting the relative ease of aromatization of the various precursors. Moreover, it can be complemented with that of the ring A methylated derivatives ( $m/z$  245).

The identification of pyrogenic hydrocarbons should also be based upon the aromatic fraction. Although smoke samples from the fire of the tanker were not available for analysis, it is well known that the profiles exhibited by soot from fossil fuels combustion are characterized by PAH patterns dominated by non-alkylated species, and a greater abundance of 4–6 ring components, relative to those of 2–3 rings which are dominant in crude oils. This feature is even enhanced in the long-range atmospheric transport of the soot particles (Simó *et al.*, 1997). By examining the relative abundances of parent PAHs it is possible to identify sources of PAHs and broadly determine the relative contribution of each source to coastal sediments (Broman *et al.*, 1988; Yunker *et al.*, 1996).

#### Sedimentary distribution

*Aliphatic hydrocarbons.* The GC profiles of the aliphatic fractions recovered from the sediment samples

showed the occurrence of petrogenic contamination and the effects of evaporation and degradation (weathering) on the spilled oil (Fig. 2). The concentrations of unresolved hydrocarbons (UCM) given in Table 1 reflect the movement of the oil slick after the accident. Sites 4, 5, 8 and 9 were the most affected and remained still heavily contaminated four months after the accident. The latter two stations (8 and 9) contained significant amounts of oil even one year later, probably favoured by the muddy texture of the sediment. On the other hand, Stations 3, 6 and 7 were apparently less affected and reached rather quickly concentrations similar to those found in the open sea Stations (1 and 2). Concentrations of UCM in sediments below  $10 \mu\text{g g}^{-1}$  are common in coastal environments distant from hydrocarbon inputs (Tolosa *et al.*, 1996).

Evaporation/dissolution and biodegradation mainly accounted for the strong decrease of hydrocarbon concentrations in the surface sediments during the months following the spill. As it can be seen in the GC profiles, the fractions lower than C-15 were completely lost in April, and in July all *n*-alkanes were degraded, leaving pristane (Pr), phytane (P) and other polycyclic compounds (St: steranes; H: hopanes) as the major resolved peaks. Since then, some biogenic alkanes became recognizable. The occurrence of *n*-C17 and the marked *n*-alkane odd–even carbon number predominance in the C25–C33 range were indications, respectively, of marine algal and higher plant inputs (Fig. 2(d) and (e)).

However, the depletion of the surface pollution could also be originated by the migration of the oil into deeper layers. This was observed in the analysis of the subsurface sections, particularly in those sediments of higher sandy nature. Eleven months after the accident, for example, the subsurface sediment (5–10 cm) of Stations 4 and 5 still contained, respectively, 180 and  $320 \mu\text{g g}^{-1}$  of unresolved aliphatic hydrocarbons (Table 1). Despite this, the buried hydrocarbons were not passively stored, they were remobilized during rough sea events and made available to benthic fauna, which increased their tissue

TABLE 1

Concentrations of aliphatic UCM (in  $\mu\text{g g}^{-1}$ ) and parent PAHs in surface (0–5 cm) and subsurface (5–10 cm, in parenthesis) sediments collected in Stations 1–9 along 1993.

Pollution indicators	Sampling period	Sampling stations (water depth)								
		1 (95 m)	2 (100 m)	3 (36 m)	4 (9 m)	5 (13 m)	6 (6 m)	7 (6 m)	8 (14 m)	9 (8 m)
UCM ( $\mu\text{g g}^{-1}$ )	April	10	5	11	180	1680	20	55	180	300
	July	– <sup>a</sup>	–	8	45 (320)	705	7	13	220 (115)	90
	September	–	–	5	30	240	–	10	135	80
	November	–	–	–	55 (180)	30 (320)	–	5	115 (130)	110
PAHs <sup>b</sup> ( $\text{ng g}^{-1}$ )	April	20	7	360	220	16200	18	135	1330	1205
	July	–	–	340	380 (580)	4140	–	210	740 (690)	950
	September	–	–	260	230	4120	–	100	390	1950
	November	–	–	n.d.	160 (250)	3910 (4840)	–	140	690 (830)	1020

<sup>a</sup> Values below  $5 \mu\text{g g}^{-1}$  (UCM) or  $5 \text{ng g}^{-1}$  (PAHs). n.d.: not determined.

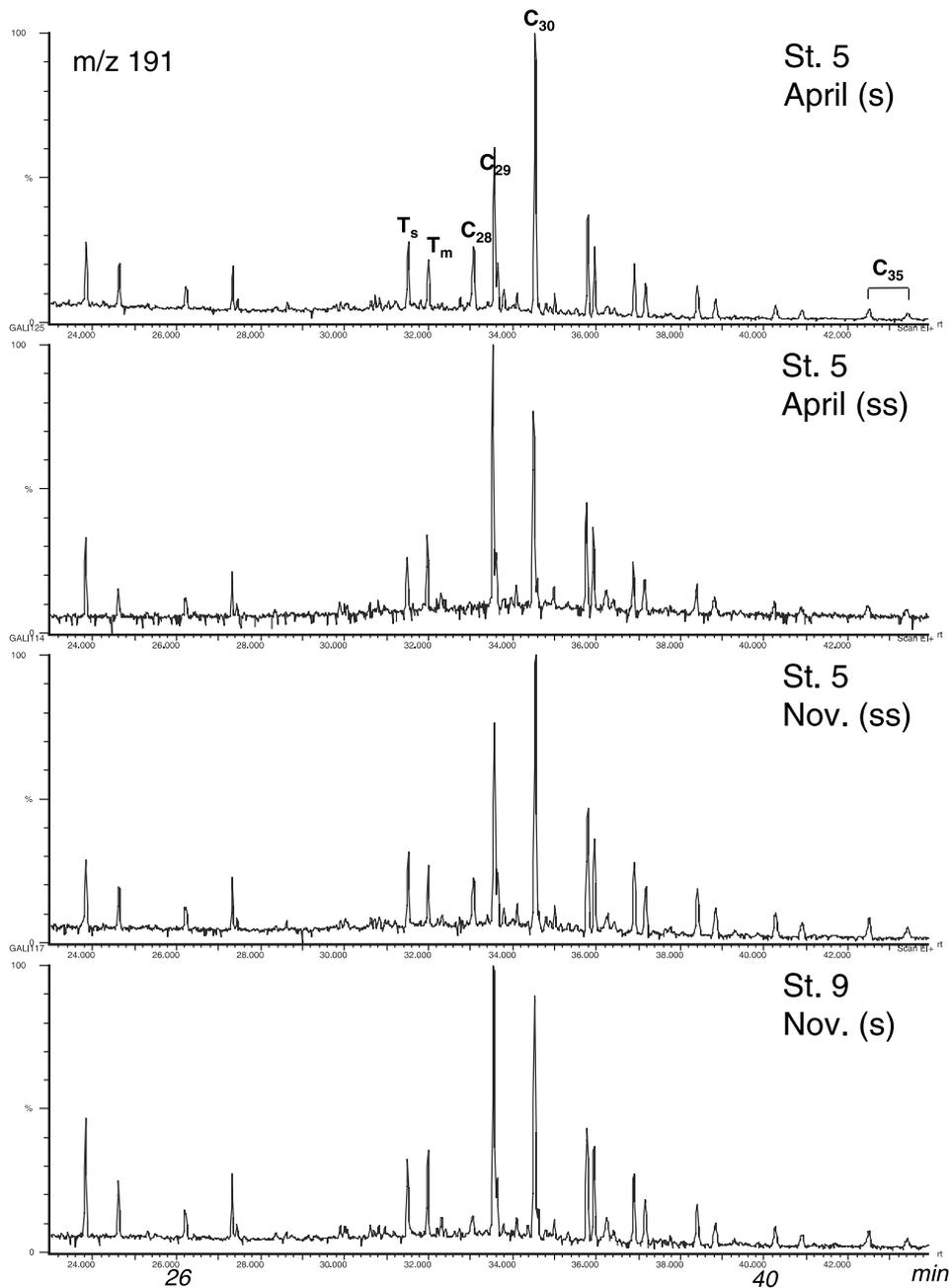
<sup>b</sup>  $\Sigma$  of phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b] + [k]fluoranthenes, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene.

concentrations in the following winter, one year after the accident (Porte *et al.*, 2000).

In order to assess the correspondence of these hydrocarbons with the *Aegean Sea* spilled oil a detailed study of the fossil markers was carried out. The triterpane profiles ( $m/z$  191) (Fig. 3) exhibited the main distinctive features of the Brent tanker oil, as the occurrence of 28,30-bisnorhopane (C-28) and  $T_m/T_s$  (C-27) and C-29/C-30 ratios  $<1$ . These parameters confirmed the persistence of the oil in the sediments one year after the accident, although the C-29/C-28 ratios were always higher than in the crude, possibly

indicating a mixture with a pre-existing (chronic) pollution in the sediments. In this respect, it was also possible to recognize the vertical migration and long persistence of the oil within the sediment in Stations 4 and 5 (Fig. 3). On the other hand, it was noticed in Station 9 the early substitution/dilution of the *Aegean Sea* oil by another oil source, probably as a result of the chronic impact of the industrial city and harbour of El Ferrol.

The sterane profiles ( $m/z$  217–218) showed patterns consistent with the triterpane profiles, in the sense that they were similar to those of the spilled oil in all stations,



**Fig. 3** Mass fragmentograms of terpanes ( $m/z$  191) in surface sediments (s) of Stations 5 and 9. The vertical migration of the *Aegean Sea* oil can be recognized in the subsurface samples (ss) of Station 5.

TABLE 2

Molecular marker parameters of the *Aegean Sea* oil and sediment aliphatic hydrocarbon fractions.<sup>a</sup>

Sample	Triterpanes ( <i>m/z</i> 191)			Steranes ( <i>m/z</i> 217–218)				
	$T_m/T_s$	$C_{29}/C_{28}$	$C_{29}/C_{30}$	$C_{27}$	$C_{28}$ ( $\beta\beta$ 20R)	$C_{29}$	$C_{29}\beta\beta$ 20S/ $C_{27}\alpha\alpha$ 20R	$C_{29}\beta\beta$ 20S/ $C_{29}\alpha\alpha$ 20R
<i>Aegean Sea</i> oil	0.83	1.66	0.65	1.1	0.8	1.0	1.25	0.96
4. April	0.84	2.23	0.68	1.0	0.9	1.0	1.38	1.07
November (s)	0.90	2.14	0.60	0.7	0.8	1.0	1.45	1.11
(ss)	0.93	2.76	0.63	1.1	0.9	1.0	1.28	1.15
5. April (s)	0.86	2.27	0.66	1.1	0.8	1.0	1.37	1.29
(ss)	1.25	–	1.35	0.8	0.7	1.0	1.48	1.30
November (s)	0.84	2.49	0.68	0.7	0.7	1.0	1.65	1.33
(ss)	0.86	2.62	0.72	0.9	0.8	1.0	1.64	1.28
7. July	0.86	2.85	0.70	0.8	0.8	1.0	1.65	1.27
November	0.84	2.88	0.72	0.6	0.8	1.0	1.83	1.25
8. July	0.80	3.13	0.73	1.0	0.8	1.0	1.67	1.40
November	0.81	3.50	0.76	0.9	0.8	1.0	1.61	1.51
9. July	1.10	22	1.08	0.8	0.6	1.0	1.63	1.38
November	1.11	–	1.11	0.8	0.6	1.0	1.63	1.42

<sup>a</sup>(s) surface; (ss) subsurface sediment.

except in Nos. 8 and 9. The distribution of the C-27, C-28 and C-29 parent components was easily calculated from the *m/z* 218 fragmentogram (Table 2), that also enabled to estimate the epimeric 20S/R ratios and the abundance of C-30 homologues.

The sterane 20S/S + R epimeric ratios are basically maturity indicators, such as the hopane 22S/S + R ratios, and they usually reach the thermodynamic equilibrium values in matured crude oils, being around 0.6 for hopanes and 0.5 for steranes (0.57 and 0.48, respectively, in the case of the *Aegean Sea* oil). Therefore, they are of limited interest for fingerprinting the spilled oil in sediments. However, they may afford information on the extent of oil biodegradation because it is known that compounds with the biological 20R configuration are removed faster than 20S compounds. Moreover, 14 $\alpha$ (H), 17 $\alpha$ (H) isomers are removed faster than the 14 $\beta$ (H), 17 $\beta$ (H); and C-27 > C-28 > C-29 (Chosson *et al.*,

1993; Peters and Moldowan, 1993). All these alterations usually occur after complete elimination of acyclic isoprenoids and before any evidence of hopane destruction. Consequently, the attention was focused on the ratios particularly sensitive to this process, such as the C-29  $\beta\beta$ 20S/C-27  $\alpha\alpha$ 20R and C-29  $\beta\beta$ 20S/C-29  $\alpha\alpha$ 20R.

From the values indicated in Table 2, a depletion of the regular C-27 components occurred in Stations 4, 5 and 7, where a higher decrease of hydrocarbon concentrations was observed along the year. Moreover, a concurrent decrease of  $\alpha\alpha$  20R vs  $\beta\beta$  20S isomers can be inferred. A similar evolution was observed in a 12-years old oil spill from an Arctic beach (Wang *et al.*, 1995). Therefore, it appears that by using these fossil markers a definite degradation trend of the oil in the sediments is confirmed, although there was no straight correlation neither among parameters nor stations,

TABLE 3

Molecular marker parameters of the *Aegean Sea* oil and sediment aromatic hydrocarbon fractions.

Sample	Source ratios		Weathering ratios		C <sub>1</sub> -DBT isomers		
	C <sub>2</sub> -DBT/C <sub>2</sub> -Ph	C <sub>3</sub> -DBT/C <sub>3</sub> -Ph	C <sub>2</sub> -DBT/C <sub>2</sub> -C	C <sub>3</sub> -P/C <sub>3</sub> -C	4	2 + 3	1
<i>Aegean Sea</i> oil	0.3	0.4	5.6	5.2	1	0.60	0.36
4. April	0.5	0.5	4.7	6.1	1	0.32	0.43
November (s)	0.7	0.5	1.9	6.0	1	0.33	0.47
(ss)	0.6	0.6	3.5	6.0	1	0.40	0.45
5. April (s)	0.5	0.4	5.2	6.2	1	0.54	0.30
(ss)	0.8	0.4	3.1	2.2	1	0.54	0.33
November (s)	0.5	0.4	2.8	2.3	1	0.34	0.30
(ss)	0.6	0.3	2.5	2.5	1	0.58	0.29
7. July	0.7	0.6	4.7	6.3	1	0.36	0.38
November	0.7	0.6	2.1	2.7	1	0.30	0.33
8. July	0.8	0.6	5.7	5.3	1	0.36	0.39
November	1.0	0.6	2.6	2.6	1	0.30	0.35
9. July	0.6	1.0	1.8	4.7	1	0.50	0.40
November	0.7	1.0	1.7	4.3	1	0.52	0.38

probably by the occurrence of different environmental conditions.

**Aromatic hydrocarbons.** The GC of the aromatic fractions also showed the characteristic UCM of hydrocarbons although the prominent resolved peaks were found to consist in polyunsaturated alkanes, highly branched isoprenoids and squalene, corresponding to biogenic inputs. On the other hand, the GC-MS analysis proved the occurrence of a mixture of petrogenic and pyrogenic hydrocarbons, according to the presence of characteristic markers. Low molecular weight (2–3 aromatic ring) compounds together with their alkylated derivatives, typical constituents of petroleum, were identified, as well as larger mol. wt. (>4 aromatic ring) non-alkylated compounds, particularly peri-condensed, which derive from high temperature combustion.

The distributions of alkylated PAH homologous series have been proposed for fingerprinting crude oils, although their composition can be significantly affected by evaporation/dissolution and degradation of the lower ring and less alkylated species. Thus, alkyl naphthalenes, which are predominant in crude oils, were absent or present in only trace amounts in the sediment samples. Burns *et al.* (1997) reported that water-washing originated this loss in intertidal sediments affected by an oil spill.

The C-1–C-3 alkylphenanthrenes (Ph), chrysenes (C) and dibenzothiophenes (DBT) are more persistent and showed typical petrogenic distributions, which are common to most oils (Fig. 4), so of limited diagnostic value. However, recently, the C-2 and C-3 alkyl homologues of dibenzothiophene and phenanthrene/anthracene and the same homologues of dibenzothiophene and chrysene/benzo[*a*]anthracene, were found useful in, respectively, differentiating hydrocarbon sources and characterizing the weathering of the spilled oil in sediments (Douglas *et al.*, 1996). The corresponding ratios were shown to be stable at moderate degradation levels in different marine environments, although the study of samples collected in the Arabian Gulf after the War did not afford conclusive results (Sauer *et al.*, 1993).

The relevant ratios for the present case are shown in Table 3. The source ratios (C2-DBT/C2-Ph and C3-DBT/C3-Ph) exhibited a slight increase with respect to those of the crude oil, probably due to the faster degradation of the phenanthrene derivatives. However, it is interesting to notice that the C3-DBT/C3-Ph ratio was more consistent because it should be less affected by biodegradation, as it is known that this decreases within a homologous series with increasing alkylation. The values also indicate that the subsurface samples exhibit a higher degree of preservation. Moreover, as already inferred from the aliphatic markers, the C3-DBT/C3-Ph values in sample 9 correspond to a different oil source.

The weathering ratios (C2-DBT/C2-C and C3-DBT/C3-C) were clearly below the original crude oil values

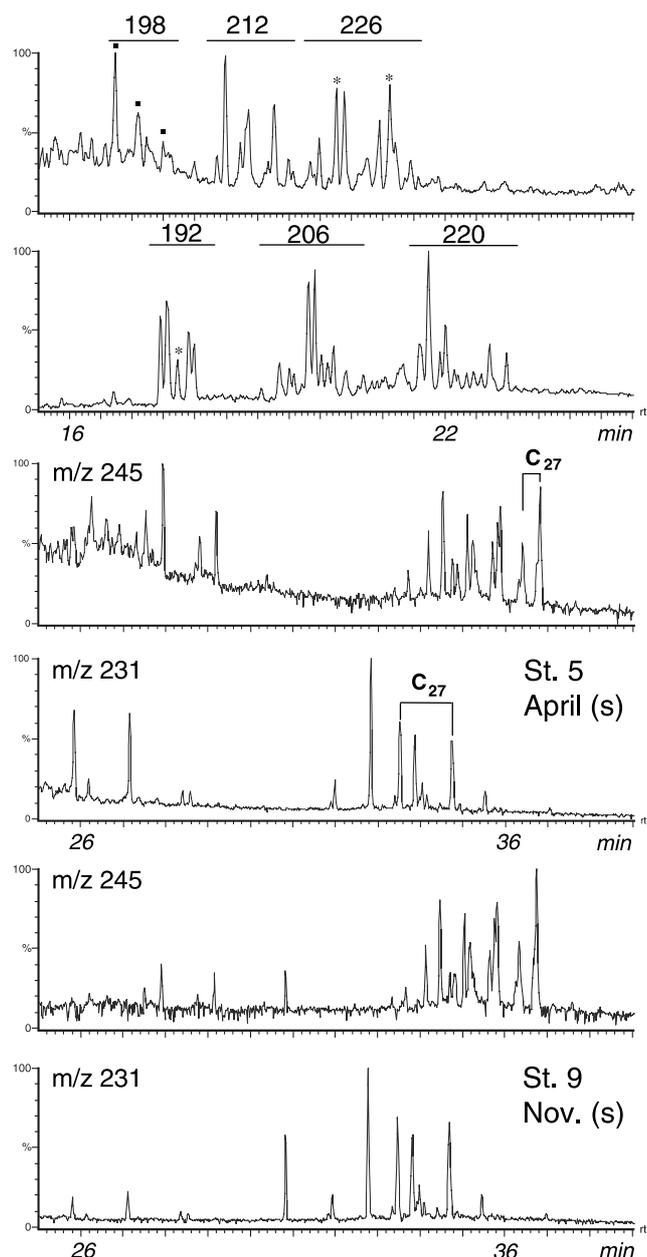


Fig. 4 Aromatic hydrocarbon markers in sediments. Triaromatic steranes ( $m/z$  231 and 245). C1–C3 alkyl-Ph ( $m/z$  192, 206 and 220) and DBT (198, 212 and 226). Pyrolytic markers (\*).

and decreased in time more significantly than those found in biota (Porte *et al.*, 2000). In the present case, the trimethyl distributions exhibited even less consistent trends because the GC-MS profiles of the trimethyl-chrysenes (C3-C) were close to the noise signal.

Besides of evaporation, that was the main responsible for the above evolution, biodegradation could also affect the relative distributions of PAHs and their S-derivatives. A conclusive evidence of advanced degradation of the oil residues was obtained from the relative distribution of methyl DBT isomers. The indices shown in Table 3 are consistent with the degradation trends already observed in laboratory experiments where we found that the 2- and 3-methyl substituted isomers were

more easily degraded in aerobic conditions than the 4-methyl derivative (Bayona *et al.*, 1986).

Of alternative use for source recognition can be the series of mono and tri-aromatic steroid hydrocarbons which are not biodegraded until steranes and triterpanes are severely affected (Wardroper *et al.*, 1984), and can be readily detected by GC-MS at, respectively,  $m/z$  253 and 231. Although these hydrocarbons are closely related to the source-dependent sterane distribution, the coelution of several components makes difficult the selection of adequate ratios for oil characterization, as performed with the saturated markers. Moreover, in

samples with high pyrolytic PAH contents the  $m/z$  253 profile was misrepresented by the coelution of the benzo-fluoranthenes and pyrenes ( $m/z$  252). For this reason we prefer considering for fingerprinting purposes the triaromatic steranes ( $m/z$  231) as well as their ring-A methylated derivatives ( $m/z$  245) (Fig. 4). These marker profiles, that were highly conservative, confirmed the wide distribution of the *Aegean Sea* oil in the area with the concurrence of other sources in Station 9.

Superimposed to this petrogenic signature was found the series of 3–6 ring PAHs, considered to be typically combustion derived. This series encompasses from the 3-

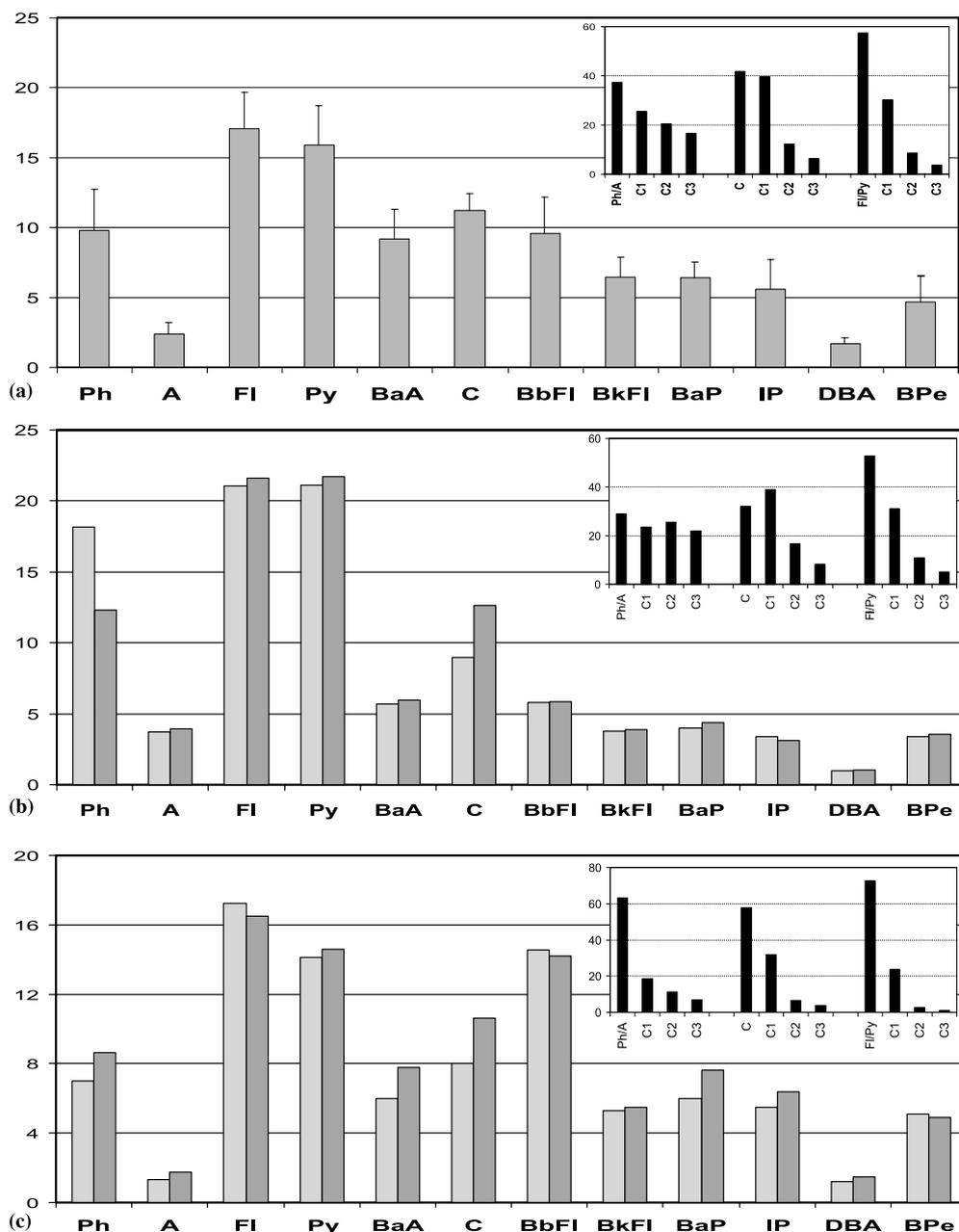


Fig. 5 Percentage distributions of parent PAHs, and alkyl-Ph, C and Fl/Py in sediments. (a) Average distribution of all surface samples, excluding Station 5. (b) Profiles corresponding to Station 5 (April, left; November, right). (c) Profiles corresponding to Stations 1 (April, left) and 3 (April, right).

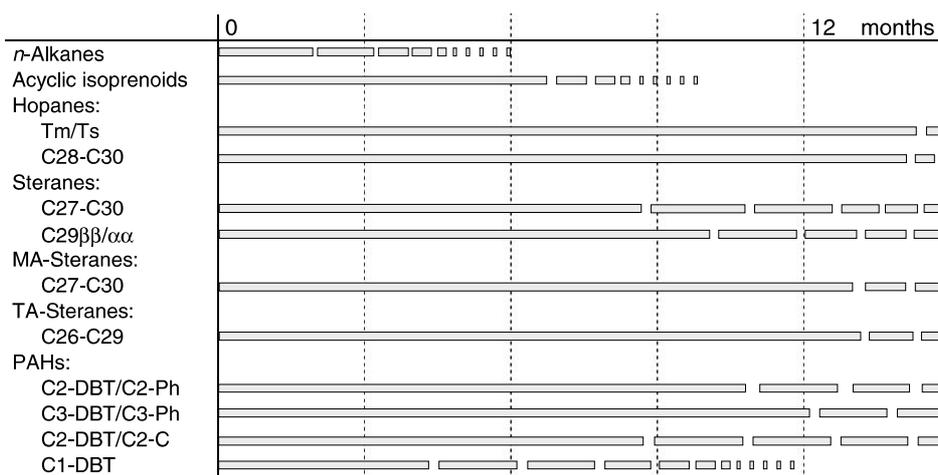


Fig. 6 Relative stability of fossil markers in the marine environment, for oil spill fingerprinting. Bars indicate the temporal span within which the corresponding indices were useful indicators in the present accident.

ring anthracene to the 6-ring indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene, including the benzo[*b*] + [*k*]fluoranthenes. Wang *et al.*, 1999) have nicely illustrated the formation of these hydrocarbons during the combustion of an oil. Elevated concentrations of pyrogenic PAHs formed during the burning of a cargo oil were also found in the accident of the tanker *Haven*, off Genova (Italy) (Douglas *et al.*, 1996), but no such detailed analysis has been performed before.

The data indicate that the whole area received these pyrogenic inputs, most probably originated in the tanker fire and conveyed by the black tide, because the concentrations showed a fair correlation with the petrogenic UCM (Table 1) ( $r = 0.942$ , excluding Station 5).

The average composition of the main parent components, as well as of their alkylated derivatives, shown in Fig. 5(a), are consistent with a mixed petrogenic-pyrolytic source. Station 5, the most heavily oiled, exhibited a higher predominance of the petrogenic phenanthrene and chrysene alkylated components. A relative decrease of the phenanthrene/chrysene ratio was observed along the observation period in this station, probably as a result of weathering processes (Fig. 5(b)), and consistently with the indices shown in Table 3. A clear input of pericondensed PAHs was found in Station 3 (Fig. 5(c)), and to some extent in Station 8, particularly in April, according to the main transport/deposition pathways of the fire plume. The pyrogenic source of these PAHs can be identified from specific isomeric ratios that have been defined for source recognition (Sicre *et al.*, 1987; Broman *et al.*, 1988; Yunker *et al.*, 1996; Burns *et al.*, 1997). Although this type of profiles are common in coastal sediments of urban/industrial areas and currently attributed to chronic atmospheric inputs (Broman *et al.*, 1988; Tolosa *et al.*, 1996), the present concentrations largely exceed the background levels found in the area (e.g., in Stations 1 and 2), thus being substantiated as originated in the accident.

Concentrations in the range of 3–450 ng of total parent PAHs per g of dry wt sediment were reported in subtidal sediments from the Arabian Gulf following the War (Readman *et al.*, 1992) and of 66–389 ng g<sup>-1</sup> in the Prince William Sound one year after the *Exxon Valdez* accident (Burns *et al.*, 1997). Baumard *et al.* (1998) considered that values of the same 12 PAHs in W Mediterranean coastal sediments below 100 ng g<sup>-1</sup> could be indicative of low pollution, whereas values higher than 1000 ng g<sup>-1</sup> corresponded to chronically polluted industrialized areas and harbours (see also Broman *et al.*, 1988 and ref. therein). In the case of the *Exxon Valdez* oil spill the sediment toxicity threshold was established in 4000 ng g<sup>-1</sup> of total pyrogenic PAHs. The sediment concentrations reported in Table 1 reflected a moderate pollution, although different from the aliphatic hydrocarbons, PAHs do not show a significant decrease in time.

## Conclusion

The variety of chemical markers existing in crude oils provide a good basis for fingerprinting marine oil spills. However, weathering processes, basically evaporation and biodegradation, may affect the corresponding patterns according to the molecular weight and chemical structure of the compounds considered. A general overview of the relative stability of the different markers found in the present study is shown in Fig. 6. Although the temporal scale can be largely dependent on the particular conditions of each site, it can be seen that the markers less sensitive to alteration are the polycyclic triterpanes and aromatized steranes. Chemical markers can be useful not only for source recognition but also for assessing the evolution of the oil spill in the environment.

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- Oceanography (IEO). Special thanks are due to J.J. Gonzalez (IEO, Vigo) for his assistance in field sampling.
- Aceves, M., Grimalt, J., Albaiges, J., Broto, F., Comellas, I. and Gassiot, M. (1988) Analysis of hydrocarbons in aquatic sediments. II. Evaluation of common preparative procedures for petroleum and chlorinated hydrocarbons. *Journal of Chromatography* **436**, 503–509.
- Albaiges, J. and Albrecht, P. (1979) Fingerprinting marine pollutant hydrocarbon by computerized gas chromatography–mass spectrometry. *International Journal of Environmental Analytical Chemistry* **6**, 171–190.
- Albaiges, J. (1980) Fingerprinting petroleum pollutants in the Mediterranean Sea. In *Analytical Techniques in Environmental Chemistry*, ed. J. Albaiges, pp. 69–81. Pergamon Press, Oxford.
- Barakat, A. O., Mostafa, A. R., Rullkotter, J. and Hegazi, A. R. (1999) Application of a multimolecular marker approach to fingerprint petroleum pollution in the marine environment. *Marine Pollution Bulletin* **38**, 535–544.
- Baumard, P., Budzinski, H. and Garrigues, Ph. (1998) Polycyclic aromatic hydrocarbons in sediments and mussels of the Western Mediterranean Sea. *Environmental Toxicology and Chemistry* **17**, 765–776.
- Bayona, J. M., Albaigés, J., Solanas, A. M., Parés, R., Garrigues, P. and Ewald, M. (1986) Selective aerobic degradation of methyl-substituted polyaromatic hydrocarbons in petroleum by pure microbial mixtures. *International Journal of Environmental Analytical Chemistry* **23**, 289–303.
- Bence, A. E., Kvenvolden, K. A. and Kennicutt II, M. C. (1996) Organic geochemistry applied to environmental assessments of Prince William Sound, Alaska, after the Exxon Valdez oil spill – a review. *Organic Geochemistry* **24**, 7–42.
- Broman, D., Colsmjo, A., Ganning, B., Naf, C. and Zebühr, Y. (1988) A multi-sediment-trap study on the temporal and spatial variability of polycyclic aromatic hydrocarbons and lead in an anthropogenic influenced archipelago. *Environmental Science and Technology* **22**, 1219–1228.
- Burns, W. A., Mankiewicz, P. J., Bence, A. E., Page, D. S. and Parker, K. R. (1997) A principal-component and least-squares method for allocating polycyclic aromatic hydrocarbons in sediment to multiple sources. *Environmental Toxicology and Chemistry* **16**, 1119–1131.
- Chosson, P., Connan, J., Dessort, D. and Lanaud, C. (1993) In vitro biodegradation of steranes and terpanes: a clue to understanding geological situations. In *Biological Markers in Sediments and Petroleum*, eds. J. M. Moldowan, P. Albrecht and R. P. Philp, pp. 320–349. Prentice-Hall, Englewood Cliffs, NJ.
- Douglas, G. S., Bence, A. E., Prince, R. C., McMillen, S. J. and Butler, E. L. (1996) Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environmental Science and Technology* **30**, 2332–2339.
- Grahl-Nielsen, O. and Lygre, T. (1990) Identification of samples of oil related to two spills. *Marine Pollution Bulletin* **21**, 176–183.
- Grantham, P. J., Posthuma, J. and DeGroot, K. (1980) Variation and significance of a North Sea core and various North Sea crude oils. In *Advances in Organic Geochemistry, 1979*, eds. A. G. Douglas and J. R. Maxwell, pp. 29–38. Pergamon Press, Oxford.
- Horstad, I., Larter, S. R., Dypvick, H., Aagaard, P., Bjornvik, A. M., Johansen, P. E. and Eriksen, S. E. (1990) Degradation and maturity controls on field petroleum heterogeneity in the Gullfaks field, Norwegian North Sea. *Organic Geochemistry* **16**, 497–510.
- Hostettler, F. D. and Kvenvolden, K. A. (1994) Geochemical changes in crude oil spilled from the Exxon Valdez supertanker into Prince William Sound, Alaska. *Organic Geochemistry* **21**, 927–936.
- Nunes, T. (1993) Special report from Spain: The 'Aegean Sea' oil spill. *ICES/CIESM Information* **22**, 7–8.
- Page, D. S., Foster, J. C., Fickett, P. M. and Gilfillan, E. S. (1988) Identification of petroleum sources in an area impacted by the Amoco Cadiz oil spill. *Marine Pollution Bulletin* **19**, 107–115.
- Peters, K. E. and Moldowan, J. M. (1993) *The Biomarker Guide*. Prentice-Hall, Englewood Cliffs, NJ, 345 pp.
- Porte C., Biosca, X., Pastor, D., Solé, M. and Albaigés, J. (2000) The Aegean Sea oil spill. II. Temporal study of the hydrocarbons accumulation in bivalves. *Environmental Science and Technology* **34**, 5067–5075.
- Readman, J. W., Fowler, S. W., Villeneuve, J. P., Cattini, C., Oregioni, B. and Mee, L. D. (1992) Oil and combustion-product contamination of the Gulf marine environment following the war. *Nature* **358**, 662–664.
- Sauer, T. C., Brown, J. S., Boehm, P. D., Aurand, D. V., Michel, J. and Hayes, M. O. (1993) Hydrocarbon source identification and weathering characterization of intertidal and subtidal sediments along the Saudi Arabian coast after the Gulf War oil spill. *Marine Pollution Bulletin* **27**, 117–134.
- Sicre, M. A., Marty, J. C., Saliot, A., Aparicio, X., Grimalt, J. and Albaigés, J. (1987) Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea. *Atmospheric Environment* **21**, 2247–2259.
- Simó, R., Grimalt, J. O. and Albaigés, J. (1997) Loss of unburned-fuel hydrocarbons from combustion aerosols during atmospheric transport. *Environmental Science and Technology* **31**, 2697–2700.
- Solé, M., Porte, C., Biosca, X., Mitchelmore, C. L., Chipman, J. K., Livingstone, D. R. and Albaigés, J. (1996) Effects of the 'Aegean Sea' oil spill on biotransformation enzymes, oxidative stress and DNA-adducts in digestive gland of the mussel *Mytilus edulis*. *Comparative Biochemistry and Physiology* **113C**, 257–265.
- Soler, M., Grimalt, J. O. and Albaigés, J. (1989) Distribution of aliphatic, aromatic and chlorinated hydrocarbons in mussels from the Spanish Atlantic coast (Galicia). An assessment of pollution parameters. *Chemosphere* **19**, 1489–1498.
- Tibbetts, P. J. C., Rowland, S. J., Tovey, L. L. and Large, R. (1983) Investigation of the sources of aliphatic hydrocarbons in the mussel *Mytilus edulis* from North Sea oil platforms by capillary GLC and CGCMS. In *Chemistry and Analysis of Hydrocarbons in the Environment*, eds. J. Albaiges, R. Frei and E. Merian, pp. 217–233. Gordon and Breach, New York.
- Tolosa, I., Bayona, J. M. and Albaigés, J. (1996) Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in north-west Mediterranean sediments: spatial and temporal variability, fluxes and budgets. *Environmental Science and Technology* **30**, 2495–2503.
- Wang, Z., Fingas, M. and Sergy, G. (1995) Chemical characterization of crude oil residues from an Arctic beach by GC/MS and GC/FID. *Environmental Science and Technology* **29**, 2622–2631.
- Wang, Z., Fingas, M. and Page, D. S. (1999) Oil spill identification. *Journal of Chromatography A* **843**, 369–411.
- Wardroper, A. M. K., Hoffmann, C. F., Maxwell J. R., Barwise, A. J. G., Goodwin, N. S. and Park, P. J. D. (1984) Crude oil biodegradation under simulated and natural conditions. II. Aromatic steroid hydrocarbons. *Organic Geochemistry* **6**, 605–617.
- Wolff, G. A., Preston, M. R., Harriman, G. and Rowland, S. J. (1993) Some preliminary observations after the wreck of the oil tanker Braer in Shetland. *Marine Pollution Bulletin* **26**, 567–571.
- Yunker, M. B., Snowdon, L. R., Macdonald, R. B., Smith, J. N., Fowler, M. G., Skibo, D. N., McLaughlin, F. A., Danyushevskaya, A. I., Petrova, V. I. and Ivanov, G. I. (1996) Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environmental Science and Technology* **30**, 1310–1320.