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Prestige Oil Spill. III. Fate of a Heavy Oil in the Marine Environment

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More than 200 oil samples were collected along the Northern Spanish coast, from December 2002 to December 2003, as part of the extensive monitoring program carried out by the Spanish Marine Safety Agency after the *Prestige* heavy oil spill (November 13, 2002). The GC FPD/FID and comprehensive GC \times GC/TOFMS sample profiles revealed the main characteristics of the oil residues. Chemical fingerprinting of the aliphatic and aromatic fractions by GC/MS was performed to determine the source of the oil as well as to follow its weathering at sea. The $(n\text{-C}_{13} + n\text{-C}_{14})/(n\text{-C}_{25} + n\text{-C}_{26})$, $n\text{-C}_{18}$ /phytane, and methylnaphthalene $[(N + N1)/N2]$ ratios were found to be useful for assessing the evaporation, biodegradation, and dissolution processes, respectively. Other indicators of more advanced degradation processes, including photo-oxidation, were unaltered, showing the low incidence of natural weathering processes on the spilled heavy oil 1 year after the accident. The survey also demonstrated the occurrence of continued discharges of ballast waters at sea and the need for a more stringent surveillance of the area, beyond accidental oil spills.

Introduction

Since the grounding of the *Torrey Canyon* in the English Channel in 1967, the history of oil tanker accidents has been populated from time to time by dramatic events (1, 2). Particularly, this type of accident has repeatedly endangered the Galicia coast (NW Spain) where on November 13, 2002, the 26-year-old single-hull oil tanker *Prestige*, carrying 77 000 tonnes of Russian heavy fuel oil (M-100 type), sprang a leak 28 nautical miles offshore, and on November 19, after 6 days of erratic towing, broke in two and sank in the Galicia Bank ($42^{\circ}15' \text{ N}$; $12^{\circ}08' \text{ W}$) (Figure 1). At the end, around 60 000 tonnes of oil was spilled, stranded at the shores of Galicia, Asturias, Cantabria, and Basque Country (3).

Although heavy oil spills have already occurred not far from this site, in the Brittany coast of France in 1980 (*Tanio*, 6000 tonnes) and 1999 (*Erika*, 15 000 tonnes), the importance of the *Prestige*, together with the large spreading of the oil and the long residence time in the sea, prompted an extensive survey of the region to determine defensibly the sources of the recovered oil and to assess the effect of weathering for better defining restoration strategies.

Once in the marine environment, any spilled oil undergoes a variety of physical, chemical, and biological processes (weathering), including evaporation, dissolution, emulsification, microbial degradation, photo-oxidation, adsorption to suspended matter, and deposition on the sea floor, that

determine its ultimate fate and impact on the environment. The key processes and their general trends are well-known (4), and a large number of models has been designed to predict the trajectories and behavior of spills in the sea and to evaluate their impact on aquatic organisms and habitats (5, 6). However, field data are always necessary to validate the existing information, which is lacking in the case of heavy oils.

Weathering processes produce changes in the chemical composition of the spilled oil that can be used to monitor the fate of the oil in the marine environment and to refine the diagnostic value of the source recognition indices (7). The most consistent methodology for oil spill characterization is based on the chemical fingerprinting approach, where a series of molecular markers can be profiled by GC/FID and GC/MS (8). In recent years, significant improvements have been made on this methodology in response to the oil spill investigation needs (9–11), including the application of multivariate statistical methods for data analysis (12).

Recently, a detailed chemical fingerprinting study of the *Prestige* heavy oil for assessing in vitro and field microbial degradation has been performed (13, 14). In the present work, we present the results of an extensive survey carried out by the Spanish Marine Safety Agency (SASEMAR) at the northern coast of Spain, between December 2002 and December 2003, following the oil spill. More than 200 oil samples were collected in the region (at sea, at the continental shelf, and stranded on the coast) and characterized by chemical fingerprinting of both the aliphatic and the aromatic fractions to obtain a comprehensive picture of the fate of the spill in the marine environment and, indirectly, to identify the molecular indicators to be used for oil source recognition under the possible occurrence of illegal discharges in the area after the spill.

Experimental Procedures

Chemicals. Dichloromethane, *n*-pentane, and *n*-hexane were obtained from Merck (SupraSolv) (Darmstadt, Germany). Solid-phase cartridges (SPE) of cyanopropyl-silica (SiO_2/CN , 1.0:0.5 g, 6 mL) were obtained from Interchim (Montluçon, France). Aliphatic hydrocarbon standards (*n*- C_{15} –*n*- C_{36} and pristane) were obtained from Fluka Chemie (Buchs, Switzerland), and a standard solution containing the 16 EPA PAHs (10 ng/ μL in cyclohexane) was purchased from Dr. Ehrenstorfer-Schäfers (Augsburg, Germany).

Sample Collection. Oil patches from the water surface and onshore began to be collected after the massive release of oil by different ships and ground teams that were permanently surveying the area after the accident. Sampling was focused not on the major oil paths or the recently oiled shorelines but on the slumps appearing at sea or arriving at the coast from time to time. Samples were collected with a metal spoon, placed in pre-cleaned amber glass jars, labeled with the collection date and location (latitude/longitude) and stored in a portable refrigerator for transport to the laboratory.

Chemical Fractionation and Analysis. The oil fractionation procedure has been reported elsewhere (15). Briefly, an aliquot (5–10 mg) of the oil residue was dissolved in *n*-pentane to precipitate the asphaltenes, and the evaporated residue was fractionated in a previously conditioned cyanopropyl-silica SPE column (6 mL of *n*-hexane). Two fractions were obtained by eluting with 4 mL of hexane (FI) and 5 mL of *n*-hexane-dichloromethane (50%) (FII) under positive pressure. Then, these two fractions containing the aliphatic and aromatic hydrocarbons, respectively, were

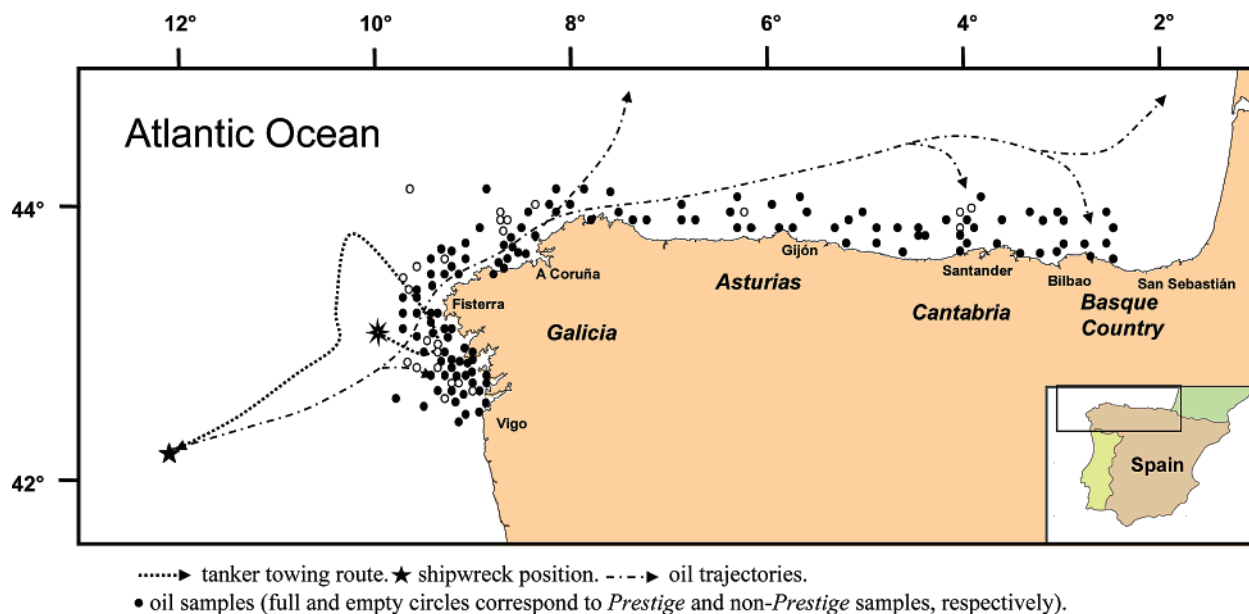


FIGURE 1. Sample locations along the Northern Spanish coast with indication of the main oil trajectories.

concentrated and analyzed by gas chromatography–mass spectrometry (GC/MS), using a Trace Thermo Finnigan system (Austin, TX) equipped with an AS 200 autosampler, a split/splitless injector, and a HP-5 MS capillary column of 30 m \times 0.25 mm i.d. \times 0.25 μ m film (J&W Scientific, Folsom, CA). The initial column temperature was held for 1 min at 70 $^{\circ}$ C, programmed at 15–150 $^{\circ}$ C/min (ramp 1), and then ramped at 6 $^{\circ}$ C/min (ramp 2) to a final temperature of 320 $^{\circ}$ C that was held for 10 min. The injector temperature was 310 $^{\circ}$ C, and the carrier gas was helium. Data were acquired in the full scan mode from 50 to 490 amu (2.4 scans/s) with 5 min of solvent delay and were processed by the X-calibur software.

The peak areas of the target analytes were measured in the reconstructed ion chromatograms at m/z 85 for aliphatics, m/z 217–218 for steranes, m/z 191 for hopanes, and the corresponding molecular ions for the aromatic hydrocarbons. Peak area measurements were performed in the linear range of the MS. The reproducibility, as RSDs of three replicates, was better than 3.0%.

Selected samples were analyzed on a dual GC FID/FPD system (Carlo Erba HRGC 5300 mega series gas chromatograph, Milan, Italy) and by comprehensive GC \times GC/TOFMS. In the first case, a 1:1 split was used at the end of the GC column (HP-5 MS) of 30 m \times 0.25 mm i.d. \times 0.25 μ m film (J&W Scientific). In the second case, the GC \times GC/TOFMS system consisted of a HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) coupled to a Pegasus II time-of-flight mass spectrometer (LECO, St. Joseph, MI), working at -70 eV, transfer line at 280 $^{\circ}$ C, ion source at 250 $^{\circ}$ C, and scanning from 70 to 800 m/z at 50 Hz. Thermal modulation was performed with a homemade longitudinally air modulated cryogenic system described elsewhere along with other methodological details (16). An orthogonal analytical system has been chosen, the first dimension consisting of a ZB-5 column (95% dimethyl/5% diphenyl polysiloxane) of 30 m \times 0.25 mm i.d. \times 0.25 μ m film (Phenomenex, Torrance, CA) and the second on a BPX50 column (50% phenyl-polyphenylene-siloxane) of 1 m \times 0.10 mm i.d. \times 0.10 μ m film (SGE, Ringwood, Victoria, Australia). The oven temperature was held at 70 $^{\circ}$ C (1 min) and raised to 360 $^{\circ}$ C at 5 $^{\circ}$ C/min, keeping the final temperature for 20 min. The modulation period was 5 s.

Results and Discussion

Oil Spill Identification. The fuel oil carried by the *Prestige* tanker was a heavy residue ($d_{15}^{20} = 0.993$ kg/L, $S = 2.28\%$) containing 22 and 49% of aliphatic and aromatic hydrocarbons, respectively, and 29% of resins and asphaltenes (13). Representative gas chromatograms of the collected samples are shown in Figure 2. Figure 2A shows the FID and FPD profiles of the *Prestige* fuel oil, the former characterized by a bimodal distribution of n -alkanes centered at n -C₁₄ and n -C₂₄ and extending up to at least n -C₄₀, typical of a petroleum residue diluted with a middle distillate, possibly to comply with the commercial specifications. The series of regular acyclic isoprenoids C₁₄ to C₂₀ is also present, with a pristane/phytane ratio of 0.9. The FPD profile is dominated by the benzo and dibenzothiophene series. On the other hand, Figure 2B shows different profiles, usually displayed by samples not corresponding to the *Prestige* oil, which exhibit high contents of n -alkanes of high molecular weight and a reduced unresolved complex mixture, characteristic of tank and bilge cleanings (17).

The oil source correlation of the collected samples was confirmed on the basis of some biomarker and PAH indices, proposed for differentiating sources of spilled oils (18–20). The *Prestige* oil is characterized by tetra- and pentacyclic terpane (27Ts and 29 $\alpha\beta$) and C-29 $\alpha\alpha$ S/R and $\beta\beta/\alpha\alpha$ sterane indices significantly below 50 (Table 1). These four parameters were found to be the most meaningful to highlight the *Prestige* oil pollution in sediment and biota surveys carried out in the region after the accident (21, 22). The ratios of C₂ and C₃ alkyl dibenzothiophenes and phenanthrene/anthracenes (D2/P2 and D3/P3), exhibiting relatively higher values (34–40) according to the S content of the oil, were also found rather conservative at low degradation rates (13).

The median values of the source indices corresponding to the collected samples along the whole sampling period are shown in Table 1. Stout et al. (20) reported that the analytical precision that can be expected in the calculation of these indices is generally high. A RSD variation <5% seems reasonable as a threshold for source confirmation. As shown in Table 1, this level of variation is well-attained in the analyzed samples, confirming their common origin. The higher variability of the pristane/phytane ratio could be attributed to the effect of weathering. Slight deviations of the

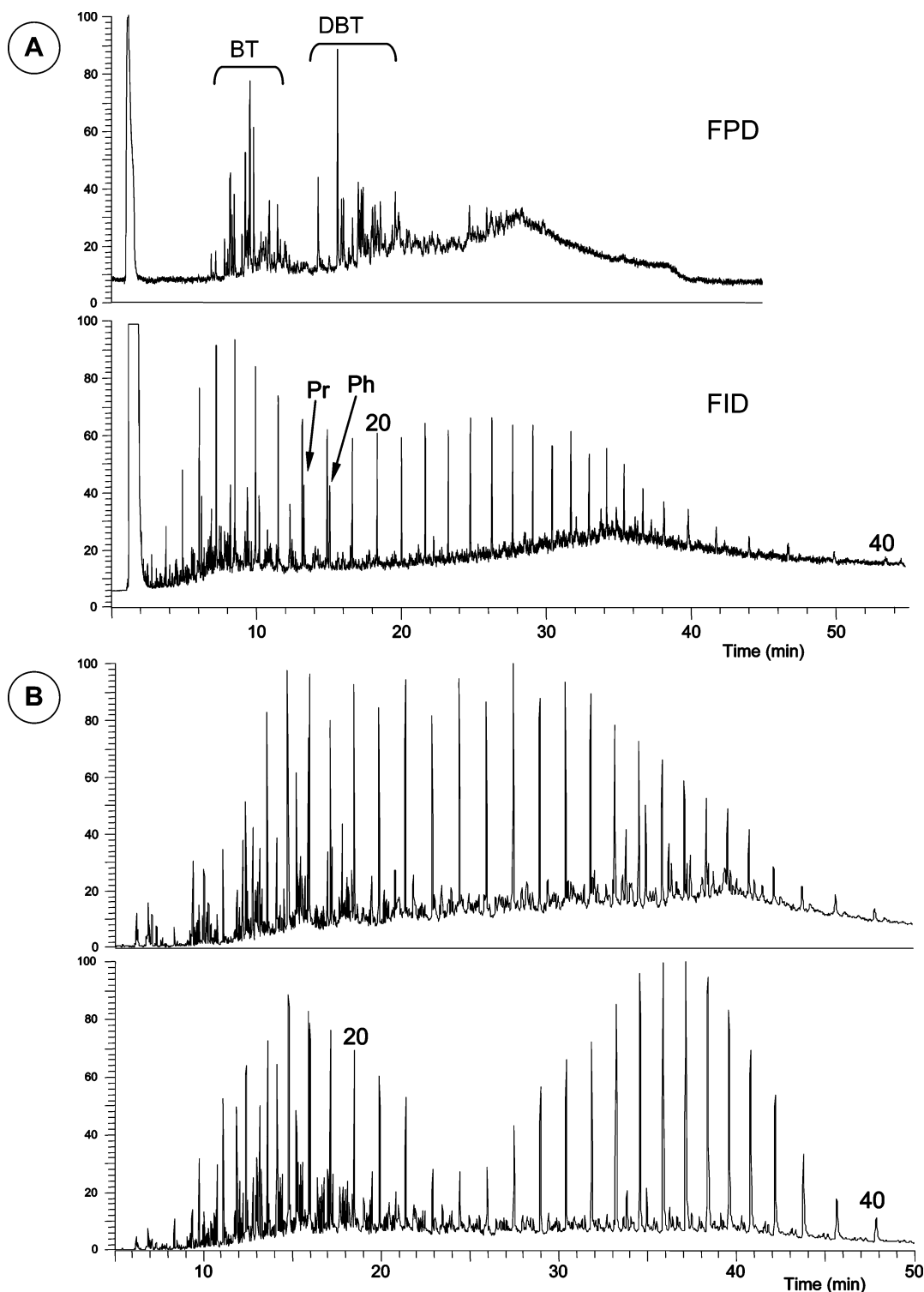


FIGURE 2. (A) GC FID/FPD profiles of the original *Prestige* oil. (B) Representative gas chromatograms of samples identified as tanker washing residues. BT and DBT: benzo- and dibenzothiophenes. Numbers over the peaks indicate the number of carbon atoms of *n*-alkanes.

other ratios from the values of the *Prestige* oil were also found, possibly due to weathering as well, as the trends are consistent with those observed in a field remediation study carried out in the area (14).

On the other hand, 17% of the total samples analyzed during this period did not match the *Prestige* oil, and most of these (52%) were found off A Coruña (Figure 1) during May to June 2003, corresponding to a common spill (Table 1). This demonstrates the continued occurrence of oil discharges at sea and the need for a more strict surveillance

of the areas supporting heavy tanker traffic, as has been documented for the Straits of Malacca (23).

Fate of the Oil. The fate and behavior of spilled oils in the environment depends on weathering processes since these cause considerable changes in their chemical and physical properties (18, 24, 25). The *Prestige* oil was drifting on the seawater surface for almost 1 year (since November 2002) (Figure 1), with final stranding on the coast, far away of the wreck, mainly during May to August 2003. Thus, it was highly exposed to major environmental parameters (e.g., water

TABLE 1. Diagnostic Ratios Used as Source Indicators for Oil Samples and Median Values Given for the *Prestige* Oil Residues ($n = 152$) and Other Samples Collected in the Area during May to June 2003 ($n = 15$)

diagnostic ion (m/z)	index	definition	structures	<i>Prestige</i> oil			other
				median values	% RSD	original oil ¹³	median values
113	Pr/Ph	pristane/phytane	Pr: 2,6,10,14-tetramethylpentadecane Ph: 2,6,10,14-tetramethylhexadecane	0.8	6.2	0.9	1.2
191	%27Ts	$100 \times Ts/(Ts + Tm)$	Ts: 18 α (H)-22,29,30-trisnorhopane Tm: 17 α (H)-22,29,30-trisnorhopane	23.1	3.7	22	48
191	%29 $\alpha\beta$	$100 \times 29\alpha\beta/(29\alpha\beta + 30\alpha\beta)$	29 $\alpha\beta$: 17 α (H),21 β (H)-30-norhopane 30 $\alpha\beta$: 17 α (H),21 β (H)-hopane	42.2	3.7	43	45
217	%27dia	$100 \times 27d(R + S)/[27d(R + S) + 27\beta\beta(R + S)]$	27d: 13 β (H),17 α (H)-diacholestane (20S and 20R) 27 $\beta\beta$: 14 β (H),17 β (H)-cholestane (20R and 20S)	35.1	3.1	36	43
217	%29 $\alpha\alpha$ S	$100 \times 29\alpha\alpha S/(29\alpha\alpha S + 29\alpha\alpha R)$	29 $\alpha\alpha$: 24-ethyl-14 α (H),17 α (H)-cholestane (20R and 20S)	48.7	2.9	45	52
217	%29 $\beta\beta$ RS	$100 \times 29\beta\beta(R + S)/[29\beta\beta(R + S) + 29\alpha\alpha(R + S)]$	29 $\beta\beta$: 24-ethyl-14 β (H),17 β (H)-cholestane (20R and 20S)	47.9	3.4	47	54
218	%27 $\beta\beta$	$100 \times [27\beta\beta(R + S)]/[27\beta\beta(R + S) + 28\beta\beta(R + S) + 29\beta\beta(R + S)]$	27 $\beta\beta$: 14 β (H),17 β (H)-cholestane (20R and 20S)	34.9	3.0	37	36
218	%28 $\beta\beta$	$100 \times [28\beta\beta(R + S)]/[27\beta\beta(R + S) + 28\beta\beta(R + S) + 29\beta\beta(R + S)]$	28 $\beta\beta$: 24-methyl-14 β (H),17 β (H)-cholestane (20R and 20S)	25.3	4.1	27	21
218	%29 $\beta\beta$	$100 \times [29\beta\beta(R + S)]/[27\beta\beta(R + S) + 28\beta\beta(R + S) + 29\beta\beta(R + S)]$	29 $\beta\beta$: 24-ethyl-14 β (H),17 β (H)-cholestane (20R and 20S)	38.9	1.9	36	43
212/206	D2/P2	$100 \times C2 - DBT/(C2 - DBT + C2 - P)$	DBT: dibenzothiophene	31.6	3.2	34	42
226/220	D3/P3	$100 \times C3 - DBT/(C3 - DBT + C3 - P)$	P: phenanthrene	38.4	2.0	40	44
212/256	D2/C2	$100 \times C2 - DBT/(C2 - DBT + C2 - C)$	C: chrysene	66.1	1.9	67	82
226/270	D3/C3	$100 \times C3 - DBT/(C3 - DBT + C3 - C)$		68.4	1.8	70	86

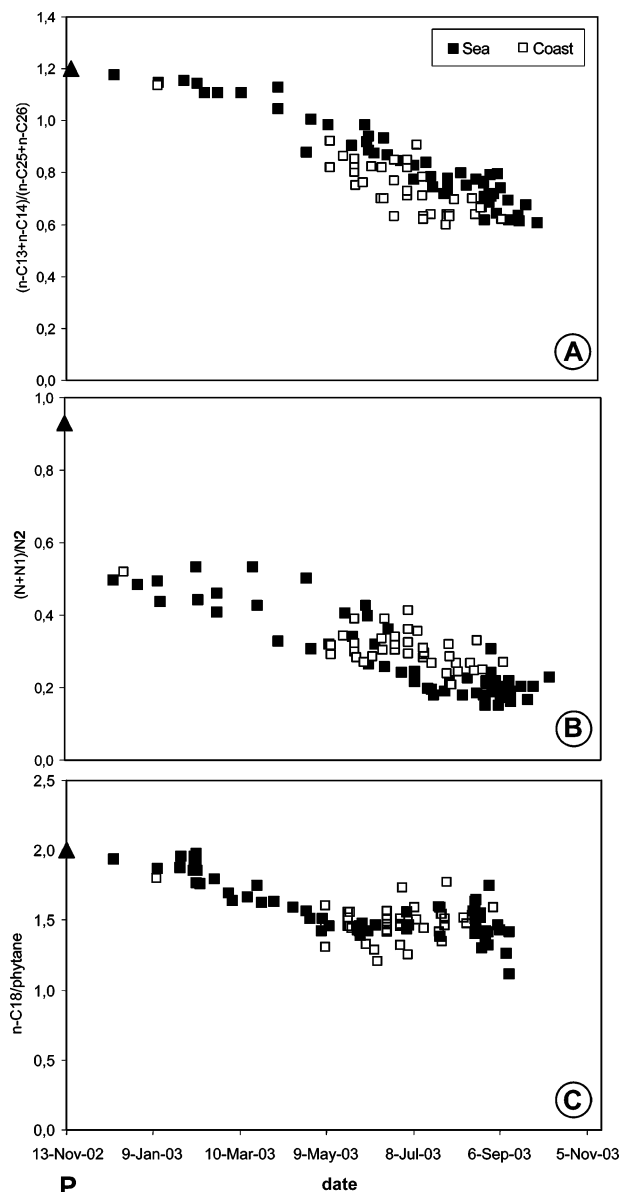


FIGURE 3. Weathering ratios of selected samples collected along the Northern Spanish coast. (A) *n*-Alkanes ($n\text{-C}_{13} + n\text{-C}_{14}/(n\text{-C}_{25} + n\text{-C}_{26})$). (B) Methylnaphthalenes $[(N + N1)/N2]$. (C) $n\text{-C}_{18}$ /Phytane. P: *Prestige* oil ratios.

flushing, aeration and aerosol partitioning, solar irradiation, etc.), and any weathering mechanism (e.g., emulsification, evaporation, dissolution, photo-oxidation, and biodegradation) could feasibly have occurred. Weathering processes are interlinked but can be monitored by the detailed analysis of compositional changes of the spilled oil.

Evaporation. A major change observed in the aliphatic fraction of the collected samples corresponding to *Prestige* oil residues was the gradual decrease of the *n*-alkanes in the $<n\text{-C}_{20}$ range, as illustrated in Figure 3, where the temporal evolution of the defined ratio $(n\text{-C}_{13} + n\text{-C}_{14})/(n\text{-C}_{25} + n\text{-C}_{26})$ has been plotted. The loss of light hydrocarbons by evaporation is the primary cause of the rapid volume reduction of the spilled oil, with the subsequent increase of its viscosity and density and the formation of stable oil–water emulsions. In general, the collected samples at sea were in the form of emulsions containing 40–50% water, an aspect that was to be taken into account in assessing the amounts of oil recovered. On the basis of laboratory evaporative studies and the values estimated by the oil depletion equation

established by Douglas et al. (26), a maximum of approximately 5% of the oil would only be lost by evaporation, due to its heavy nature.

Usually, the rate of *n*-alkane evaporation at sea is rapid in the first weeks after the spill and subsequently slows down until it becomes negligible (27). However, in the present case, a steady depletion trend was observed during the whole period, probably due to the patchy nature of the spilled product (Figure 3A). Moreover, it is interesting to notice that samples collected at the coast (beaches and rocky shores) showed higher depletion rates than open seawater samples, probably as a result of their exposure to higher temperatures (evaporation) or to the indigenous hydrocarbon degrading bacteria present in the oil impacted shorelines (biodegradation) (14).

Dissolution. Some of the oil components that are subject to evaporation, namely, the low molecular weight aromatic hydrocarbons, can also dissolve into the water column, largely influenced by the hydrodynamic conditions of the surface waters. Thus, evaporation and dissolution are competitive processes. Although the volume loss of spilled oil by dissolution can be negligible from a practical perspective, it can be significant from an ecotoxicological standpoint.

The most important change observed in the aromatic fraction of the collected samples was the decrease of the relative abundance of naphthalene to below detection limits. GC \times GC is a useful technique for characterizing this fraction due to its enhanced orthogonal chromatographic resolution and to the obtained chemical ordering of the compounds (28). In this case, chemical ordering is based on the aromaticity degree in the second dimension and on the alkylation degree in the first dimension. The GC \times GC/TOFMS profile of the original fuel shown in Figure 4 clearly resembles that obtained by GC/MS of the aromatic fraction. In turn, the profile of one of the collected samples is highly depleted in naphthalene and its low alkylated derivatives. This trend is consistent with that anticipated for dissolution. In fact, the hydrocarbon profile found in the *Prestige* fuel oil water accommodated fraction (WAF) was largely dominated by alkylnaphthalenes, although decreased with the alkyl substitution (29). Around 30% of naphthalene in the original oil was dissolved in water, whereas $C_1\text{--}C_2\text{--}$, and $C_3\text{--}$ derivatives were 12, 5, and 2.4%, respectively. Overall, 3.4% of the fuel oil aromatic fraction was found in the WAF. As a result, the oil residue was depleted in the same components, which account for less than 2% of the original oil. The relative loss of naphthalene and methylnaphthalenes with respect to $C_2\text{--}$ naphthalenes, defined by the $[(N + N1)/N2]$ ratio, was particularly evident during the initial phase of the spill, as illustrated in Figure 3B.

Biodegradation. Biodegradation originated the compositional changes dominated by the molecular structure of the hydrocarbons. In this respect, *n*-alkanes are degraded at faster rates than acyclic isoprenoids (30), and the early effect of microbial degradation is currently monitored by the $n\text{-C}_{17}$ /pristane and $n\text{-C}_{18}$ /phytane ratios. Figure 3C indicates a delay of about 2 months before the degradation of *n*-alkanes is evidenced, and after a certain progression does not go further for the rest of the year. It is possible that the limited extension of degradation can be due to the fact that the oil is in the form of compact tar residues, which are only available to bacteria at the surface. Other series of long chain *n*-alkyl derivatives eluting in the same fraction, namely, *n*-alkylcyclohexanes and benzenes, were also unaltered, indicating the reduced weathering of the oil.

The general biodegradation pattern of the aromatic hydrocarbons indicates that biodegradation decreases with the increase of alkylation. However, microbial degradation was demonstrated to be isomer specific (7, 31, 32), so that when partial biodegradation of alkyl PAHs occurs, the relative

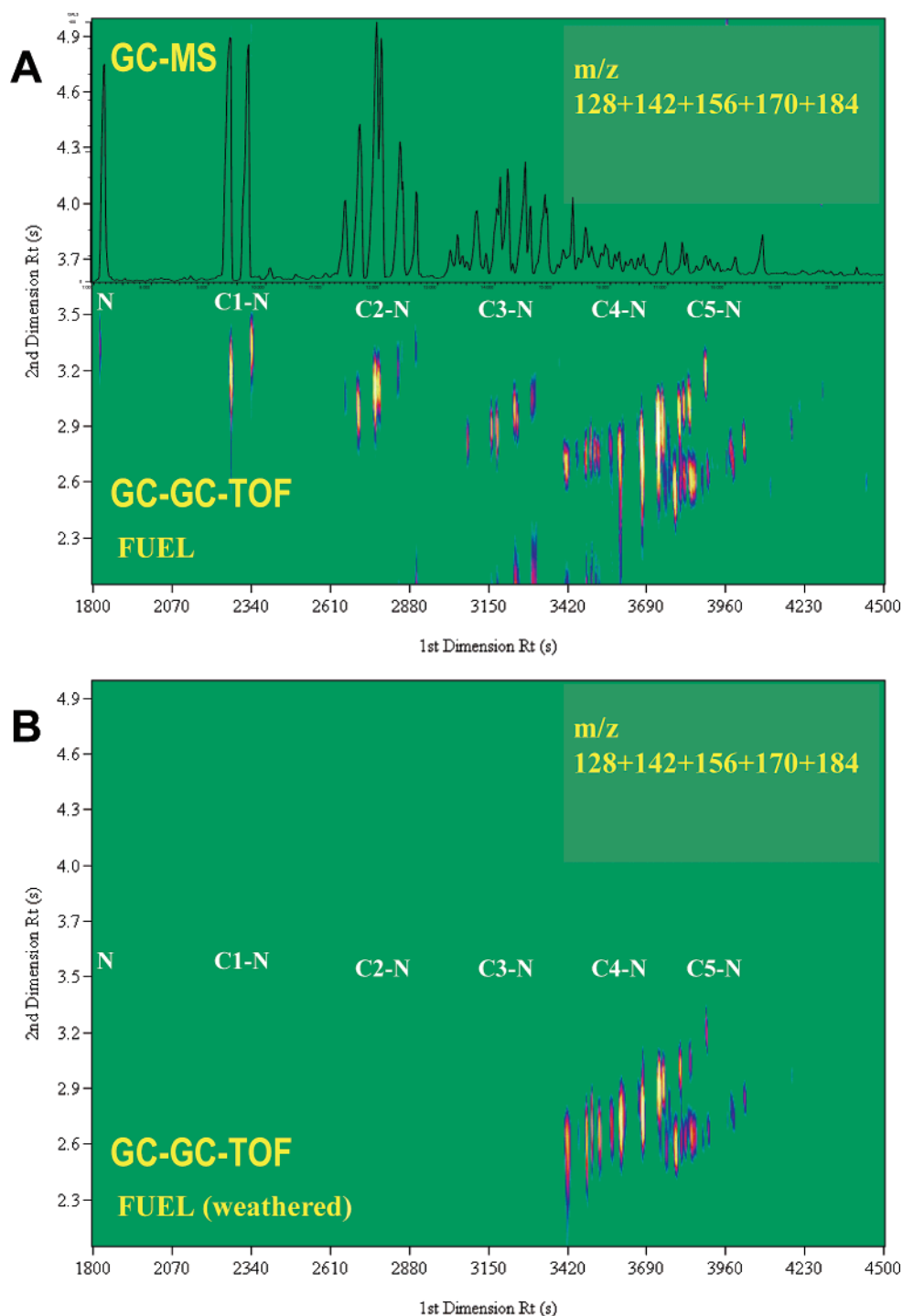


FIGURE 4. Mass fragmentogram of alkyl naphthalenes (m/z 128 + 14n) and the corresponding GC \times GC/TOFMS contour plot of the *Prestige* oil (A) and one field sample (B).

losses of different isomers may provide useful indicators of the extent of the oil biodegradation. Early indicators of biodegradation have been reported within methylphenanthrenes (MP) and dibenzothiophenes (MD), where 9-MP and 4-MD appeared to be more resistant than the others (18, 31). The plots of relevant ratios shown in Figure 5 indicate that only the 1M/9P ratio seems to exhibit a slight decreasing trend, paralleling that of the *n*-alkanes (Figure 3C). Therefore, it appears that although biodegradation might have played a role in the oil weathering, it is not dominant, as already has been observed in other oil spills (27, 33).

On the other hand, C_2 and C_3 alkyl homologues of dibenzothiophene (D2 and D3) and chrysene/benzo[*a*]-

anthracene (C_2 and C_3) were found to be useful for characterizing the weathering of the spilled oil in sediments (19). The corresponding ratios for the present case (D2/ C_2 and D3/ C_3) were rather conservative (Table 1), suggesting the low alteration of the oil and providing useful source indices.

Photo-oxidation. Opposite to biodegradation, there is evidence that alkyl substituted aromatic hydrocarbons are photochemically oxidized at a faster rate than the parent compounds. In a laboratory experiment, Garret et al. (34) found that C_3 -phenanthrenes and chrysenes are approximately 50% degraded, whereas the parent compounds appear to be quite resistant. Therefore, the ratios between C_3 and

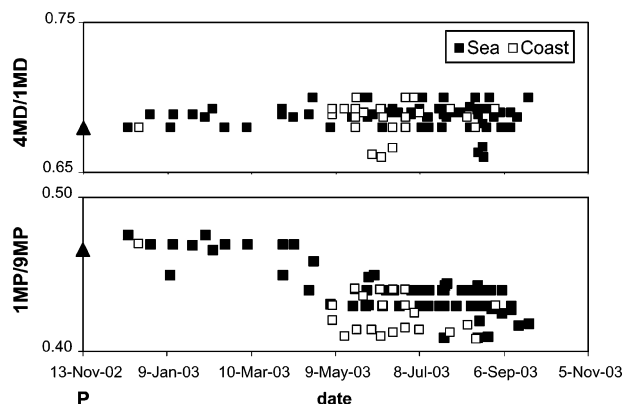


FIGURE 5. Methylphenanthrene (MP) and dibenzothiophene (MD) ratios of the *Prestige* oil (P) and selected samples collected along the Northern Spanish coast.

parent derivatives of phenanthrene (P) and chrysene (C) could be adequate indicators of the relative incidence of this weathering process. However, microbial degradation results in the depletion of unsubstituted species relative to their alkylated homologues, so that it is likely that concurrent photo- and biodegradation may give rise, at moderate levels, to profiles similar to those of the fresh oil.

The corresponding values of the collected samples did not exhibit any noticeable temporal trend. Therefore, taking into account that, as shown previously, biodegradation of the samples was rather limited, this may indicate that photo-oxidation has not been significant at sea during this period.

In summary, the present data show a high persistence of the spilled heavy oil at sea, 1 year after the accident, with very low incidence of the natural weathering process. These are only slightly enhanced when the oil was stranded on the shorelines, thus stressing the need for mechanical removal from the sea surface and the coastal areas, as well as for the application of bioremediation techniques, which have been found to be appropriate in this case (14). On the other hand, the incidental occurrence of oil samples from other sources in certain areas affected by the spill strongly supports the need for a continued surveillance of the coastal areas holding heavy tanker traffic.

Acknowledgments

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