Marine Pollution Bulletin 60 (2010) 1667–1673

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Phase distribution of hydrocarbons in the water column after a pelagic deep ocean oil spill

Saioa Elordui-Zapatarietxe[a], Antoni Rosell-Melé[a,b,c,*], Núria Moraleda[a], Imma Tolosa[d], Joan Albaigés[e]

[a] Institute of Environmental Science and Technology, Universitat Autònoma de Barcelona, Bellaterra 08193, Catalonia, Spain
[b] College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, United States
[c] ICREA, Passeig Lluís Companys, 23, Barcelona 08010, Catalonia, Spain
[d] Marine Environment Laboratories, International Atomic Energy Agency, 4 quai Antoine 1er, MC 98000, Monaco
[e] Institute of Environmental Assessment and Water Research, CSIC, Jordi Girona 18, Barcelona 08034, Catalonia, Spain

ARTICLE INFO

Keywords:
Prestige
Northeastern Atlantic
Deep sea oil spill
PAHs
Dissolved phase
Hydrocarbons

ABSTRACT

Spills from wrecks are a potential major source of pollution in the deep ocean. However, not much is known about the fate of a spill at several kilometers depth, beyond the oceans continental shelves. Here, we report the phase distribution of hydrocarbons released from the wrecks of the *Prestige* tanker, several years after it sank in November 2002 to depths between 3500 and 3800 m. The released oil reached the surface waters above the wrecks without any signs of weathering and leaving an homogenous signature throughout the water column. At depths of several kilometers below the sea surface, the occurrence and spread of the deep sea oil spill could be evaluated better by quantifying and characterizing the dissolved hydrocarbon signature, rather than just the investigation of hydrocarbons in the suspended particulate matter.

1. Introduction

Accidental marine pollution in the pelagic ocean is usually associated with oil tanker spills, but in recent years the scientific community has become more aware of the potential pollution that could originate from shipwrecks (Girin, 2004). There are thousands of sunken ships worldwide containing an estimated 2.5–20.4 million tonnes of oil (Michel et al., 2005), which represents between 180 and 1500 times the oil spilled annually at surface when considering an annual spill rate of 14,000 Tn year^{-1} for the period 2000–2007 (ITOPF, 2009). Almost two thirds of the potentially polluting wrecks are concentrated in the South Asian Pacific (35%) and the North Atlantic Ocean (27%), and correspond to vessels that sank decades ago, mainly during World War II (Michel et al., 2005).

Wrecks are likely to release their cargo when they eventually corrode past a certain stage, and the removal of the oil from shipwrecks before a large scale spill occurs has been encouraged by different sectors (Basta and Kennedy, 2004). This leads to the need to evaluate the individual risk posed by each sunken vessel. However, to date little is known about the fate of a deep sea oil spill, particularly beyond the continental shelf where many of the wrecks are found and existing dispersion models of hydrocarbons are not likely to be applicable to spills that have been occurring over long time scales of months or years in the deep sea (e.g. Turrell, 1994). Potentially, some of the oil may remain at great depth, or part of the plume could be trapped in the water column below the thermocline (Daling et al., 2003). A further difficulty is to determine the exact location of a shipwreck in the deep ocean seafloor.

To shed some light on this issue we have investigated the wrecks of the *Prestige* oil tanker as a case study of an oceanic deep spill. On November 13, 2002, the vessel broke in two 240 km off NW Spain, sunk at 3565 m (the stern) and 3800 m (the bow) with about 58,000 tonnes of heavy fuel oil (Albaiges et al., 2006), and leaking from several cracks in the structure. Most of the cracks were sealed in 2003, and the vast majority of the oil that still remained in one of the wrecks was allegedly completely removed in summer 2004 as reported widely in the media. In March 2006, an oceanographic expedition was undertaken to the area of the *Prestige* shipwreck and at the sea surface, near the sinking area, iridescent slicks were observed, but the severe weather did not allow their sampling. Another cruise was undertaken to the sinking area in October 2006, and the occurrence of oil slicks of different thickness and size, and small tar balls was observed. Excellent weather conditions facilitated their sampling as well as a detailed sampling of the water column near the wrecks. In this paper we discuss the origin of the oil slicks found in the ocean surface above the *Prestige* shipwrecks, and the implications for future studies of deep sea spills.

---

* Corresponding author at: Institute of Environmental Science and Technology, Universitat Autònoma de Barcelona, Bellaterra 08193, Catalonia, Spain. Tel.: +34 541 737 9867; fax: +34 541 737 2064.
E-mail address: antoni.rosell@uab.cat (A. Rosell-Melé).

0025-326X/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2010.07.001

2. Experimental section

2.1. Sampling

In October 2006, oil was taken from slicks floating on the ocean surface by means of aluminium webs from the bow of a dinghy. These were wrapped in aluminium foil and frozen until analysis. Between 10 and 20 L of seawater were collected with Go-Flo and Niskin bottles at five depths, corresponding to the main water masses (Ruiz-Villarreal et al., 2006) at the location of the sinking of the *Prestige* (42° 12,487′ N, 12° 03,121′ W): 5 m (superficial waters, SW), 400 m (Eastern North Atlantic Central Water, ENACW), 1000 m (Mediterranean Water, MW), 2000 m (Labrador Sea Water, LSW), bottom (North Atlantic Deep Water, NADW). The seawater was stored in high density polyethylene containers and immediately carried to the ship laboratory. The filtration of the suspended particulate matter (SPM) and extraction of the dissolved phase (DP) were carried out consecutively by placing a glass microfiber filters (GMF) (Millipore, Cork, Ireland) on top of a C_{18} bonded silica (ENVI-Disk) (Supelco, Bellefonte, PA, USA) extraction disks in 47 mm diameter filter holders. Two PVC manifolds with three cups each (Millipore) were connected to two vacuum pumps, which allowed parallel filtration of six different samples reducing the seawater storage time and thus avoiding the redistribution of contaminants between the DP and SPM (Wolska et al., 1999). After filtration of up to 10 L of seawater, both the GMF and the extraction disk were replaced to avoid analyte breakthrough. Conditioning of the disks was carried out by rinsing them while in the filter holder sequentially with 10 mL of hexane, 10 mL of methanol and seawater for 3 min each, and then elimination of the solvent by connecting the filter holder to the vacuum.

2.2. Analytical procedure for oil samples

Samples of the oil slicks were fractionated using a glass column packed with 6 g of silica (40–60 mesh, Acros Organics, Geel, Belgium), 6 g of aluminium oxide (70–230 mesh, Merck, Darmstadt, Germany), and 2 g of sodium sulphate (>99%, Merck). Between 10 and 20 mg of the oil sample were dissolved in hexane, spiked with a solution of anthracene-d_{10} (Acros Organics) and pyrene-d_{10} (Sigma–Aldrich, St. Louis, Mo, USA) in isooctane and added at the top of the column as internal standards. The aliphatic hydrocarbons were eluted in the first fraction with 17 mL of hexane, and the aromatic hydrocarbons with 20 mL of hexane:dichloromethane (2:1, v/v). The original oil carried by the *Prestige* was fractionated using solid phase extraction as described elsewhere (Alzaga et al., 2004). The recovered fractions were concentrated until near dryness, before further analysis by gas chromatography–mass spectrometry (GC–MS).

2.3. Compound specific carbon isotope analysis ($\delta^{13}C$)

Measurements were performed using a Hewlett–Packard HP5890 GC coupled to a Finnigan MAT Delta C isotope-ratio mass spectrometer (IRMS) via a combustion furnace heated at 940 °C. A 2 μL aliquot of the aliphatic fraction in isooctane was injected via an on column injector onto a capillary Agilent (Santa Clara, CA, USA) HP5 column (60 m × 0.32 mm i.d.x 0.25 mm film thickness). The GC oven temperature was programmed as follows: initial temperature was set at 60 °C and held for 2 min, then raised to 100 °C at a rate of 10 °C min^{-1}, then to 310 °C at 4 °C min^{-1} and held at this temperature for 43 min. Samples were analyzed in triplicate. Before and after each analysis pulses of reference CO_2 were bled into the source in order to calibrate it relative to Pee Dee Belemnite. Between samples, a standard mixture composed of three *n*-alkanes with known isotope composition was injected to control the performance of the instrument.

2.4. Analytical procedure for seawater samples

Analysis of the hydrocarbons in the SPM was performed using microwave assisted extraction on a CEM-MARS 5 system (Matthews, NC, USA), equipped with Greenchem pressure vessels with 14 Teflon® vessels (100 mL). Freeze dried filters were inserted uncut in the vessels and spiked with anthracene-d_{10} and pyrene-d_{10} as recovery standards. After adding 15 mL of trace analysis grade (Suprasolv, Merck) hexane:acetone 1:1 (v/v) and a magnetic agitation bar the vessel was sealed. The extraction was carried out at 1200 W and 115 °C for 2 min, and left to cool to below 35 °C before they were opened.

Organic extracts were fractionated by column chromatography using 1 g of silica and 1 g of alumina, previously activated at 110 °C and deactivated with 5% of milli-Q water (w/w). The first fraction (containing aliphatic hydrocarbons) was collected eluting with 2.5 mL of hexane, and the second fraction (aromatic hydrocarbons) eluting with 10 mL of hexane:dichloromethane 2:1 (v/v). The extracts were concentrated by rotary evaporation, and then with a gentle stream of N_2 to near dryness.

C_{18} extraction disks were processed in a glass filter holder where they were soaked with 10 mL of methanol for 3 min, before connecting the holder to vacuum to elute and collect the solvent. The same process was repeated with 10 mL of dichloromethane and finally with 10 mL of hexane. These last two fractions were collected together. The methanol fraction was extracted three times with 2 mL of hexane in a separatory funnel, and the hexane combined with the dichloromethane/hexane fraction. Recovery standards were added to the apolar extracts before fractionation by flash chromatography as described above for the SPM.

2.5. Instrumental analysis

The quantification of hydrocarbons was carried out in a Konik HRGC 4000B GC coupled to a Konik MS Q12 mass spectrometer (Sant Cugat del Vallès, Spain). The GC was fitted with a capillary Agilent DB5 MS column (30 m × 0.25 mm, I.D. × 0.25 μm film thickness). The initial column temperature was held for 1 min at 70 °C, then programmed to 320 °C at a rate of 6 °C min^{-1} and kept at this temperature for 10 min, for the aromatic hydrocarbons, while the program was slightly modified for the aliphatic hydrocarbons, being the temperature program from 70 to 150 °C at 15 °C min^{-1} and from 150 °C to 320 °C at 6 °C min^{-1}. Helium was used as carrier gas at a constant flow of 1.5 mL min^{-1}. The injection was made in the split/splitless mode at 300 °C. Data were acquired in the selective ion monitoring (SIM) mode at a 70 eV and processed by the Konikrom Data Reduction software. Quantification was performed calculating the response factors for each compound at different concentrations, correcting the values with the internal standards. A solution of 17 polyaromatic hydrocarbons (PAHs) containing acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, perylene, phenanthrene and pyrene purchased from Dr. Ehrenstorfer (Augsburg, Germany) were used to calculate the response factors for PAHs, and a mixture of C_{16}, C_{20}, C_{28}, C_{32} and C_{36} *n*-alkanes obtained from Sigma–Aldrich for aliphatic hydrocarbons.

2.6. Quality assurance and quality control (QA/QC)

Field blanks were obtained from milli-Q water that was transferred to the polyethylene containers, and filtered and extracted

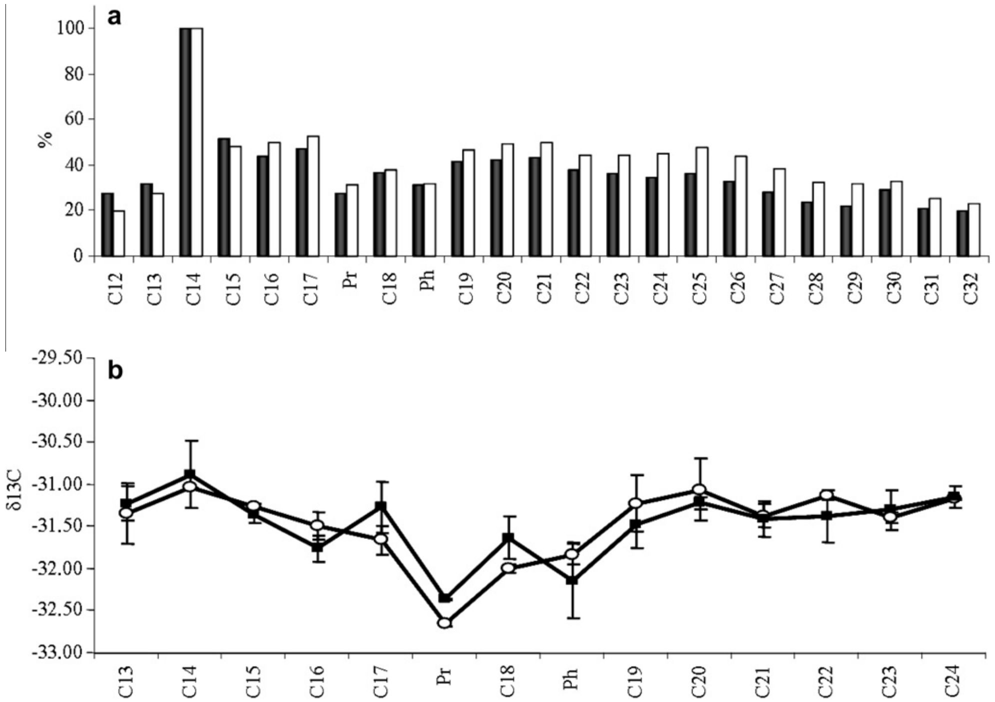

Fig. 1. Comparison of the chemical and isotopic signatures of the fuel oil found above the wreck in October 2006 with the one originally carried by the tanker. (a) C_{12}–C_{32} *n*-alkane distribution in the *Prestige* fuel oil (black squares) and the collected oil slicks (white dots). (b) Isotopic composition of the C_{13}–C_{24} *n*-alkanes from the *Prestige* fuel oil (black), and from the collected oil slicks (white).

in the same way as the field samples. For each extraction batch in the laboratory analyses a procedural blank and a filter blank were performed.

Recoveries of the analyses were between 67% and 103% for the GMF and the reported values were corrected for their recoveries. Detection limits for each hydrocarbon were calculated based on the average concentration of the compound in the field blanks plus three times the standard deviation. They ranged from 0.01 ng L^{-1} to 0.14 ng L^{-1} for the PAHs, and 0.05 ng L^{-1} to 1.7 ng L^{-1} for the aliphatic hydrocarbons.

Spiking experiments were carried out in the laboratory to determine the suitability and efficiency of C_{18} extraction disks to preconcentrate PAHs from the water. Some 8 L of milli-Q water were poured in glass flasks and spiked with a mixture of 17 PAHs (see previous section; 100 ng L^{-1} per compound). The bottles were covered and left 48 h at room temperature. After this time the water was extracted as described in the previous section. Triphenylamine (Sigma–Aldrich) was used as an injection standard and response factors were calculated relative to this compound. Recuperation of individual PAHs ranged from 58% to 90%, decreasing according to the molecular weight of the compound as previously observed in similar experiments (Michor et al., 1996), and illustrating the suitability of the disks to extract dissolved PAHs from the seawater.

3. Results and discussion

3.1. Origin of the oil slicks

The presence of oil slicks above the *Prestige* wrecks does not constitute proof *per se* that they are the origin of any spillage, as water masses can potentially transport oil away from its source. Consequently, several complementary approaches were used to verify that the oil collected in the sea surface in October 2006 in fact originated from the *Prestige* wrecks. The *n*-alkanes and isoprenoids of the oil slicks displayed a bimodal distribution that matched well that of the original *Prestige* fuel oil (Fig. 1a). The molecular marker diagnostic ratios (Table 1) of some of these samples were also practically identical to those of the original fuel oil. Overall the oil did not show signs of biodegradation despite the time past since the incident. Finally, the δ^{13}C values of the individual *n*-alkanes of the slicks, used as a complementary tool to confirm the origin of the oil found at sea, also agreed well with those from the original *Prestige* oil (Fig. 1b).

We are thus able to ascertain that the oil from the slicks was the one carried by the *Prestige*, and that their presence in the ocean was most likely related to a deep sea oil spill, or leak, from the wrecks. Given the absence of any weathering in the slicks chemical signature, as indicated by the unchanged biomarker ratios in Table 1, we ruled out that the origin of the slicks found in the sea surface was from the remobilization of the oil in the ocean floor.

Table 1
Biomarker indices measured in three samples (A, B and C) from oil slicks collected on 30/10/2006 above the location of the *Prestige* wrecks (A: 42° 12,14′ N, 12° 05,0′ W, B: 42° 12,49′ N, 12° 03,12′ W, C: 42° 12,49′ N, 12° 03,12′ W). “*Prestige* values” drawn from mean values of 200 samples from the *Prestige* fuel oil collected during 2003.

	A	B	C	*Prestige*
n-C_{17}/Pristane	–	1.7	1.6	1.5
n-C_{18}/Phytane	–	1.6	1.5	1.4
Pristane/Phytane	0.8	0.9	0.9	0.9
%27Ts[a]	24	22	24	23
%29αβ[a]	46	46	46	44
%32αβ S[a]	57	58	57	59
%27d[a]	33	35	33	35
%29αα S[a]	52	50	54	49
%29ββ (R + S)[a]	52	47	49	48
%27ββ[a]	35	34	35	35
%28ββ[a]	25	24	25	25
%29ββ[a]	40	41	40	40

[a] Indices defined elsewhere (Diez et al., 2007).

3.2. PAH in the suspended particulate matter

The hydrocarbon concentrations in the water column of the *Prestige* sinking area in March and October 2006 were substantially different (Fig. 2). The SPM ΣPAHs (sum of individual PAHs concentrations) in March were between 0.3 and 2.1 ng L^{-1}. These values are not far from the background reference concentration established for the area of the NE Atlantic (0.7–1.6 ng L^{-1}, sum of 15 parent PAHs) (OSPAR_Commission, 2004). In contrast, SPM ΣPAHs levels found in October (308–1218 ng L^{-1}) were three orders of magnitude higher than in March 2006, well above the background levels. These values are similar to the near shore levels determined in December 2002 off Costa da Morte (0.29–5.8 μg L^{-1}, sum of 25 PAHs), in the most affected coastal areas by the *Prestige* oil spill (González et al., 2006).

In both sampling periods the vertical profile of SPM ΣPAHs was characterized by the highest hydrocarbon concentration in the most superficial (5 m) and the deepest (3706 m) samples, and a decrease in the abundance of the mid-depth layers. The higher concentrations at the upper layers are not surprising given the presence of oil slicks in the sea surface. Near the ocean floor, high concentrations may be due to secondary contamination of the water body due to sediment resuspension (Nemirovskaya, 2007), or to the nearby oil source. The main difference exhibited by the two periods was that in March, the maximum abundance was found at 5 m depth and doubled the concentration of the bottom layer, while in October the concentration in the deepest water mass triplicated the one near the surface. This seems to confirm the occurrence of a major deep sea oil spill coming from the *Prestige* wrecks in October, but not in March. Alternatively, the exact location of the retrieval of the samples from the deep sea during the two periods is unconstrained because the research vessel used, the *Cornide de Saavedra*, did not have a dynamical positioning system, and drifted at different speeds in each cruise. Consequently, the highest concentrations of hydrocarbons observed at depth in October in comparison to March could be related to the proximity of the sampling device to the spill source.

In general, the relative distribution of the SPM PAHs was quite uniform in the water column. Naphthalene and its alkyl derivatives represented 95–99% of the total mixture (Fig. 3). The relative distribution of the individual PAHs in the SPM also exhibited divergences during the two sampling periods. In March, the mixture was dominated by phenanthrene and methylphenanthrenes, followed by naphthalene and its alkyl derivatives. In fact, the relative importance of the latter group was higher at 5 m and 3706 m depth, in accordance with the maximum concentration of the ΣPAHs. Compounds with more than five rings were below the detection limit in all samples. In October, the SPM PAH mixture is also clearly dom-

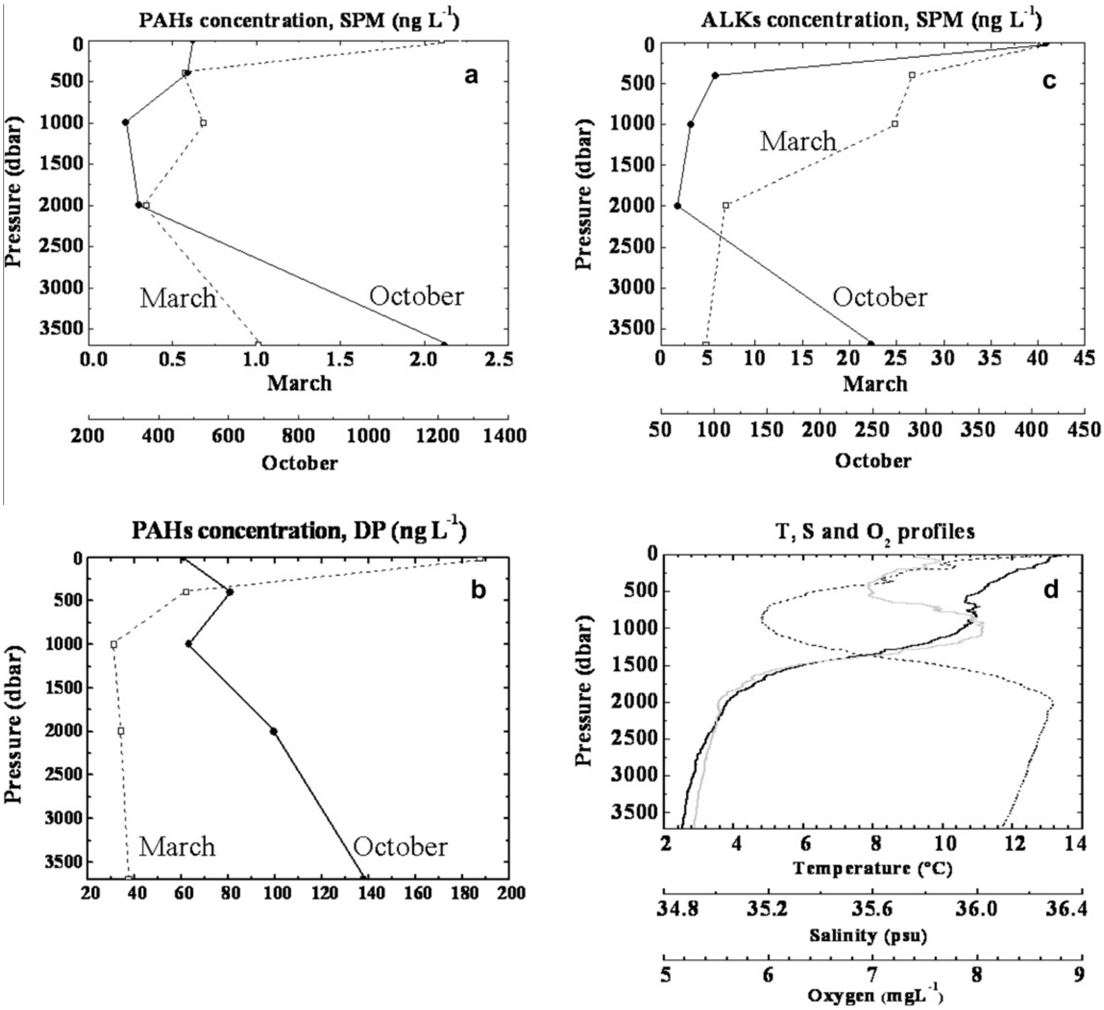

Fig. 2. Total concentration of PAHs (a and b) and *n*-alkane (c) distributions in the suspended particulate matter (SPM) and dissolved phase (DP) in the water column above the *Prestige* wrecks in March (white squares, dashed line) and October (black dots, solid line) 2006. Temperature (black line), salinity (grey line) and oxygen concentration (dotted line) profiles registered in the area in October (d) are also plotted to illustrate the variable hydrography of the water column in the area of the sinking.

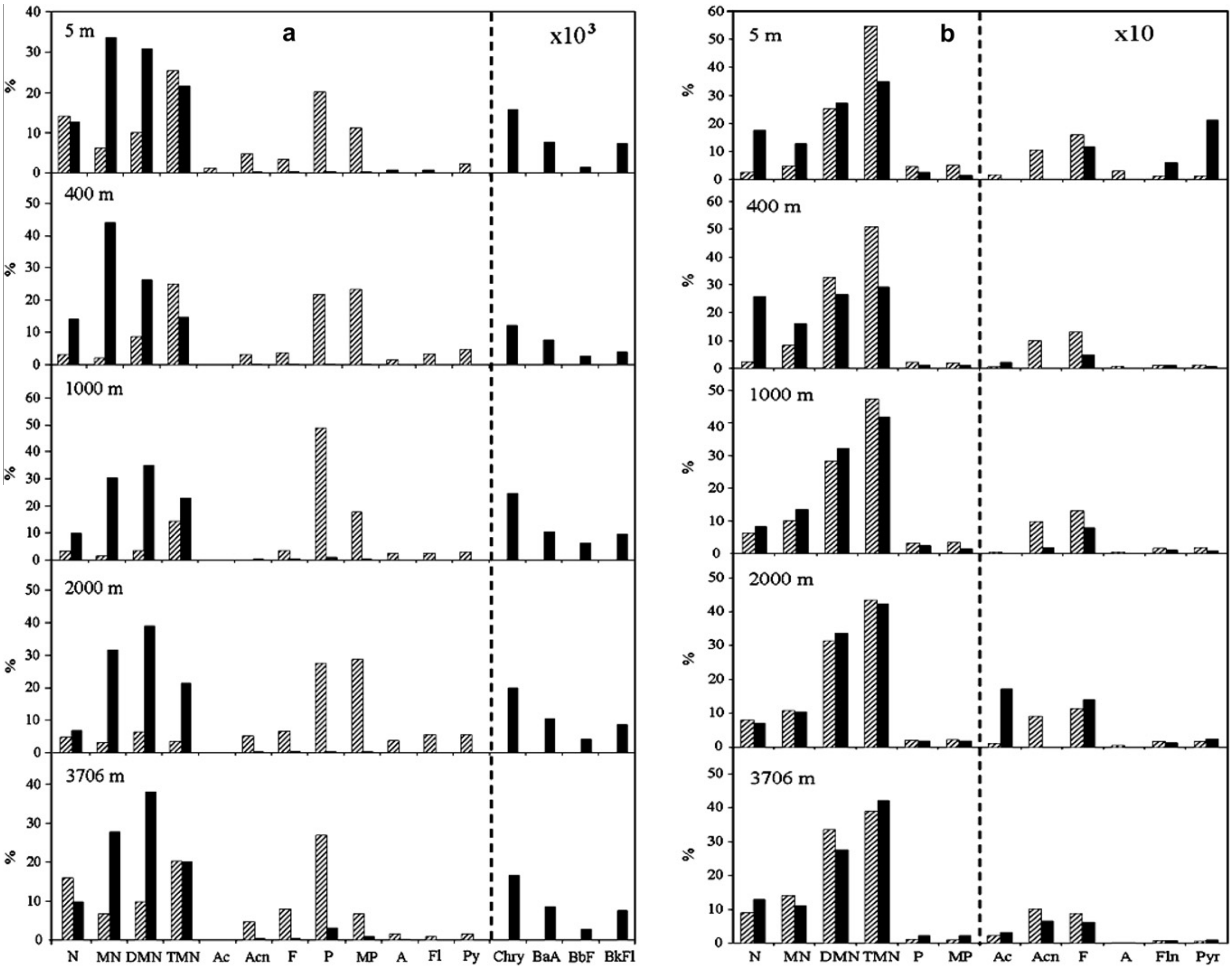

Fig. 3. Relative distribution of PAHs in the suspended particulate matter (SPM) (a) and dissolved phase (DP) (b) of the water column at the *Prestige* shipwreck sinking area in March (striped bars) and October (black bars) 2006. N: naphthalene, MN: methylnaphthalenes, DMN: dimethylnaphthalenes, TMN: trimethylnaphthalenes, Ac: acenaphthylene, Acn: acenaphthene, F: fluorene, P: phenanthrene, MP: methylphenanthrenes, A: anthracene, Fl: fluoranthene, Py: pyrene, Chry: chrysene, BaA: benzo[*a*]anthracene, BbF: benzo[*b*]fluorene, BkFl: benzo[*k*]fluoranthene. Compounds not represented in the DP were found below detection limit in both sampling periods.

inated by alkylated naphthalenes, a fact that was also observed after the main black tides in the affected areas by the *Prestige* (González et al., 2006), and that agrees with the fresh character of the oil found in the sea surface, suggesting that the spilled product was recently leaked from the wreck and had not undergone appreciable weathering.

3.3. PAH in the dissolved phase

Unlike in the SPM, total dissolved PAHs (DP ΣPAHs) concentrations were within the same range during both cruises, between 31.3–187.8 ng L^{-1} and 61–137 ng L^{-1} in March and October respectively (Fig. 2b), and well above the background reference concentrations for the NE Atlantic (OSPAR_Commission, 2004). These ΣPAHs levels were between 1 and 2 orders of magnitude higher than the ones described in previous studies of open ocean waters, where concentrations are usually lower than 1 ng L^{-1} (Dachs et al., 1997; Lipiatou et al., 1997; Maldonado et al., 1999; Schulz-Bull et al., 1998). In fact, the values found at the *Prestige* station in March 2006 were similar to the levels found in the DP near the coast after the *Erika* oil spill (Tronczynski et al., 2004), of around 20.9–139 ng L^{-1}. The relative distribution of individual DP compounds in the PAH mixture was also similar in both sampling periods (Fig. 3b), and not dissimilar to the principal components found in the seawater accommodated fraction for the *Prestige* fuel oil (González et al., 2006). Thus, it seems likely that the DP hydrocarbons indicate a deep spill from the *Prestige* wrecks during both sampling periods.

3.4. Aliphatic hydrocarbons in the suspended particulate matter

In March, the total concentration of SPM aliphatic hydrocarbons (C_{14}–C_{35} *n*-alkanes together with pristane and phytane) in the water column ranged from 4.8 to 40.5 ng L^{-1}, decreasing with depth (Fig. 2c). These concentrations agreed with values reported for open surface waters in the Mediterranean (Dachs et al., 1999; Marti et al., 2001) and the Black Sea (Maldonado et al., 1999). In contrast, the samples collected in October showed a vertical profile quite similar to the one found for the PAHs in the same period, with maximum concentrations in the superficial waters, a depletion in the mid-depth waters and enrichment near the bottom. As for the PAHs, this trend could be attributed to the contribution of the oil coming from the *Prestige* wrecks. Higher concentration in the total aliphatic hydrocarbons in October seemed to confirm the occurrence of a deep sea spill, although the increment was less spectacular than in the aromatic fraction, only of about one order of magnitude. Total aliphatic hydrocarbon concentrations were between 65.7 and 413.7 ng L^{-1}, values that are well above previously reported concentrations in the open ocean.

Similarly to the distribution of the PAHs, the relative distribution of individual *n*-alkanes in the mixture changed noticeably between the samples collected in the two cruises (Fig. 4). In March,

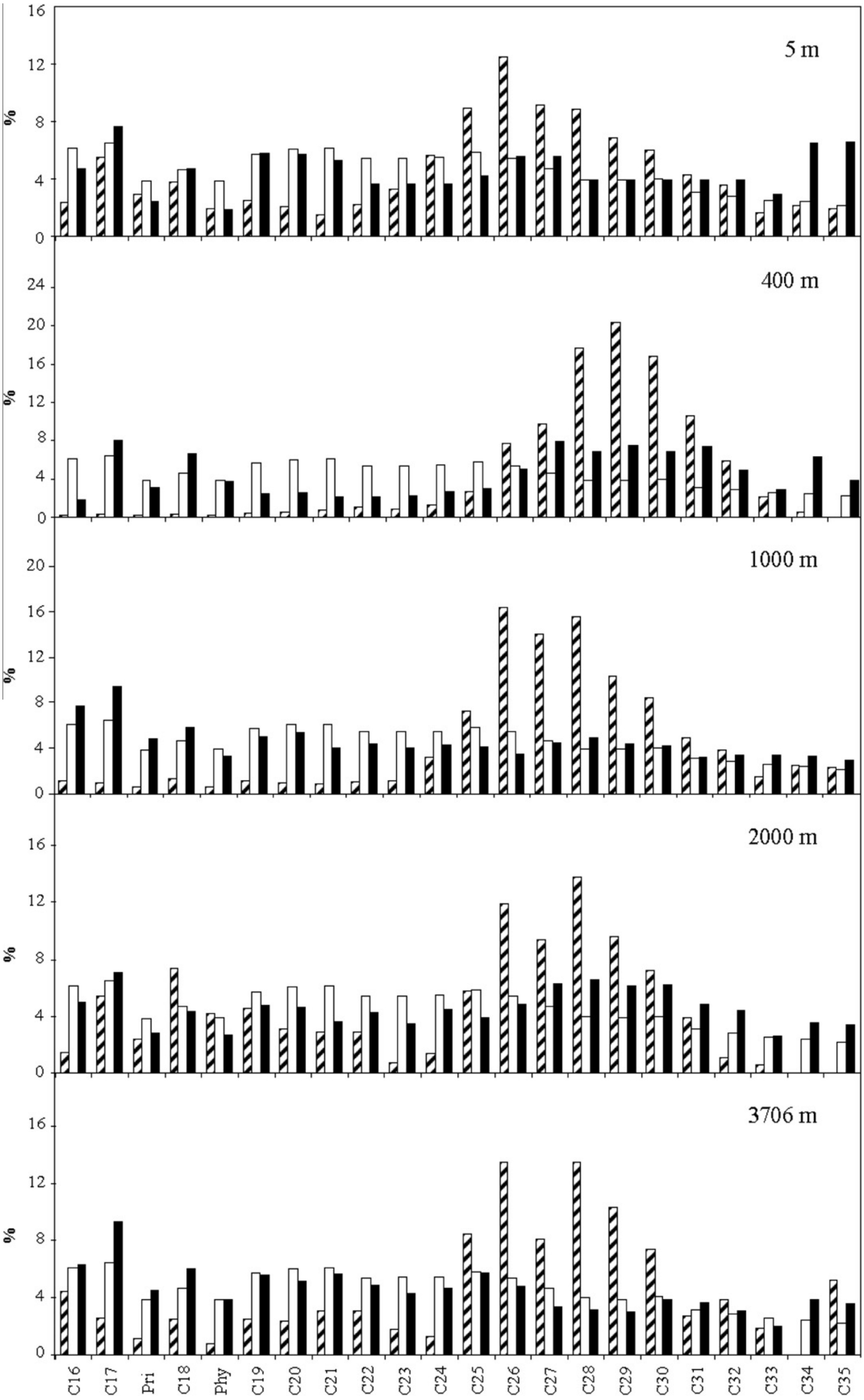

Fig. 4. Distribution of individual *n*-alkanes, including pristane (Pr) and phytane (Ph) in the SPM from different depths in March (striped bars) and October (black bars) 2006. The distribution of *n*-alkanes in the oil slicks found in the sinking area in October 2006 (white bars) is shown for comparison in the 4 insets.

the mixture was dominated by C_{25}–C_{30} hydrocarbons at all depths, being the distribution rather dissimilar to that of the *Prestige* oil. The odd-to-even carbon number ratio was 1 in the superficial waters, and above 1 in the remaining depths, indicating the occurrence of biogenic aliphatic hydrocarbon inputs. The profile of *n*-alkanes in October was remarkably uniform in the water column, close to the distribution pattern of the *Prestige* oil, particularly for the most superficial and deepest samples. In the mid-depth samples, C_{16}, C_{17} and C_{27} to C_{35} *n*-alkanes were generally present at higher proportion than the other components, indicating the presence of some biogenic components (Avigan and Blumer, 1968), although the odd-to-even carbon number ratio showed values around 1 for all depths, as expected for a major contribution of petrogenic hydrocarbons to the aliphatic fraction (Marti et al., 2001).

3.5. Phase distribution of PAH

The relative importance of the DP and SPM as a PAH pool in the water column of the *Prestige* station varied drastically between the two sampling periods. In March, the aqueous phase accumulated between 97% and 99% of the total PAHs found in the water column of the sinking area, whereas in October, the phase distribution pattern became inverted. The vast majority of the PAHs were associated to the SPM (77–90% of the total PAHs). We attribute these differences in phase partitioning to either a greater proximity of the sampling devices to the oil source in October and/or the relative age of the spilled oil during both sampling periods. Thus, arguably, in October the spilled oil had not been long enough in the water to reach partition equilibrium. Equilibrium concentration between DP and SPM is not immediately reached after the spill, in fact it can take from days to weeks (Broman et al., 1996), which can also explain the relatively low importance of the DP as a PAH pool soon after the deep sea spill.

4. Conclusions

The wrecks of the *Prestige* tanker were releasing oil to the deep pelagic ocean environment, from 3800 m depth, 3 years after the wrecks had been sealed for leaks. The oil reached the surface waters above the wrecks without any signs of weathering and leaving an homogenous signature throughout the water column. Therefore, a deep spill at near 4000 m depth, in a relatively hydrodynamically complex region, with water masses of distinct temperature and salinity as in the NE Atlantic, may release oil that will surface with a chemical signature identical to the source. However, at mid-depths, the spread of a deep sea spill can be better evaluated by the dissolved hydrocarbon signature, rather than the SPM, which may decrease quickly away from primary or secondary sources of oil. The identified and unexpected deep spill from the *Prestige* provides some clues for the appraisal of the contribution of deep spills from wrecks to the pelagic ocean, even when the location of the wrecks is not known with certainty, as it is in most cases.

Acknowledgment

Authors acknowledge the Spanish government for funding (VEM2003-20583) and the Generalitat of Catalonia for a studentship to S.E.Z. Erin McClymont, Ester Garcia, Raquel Hernandez, Alfredo Martinez, Carolina Olid, Sara Orgué, Barend van Droogue and the crew of the *Cornide de Saavedra* are thanked for their assistance during the expeditions, Juan J. Gonzalez and Demetrio de Armas for providing logistical support during the October 2009 cruise, and Manh Hieu for laboratory assistance. The IAEA is grateful for the support provided to its Marine Environment Laboratories by the Government of the Principality of Monaco.

References

Albaiges, J., Morales-Nin, B., Vilas, F., 2006. The Prestige oil spill: a scientific response. Mar. Pollut. Bull. 53 (5–7), 205–207.

Alzaga, R., Montuori, P., Ortiz, L., Bayona, J.M., Albaiges, J., 2004. Fast solid-phase extraction-gas chromatography–mass spectrometry procedure for oil fingerprinting – application to the prestige oil spill. J. Chromatogr. A 1025 (1), 133–138.

Avigan, J., Blumer, M., 1968. On the origin of pristane in marine organisms. J. Lipid Res. 9, 350–352.

Basta, D.J., Kennedy, D.M., 2004. The need for a proactive approach to underwater threats. Mar. Technol. Soc. J. 38, 9–11.

Broman, D. et al., 1996. Significance of bacteria in marine waters for the distribution of hydrophobic organic contaminants. Environ. Sci. Technol. 30 (4), 1238–1241.

Dachs, J., Bayona, J.M., Fillaux, J., Saliot, A., Albaiges, J., 1999. Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. Mar. Chem. 65 (3–4), 195–210.

Dachs, J., Bayona, J.M., Raoux, C., Albaiges, J., 1997. Spatial, vertical distribution and budget of polycyclic aromatic hydrocarbons in the western Mediterranean seawater. Environ. Sci. Technol. 31 (3), 682–688.

Daling, P., Moldestad, M., Johansen, O., Lewis, A., Rodal, J., 2003. Norwegian testing of emulsion properties at sea: the importance of oil type and release conditions. Spill Sci. Technol. Bull. 8, 123–136.

Diez, S., Jover, E., Bayona, J.M., Albaiges, J., 2007. Prestige oil spill. III. Fate of a heavy oil in the marine environment. Environ. Sci. Technol. 41 (9), 3075–3082.

Girin, M., 2004. European experience in response to potentially polluting shipwrecks. Mar. Technol. Soc. J. 38, 21–25.

González, J.J. et al., 2006. Spatial and temporal distribution of dissolved/dispersed aromatic hydrocarbons in seawater in the area affected by the Prestige oil spill. Mar. Pollut. Bull. 53, 250–259.

ITOPF, 2009. Oil Tanker Spill Statistics.

Lipiatou, E. et al., 1997. Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea. Deep-Sea Res. Part Ii-Top. Stud. Oceanogr. 44 (3–4), 881–905.

Maldonado, C., Bayona, J.M., Bodineau, L., 1999. Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the northwestern Black Sea water. Environ. Sci. Technol. 33 (16), 2693–2702.

Marti, S., Bayona, J.M., Albaiges, J., 2001. A potential source of organic pollutants into the northeastern Atlantic: the outflow of the Mediterranean deep-lying waters through the Gibraltar Strait. Environ. Sci. Technol. 35 (13), 2682–2689.

Michel, J., et al., 2005. Potentially Polluting Wrecks in Marine Waters International Oil Spill Conference, Miami, Florida, USA.

Michor, G., Carron, J., Bruce, S., Cancilla, D.A., 1996. Analysis of 23 polynuclear aromatic hydrocarbons from natural water at the sub-ng/l level using solid-phase disk extraction and mass-selective detection. J. Chromatogr. A 732, 85–99.

Nemirovskaya, I.A., 2007. Hydrocarbons in the water and bottom sediments of a region with continuous petroleum contamination. Geochem. Int. 45 (7), 638–651.

OSPAR_Commission, 2004. OSPAR/ICES Workshop on the Evaluation and Update of the Background Reference Concentrations (BCRs) and Ecotoxicological assessment Criteria (EACs) and How these Assessment Tools should be used in Assessing Contaminants in Water, Sediment and Biota, ICES.

Ruiz-Villarreal, M. et al., 2006. Oceanographic conditions in North and Northwest Iberia and their influence on the Prestige oil spill. Mar. Pollut. Bull. 53 (5–7), 220–238.

Schulz-Bull, D.E., Petrick, G., Bruhn, R., Duinker, J.C., 1998. Chlorobiphenyls (PCB) and PAHs in water masses of the northern North Atlantic. Mar. Chem. 61 (1–2), 101–114.

Tronczynski, J. et al., 2004. Contamination of the Bay of Biscay by polycyclic aromatic hydrocarbons (PAHs) following the T/V "Erika" oil spill. Aquatic Living Resour. 17 (3), 243–259.

Turrell, W.R., 1994. Modeling the Braer oil-spill – a retrospective view. Mar. Pollut. Bull. 28 (4), 211–218.

Wolska, L., Galer, K., Gorecki, T., Namiesnik, J., 1999. Surface water preparation procedure for chromatographic determination of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. Talanta 50 (5), 985–991.