



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

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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.

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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.

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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, EN-ACW), 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 C₁₈ 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-d₁₀ (Acros Organics) and pyrene-d₁₀ (Sigma–Aldrich, St. Louis, Mo, USA) in isoctane 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 ($\delta^{13}\text{C}$)

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 isoctane was injected via an on column injector onto a capillary Agilent (Santa Clara, CA, USA) HP5 column (60 m \times 0.32 mm i.d. \times 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 CO₂ 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-d₁₀ and pyrene-d₁₀ 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 N₂ to near dryness.

C₁₈ 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 \times 0.25 mm, I.D. \times 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 C₁₆, C₂₀, C₂₈, C₃₂ and C₃₆ *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

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