

Spatial and temporal distribution of dissolved/dispersed aromatic hydrocarbons in seawater in the area affected by the *Prestige* oil spill

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Abstract

Seawater samples collected at three depths from 68 stations along the Northern Spanish coast were analysed for dissolved/dispersed petroleum aromatic hydrocarbons by UV-fluorescence and for 25 individual compounds by GC–MS. Sampling was performed in December 2002, just after the *Prestige* oil spill, and in February–March and September 2003. Higher concentrations of total aromatic hydrocarbons were found at all depths in the samples collected during December 2002 off the Galicia coast, with levels ranging between 0.19 and 28.8 µg/L eq. oil (0.1–4.8 µg/L chrysene eq.). These values decreased in the following cruises, till <0.05–2.86 µg/L oil eq. (av. 0.23 µg/L chrysene eq.) in September 2003, possibly representing the background levels for the region. However, in the Cantabrian coast they were still high at the surface in the March cruise, probably by the late arrival of the fuel-oil to this area. Some coastal hot spots were also identified, with values up to 29.2 µg/L fuel-oil eq., close to river mouths and urban areas.

The individual PAH distributions in the December 2002 sampling off-Galicia were dominated by alkyl-naphthalene derivatives, consistently with the pattern distribution shown by the fuel-oil water accommodated fraction. The higher concentrations were found in the subsurface samples along the Costa da Morte, the area most heavily affected by the spill (av. 0.46 µg/L Σ16 PAHs). The rest of the samples collected in other areas exhibited lower concentrations and a more even distribution of 2–4 ring PAHs, that ranged from 0.09 to 0.37 µg/L (av. 0.15 µg/L Σ16 PAHs), with decreasing trends offshore and downward the water column. In September 2003, the values were rather uniform, averaging 0.09 µg/L (Σ16 PAHs).

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1. Introduction

On 13th November 2002, the tanker *Prestige*, transporting 77,000 tons of a Russian heavy fuel-oil (type M-100), started to leak oil 30 miles off the Galicia coast (NW Spain). After six days of erratic tow along the coast the tanker broke in two and sunk at the Galicia bank (3800 m depth, 150 miles offshore) (Fig. 1). The winds and sea-

currents drove the patches of about 60,000 tons of emulsified oil towards the shore, affecting more than 800 km of the NW Spanish coast.

A detailed understanding of the fate of any spilled oil is required in order to foresee the extension of the environmental damage and to develop effective restoration strategies. The first processes affecting the spilled oil are dispersion and dissolution. The composition and concentration of the soluble fraction will determine the early impact of the spilled product on marine biota. In this respect, aromatic hydrocarbons are of special concern as they exhibit higher solubility and toxicity in the aquatic environment. Greater

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acute toxicity is generally associated with the lower molecular weight polycyclic aromatic hydrocarbons (PAHs) whereas some of the higher molecular weight PAHs forms carcinogenically active metabolites (Neff, 2002).

Two main approaches have been followed for the determination of dissolved/dispersed petroleum hydrocarbons in seawater, namely using UV-fluorescence or GC–MS for the analysis of total or individual hydrocarbons, respectively (Grasshoff et al., 1999). Although in general UV-fluorescence has been replaced by more specific methods, it is still being used for monitoring spatial and temporal concentration gradients of petroleum hydrocarbons in seawater because of its simplicity, sensitivity and easy application (Gordon et al., 1978; Law, 1981; Wattayakoran et al., 1998; Zanardi et al., 1999). Moreover, it has been employed in the assessment of several oil spills (Mackie et al., 1978; Law, 1978; Marchand, 1980; González et al., 1997). However, recent data mainly refer to individual PAHs for a better source apportionment and ecotoxicology assessment (Kennicutt et al., 1991; Neff and Stubblefield, 1995; Law et al., 1997; Reddy and Quinn, 2001; Pécseli et al., 2002).

In order to evaluate the spatial and temporal distribution of dissolved/dispersed petroleum hydrocarbons (DDPH) in the water column after the *Prestige* fuel-oil spill, both total hydrocarbons, determined by UV-fluorescence, and the individual distribution of 25 PAHs, determined by GC–MS, were considered. Seawater samples were collected during three cruises covering the NW Spanish coast in December 2002, just after the accident, and the whole Northern coast in February–March and September 2003.

In addition, to better assess the occurrence of the *Prestige* fuel-oil components in the seawater, the distribution patterns of individual aromatic hydrocarbons found in the samples collected in the affected area were compared with those obtained in the laboratory after accommodation of the fuel-oil in artificial seawater. The water accommodated fraction (WAF) was prepared following the Chemical Response to Oil Spills Ecological Research Forum (CROSERF) guidelines, aiming at obtaining intercomparable results for chemical and toxicological testing of oil WAFs (Singeri et al., 2000).

2. Experimental

2.1. Materials and reagents

All glassware was cleaned with LA 13 Derquim (Panreac, Spain) during 48 h, followed by clearing with water and Milli-Q water. Suprasolv grade hexane and dichloromethane were obtained from Merck (Darmstadt, Germany) and chrysene (98%) from Sigma–Aldrich (Steinheim, Germany).

A PAH mixture containing naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene and benzo[*ghi*]per-

ylene at 10 mg/L in cyclohexane was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Alternatively, a standard reference material SRM 2260 “24 Aromatic Hydrocarbons in Toluene” (NIST, Gaithersburg, MD, USA), containing some methyl derivatives was also used. The following perdeuterated standards, used as surrogates, were obtained from Cambridge Isotope Laboratories (Andover, USA): naphthalene-*d*₈ (99%), anthracene-*d*₁₀ (98%), pyrene-*d*₁₀ (98%) and benzo[*a*]pyrene-*d*₁₂ (98%).

2.2. Sampling

The stations shown in Fig. 1 were sampled at three depths, from 7 to 13 December 2002 in the area of Galicia (stations 1–34) and from 9 February–22 March and 2–8 September 2003 in the whole NW Atlantic coast (stations 1–68).

Subsurface seawater (1 m depth) was sampled with 2 L amber glass bottles held in a stainless-steel frame and deployed before the total stopping of the vessel, in order to avoid local contamination. Mid depth and bottom (2–3 m above the sediment) waters were sampled with Go-Flo bottles and immediately transferred to the 2 L glass bottles. Then, 25 mL of hexane and 1 mL of HgCl₂ solution were added. The bottles were kept at 4 °C before extraction in the laboratory within the following 24 h. For the analysis of individual PAHs the seawater was acidified with HCl 6 N until pH < 2, following the EPA recommendation.

2.3. Analytical procedure

2.3.1. Total hydrocarbons in seawater

The unfiltered seawater samples were analysed by UV-fluorescence for dissolved/dispersed hydrocarbons according to the MARPOLMON protocol (UNESCO, 1984). Two litres of seawater were extracted three times with 25 mL of hexane. The organic extracts were combined, dried over anhydrous Na₂SO₄, concentrated to 5 mL by vacuum evaporation and the fluorescence measured at the ex/em wavelengths of 310/360 nm with a Perkin–Elmer LS 50B spectrofluorometer.

The calibration was made with hexane solutions of chrysene and *Prestige* oil (between 0.03 and 2000 µg/L and 0.1 and 15,000 µg/L of chrysene and fuel-oil, respectively). In the UNESCO/IOC method (1984) the idea was that expressing concentrations on the basis of chrysene equivalents would give a better intercomparison of published data, however, in practice samples of standard chrysene from different suppliers give different fluorescence, so that values are of lower interest. Therefore, concentrations in chrysene equivalents are not reported individually although in the present case they have been found to be about 1/6 of the fuel-oil values. The detection limits (DL = average + 3SD) were 0.05 and 0.15 µg/L equivalents of chrysene and fuel-oil, respectively. The method was tested for reproducibility using six samples from three different sites.

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