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ScienceDirect
Journal of Marine Systems 72 (2008) 350–357
JOURNAL OF MARINE SYSTEMS
www.elsevier.com/locate/jmarsys

# Influence of the heavy fuel spill from the *Prestige* tanker wreckage in the overlying seawater column levels of copper, nickel and vanadium (NE Atlantic ocean)

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Received 17 July 2006; received in revised form 11 December 2006; accepted 20 December 2006
Available online 4 December 2007

**Abstract**

The water column above the *Prestige* wreckage was sampled during two consecutive campaigns: *Prestinaut* (December 2002) two weeks after the tanker sunk and *HidroPrestige0303* (March 2003) one month after the sealing of the main fuel leaks. Samples of the original cargo fuel and the emulsified fuel in the surface of the ocean were also collected. Analysis of the fuel indicated the release of 135 kg of Cu, 1700 kg of Ni and 5300 kg of V from the original fuel to the water column, remaining 35 kg of Cu, 3100 kg of Ni and 13,800 kg of V in the emulsified fuel. The metal partitioning between the water column and the emulsioned floating fuel, Cu > Ni ~ V, are in accordance with the stability index for the metal–nitrogen bond in metalloporphyrins. This release had an impact on dissolved trace metal concentrations in the water column. An increase on dissolved copper (2.8–4.7 nM) and nickel (2.2–8.0 nM) with respect to natural values (1–3 nM for Cu and 1.6–5 nM for Ni) was observed. Values for vanadium (28–35 nM) were in the range of pristine North Atlantic waters (30–36 nM). This contamination was especially observed in the upper water column (0–50 m), associated with the mixing of seawater with the fuel moving upwards, and in deep waters, where the residence time of fuel is higher. Future research in this field should focus on the environmental variables and the processes that control the release of contaminants from fuels for a better assessment of the contamination in oil-spill events.


*Keywords:* Copper; Nickel; Vanadium; Seawater; Contamination; Oil spill; Heavy fuel; *Prestige* tanker; NE Atlantic Ocean

## 1. Introduction

In the complex mixture of hydrocarbons that are crude oils, non-hydrocarbon compounds – including metals and sulphur – may represent up to 25% of the oil (Clark, 2001). Metal concentrations in fossil fuels may vary according to their oilfield source (Filby and Van Berkel, 1987), though the highest values are generally found for nickel and vanadium.

Due to their low volatility, metals are concentrated in the residual heavy fuels during the fractional distillation of petroleum (Butt, 1986), remaining in the black, viscous distillation tower bottoms. This product, named as heavy fuel-oil no. 6 (U.K. classification; Reid, 1973) contains from 10 to 500 μg $g^{-1}$ of V and Ni in complex organic molecules, mainly in the form of metalloporphyrins (Perry and Chilton, 1973). Other metal concentrations reported in the literature for this

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doi:10.1016/j.jmarsys.2006.12.005

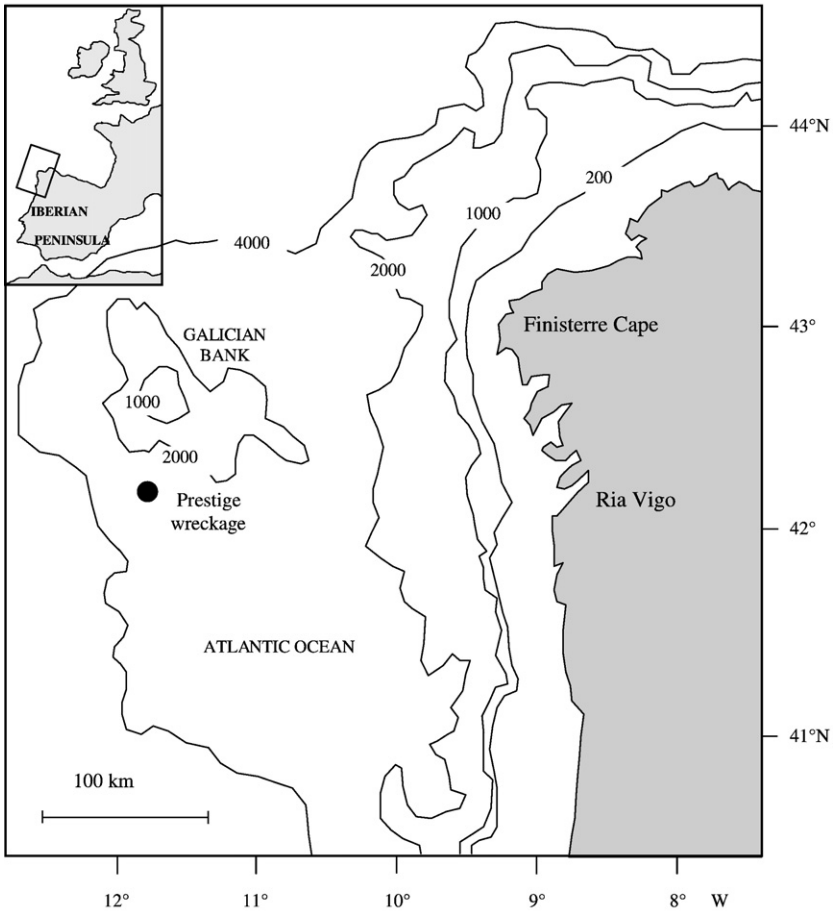


Fig. 1. Study area map.

type of fuels range from 0.8–1.0 μg $g^{-1}$ for Cd, 2 μg $g^{-1}$ for Pb and Co, 1–73 μg $g^{-1}$ for Zn, and 3–148 μg $g^{-1}$ for Cu (Allouis et al., 2003; Reddy et al., 2005).

This heavy fuel-oil no. 6 was the type of fuel transported by the *Prestige* tanker; recent studies have shown that it was rich in sulphur (2.6%; Albaigés and Bayona, 2002) and contained significant amounts of metals (Prego et al., 2005), especially V (~400 μg $g^{-1}$) and Ni (~100 μg $g^{-1}$). In spite of the relative importance of trace metals in these heavy fuels and crude oils, little attention has been paid to their potential contamination derived from oil spills, being the hydrocarbons the only pollutants extensively studied (Patin, 1999). This is reflected in the few publications studying the metal enrichment of the environment following oil-spill events. Apart from the ones published after the *Prestige* accident in the coast of Galicia (Prego and Cobelo-García, 2004; Santos-Echeandia et al., 2005), there are few references for similar situations, i.e. the Kuwait coasts after the Gulf War (Fowler et al., 1993), the fresh and marine Egyptian waters contaminated from tanker oil loading and waste discharge (Shimy 1997), and the drilling wastes from petroleum production in platforms (Middleditch, 1981), the later amounting up to 22,000 t of oil and about 100,000 t of inorganic chemicals into the North Sea (Davies and Kingstone, 1992).

Unfortunately, oil-tanker accidents occur occasionally, representing 12% of the total oil input to the marine environment (Baker, 2001). In the last 40 years around 100 oil-spill related accidents took place all around the world (e.g. *Exxon Valdez*, Alaska in 1989; Gulf War, Persian Gulf in 1991), being the west coast of Europe the most damaged place (e.g. *Amoco Cadiz*, France in 1978; *Erika*, France in 1999; *Baltic Carrier*, Germany and Denmark in 2001). Almost half of this quantity occurred in the Iberian Peninsula (e.g. *Polycommander* in 1970; *Urquiola* in 1976; *Aegean Sea* in 1992), being the *Prestige* accident in 2002 the last example of these kinds of catastrophes.

On 13th November 2002, the *Prestige* oil tanker, transporting 77,000 t of fuel, started to crack and vast