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The comparison of two heavy fuel oils in composition and weathering pattern, based on IR, GC-FID and GC–MS analyses: Application to the *Prestige* wreckage

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ABSTRACT

This paper compares the weathering patterns of two similar fuel oils: a fuel oil spilled after a ship accident (*Prestige-Nassau*, off the Galician coast -NW Spain-) and a fuel designed to cope with the numerous quests for samples to carry out scientific studies (IFO). Comparative studies were made to evaluate the capability of common fingerprinting analytical techniques to differentiate the fuels, as well as their capabilities to monitor their weathering. The two products were spilled under controlled conditions during ca. four months to assess how they evolved on time. Mid-IR spectrometry and gas chromatography (flame ionization and mass spectrometry detectors) were used. IR indexes related to total aromaticity, type of substituents (branched or linear chains) and degree of aromatic substitution reflected well the differences between the fuels during weathering. Regarding the chromatographic measurements, the *n*-alkanes became highly reduced for both fuel oils and it was found that the PAHs of the synthetic fuel (IFO) were more resistant to weathering. Regarding biomarkers, the different profiles of the steranes, diasteranes and triaromatic steroids allowed for a simple differentiation amongst the two products. The %D2/P2 ratio differentiated both products whereas the %N3/P2 one ordered the samples according to the extent of their weathering.

1. Introduction

The strategic location of the Galician coast (NW Spain) caused repeated threats of hydrocarbon pollution, including accidental oil spills from tankers, undue ballast releases and residues of ship bilges cleanups. The wreckage of the ship *Prestige-Nassau* was the fifth large oil tanker spillage occurred at the Galician coast since 1970 and, as it happened with other recent disasters (e.g. *Cosco Busan*, at San Francisco Bay, releasing 220 oil tons, and *Hebei Spirit*, South Corea, pouring ca. 10,000 oil tons) caused important environmental damages.

The oil tanker *Prestige* became damaged in a heavy storm on the 13th of November of 2002, suffering a breach on her hull. On Tuesday, 19th November, the vessel split in two halves and sank off the Galician coast. She carried out ca. 77,000 tons of a heavy fuel oil, of which *circa* 63,000 tons were released to the marine ecosystem. The *Prestige* fuel oil was as an M100 (Russian classification) or 'fuel oil n° 6' (English terminology), with 0.9980 specific gravity, 22% aliphatic, 49% aromatic hydrocarbons, and around 29% of resins and asphaltenes; it was also very similar to typical IFO 650 fuel oils (Intermediate Fuel Oil, 650 cSt at 50 °C; 30,000 cSt at 15 °C). This was a very viscous product, almost insoluble, with an oil-characteristic smell,

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difficult to disperse and with a pronounced trend to form stable emulsions. Such a heavy fuel is obtained at the end of petroleum refinery distillations and lighter distillates are required sometimes to facilitate their mixing and/or movement, although the authors were informed that solvents had not been added to the *Prestige* cargo.

The dramatic short-term environmental impact affected more than 2500 km of coastal areas from N Portugal to SW France, and it boostered the international scientific community to study the spillage. To address the enormous amount of quests for oil samples and guarantee their homogeneity, the Spanish Government (through the Ministry of Public Works) supplied scientists a quite similar blend termed ''Intermediate Marine Fuel Oil'' (IFO Marine) on 2005, with specific gravity and viscosity amounting 0.9724 and 500 cSt (50 °C) respectively. No more specific details were given.

The particular evolution an oil undergoes while it is floating and drifting on the sea is affected by many physicochemical weathering processes which, in turn, are strongly dependent on the particular composition of the spilled product and the physical-, marine- and solar-conditions. Moreover fuel persistence, toxicity and bioavailability are strongly determined by its particular composition as well. The compositional characteristics of a spillage are currently characterized by the so-called fingerprinting analytical methods. They comprise a suite of analytical tools intended to ascertain the origin of the spillage. They can determine either the whole chemical fingerprints (e.g. mid-IR spectroscopy (Fernández-Varela et al., 2005)) or, more common, individual compounds (e.g. gas chromatography methods (Barakat et al., 2001; Wang and Fingas, 2003)). In any case, the determination of the source of the spilled product is made by a matching step against several (previously characterized) suspicious sources. It is worth, therefore, assessing the ability of the most usual fingerprint methods to differentiate among two similar products weathered under natural conditions during a reasonably extended period of time. Hence, comparison of the weathering patterns of the *Prestige*'s fuel oil and the ''*Prestige*-like'' IFO blend was carried out.

The aims of this paper are, therefore: i) to compare the chemical composition of both products, ii) to assess how they evolved on time (ca. four months) after they were spilled under controlled conditions and iii) to inspect which variables, among those provided by the oil-screening techniques give rise to a differentiation among the two products. Three analytical techniques will be employed: ATR-MIR (Attenuated Total Reflectance Mid-Infrared Spectrometry) because of its proved usefulness as a screening technique, GC-FID (Gas Chromatography-Flame Ionization Detector) and GC–MS (Gas Chromatography–Mass Spectrometry), which give insight on the detailed chemical composition. A final objective is, following, to determine if they can differentiate the two products, even when they were weathered.

2. Materials and methods

2.1. Samples

Both products were released (ca. 500 mL) on a two-compartment special metallic container filled with sea water (60–70 L) and weathered during three and a half months. The thickness of the oil layer was around 0.15 cm when pouring the oil. As part of the oil became 'stacked' to walls in subsequent days all samples were withdrawn from the center of the container. A closed-circuit water pump agitated continuously the system by pouring water over the oil–water surface so that washing, emulsion, wave agitation and sea movement were simulated as close as possible. Aliquots were sampled at preset intervals; namely, 5, 10, 24, 36, 48, 60, 72, 84 h, and 7, 11, 14, 21, 28, 42, 56 and 101 days. Samples identified as 0 in the figures correspond to original unweathered fuels. Atmospheric conditions were registered for each aliquot (approx. 25 mL, Fernández-Varela et al., 2005) as weathering was performed in open air. Only three days were of sunny weather and the air temperature ranged from 7 to 16 °C since the fuels were spilled at the same months than the *Prestige* release occurred.

The organic phase was transferred to 50 mL Pyrex centrifuge tubes, approximately 1 g of sodium sulphate (Merck, 99.0%, Damstard, Germany) was added, and centrifuged at 3000 r.p.m. during 30 min. In case of emulsions appeared, NaCl (Panreac, 99.5%, Barcelona, Spain) and another gram of sodium sulphate were added until the emulsion broken down. Stable emulsified samples obtained after the first month were treated on a single step thermostatizing them at 50–60 °C (±1 °C) while centrifuging at 3000 r.p.m. for 30–40 min (Seta Oil Test Centrifuge, Surrey, United Kingdom). No further cleanup procedures were applied before the chromatographic measurements.

2.2. Analytical measurements

Many analytical procedures were developed two decades ago for oil source identification and matching purposes. Most of them relied on gas chromatography coupled to FID and/or MS detection and yielded standardized protocols to determine the hydrocarbon fingerprint, specific chemicals, the persistence of several species, and to set specific ratios (see, e.g. Barakat et al., 1999; Boehm et al., 1997; Wang et al., 2001).

Gas chromatography (GC) is of paramount importance to determine individual species and study how they evolve during weathering. Particularly, GC-FID is well-established, robust, cheap and constitutes a fast procedure to fingerprint aliphatic hydrocarbons. Aromatic compounds and oil-specific biomarkers are determined coupling gas chromatography and mass spectrometry detectors (GC–MS).

General-purpose analytical techniques such as mid-infrared spectrometry (IR), are fast, inexpensive and can be deployed on contaminated sites thanks to newest portable equipments. In particular, the attenuated total reflectance-Fourier transform mid-IR spectrometry (ATR-MIR) is a very simple, fast and useful tool that has been used recently to monitor the weathering processes and perform fast screening tests (Fernández-Varela et al., 2005; Fresco-Rivera et al., 2007).

2.2.1. Infrared spectrometry

A 16PC Perkin-Elmer mid-IR spectrometer (Ge–KBr beamsplitter, DTGS detector, 4 cm^{-1} nominal resolution, strong Beer–Norton apodization) with a horizontal, ATR device (ZnSe, trapezoidal, 45°, 12 reflections) was used throughout (50 scans per spectrum, 4000–600 cm^{-1} measuring range, corrected for