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Fast preparation of the seawater accommodated fraction of heavy fuel oil by sonication

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ABSTRACT

The seawater accommodated fraction (SWAF) of oil is widely used for the assessment of its toxicity. However, its preparation in the laboratory is time consuming, and results from different authors are difficult to compare as preparation methods vary. Here we describe a simple and fast set up, using sonication, to produce reproducible SWAF in the laboratory. The system was tested on heavy fuel oil placed on seawater at different salinity and temperature conditions. Maximum dissolution of the oil was achieved after 24 h, independently of both seawater salinity and temperature. Our findings are discussed in relation to the fate of the oil from the deep spill of the *Prestige* tanker. Changes in temperature in the open ocean are bound to have larger impact in the concentration of the SWAF than the corresponding values of sea water salinity. We anticipate that in this type of incident the highest SWAF, as the oil reaches the sea surface, should be expected in the warmest and less saline waters of the water column.

1. Introduction

The seawater accommodated fraction (SWAF) of a crude oil is a mixture mainly composed by light polycyclic aromatic hydrocarbons (PAHs), phenols and heterocyclic compounds containing nitrogen and sulphur (Saeed and Al-Mutairi, 2000). Several of these PAHs are known to be neurotoxic, mutagenic and carcinogenic (Khan et al., 1995; Fernandez et al., 2006). Since the SWAF is the fraction which is more readily bioavailable soon after an oil spill, it has been widely used for the assessment of the toxicity of the oils in different living organisms, such as crustaceans (Maki et al., 2001; Martinez-Jeronimo et al., 2005), fish (Akaishi et al., 2004) and microbiota (Ohwada et al., 2003). The SWAF can also produce long term effects in areas that are not directly affected by the spill (Navas et al., 2006).

The preparation in the laboratory of the SWAF is usually carried out by gently stirring the oil and seawater by means of a low energy mixing system to avoid the formation of oil in water emulsions (Ali et al., 1995; Rayburn et al, 1996; Ziolli and Jardim, 2002). Consequently, the procedure is slow, taking several days for the concentration of the SWAF to reach a steady state (Hokstad et al., 1999; Page et al., 2000). Moreover, the preparation of replicates of the SWAF is tedious and time consuming. On the other hand, in the assessment studies of the toxicological effects on biota, it is convenient to prepare the SWAF rapidly, as it is not possible to add a biocide to the water to avoid the onset of bacterial activity after 24 h (Singer et al., 2000).

The final composition of the SWAF depends chiefly on parameters such as oil–water ratio, stirring and settling time, salinity and temperature (Ziolli and Jardim, 2002; Martinez-Jeronimo et al., 2005). Given that there is not a common procedure for its preparation the results from different authors are difficult to compare (Singer et al., 2000). Therefore, it is not easy to assess, for instance, how oceanic water masses properties may affect the formation and composition of the SWAF in different spill conditions. For example, in the incident of the *Prestige* tanker tens of thousands of tonnes of heavy fuel oil were released from the wreck at more than 3500 m water depth (Albaigés et al., 2006). On its way towards the surface, the oil had to cross up to five water masses with different temperature and salinity conditions (Ruiz-Villarreal et al., 2006). Consequently, the concentration and composition of the SWAF in each water mass was likely to be different.

In this paper we propose a simple, fast and reproducible method for the preparation of SWAF. We apply a high energy mixing system, using an ultrasonic bath, but avoiding the formation of oil–water emulsions. The method is appraised by studying the changes in the concentration of PAHs in the SWAF of a heavy fuel oil in some of the salinity and temperature conditions commonly found in the North Atlantic Ocean, in the area of the incident of the *Prestige* tanker.

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2. Materials and methods

2.1. Fuel oil and seawater

The fuel oil employed was a marine fuel oil IFO 380, with a density of 0.981 kg L^{-1} at 15 °C, provided by the Coordination Technical Bureau from the Scientific Intervention Program Against Accidental Marine Spills (Vigo, Spain) in April 2005. It was similar in its physicochemical properties to that carried by the *Prestige* tanker.

Natural seawater was obtained from the Gulf of Biscay (33.3 psu; Cantabrian Sea) and from the Mediterranean Sea (37.7 psu). The salinity was measured using a YSI FT Model 556 conductimeter (YSI, Ohio, USA). The seawater was sterilized by adding $HgCl_2$ and filtrated before use through a precleaned glass fibre filter (0.7 μm, Ø 47 mm, APFF type, Millipore, Ireland) to remove suspended particulate material. To determine background levels of hydrocarbons in the natural SWAF, three aliquots of 400 mL from each water type were extracted with the same procedure used to analyze the SWAF, as described in the next section. The background PAH concentrations were subtracted from those found in the SWAF samples prepared in the laboratory.

The effect of temperature in the dissolution of fuel oil was appraised at two temperatures, i.e. 20 °C (i.e. coded high temperature or HT in the text and figures) and 3 °C (i.e. low temperature or LT). These temperatures were chosen as representative of the values of the surface and bottom water masses in the sinking area of the *Prestige* tanker, in the North Eastern Atlantic, 150 nautical miles offshore from the Spanish coast (Ruiz-Villarreal et al., 2006).

The effect of salinity was studied using natural seawater from the Gulf of Biscay (low salinity or LS), and from the Mediterranean Sea (high salinity or HS). The salinity of both of them was measured directly in the storing tanks, before and after the experiments to monitor any changes due to evaporation.

2.2. Preparation of SWAF

The dissolution apparatus (Fig. 1) was adapted from Ali et al. (1995). Seawater (1 L) was poured into a 1.5 L volume glass flask (94 mm I.D. × 200 mm height). Two PTFE tubs (0.7 mm I.D. × 500 mm length) were inserted in the cap, one of them kept over the surface of the seawater to blow nitrogen, and the other used for the collection of water samples inserted deep into the seawater. Fuel was added in a 1:500 (v/v) oil to water ratio, close to the surface of the seawater by means of a stainless steel spatula. The surface area to volume ratio was 0.03 and the headspace represented the 33% of the flask volume. The cap on the flask was sealed with PTFE film first, and then with plastic film. All the apparatus was placed carefully in an ultrasonic bath, sonicated for 30 min with an energy of 360 W and left to settle down at a constant temperature.

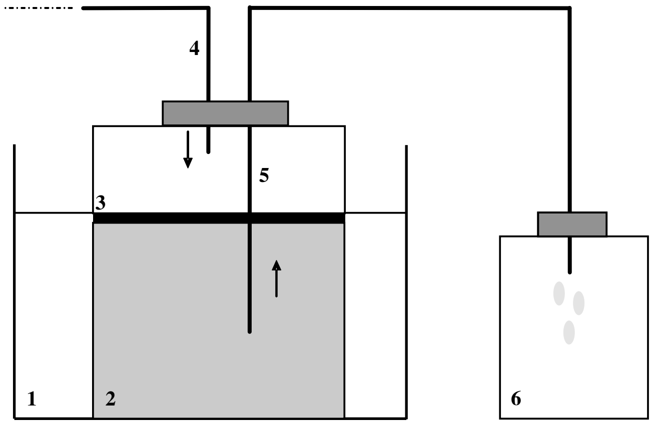

Fig. 1. The dissolution apparatus. (1): Ultrasonic bath; (2): SWAF preparation flask; (3): oil slick; (4): tube for N_2 application; (5): tube for sample retrieval; (6): sample recovery jar.

The apparatus was covered with aluminium foil to minimize the photodegradation of the fuel oil during the experiment. To maintain the sonication conditions reproducible, the location of the flask and the water level in the ultrasonic bath were exactly the same in all the experiments. Emulsions did not form as long as the flasks did not vibrate substantially in the bath. Cork plates were used to avoid direct contact between the flasks and the bath walls.

The retrieval of the water samples was carried out by applying a gentle stream of nitrogen through the tube over the seawater surface, while SWAF aliquots were collected in a clean glass flask through the tube inserted in the bottom. Special attention was paid not to disturb the water surface during this process to avoid dispersion of the oil.

The temperature was controlled mainly at two different stages of the SWAF preparation. First of all, natural seawater in the flasks, and distilled water filling the ultrasonic bath was added at the corresponding temperature at the beginning of each preparation experiment. Some of the seawater was simply stored in closed tanks in the laboratory at room temperature, maintained at 20 ± 2 °C, while water at 3 °C was obtained using a refrigeration system. This parameter was also controlled during the equilibration time. Half of the replicas were left to equilibrate at 3 °C, and the other half at 20 °C. The temperature of the water in the ultrasonic bath was measured before and after stirring and a maximum increment of 2 °C was observed.

Four experiments (at two different temperatures and salinities) were carried out in triplicate. In each type of experiment two identical sets were prepared for different purposes. In the first one, between 1 and 3 mL aliquots of water were collected at 0, 24, 48, 72, 96 and 120 h to monitor the progress of the oil dissolution by fluorescence analysis. In the second, 400 mL of water were collected after 24 h for the identification and quantification of individual PAHs.

The significance of the different experimental effects were confirmed using a one way ANOVA ($p < 0.05$ for all the preparation parameters) and several post-hoc tests (Tuckey HSD and Bonferroni), to make pairwise comparison of the average concentration and appraise which factor had the strongest influence in the dissolution of fuel oil in the seawater.

In parallel, another experiment was prepared where the fuel-water mixture was not sonicated to assess the differences in the solubility of the fuel in comparison to the proposed method with sonication. The experiment without sonication performed in triplicate under HT and HS conditions. Besides the oil–water mixing, the rest of the process was followed exactly as in the sonication experiments.

2.3. Characterization of PAHs in sea water and fuel oil

Sea water (400 mL) was filtered through a Durapore membrane (0.22 μm and Ø 47 mm, Millipore) in order to eliminate the particulate bulk oil material generated when using high energy stirring systems (Singer et al., 2000). The filtrated sea water was poured into a separatory glass funnel, spiked with a solution of anthracene-d_{10}, and extracted three times with 50 mL of dichloromethane (Suprasolv, Merck, Germany). The combined extracts were passed through a glass column filled with cotton wool and 7 g of dried Na_2SO_4 (>99%, Merck) to eliminate residual seawater, and