Determination of Polynuclear Aromatic Hydrocarbons in Seawater following an Experimental Oil Spill by Stir Bar Sorptive Extraction (SBSE) and Thermal Desorption GC-MS

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Abstract

Each case of oil spill involves a series of questions in terms of response, but also concerning an potential toxicity induced in the water column by the solubilization of some aromatic compounds. However, this process is difficult to predict as it is balanced by the evaporation phenomenon, and most field techniques have limits of quantification higher than the sensitivity that can be required in sensitive areas. Moreover, each oil is characterized by a specific composition, which leads to a particular amount and distribution of aromatics, hence the need for tools that allow the potential toxicity of a spill to be rapidly assessed.

The objective of this study was to obtain experimental data on the behavior of a crude oil by analyzing its water-soluble fractions in real conditions. The experimental program took advantage of a sea trial carried out in the North Sea from 28th September to 1st October 2009 by Rijkswaterstaat (Netherlands), and which involved two spills of crude oil, of 1 and 5 m^3 respectively. The first slick was immediately treated with dispersants while the second remained at sea 2 days for monitoring. Water samples containing dissolved oil fractions were regularly taken, at 1.5 and 8 m depths, for analyses using different chemical and biological techniques. As regards *Cedre*'s work, most of the samples collected just below the centre of the slick were analyzed by the SBSE-GC/MS technique in order to quantify dissolved Polycyclic Aromatic Hydrocarbons (PAHs). This technique of extraction (Stir Bar Sorptive Extraction) coupled with a GC/MS system allows quantification of dissolved apolar organic compounds at low levels, around 0.5 ng/L.

Results of analyses showed a continuous decrease of concentrations over time, either at 1.5 or at 8 m water depth. Moreover, concentrations measured at 8 m depth appeared to be more significant in comparison with samples collected just below the water surface (1.5 m).

1   Introduction

The identification and quantification of semi-volatile contaminants dissolved in water is generally performed in the laboratory after several steps following the sampling, mainly extraction, concentration and purification processes. These analyses are in most cases time-consuming, and many steps involved increases the risk of contamination, particularly when dealing with trace levels. Moreover, in case of oil spills, the shipment of samples can be difficult, and the conditions of their preservation questionable. The comparison of various extraction techniques used to analyzed water samples have been discussed and showed the reliability of the SBSE

compared to traditional liquid-liquid extractions (Hyötyläinen and Riekkola, 2007, *Trends in Analytical Chemistry*).

Consequently, the combination of SBSE (Stir Bar Sorptive Extraction) performed on-site followed by analysis in the laboratory afterwards represents an interesting solution. This technique, which was successfully applied in previous monitoring studies conducted in order to assess baseline levels, was applied in the context of an accidental oil spill. It must be noticed that this technique was also tested with a field GC/MS but some limitations appeared (Roy et al., 2005, *Talanta*).

The experimental program carried out in the North Sea, from 28th September to 1st October 2009, involved two spills of Grane crude oil, of 1 and 5 m^3 respectively. The first slick was immediately treated with dispersants while the second was monitored for 2 days. Water samples containing dissolved oil fractions were regularly taken, at 1.5 and 8 m depths. Unexpectedly, the oil showed a great natural dispersion, and the slick could be monitored only during the first 26 hours following the spill.

The objective of the analyses conducted by *Cedre* was to assess the behavior of the dissolved fraction of hydrocarbons during a crude oil spill. In this study, polycyclic aromatic hydrocarbons (PAHs), included parents and alkylated compounds, were the target molecules.

2 Material and Methods
2.1 Experimental Spill at Sea and Sampling Strategy

Following the experimental release at sea, several samples were collected in the water column at two water depths, 1.5 and 8 m, and at different locations considering the slick shape: outside, to get a control, in the middle for the "inside" location, and at the edge. Samples were collected in 5 L flasks in duplicate by using a dingy, and were then dispatched onboard the research vessel (a small laboratory was set up on the ARCA's deck). Concerning the SBSE analyses, 100 mL water samples (analyzed in triplicate) were immediately added with internal standards, and the bars introduced for a 2 hours stirring. Only one "outside" sample was analyzed as a control, and only the "inside" samples were considered in the study.

2.2 Measurements
2.2.1 Principle of the SBSE Analyses

The SBSE (Stir Bar Sorptive Extraction) consists in the concentration of apolar dissolved compounds by the apolar phase (PolyMethylPolySiloxane) deposited on a stir bar. The extraction is ensured by a stirring at 900 rpm for 2 hours. The quantification is achieved by introducing internal standards at the beginning of the sample preparation procedure. These standards (5 perdeuterated PAHs) are introduced in a methanolic solution in order to get a complete solubilization, and this final 10% content in methanol also prevent compounds from being sorbed on the glass walls. As 100 mL water samples were analyzed, they were added with 10 mL of methanol containing 10 ng of each perdeuterated PAH (final concentration of 100 ng/L). After the extraction, bars were recovered, rinsed with distilled water, dried over paper and placed on the automatic sampler in order to thermally desorb the compounds which are then introduced in the GC/MS equipment.

2.2.2 Target Molecules and Limits of Quantification

The quantification of dissolved PAHs was focused on parents and alkylated molecules. As regards the parents'ones, the 16 PAHs of the US EPA list were completed with biphenyl, benzo[e]pyrene and perylene, and also two sulphur aromatics (benzothiophene and dibenzothiophene). For most of PAHs, from naphthalene to chrysene, alkylated derivatives characterized by up to 3 additional carbons atoms, were also quantified relatively to the parent PAH.

2.2.3 Calibration

For each of the 21 parent PAHs, a calibration curve was established relatively to one internal standard chosen according to the similarity of its chemical structure. Six levels were used: 0.5, 1, 5, 10, 50 and 100 ng/L.

2.2.4 Analytical Conditions

Stir Bars covered with PDMS (20 mm long and 0.5 mm film thickness) were purchased from the Gerstel company (Switzerland).

The analysis was performed by Gas Chromatography coupled to Mass Spectrometry (GC/MS). The GC was an HP 7890N (Hewlett-Packard, Palo Alto, CA, USA) equipped with a Twister Desorption Unit combined with a Cooled Injection System (TDU and CIS-4, Gerstel, Switzerland). The thermal desorption was performed in splitless mode (TDU temperature program: from 50°C to 300°C (15 minutes) @ 60°C/min) and the cryofocussing was performed at -50°C by using liquid nitrogen. The interface temperature between the TDU and the CIS-4 units was maintained at 300°C. The injection was performed in splitless mode (CIS temperature program: from -50°C to 300°C (10 min) at 10°C/min). The GC temperature program was: from 50°C (1 min) to 300°C (20 min) at 5°C/min. The carrier gas was helium at a constant flow of 1 mL/min. The capillary column used was a HP-5 ms (HP, Palo Alto, USA): 30 m x 0.25 mm ID x 0.25 μm film thickness. The GC was coupled to an HP 5975 Mass Selective Detector (MSD) (Electronic Impact: 70 eV, voltage: 1200 V). The interface temperature was 300°C. PAHs quantifications were done using Single Ion Monitoring mode with the molecular ion of each compound at a minimum of 1.5 cycle/s.

PAHs were quantified relatively to the perdeuterated PAHs introduced at the beginning of the sample preparation procedure. Perdeuterated PAHs (Naphthalene d_8, Biphenyl d_{10}, Phenanthrene d_{10}, Chrysene d_{12} and Penzo[a]pyrene d_{12} in acetone, each compound at the concentration of 1 μg/mL) were purchased from LGC Standards (France).

3 Results
3.1 Qualitative Analysis

The sampling of water-soluble fractions following an oil spill is generally difficult due to the great amount of pollutants either remaining at the sea surface or partially dispersed in the water column. Consequently, for each chromatogram, the presence of potential dispersed oil had to be checked. This was done by extracting the pattern specific to saturated compounds (fragment m/z =57) which was then compared to the one obtained on the crude oil itself. No sample showed a distribution sufficiently close to the oil to suggest the presence of oil droplets.
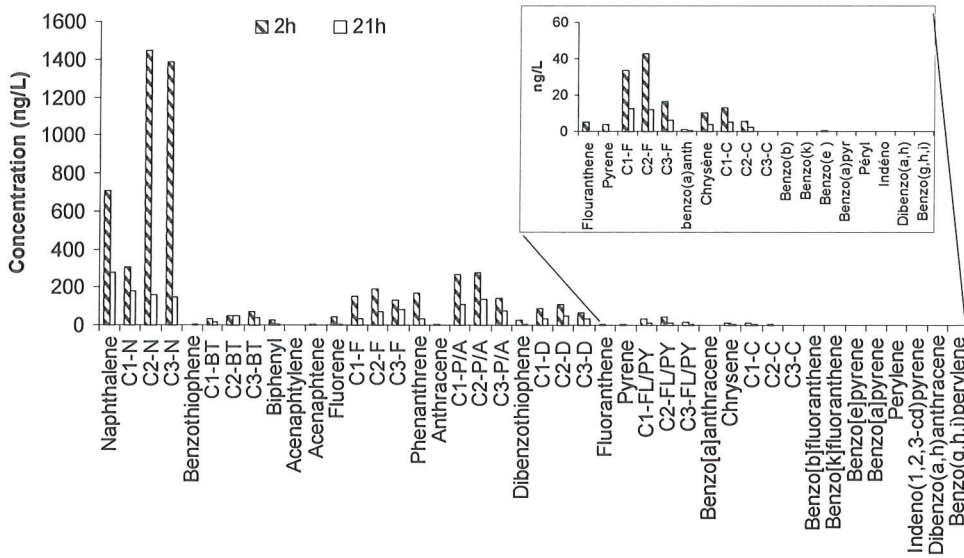
An example of chromatogram illustrating the PAHs patterns of a dissolved fractions is presented figure 1 (Nd_8 and Pd_{10} correspond to the Naphthalene d_8 and Phenanthrene d_{10} used as internal standard, C_1-N to C_3-N correspond to the alkylated Naphthalenes, and C_1-P/A to C_3-P/A correspond to the alkylated Phenanthrenes and Anthracenes). In this example, the naphthalene is more abundant than C_1-Naphthalenes, which is not the case in crude oils (Wang and Fingas, 1999).
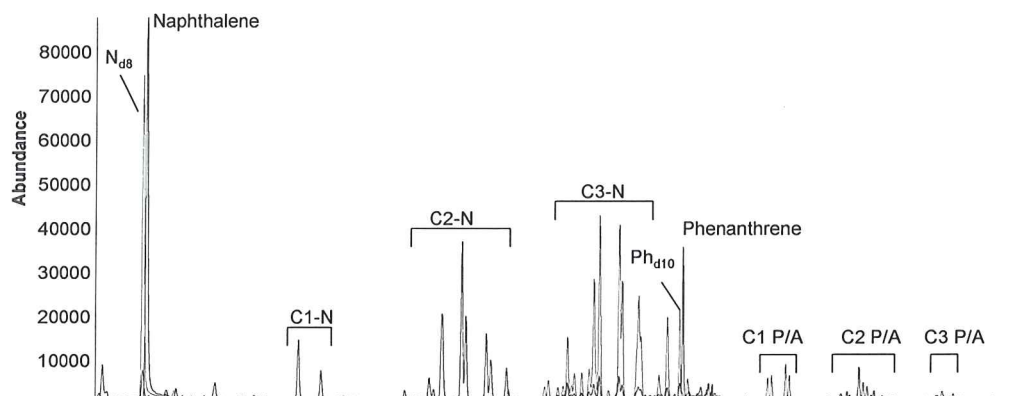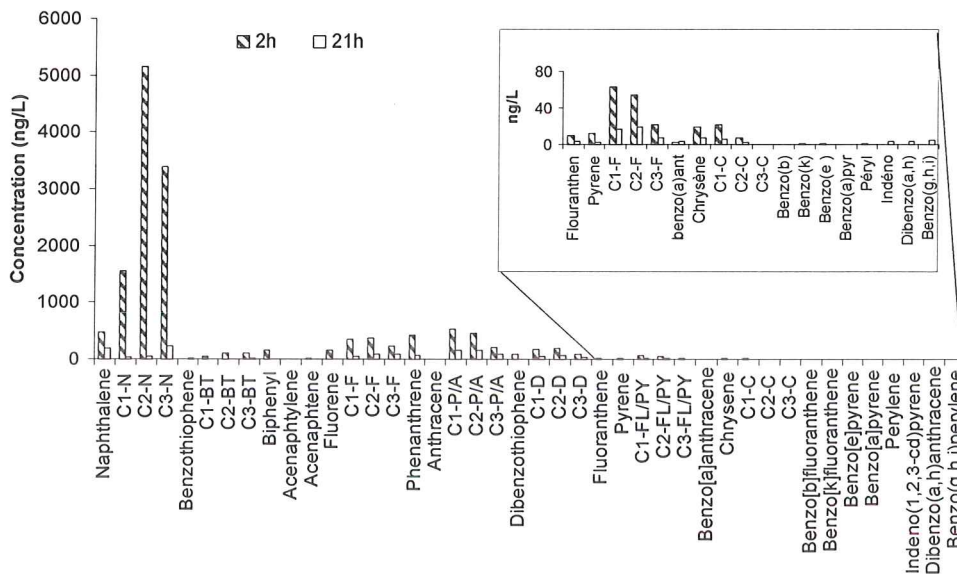

Figure 1   **Extracted ion chromatogram of Naphthalenes and Phenanthrenes/Anthracenes (1.5 m depth 2 hours after the spill)**

3.2   PAHs Profiles over Time

Two hours after the oil spill, concentrations of PAHs, either at 1.5 m or 8 m depth, ranged from few ng/L for the heaviest molecules to thousands of ng/L for the lightest. The PAHs patterns (illustrated figure 2 and 3) show a great abundance of the naphthalenes, which then decreased over time due to the progressive evaporation of light fractions. The heaviest PAHs concentrations also showed a decrease but relatively less important, and these molecules were still detected at significant levels at the end of the experiment.

Guyomarch, J. and S. Van Ganse, Determination of Polynuclear Aromatic Hydrocarbons in Seawater following an Experimental Oil Spill by Stir Bar Sorptive Extraction (SBSE) and Thermal Desorption GC-MS, Proceedings of the Thirty-third AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 181-187, 2010.

Figure 2   **PAHs profile at 1.5 m water depth 2 hours and 21 hours after the oil spill**
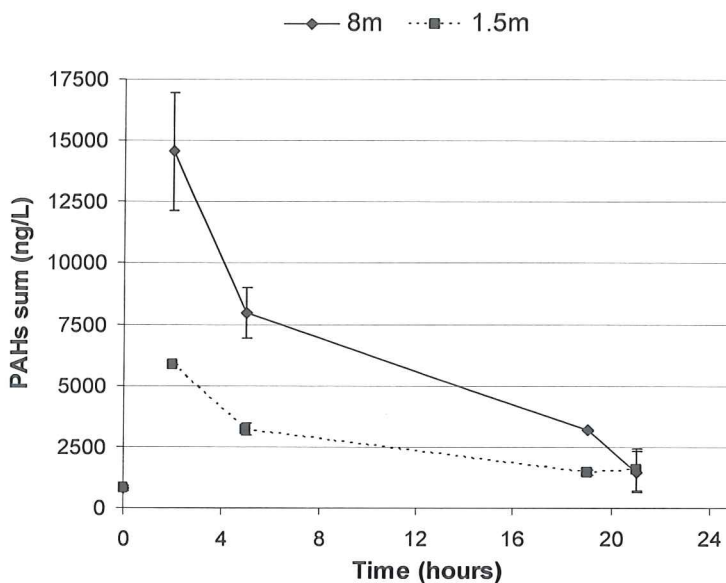

Figure 3   **PAHs profile at 8 m water depth 2 hours and 21 hours after the oil spill**

3.3   Total PAHs Concentration over Time

The quantitative analyses of the various water samples showed an initial increase up to a maximum close to 6000 ng/L at 1.5 m (15000 ng/L at 8 m), followed afterwards by a regular decrease. The concentrations were higher at 8 m, in comparison with the sub-surface samples (Figure 4). This could be explained by the great natural dispersion observed during the field trial: PAHs could come not only from the slick itself, but also from the oil droplets remaining in a lower part of the water column.

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Figure 4   Evolution of PAHs concentrations versus time at 1.5 and 8 meters

4   Conclusions

The SBSE extraction, in combination with a GC/MS analysis, applied in the framework of this experimental oil spill proved to be adapted to on-site measurements. Low limits of quantifications can be reached, and the sample preparation procedure, simple and performed onboard, reduces the possibilities of contamination. The quantitative results were not expected as the concentrations were significantly higher at 8 m water depth in comparison with 1.5 m samples. This could be explained by the great natural dispersion observed during the field trial. This study also demonstrates the great decrease of concentrations over time, but many PAHs were still quantified at the end of the experiment. Taking into account the high toxicity of these molecules at low levels (Goanvec et al., 2008, *Journal of Fish Biology*), a continuous monitoring should be recommended in the case of a real spill, and the SBSE technique represents an interesting solution due to its simplicity and sensitivity.

5   Acknowledgements

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6   References

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