

## Oil Weathering, Impact Assessment and Response Options Studies at the Pilot Scale: Improved Methodology and Design of a New Dedicated Flume Test

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### Abstract

Each case of spill entails a series of questions concerning the fate and behavior of the petroleum product, either crude or refined oil. It is subjected to weathering processes such as evaporation, emulsification, dispersion and photo-oxidation. These processes occur under natural conditions due to sea surface agitation by wind, waves and currents and to the exposure of the oil to solar light. According to its weathering stage, the state of the oil is continuously changing in terms of chemical composition and physical properties. Understanding these transformations is a key element in evaluating the potential impacts, optimizing the response options and implementing the emergency response plan to spillage.

The objective of this paper is to describe the methodology applied to get experimental data on the physical-chemical evolution and behavior of spilled oils. The various weathering processes are simulated realistically in the new flume test implemented at *Cedre*, in which different marine or inland water conditions can be recreated. It is equipped with wind, current and waves generators, the temperature can be adjusted from 1°C to 30°C and the intensity of UV lights is in agreement with natural irradiation. The process of the design of this new equipment is also described, as well as its validation.

The different parameters measured or assessed on the 15 samples collected during the one week experiments are: density, viscosity, water content and kinetics of emulsification, chemical composition and kinetics of evaporation, flash point, emulsion stability, oil adhesion and chemical dispersibility. In addition, *in situ* dispersibility tests can be carried out, and combined by an assessment of the quality of the dispersion through droplets size measurements.

Finally, some on-going projects are described as they can be combined with weathering studies, thus providing data on the various issues related to oil spills: impact of the oil, possibility of using *in situ* burning techniques, expected efficiency of cleaning techniques...

### 1 Introduction

The weathering of crude oils or refined products is complex as different processes (evaporation, dispersion, emulsification, photo-oxidation, ...) take place simultaneously, mainly governed by environmental conditions. In addition, each crude oil has its own chemical composition, and the extent of the various processes depends on its initial physical-chemical characteristics. Laboratory protocols can be applied in order to assess more realistically the oil weathering, and to get additional information such as the time-window of opportunity for dispersant use. Different laboratory methodologies exist to simulate different weathering processes. For example, evaporation can be simulated by a simple distillation at various temperatures while the Mackay method using rotary funnels is used to create water-in-oil emulsions. However, no laboratory method takes into account all the parameters simultaneously, thus simulating the whole weathering process which is affected by the

interactions between various phenomena: evaporation is limited by the formation of emulsions; the emulsification process can be balanced with natural dispersion...

In order to simulate these various processes realistically and simultaneously, *Cedre* has equipped its facilities in 1997 with an hydraulic canal, the Polludrome, in which different marine (as well as inland) water conditions could be recreated: wind, current, waves and solar radiations. This canal consisted of a loop set in an air-conditioned room, in which the water can be circulated and equipped with a wave generator (adjustable period), a current generator and UV lights. With this equipment, it was possible to weather a dedicated oil in similar climatic conditions as the ones which can be encountered in the oil field from which it is extracted or in the area of shipment. This equipment was used to study the behavior and weathering of many chemicals and oils, in particular in the framework of the response to real accidents such as the *ERIKA* spill in 1999, or the *PRESTIGE* in 2002.

Over the last 15 years, around 40 crude oils were spilled in the flume test in order to monitor the evolution of their physical-chemical properties. Data obtained from these experiments were used by people in charge of the elaboration and implementation of response plans in case of accidental oil spills. The objective was to help them choose the most appropriate response options according to the weathering stage of the oil. In addition, such a database could be used in a longer term with a view of predicting the behavior of one oil according to its initial physical-chemical properties.

It must be noted that the device was also used to assess recovery ships at small scale, test sorbents or study the behavior and drift of chemicals, coal and algae on the sea floor.

After 15 years of intensive use, the flume test was significantly corroded on some points and some equipments were affected by changes of their performances, in particular the wave beater. With many years of experience in using this tool, a reflexion was carried out at *Cedre* in order to define the specifications of a new flume test, in terms of simulations of the environmental parameters, but also as regards the conditions of use.

This paper describes the evolutions of the equipment and examples of results, and provides an update of the methodology previously described (Guyomarch *et al.*, 2000). Finally, some synergies have been identified with the other characterizations and experimental tools developed at *Cedre*, hence the implementation of on-going studies combining various aspects of the response (oil weathering, environmental impact, assessment of cleaning techniques...).

## 2 Background

Each case of spill entails a series of questions concerning the fate, behavior and environmental impact of the crude oil or refined product involved. Subjected to weathering processes such as evaporation, emulsification, photo-oxidation and dissolution possibly combined with natural dispersion, the state of the oil is continuously changing in terms of chemical composition and physical properties. Moreover, part of the most soluble compounds is transferred from the slick to the water column, thus inducing other potential impacts. These processes occur under natural conditions due to sea surface agitation by wind, waves and currents and to the exposure of the oil to solar light.

As weathering progresses, the state of the oil is continuously changing: the light fractions evaporate gradually, its density gets higher, and part of the oil can disperse naturally in the water column while the oil remaining on the water surface gets emulsified with sea water and is oxidized by ultra-violet radiations. Oils generally become more and more viscous and can turn into a new persistent pollutant in the environment. Weathered oil behavior may be very different from the behavior of the original oil. Understanding these transformations is a key element in evaluating the potential impacts, optimizing the response options according

to the weathering stage of the spilled oil and implementing the emergency response plan to spillage.

The knowledge of these transformations is a key element in evaluating potential impacts and in optimizing the emergency response to a spill. Each spill induces a series of questions:

- What is the fate of the pollutant and what is the rate and extent of its weathering?
- Can natural dispersion occur?
- Does the oil emulsify? What is the emulsification rate? What is the real stability of the emulsion?
- Is it chemically dispersible? For how long? Which dispersant would be the most suitable?
- Is it possible to apply the *in situ* burning technique?
- Is it likely to be mechanically recovered? Can the recovered emulsion be broken using demulsifiers? Which demulsifiers are suitable?
- What is the potential for bioremediation? What is the oil biodegradability?
- What is the potential toxicity of the water soluble fractions (WSFs)?

When a spill occurs, it is often too late for investigating these questions. Therefore, these questions must be addressed during the emergency response planning process in order to allow responders to take quick, appropriate and justified decisions in case of a spill.

Different mathematical models have been designed over these last few years to predict the fate and behavior of various oils. However, during recent large spills, these predictions did not prove to be always as reliable as they should be. Therefore, the models have to include specific characteristics of the oils and also, if possible, experimental simulations of the oil behavior when spilled at sea have to be carried out to adjust the predictions.

### **3 Design of the New Flume Test**

#### **3.1 Main Modifications of the Device**

The replacement of a tool used for many years by different people involved in various fields was the occasion of gathering all the views concerning the past experience and the potential applications in the future. It must be noted that the only pre-requisite was to keep the geometry of the loop configuration which was initially combined with the possibility of using a straight section of the canal. These requirements were explained by the necessity of comparing future with past experiments.

The main conclusions which were drawn from the discussions were:

- The combination of the *loop* and *straight* configurations was given up as it created difficulties in terms of water tightness, hydrodynamic turbulences and homogeneity of the structure.
- The withdrawal of the straight section led to the possibility of dividing the 100 m<sup>2</sup> climate room in two areas separated by a removable door, with two different systems of temperature regulation.
- The flume test had to be mobile in the case of the entire climate room should be necessary for a specific experiment.

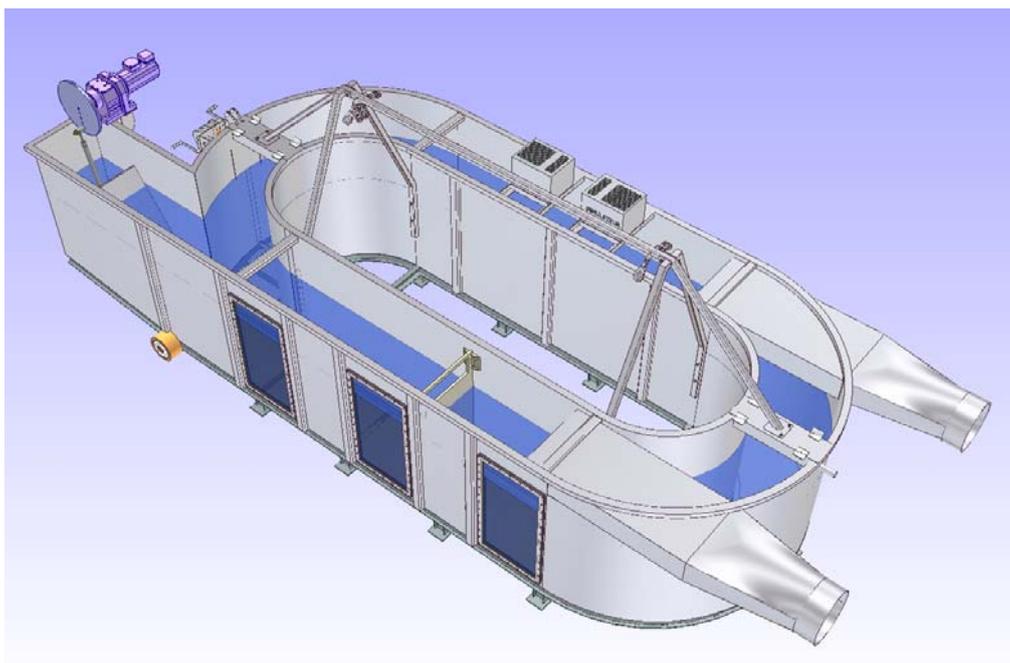
As regards the conception of the canal used for weathering studies, the main changes or improvements were as follows:

- Equipment made of 4 mm stainless steel (3 mm for the cover) instead of aluminum.
- Reduction of the size of the windows and withdrawal of the small ones previously located just above the bottom,
- The cover was made of two parts instead of around 10 different pieces, and operated by using a winch,

- The wind generator was kept but the geometry of the diffusion in the canal was modified to generate less turbulences. The location of the fumes extractor was also changed.

The final project adopted before manufacturing is illustrated in Figure 1. The dimensions of the canal and the conditions of the simulations are as follows:

- Canal dimensions:  $L = 12$  m,  $l = 0.6$  m,  $h = 1.4$  m
- Temperature: from 1 to 30°C
- Waves height and frequency, wind and current speed adjustable
- UV lights: 2 units of 2 000 W each



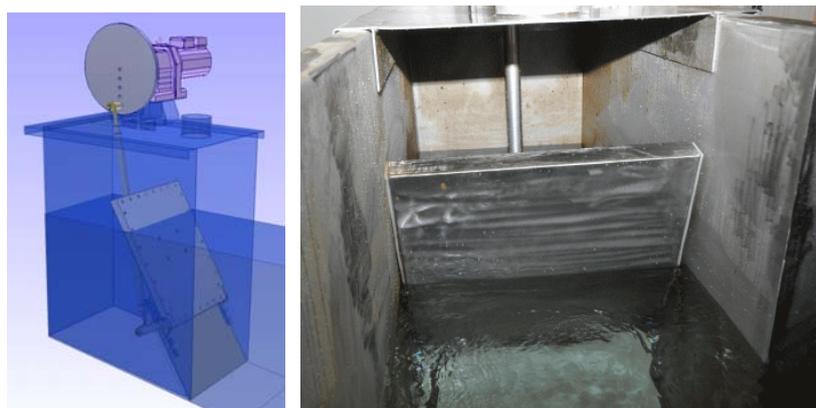
**Figure 1**      **The *Polludrome***

## **3.2 Specific Equipments**

### **3.2.1 Wave Generator**

The overall design of the wave generator is illustrated in Figure 2. This solution was chosen as it offered a regular and reproducible wave without the drawbacks of the jolts generated by the previous version (wedge-shaped section plunged into the water by a hydraulic cylinder). Contact was made with *Cedre*'s partners in order to model the agitation generated by the system. However, the considerable reflection off the walls and the complexity of the waves overlaying each other proved incompatible with such a numerical simulation.

During the set-up design stage, it was decided that the aim would be to include many different settings in order to offer numerous combinations. Four bottom plate anchor points were positioned along the two oblique attachment rails, and the connecting rod can also be attached in 4 different positions on the rotating disc. The speed of this disc itself can be adjusted by a rheostat.



**Figure 2 Views of the Wave Beater**

### 3.2.2 Simulation of Solar Radiation

The difficulty in designing a specialised system caused us to look towards industrial solutions. Solar radiation simulation units are currently used in paint weathering tests, in particular in the automotive industry. We opted for two 2000 W units (Figure 3), generating an intensity of 1000 W on the slick (manufacturer data).

As the area exposed to radiation is around 1.5 metres long by 60 cm wide, the light intensity per surface unit is approximately 2000 W/m<sup>2</sup>. As a slick drifting in the canal is only exposed to this radiation periodically, the average intensity is approximately 200 W/m<sup>2</sup>. This value is close to those found at the equator, and around twice that measured in Western Europe. It is therefore possible to recreate a wide variety of conditions using one or more generators, whereby lower irradiation rates (in particular Arctic conditions) are simulated by periodically shutting down the systems.



**Figure 3 Views of the UV Generators**

## 4 Experimental Weathering at the Pilot Scale

### 4.1 Material and Methods

#### 4.1.1 Conditions of Test

The tests were performed at a representative temperature of the area of production or shipment of the oil, and at the same surface energy (waves and wind, current about sea state 3). It is also possible to simulate different weather conditions on request.

For each oil, *Cedre* studied the weathering of a sample in its hydraulic canal during 7 days in order to know its fate and behavior during the first hours and first days after an oil spill. Full salinity seawater (33 ppt) was used in tests, or other conditions on request.

Assuming a moderate wind speed (around 10 knots), a sea state 3 on the Douglas scale was simulated in the canal (this sea state corresponds to wave heights between 0.5 and 1.25 m in real conditions). 15 liters of oil were poured onto the water surface to allow an extensive sampling as presented Table 1. During the tests, surface oil samples were taken periodically to determine the oils characteristics. In addition, the weathered crude oils were subjected to dispersibility tests using the IFP laboratory protocol according to the NF T 90-345 French Standard (AFNOR, 1990).

**Table 1 Sampling Times**

Sample reference	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>	T <sub>6</sub>	T <sub>7</sub>	T <sub>8</sub>	T <sub>9</sub>	T <sub>10</sub>	T <sub>11</sub>	T <sub>12</sub>	T <sub>13</sub>	T <sub>14</sub>	T <sub>15</sub>	T <sub>16</sub>
Time (hours)	1	2	4	6	8	14	22	26	30	48	53	72	77	96	101	168

#### 4.1.2 Monitoring of Physical-Chemical Parameters

Table 2 illustrates the various physical-chemical parameters monitored during the weathering experiments, and also the response strategies assessed according to standard (dispersibility) or specific (oil adhesion) laboratory tests

**Table 2 Physical-Chemical Parameters and Response Strategies**

##### *Physical-Chemical parameters*

Evaporation and chemical Composition	- Modification of the oil composition - Kinetics of evaporation and maximum evaporation rate
Flash Point	- Evolution of flash point
Emulsification	- Kinetics of emulsification and maximum water content - Assessment of the possibilities of using demulsifiers - Changes in the stability of the emulsion
Density	- Evolution of the surface oil and/or emulsion density
Viscosity	- Evolution of the oil and/or emulsion viscosity

##### *Treatment possibilities*

Dispersibility	- Chemical dispersibility of the oil and/or emulsion - Window of opportunity for the use of dispersants
Oil Adhesion	- Adhesion of the oil to oleophilic surfaces; oil ability to be skimmed
Oil Biodegradation	- Assessment of the possibility to biodegrade the oil and to run bioremediation operations

## 4.2 Methods of Measurements

### 4.2.1 Evaporation and Chemical Composition

The evolution of the oil composition was assessed by fractionation into 4 chemical families (saturates, aromatics, resins and *n*-pentane asphaltenes). The total oil evaporation was assessed on the basis of the evolution of saturates. The Weathering Index described by Wang *et al.* (1995) was used and the calibration curve was established from samples evaporated in the laboratory by distillation at various temperatures (typically topped at 150, 200 and 250°C;

see section 8.1). The same calibration curve was also obtained from density measurements. Finally, total losses could also be assessed by analyzing oil samples by High Temperature Gas Chromatography – Flame Ionization Detection (HTGC-FID). This technique proved to be particularly adapted to products characterized by a significant proportion of heavy compounds, containing more than 40 carbon atoms.

#### 4.2.2 Flash Point

The flash point was measured according to the NF EN ISO 13736 norm (AFNOR, 2008) on non-emulsified oil samples (Abel method equivalent to IP 170). This parameter was assessed until it reached 100°C considering this value as a reasonable limit in term of risk of ignition of an oil slick.

#### 4.2.3 Pour Point

The pour point was measured according to the ISO 3016 norm (AFNOR, 2008) equivalent to ASTM D97, on the fresh crude oil and also on corresponding residues obtained by distillation at 150, 200 and 250°C.

#### 4.2.4 Emulsification

Emulsification was assessed by measuring the water content in the oil samples according to three different ways:

- the water which separated naturally from the oil.
- the water which settled after addition of 0.1% demulsifier (*Demulsip*),
- the water that was distilled using the ISO 3733 Dean & Stark method, equivalent to the ASTM D95-05 (2010) Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation.

From these measurements, it was possible to determine the kinetics of emulsification as well as the maximum water uptake. The assessment of the stability of the emulsion resulted from the comparison of these data.

#### 4.2.5 Density

The density of the samples of surface oil was determined according to the ASTM method D70-09e1 Standard Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials (Pycnometer Method) (ASTM, 2009). This measurement gave the real density of the emulsion that would remain on the sea surface.

#### 4.2.6 Viscosity

The viscosity of the oil samples was measured by establishing the rheological curve using a Haake VT 550 viscosimeter at test temperature, to get the evolution of the viscosity at dedicated shear rates (e.g. 1, 10, 100 s<sup>-1</sup>).

#### 4.2.7 Dispersibility

The natural dispersion (combined with the possible dissolution) was measured from water column samples.

The chemical dispersibility of the surface oil was measured by using the IFP test method (NF T 90-345 French Standard) at test temperature and with a reference dispersant (Finasol OSR 52). Tests were performed using samples collected during the oil weathering according to their viscosity evolution, and at least after 24, 48, 72 and 168 hours .

Finally, at the end of the weathering experiment, one dispersant could be directly applied on the slick at its final state (high viscosity and high water content) in the flume test to obtain a more representative value of the dispersant efficiency in real conditions.

#### 4.2.8 Oil Adhesion

The evolution of oil adhesion was measured by weighing the amount of oil that sticks on a given oleophilic plate. This test provides information of the possibility of using oleophilic skimmers.

#### 4.2.9 Oil Biodegradation

The biodegradability of the oil was assessed by determining its final composition (fractionation into 4 chemical families) and by analyzing the various compounds in the aromatic and saturate fractions by using gas chromatography/mass spectrometry (GC/MS). The GC/MS analysis was used to identify the proportion of resolved peaks and Unresolved Complex Mixture (UCM) in both chemical families. Biodegradability was calculated according to the rates defined in the International Maritime Organization guidelines (IMO, 2004) for each category of compounds.

### 4.3 Chemical Analysis of Crude Oils

#### 4.3.1 PolyAromatic Hydrocarbons (PAHs) and *n*-Alkanes

Each crude oil sample was spiked with internal standards (perdeuterated PAHs) and purified on a cyano micro-column in order to remove polar compounds. Saturated and aromatic compounds were analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). PAHs were quantified relatively to the perdeuterated PAHs introduced at the beginning of the sample preparation procedure (perdeuterated eicosane as regards the alkanes). Target molecules, as regards the PAHs, were the 16 PAHs of the US EPA list completed with biphenyl, benzo[e]pyrene and perylene, and also two sulfured aromatics (benzothiophene and dibenzothiophene). For most PAHs, from naphthalene to chrysene, alkylated derivatives characterized by up to 4 additional carbons atoms were also quantified relatively to the parent PAH. Perdeuterated PAHs (Naphthalene  $d_8$ , Biphenyl  $d_{10}$ , Phenanthrene  $d_{10}$ , Chrysene  $d_{12}$  and Benzo[a]pyrene  $d_{12}$ ) and Eicosene  $C_{20}D_{42}$  were obtained from LGC Standards (Molsheim, France). Calibration curves were established from *n*-alkanes and PAHs mixtures obtained from Ultra Scientific. These mixtures contained *n*-alkanes from  $nC_8$  to  $nC_{32}$ , and as regards PAHs, all the parent PAHs mentioned previously.

#### 4.3.2 Simulated Distillation

The boiling point distribution of the various samples could be established by simulated distillation using the HTGC-FID techniques. Retention times were converted into boiling points by using a calibration curve established by analyzing an *n*-alkanes mixture, from  $nC_{10}$  to  $nC_{100}$ .

#### 4.3.3 Oil Fingerprint

Oil samples were purified by low pressure liquid chromatography and analyzed by GC/MS. The oils fingerprints were established according to the CEN (European Committee for Standardization) technical report " Oil spill identification – Waterborne petroleum and petroleum products – Part 2: Analytical methodology and interpretation of results " (CEN, 2006).

#### 4.3.4 Chemical Parameters

Asphaltenes content was determined on the residue obtained by distillation at 250°C according to the IP-143/90 norm "Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products" (Institut of Petroleum, 1985). This gravimetric method was more reliable when applied to non-volatile oils, such as 250°C+ residues. The results was then extrapolated to other residues and to the fresh oil by taking into account the evaporation rate

measured following the distillation. This determination could be completed with a SARA (Saturates/Aromatics/Resins/Asphaltenes) separation with limitations as regards saturates and aromatics in case of significant content of volatile products (most of SARA analyses are gravimetric methods).

Wax content was measured on the same residue after the precipitation of asphaltenes (the measurement performed directly on the residue was liable to conduct to co-precipitation of asphaltenes and waxes). The protocol, which was described by Bridié *et al.* (1980), consisted in a precipitation in a mixture of MEK (methylethylketone) and DCM (dichloromethane) 1:1 at -10°C.

## 5 Characterizations of the Water Column

### 5.1 Oil Droplet Size Distribution in Case of Natural Dispersion

Oil weathering studies in the marine environment go hand-in-hand with the assessment of the oil's chemical dispersibility. The possibility of dispersant application is estimated throughout experiments by analysing certain samples using the IFP dispersant efficiency assessment protocol. This quantitative information however only provides a partial vision of the phenomena liable to occur at sea. The opportunity for dispersant use can be assessed, from a physical-chemical perspective, according to two criteria: the treatment efficiency (proportion of oil dispersed or else oil concentration in the water column), but also the quality of dispersion. "Acceptable" efficiency in the case of large droplets can result in the resurfacing of the pollutant in the medium term, and therefore in the spread of the pollution at the surface rather than its "dilution".

It therefore appeared necessary to include a characterisation of the physical form of the dispersed pollutant (natural or chemical dispersion) in oil behaviour experiments, as this is a determining factor in its behaviour and fate in the water column. Following an analysis of the different systems available on the market, a laser particle size analyser was purchased from Malvern (MasterSizer 2000, Figure 4). It must be noted that the sampling is performed by using a peristaltic pump placed after the measuring cell to avoid droplets coalescence.



**Figure 4** Laser particle size analyser (optical unit and input system)

## 5.2 Quantification of Water Soluble Fractions (WSFs)

The PAHs listed in section 4.3.1 were quantified by using the SBSE (Stir Bar Sorptive Extraction) technique combined with a GC/MS analysis as previously described (Guyomarch and Van Ganse, 2010; Balcon *et al.*, 2011). The limits of quantification were below  $1 \text{ ng.L}^{-1}$  for all the compounds assuming a sample volume of 100 mL. The principle and the deuterated compounds used for the internal calibration were the same as described for oil samples. It must be noted that this technique could only be applied to soluble fractions, and the presence of potential dispersed oil was checked by looking at the saturated pattern ( $m/z = 57$ ).

## 6 Validation of the new *Polludrome*

### 6.1 Adjustment of the parameters

To obtain the evolution of oils spilt similarly to those observed with the previous *Polludrome*, the geometry of the ring flume was maintained, as were its main characteristics. The water depth and the current and wind generation mechanisms have remained relatively unchanged. On the other hand, the wave generating system has been completely redesigned, resulting in a very different propagation of surface agitation. A very localised high energy point has been replaced with waves that now run throughout the entire ring. Adjustments to wave height and the level of energy generated have therefore been empirical and qualitative in comparison to previous observations. The wave size, measured at the reference level taken in the middle of the window closest to the generator, is  $\pm 17 \text{ cm}$ , and the waves break slightly within the first 3 metres.

### 6.2 Comparative Weathering Tests of a Crude Oil

Among the first oils studied in the previous *Polludrome*, a crude oil tested in October 2010 appeared to be of particular interest with a view to reproducing the results in the newly revised flume tank. The specificity of this oil was that it formed relatively viscous emulsions in comparison to other available oils, while remaining at the limit of natural dispersion.

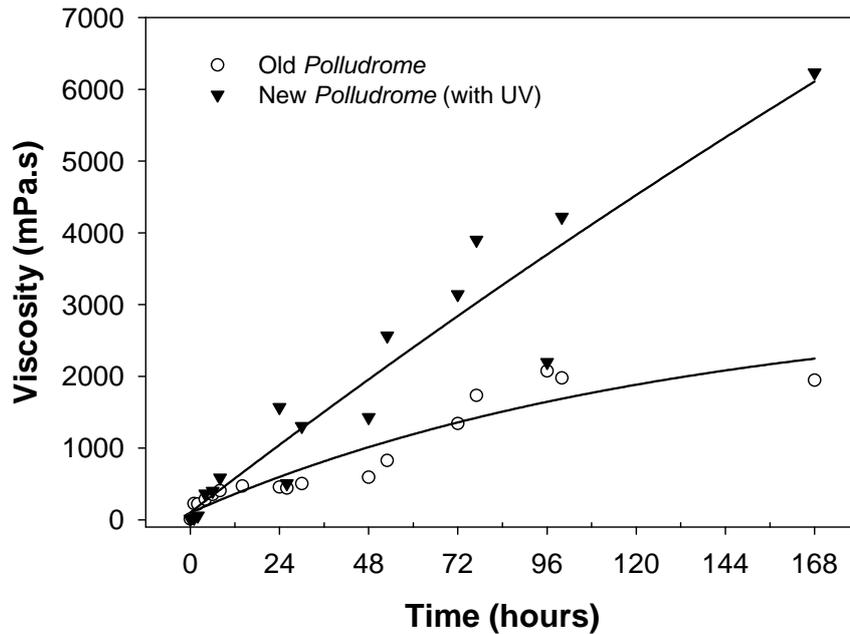
The measurements taken during these validation trials aimed to determine the water content and viscosity of emulsions, the most representative characteristics of the oil's overall evolution.

In the following graphs, the evolution of the different parameters is expressed according to the weathering time and, whenever possible, a regression model was applied. This modelling is the result of a statistical analysis performed using the software Sigmaplot 9.0.

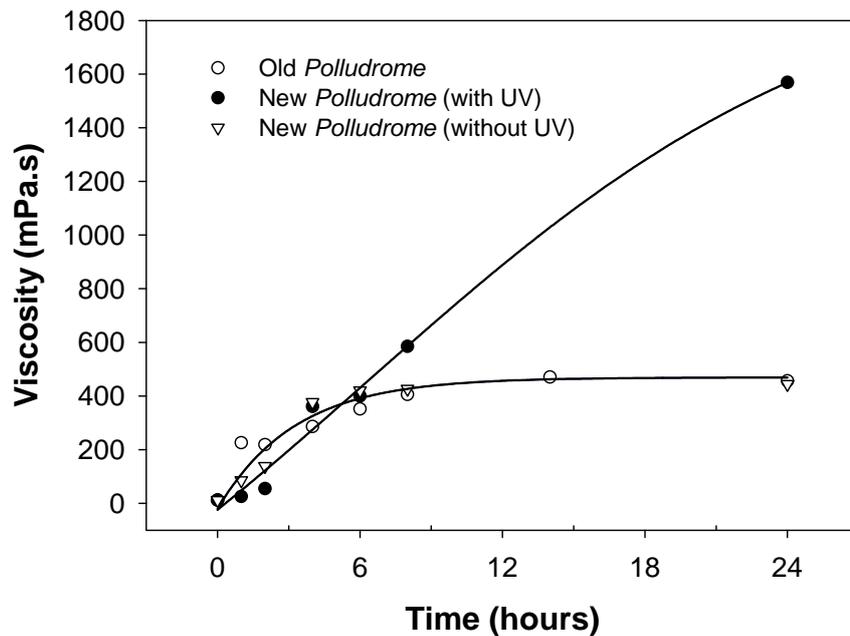
#### 6.2.1 Viscosity

Studies of the evolution in viscosity showed major discrepancies between the two systems, whereby the new equipment gave far higher values (Figure 5). Given the major overhaul of the solar radiation simulation system, a second trial was conducted without activating this equipment, thus providing conditions closer to those applied previously.

Figure 6 illustrates very similar evolutions over the first 24 hours, however comparisons could not be pursued beyond this period due to the quantity of oil spilt. These comparative trials showed that the energy level generated by the new system is comparable to the previous system, at least in terms of the characteristics of the emulsions generated. Furthermore, the effects of the UV radiation simulator can be perceived from the first hours of weathering.



**Figure 5** Comparison of the Viscosity Evolutions Obtained by the Two Device

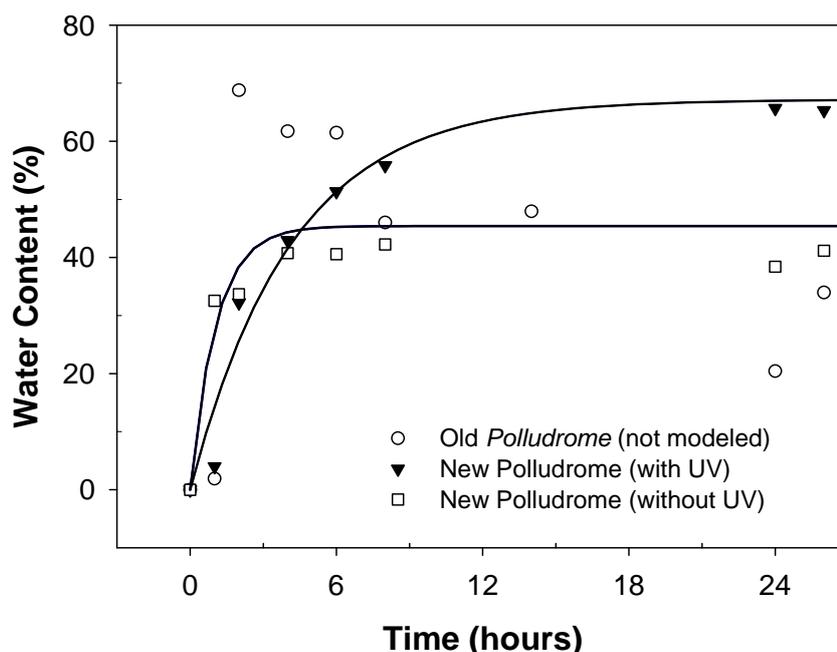


**Figure 6** Comparison of the Viscosity Evolutions within the First 24 Hours

### 6.2.2 Water Content

Different trial configurations lead to variable evolutions in water content, whether in terms of the maximum reached or kinetics (Figure 7).

The new system is set apart by a lower variability in results, as the experimental data is globally in agreement with the regression models generally applied to the evolution of this parameter (exponential growth to a maximum). These differences with the previous version of the *Polludrome* can be explained by a greater distribution of the agitation energy across the entire flume, while the “wedge” wave generator provided greater but more localised energy.



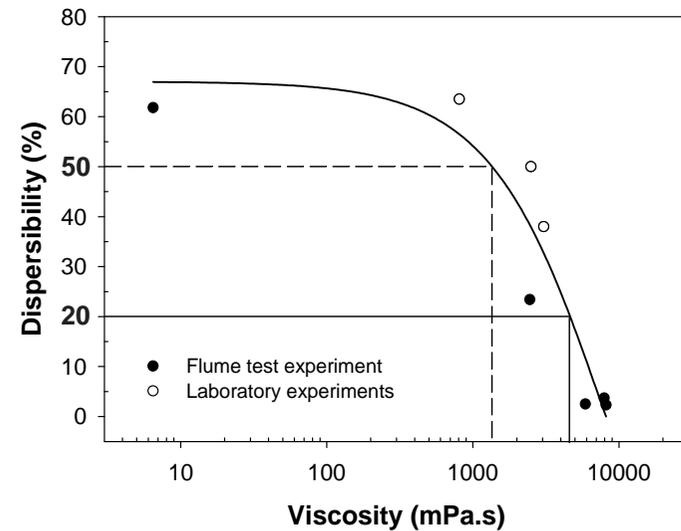
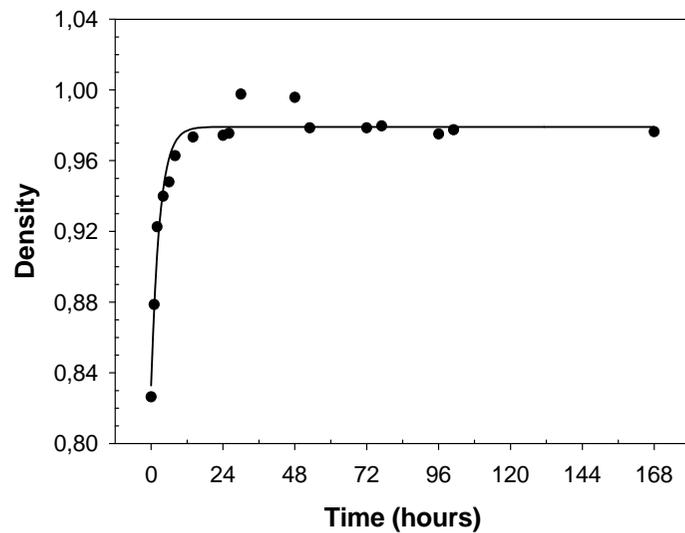
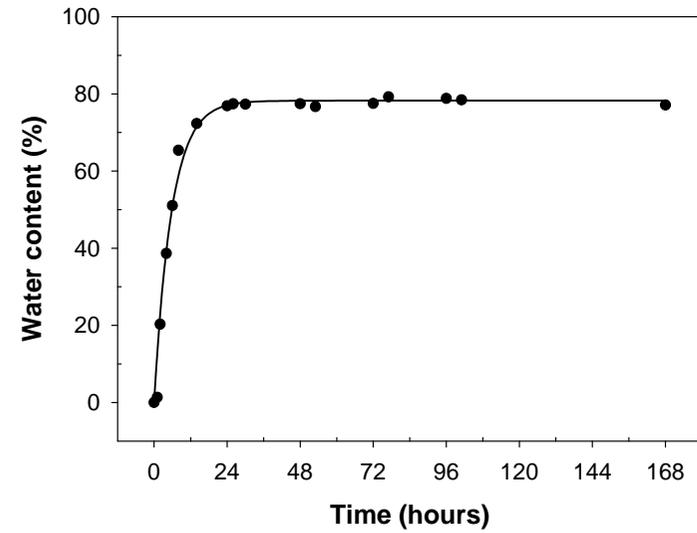
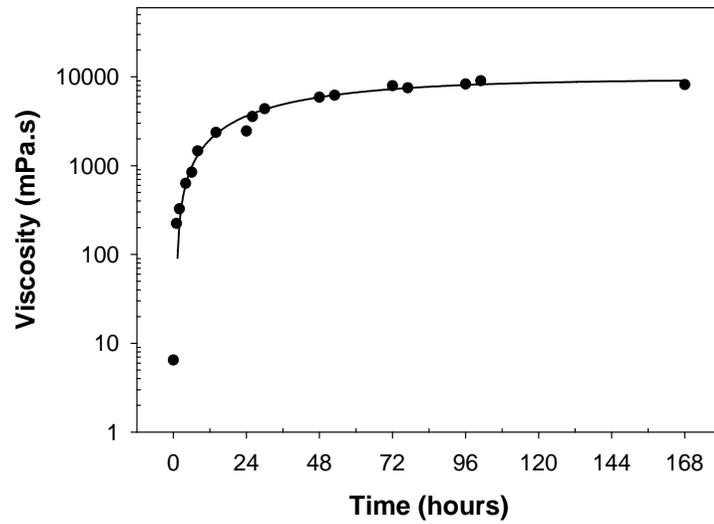
**Figure 7 Evolution of the Water Content**

The influence of UV radiation is in agreement with the evolution in viscosity, as the activation of the simulator resulted in higher water contents. The trial conducted without the simulators resulted in average water contents close to those obtained from the experiment performed in 2010, the comparison however being very biased given the very high heterogeneity of the values measured.

## 7 Examples of Results Obtained with the New *Polludrome*

Examples of evolutions of various physical-chemical parameters during flume test experiment are illustrated Figure 8 to 11. In particular, the oil dispersibility was plotted versus oil viscosity, in order to assess the limit of viscosity for dispersant use. The criteria chosen to distinguish the various categories of dispersibility (easily dispersible, uncertainly dispersible and poor dispersible) was based on the dispersant efficiency measured according to the IFP test, and the corresponding dispersibility obtained in flume test experiments which was considered as more representative of real operations (Guyomarch and Merlin, 1999). Finally, the criteria adopted to qualify the potential success of such operations were dispersibility of respectively 50% and 20% according to IFP test. It must be noted that the upper limit was in agreement with other studies (Daling *et al.*, 1997) while the second was slightly greater (20% vs 5%).

The experiments that were conducted in the flume tests are simulations of the various processes that can occur under natural conditions. However, due to the experimental protocol, particularly the fumes extraction and the simulated mixing energy, kinetics had to be slightly adapted when extrapolating this set of data to given environmental conditions. Previous studies have demonstrated that the hydraulic canal could speed up some processes (evaporation, emulsification) and, consequently, parameters that were linked with (density, flash point). On the other hand, viscosity proved to follow similar kinetics in comparison with the field, for low mixing energy, except the maximum values that were lowered in case of high asphaltenes content (Guyomarch *et al.*, 2002). As regards this last point, the implementation of a new system, which simulates more realistically the solar radiations, should make the experiments even more realistic.



**Figures 8 to 11 Examples of Evolutions of Physical-Chemical Parameters**

## **8 Complementary Weathering and Dispersibility Test at the Lab Scale**

### **8.1 Experimental Weathering in the Laboratory**

Samples weathered in the flume test at the pilot scale can also be artificially evaporated and emulsified at the laboratory scale. To simulate the main weathering processes at sea, the oil was exposed to a systematic, stepwise procedure including distillation and emulsification processes, thus leading to 10 different samples representative of the potential evolutions (Daling and Strøm, 1999). Topping temperatures are 150, 200 and 250°C and water content 50%, 75% and maximum. It must be noticed that the 250°C+ residue is particularly important as it approximately corresponds to the maximum evaporation at sea. Moreover, this residue is particularly adapted to gravimetric methods (asphaltenes and wax content measurements) thanks to its lack of volatile components.

This “bench-scale experiment” was performed at one representative test temperature, taking into account local conditions, but could be extrapolated to various temperatures and wind speeds by using modelling softwares. This test matrix is in agreement with the set of data required by the SINTEF Oil Weathering Model.

#### **8.1.1 Sample Preparation**

The crude oil sample was evaporated at various rates by distillation according to the protocol developed at IKU/SINTEF (Norway). The distillation technique was described by Stiver and Mackay (1984) as a modified ASTM D86/82 method.

The oil emulsification was achieved by using the modified Mackay-Zagorsky method using rotary funnels (Hokstad *et al.*, 1993). The principle of the method is to form water-in-oil emulsions by rotating cylindrical separatory funnels containing water and oil. The rotation simulates the mixing energy wave activity at sea.

#### **8.1.2 Measurements**

Fresh oils, oil residues obtained from distillations, and emulsions resulting from the emulsification of these residues, were characterized by their density and viscosity. The pour point and flash point of non-emulsified oils were also determined. The methods used were previously described (see section 4.2).

### **8.2 Comparison of the Relative Efficiency of Dispersants**

The sampling schedule and the uncertainty as regards dispersants efficiency do not allow the testing of various dispersants on samples collected in the flume. Therefore, emulsions used for these comparative tests have to be separately prepared in the laboratory. The weathering stage adopted for these comparative tests is chosen according to the results of the flume test experiment, which can be conducted only on the reference dispersant. The dispersibility has to be in the range 20-50% to allow significant differences for samples viscous enough to be difficultly treated. These tests are performed at least in duplicates to enable reliable conclusions.

## **9 Overview of the Related Devices and Ongoing Projects**

The weathering experiments have been performed at *Cedre* for many years, but, since the first test, various other devices and tests protocols were implemented and can be combined with these studies.

The impact of the oil can be assessed by testing the effect of the product at different weathering stages by using the ecotoxicology bench as described by Dussauze *et al.* (2012). The toxicity of the water soluble fractions obtained in the flume test can also be directly

assessed. It must be noted that the quantification of the dissolved molecules is performed at *Cedre* as described in section 5.2. The technique used for that purpose also enables extensive sampling. Finally, the ecotoxicology bench can also deal with dispersed oil, generated either in the flume or at the laboratory scale according to a dedicated protocol. The organisms exposition is also characterized by hydrocarbons measurements (particulate and/or dissolved fractions) and droplets size distributions as described in section 5.1.

The persistence of the oil on rocky shore, and particularly the possibilities of cleaning it by using high pressure washing, can be assessed. The principle of the test described by Jezequel *et al.* (2009, 2011) consists in applying the weathered oil on different calibrated granite tiles. An automated system enables the testing of various cleaning conditions (temperature and pressure of the water) or procedures (with or without cleaning agents) in a reproducible way.

Finally, the next development scheduled for the beginning of 2013 will consist in a test dedicated to the possibility of using the *in situ* burning technique. A device will recreate the conditions of ignition of an oil slick, and this protocol could be applied to samples collected in the flume at various weathering stages.

## 10 Conclusion

The reflection on the design of a new flume tank, followed by its construction and validation, were the opportunity to redefine the experimental conditions as well as the test and measurement methods.

The initial modularity, which offered the possibility of a straight section or a ring configuration for weathering studies, was abandoned due to the constraints involved in its implementation. Due to this choice, the surface area required for the *Polludrome* could be reduced, and a new air conditioned room could therefore be fitted out. However, it is still possible to expand back to the initial surface area, thanks to a flexible set-up: the two rooms are separated by a sliding door and the new *Polludrome* is a mobile unit, meaning that it can be removed from the room if other applications require it to be.

The validation trials proved conclusive, even if some elements differed significantly from those adopted for the previous version. The wave generator, altered to remain reproducible over the years, produces agitation that is better distributed throughout the ring, and no longer a very localised high energy point close to the generator. The comparative trials conducted on a crude oil showed similar evolutions in viscosity, indicating similar average energy levels. It is however worth noting that water content measurements for the emulsions formed with the new system are less variable, in accordance with the new surface agitation characteristics.

Furthermore, the solar radiation simulator appears to be more in accordance with the intensities measured in real conditions, making simulations more realistic but leading to inevitable divergences with previous studies in terms of maximum viscosity values.

Finally, the renewal of this equipment is part of an effort to develop realistic simulation tools for operational purposes. These systems are complementary and now enable us to offer, in addition to weathering studies, oil impact assessments through ecotoxicological tests, as well as *in situ* burning or specific clean-up tests.

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## 12 References

AFNOR, *Détermination du point d'éclair - Méthode Abel en vase clos*, NF EN ISO 13736, Saint Denis La Plaine : AFNOR, 22 p., 2008.

AFNOR, *Produits pétroliers. Détermination du point d'écoulement*, ISO 3016, Saint Denis La Plaine : AFNOR, 1994.

AFNOR, *Essais des eaux - Produits dispersants - Évaluation en milieu marin de l'efficacité vis-à-vis de la dispersion du pétrole*, NF T90-345, Saint Denis La Plaine : AFNOR, 1990

ASTM, *Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation*, ASTM D95 - 05(2010), West Conshohocken : ASTM, 6 p. 2010.

ASTM, *Standard Test Method for Density of Semi-Solid Bituminous Materials (Pycnometer Method)*, ASTM D70 - 09e1, West Conshohocken : ASTM, 4 p., 2009.

Balcon, A-L., R. Kanan, S. Van Ganse and J. Guyomarch, "Analysis of Dissolved BTEX and PAHs in Seawater following an Oil Spill: Development of Sensitive, Operational Methods for Rapid Diagnosis", in *Proceedings of the 2011 International Oil Spill Conference*, Portland, Oregon, USA, 2011.

Bridié, A.L., T.H. Wanders, W.V. Zegveld and H.B. Van der Heijde, "Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse", *Marine Poll. Bull.*, Vol. 11, N°12, pp. 343-348., 1980.

CEN, *Oil Spill Identification – Waterborne Petroleum and Petroleum Products – Part 2: Analytical Methodology and Interpretation of Results*, CEN/TR 15522-2:2006, Brussels : European Committee for Standardization, 2006.

Daling, P.S., and T. Strøm, "Weathering of Oil at Sea; Model/Field Data Comparisons", *Spill Science & Technology Bulletin*, Vol. 5, N°. 1, pp. 63-74, 1999.

Daling, P.S., O.M. Aamo, A. Lewis and T. Strøm-Kristiansen, "SINTEF/IKU Oil-Weathering Model: Predicting Oils Properties at Sea", in *1997 International Oil Spill Conference (IOSC)*, Fort Lauderdale, Florida, USA: April 7-10, 1997, Washington : American Petroleum Institute (API), pp. 297-307, 1997.

Dussauze, M., S. Le Floch, F-X. Merlin, M. Theron and K. Pichavant, Tool for the Impact Assessment of Chemicals on Marine Organisms, in *Interspill London 2012 - Conference & Exhibition* : 13-15 March 2012, ExCel, London, UK, 2012.

Guyomarch, J. and F. Merlin, "Study of the Feasibility of Chemical Dispersion of Viscous Oils and Water-in-oil Emulsions", in *Proceedings of the twenty-second Arctic and Marine Oil Spill Program (AMOP) technical seminar*, Calgary, Alberta, Canada: June 2 to 4, 1999, Environment Canada, Ottawa, Ontario, Canada, Vol. 1, pp. 219-230, 1999.

Guyomarch, J., “Methodology for Assessing Oil Weathering in a Dedicated Hydraulic Canal: Evolution of the Physical-Chemical Properties and Dispersibility of Various Crudes”, in *Proceedings of the twenty-third Arctic and Marine Oil Spill Program (AMOP) technical seminar*, Vancouver, British Columbia, Canada, : June 14-16, 2000, Environment Canada, Ottawa, Ontario, Canada, Vol. 1, pp. 37-57, 2000.

Guyomarch, J., E. Mamaca, M. Champs and F-X. Merlin, “Oil Weathering and Dispersibility Studies : Laboratory, Flume, Mesocosms and Field Experiments”, in *Third R&D Forum on High-density Oil Spill Response (IMO)*, Brest (FRANCE): 11-13 March 2002, London : International Maritime Organization, pp. 174-186, 2002.

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”, in *Proceedings of the thirty-third AMOP Technical Seminar on Environmental Contamination and Response*, Halifax, Nova Scotia, Canada : June 07-09 2010, Environment Canada, Ottawa, Ontario, Canada, Vol. 1, pp.181-188, 2010.

Hokstad, J. P., P.S. Daling, A. Lewis and T. Strøm-Kristiansen, “Methodology for Testing Water-in-Oil Emulsions and Demulsifiers. Description of Laboratory Procedures”, in *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings Marine Spill Response Corporation*, Washington DC, MSRC Technical Report Series 93-108, pp. 239-253, 1993.

International Maritime Organization, *Bioremediation in Marine Oil Spills: Guidance Document for Decision Making and Implementation of Bioremediation in Marine Oil Spills*, London: International Maritime Organization, 49 p., 2004.

IP 143/90 (or ASTM D3279-90), “Asphaltene (Heptane Insolubles) in Petroleum Products”, in *Standards for Petroleum and its Products*, London : Institute of Petroleum, pp. 143.1-143.7, 1985.

Jézéquel, R., and F-X. Merlin, “Experimental Study of High Pressure Washing Efficiency of Oily Rocky Shores: Influence of Viscosity of Oil and Cleaning Agent Use”, in *Proceedings of the 2011 International Oil Spill Conference*, Portland, Oregon, USA, 2011.

Jézéquel, R., J. Lebastard and F-X. Merlin, “Influence of Weathering of Heavy Fuel Oil on High Pressure Washing Efficiency with and without Cleaning Agent”, in *Proceedings of the thirty-second AMOP Technical Seminar on Environmental Contamination and Response*, Vancouver, British Columbia, Canada : June 9-11 2009, Environment Canada, Ottawa, Ontario, Canada, Vol. 1, pp. 177-193, 2009.

Stiver, W., and D. MacKay, “Evaporation Rate of Spills of Hydrocarbons and Petroleum Mixtures”, *Environmental Science & Technology*, Vol. 1, N°11, pp. 834-839, 1984.

Wang, Z., and M. Fingas, “Study of the Effects of Weathering on the Chemical Composition of a Light Crude Oil Using GC/MS GC/FID”, *Journal of Microcolumn Separations*, Vol. 7, N° 6, pp. 617-639, 1995.