DELIVERABLE D3.2

SUMMARY OF WP3

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Appendices

Acknowledgement

The work described in this report was supported by the Directorate-General for European Civil Protection and Humanitarian Aid Operations (DG-ECHO) of the European Union through the Grant Agreement number 874387 - IMAROS – UCPM-2019-PP-AG, under to the Topic “Preparedness", corresponding to the General objective "Strengthening preparedness for responding to multisector emergencies, including health, CBRN, environment and marine pollution in Europe and its Neighbourhoods" and to the specific Objective "Strengthening capacities for emergency response".

The main objective of Work Package 3 (WP 3) is to get knowledge of the chemical composition and physical properties of relevant Low Sulphur Fuel Oil (LSFO), by analysing samples at the laboratory and at the pilot scale. Knowledge of chemical and physical properties of the oil is crucial in order to evaluate response strategy and potential environmental impacts.

Additional objectives are:

- Thanks to physical-chemical results obtain in this WP, to select relevant products for testing in WP 4;
- To make data from WP 3 reference data for oil spill identification for spills from unknown sources (Oil spill forensics, COSIWEB);
- To make data from WP 3 input data to existing modelling tools and databases for decision support.

The WP is divided in five different tasks that are briefly described below. The main conclusions of each task are also presented in this section. Detailed reports are attached either as appendix of this document or submitted as dedicated deliverables.

I. Task 3.1: Physico-chemical characterisation

This task was carried out at Cedre. Detailed report is presented in Appendix 1.

This task consisted in an initial physical-chemical screening of a broad range of small oil samples (2 L) collected in WP 2.

Twelve LSFO were obtained from 7 providers (oil deliverers and refineries). Two samples were ULSFO (Ultra Low Sulphur Fuel oil, sulphur content ≤ 0.1%), while eleven were VLSFO (Very Low sulphur Fuel Oil, sulphur content ≤ 0.5%). One more sample was taken from the Wakashio, bulk carrier stranded on the Mauritius Island coral reef in July 2020 and loaded with 3 800 tons of VLSFO.

Task 3.1 has consisted in a detailed screening of those 13 samples. Viscosity and density at 5°C and 15°C, flash point, pour point, asphaltenes and waxes contents, evaporation rate (samples topped at 250°C) and OSCAR composition were determined for the 13 fresh samples. Dispersibilty tests were conducted at 15°C in order to study this response option on such kind of products. The 250°C+ residues were characterised for viscosity and density at

5°C and 15°C, pour point and dispersibility. Finally, when possible, those residues were emulsified with 50% water content and the resulting emulsions were characterised in terms of viscosity and density at 15°C. Dispersibility of those emulsions at 15°C was also evaluated. This set of samples and data allows the assessment of oils behaviour and gives first insight on appropriate response options.

The main result from this screening phase is the **high variability of the results obtained** for each of the studied parameters. No obvious difference was observed between ULSFO and VLSFO.

Concerning the fresh oils:

- Viscosities range from 375 mPa.s at 15°C and 1826 mPa.s at 5°C to solid oils;
- All the oils exhibit a density below 1.00 ;
- Pour points highly vary, from -27°C to +27°C, implying different behaviours if released at sea;
- Persistency in the environment should be observed with evaporation rate ranging from 2.6% to 28.1%;
- Asphaltenes contents range from 0.3% to 3.7%, values higher than the threshold limit usually sets for emulsion formation;
- Some oils exhibit high wax content with a highest value reaching 20.6%;
- Some oils exhibit a potential for chemical dispersibility with efficiency slightly higher than 50% for IFP tests;
- Finally, flash points are all above 60°C, with a minimum of 77°C.

Once weathered, some oils turn highly viscous and sticky. Oils should still float (maximum density: 1.00), except if the product is spilt in concentrated suspended material environments. Immersion may also be problematic for spills occurring in freshwaters. Pour point may evolve a lot between fresh and weathered products, generally in relationship with the evaporation rate. Finally, dispersibility of weathered oils is drastically reduced.

Those data highlight the fact that those products will behave and weather differently in case of spillage at sea. Response options will subsequently have to be adapted, depending on the oil characteristics.

II. Task 3.2: Oil weathering

This task was carried out at Cedre. Detailed report is presented in Appendix 2.

Three VLSFO were selected from a first experimental phase (Task 3.1: Physical-chemical characterisation) in order to study them within Cedre's facilities, both at laboratory and pilot scales (in the Polludrome®).

The objective of this study (Task 3.2: Oil weathering) is to obtain experimental data on the behaviour, fate, and treatment possibilities of those three VLSFO.

Pilot scale tests were performed at representative weather conditions encountered in the European waters: the air temperatures were set at 5 °C and 15 °C. They were run assuming a moderate situation (around sea state 3 on the Douglas scale, which corresponds in real conditions to wave heights between 0.5 and 1.25 m) with a simulated wind speed of 10 knots. One test was performed in freshwater condition in order to simulate a potential spill occurring in lakes. Additional tests were carried out at the laboratory scale (at 5°C and 15°C) in order to obtain a set of experimental data which can be implemented in oil weathering models. Dedicated experiments were conducted to assess the oil dispersibility and when possible, the time-window of opportunity for dispersant use as well as a comparison of effectiveness of different dispersants.

The main results from the experiments are as follows:

- The three VLSFO behave and weather differently, highlighting the variability existing among those products;
- Pour points vary from +3°C to +27°C, leading to some potential difficulties in terms of recovery for oils exhibiting high pour points;
- Density of weathered oils can reach 1.00, leading to potential submersion issues if the oil is poured in freshwater or in coastal waters characterised by high suspended matter;
- The flash point of the three fresh oils is above 85°C, meaning that in terms of safety, operations could be conducted directly after the spill;
- Some oils seem to be dispersible when fresh. However, as soon as they weather, they become rapidly not dispersible. This response option seems thus limited for this kind of products.

It should be noted that dispersibility tests (related to the task 4.2 - WP 4) were performed in the frame of this task, on the samples collected at the laboratory or in the Polludrome®

III. Task 3.3: Ecotoxicity

This task was carried out at Cedre. Detailed report is presented in Appendix 3.

Ecotoxicity tests were performed on 3 marine organisms: the marine algae *Phaeodactylum tricornatum*, the marine copepod *Acartia tonsa* and the amphipod *Corophium sp*.
The tests were conducted in accordance with the "Harmonised Offshore Chemical Notification Format" (OSPARCOM).

Three VLSFO, tested at different concentrations, served as tested substances. The algae and the copepods were exposed to the soluble fraction of the oils collected thanks to WAF (Water Accommodated Fraction) preparations. Amphipods were exposed to direct contact with the oils during sediment bioassay.
Algal growth inhibition (for algae) and average mortality (for copepods and amphipods) was calculated in order to determine EC_{50} (effective concentration, for algae) or LC_{50} (lethal concentration, for copepods and amphipods), respectively resulting in 50 % inhibition of growth rate or in the loss of 50 % of the population studied.

The study led to the following conclusions:

- Marine algal growth inhibition test: even for the highest PAH concentration tested, the growth rate was still very close to the one of the control. EC_{50} at 72 hours could not be determined for the 3 VLSFO tested.
  No toxicity was observed on *Phaeodactylum tricornatum* by testing those 3 VLSFO.

- Determination of acute lethal toxicity to marine copepods: for the 3 VLSFO tested, LC_{50} was below the lowest PAH concentration tested (i.e. the lowest PAH concentration tested led already to a mortality higher than 50 %), **demonstrating to a high sensibility of those organisms. However, the sensitivity observed may be explained by a stress (potentially induced by the transport time) of the tested organisms**.

- Sediment bioassay using the amphipod *Corphium sp.:* **an impact of the oil on the mortality rate was observed.** The determination of LC_{50} seems related to the PAH quantification in the 3 oils, with the lowest LC_{50} calculated for IM-15.

Additionally, PAH quantification for the three VLSFO tested are in the same range as traditional fuel oils already analysed at Cedre. In addition, WAF toxicity measured by SINTEF on the thirteen LSFO collected in the frame of the Task 3.1 (Faksness and Daling, 2022[1]) is also in the same range as traditional fuel oils. **The toxicity of the LSFO tested seems thus to be in the same range as the one observed for traditional fuel oils.**

IV. Task 3.4: Identification /forensics

Detailed report related to this task is part of the Deliverable D3.3 – Dataset available in COSIWEB.

Samples were prepared and analysed in accordance with the recommendations of the CEN Technical Report (European committee for standardization) “Oil Spill Identification – Waterbone petroleum and petroleum products – Part 2: analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses”. GC-FID analysis was used in a first phase for the screening of the samples (general shapes of the oils and *n*-alkanes distributions). The second step of the method of comparison consisted in GC-MS analyses to determine polycyclic aromatic hydrocarbons (PAHs), saturates (linear alkanes and isoprenoids) and geochemical markers (biomarkers: hopanes, steranes/diasteranes and triaromatic steranes).
Samples were entered in the COSIWEB database. This allows users to rapidly compare data simultaneously with all the oils included in the database.

Briefly, the main conclusion of the task are:

- From the total ion chromatogram it is not possible to know if the oil is a low sulphur oil;
- The Ion chromatograms and the of calculations of the C1-, C2-, C3-dibenzothiophens and BNT can show that there is less sulphur present in an oil;
- Steranes, diasteranes and triaromatic steranes can show if there are waxes present.

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[1] Chemical composition of fuel oils : Faksness and Daling, SINTEF report n° 2022:00383 - Unrestricted

V. Task 3.5: Modelling weathering of Low Sulphur Fuel Oil

The outcome of this task is a report summarizing the main findings of the task and suggesting best practice to be implemented in the different existing national models. It corresponds to the deliverable D3.4: Modelling Low Sulphur Fuel Oil Weathering.

Briefly, data obtained from laboratory analysis were compiled into different modelling tools. Objectives were:

- to prepare data from tasks 3.1 and 3.2 and compile them as input to different modelling tools;
- In the Bonn Agreement area, most contracting parties operate their own national oil drift and fate models. The objective of this task is to assess the ability of these existing models to simulate the physical behaviour and the weathering processes for the low sulphur fuel oil tested in the flume tank experiments (task 3.2).

APPENDIX 1

Task 3.1 – Physical-chemical characterization

WP3

DELIVERABLE D3.2

TASK 3.1: PHYSICAL-CHEMICAL CHARACTERISATION

“PHYSICAL-CHEMICAL CHARACTERISATION OF 13 LSFO”

FINAL REPORT

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EXECUTIVE SUMMARY

When spilled at the water surface, oils are subjected to weathering processes such as evaporation, emulsification, dispersion, photo-oxidation, and biodegradation. These processes naturally occur due to water agitation generated by currents, wind and/or waves, to the sun exposure (UV oxidation), and to bacteria's and micro-organisms activity. Throughout the weathering processes, the oil continuously changes in terms of chemical composition and physical properties. Oil generally becomes more and more viscous and can turn into a new persistent pollutant in the environment. The behaviour of weathered oil is often different from the one of the oil initially spilled. Understanding these transformations is a key element in evaluating the potential impacts and optimizing the emergency response to spillage.

In the frame of the European project IMAROS and of the Task 3.1 (Physical-chemical characterisation) of the Work Package 3 (WP3: Chemical characterisation), twelve Low Sulphur Fuel Oils (LSFO) were obtained from 7 providers (oil deliverers and refineries). Two samples were ULSFO (Ultra Low Sulphur Fuel oil, sulphur content ≤ 0.1%), while eleven were VLSFO (Very Low sulphur Fuel Oil, sulphur content ≤ 0.5%). One more sample was taken from the Wakashio, bulk carrier stranded on the Mauritius Island coral reef in July 2020 and loaded with 3 800 tons of VLSFO.

Task 3.1 has consisted in a detailed screening of those 13 samples. Viscosity and density at 5°C and 15°C, flash point, pour point, asphaltenes and waxes contents, evaporation rate (samples topped at 250°C) and OSCAR composition were determined for the 13 fresh samples. Dispersibilty tests were conducted at 15°C in order to study this response option on such kind of products. The 250°C+ residues were characterised for viscosity and density at 5°C and 15°C, pour point and dispersibility. Finally, when possible, those residues were emulsified with 50% water content and the resulting emulsions were characterised in terms of viscosity and density at 15°C. Dispersibility of those emulsions at 15°C was also evaluated.

The main result from this screening phase is the high variability of the results obtained for each of the studied parameters. No obvious difference between ULSFO and VLSFO was observed.

Concerning the fresh oils:

- *Viscosities range from 375 mPa.s at 15°C and 1826 mPa.s at 5°C (IM-5) to solid oils (IM-1 ; IM-2 and IM-9);*
- *All the oils exhibit a density below 1.00;*
- *Pour points highly vary, from -27°C (IM-6) to +27°C (IM-2), implying different behaviours if released at sea with, depending on the water temperature, potential solidification of oils characterized by the highest pour points;*
- *Persistency in the environment should be observed with evaporation rate ranging from 2.6% (IM-11) to 28.1% (IM-6);*
- *Asphaltenes contents range from 0.3% (IM-1) to 3.7% (IM-10), values higher than the threshold limit usually sets for emulsion formation;*
- *Some oils exhibit high wax content with a highest value reaching 20.6% (IM-9);*
- *Some oils exhibit a potential for chemical dispersibility with efficiency slightly higher than 50% for IFP tests;*

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- *Finally, flash points are all above 60°C, with a minimum of 77°C (IM-13).*

Once weathered, some oils turn highly viscous and sticky. Oils should still float (maximum density: 1.00), except if the product is spilt in highly concentrated suspended material environments. Immersion may also be problematic for spills occurring in freshwaters. Pour point may evolve a lot between fresh and weathered products, generally in relationship with the evaporation rate. Finally, dispersibility of weathered oils is drastically reduced.

Those data highlight the fact that those products will behave and weather differently in case of spillage at sea. Response options will subsequently have to be adapted, depending on the oil characteristics. It also highlights the necessity to rapidly obtain physical-chemical information on the oil involved in the spillage and if possible to take samples in case of oil spill to be able analyse it.

The objectives of this Tasks 3.1 were to characterise the oils collected from the deliverers and refineries and to select the 3 most pertinent ones for further experiments. Experiments that follow the Task 3.1 are part of the WP3 (Task 3.2: Weathering at the laboratory and pilot scale; Task 3.3: Exotoxicity) and of the WP4 dedicated to the response options (Task 4.1: Mechanical Recovery; Task 4.2: Dispersants; Task 4.3: In Situ Burning and Task 4.4: Shoreline clean-up).

GLOSSARY

ASTM	American Society for Testing Materials
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
DOR	Dispersant Oil Ratio
IFP test	Dispersibility test formerly developed by the French Petroleum Institute (*Institut Français du Pétrole*, name no longer used for this organism, which is now *IFP énergie nouvelles*). This method is a low-energy test, estimated to represent non-breaking waves conditions. It is identified within the NF T 90-345 French Standard
IP	Institute of Petroleum (UK-based professional organization)
MNS test	The **MNS** (*Mackay–Nadeau–Steelman*) dispersibility test is estimated to represent a medium to high sea-state condition
OWM	Oil Weathering Model
PAH	Polycyclic Aromatic Hydrocarbons
TBP	True Boiling Point
UCM	Unresolved Complex Mixture: compounds that cannot be separated by gas chromatography. They appear as a hump, generally correspond to highly branched alkanes which are reluctant to biodegradation
WSL	Warren Spring Laboratory dispersibility test used for approval purpose in the UK

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1 CONTEXT AND OBJECTIVES

Each spill entails a series of questions concerning the fate and behaviour of the oil involved, and consequently about the oil spill response techniques to be used. Subjected to weathering processes such as evaporation, emulsification, dispersion, photo-oxidation, or biodegradation, the oil is continuously changing in terms of chemical composition and physical properties. These processes occur under natural conditions due to water surface agitation (wind, waves, turbulence, and currents) sun exposure (UV), and also bacteria and micro-organisms activity.

As the weathering progresses, the oil is continuously changing: the light fractions evaporate gradually; oil density increases while it gets emulsified with water and is oxidized by ultra-violet radiations. Oils generally become more and more viscous and can become a new persistent pollutant in the environment. Weathered oil behaviour is often different from the original one. Understanding these transformations is a key element in evaluating the potential impacts, optimising the response options according to the weathering stage of the spilled oil, and implementing the oil spill contingency plan.

The objective of the Task 3.1 of the IMAROS project was to perform a physical-chemical characterisation of the 13 LSFO collected by the project partners in order to improve our knowledge on those products. Fresh oils and weathered samples were analysed. Analyses were carried out in Cedre’s testing facilities, at laboratory scale. The tests were performed at 5°C and 15°C, representative weather conditions encountered in the European waters.

2 BACKGROUND

In order to assess the fate and behaviour of a dedicated oil in case of accidental release, various approaches can be considered, from the simplest one to the most complicated one:

- The initial physical-chemical characteristics of the oil can be used to get a general idea of its fate. The density is representative of the buoyancy of the product, its True Boiling Point (TBP) curve provides a reliable estimation of the maximum evaporation rate, the viscosity informs on the spreading and potential use of response techniques such as dispersion or recovery, … This set of data can also be implemented in modelling software such as ADIOS 2 which mainly deals with initial properties.

- Laboratory protocols can be applied in order to asses more realistically the oil weathering, and to get additional information such as the time-window of opportunity for dispersant use. Finally, pilot scale experiments can be conducted in order to simulate these various processes realistically and simultaneously.

Answering the Task 3.1 of the European project IMAROS, this study intends to perform the physical-chemical characterisation of 13 LSFO through laboratory tests and the potential fate and behaviour at sea of those products, considering European environmental conditions. Three of those products will be chosen for further experiments (Tasks 3.2, 3.3, 4.1, 4.2 and 4.3), among them weathering at the laboratory and pilot scales (Task 3.2) and response options (Tasks of WP4).

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3 MATERIALS AND METHODS

3.1 Samples

Thirteen samples of 2L were obtained for this study. Samples were coming from 7 different oil deliverers or refineries across Europe. Two samples were ULSFO and 11 were VLSFO. Samples were labelled IM-1, IM-2, …, IM-13. IM-5 was the sample collected from the Wakashio bulk carrier.

Table 1 details the nature and the country of origin of the collected samples.

Table 1 Labelling, nature and country of origin of the 13 tested LSFO

Samples	Nature	Country of origin
IM-1	ULSFO	Sweden
IM-2	VLSFO	Sweden
IM-3	VLSFO	Belgium
IM-4	VLSFO	Belgium
IM-5	VLSFO	Wakashio sample
IM-6	VLSFO	Malta
IM-7	VLSFO	Belgium
IM-8	VLSFO	The Netherlands
IM-9	ULSFO	The Netherlands
IM-10	VLSFO	The Netherlands
IM-11	VLSFO	The Netherlands
IM-12	VLSFO	Cyprus
IM-13	VLSFO	Spain

The visual appearance of the 13 oils was black and dense. Three of them were solid at ambient temperature (IM-1, IM-2 and IM-9).

3.2 Laboratory protocols

Fresh oils were first analysed. They were characterised by the following measurements: viscosity and density at 5°C and 15°C, pour point, flash point, sulphur content, wax and asphaltenes contents, evaporation rate and full detailed chemical characterisation (OSCAR composition).

Distillations to a vapour temperature of 250°C were performed in order to obtain a residue simulating a weathered oil at sea. This residue is particularly important as it approximately corresponds to the maximum evaporation at sea. Moreover, it is particularly adapted to gravimetric methods thanks to its lack of volatile components, allowing the wax and asphaltenes contents determination. The residue was characterised in terms of viscosity and density at 5°C and 15°C, pour point, wax and asphaltenes contents.

When possible, those residues were emulsified at 50% water content. Emulsions were characterised for viscosity and density at 15°C.

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IFP dispersibilty tests at 15°C were performed to assess the oils dispersibility. The fresh and the weathered oils (250°C+ residues and emulsions) were tested.

Table 2 summarizes the analyses performed on the fresh oils and the 250°C residues.

Table 2 Test matrix of characterisations performed on the oils

Characterisations	Fresh Oil	250°C+ residue	Emulsion 50% water content
Volume topped (%)	-	m	-
Residue (% wt.)	-	m	-
Specific gravity at 5°C and 15°C	m	m	m
Pour Point (°C)	m	m	-
Flash Point (°C)	m	nd	-
Viscosity at 5°C and 15°C (mPa.s)	m	m	m
Sulphur content (%)	m	-	-
OSCAR characterisation	m	nd	-
Viscosity at 15°C of 50% water emulsion (mPa.s)	-	m	-
Wax / Asphaltenes	c	m	-
IFP dispersibility at 15°C	m	m	m

m: to be measured
nd: not determined
-: not relevant
c: calculated from the value measured on the 250°C+ residue

Appendix 1 details the methods of measurements used in this study.

3.2.1 Oil evaporation and photo-oxidation

To simulate the maximum evaporation at sea the fresh oils were topped at 250°C (vapour temperature). Evaporated samples are obtained by distillation according to the protocol developed at IKU/SINTEF (Norway). The distillation technique is described by Stiver and Mackay (1984) as a modified ASTM D86/82 method. The objective of this protocol is not to get the distillation curve of an oil, as intended by the ASTM method, but to obtain oil residues at given temperatures.

3.2.2 Oil emulsification

The oil emulsification is achieved by using the modified Mackay-Zagorsky method using rotary funnels (Hokstad et al., 1993[1]). The principle of the method is to form water-in-oil

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[1] 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

emulsions by rotating cylindrical separatory funnels containing water and oil. The rotation simulates the mixing energy wave activity at sea. To form a water-in-oil emulsion of 50% water content, the rotation is started with equal volumes of water and oil.

3.2.3 Effectiveness of Chemical dispersants

Different dispersibility tests can be conducted, each protocol having its specificity. However, all of them were initially designed for the comparison of dispersants products (in particular the WSL and IFP tests). Some of them can be used for the assessment of an oil dispersibility in real conditions, particularly the IFP and MNS tests which were correlated to field or pilot scale experiments. During this screening phase, oil dispersibility was assessed through IFP tests.

All the dispersibility tests are carried out twice (duplicates), and the relative differences of results between two similar tests have not to differ more than 14% (in that case, a third test has to be performed). However, this criterion cannot be strictly applied for efficiencies lower than 40%, and in that case, results have not to differ more than 3% compared to the mean value (10% ± 2% for example).

The chemical dispersibility of the oil samples was measured at 15 °C, one of the 2 reference temperatures of the study, and using the “model” dispersant. The IFP flow through test method (French standard NF T 90-345), which is characterized by a low energy and a dilution process from a main tank to a dilution tank was applied. The test equipment was checked with Cedre reference oil (FOREF: mixture of Heavy Fuel Oil and Arabian Light topped at 110°C, viscosity of 1 200 ± 100 mPa.s at 20°C) and with the “model” dispersant formulated at Cedre (see *Appendix 1*). Under these test conditions, the efficiency has to be 75 ± 3%. The oil, dispersed in the water column and entrained in the dilution beaker, was extracted by dichloromethane and the concentration measured by spectrophotometry at 390 nm.

This method has been extensively used and studied over the last few years at Cedre and is fully documented. Results obtained at these laboratory scales have been correlated to potential efficiency during field operations[2]. The IFP test is a low-energy system which allows significant differences among products (oil nature, weathering stage …). The IFP test is representative of medium conditions, for a sea state around 2-3. Moreover, it provides information not only on the efficiency of the dispersant, but also on the quality of the dispersion due to the dilution process.

3.3 Physical-chemical properties

Sulphur content

The sulphur content was measured according to the NF EN ISO 8754, on the fresh oils.

Pour point

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[2] Chever F., K. Duboscq, J. Receveur, C. Audegond and J. Guyomarch. “Determination of limits of viscosity for dispersant use: quantitative and qualitative assessment of the dispersibility of water-in-oil emulsions at the laboratory (IFP and MNS tests) and in the Polludrome”. *Proceedings of the 39th Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, 7-9 June 2016, Halifax (Nova Scotia), Canada.

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

Flash point

The flash point was measured on the fresh oils according to the NF EN ISO 13736 norm (Abel method). This measurement was performed using an Anton Paar ABA 4 Abel flash point tester.

Viscosity

The viscosity of the oil samples (fresh oils and residues) was measured by using an Anton Paar viscosimeter (Rheolab QC) at dedicated shear rates (from 1 to 100 s^{-1}) and the 100 s^{-1} values, mean of 60 measurements at 15°C and mean of 10 measurements at 5°C, calculated. As regards emulsions formed from residues, their viscosity was measured at the test temperature considering the same shear rates but the 10 s^{-1} value was calculated in these cases. The equipment was calibrated by analysing reference oils.

Note : in the case of newtonian fluids such as most of crude oils, the value of the viscosity is a constant over a wide range of shear rates. Non emulsified oils were measured at 100 s^{-1}. As far as they get emulsified, these fluids follow a non-newtonian behaviour, generally shear thinning, which mean that the viscosity decreases as the shear rate increases. Therefore, viscosities of emulsions have to be expressed with the shear rate used to perform the measurement. Viscosity of emulsions is generally measured at 10 s^{-1}, which constitutes an implicit standard in the field of oil pollution studies.

The relationship between this dynamic viscosity η, expressed in mPa.s or cP, and the corresponding kinematic viscosity υ (cSt), is as follows:

$$\upsilon = \frac{\eta}{\rho}$$

ρ represents the fluid density, generally close to 1 for water-in-oil emulsions. Therefore, the viscosity measurement can be expressed, with the same figures, either in cP, mPa.s or cSt.

Temperature-sweep (viscosity) with a temperature range from 50°C to 0°C was also measured. As detailed in Rist Sørheim et al. (2020)[3] this method uses oscillated force to avoid wax lattice disturbance, hence the viscosity development can be followed over a wide temperature range. The temperature sweep is thus considered as a robust method when comparing viscosities of high viscous oils where the pour points are considerably higher than the test temperature.

Specific gravity

The density of the fresh oil and residues samples was determined according to the ASTM method D5002 “Standard Test Method for density and relative density of crude oils by digital density analyser” (ASTM, 2013). This measurement was performed using an Anton Paar D4500 analyzer.

Asphaltenes and waxes

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[3] Kristin Rist Sørheim, P. Daling, D. Cooper, I. Buist, L.G. Faksness, D. Altin, T.A. Pettersen, O.M. Bakken, 2020, Characterization of low sulfur fuel oils (LSFO) – A new generation of marine fuel oils, SINTEF Report OC2020 A-050

Asphaltenes content was measured on the residues obtained by distillation at 250°C according to the IP-143/90 norm “Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products”. This gravimetric method is more reliable when applied to non-volatile oils, such as 250°C+ residues. The result is then extrapolated to the fresh oils by taking into account the evaporation rate measured following the distillation.

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

3.4 Detailed chemical analyses

A detailed chemical characterisation of the oils was performed:

- The boiling point curve was obtained up to 520°C using simulated distillation, in addition to the True Boiling Point (TBP) curve established during the sample preparation.
- A detailed chemical composition was obtained according to 3 different chemical analyses as presented in *Table 3*:
    - Volatiles Organic Compounds (VOCs) were quantified by Headspace-GC/MS (list of 31 molecules),
    - semi-volatiles compounds, mainly PAHs, were analysed by GC/MS (liquid injection) according to a list of 43 molecules (or groups of molecules),
    - the distribution of compounds not individually quantified was established according to their number of carbons up to C_{25} based on a GC/FID analysis.

Chemical composition results are detailed in *Appendix 2*, HAP results in *Appendix 3* and TBP curves in *Appendix 4*.

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Table 3 ***Detailed list of the target molecules and definition of the dissolution potential***

Composition (% weight)	Individuals compounds	Analysis
C_1-C_4 (dissolved gas)	-	Crude assay
C_5-saturates (n-/iso-/cyclo)	*n*- pentane, isopentane, cyclopentane	HS-GC/MS
C_6- saturates (n-/iso-/cyclo)	*n*-hexane, methylpentane (2), methylcyclopropane, cyclohexane	
C_7- saturates (n-/iso-/cyclo)	*n*-heptane, dimethylpentane, methylhexane, methylcyclohexane	
C_8- saturates (n-/iso-/cyclo)	*n*-octane, methylheptane	HS-GC/MS
C_9- saturates (n-/iso-/cyclo)	*n*-nonane	HS-GC/MS
Benzene	benzene	HS-GC/MS
C_1-Benzene	Toluene	
C_2-Benzenes	o-, m-, p-xylène, ethylbenzene	
C_3-Benzenes	methylethylbenzenes (3), trimethylbenzenes (3), propylbenzene	
C_4 & C_5-Benzenes	n-butylbenzene, tetraméthylbenzene, n-pentylbenzene	
C_{10}- saturates (n-/iso-/cyclo)	No quantification of individual compounds	GC/FID
C_{11}-C_{12} (total saturates + aromatics)		
C_{13}-C_{14} (total saturates + aromatics)		
C_{15}-C_{16} (total saturates + aromatics)		
C_{17}-C_{18} (total saturates + aromatics)		
C_{19}-C_{20} (total saturates + aromatics)		
C_{21}-C_{25} (total saturates + aromatics)		
C_{25}+ (total)		
Naphthalenes 1 (C_0-C_1 alkylated)	N, N1	GC/MS
Naphthalenes 2 (C_2-C_3 alkylated)	N2, N3	GC/MS
PAHs 1 (medium solubility)	BT, BT1, BT2, BT3, BT4, N4, B, ANA, ANY, F, F1, P, A, P1, D, D1	
PAHs 2 (low solubility)	F_2, F_3, P_2, P_3, P_4, D_2, D_3, D_4, FL, PY, FL_1, FL_2, FL_3, BAA, C, C_1, C_2, C_3, BBF, BKF, BEP, BAP, PE, DBA, IN, BPE	GC/MS
Phenols (C_0-C_4)	Phenol, C_1 to C_4-Phenols	GC/MS

☐ High dissolution potential

🟦 Medium dissolution potential

🟧 Low dissolution potential

4 RESULTS OF LABORATORY SCALE TESTS

4.1 Gas chromatographic (GC-FID) characterisation

GC-FID analysis is used for the screening of samples: general shapes of the oils and n-alkanes distributions can be compared. n-alkanes are represented as narrow regular peaks. Components with the lowest boiling points appear with the lowest retention time (left part of the graphs). Heaviest compounds (> nC_{40}) cannot be analysed with this technique. “Unresolved Complex Mixture” (UCM) appears as a broad bump below the sharp peaks.

Based upon the visual comparison of the chromatograms, the oils exhibit different hydrocarbons profiles, reflecting variability in terms of physical – chemical properties (*Figure 1*).
Some samples exhibit a wide range of n-alkanes (nC_{10} – nC_{36}) (IM-9). Content of light compounds (< nC_{17}) gives insight of evaporative loss. Samples with a significant content of light compounds (IM-6, IM-12, IM-13) usually reflect a high evaporative rate. Some samples exhibit high peaks of naphtalenes, represented on the graphs by the irregular peaks between 10 and 15 minutes (IM-1, IM-3, IM-4, IM-6). Naphtalene contents give insights on oils ecotoxicity. Abundance of compounds eluting after nC_{20} reflects a high wax content (IM-1, IM-2, IM-9).
A high similarity between the samples IM-10 and IM-11 is observed. Those samples, coming from the same provider, are probably identical.

It should be noted that the 2 ULSFO (IM-1 and IM-9) do not exhibit differences with the VLSFO.

These chromatograms illustrate the diversity of hydrocarbons profiles, and so of physical-chemical properties. However, as the heaviest compounds are not analysed by this technique, it cannot explain by itself the oils behaviour.

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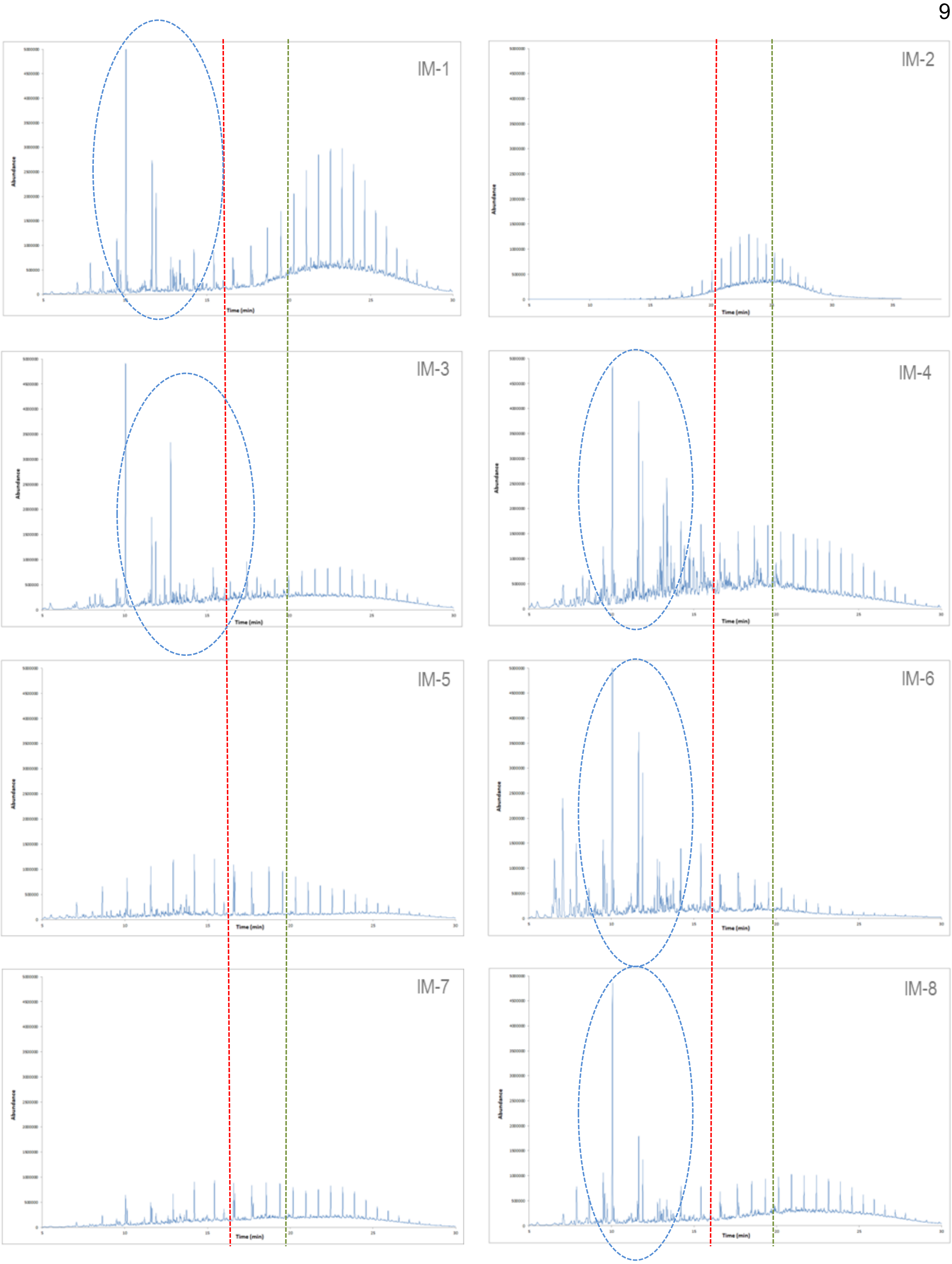

Figure 1 GC-FID chromatograms (compounds abundance in function of retention time in minutes) of the 13 fresh LSFO. All the graphs are represented with the same scales. On the left of the red dashed line are represented n-alkanes < nC17. On the right of the green dashed line are represented n-alkanes > nC20. Naphtalenes are represented with blue circles.

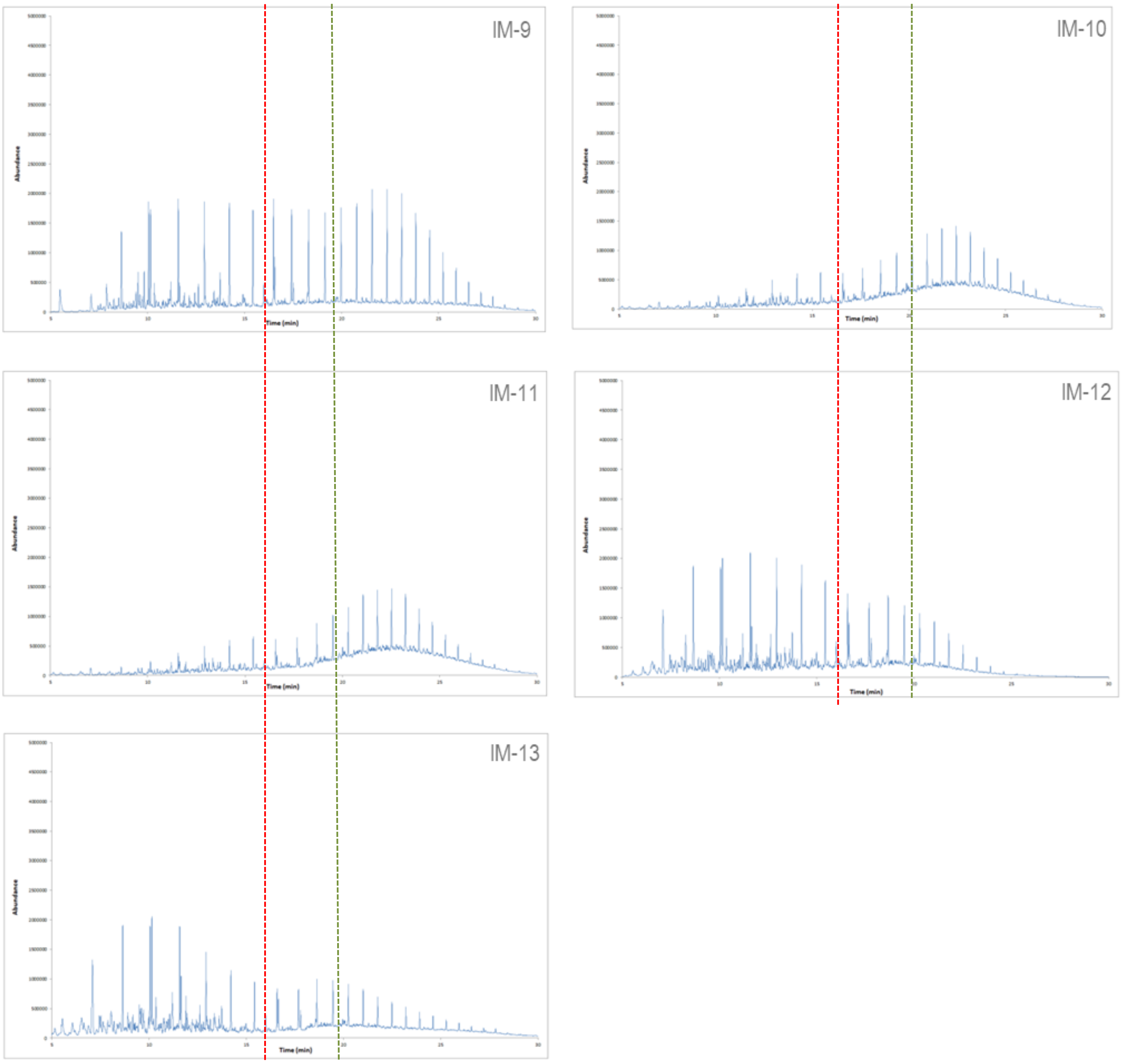

Figure 1 (cont.) ***GC-FID chromatograms (compounds abundance in function of retention time in minutes) of the 13 fresh LSFO. All the graphs are represented with the same scales. On the left of the red dashed line are represented n-alkanes < nC17. On the right of the green dashed line are represented n-alkanes > nC20. Naphtalenes are represented with blue circles.***

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4.2 True Boiling point (TBP) curve

The boiling point distributions obtained from the distillations at the laboratory scale are presented in *Appendix 4*, as well as the True Boiling Point (TBP) curves up to 520°C, combination of these experimental data and simulated distillation.

Table 4 presents the maximum evaporation rate reached for each oil at 520°C. Those results highlight the variability of the samples with distillation rate varying between 27 % (IM-2) and 74 % (IM-9).

Table 4 ***Maximum evaporation rate (%) obtained from simulated distillations (GC-FID)***

Sample	Max. distillation rate (%)
IM-1	29
IM-2	27
IM-3	51
IM-4	43
IM-5	50
IM-6	66
IM-7	50
IM-8	70
IM-9	74
IM-10	39
IM-11	38
IM-12	58
IM-13	46

4.3 Physico-chemical properties

The characterisation of the initial fresh oils is presented in *Table 5. Table 6* gathers the physical-chemical characterisations of the residues obtained from the 250°C distillation. Finally, characterisations obtained on emulsions formed from the 250°C+ residues with 50% water content are presented in *Table 7.*

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Table 5 Physical-chemical characterisation of the 13 fresh LSFO at 5°C and 15°C

Sample	S content (%)	Density 5°C	Density 15°C	Viscosity 5°C (mPa.s) (1) (2)	Viscosity 15°C (mPa.s) (1)	Pour Point (°C)	Flash point (°C)	Asph. (%) (3)	Waxes (%)(3)	Evaporation (vol. %)
IM-1	0.08	0.96	0.95	solid	solid	27	>100	0.3	17.3	3.8
IM-2	0.46	0.94	0.93	solid	solid	27	>100	0.5	12.1	5.2
IM-3	0.46	0.99	0.98	4 858	1 293	0	99.5	2.3	4.8	8.6
IM-4	0.48	0.95	0.95	2 808	703	21	93	2.2	8.1	9.0
IM-5	0.47	0.92	0.91	1 826	375	9	84	0.6	5.1	10.5
IM-6	0.45	0.98	0.97	2 244	892	-27	78	3.0	7.6	28.1
IM-7	0.49	0.95	0.94	4 415	19 117	15	>100	1.7	6.2	6.7
IM-8	0.49	0.97	0.96	15 585	3 348	9	>100	1.6	9.9	15.4
IM-9	0.08	0.90	0.90	solid	solid	30	>100	1.6	20.6	21.6
IM-10	0.47	0.95	0.94	12 443	2 451	0	>100	3.7	9.1	2.9
IM-11	0.49	0.95	0.94	8 171	1 964	0	>100	3.4	9.0	2.6
IM-12	0.48	0.95	0.94	10 679	3 042	-9	83.5	1.8	18.6	21.4
IM-13	0.48	0.96	0.96	24 994	6 240	-6	77	2.3	8.7	16.9

(1) Viscosity measured with a shear rate of 100 s^{-1}

(2) At 5°C, the mean of the 10 first values was calculated

(3) Values recalculated for the fresh oils, from the 250°C residues, taking into account the evaporation rate at 250°C

Table 6 *Physical-chemical characterisation of the 13 "250°C+ residues" at 5°C and 15°C*

Sample	Density 5°C	Density 15°C	Viscosity 5°C (mPa.s) (1) (2)	Viscosity 15°C (mPa.s) (1)	Pour point (°C)
IM-1	0.91	0.91	solid	solid	27
IM-2	0.93	0.92	solid	solid	30
IM-3	1.00	0.99	22 139	4 345	3
IM-4	0.97	0.96	4 039	1 156	21
IM-5	0.93	0.92	4 230	938	15
IM-6	1.00	1.00	solid/sticky	*252 759* *(4)*	6
IM-7	0.96	0.95	10 349	2 209	12
IM-8	0.97	0.97	124 826	19 117	3
IM-9	0.91	0.91	Solid	23 248	30
IM-10	0.98	0.97	13 553	4 345	nd(5)
IM-11	0.95	0.94	9 507	2 716	-9
IM-12	0.97	0.97	solid/sticky	*144 065* (4)	18
IM-13	- (3)	- (3)	solid/sticky	*272 261* (4)	6

(1) Viscosity measured with a shear rate of 100 s^{-1}
(2) At 5°C, the mean of the 10 first values was calculated
(3) No measurement possible
(4) Very sticky
(5) Not determined

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Table 7 ***Physical-chemical characterisation of the emulsions formed from the 250°C+ residues with 50% water content, at 5°C and 15°C***

Sample	Density 15°C	Viscosity 15°C (mPa.s) (2)	Water content (%)
IM-1	0.94	9 674	51.6
IM-2	0.85	22 259	44.4
IM-3	0.99	6 401	44.2
IM-4	0.97	5 077	47.1
IM-5	0.94	5 997	45.9
IM-6	nd (1)	798 826	40.6
IM-7	0.97	13 112	45.9
IM-8	0.95	28 832	31.7
IM-9	Not possible to form the emulsion		
IM-10	nm(3)	nm(3)	nm(3)
IM-11	0.97	13 035	50.0
IM-12	Not possible to form the emulsion		
IM-13	Not possible to form the emulsion		

(1) Not possible to perform the measurement due to the highly viscous product
(2) Viscosity measured with a shear rate of 10 s^{-1}
(3) Nm: not measured.

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Sulphur content has been measured to confirm the oils nature. The 2 samples containing 0.08% sulphur content correspond to the ULSFO IM-1 and IM-9 (ULSFO are characterized by a sulphur content below 0.1%). The sulphur content of the 11 VLSFO vary from 0.45% (IM-6) to 0.49% (IM-7, IM-8 and IM-11) (VLSFO are characterized by a sulphur content below 0.5%).

As already mentioned in the section 4.1, the analyses suggest that samples IM-10 and IM-11 are coming from the same stock.

Waxes and Asphaltenes:

In terms of chemical composition, asphaltenes contents vary from 0.3% (IM-1) to 3.7% (IM-10) (*Figure 2*) and are *a priori* in agreement with conditions required to form water-in-oil emulsions, the threshold limit of asphaltenes content being generally estimated around 0.2 to 0.3% when measured as insoluble in *n*-heptane. The average value for the 13 oils is 1.9%. The wax content variation is high, from 4.8% (IM-3) to 20.6% (IM-9), with an average value of 10.5%. For most of the samples exhibiting high wax contents, the pour point is generally high, well above the minimum seawater temperature. This will induce a solidification of those oils when in contact with the seawater. The 2 ULSFO present a high wax content.

For comparison, this variability reflects the one observed for the crude oils. The average values calculated on the 82 crude oils tested at Cedre are for these parameters, respectively 0.95% (values varying between 0.02 and 8.7%) and 8.02% (values varying between 0.02 and 42.3%).

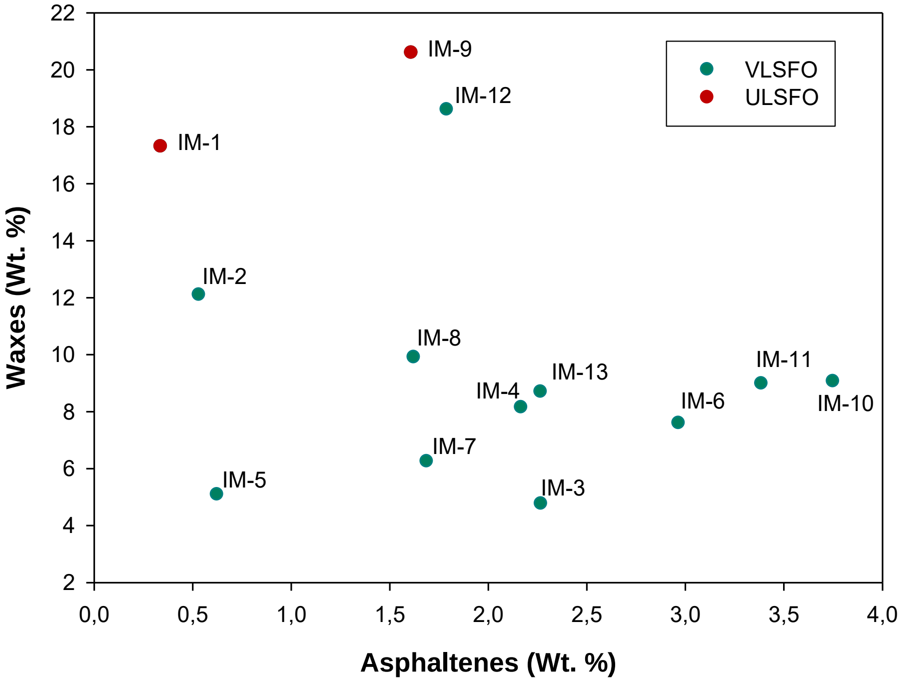

Figure 2 **Distribution of the 13 LSFO tested at Cedre based on asphaltenes and wax contents. ULSFO are represented with red dots.**

Viscosity:

Viscosity of the fresh oils vary from 375 mPa.s at 15°C and 1826 mPa.s at 5°C (IM-5) to solid oils (IM-1, IM-2 and IM-9) at 5°C and 15°C (*Table 5*).

Reliable measurements of highly viscous and/or waxy oils are difficult to obtain, particularly at low temperature. At 5°C, viscosity was measured on the 10 first values instead of

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the 60 first ones because of instability of the measures due to the rheofluidifiant properties of the products.

The 2 ULSFO tested are characterized by a solid state at ambient temperature.

Once weathered, viscosity increases up to more than 100 000 mPa.s for IM-6, IM-12 and IM-13 at 15°C (*Table 6*). Measurements were even not possible for those 3 oils at 5°C because of their stickyness.

When possible, emulsions were formed from the 250°C+ residue, with 50% water content. Three emulsions were unable to form: IM-9, IM-12 and IM-13 (*Table 7*). For the 10 other oils, at 15°C, emulsions viscosity varies from ~5 000 (IM-4) to ~800 000 mPa.s (IM-6). **Those results highlight the differences encountered among the LSFO and so the different expected behaviors once spilt at sea.**

The temperature-sweeps for 12 LSFO are shown on *Figure 3* (not enough volume was remaining for IM-10). For all the oils, viscosities vary significantly in the range of seawater temperature (~ 5°C-15°C). The viscosity evolution of 4 oils (IM-1, IM-2, IM-4 and IM-9) was modeled, using an exponential decay curve, from ~30°C to 50°C because of a dispersion of some values in this range. This dispersion was particularly marked for the 2 ULSFO (IM-1 and IM-9), with a variability of ± 15-20 mPa.s at 50°C. This may be due to the high pour point of those oils. At 50°C, viscosities range from 2 mPa.s (IM-4) to 241 mPa.s (IM-13).

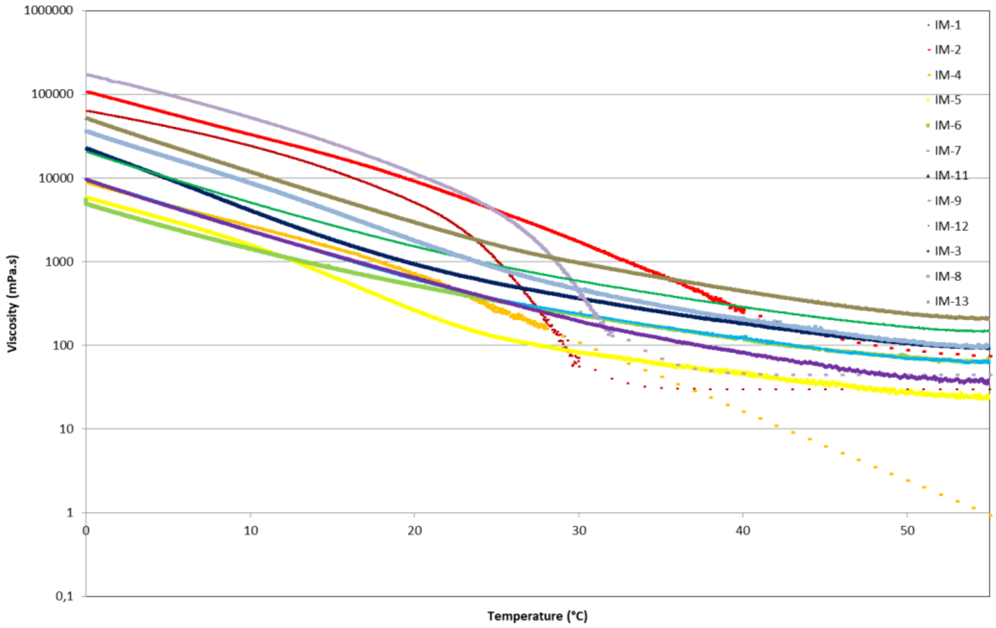

Figure 3 *Temperature sweep measurements (viscosities) of the LSFO*

	IM-1	IM-2	IM-3	IM-4	IM-5	IM-6	IM-7	IM-8	IM-9	IM-11	IM-12	IM-13
Viscosity (mPa.s) at 50°C (10s^{-1})	30	87	41	2	27	72	70	110	43	108	166	241

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Density:

The ULSFO IM-9 exhibits the lowest density (0.90 at 5°C and 15°C) and the VLSFO IM-3 the highest (0.99 at 5°C and 0.98 at 15°C). ULSFO are not characterized by lower densities as IM-1 exhibits a density of 0.95-0.96. **Based on this set of 13 samples, LSFO should float at the water surface. However, it should be noted that depending on the salinity and on the suspended material concentration, some oils may be entrained into the water column.**

Pour point:

Pour points highly vary, ranging from -27°C (IM-6) to +30°C (IM-9) for the fresh oils (Figure 4). This variability induces different behaviors if spilt at sea and implies the choice of different response options, especially of different recovery techniques. **Depending on the water temperature, oil solidification will occur for oils characterized by the highest pour points.**

As the oil weathers, the pour point may evolve significantly, as observed for the sample IM-6, with an increase from -27°C to 6°C. For some of those samples, the great increase of pour point could be linked to a high evaporation rate (IM-6, IM-12 and IM-13). The 2 ULSFO tested exhibit high and stable pour point (IM-1 and IM-9).

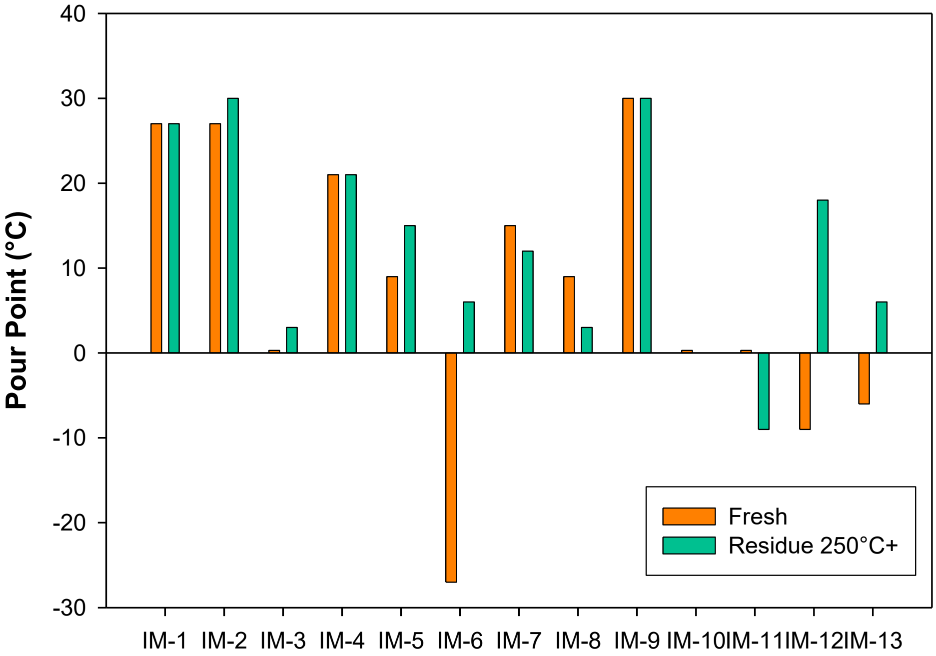

Figure 4 Pour point (°C) of the fresh oils and of the 250°C+ residues

Evaporation rate (vol. %):

Evaporation rate vary from 3 % (IM-10 and IM-11) to 28 % (IM-6) (*Figure 5*). The 2 ULSFO tested exhibit a high difference, with values of 4% for IM-1 and 22% for IM-9. **Those results highlight the fact that most of the products will be persistent in the aquatic environment, with a maximum of 30% of evaporation.**

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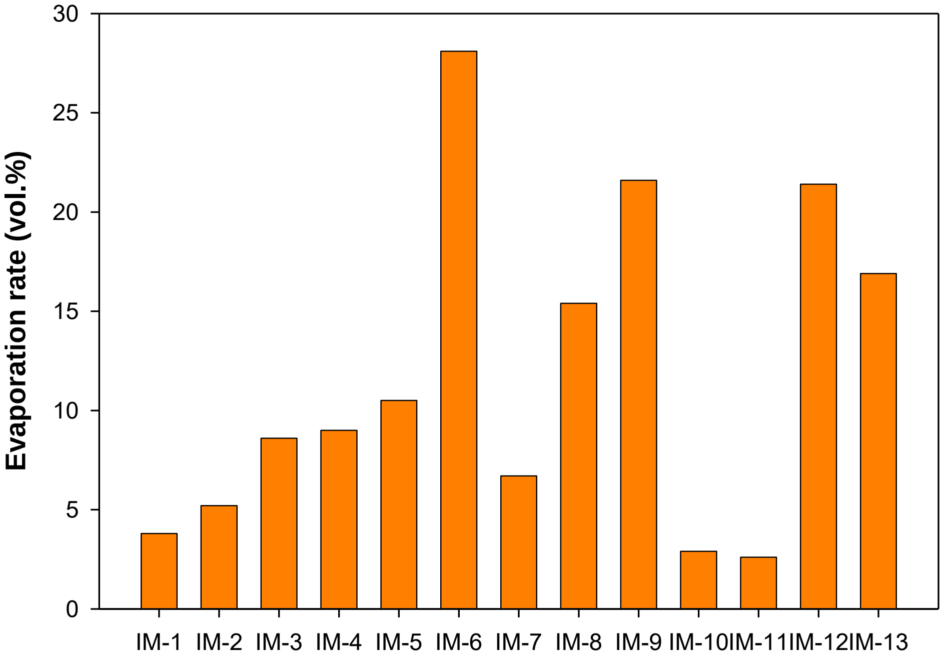

Figure 5 Evaporation rate (vol. %) of the 13 LSFO tested

4.4 Dispersibility tests

The tests conducted using reference conditions (see *Appendix 5*) allowed calibration of the IFP equipment (the efficiency of 73 % obtained in standard conditions is in agreement with the reference value which is 76 % ± 3 %).

Based on laboratory tests, the dispersibility of one oil is assessed according to 3 different levels: *dispersible*, *possibly dispersible* (dispersible with uncertainties), and *poorly dispersible*. Considering previous studies conducted at Cedre on the IFP test, two threshold values of dispersibility were defined to distinguish these 3 categories:

- Oils are considered as *dispersible* for IFP efficiency greater than 50%,
- Oils are considered as *possibly dispersible* for IFP efficiency in the range 20% - 50%,
- Oils are *poorly dispersible* for IFP efficiency lower than 20%.

Tests were carried out on the 13 fresh oils and on some of the 250°C+ residues (depending on the viscosity values of the residues, IM-6, IM-12 and IM-13 were not analysed), by using the model dispersant at 15°C. The dispersibilty of the emulsions (250°C+ residue + 50% water content) was also evaluated, on the same samples as the residues. Results are presented in *Table 8* and on *Figure 6*. Details are presented in *Appendix 5*. It should be noted that a high variability was observed between replicates, even with 3 measurements (*Appendix 5*). Only the average values are represented in the *Table 8* and on *Figure 6*.

Table 8 IFP dispersibilty (%) and viscosities of the fresh oils, the 250°C residues and the emulsions with 50%water content, at 15°C

	Mean IFP dispersibility at 15°C (%)			Viscosity at 15°C (mPa.s)		
Sample	Fresh oils	250°C residues	Emulsions (250°C / 50%)	Fresh oils	250°C residues	Emulsions (250°C / 50%)
IM-1	0.4	0.6	0.0	solid	solid	9 674
IM-2	0.2	0.4	0.8	solid	solid	22 259
IM-3	2.0	3.6	0.9	1 293	4 345	6 401
IM-4	0.2	2.8	2.9	703	1 156	5 077
IM-5	54.3	36.6	14.7	375	938	5 997
IM-6	58.4	nd	nd	892	252 759	798 826
IM-7	36.3	47.8	0.6	19 117	2 209	13 112
IM-8	2.6	3.1	0.4	3 348	19 117	28 832
IM-9	0.6	0.0	nd	solid	23 248	nd
IM-10	46.8	5.4	0.0	2 451	4 345	nd
IM-11	48.3	39.7	5.4	1 964	2 716	13 035
IM-12	22.8	nd	nd	3 042	144 065	nd
IM-13	46.9	nd	nd	6 240	272 261	nd

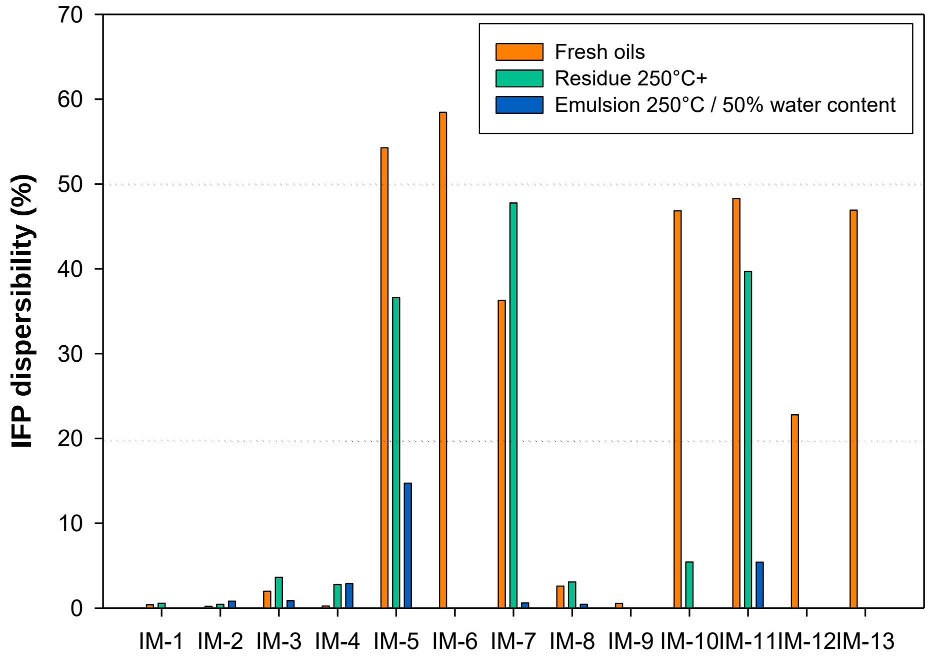

Figure 6 IFP dispersibility (%) of the fresh oils, the 250°C+ residues and the emulsions formed from the 250°C+ residues with 50% water content, at 15°C. The 2 dashed lines represent the 2 threshold values of 20% and 50%.

Fresh, 2 VLSFO may be dispersible (IM-5 and IM-6) whereas 5 VLSFO are potentially dispersible (IM-7, IM-10, IM-11, IM-12 and IM-13). Six oils (among them the 2 ULSFO) seem to be not dispersible. Once weathered (250°C+ residue), 3 oils remain potentially dispersible (IM-5, IM-7 and IM-11). The emulsions studied are not dispersible.

In general, the oils tested show limited dispersibility efficiency, especially once weathered.

5 Elements for OSR techniques potentially available

5.1 Safety: flammability

In terms of safety, considering the 13 tested samples, recovery operations from ships can be conducted directly after a spill given that flash points of the fresh oils are well above the ambient temperature. However, if the flash point of the spilt LSFO is not known, at sea operations should be carried out provided that a specific safety procedure is implemented to check for flammable hydrocarbon vapours (using gas detectors for example). This risk of ignition of the volatile vapours emitted by the oil being governed by the release characteristics and environmental conditions. The need to maintain monitoring should be regularly reconsidered.

5.2 Chemical dispersibility

Dispersibility test (according to IFP tests) performed at 15°C on the fresh oils, the residue 250°C+ and the emulsions formed from the residue 250°C+ with 50% water content show that some LSFO could be treated with dispersant when fresh. However, when weathered, the efficiency of this technique seems highly reduced. This response option seems thus to be very limited considering spills involving LSFO.

This response option will be more extensively studied in the frame of the Task 3.2 (weathering), on a selection of 3 samples, at the laboratory and the pilot scale.

5.3 Recovery

Considering the differences of pour point and of viscosity of the fresh and weathered LSFO tested in this study, the choice of the skimmer systems will be crucial and highly dependent of the product involved. Some LSFO will solidify immediately, adding challenge to the recovery operations. Some other oils will become highly viscous and sticky.

This important part of the project will be extensively studied on 3 selected oils in the frame of the WP4 (response options). It will be the subject of the Task 4.1, characterised by coupled experiments between NCA and Cedre.

6 Conclusion

Thirteen samples of ULSFO/VLSFO were analysed at the laboratory for physical-chemical characterization. Those samples have demonstrated the high variability existing in those new generation fuel oils. Some oils, fluid, may be dispersible on first hours after a spill and can be recovered with existing skimmer systems. Some other oils may represent a challenge if spilt in the aquatic environment. Very viscous or turning to very sticky weathered products, they may be difficult to recover with existing equipment and will be resistant to chemical dispersion. Considering the 2 ULSFO tested in this study, no difference was observed with VLSFO.

Based on those results, 3 products will be selected for weathering study at the laboratory and pilot scales in order to better evaluate the weathering of the oils as well as their behavior and the response options recommended (Task 3.2 of the WP3). Ecotoxicity tests will also be performed on those samples (Task 3.3 of the WP3). Finally, WP4 dedicated to the response option will be implemented, with dedicated tasks on mechanical recovery (Task 4.1), *In Situ* Burning (Task 4.3) and Shoreline Clean-up (Task 4.4)

APPENDIX

APPENDIX 1

Methods of measurements

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Methods of measurements

Chemical Composition and Evaporation

Chemical composition

The evolution of the oil composition was assessed by fractionation into 4 chemical families (saturates, aromatics, resins and asphaltenes). Asphaltenes were precipitated in *n*-pentane and were filtered on a glass fibre filter. The maltene fraction was separated on a silica-alumina column. Saturates were eluted with *n*-pentane, aromatics with a *n*-pentane/dichloromethane 80/20 mixture, and resins with a mixture methanol/ dichloromethane 50/50. The various fractions were weighed after evaporation of the solvent and stabilization of the masses. The mass balanced was calculated assuming that saturates and aromatics evaporates similarly whereas resins and asphaltenes do not evaporate.

Evaporation

The saturate and aromatic fractions were analysed using gas chromatography. Chromatograms of these volatile compounds at different weathering times show the evolution of their distribution. The lighter molecules disappear progressively and the quantitative analysis of samples compared to the initial oil can give the evaporation rate. These analyses performed at various weathering times provide an assessment of the kinetics of evaporation. Considering the low rate of dissolution and natural dispersion compared to evaporation, water soluble fractions were not taken into account to assess the proportion of oil that evaporated.

To assess the evaporation rate of the whole oil, a calibration was established in the laboratory. Different samples of the initial oil were artificially evaporated and then analysed (*table 1*). This qualitative determination led to the calculation of a Weathering Index (WI), proposed by Wang and Fingas (1994), which was plotted versus the evaporation rate. The calibration curve established that way was then applied to real samples to get their evaporation rates.

The Weathering Index is defined in the general following equation:

$$WI = \frac{L_1 + L_2 + L_3 + L_4}{H_1 + H_2 + H_3 + H_4}$$

L_1, L_2, L_3 and L_4 represent components that volatilize while H_1, H_2, H_3 and H_4 represent the non-volatile compounds in the oil (the choice of these target compounds depends on the initial composition of the oil; in our case. the light compounds were the linear alkanes $n\mathrm{C}_{11}$ to $n\mathrm{C}_{14}$. while the heavy molecules were $n\mathrm{C}_{25}$ to $n\mathrm{C}_{28}$). Consequently, as the oil evaporates, the Weathering Index decreases and a calibration curve similar to the one presented *figure 1* can be obtained:

Table 1 *Example of characterisation of distilled samples of one crude oil*

	Sample 1	Sample 2	Sample 3
Distillation temperature (°C)	150	200	250
Evaporation rate (%)	12.1	20.7	29.7
Density @ 1°C / 10°C	0.908 / 0.901	0.921 / 0.913	0.933 / 0.925
Weathering Index	-	-	-

The calculation of the maximum evaporation rate can also be checked by comparing the oil density at its final weathering state with samples obtained in the laboratory and characterized by their evaporation rate

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(measured by gravimetry).

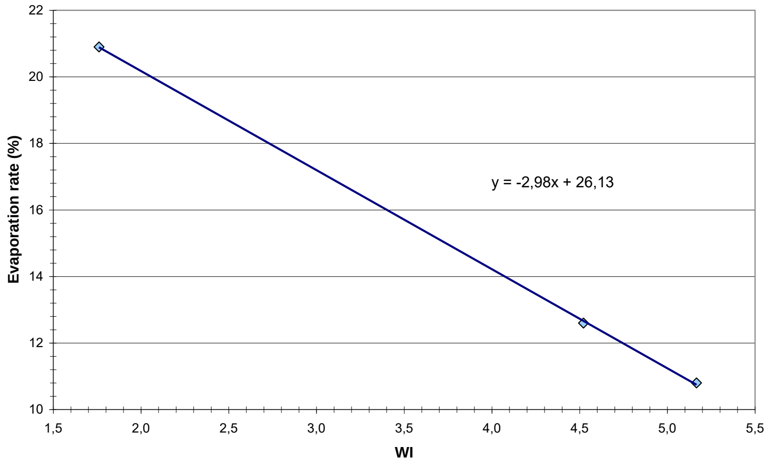

Figure 1 *Calibration curve established to measure the evaporation rate of weathered oils*

IFP Dispersibility

The chemical dispersibility were measured using the IFP test method (NF 90-345 French Standard) at 15°C and with a reference dispersant (*model dispersant*).

In order to calibrate the experimental design, additional dispersibility tests were carried out with the same dispersant using the French procedure for dispersant approval (test performed at 20°C; reference oil : FOREF, mixture of Heavy Fuel Oil and Arabian Light topped at 110°C, viscosity of 1000 mPa.s at 20°C). Under these conditions, the reference value is 76% ± 3 and the results of the calibration have to be within this range.

Oil was extracted using dichloromethane and the concentration was measured by UV spectrophotometry at 580 nm.

Table 2 *Composition of the model dispersant*

Denomination	% weight
Dipropylene-glycol-n-butyl-ether	18.5
Span-80	6.5
Tween-80	12.9
Tween-85	19.1
Aerosol-OT-75 (14/05/14)	27.8
Exxsol-D80	15.2
Total	100.0

Oil Composition – Quantification of Individual Components (PAHs. n-alkanes)

The PAHs and *n*-alkanes concentrations were measured on the crude oil in its initial state.

10 mg of the oil sample were spiked with internal standards (perdeutarated PAHs and eicosane). Compounds were then analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). The GC was an HP 7890 series II (Hewlett-Packard. Palo Alto. CA. USA) equipped with a Multi Mode Injector (MMI) used in the pulsed splitless mode (Pulse Splitless time: 1 min. Pulse Pressure: 15 psi). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 320°C (20 min) at 3°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a HP 5-ms (Hewlett-Packard.Palo Alto. CA. USA): 50 m x 0.25

mm ID x 0.25 µm film thickness. The GC was coupled to a HP 7000 triple quadripole used in the Electronic Impact mode (Electronic Impact: 70 eV. voltage: 2000V). PAHs and *n*-alkanes quantifications were done using Single Ion Monitoring mode with respectively the molecular ion of each compound and a common fragment (generally m/z = 57) at a minimum of 2 cycles/s.

PAHs and *n*-alkanes were quantified relatively to the perdeuterated PAHs and eicosane introduced at the beginning of the sample preparation procedure.

Oil Composition – Quantification of Individual Components (COVs)

10 mg of the oil sample and 10 mL of reverse-osmosis purified water are added in a 20 mL flask. which is then spiked with 50 µL of the methanolic solution of internal standards (6 perdeuterated alkanes, from C_5 to C_{10}, and C_0 to C_4- perdeuterated benzenes). The flask is then closed with a cap.

Headspace (HS) parameters

Following an incubation time of 5 minutes at 60°C (stirring at 500 rpm with a 1 second break every 60 seconds), 1000 µL of the air is sampled and injected in the GC-MS system.

GC-MS analysis

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 Cooled Injection System CIS-4 (Gerstel. Switzerland). The injection was performed in splitless mode (CIS temperature: 225°C). The GC temperature program was: from 35°C (5 min) to 80°C (0 min) at 11°C/min, then 250°C (0 min) at 16°C/min. The carrier gas was helium at a constant flow of 1 mL/min. The capillary column used was a RXi-624 Sil MS (Restek. Bellefonte. PA. USA): 30 m x 0.25 mm ID x 1.4 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 230°C. Alkanes and monoaromatics quantifications were done using Single Ion Monitoring mode at a minimum of 2 cycles/s.

Monoaromatics and and alkanes were quantified relatively to the perdeuterated linear alkanes, benzene and alkylated benzenes introduced at the beginning of the sample preparation procedure.

Oil Composition – Distribution according to the number of carbon atoms

10 mg of the oil were solubilized by 10 mL of CS_2. No purification was performed prior to the analysis.
The analysis was performed by high temperature gas chromatography coupled to a flame ionization detector (HTGC-FID). The GC was an HP 7890N (Hewlett-Packard. Palo Alto. CA. USA) equipped with an “on-column” injector. The injector program was: from 50°C to 400°C at 6°C/s. The oven temperature program: from 50°C (1 min) to 420°C (10 min) at 15°C/min. The carrier gas was hydrogen at a constant flow (15 mL/min). The capillary column used was a DB-HT Simdist (100% diméthylsiloxanne): 5 m x 0.53 mm x 0.15 µm film thickness. The chromatograph was coupled to a FID detector maintained at 425°C. The volume injected was 1 µL.

Co-funded by the European Union

APPENDIX 2

Detailed chemical composition of the oils

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Table 1 *Results of the OSCAR characterisation of the fresh samples (Individual compounds)*

Composition (% weight)	IM-1	IM-2	IM-3	IM-4	IM-5	IM-6	IM-7
C_1-C_4 (dissolved gas)	0.74	0.00	0.34	0.03	0.08	0.00	0.17
C_5-saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_6- saturates (n-/iso-/cyclo)	0.00	0.01	0.01	0.00	0.00	0.00	0.00
C_7- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_9- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Benzene	0.00	0,00	0,00	0.00	0.00	0.00	0.00
C_1-Benzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_2-Benzenes	0.00	0.00	0.00	0.01	0.00	0.00	0.00
C_3-Benzenes	0.01	0.00	0.01	0.02	0.02	0.22	0.00
C_4 & C_5-Benzenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_{10}- saturates (n-/iso-/cyclo)	0.00	0.04	0.06	0.58	2.09	1.92	0.32
C_{11}-C_{12} (total saturates + aromatics)	2.76	0.03	3.32	3.40	3.88	7.52	2.15
C_{13}-C_{14} (total saturates + aromatics)	3.01	0.03	5.12	5.49	5.32	6.43	3.66
C_{15}-C_{16} (total saturates + aromatics)	3.01	0.12	5.54	8.14	5.31	6.05	5.73
C_{17}-C_{18} (total saturates + aromatics)	3.02	0.48	5.60	6.80	4.97	4.60	5.61
C_{19}-C_{20} (total saturates + aromatics)	4.46	1.42	5.37	6.30	4.04	3.86	5.83
C_{21}-C_{25} (total saturates + aromatics)	19.30	10.89	12.94	11.43	8.86	5.82	13.22
C_{25}+ (total)	61.16	86.72	57.54	52.73	63.02	58.65	61.45
Naphthalenes 1 (C_0-C_1 alkylated)	1.36	0.00	1.34	1.18	0.17	2.78	0.37
Naphthalenes 2 (C_2-C_3 alkylated)	0.30	0.01	0.23	1.05	0.22	0.30	0.20
PAHs 1 (medium solubility)	0.52	0.04	1.57	1.44	0.29	1.31	0.39
PAHs 2 (low solubility)	0.35	0.21	1.01	1.40	0.54	0.54	0.90
Phenols (C_0-C_4)	-	-	-	-	-	-	-

☐	High dissolution potential
🟦	Medium dissolution potential
🟧	Low dissolution potential

Table 1 (cont.) *Results of the OSCAR characterisation of the fresh samples (Individual compounds)*

Composition (% weight)	IM-8	IM-9	IM-10	IM-11	IM-12	IM-13
C_1-C_4 (dissolved gas)	0.53	1.06	8.52	0.06	0.00	0.07
C_5-saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00
C_6- saturates (n-/iso-/cyclo)	0.01	0.00	0.00	0.00	0.00	0.00
C_7- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00
C_8- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.00	0.00
C_9- saturates (n-/iso-/cyclo)	0.00	0.00	0.00	0.00	0.01	0.01
Benzene	0.00	0.00	0.00	0.00	0.00	0.00
C_1-Benzene	0.00	0.00	0.00	0.00	0.00	0.00
C_2-Benzenes	0.00	0.00	0.00	0.00	0.00	0.00
C_3-Benzenes	0.00	0.00	0.01	0.01	0.02	0.01
C_4 & C_5-Benzenes	0.00	0.00	0.00	0.00	0.00	0.00
C_{10}- saturates (n-/iso-/cyclo)	0.00	0.83	0.53	0.57	1.91	2.65
C_{11}-C_{12} (total saturates + aromatics)	3.62	5.29	0.77	0.84	6.24	5.01
C_{13}-C_{14} (total saturates + aromatics)	2.88	5.41	1.68	1.84	6.00	4.62
C_{15}-C_{16} (total saturates + aromatics)	2.98	4.99	2.39	2.63	5.70	3.07
C_{17}-C_{18} (total saturates + aromatics)	2.76	4.97	2.80	2.94	4.72	2.28
C_{19}-C_{20} (total saturates + aromatics)	3.63	4.55	3.86	4.08	4.44	2.72
C_{21}-C_{25} (total saturates + aromatics)	11.04	10.73	14.84	16.59	7.00	5.99
C_{25}+ (total)	69.38	61.04	63.32	69.08	62.04	72.04
Naphthalenes 1 (C_0-C_1 alkylated)	1.08	0.58	0.05	0.06	0.51	0.42
Naphthalenes 2 (C_2-C_3 alkylated)	0.22	0.11	0.16	0.18	0.23	0.14
PAHs 1 (medium solubility)	0.54	0.19	0.33	0.37	0.33	0.24
PAHs 2 (low solubility)	1.33	0.25	0.74	0.75	0.85	0.73
Phenols (C_0-C_4)	-	-	-	-	-	-

⬜	High dissolution potential
🟦	Medium dissolution potential
🟧	Low dissolution potential

APPENDIX 3

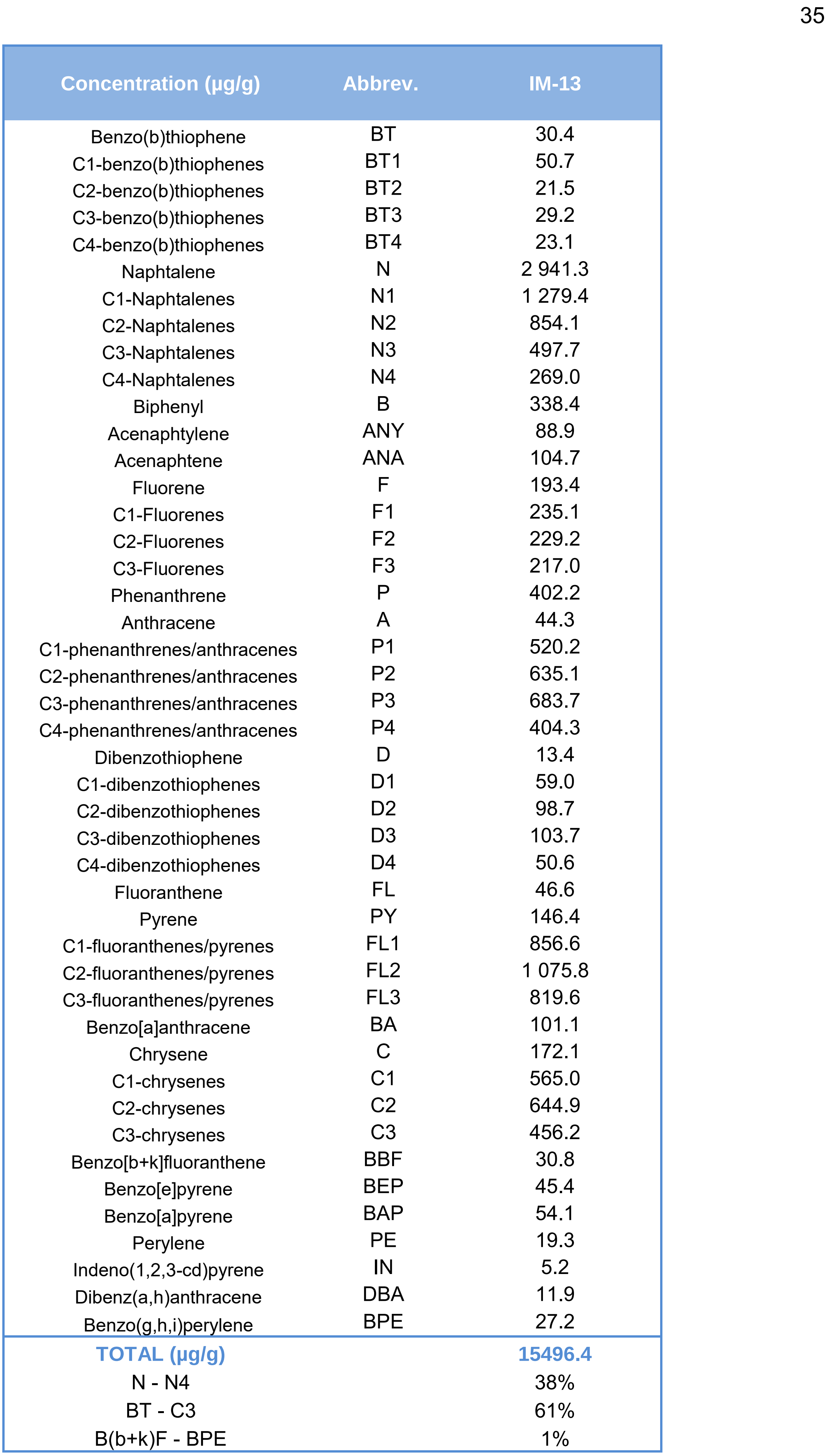
HAP quantification

Concentration (µg/g)	Abbrev.	IM-1	IM-2	IM-3
Benzo(b)thiophene	BT	9.4	0.0	70.8
C1-benzo(b)thiophenes	BT1	5.6	0.0	117.4
C2-benzo(b)thiophenes	BT2	7.8	0.0	162.3
C3-benzo(b)thiophenes	BT3	12.9	0.0	182.1
C4-benzo(b)thiophenes	BT4	3.4	0.0	377.0
Naphtalene	N	9 422.1	0.5	10 032.9
C1-Naphtalenes	N1	4 241.3	32.6	3 378.9
C2-Naphtalenes	N2	2 045.5	50.2	1 521.4
C3-Naphtalenes	N3	1 008.3	64.8	753.0
C4-Naphtalenes	N4	473.4	61.6	454.1
Biphenyl	B	1 563.4	0.0	7 200.5
Acenaphtylene	ANY	90.8	0.0	346.7
Acenaphtene	ANA	603.5	0.5	499.4
Fluorene	F	548.2	5.8	1 050.5
C1-Fluorenes	F1	426.3	67.7	799.7
C2-Fluorenes	F2	358.9	101.5	641.8
C3-Fluorenes	F3	319.0	117.1	633.1
Phenanthrene	P	806.2	45.0	2 287.7
Anthracene	A	75.5	2.4	342.6
C1-phenanthrenes/anthracenes	P1	608.4	182.4	1 497.1
C2-phenanthrenes/anthracenes	P2	639.0	311.9	1 279.0
C3-phenanthrenes/anthracenes	P3	552.6	346.6	1 003.0
C4-phenanthrenes/anthracenes	P4	341.7	244.6	504.6
Dibenzothiophene	D	8.5	0.0	58.1
C1-dibenzothiophenes	D1	29.9	37.2	338.8
C2-dibenzothiophenes	D2	64.8	78.9	281.2
C3-dibenzothiophenes	D3	81.4	95.0	409.0
C4-dibenzothiophenes	D4	40.4	55.1	195.0
Fluoranthene	FL	33.9	2.5	233.0
Pyrene	PY	68.5	4.9	442.5
C1-fluoranthenes/pyrenes	FL1	248.0	123.9	1 251.4
C2-fluoranthenes/pyrenes	FL2	234.1	171.7	1 062.8
C3-fluoranthenes/pyrenes	FL3	204.9	188.7	673.4
Benzo[a]anthracene	BA	17.6	4.3	164.3
Chrysene	C	57.7	38.5	239.0
C1-chrysenes	C1	84.9	83.9	440.5
C2-chrysenes	C2	98.2	92.0	433.7
C3-chrysenes	C3	79.0	75.8	270.9
Benzo[b+k]fluoranthene	BBF	11.4	10.2	76.2
Benzo[e]pyrene	BEP	16.4	9.2	64.2
Benzo[a]pyrene	BAP	4.2	1.3	81.9
Perylene	PE	1.3	3.8	15.5
Indeno(1,2,3-cd)pyrene	IN	0.0	0.0	13.1
Dibenz(a,h)anthracene	DBA	0.0	0.0	8.7
Benzo(g,h,i)perylene	BPE	4.0	3.9	31.9
TOTAL (µg/g)		**25551.9**	**2716.0**	**41920.4**
N - N4		67%	8%	39%
BT - C3		33%	91%	61%
B(b+k)F - BPE		0%	1%	1%

Concentration (µg/g)	Abbrev.	IM-4	IM-5	IM-6
Benzo(b)thiophene	BT	116.9	20.5	31.5
C1-benzo(b)thiophenes	BT1	425.1	46.0	46.3
C2-benzo(b)thiophenes	BT2	585.1	18.4	24.1
C3-benzo(b)thiophenes	BT3	498.9	36.3	51.6
C4-benzo(b)thiophenes	BT4	365.8	19.6	28.7
Naphtalene	N	6 826.4	851.0	20 527.7
C1-Naphtalenes	N1	5 008.1	801.0	7 236.5
C2-Naphtalenes	N2	6 047.8	1 240.6	2 268.3
C3-Naphtalenes	N3	4 447.7	952.5	683.1
C4-Naphtalenes	N4	2 270.9	577.0	301.8
Biphenyl	B	965.6	380.5	2 845.8
Acenaphtylene	ANY	159.8	0.0	896.5
Acenaphtene	ANA	521.6	26.4	828.9
Fluorene	F	729.6	141.4	1 709.4
C1-Fluorenes	F1	1 263.0	367.7	1 417.7
C2-Fluorenes	F2	1 436.2	494.6	657.7
C3-Fluorenes	F3	1 071.5	510.5	263.5
Phenanthrene	P	1 856.5	259.2	2 925.6
Anthracene	A	272.5	9.6	337.4
C1-phenanthrenes/anthracenes	P1	3 513.7	696.3	1 584.7
C2-phenanthrenes/anthracenes	P2	3 207.3	987.9	636.3
C3-phenanthrenes/anthracenes	P3	1 850.2	801.0	306.9
C4-phenanthrenes/anthracenes	P4	706.5	391.0	110.0
Dibenzothiophene	D	226.2	143.1	0.0
C1-dibenzothiophenes	D1	606.3	169.6	31.5
C2-dibenzothiophenes	D2	733.0	231.0	55.4
C3-dibenzothiophenes	D3	500.2	182.7	52.6
C4-dibenzothiophenes	D4	178.2	78.8	11.4
Fluoranthene	FL	114.7	10.4	336.0
Pyrene	PY	360.2	45.8	564.1
C1-fluoranthenes/pyrenes	FL1	1 236.0	324.3	1 168.3
C2-fluoranthenes/pyrenes	FL2	1 013.8	394.9	508.1
C3-fluoranthenes/pyrenes	FL3	586.4	353.7	179.2
Benzo[a]anthracene	BA	91.9	14.4	153.6
Chrysene	C	187.7	50.9	168.4
C1-chrysenes	C1	346.9	155.2	152.4
C2-chrysenes	C2	223.4	202.4	68.1
C3-chrysenes	C3	140.6	183.2	38.8
Benzo[b+k]fluoranthene	BBF	29.1	9.8	65.7
Benzo[e]pyrene	BEP	27.9	15.1	46.8
Benzo[a]pyrene	BAP	31.7	6.9	78.6
Perylene	PE	7.2	4.7	13.2
Indeno(1,2,3-cd)pyrene	IN	2.3	0.8	11.8
Dibenz(a,h)anthracene	DBA	0.0	0.0	1.6
Benzo(g,h,i)perylene	BPE	24.4	7.2	42.8
TOTAL (µg/g)		**50814.7**	**12214.3**	**49468.3**
N - N4		48%	36%	63%
BT - C3		51%	63%	37%
B(b+k)F - BPE		0%	0%	1%

Concentration (µg/g)	Abbrev.	IM-7	IM-8	IM-9
Benzo(b)thiophene	BT	15.9	20.4	9.7
C1-benzo(b)thiophenes	BT1	51.9	52.3	15.1
C2-benzo(b)thiophenes	BT2	65.6	56.6	0.5
C3-benzo(b)thiophenes	BT3	121.5	80.1	31.4
C4-benzo(b)thiophenes	BT4	112.5	115.3	13.4
Naphtalene	N	2 554.4	8 080.9	4 903.7
C1-Naphtalenes	N1	1 118.9	2 818.4	1 006.7
C2-Naphtalenes	N2	1 066.2	1 440.9	549.8
C3-Naphtalenes	N3	930.3	801.7	564.8
C4-Naphtalenes	N4	596.7	429.7	356.1
Biphenyl	B	334.1	950.0	310.5
Acenaphtylene	ANY	42.3	71.2	30.5
Acenaphtene	ANA	117.9	348.7	44.1
Fluorene	F	194.3	375.8	75.0
C1-Fluorenes	F1	375.0	446.0	339.9
C2-Fluorenes	F2	505.4	453.1	278.5
C3-Fluorenes	F3	509.8	390.2	255.6
Phenanthrene	P	498.4	841.1	296.5
Anthracene	A	61.9	110.5	21.9
C1-phenanthrenes/anthracenes	P1	1 098.8	1 300.3	316.0
C2-phenanthrenes/anthracenes	P2	1 422.0	1 716.0	530.5
C3-phenanthrenes/anthracenes	P3	1 119.7	1 700.2	429.0
C4-phenanthrenes/anthracenes	P4	598.4	974.0	180.6
Dibenzothiophene	D	58.0	49.3	9.2
C1-dibenzothiophenes	D1	209.4	190.6	41.4
C2-dibenzothiophenes	D2	327.4	331.2	50.5
C3-dibenzothiophenes	D3	338.6	381.9	45.0
C4-dibenzothiophenes	D4	135.7	157.3	11.4
Fluoranthene	FL	42.3	96.8	12.4
Pyrene	PY	167.0	349.2	27.4
C1-fluoranthenes/pyrenes	FL1	820.9	1 635.7	131.5
C2-fluoranthenes/pyrenes	FL2	989.8	1 741.7	140.2
C3-fluoranthenes/pyrenes	FL3	753.0	1 139.3	113.3
Benzo[a]anthracene	BA	69.6	147.2	6.4
Chrysene	C	131.0	243.9	52.7
C1-chrysenes	C1	380.3	709.0	96.7
C2-chrysenes	C2	437.2	706.1	94.6
C3-chrysenes	C3	310.8	499.8	69.4
Benzo[b+k]fluoranthene	BBF	47.4	49.2	16.3
Benzo[e]pyrene	BEP	45.6	70.6	20.0
Benzo[a]pyrene	BAP	38.0	65.2	3.3
Perylene	PE	18.4	18.4	7.4
Indeno(1,2,3-cd)pyrene	IN	11.8	4.3	0.0
Dibenz(a,h)anthracene	DBA	16.9	7.7	0.0
Benzo(g,h,i)perylene	BPE	42.2	32.9	5.3
TOTAL (µg/g)		**18903.1**	**32200.4**	**11514.3**
N - N4		33%	42%	64%
BT - C3		66%	57%	35%
B(b+k)F - BPE		1%	1%	0%

Concentration (µg/g)	Abbrev.	IM-10	IM-11	IM-12
Benzo(b)thiophene	BT	1.8	17.0	52.3
C1-benzo(b)thiophenes	BT1	43.5	45.6	139.7
C2-benzo(b)thiophenes	BT2	50.0	46.7	27.7
C3-benzo(b)thiophenes	BT3	71.5	80.0	49.1
C4-benzo(b)thiophenes	BT4	57.7	60.5	29.8
Naphtalene	N	145.1	145.2	3 781.5
C1-Naphtalenes	N1	435.7	449.0	1 327.6
C2-Naphtalenes	N2	866.3	887.1	1 272.7
C3-Naphtalenes	N3	903.3	929.8	1 027.8
C4-Naphtalenes	N4	611.9	620.7	596.2
Biphenyl	B	428.6	436.4	240.1
Acenaphtylene	ANY	1.3	9.1	56.5
Acenaphtene	ANA	36.8	38.9	80.4
Fluorene	F	167.2	169.3	156.6
C1-Fluorenes	F1	310.8	326.0	362.9
C2-Fluorenes	F2	541.2	551.0	531.5
C3-Fluorenes	F3	501.1	536.0	405.5
Phenanthrene	P	362.3	343.2	394.0
Anthracene	A	44.5	35.0	51.4
C1-phenanthrenes/anthracenes	P1	1 171.9	1 198.3	919.8
C2-phenanthrenes/anthracenes	P2	1 602.2	1 572.8	1 310.3
C3-phenanthrenes/anthracenes	P3	1 237.6	1 114.9	1 077.3
C4-phenanthrenes/anthracenes	P4	584.7	533.0	496.0
Dibenzothiophene	D	53.8	52.1	35.4
C1-dibenzothiophenes	D1	208.4	209.0	129.2
C2-dibenzothiophenes	D2	357.7	359.3	252.5
C3-dibenzothiophenes	D3	318.2	296.7	219.0
C4-dibenzothiophenes	D4	133.9	112.7	91.0
Fluoranthene	FL	65.1	20.0	37.8
Pyrene	PY	147.1	111.8	152.5
C1-fluoranthenes/pyrenes	FL1	686.5	640.0	844.0
C2-fluoranthenes/pyrenes	FL2	707.0	648.8	976.3
C3-fluoranthenes/pyrenes	FL3	500.5	419.1	734.6
Benzo[a]anthracene	BA	72.7	29.2	71.6
Chrysene	C	124.6	61.6	117.1
C1-chrysenes	C1	228.7	201.9	387.4
C2-chrysenes	C2	183.8	158.6	414.6
C3-chrysenes	C3	129.5	111.4	348.4
Benzo[b+k]fluoranthene	BBF	113.6	11.6	19.8
Benzo[e]pyrene	BEP	57.3	12.6	41.6
Benzo[a]pyrene	BAP	45.2	5.3	30.5
Perylene	PE	47.7	3.8	11.7
Indeno(1,2,3-cd)pyrene	IN	62.0	6.4	3.9
Dibenz(a,h)anthracene	DBA	71.0	0.0	6.1
Benzo(g,h,i)perylene	BPE	125.0	55.0	78.0
TOTAL (µg/g)		**14616.5**	**13672.1**	**19389.6**
N - N4		20%	22%	41%
BT - C3		76%	77%	58%
B(b+k)F - BPE		4%	1%	1%



Concentration (µg/g)	Abbrev.	IM-13
Benzo(b)thiophene	BT	30.4
C1-benzo(b)thiophenes	BT1	50.7
C2-benzo(b)thiophenes	BT2	21.5
C3-benzo(b)thiophenes	BT3	29.2
C4-benzo(b)thiophenes	BT4	23.1
Naphtalene	N	2 941.3
C1-Naphtalenes	N1	1 279.4
C2-Naphtalenes	N2	854.1
C3-Naphtalenes	N3	497.7
C4-Naphtalenes	N4	269.0
Biphenyl	B	338.4
Acenaphtylene	ANY	88.9
Acenaphtene	ANA	104.7
Fluorene	F	193.4
C1-Fluorenes	F1	235.1
C2-Fluorenes	F2	229.2
C3-Fluorenes	F3	217.0
Phenanthrene	P	402.2
Anthracene	A	44.3
C1-phenanthrenes/anthracenes	P1	520.2
C2-phenanthrenes/anthracenes	P2	635.1
C3-phenanthrenes/anthracenes	P3	683.7
C4-phenanthrenes/anthracenes	P4	404.3
Dibenzothiophene	D	13.4
C1-dibenzothiophenes	D1	59.0
C2-dibenzothiophenes	D2	98.7
C3-dibenzothiophenes	D3	103.7
C4-dibenzothiophenes	D4	50.6
Fluoranthene	FL	46.6
Pyrene	PY	146.4
C1-fluoranthenes/pyrenes	FL1	856.6
C2-fluoranthenes/pyrenes	FL2	1 075.8
C3-fluoranthenes/pyrenes	FL3	819.6
Benzo[a]anthracene	BA	101.1
Chrysene	C	172.1
C1-chrysenes	C1	565.0
C2-chrysenes	C2	644.9
C3-chrysenes	C3	456.2
Benzo[b+k]fluoranthene	BBF	30.8
Benzo[e]pyrene	BEP	45.4
Benzo[a]pyrene	BAP	54.1
Perylene	PE	19.3
Indeno(1,2,3-cd)pyrene	IN	5.2
Dibenz(a,h)anthracene	DBA	11.9
Benzo(g,h,i)perylene	BPE	27.2
TOTAL (µg/g)		**15496.4**
N - N4		38%
BT - C3		61%
B(b+k)F - BPE		1%

APPENDIX 4

True Boiling Point (TBP) curve

Combination of laboratory data (up to 250°C) and simulated distillation (from 200 to 520°C)

Table 1 *Results of laboratory and simulated distillation of the fresh IM-1 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
25	0.1	200	1.5
30	0.1	210	2.4
40	0.1	220	2.7
50	0.1	230	3.5
60	0.1	240	3.8
70	0.1	250	4.3
80	0.1	260	4.7
90	0.1	270	5.2
95	0.2	280	5.6
105	0.2	290	6.0
110	0.2	300	6.5
115	0.2	310	7.1
120	0.3	320	7.7
125	0.3	330	8.7
130	0.4	340	9.8
135	0.5	350	11.3
140	0.5	360	13.0
145	0.5	370	14.9
150	0.5	380	16.8
155	0.5	390	18.8
160	0.6	400	20.6
165	0.6	410	22.4
170	0.6	420	23.9
175	0.6	430	25.2
180	0.6	440	26.3
185	0.6	450	27.1
190	0.7	460	27.6
195	0.7	470	28.0
200	0.7	480	28.2
205	0.7	490	28.3
210	0.8	500	28.5
215	0.9	510	28.6
220	1.1	520	28.6
225	1.3		
230	2.0		
235	2.9		
240	3.4		
245	3.6		
250	3.8		

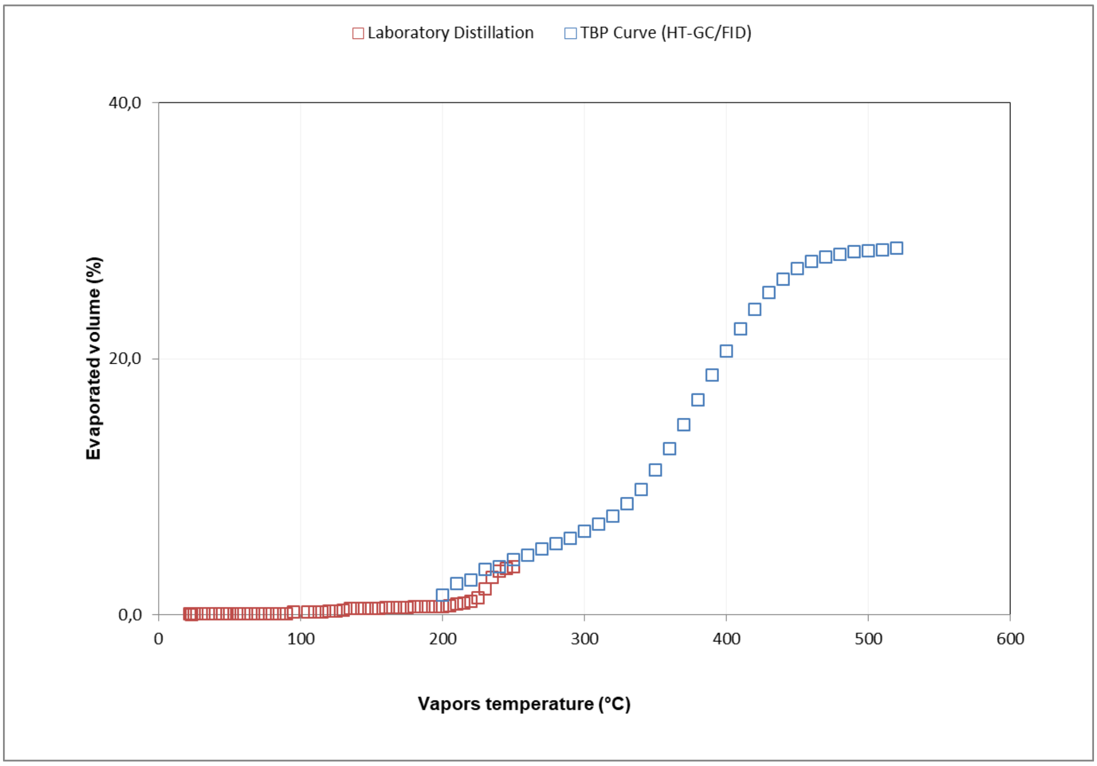


Figure 1 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-1 sample*

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Table 2 *Results of laboratory and simulated distillation of the fresh IM-2 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
21	0.0	210	3.7
25	0.0	220	3.7
30	0.0	230	3.7
40	0.0	240	3.8
50	0.0	250	3.8
60	0.0	260	3.9
80	0.0	270	4.0
85	0.0	280	4.1
90	0.0	290	4.2
100	0.0	300	4.5
105	0.0	310	4.8
110	0.0	320	5.3
115	0.0	330	5.9
120	0.0	340	6.8
125	0.0	350	8.1
130	0.0	360	9.9
135	0.1	370	12.1
140	0.1	380	14.6
145	0.2	390	17.9
150	0.3	400	21.5
155	0.3	410	25.5
160	0.3	420	26.6
165	0.5	430	26.6
170	0.5	440	26.6
175	0.6	450	26.7
180	0.7	460	26.7
185	0.8	470	26.7
190	0.9	480	26.7
195	1.1	490	26.7
200	1.2	500	26.7
210	1.7	510	26.7
215	2.3	520	26.7
220	2.5		
225	2.8		
230	2.8		
235	3.4		
240	3.7		
245	4.3		
250	5.2		

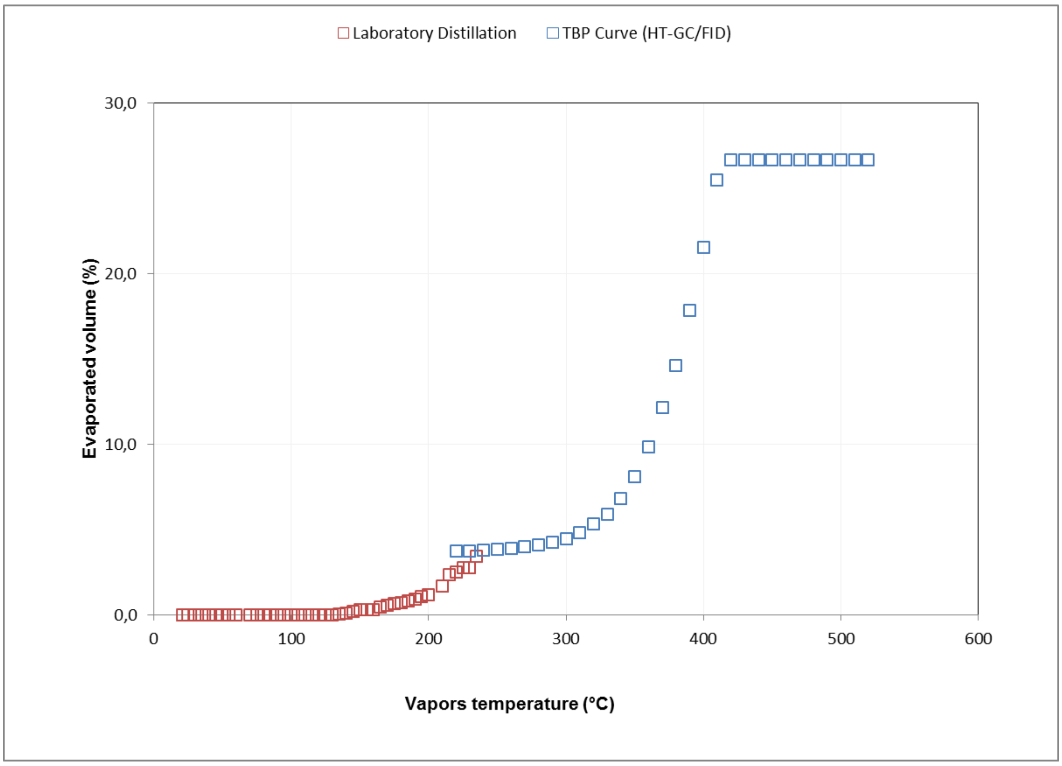

Figure 2 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-2 sample*

Table 3 *Results of laboratory and simulated distillation of the fresh IM-3 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
20	0.0	200	3.5
21	0.3	210	5.6
24	0.3	220	6.4
27	0.3	230	8.2
39	0.3	240	9.3
80	0.3	250	11.5
85	0.4	260	12.9
90	0.4	270	14.4
95	0.4	280	16.2
95	0.6	290	17.8
105	0.7	300	19.6
110	0.8	310	21.6
125	0.9	320	23.6
140	0.9	330	25.6
160	0.9	340	27.6
175	1.1	350	29.8
190	1.2	360	31.9
200	1.4	370	34.1
205	1.5	380	36.3
210	1.8	390	38.4
215	2.1	400	40.4
220	2.7	410	42.3
225	3.3	420	44.1
232	4.4	430	45.7
236	5.5	440	47.0
240	6.3	450	48.1
245	7.1	460	48.9
250	8.6	470	49.5
		480	49.8
		490	50.1
		500	50.3
		510	50.5
		520	50.7

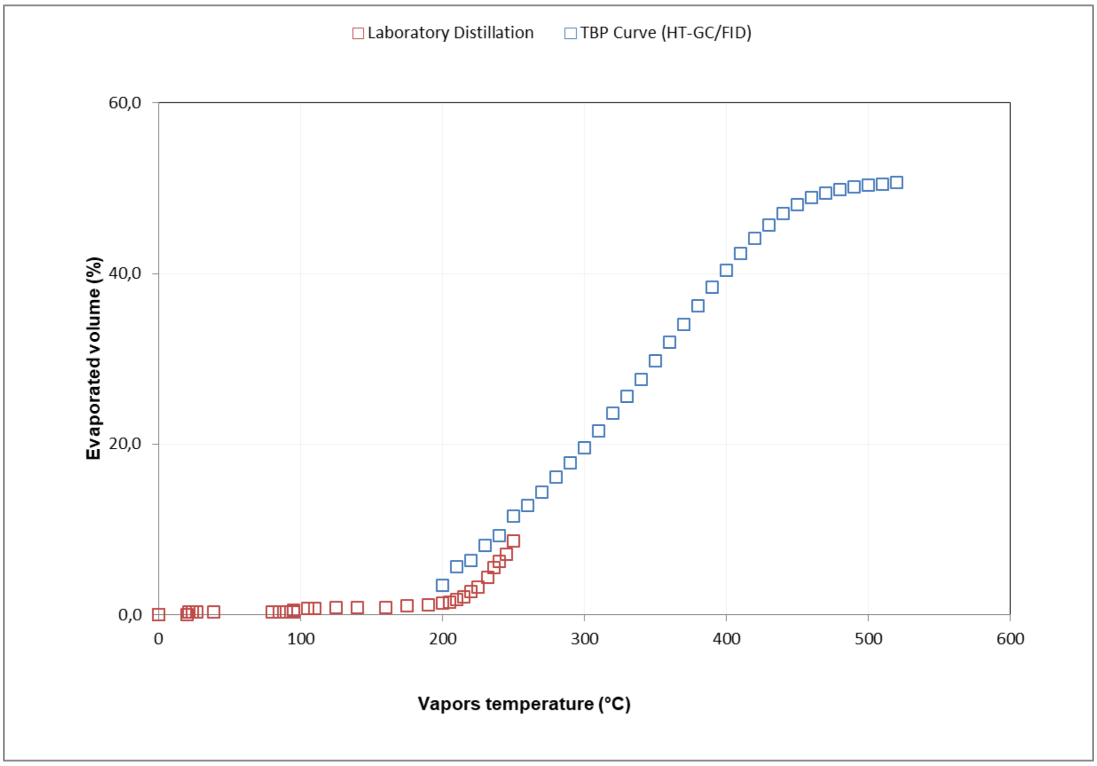

Figure 3 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-3 sample*

Table 4 *Results of laboratory and simulated distillation of the fresh IM-4 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
20	0.0	200	3.2
21	0.0	210	4.7
22	0.0	220	5.7
25	0.0	230	7.9
33	0.0	240	9.0
33	0.0	250	11.4
42	0.0	260	13.0
75	0.0	270	15.0
90	0.0	280	16.9
100	0.0	290	18.8
110	0.0	300	20.7
125	0.0	310	22.6
145	0.5	320	24.3
160	0.5	330	26.6
170	0.7	340	28.5
180	0.8	350	30.5
190	1.0	360	32.3
200	1.1	370	33.9
207	1.5	380	35.3
215	2.0	390	36.6
222	2.5	400	37.9
230	4.2	410	39.0
235	5.3	420	39.9
240	6.7	430	40.7
245	8.2	440	41.4
250	9.0	450	41.9
		460	42.3
		470	42.5
		480	42.7
		490	42.8
		500	42.9
		510	43.0
		520	43.0

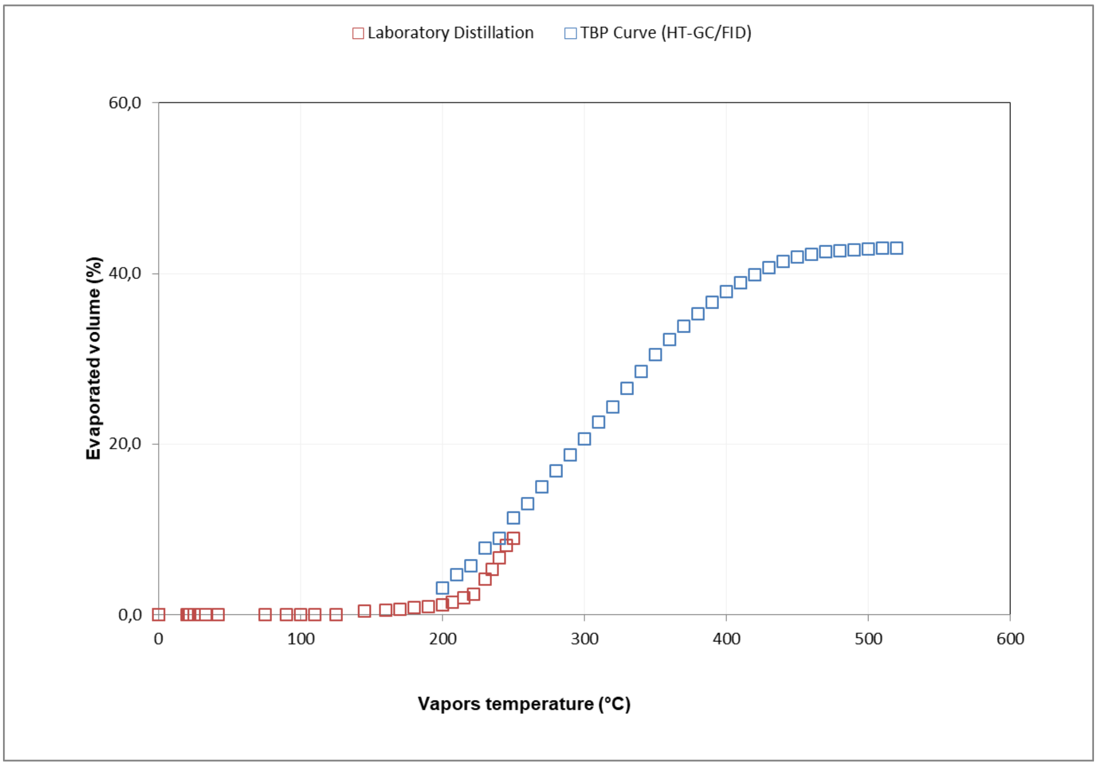

Figure 4 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-4 sample*

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Table 5 *Results of laboratory and simulated distillation of the fresh IM-5 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
21	0.0	200	5.0
21	0.1	210	6.3
22	0.1	220	7.5
22	0.1	230	9.1
23	0.1	240	10.5
25	0.1	250	12.7
30	0.1	260	14.6
40	0.1	270	16.5
50	0.1	280	18.5
65	0.1	290	19.9
75	0.1	300	22.0
80	0.1	310	23.7
90	0.1	320	25.0
95	0.2	330	26.8
99	0.5	340	28.5
100	1.1	350	30.2
105	1.2	360	31.9
115	1.2	370	33.5
120	1.3	380	35.1
130	1.6	390	36.8
140	1.7	400	38.7
150	1.8	410	40.5
160	1.9	420	42.3
170	1.9	430	43.9
180	2.1	440	45.4
190	2.2	450	46.6
195	2.3	460	47.5
200	2.4	470	48.2
205	2.7	480	48.7
210	3.3	490	49.1
215	3.6	500	49.4
220	4.4	510	49.6
226	5.6	520	49.8
230	6.4		
235	7.7		
240	8.5		
245	9.3		
250	10.5		

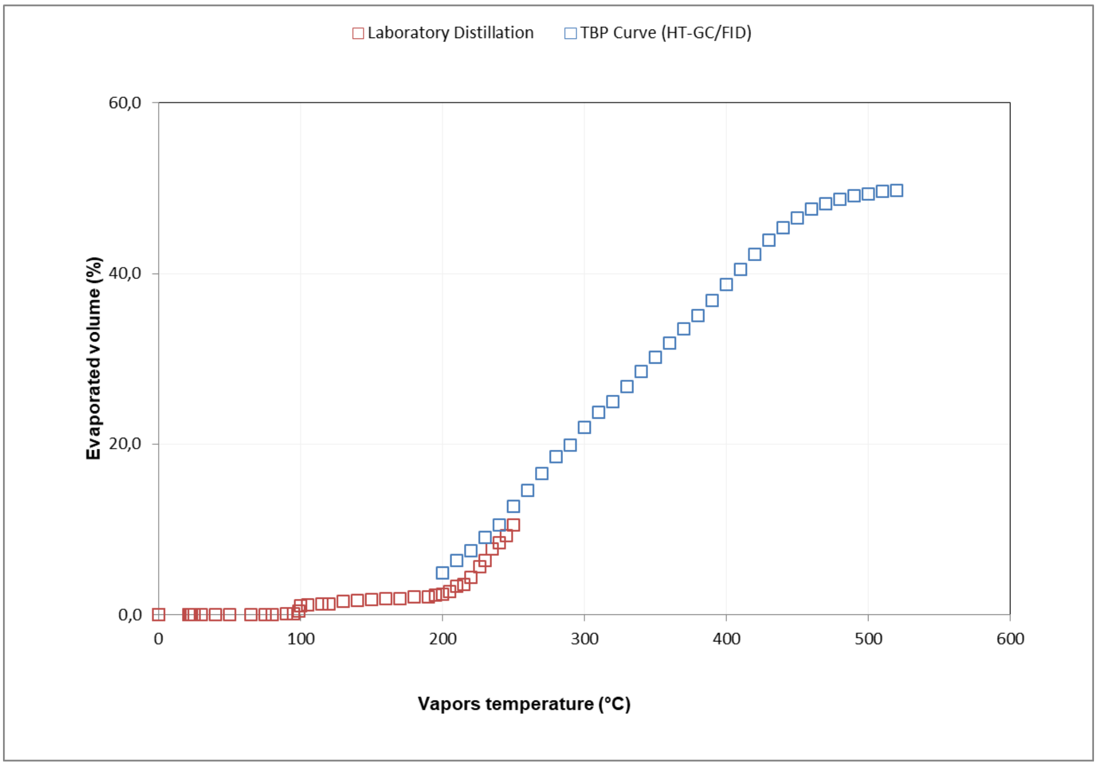

Figure 5 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-5 sample*

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Table 6 *Results of laboratory and simulated distillation of the fresh IM-6 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
30	0	200	13.4
50	0	210	19.6
77	0	220	21.5
90	0	230	26.3
135	0.1	240	28.1
130	0.6	250	31.2
105	0.7	260	33.9
100	0.8	270	36.4
120	0.9	280	39.0
135	1.0	290	41.2
160	1.3	300	43.5
141	1.5	310	46.0
150	2.0	320	48.0
155	2.3	330	50.4
160	2.4	340	52.5
165	2.5	350	54.6
170	2.9	360	56.3
175	3.7	370	57.9
170	5.1	380	59.1
165	6.1	390	60.1
170	6.4	400	61.0
180	6.8	410	61.8
185	7.3	420	62.5
190	8.6	430	63.2
195	8.1	440	63.8
190	9.8	450	64.3
195	10.9	460	64.8
200	11.2	470	65.2
210	11.9	480	65.5
210	14.0	490	65.7
215	14.2	500	65.9
220	15.9	510	66.0
223	19.0	520	66.2
225	19.0		
230	20.4		
235	21.1		
240	23.7		
245	25.6		
250	28.1		

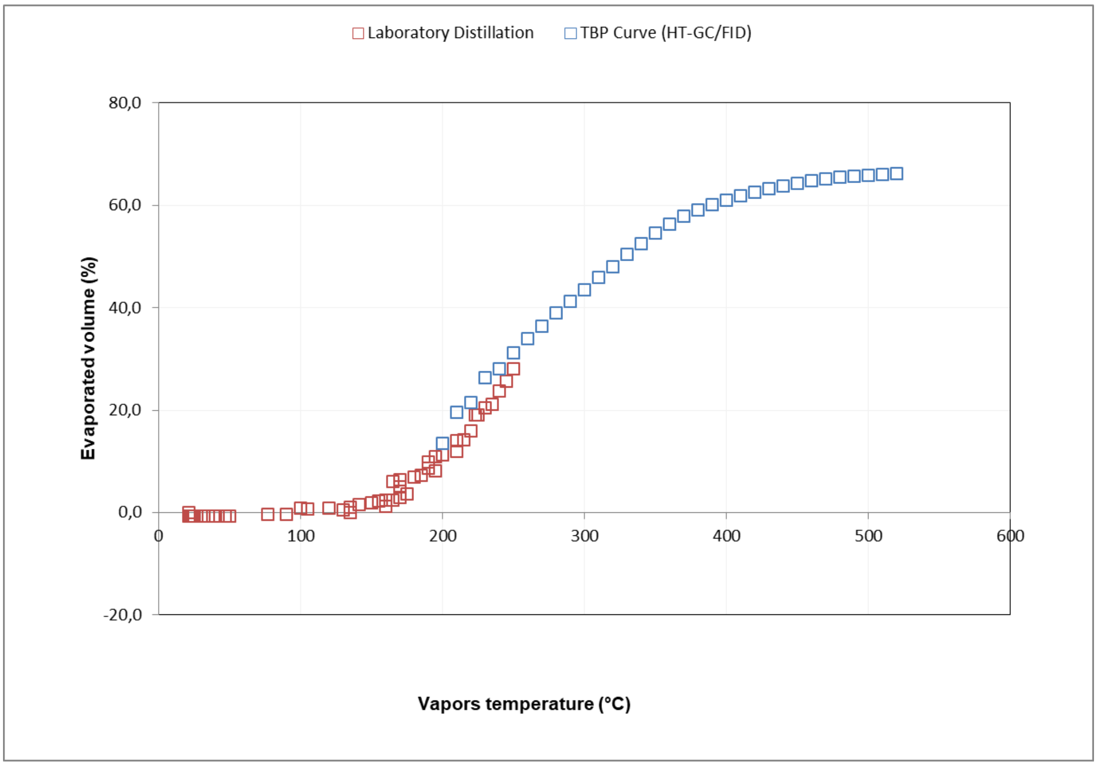

Figure 6 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-6 sample*

Table 7 *Results of laboratory and simulated distillation of the fresh IM-7 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
20	0.2	200	2.6
24	0.2	210	3.6
26	0.2	220	4.4
30	0.2	230	5.6
32	0.2	240	6.7
35	0.2	250	8.2
40	0.2	260	9.8
50	0.2	270	11.6
90	0.4	280	13.6
95	0.5	290	15.3
105	0.5	300	17.5
110	0.5	310	19.5
120	0.6	320	21.7
125	0.6	330	24.2
130	0.7	340	26.6
135	0.7	350	29.0
145	0.7	360	31.3
160	0.8	370	33.8
180	1.0	380	36.3
185	1.2	390	38.7
190	1.2	400	41.1
195	1.2	410	43.2
200	1.3	420	45.0
205	1.5	430	46.5
210	1.5	440	47.6
215	1.9	450	48.5
220	2.2	460	49.2
225	2.7	470	49.6
230	3.2	480	49.9
235	3.9	490	50.0
240	5.3	500	50.2
245	5.8	510	50.3
250	6.7	520	50.4

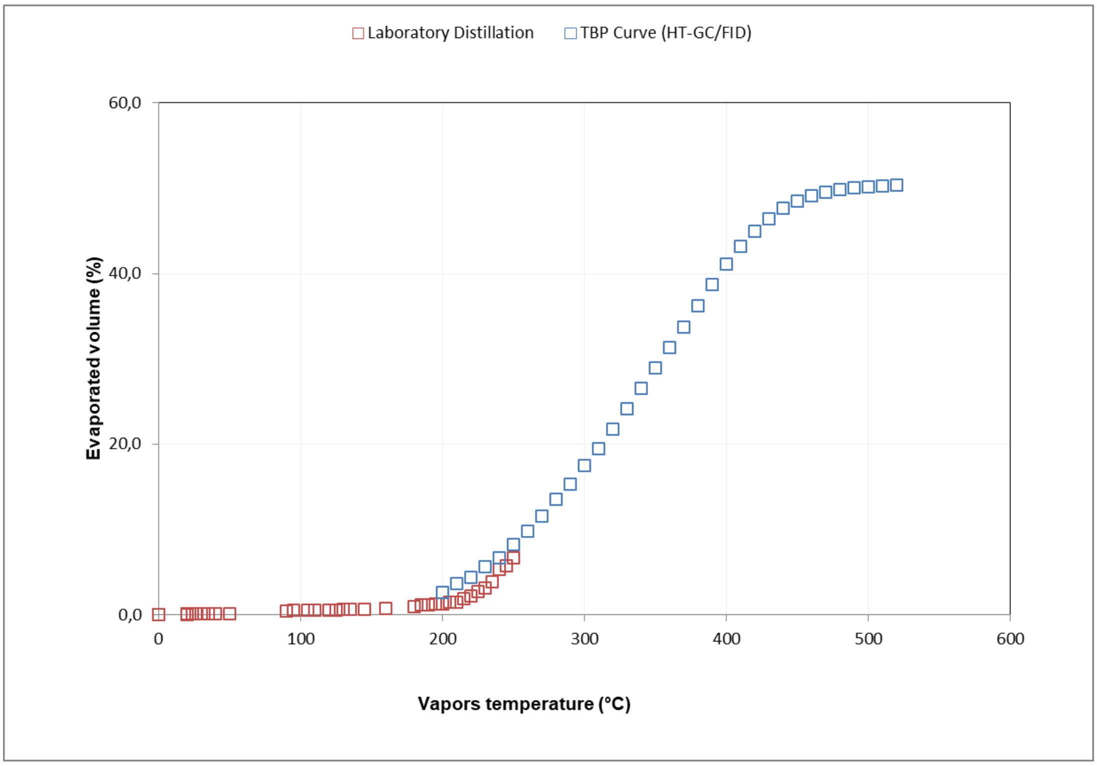

Figure 7 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-7 sample*

Table 8 *Results of laboratory and simulated distillation of the fresh IM-8 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
21	0.5	200	8.2
26	0.5	210	11.2
30	0.5	220	12.2
35	0.5	230	14.4
75	0.5	240	15.4
80	0.7	250	17.1
85	0.8	260	18.4
95	0.9	270	20.0
100	0.9	280	21.7
116	0.9	290	23.2
125	1.0	300	24.9
130	1.3	310	27.1
140	1.3	320	29.2
145	1.4	330	31.9
150	1.6	340	34.8
155	1.7	350	37.9
160	1.8	360	41.3
165	1.8	370	44.7
170	2.3	380	48.0
175	2.6	390	51.2
185	3.0	400	54.3
185	4.6	410	57.2
190	5.3	420	59.9
195	5.3	430	62.3
200	5.5	440	64.3
205	6.2	450	66.0
210	6.8	460	67.3
215	7.9	470	68.1
220	9.0	480	68.7
230	9.8	490	69.1
235	12.3	500	69.5
240	12.8	510	69.7
245	14.6	520	69.9
250	15.4		

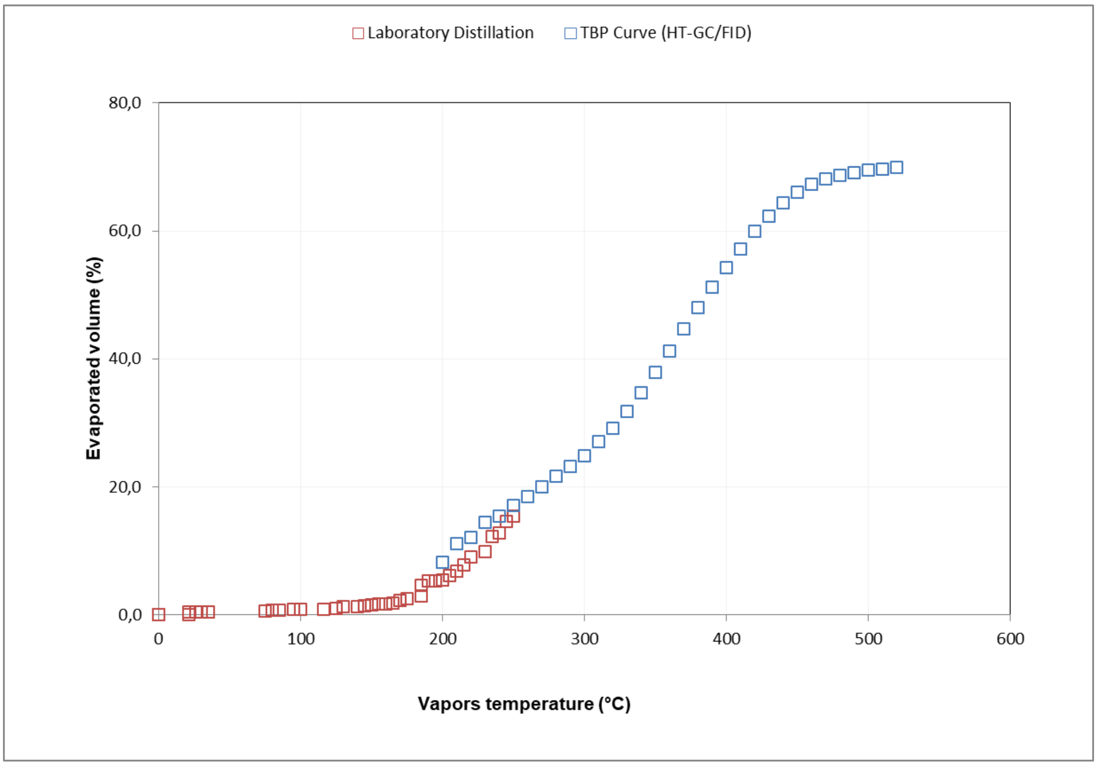

Figure 8 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-8 sample*

Table 9 *Results of laboratory and simulated distillation of the fresh IM-9 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
25	1.1	200	12.4
30	1.1	210	15.7
40	1.1	220	17.4
50	1.3	230	19.9
60	2.0	240	21.6
70	2.2	250	23.9
75	2.3	260	25.8
80	2.4	270	28.1
85	2.5	280	30.4
90	2.6	290	32.1
95	2.8	300	35.0
100	3.0	310	37.7
105	3.3	320	40.4
110	3.6	330	43.1
120	4.0	340	45.3
125	4.4	350	48.2
130	4.7	360	51.0
135	4.7	370	53.9
140	4.8	380	56.7
150	5.0	390	59.5
155	5.3	400	62.1
160	5.4	410	64.5
165	6.5	420	66.7
170	6.9	430	68.6
180	7.4	440	70.2
185	8.1	450	71.5
190	9.4	460	72.5
200	11.6	470	73.0
205	11.7	480	73.4
210	11.7	490	73.7
215	11.7	500	73.8
220	14.6	510	74.0
225	15.0	520	74.1
230	15.9		
235	18.3		
240	20.3		
245	20.5		
250	21.6		

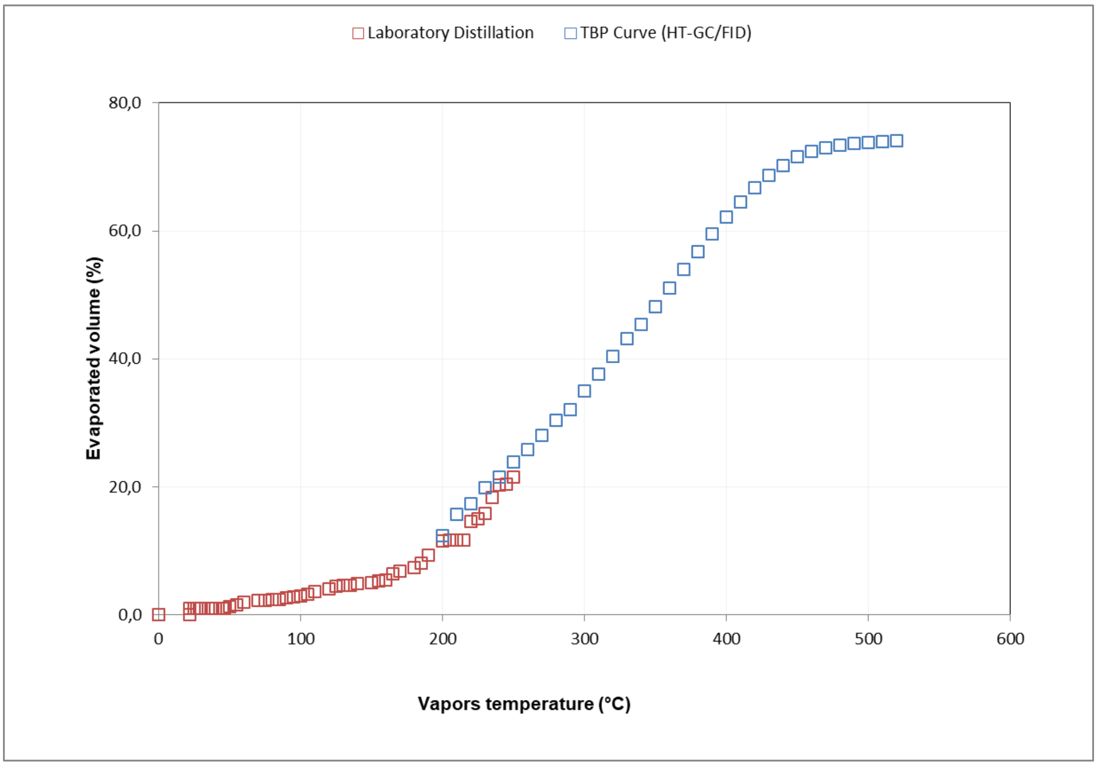

Figure 9 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-9 sample*

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Table 10 *Results of laboratory and simulated distillation of the fresh IM-10 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
170	0.3	210	1.1
185	0.5	220	1.5
190	0.5	230	2.0
210	0.9	240	2.6
215	1.1	250	3.3
220	1.3	260	4.0
225	1.6	270	4.8
230	1.8	280	5.6
235	2.0	290	6.4
240	2.2	300	7.4
245	2.5	310	8.6
250	2.9	320	9.8
		330	11.5
		340	13.4
		350	15.6
		360	18.2
		370	21.1
		380	24.0
		390	26.8
		400	29.5
		410	31.8
		420	33.7
		430	35.3
		440	36.5
		450	37.4
		460	38.0
		470	38.4
		480	38.6
		490	38.7
		500	38.8
		510	38.9
		520	39.0

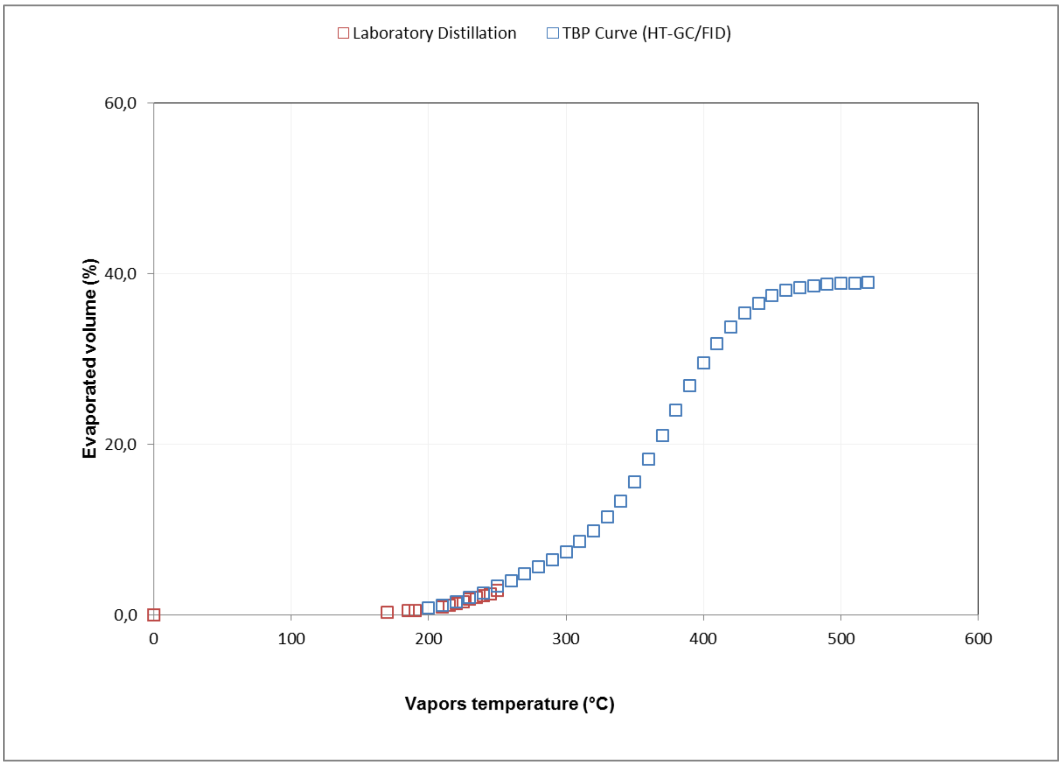

Figure 10 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-10 sample*

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Table 11 *Results of laboratory and simulated distillation of the fresh IM-11 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
20	0.0	200	0.9
21	0.0	210	1.3
23	0.0	220	1.6
25	0.0	230	2.1
29	0.0	240	2.6
31	0.0	250	3.4
32	0.0	260	4.0
32	0.0	270	4.8
36	0.0	280	5.6
36	0.0	290	6.4
36	0.0	300	7.3
36	0.0	310	8.3
49	0.1	320	9.4
90	0.1	330	10.9
100	0.1	340	12.7
115	0.1	350	14.9
170	0.1	360	17.4
180	0.3	370	20.2
185	0.4	380	23.1
215	0.6	390	25.9
221	0.7	400	28.6
225	0.8	410	30.9
227	1.3	420	32.8
230	1.5	430	34.4
235	1.5	440	35.6
240	1.8	450	36.5
245	2.3	460	37.1
252	2.6	470	37.5
		480	37.7
		490	37.9
		500	38.0
		510	38.0
		520	38.1

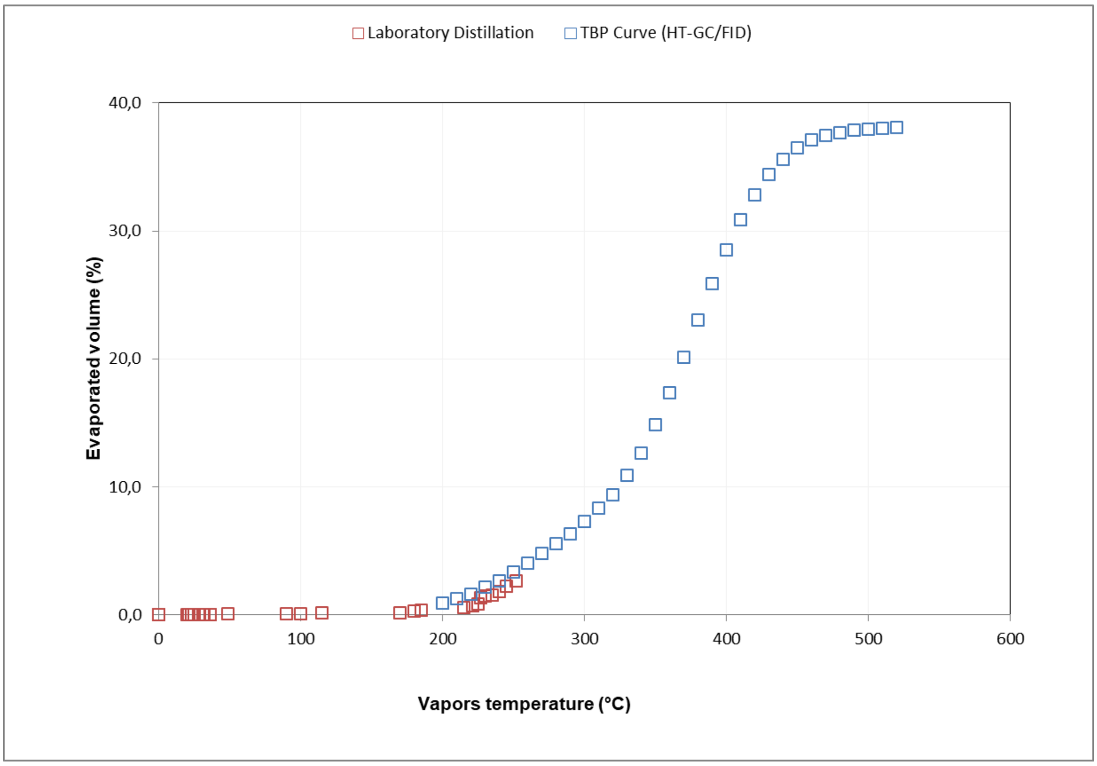

Figure 11 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-11 sample*

Table 12 *Results of laboratory and simulated distillation of the fresh IM-12 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
25	0.0	200	11.6
30	0.0	210	14.6
35	0.0	220	16.6
80	0.0	230	19.3
100	0.0	240	21.4
110	0.0	250	24.0
120	0.1	260	26.4
124	0.1	270	28.9
133	0.2	280	31.4
136	0.4	290	33.5
143	0.5	300	36.1
145	1.1	310	38.6
130	1.7	320	40.9
150	2.0	330	43.6
155	2.1	340	46.2
165	2.1	350	48.7
170	2.4	360	50.8
175	2.8	370	52.7
175	3.9	380	54.1
183	5.1	390	55.2
185	6.2	400	56.0
190	6.4	410	56.5
190	6.8	420	56.8
197	7.8	430	57.1
204	8.1	440	57.3
205	9.2	450	57.5
210	10.0	460	57.6
215	10.3	470	57.6
215	11.3	480	57.7
220	11.7	490	57.7
220	12.4	500	57.7
220	14.6	510	57.7
225	15.6	520	57.7
230	16.6		
235	17.8		
240	18.7		
245	19.5		
250	21.4		

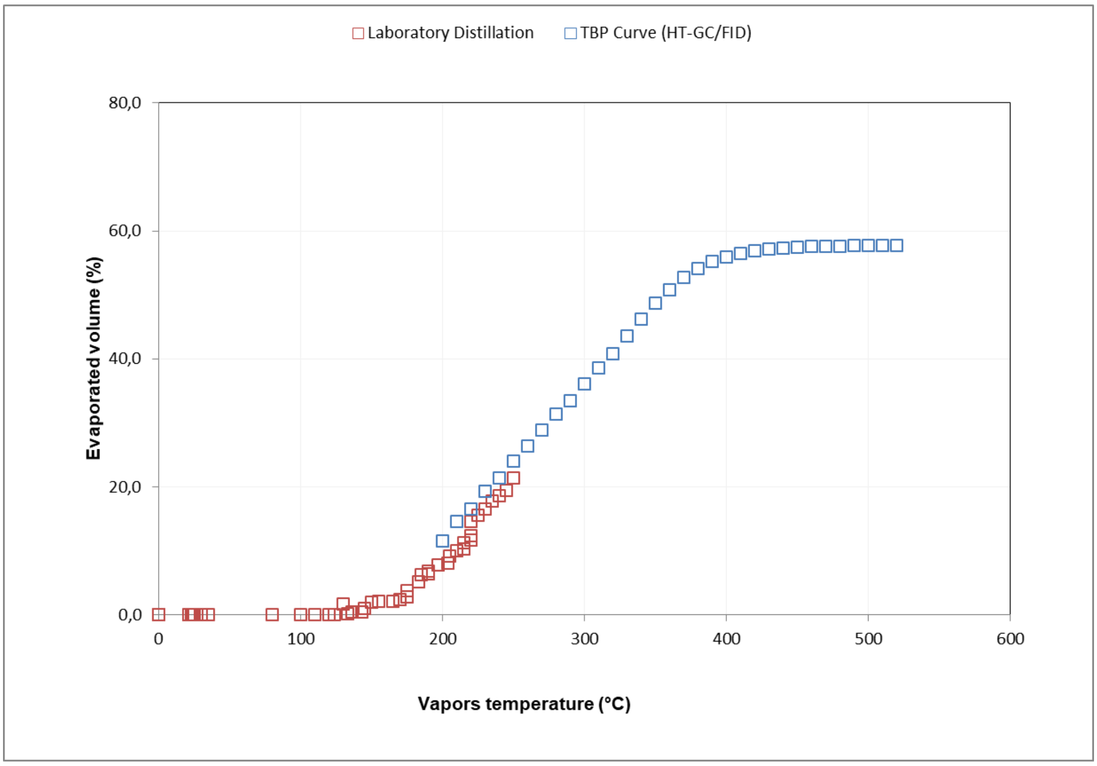

Figure 12 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-12 sample*

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Table 13 *Results of laboratory and simulated distillation of the fresh IM-13 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
22	0.1	200	9.3
22	0.1	210	11.7
26	0.1	220	13.3
30	0.1	230	15.4
40	0.1	240	16.9
45	0.1	250	18.5
50	0.1	260	19.9
65	0.1	270	21.1
85	0.2	280	22.3
100	0.3	290	23.3
110	0.4	300	24.6
135	0.5	310	25.9
145	0.7	320	27.2
150	0.7	330	28.9
160	0.8	340	30.7
165	1.3	350	32.4
170	1.6	360	34.1
172	2.3	370	35.6
175	3.4	380	37.0
180	4.3	390	38.3
185	4.6	400	39.5
190	6.4	410	40.6
195	7.9	420	41.6
215	9.1	430	42.6
220	10.5	440	43.4
225	11.9	450	44.2
230	12.6	460	44.7
235	13.2	470	45.1
240	16.4	480	45.4
245	16.6	490	45.7
250	16.9	500	45.8
		510	46.0
		520	46.1

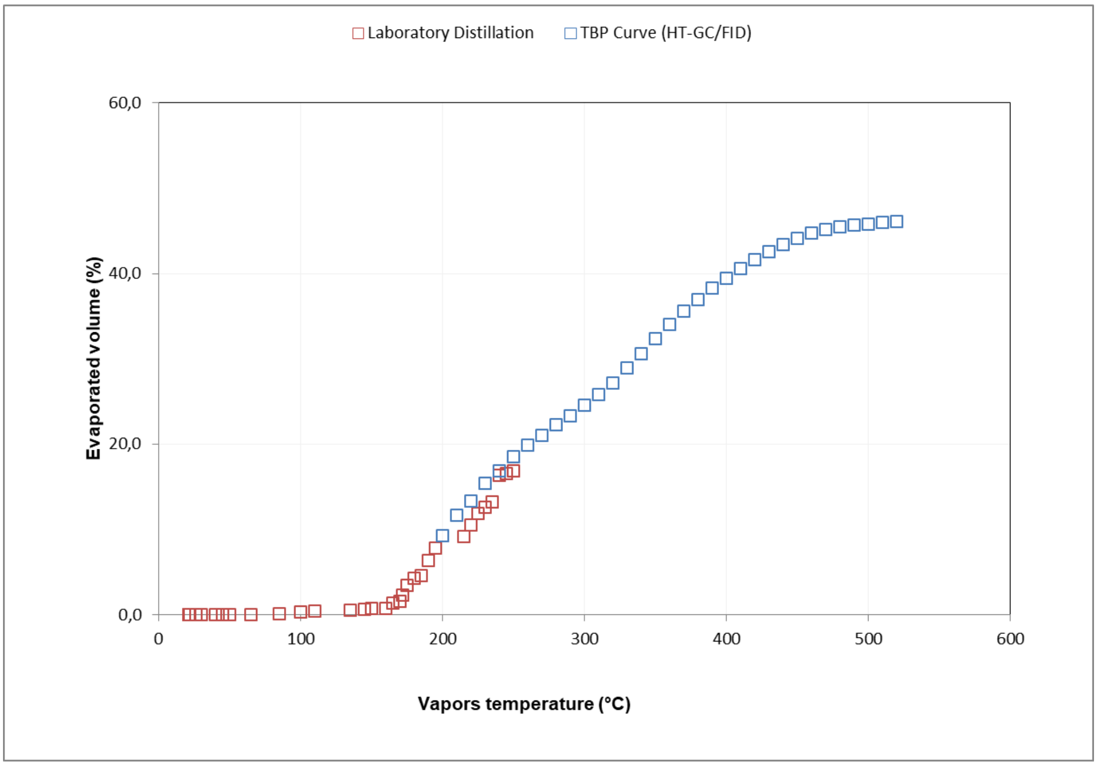

Figure 13 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-13 sample*

APPENDIX 5

Results of dispersibility tests

(***Model dispersant***)

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Table 1 *Results of IFP tests performed on the fresh oils at 15°C*

Sample	Dispersibility # 1	Dispersibility # 2	Dispersibility # 3	Average	AD
IM-1	0.5	0.3	nm	**0.4**	0.2
IM-2	0.4	0.0	nm	**0.2**	0.4
IM-3	2.0	1.9	nm	**2**	0.1
IM-4	0.4	0.1	nm	**0.2**	0.3
IM-5	52.1	33.4	77.2	**54**	*81 (1)*
IM-6	60.0	56.8	nm	**58**	*5 (1)*
IM-7	25.4	37.5	45.9	**36**	20
IM-8	5.2	0.0	nm	**3**	5
IM-9	0.9	0.2	nm	**0.6**	0.7
IM-10	20.9	48.1	71.5	**47**	*108 (1)*
IM-11	46.5	50.1	nm	**48**	*7 (1)*
IM-12	21.2	24.4	nm	**23**	3.2
IM-13	39.1	26.0	75.7	**47**	*106 (1)*

(1) For values above 40%, RD was calculated

Table 2 *Results of IFP tests performed on the residues of 250°C distillations. at 15°C*

Sample	Dispersibiltiy # 1	Dispersibiltiy # 2	Dispersibiltiy # 3	Average	AD
IM-1	1.1	0.0	nm	**0.6**	1.1
IM-2	0.6	0.3	nm	**0.4**	0.3
IM-3	1.6	5.7	nm	**4**	4.1
IM-4	3.1	2.4	nm	**3**	0.7
IM-5	15.2	51.7	42.7	**37**	36
IM-6	Not determined				
IM-7	23.0	47.5	72.8	**48**	104
IM-8	0.8	5.4	nm	**3**	4.6
IM-9	0.0	0.0	nm	**0.0**	0.0
IM-10	2.5	8.3	nm	**5**	5.8
IM-11	21.7	48.6	48.7	**40**	27
IM-12	Not determined				
IM-13	Not determined				

Table 3 *Results of IFP tests performed on the emulsions formed on the 250°C+ residues with 50% water content*

Sample	Dispersibiltiy # 1	Dispersibiltiy # 2	Average	AD
IM-1	0.0	0.0	**0.0**	0.0
IM-2	0.7	0.9	**0.8**	0.2
IM-3	1.4	0.3	**0.9**	1.1
IM-4	4.2	1.6	**2.9**	2.6
IM-5	13.5	15.9	**14.7**	2.4
IM-6	Not determined			
IM-7	0.6	0.6	**0.6**	0.0
IM-8	0.3	0.6	**0.4**	0.3
IM-9	Emulsion not formed			
IM-10	0.0	0.03	**0.0**	0.3
IM-11	6.9	4.0	**5.4**	2.9
IM-12	Emulsion not formed			
IM-13	Emulsion not formed			

RD (Relative Difference) is calculated as the ratio between the Absolute Difference (between two duplicates) and the average. It has to be lower than 14% for efficiencies greater than 40%:

$$RD = \frac{abs(E1 - E2)}{mean(E1.E2)} < 14$$

For efficiencies lower than 40%. the Absolute Difference has to be lower than 6%:

$$AD = abs(E1 - E2) < 6$$

APPENDIX 2

Task 3.2 – Oil weathering

WP3

DELIVERABLE D3.2

TASK 3.2: OIL WEATHERING

"WEATHERING AND DISPERSIBILITY STUDY OF 3 VLSFO AT THE LABORATORY AND PILOT SCALE IN SIMULATED LOCAL WEATHER CONDITIONS"

FINAL REPORT

Co-funded by the European Union

EXECUTIVE SUMMARY

When spilled at the water surface, oils are subjected to weathering processes such as evaporation, emulsification, dispersion, photo-oxidation, and biodegradation. These processes naturally occur due to water agitation generated by currents, wind and/or waves, to the sun exposure (UV oxidation), and to bacteria's and micro-organisms activity. Throughout the weathering processes, the oil continuously changes in terms of chemical composition and physical properties. Oil generally becomes more and more viscous and can turn into a new persistent pollutant in the environment. The behaviour of weathered oil is often different from the one of the oil initially spilled. Understanding these transformations is a key element in evaluating the potential impacts and optimizing the emergency response to spillage.

In the frame of the European project IMAROS, 3 Very Low Sulphur Fuel Oils (VLSFO) were selected from a first experimental phase (Task 3.1: Physical-chemical characterisation, total of 13 samples) in order to study them within its facilities, both at laboratory and pilot scales (in the Polludrome®). The objective of this study (Task 3.2: Oil weathering) was to obtain experimental data on the behaviour, fate, and treatment possibilities of the 3 VLSFO (identified as IM-5, IM-14 and IM-15).

Tests were performed at representative weather conditions encountered in the European waters: the air temperatures were set at 5 °C and 15 °C. They were run assuming a moderate situation (around sea state 3 on the Douglas scale, which corresponds in real conditions to wave heights between 0.5 and 1.25 m) with a simulated wind speed of 10 knots. One test was performed in freshwater condition in order to simulate a potential spill occurring in lakes. Additional tests were carried out at the laboratory scale in order to obtain a set of experimental data which can be implemented in oil weathering models. Dedicated experiments were conducted to assess the oil dispersibility, the time-window of opportunity for dispersant use and to compare the effectiveness of different dispersants.

The main results from the experiments are as follows:

- *The 3 VLSFO behaves and weathers differently, highlighting the variability existing among those products.*
- *Pour points vary from +3°C (IM-15) to +27°C (IM-14), leading to some potential difficulties in terms of recovery for oils exhibiting high pour points.*
- *Density of weathered oils can reach 1.00, leading to potential submersion issues if the oil is poured in freshwater or in coastal waters characterised by high suspended matter.*
- *The flash point of the 3 fresh oils is above 85°C, meaning that in terms of safety, operations could be conducted directly after the spill.*
- *Some oils seem to be dispersible when fresh. However, as soon as they weather, they become rapidly not dispersible. This response option seems thus limited for this kind of products.*

GLOSSARY

ASTM	American Society for Testing Materials
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
DOR	Dispersant Oil Ratio
DER	Dispersant Emulsion Ratio
IFP test	Dispersibility test formerly developed by the French Petroleum Institute (*Institut Français du Pétrole*, name no longer used for this organism, which is now *IFP énergie nouvelles*). This method is a low-energy test, estimated to represent non-breaking waves conditions. It is identified within the NF 90-345 French Standard
IP	Institute of Petroleum (UK-based professional organization)
MNS test	The **MNS** (*Mackay–Nadeau–Steelman*) dispersibility test is estimated to represent a medium to high sea-state condition
OWM	Oil Weathering Model
PAH	Polycyclic Aromatic Hydrocarbons
TBP	True Boiling Point
T_0, T_f	Values determined at the beginning (T_0) and end (T_f) of the *Polludrome* weathering experiments

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1 CONTEXT AND OBJECTIVES

Each spill entails a series of questions concerning the fate and behavior of the oil involved, and consequently about the oil spill response techniques to be used. Subjected to weathering processes such as evaporation, emulsification, dispersion, photo-oxidation, or biodegradation, the oil is continuously changing in terms of chemical composition and physical properties. These processes occur under natural conditions due to water surface agitation (wind, waves, turbulence, and currents) sun exposure (UV), and also bacteria and micro-organisms activity.

As the weathering progresses, the light fractions evaporate gradually, oil density increases while it gets emulsified with water and is oxidized by ultra-violet radiations. Oils generally become more and more viscous and can become a new persistent pollutant in the environment. Weathered oil behavior is often different from the original one. Understanding these transformations is a key element in evaluating the potential impacts, optimising the response options according to the weathering stage of the spilled oil, and implementing the oil spill contingency plan.

The objective of the present study was to characterise and assess the behaviour of 3 LSFO in the frame of the European project IMAROS, according to their weathering once released at sea. Experiments were carried out in Cedre's testing facilities both at pilot and laboratory scales. The tests were performed at the representative weather conditions encountered in the European waters: 5 °C and 15 °C. The goal was to estimate the most appropriate response options according to the weathering stage of the oils. Specific response options are tested in a dedicated work package (WP4): Mechanical recovery (Task 4.1), *in situ* burning (Task 4.3) and shoreline clean-up (Task 4.4). The use of dispersants (Task 4.2) is the only response option tested in the frame of this task given its strong link with oil behavior/weathering.

2 SELECTION OF SAMPLES

Following the Task 3.1 and the crosscutting WP2/WP3 workshop, 3 samples were selected for weathering at the laboratory and the pilot scales:

- IM-5 : VLSFO from the Wakashio bulk carrier, characterized by a pour point of 15°C,
- IM-2 : VLSFO from Sweden, characterized by a high pour point (+27°C),
- IM-6 : VLSFO from Malta, characterized by a very low pour point (-27°C)

Those samples were selected because of their variability, especially in terms of pour point, among all the oils tested.

When starting the purchase process for getting the oils in large quantities (3 m^3) for weathering and recovery tests, few months after obtaining the 2L required for the Task 3.1, it appeared that the VLSFO stocks had changed. The oils received for Task 3.2 are thus different from those from Task 3.1. Consequently, it was decided to change the identification number of those large samples.

The following was decided:

- VLSFO IM-5: the same identification number was kept as the same batch was used for the tasks 3.1 and 3.2.
- VLSFO from Sweden: The identification IM-2 related to the task 3.1 has been changed to IM-14 for task 3.2.
- VLSFO from Malta: The identification IM-6 related to the task 3.1 has been changed to IM-15 for task 3.2.

This report presents the results obtained in the study of the samples IM-5, IM-14 and IM-15.

3 BACKGROUND

In order to assess the fate and behaviour of a dedicated oil in case of accidental release, the following various approaches can be considered, from the simplest one to the most complicated one:

- The initial physical-chemical characteristics of the oil can be used to get a general idea of its fate. The density is representative of the buoyancy of the product, its True Boiling Point (TBP) curve provides a reliable estimation of the maximum evaporation rate, the viscosity informs on the spreading and potential use of response techniques such as dispersion or recovery, … This set of data can also be implemented in modelling software such as ADIOS 2 which mainly deals with initial properties.
  This approach has been chosen in the task 3.1.

- Laboratory protocols can be applied in order to asses more realistically the oil weathering, and to get additional information such as the time-window of opportunity for dispersant use. Different laboratory methodologies can be used to simulate various 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…
  These results, in addition to initial characteristics, can also be implemented in particular modeling software such as the oil weathering model developed at SINTEF (Norway).
  A simplified version of those protocols has been carried out in the task 3.1 and a full one in the task 3.2.

- Finally, pilot scale experiments can be conducted in order to simulate these various processes realistically and simultaneously. Cedre has equipped its facilities with an hydraulic canal (the *Polludrome®*) in which different marine (as well as inland) water conditions can be recreated: wind, current, waves, solar radiations and temperature. With this equipment, it is possible to weather dedicated oil in similar climatic conditions as the ones which can be encountered in the oil field from which it is extracted (or the area of shipment).
  This approach has been followed in the frame of the task 3.2.

In addition, studies conducted during the previous years demonstrated that modern dispersants were able to treat better and better oils with higher viscosities. However, significant differences of efficiency have been observed between different oils, demonstrating the role of the oil composition on the intrinsic oil dispersibility. In other words, for the same treatment product, oil dispersibility depends on the type of the oil and on its weathering stage. Moreover, differences of efficiency toward the same oil between dispersant products have been shown, especially when the oil becomes weathered and more difficult to be chemically dispersed. Therefore, it is necessary to assess, for a dedicated oil, its dispersibility according to its weathering stage and to identify the dispersant products which are the most efficient.

Answering the Task 3.2 (oil weathering) of the European project IMAROS, this study intends to assess, through laboratory and pilot scale tests, the potential fate and behaviour at sea of 3 LSFO considering European environmental conditions. Additional tests were also carried out in order to assess the time-window of opportunity for dispersant use combined with the comparison of various treatment products.

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4 GENERAL PRINCIPLES OF SIMULATION OF WEATHERING AND DISPERSIBILITY

The tests were conducted according to a methodology developed at Cedre[1],[2] strongly related to the use of the *Polludrome®*; it is a combination of measurements according to French, ASTM or IP norms, and characterizations performed by using protocols developed at Cedre. Characterisations and analyses conducted at the laboratory scale were in agreement with inputs generally required by modelling softwares that could be subsequently used.

Various compounds (*n*-alkanes, BTEX and other COV, and PAHs) in the oils, as well as their global composition, were quantified in agreement with the OSCAR model requirements.

4.1 Oil weathering studies at the laboratory scale

To simulate the main weathering processes at sea, the oils were exposed in laboratory to a systematic, stepwise procedure (*Table 1*) including distillation and emulsification processes. The oils were topped at 3 different temperatures (vapours temperatures of 150, 200 and 250°C), the 250°C distillation being performed twice in order to complete the weathering simulation with a sample corresponding to 4 days of exposition to photo-oxidation processes. These residues were then emulsified with seawater at various levels (50%, 75% and maximum uptake), thus leading, taking into account the initial crude oil, to 17 different samples representative of the potential evolutions at sea (Daling and Strøm, 1999 [3]). Each sample, emulsified or not, was characterized by various physical measurements (viscosity, density, pour point …), in addition to a full characterisation of the initial oil (in particular wax and asphaltenes contents).

These “bench-scale” experiments were performed at the 2 reference temperatures of 5 °C and 15 °C, but could be extrapolated to various temperatures and wind speeds by using modelling softwares. This test matrix is, in particular, in agreement with the set of data required by the SINTEF Oil Weathering Model.

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.

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[1] J. Guyomarch, E. Morin, A. Goutard and F-X.Merlin, 2001.“Experimental Oil Weathering Studies in Hydraulic Canal and Open Pool to Predict Oils Behaviour in Case of Casual Spillage”.*Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C.

[2] J. Guyomarch, S. Le Floch and R. Jezequel, 2012. “Oil Weathering, Impact Assessment and Response Options Studies at the Pilot Scale:Improved Methodology and Design of a New Dedicated Flume Test”. Proceedings of the 35th Arctic and Marine Oilspill Program(AMOP) Technical Seminar, Environment Canada, Ottawa, Ontario.

[3] Daling, P. S. and Strøm, T., 1999: “Weathering of Oils at Sea: Model/Field Data Comparisons”, in *Spill Science and Tech. Bull.*, 5 (1), pp. 63-74.

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Table 1 ***Test matrix of characterisations and preparations performed on the oils***

Characterisations	Fresh Oil	Residues of distillation (vapors temperature)			
		150°C+	200°C+	250°C+	250°C ph. ox.
Volume topped (%)	-	m	m	m	-
Residue (% wt.)	-	m	m	m	-
Specific gravity	m	m	m	m	m
Pour Point (°C)	m	m	m	m	m
Flash Point (°C)	m	m	m	m	m
Viscosity (mPa.s)	m	m	m	m	m
Viscosity of 50% emulsion (mPa.s)	-	m	m	m	m
Viscosity of 75% emulsion (mPa.s)	-	m	m	m	m
Viscosity of max. water emulsion (mPa.s)	-	m	m	m	m
Maximum water content (%)	-	m	m	m	m
Halftime for water uptake (hours)	-	m	m	m	m
Wax / Asphaltenes	c	c	c	m	-
True Boiling Point (TBP) curve up to 250°C					

m: to be measured
-: not relevant
c: calculated from the value measured on the 250°C+ residue

4.2 Assessment of the crude oil dispersibility

4.2.1 Time-window of opportunity for dispersant use

In addition to the fresh oils, three samples corresponding to respectively 6, 36 and 96 hours at sea, have to be analysed. The environmental and release conditions that correspond to this weathering are as follows: wind speed of 5 m.s^{-1} and water surface temperature close to 10°C. To simulate this weathering in laboratory, the behaviour of several light crude oils has been simulated using the ADIOS 2 model in the environmental conditions mentioned previously. A relationship was then established between the evaporation rate at 6, 36, and 96 hours and the corresponding distillation properties. It appeared that the oil cut that evaporated within 6 hours was below 200°C, and for the period 6-36 hours, the oil cut was 200-250°C (these observations are in agreement with those formulated in the DIWO study conducted by IKU/SINTEF (1997)). Finally, to simulate the maximum weathering stage at sea, obtained after around 96 hours according to previous flume test experiments performed at Cedre, the 250°C+ residue was photo-oxidized.

Consequently, to simulate the evaporation at sea for periods of 6, 36 and 96 hours, the samples were respectively topped at 200°C and 250°C (vapor temperature). The 96 hours oil was obtained by exposing the 250°C residue to UV-light for 4 days. As regards the emulsification process, these 3 residues were emulsified at 50%, 75% and at the maximum water content.

The efficiency of the selected dispersant (model dispersant) was assessed on both fresh oil and weathered samples according to the IFP and MNS protocols. The emulsion viscosity was checked at each step of the study to ensure the reliability of the observed evolutions, thus allowing the definition of the time-window of opportunity for dispersant use. The test matrix is presented in *Table 2*. These tests were conducted in duplicates (or in triplicates in case of too high variability) using a regular Dispersant Oil Ratio (DOR) or Dispersant Emulsion Ratio (DER) of 1:20.

Table 2 ***Tests matrix used to assess the time-window of opportunity for dispersant use***

Sample / Water content	Fresh oil	200°C+	250°C+	250°C+ Photo-ox.
0%	✓	-	-	-
50%	-	✓	-	-
75%	-	-	✓	-
% max.	-	-	-	✓

All tests have to be carried out twice (duplicates), results between two similar tests should not differ more than 14% considering relative differences (in that case, a third test will be performed).

In case of obvious non dispersibility, one replicate is carried out. Additionally if a sample is not dispersible for a weathered time given, further tests are stopped.

4.2.2 Comparison of the dispersants efficiency

The objective of this part was to compare the relative efficiency of 4 selected dispersants *(Model*, *Dasic Slickgone NS*, *Finasol OSR 52* and *Corexit 9500A*) according to a low-energy test (IFP test), more relevant with a view of making differences between products. 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 in these tests had to be separately prepared in the laboratory.

According to the viscosity measurements performed on the emulsions prepared in the laboratory and in relationship with the results obtained in order to assess the time-window of opportunity for dispersant use, two “laboratory” samples were selected for these comparative dispersibility tests, conducted at 15°C (*Table 3*). As mentioned previously, tests were performed, at least, in duplicates. If the fresh samples are not dispersible with the reference dispersant, only one sample was tested (the fresh oil) using the three commercial dispersants.

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Table 3 Test Matrix for comparative efficiency of dispersants

Test@15°C Dispersant	Sample 1	Sample 2
Model Dispersant	✓	✓
DasicSlickgone NS	✓	✓
Corexit 9500A	✓	✓
Finasol OSR52	✓	✓

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4.3 Pilot-scale oil weathering study (*Polludrome®*)

4.3.1 Experimental protocol and conditions of test

The tests were performed in Cedre's hydraulic canal (the *Polludrome®*), which was used with the water being continuously circulated to simulate open sea conditions (*Figure 1*).

The test conditions were: wave height of 20 cm, current speed of 0.4 m/s, water depth of 0.90 m; the volume of seawater was 7 m^3 and the air temperature was set at 5 °C and 15 °C. Tests were run assuming a moderate situation (around sea state 3 on the Douglas scale, which corresponds in real conditions to wave heights between 0.5 and 1.25 m) with a simulated wind speed of 10 knots (it must be noted that the device is equipped with an exhaust fan for safety reasons, and the corresponding wind speed was assessed by calibrations and comparisons with evolutions in real environmental conditions). The photo-oxidation process (solar energy) was recreated by the use of a UV light, on a 12 hours cycle, corresponding to the solar radiations intensity encountered in the North Sea.

The weathering of the oils were monitored in the *Polludrome®* during 7 days in order to evaluate their fate and behaviour during the first hours and first days after an oil spill. During the tests, surface oil samples were periodically (*Table 4*) taken to determine or asses the oil characteristics. The testing progress and protocol applied are summarized in *Appendix 2*.

In addition, the weathered oils were subjected to dispersibility tests using the IFP (NF T 90-345 French Standard) and MNS laboratory protocols after 24, 48, 72 and 168 hours. If the oil becomes not dispersible for one sampling time, dispersibility tests are not performed for the following sampling times.

Figure 1 ***The Polludrome® and picture of the weathering of a crude oil***

It must be noted that these experiments can simulate short-term weathering (up to 1 or 2 weeks) but cannot completely recreate long-term processes or incorporation of mineral fines, phenomena liable to stabilize emulsions.

Table 4 Typical sampling times

Sample reference	T0	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16
Time (hours)	0	1	2	4	6	8	14	24	27	30	48	53	72	77	96	101	168

4.3.2 Evolution of physical-chemical properties

Table 5 Characterisations of the oil samples collected during the weathering experiments

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	
Oil Dispersibility	- Definition of the time-window of opportunity for dispersant use
Oil Adhesion	- Adhesion of the oil to oleophilic surfaces; oil ability to be skimmed

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5 MATERIALS AND METHODS

5.1 Laboratory protocols for oil weathering

5.1.1 Oil evaporation and photo-oxidation

To simulate the evaporation at sea, the samples were respectively topped at 150°C, 200°C and 250°C (vapour temperature). A photo-oxidation step has been added on the residue obtained at 250°C to simulate the evaporation at sea and exposure to solar radiations for a period of 96 hours. These relationships were established using the ADIOS 2 modelling software.

Samples of oils evaporated at various rates are obtained by distillation according to the protocol developed at IKU/SINTEF (Norway). The distillation technique is described by Stiver and Mackay (1984) as a modified ASTM D86/82 method. The objective of this protocol is not to get the distillation curve of an oil, as intended by the ASTM method, but to obtain oil residues at given temperatures.

5.1.2 Oil emulsification

The oil emulsification is achieved by using the modified Mackay-Zagorsky method using rotary funnels (Hokstad et al., 1993[4]). 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. To form a water-in-oil emulsion of 50% water content, the rotation is started with equal volumes of water and oil (to make a 75% water content emulsion, 3 parts of water to 1 part of oil, and for the maximum water content, an excess of water).

5.1.3 Effectiveness of Chemical dispersants

Different dispersibility tests can be conducted, each protocol having its specificity. However, all of them were initially designed for the comparison of dispersants products (in particular the WSL and IFP tests). Some of them can be used for the assessment of an oil dispersibility in real conditions, particularly the IFP and MNS tests which were correlated to field or pilot scale experiments.

All the dispersibility tests are carried out twice (duplicates), and the relative differences of results between two similar tests have not to differ more than 14% (in that case, a third test has to be performed). However, this criterion cannot be strictly applied for efficiencies lower than 40%, and in that case, results have not to differ more than 3% compared to the mean value (10% ± 2% for example). In case of obvious non dispersibility, one replicate is carried out. Additionally if a sample is not dispersible for a weathered time given, further tests are stopped.

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[4] 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

Time-window of opportunity for dispersant use: IFP and MNS test protocols

The chemical dispersibility of the oil samples was measured at 5°C and 15°C, the reference temperatures of the study, and using the model dispersant. Two different protocols of tests were applied:

- the IFP flow through test method (French standard NF T 90-345), which is characterized by a low energy and a dilution process from a main tank to a dilution tank. The test equipment was checked with Cedre reference oil (FOREF: mixture of Heavy Fuel Oil and Arabian Light topped at 110°C, viscosity of 1 200 ± 200 mPa.s at 20°C) and with a model dispersant formulated at Cedre. Under these test conditions, the efficiency has to be 75 %. The oil dispersed in the water column and entrained in the dilution beaker was extracted by dichloromethane and the concentration measured by spectrophotometry at 390 nm.
- The MNS protocol is a high energy test, which is provided by an air flow controlled by the measurement of a pressure drop. Various settings are possible and a standard value of 25 mm was applied in this study. The equipment was checked based on the conditions specified for the IFP test.

The choice of these methodologies can be explained as follows:

- These methods have been extensively used and studied over the last few years at Cedre and are fully documented. Results obtained at these laboratory scales have been correlated to potential efficiency during field operations[5].
- The IFP test is a low-energy system which allows significant differences among products (oil nature, weathering stage …). The IFP test is representative of medium conditions, for a sea state around 2-3. Moreover, it provides information not only on the efficiency of the dispersant, but also on the quality of the dispersion due to the dilution process.
- The MNS test protocol was also used as it represents stronger conditions of energy, and can then provide information of the maximum viscosity of an emulsion which could be treated with dispersants (the 25 mm settings is representative of medium-strong conditions, for a sea state around 4).

Comparison of dispersants efficiency: IFP test protocol

The IFP test is a low-energy system which allows significant differences among dispersants products. Therefore, this methodology is part of the French approval procedure as regards chemical dispersants and is currently used at Cedre to control the quality of dispersants stockpiles.

5.2 Physical-chemical properties

Pour point

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[5] Chever F., K. Duboscq, J. Receveur, C. Audegond and J. Guyomarch. “Determination of limits of viscosity for dispersant use: quantitative and qualitative assessment of the dispersibility of water-in-oil emulsions at the laboratory (IFP and MNS tests) and in the Polludrome”. *Proceedings of the 39th Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, 7-9 June 2016, Halifax (Nova Scotia), Canada.

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

Flash point

The flash point was measured on the fresh oils and their corresponding residues obtained by distillation at 150, 200 and 250°C, according to the NF EN ISO 13736 norm (Abel method). This measurement was performed using an Anton Paar ABA 4 Abel flash point tester.

Viscosity

The viscosity of the oil samples (fresh oil and residues) was measured by using a Rheolab QC (Anton Paar) viscosimeter at dedicated shear rates (from 1 to 100 s^{-1}) and the 100 s^{-1} value, mean of 60 measurements, calculated. As regards emulsions formed from residues, their viscosity was measured at the test temperature considering the same shear rates but the 10 s^{-1} value was calculated in these cases. To ensure reliable comparisons of the dispersant effectiveness according to the nature of the products, viscosity of the tested emulsions had to be controlled for each series of tests. The equipment was calibrated by analysing reference oils.

Note : *in the case of newtonian fluids such as most of crude oils, the value of the viscosity is a constant over a wide range of shear rates. In this experimental study, they were measured at 100* s^{-1}*, which allows a more stable measurement for the low viscosities. As far as they get emulsified, these fluids follow a non-newtonian behaviour, generally shear thinning, which mean that the viscosity decreases as the shear rate increases. Therefore, viscosities of emulsions have to be expressed with the shear rate used to perform the measurement. Viscosity of emulsions is generally measured at 10* s^{-1}*, which constitutes an implicit standard in the field of oil pollution studies. The relationship between this dynamic viscosity* η*, expressed in mPa.s or cP, and the corresponding kinematic viscosity* υ *(cSt), is as follows:*

$$\upsilon = \frac{\eta}{\rho}$$

ρ *represents the fluid density, generally close to 1 for water-in-oil emulsions. Therefore, the viscosity measurement can be expressed, with the same figures, either in cP, mPa.s or cSt.*

Specific gravity

The density of the fresh oil and residues samples was determined according to the ASTM method D5002 Standard Test Method for density and relative density of crude oils by digital density analyzer (ASTM, 2013). This measurement was performed using an Anton Paar D4500 analyzer.

Asphaltenes and waxes

Asphaltenes contents were measured 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”. This gravimetric method is more reliable when applied to non-volatile oils, such as 250°C+ residues. The result is then extrapolated to other residues and to the fresh oil by taking into account the evaporation rate measured following the distillation.

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

5.3 Chemical analyses in agreement with the OSCAR model

In order to fully comply with the inputs required by the OSCAR model, a detailed chemical characterization of the oils was performed (*Table 6*):

- The boiling point curve was obtained up to 450°C using simulated distillation, in addition to the True Boiling Point (TBP) curve established during the sample preparation.
- A detailed chemical composition was obtained according to 3 different chemical analyses as presented in *Table 6*:
    - Volatiles Organic Compounds (VOCs) were quantified by Headspace-GC/MS (list of 31 molecules),
    - semi-volatiles compounds, mainly PAHs, were analysed by GC/MS (liquid injection) according to a list of 43 molecules (or groups of molecules),
    - the distribution of compounds not individually quantified was established according to their number of carbons up to C_{25} based on a GC/FID analysis.

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Table 6 ***Detailed list of the target molecules and definition of the dissolution potential***

Composition (% weight)	Individuals compounds	Analysis
C_1-C_4 (dissolved gas)	-	Crude assay
C_5-saturates (n-/iso-/cyclo)	*n*- pentane, isopentane, cyclopentane	HS-GC/MS
C_6- saturates (n-/iso-/cyclo)	*n*-hexane, methylpentane (2), methylcyclopropane, cyclohexane	
C_7- saturates (n-/iso-/cyclo)	*n*-heptane, dimethylpentane, methylhexane, methylcyclohexane	
C_8- saturates (n-/iso-/cyclo)	*n*-octane, methylheptane	HS-GC/MS
C_9- saturates (n-/iso-/cyclo)	*n*-nonane	HS-GC/MS
Benzene	benzene	HS-GC/MS
C_1-Benzene	Toluene	
C_2-Benzenes	o-, m-, p-xylène, ethylbenzene	
C_3-Benzenes	methylethylbenzenes (3), trimethylbenzenes (3), propylbenzene	
C_4 & C_5-Benzenes	n-butylbenzene, tetraméthylbenzene, n-pentylbenzene	
C_{10}- saturates (n-/iso-/cyclo)	No quantification of individual compounds	GC/FID
C_{11}-C_{12} (total saturates + aromatics)		
C_{13}-C_{14} (total saturates + aromatics)		
C_{15}-C_{16} (total saturates + aromatics)		
C_{17}-C_{18} (total saturates + aromatics)		
C_{19}-C_{20} (total saturates + aromatics)		
C_{21}-C_{25} (total saturates + aromatics)		
C_{25}+ (total)		
Naphthalenes 1 (C_0-C_1 alkylated)	N, N1	GC/MS
Naphthalenes 2 (C_2-C_3 alkylated)	N2, N3	GC/MS
PAHs 1 (medium solubility)	BT, BT1, BT2, BT3, BT4, N4, B, ANA, ANY, F, F1, P, A, P1, D, D1	
PAHs 2 (low solubility)	F_2, F_3, P_2, P_3, P_4, D_2, D_3, D_4, FL, PY, FL_1, FL_2, FL_3, BAA, C, C_1, C_2, C_3, BBF, BKF, BEP, BAP, PE, DBA, IN, BPE	GC/MS
Phenols (C_0-C_4)	Phenol, C_1 to C_4-Phenols	GC/MS

⬜	High dissolution potential
🟦	Medium dissolution potential
🟧	Low dissolution potential

6 RESULTS OF LABORATORY SCALE TESTS

Results of experiments performed on the 3 LSFO are presented hereafter. They are presented in two stages. The first part is dedicated to the assessment of the oil behaviour based on the most relevant parameters: chemical composition, pour point, maximum viscosity and water content expected at 5 °C and 15 °C. The second part presents all the results of the dispersibility tests performed on the oils.

6.1 Characterization of the fresh oils, residues of distillation and emulsions

The characterisation of the initial oils, residues and emulsions formed from these residues are presented in *Table 7* for the sample IM-5, in *Table 8* for the sample IM-14 and in *Table 9* for sample IM-15. It must be noted that, due to the shear thinning behaviour of these oils (i.e. characterized with a decrease of viscosity with an increasing shear rate), the viscosity of the non-emulsified residues was measured at 10 s^{-1} and 100 s^{-1}.

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Table 7 Physical-chemical characterisation at 5°C and 15°C of the IM-5 sample

	Characterisations	Fresh	Residues of distillation (vapours temperatures)			
			150°C	200°C	250°C	250°C Photo-ox.
Fresh oil	Evaporation rate (% wt.)	-	1.7	2.6	8.8	-
	Evaporation rate (% vol.)	-	1.8	2.7	9.5	-
	Specific gravity at 20°C (g/L)	0.909	0.909	0.910	0.915	0.920
	Pour Point (°C)	+15	+18	+21	+21	+21
	Flash Point (°C)	90	98.5	>100	>100	>100
	Asphaltenes (% wt.)	0.56	0.57	0.57	0.61	0.65 (2)
	Wax (% wt.)(1)	8.9	9.1	9.2	9.8	10.4 (2)
Experiment at 5 °C	*Density*	*0.919*	*0.920*	*0.921*	*0.927*	*0.931*
	Viscosity of non-emulsified oils (mPa.s)[3]	1418	1338	1506	3216	6174
	Viscosity of non-emulsified oils (mPa.s)[4]	3051	1781	2145	5373	13443
	Viscosity of 50% water content emulsion[4]	-	5018	6816	15348	26858
	Viscosity of 75% water content emulsion[4]	-	16013	15811	24488	42008
	Viscosity of max. water content emulsion[4]	-	17720	21754	31458	30292
	Max. water content (%)	-	*71*	*64*	*62*	*62*
	Halftime for water uptake (min)	-	21.9	15.4	33.2	26.0
Experiment at 15 °C	*Density*	*0.911*	*0.912*	*0.913*	*0.919*	*0.923*
	Viscosity of non-emulsified oils (mPa.s)[3]	398	499	506	977	1648
	Viscosity of non-emulsified oils (mPa.s)[4]	507	620	592	1260	2506
	Viscosity of 50% water content emulsion[4]	-	2074	2545	4892	17007
	Viscosity of 75% water content emulsion[4]	-	8238	9301	17007	23149
	Viscosity of max. water content emulsion[4]	-	12317	11930	16367	33257
	Max. water content (%)	-	*70*	*76*	*67*	*81*
	Halftime for water uptake (min)	-	5.4	5.8	11.6	29.4

- : not relevant

[1] Wax values are higher than the ones measured in task 3.1. This may be due to heterogeneity of batches.

[2] Extrapolated data from modelling

[3] viscosity (mPa.s) measured at 100 s^{-1}

[4] viscosity (mPa.s) measured at 10 s^{-1}

Some emulsions were difficult to form at the laboratory scale. This is due to the combined effect of the wax content (8.9%) and the pour point of the fresh oil (+15°C) that is the same as the maximum seawater temperature tested (+15°C).

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Table 8 Physical-chemical characterisation at 5°C and 15°C of the IM-14 sample

	Characterisations	Fresh	Residues of distillation (vapours temperatures)			
			150°C	200°C	250°C	250°C Photo-ox.
Fresh oil	Evaporation rate (% wt.)	-	0.2	0.4	1.0	-
	Evaporation rate (% vol.)	-	0.2	0.4	1.0	-
	Specific gravity at 20°C (g/L)	0.934	0.934	0.934	0.934	-
	Pour Point (°C)	+27	+27	+27	+27	+30
	Flash Point (°C)	>100	>100	>100	>100	>100
	Asphaltenes (% wt.)	0.8	0.8	0.8	0.8	-
	Wax (% wt.)$^{(1)}$	10.5	10.5	10.5	10.6	-
Experiment at 5 °C	*Density*	0.945	0.944	0.944	0.945	0.946
	Viscosity of non-emulsified oils (mPa.s)^1	21007	18145	16906	16327	27494
	Viscosity of non-emulsified oils (mPa.s)^2	71747	47255	33136	30871	92253
	Viscosity of 50% water content emulsion^2	-	/	/	/	nd
	Viscosity of 75% water content emulsion^2	-	nd	nd	nd	nd
	Viscosity of max. water content emulsion^2	-	nd	nd	nd	nd
	Max. water content (%)	-	/	/	/	/
Experiment at 15 °C	*Density*	0.937	0.937	0.936	0.937	0.941
	Viscosity of non-emulsified oils (mPa.s)^1	5347	4620	3628	4178	6631
	Viscosity of non-emulsified oils (mPa.s)^2	17121	8531	4351	5849	14560
	Viscosity of 50% water content emulsion^2	-	17381	/	/	27057
	Viscosity of 75% water content emulsion^2	-	23104	24897	28277	nd
	Viscosity of max. water content emulsion^2	-	15366	/	/	nd
	Max. water content (%)	-	46	50	46	19

- : not relevant

^{1} viscosity (mPa.s) measured at 100 s^{-1}

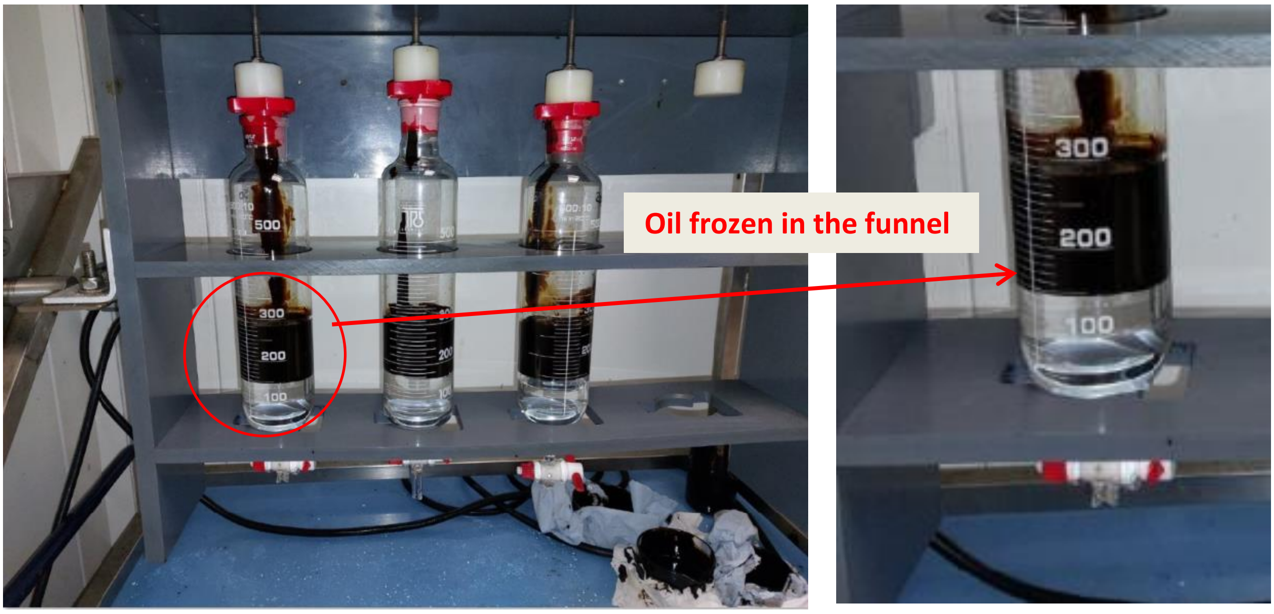
^{2} viscosity (mPa.s) measured at 10 s^{-1}

nd: not determined

/ : emulsion did not formed

At 5°C, emulsions with 50% water content could not formed (the oil freezed in the rotary funnels, see figure 2). Emulsions with higher water contents were thus not tested.

A decrease of viscosity can be observed between the fresh oil and some residues. This could be due to the evaporation of light paraffin waxes during the distillation process that tends to make the residues more fluid. Other processes due to the heating of the could also explain this behaviour but they have not been identified.



Oil frozen in the funnel

Figure 2 *Emulsions of IM-14 with 50% water content, at 5°C*

Table 9 Physical-chemical characterisation at 5°C and 15°C of the IM-15 sample

	Characterisations	Fresh	Residues of distillation (vapours temperatures)			
			150°C	200°C	250°C	250°C Photo-ox.
Fresh oil	Evaporation rate (% wt.)	-	0.2	1.4	8.6	-
	Evaporation rate (% vol.)	-	0.2	1.6	9.6	-
	Specific gravity at 20°C (g/L)	0.949	0.950	0.950	0.961	-
	Pour Point (°C)	+13	+3	+3	+12	nd
	Flash Point (°C)	94.5	94	100	> 100	>100
	Asphaltenes (% wt.)	1.3	1.3	1.3	1.4	-
	Wax (% wt.)$^{(1)}$	18.0	18.0	18.3	19.7	-
Experiment at 5 °C	*Density*	0.958	0.960	0.959	0.970	0.984
	Viscosity of non-emulsified oils (mPa.s)^{1}	15032	14494	18929	117677	nm
	Viscosity of non-emulsified oils (mPa.s)^{2}	19406	18988	23439	156705	nm
	Viscosity of 50% water content emulsion^{2}	-	24484	31215	204544	nd
	Viscosity of 75% water content emulsion^{2}	-	25644	29867	/	nd
	Viscosity of max. water content emulsion^{2}	-	59216	45887	/	nd
	Max. water content (%)	-	50	40	32	/
Experiment at 15 °C	*Density*	0.951	0.951	0.953	0.961	0.978
	Viscosity of non-emulsified oils (mPa.s)^{1}	4137	4553	4995	20569	97786
	Viscosity of non-emulsified oils (mPa.s)^{2}	4305	5179	5305	24295	175126
	Viscosity of 50% water content emulsion^{2}	-	29583	24046	/	379891
	Viscosity of 75% water content emulsion^{2}	-	30309	30793	/	nd
	Viscosity of max. water content emulsion^{2}	-	47188	/	/	nd
	Max. water content (%)	-	70	70	/	49

- : not relevant
^{1} viscosity (mPa.s) measured at 100 s^{-1}
^{2} viscosity (mPa.s) measured at 10 s^{-1}
nd: not determined
nm: not measurable
/ : emulsion did not formed

Viscosity of IM-15 greatly increases with the different distillation and emulsification steps. This can be observed when close to the pour point.

Technical specification provided by the supplier gave a pour point of +3°C for the fresh oil, similar to the pour point obtained for the 150°C and 200°C residues. The difference observed for the fresh oil (+13 °C *vs* 3 °C) could be due to a non-homogeneous mixing of the oil, especially in terms of waxes, even if the oil is heated and mixed before subsampling.

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True Boiling Point:

The boiling point distributions obtained from the distillation at the laboratory scale for the 3 oils are presented in *Appendix 9*, as well as the True Boiling Point (TBP) curve up to 520°C, combination of these experimental data and simulated distillation. Those data come from the Task 3.1.

Asphaltenes/Wax composition:

Based on the asphaltenes and wax contents, the 3 VLSFO (IM-5, IM-14 and IM-15) were plotted versus all the crude oils tested at Cedre over the last 13 years (*Figure 3*). The average values calculated on the 89 crude oils are 0.9% for asphaltenes and 8.0% for wax content. The 13 LSFO tested in the task 3.1 are also presented on *Figure 3,* in red, and their average values are higher than the crude oils ones, respectively 1.9% and 10.5%. The 3 samples IM-5, IM-14 and IM-15 are in the same range, with IM-15 exhibiting the highest amount of asphaltenes (1.3 %) and wax content (18.0%).

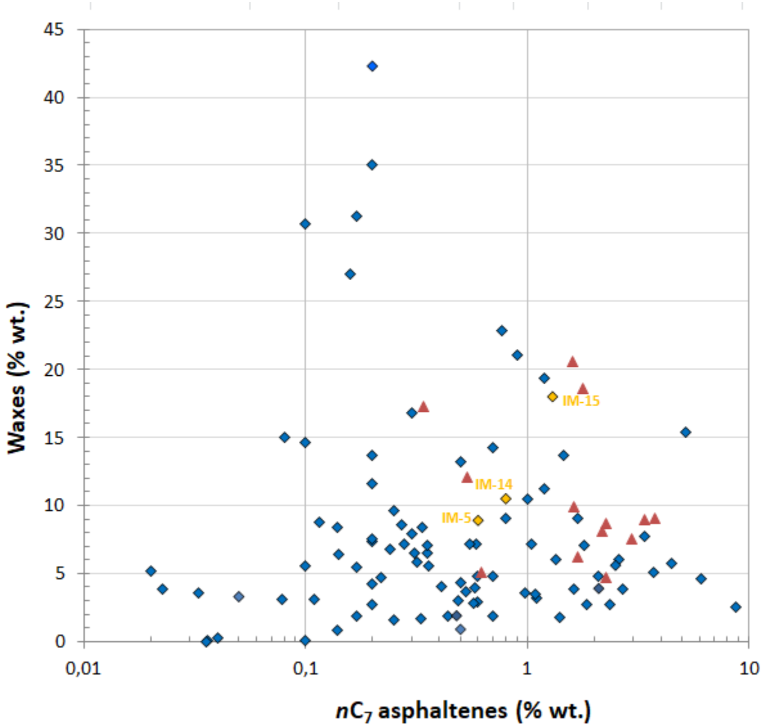

Figure 3 ***Distribution of oils tested at Cedre based on asphaltenes and wax contents. Crude oils are represented in blue, LSFO tested in task 3.1 in red and the 3 oils tested in the task 3.2 in orange.***

In terms of chemical composition, asphaltenes contents of the 3 VLSFO are *a priori* in agreement with conditions required to form water-in-oil emulsions, the threshold limit of asphaltenes content being generally estimated around 0.2 to 0.3 % when measured as insoluble in *n*-heptane.

OSCAR composition:

Results from the detailed chemical composition (OSCAR) of the 3 oils are presented in *Appendix 6*. Concerning the sample IM-5, data come from the task 3.1. HAP quantification is

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presented in *Appendix 7*.

6.2 Time-window of opportunity for dispersant use

Based on laboratory tests, the dispersibility of one oil is assessed according to 3 different levels: *dispersible*, *possibly dispersible* (dispersible with uncertainties), and *poorly dispersible*. Considering previous studies conducted at Cedre on the IFP test, two threshold values of dispersibility were defined to distinguish these 3 categories:

- Oils are considered as *dispersible* for IFP efficiency greater than 50%,
- Oils are considered as *possibly dispersible* for IFP efficiency in the range 20% - 50%,
- Oils are *poorly dispersible* for IFP efficiency lower than 20%.

Tests were carried out on the fresh oils and on samples weathered at 3 stages, approximately equivalent to respectively 6, 36 and 96 hours weathering times, by using the model dispersant according to the IFP and MNS tests. The objective of these tests was to assess the maximum viscosity of the tested oils that could be efficiently treated with dispersants. Taking into account the limits set for the fresh oils, in relationship with the evolutions of viscosity, these limits could be expressed in terms of weathering time.

In the case of the MNS tests, the two threshold values defined for these 3 categories are respectively 15% and 70%.

Summary of the results obtained are presented in *Table 10*. When the oil did not show any efficient dispersion, only one replicate was performed. When no dispersion was observed for a weathered stage, the following weathering stages were not tested afterwards.

Table 10 *Average dispersibility (%) measured or observed for the 3 VLSFO IM-5, IM-14 and IM-15, at 5°C and 15°C, during IFP and MNS test*

		IM-5		IM-14		IM-15	
Sample	Temp. (°C)	IFP	MNS	IFP	MNS	IFP	MNS
Fresh	5°C	53	66	0	0	12	0
	15°C	56	44	0	0	42	21
200°C-50°C	5°C	15	23	nd	nd	4	0
	15°C	37	39	nd	nd	11	1
250°C-75%	5°C	0	11	nd	nd	0	nd
	15°C	0	5	0	0	nd	nd
250°C-photoox-max%	5°C	0	2	nd	nd	nd	nd
	15°C	0	4	nd	nd	nd	nd

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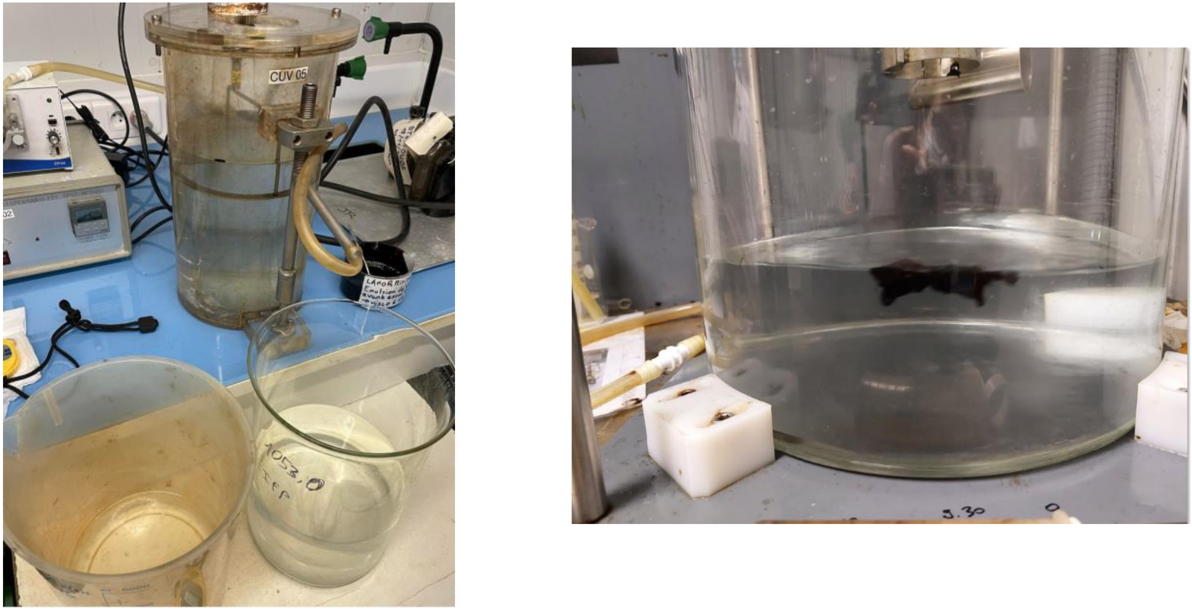
Only IM-5 exhibited a potential for dispersibility when fresh, at 5°C and 15°C. With time and weathering, the oil turned less and less dispersible. At 15°C, IM-15 seemed to be potentially dispersible when fresh. However values did not reflect a real efficient dispersion. Oil droplets formed were big and had a tendency to form a slick again at the water surface. At 5°C, IM-15 was not dispersible. Finally, IM-14 did not show any dispersibility, neither ay 5°C nor at 15°C (*Figure 4*).

IM-15 fresh, IFP test at 15°C (big droplets formed that did not reflect real dispersion)

IM-15 fresh, MNS test at 5°C



IM-14 250°C – 75% water content, at 15°C

IM-14 fresh, MNS test at 5°C

Figure 4 *Pictures taken during IFP and MNS dispersibility tests*

For the sample IM-5 dispersibility was plotted *versus* the corresponding viscosity, and experimental data were fitted by using “Exponential Decay” curves (*Figure* 5). This enabled the determination of the maximum viscosity beyond which the dispersants could not be considered as still efficient (20% limit considering IFP tests), and the range of viscosities for which the oil should be dispersible (above 50% or 70% for the IFP and MNS test respectively). Detailed results are presented in *Appendix 4*.

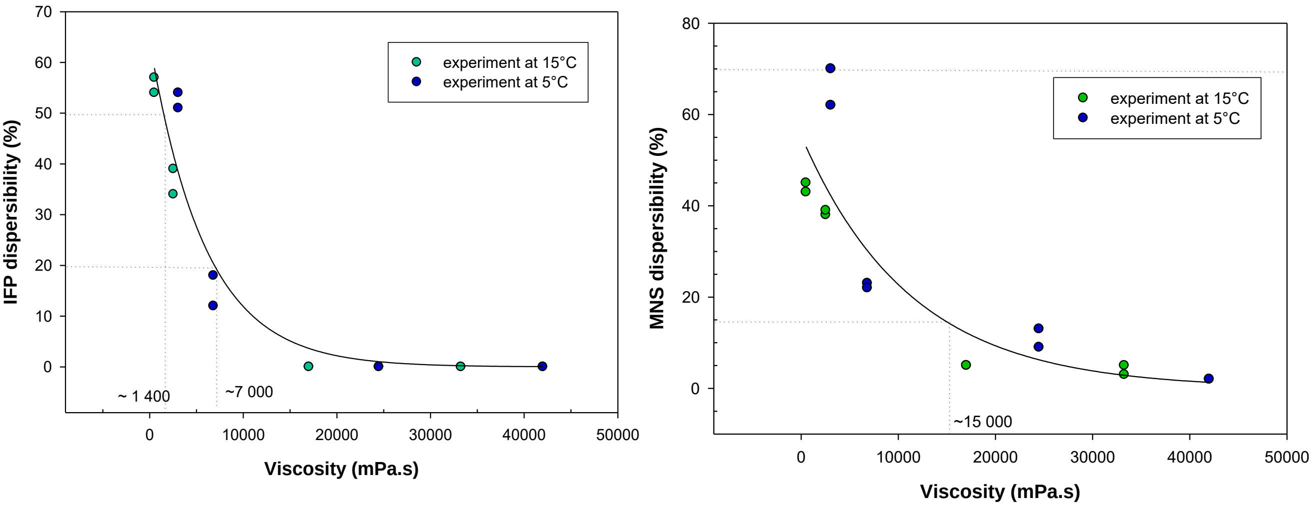


Figure 5 ***Evolutions of the Wakashio –IM-5 dispersibility according to its viscosity following IFP test and MNS tests***

The dispersibility of IM-5 sample, based on its viscosity, is summarized in *Table 11* for IFP and MNS tests. IFP tests show that the oil can be qualified as *fully dispersible* only when fresh and for moderate energy only. Dispersibility rapidly decreases: the oil becomes not dispersible for viscosities greater than 7 000 mPa.s for moderate conditions, and above 15 000 mPa.s for higher energy.

Table 11 *Dispersibility of the IM-5 oil according to the viscosity of the oil (in mPa.s), estimated thanks to IFP and MNS tests*

Dispersibility	IFP	MNS
Fully dispersible	< 1 400	-
Possibly dispersible	1 400 – 7 000	< 15 000
Poorly dispersible	> 7 000	> 15 000

As regards the MNS test, in addition to limits mentioned previously, the 5% threshold value leads to a viscosity of 25 000 mPa.s. It is considered by some institutes (SINTEF) as representative of the limit between *possibly* and *non dispersible* oils.

Considering the 3 VLSFO tested in this study, it appears that some oils can be dispersible when fresh. Nevertheless, as soon as the oils weather, they seem to rapidly become resistant to chemical dispersion. Some oils will never be dispersible, as it was observed with IM-14. Chemical dispersion seems thus to offer limited opportunities to treat an oil spill involving a VLSFO.

6.3 Comparison of the dispersants efficiency

The objective of these tests is to compare the relative efficiency of 3 dispersants (*Dasic Slickgone NS, Corexit 9500* and *Finasol OSR 52*) to the one obtained with the reference dispersant (model dispersant) at 15°C using the IFP test.

Usually, samples chosen to carry out those tests are weathered samples with dispersibility of ~40%-50% with the dispersant of reference (model dispersant in this study).

Considering IM-5, the relative efficiency of the 4 selected dispersants is illustrated on *Figure Figure* 6 and detailed results obtained for the 3 oils are presented in *Appendix 5*. The weathered samples chosen were the "150°C residue" and the "200°C / 50% water content" emulsion. Viscosity of the "150°C residue" sample was measured (620 mPa.s) but not its dispersibility with the model dispersant. This dispersibility value was extrapolated from the modelling of the IFP results at 15°C using the IFP test and is of ~ 55 %. *Corexit 9500A* is the less efficient dispersant, especially on the 150°C residue. Except for the *Dasic slickgone NS*, the efficiency logically decreases with the weathering degree. *Finasol OSR52* exhibits a high efficiency on the 150°C residue. Globally, *Finasol OSR 52* and *Dasic slickgone NS* seem to be the most efficient dispersants with values higher than the 50% threshold values for the 2 samples tested.

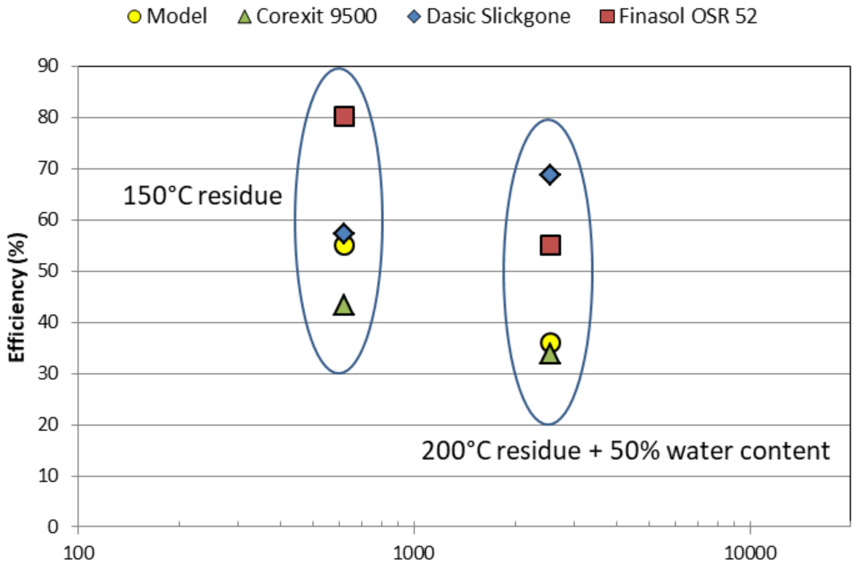


Figure 6 IM-5 comparison of the dispersants efficiency at 15 °C, using the IFP test (150°C residue and 200°C / 50% water content emulsion). X-axis corresponds to the viscosity (in mPa.s) of the tested samples.

Given that IM-14 and IM-15 did not exhibit an efficient dispersion, even when fresh, a rapid comparison was performed on a replicate of the fresh oils. Table 12 presents the results obtained. Not surprisingly, IM-14 is not dispersible either; the 15% measured with Finasol OSR 52 did not reflect an efficient dispersion but rather a fragmentation in big oil droplets. The same phenomenon as with the model dispersant was observed with the Dasic slickgone NS, the Finasol OSR52 and the Corexit 9500 A for the IM-15 sample: the dispersion did not reflect an efficient dispersion but most likely the formation of big droplets.

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Table 12 *Comparison of dispersants efficiency (in %) for the IM-14 and IM-15 fresh oils*

Dispersibility (%)		IM-14 Fresh oil	IM-15 Fresh oil
Viscosity (mPa.s)		5347	4137
Efficiency (in %)	Dasic slickgone	0	28
	Finasol OSR52	15	48
	Corexit 9500 A	0	32
	Model	0	42

7 RESULTS OF PILOT SCALE TESTS

This section describes the evolution of the physical-chemical properties of the 3 LSFO according to various environmental conditions and test protocols. The consequences of these evolutions in terms of response strategies are discussed in the operational guidelines (*section 8*). Pictures of the oil taken at different time steps and at the 2 temperatures tested are presented in *Appendix 10*.

7.1 Evolution of the physical-chemical properties at the pilot scale at 5°C and 15°C

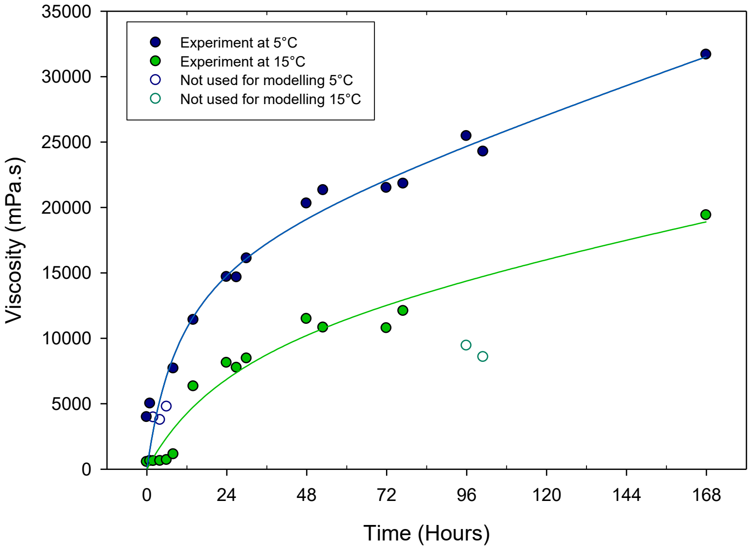
The various parameters were plotted versus the weathering time and, when possible, a regression model was applied, result of a statistical analysis using the Sigmaplot 9.0 software.

7.1.1 Viscosity

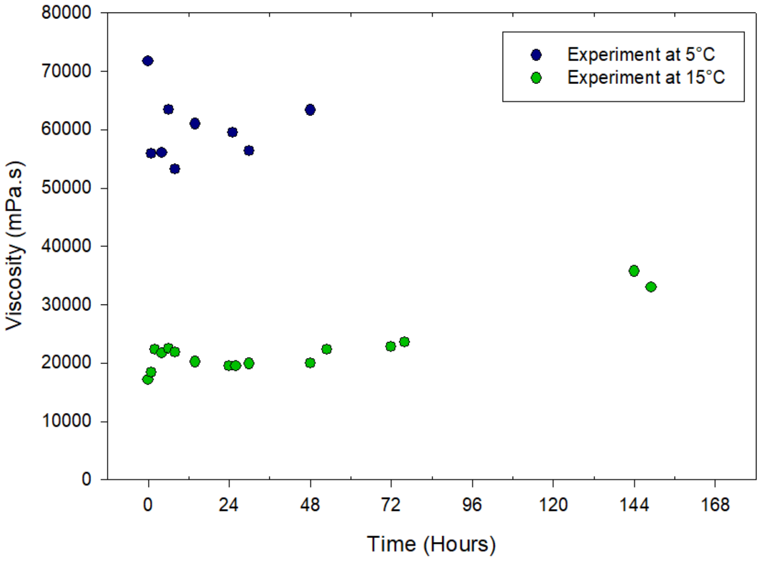
The viscosity increases (*Figure 7*) during the whole experiment for samples IM-5 and IM-15. Considering IM-5, viscosities reach a maximum value of 32 000 mPa.s and 19 000 mPa.s after one week, respectively at 5°C and 15°C. Results from the experiment conducted in freshwater follow the same trend as the ones conducted in seawater conditions. Considering IM-15, viscosities reach a maximum value of 223 000 mPa.s and 107 000 mPa.s after one week, respectively at 5°C and 15°C.

The weathering of IM-14 at 5°C was stopped before the end of the week experiments as the slicks were stuck on the flume tank walls and no free oil could be sampled. For this oil, the viscosity was quite stable over time, around 20 000 mPa.s and 60 000 mPa.s, respectively at 5°C and 15°C. This oil is representative of the behaviour sometimes observed when the pour point is significantly greater than the test temperature: the emulsified oil is not more viscous than the fresh oil, the shear thinning phenomenon being particularly important.

a) IM-5



b) IM-14



c) IM-15

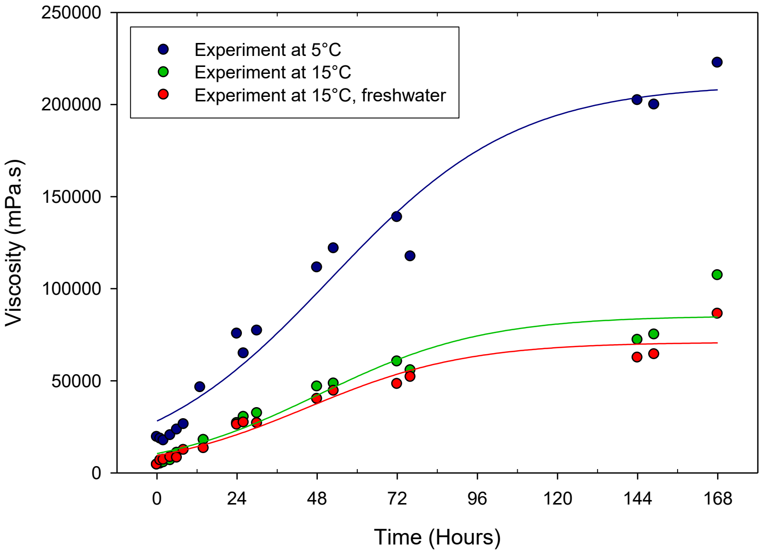


Figure 7 *Evolution of the viscosity of a) IM-5, b) IM-14 and c) IM-15*

Details concerning the viscosity measurements and related units are presented in section *4.2.*

7.1.2 Emulsification

7.1.2.1 Kinetics of emulsification and maximum water content

The water content proves to increase rapidly within the first 24 hours for the 3 VLSFO (except IM-14 at 5°C), to reach a maximum close to 80-90% for IM-5, 60% for IM-14 (15°C) and 60-70% for IM-15 (*Figure 8*). Emulsification in freshwater is similar to the ones observed in seawater conditions (see IM-15 at 15°C).

The kinetics of emulsification were quick as 90% or more of the maximum water content was reached during those first 24 hours of weathering, either at 5°C or 15°C, for the 3 products tested.

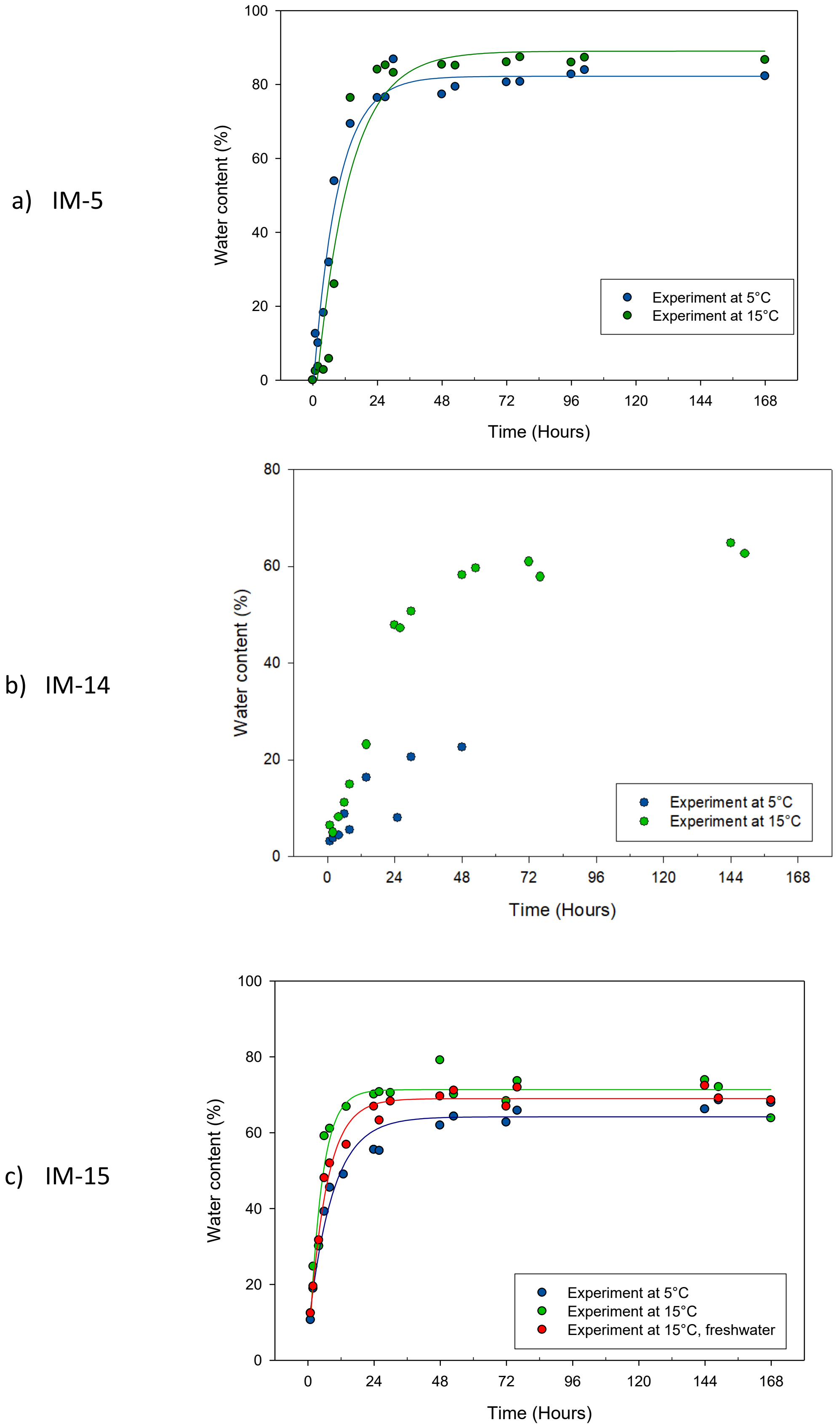


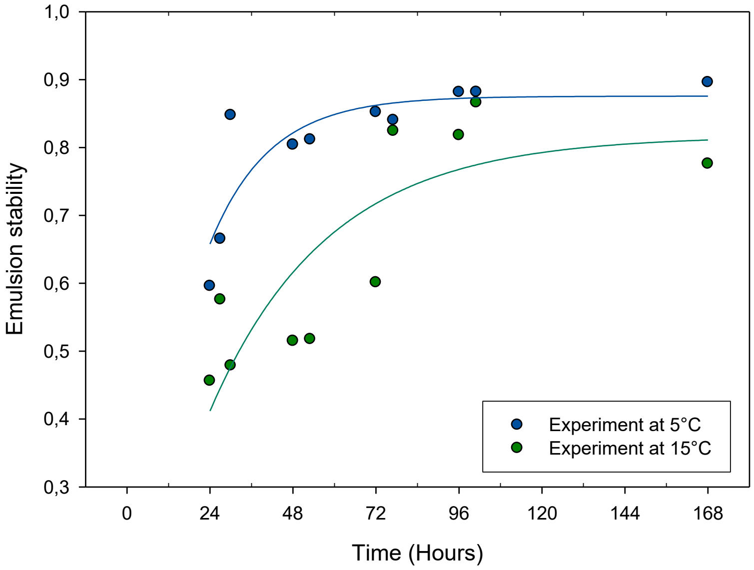
Figure 8 Evolution of the water content of a) IM-5, b) IM-14 and c) IM-15

7.1.2.2 Stability of the emulsions

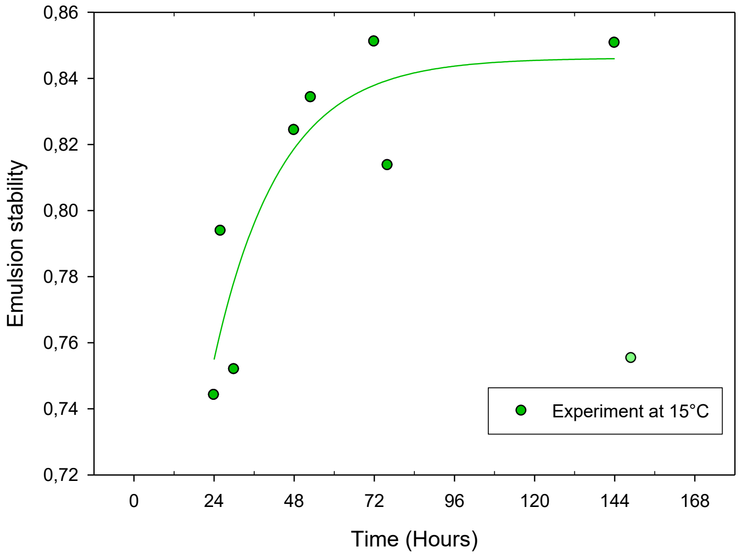
The stability of the emulsions was assessed all along the weathering experiments but results are more relevant when considering that the process is completed or almost achieved (water content close to its maximum value). Based on the kinetics of emulsification, the stability was particularly monitored after 24 hours, and its evolution plotted over time as illustrated in Figure 9. The stability ratio is calculated as the ratio between the emulsion water contents of the sample collected after addition of demulsifier and in the flume.

At 5 °C and 15 °C, the emulsions proved to more stable over time, with values reaching ~0.8 at 15°C and ~0.9 at 5°C.

a) IM-5



b) IM-14



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d) IM-15

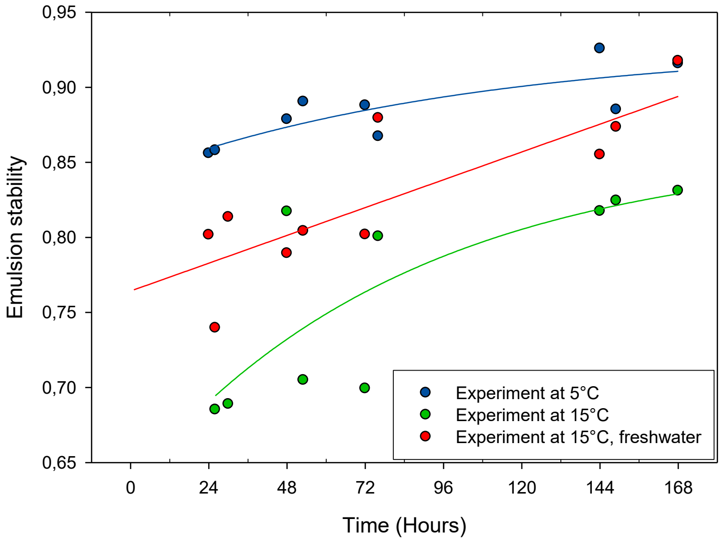

Figure 9 Evolution of the stability of the emulsion for a) IM-5, b) IM-14 and c) IM-15

7.1.3 Density

The increase of density observed for IM-5 and IM-15 during the whole experiment is in agreement with observations made as regards the kinetics of evaporation and emulsification. The density increase of water-in-oil emulsions is generated by both incorporation of water and, and volatilization of the lighter fractions of the oil could be described as follows (*d* and *f* represent respectively the density and fraction of oil or water):

$$d_{emulsion} = d_{HC} \times f_{HC} + d_{water} \times f_{water}$$

d_{HC} can then be calculated as follows: $d_{HC} = \frac{1}{1 - f_{water}} \times (d_{emulsion} - f_{water} \times d_{water}\rangle$

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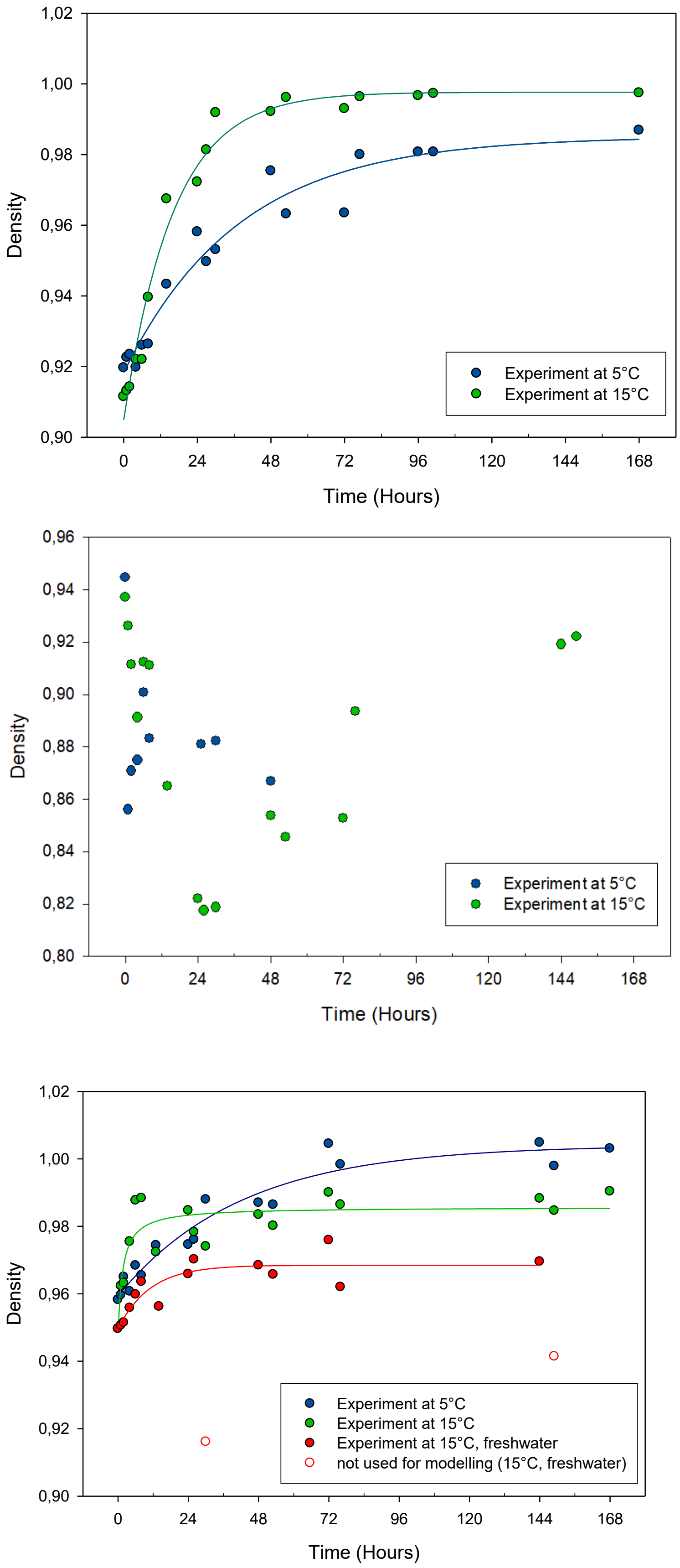

a) IM-5

b) IM-14

c) IM-15

Figure 10 Evolution of the emulsion density of a) IM-5, b) IM-14 and c) IM-15

The density of IM-14 is more variable, especially in the first 24 hours. This can be due to the nature of the oil that can catch up air in the emulsion.

At the end of the trial, sample IM-5 and IM-15 exhibit values close to 1. In open waters, characterized by low suspended matter concentration, the oil should float at the surface. However, if a spill occurs in freshwater, or close to the coast, in an area characterized by a high particulate charge playing the role of ballast, the oil could potentially be transferred into the water column. The experiment performed in freshwater leads to a final density of ~0.96, value slightly lower than the experiment carried out in seawater conditions. However, at the end of the freshwater trial, free water was clearly visible on the top of the slick, highlighting the potential for the slick to be immerged.

7.1.4 Flash point

The evolution of the flash point could not be followed throughout the duration of the experiments. The flash point is measured by heating the oil which is regularly exposed to a flame. The flash point corresponds to the temperature for which vapors get inflamed. However, as regards emulsions, the incorporated water boils at 100°C, which do not allow measurements due to projections of water inside the cup. Hence, the maximum flash point measured was not greater than 100°C (boiling point of water). Nevertheless, this threshold value is sufficient in terms of safety and higher flash points would not have an operational meaning (it must be noted that these flash points were measured according to a closed-cup method which overestimates the risk of ignition compared to open air conditions).

Tables 13 and *14* present the flash points measured for the IM-5 and IM-15 samples. IM-14 exhibited a flash point above 100°C at 5°C and 15°C, even when fresh.

Table 13 ***Evolution of the flash point of IM-5 (Abel closed-cup method)***

Weathering time (hrs)	Flash Point (°C) at 5 °C	Flash Point (°C) at 15 °C
0	91.0	91.0
1	90.0	91.5
2	92.0	94.0
4	92.0	97.5
6	95.5	> 100
8	> 100	> 100

Table 14 ***Evolution of the flash point of IM-15 (Abel closed-cup method)***

Weathering time (hrs)	Flash Point (°C) at 5 °C	Flash Point (°C) at 15 °C
0	86.5	94.5
1	88.0	98.5
2	90.5	99.5
4	92.0	> 100
6	94.0	> 100
8	94.0	> 100
13	97.0	> 100
24	>100	> 100

It appears that, even when fresh, the flash point was always largely above 60°C. This threshold corresponds, according to some regulations, to the limit between flammable and non-flammable products.

7.1.5 Evaporation and chemical composition

Considering IM-5, the evaporation kinetics illustrated in *Figure 11* was estimated by using the method 1 described in *Appendix 3*. Briefly, to assess the evaporation rate of the oil, a calibration was established in the laboratory. Different samples of the initial oil were artificially evaporated and then analysed (*table 1*). This qualitative determination led to the calculation of a Weathering Index (WI), as proposed by Wang and Fingas (1994), which was plotted versus the evaporation rate. The calibration curve established that way was then applied to real samples to get their evaporation rates.
Artificially weathered samples were obtained in the laboratory following distillations at 150°C, 200°C and 250°C. However, it must be noted that these temperatures correspond to laboratory protocols at atmospheric pressure: in natural conditions, due to the wind action, components with boiling point greater than local temperature will evaporate, and, generally, it is considered that the limit of volatility corresponds to molecules that distil up to 250°C.
The maximum evaporation rate (in volume) was found close to 3% and 8%; at 5°C and 15°C respectively. The value obtained after one week at 15°C is close to the value obtained for the 250°C residue at the laboratory (9.5 % vol.).

Considering IM-15, the evaporation kinetics was estimated by using the method 2 described in *Appendix 3*. Maximum evaporation ranged between ~10% (at 5°C) and ~15°c (at 15°C). Those

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results are in agreement with the values obtained at the laboratory scale. IM-14 did not show any ability to evaporate (~1% at 5 and 15°C, data not represented on the graph), as it was already demonstrated at the laboratory scale.

It must be noted that, in case of great waxes content, the evaporation rate is less accurately determined. Part of the slick can be enriched in waxes, while other parts are depleted in waxes. Chromatographic methods are applied assuming that the heaviest part of the oil is constant, which is not the case. In addition, the methods using the evolution of the oil density are also affected by the incorporation of air which lowers the measured values.

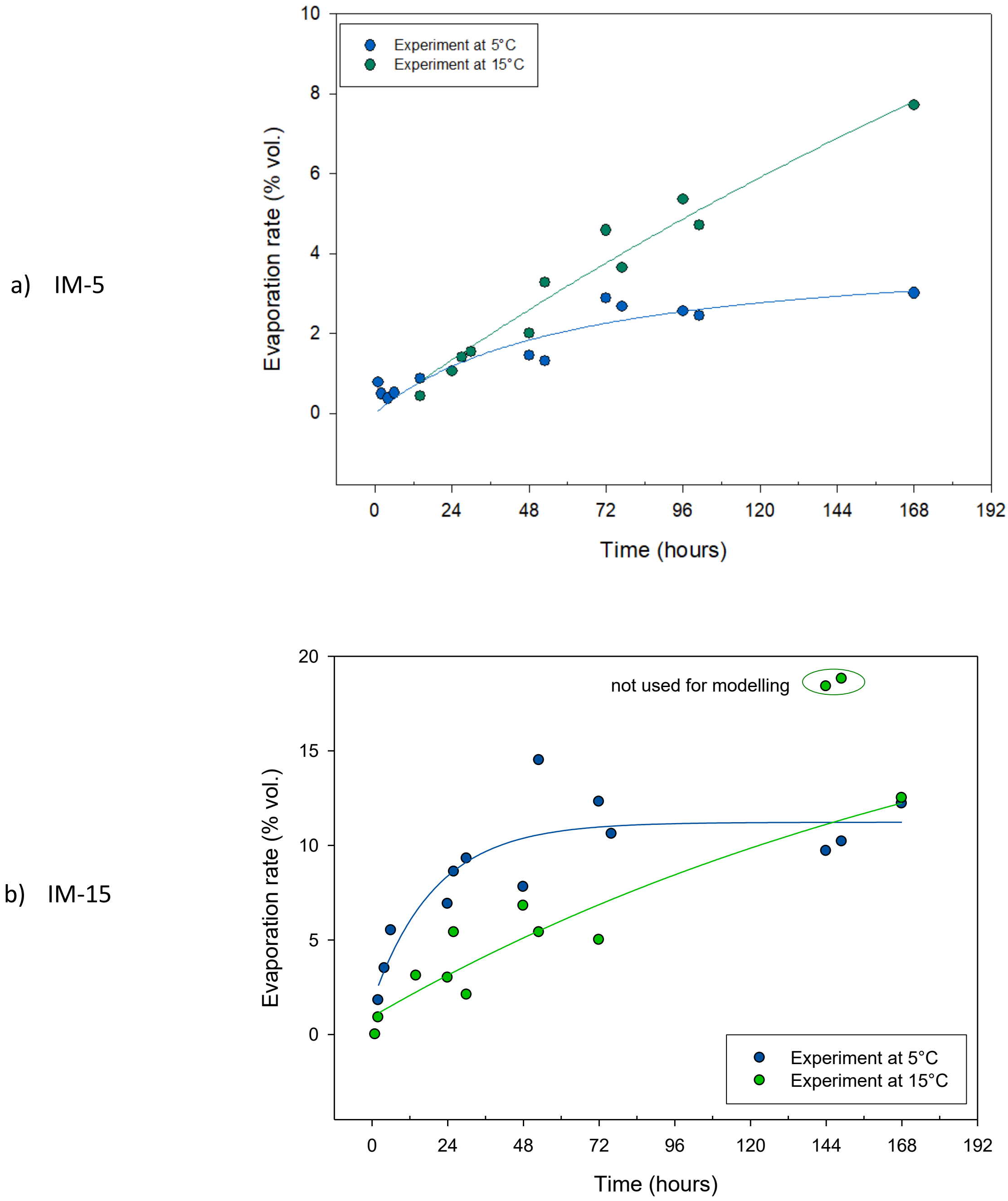

Figure 11 ***Evolution of the evaporation rate (% vol.) of a) IM-5 and b) IM-15***

7.2 Elements for OSR techniques potentially available

7.2.1 Chemical dispersibility

The tests conducted using reference conditions (see *Appendix 4*) allowed calibration of the IFP equipment (the efficiency of 73 % obtained in standard conditions is in agreement with the reference value which is 75 % ± 3 %).

Windows of dispersibility have been set by Cedre (Guyomarch *et al.*, 2012) and SINTEF (Int. Oil Spill Conf., 1997) according to IFP and MNS results: oils are considered as “dispersible” for IFP and/or MNS efficiency respectively greater than 50% and 70%, “poorly dispersible” below 20% according to Cedre when using the IFP test or below 5% according to SINTEF based on the MNS test, and dispersibility is “reduced” in between. However, based on recent studies conducted at Cedre, the 5% threshold limit defined for the MNS test appeared to be too low and could be replaced by 15% (Guyomarch *et al.*, 2016).

Considering IFP tests, IM-5 seems dispersible when fresh (at 5 and 15°C). Once weathered, the oil is not dispersible anymore. IM-5 and IM-14 did not exhibit any dispersibility, even when fresh. Values calculated for the fresh IM-15 at 15°C did not reflect any real dispersion but a slick fragmentation.

7.2.2 Recovery by using oleophilic skimmers

Oil adhesion on an oleophilic plate is assumed to represent a reliable parameter for assessing the possibility of using oleophilic skimmers to recover the oil. An increase during the very first hours (reaching more than 3000-4000 g/m^2 for all the oils except for IM-14 at 5°C), followed by a decrease with time is observed for the 3 products (*Figure 12*). This theoretical determination suggests that oleophilic skimmers could be appropriate for spills involving fresh and moderate weathered oils. However, this option might not be suitable considering weathered products. Additionally, following the viscosity evolution, mechanical skimmers can be considered.

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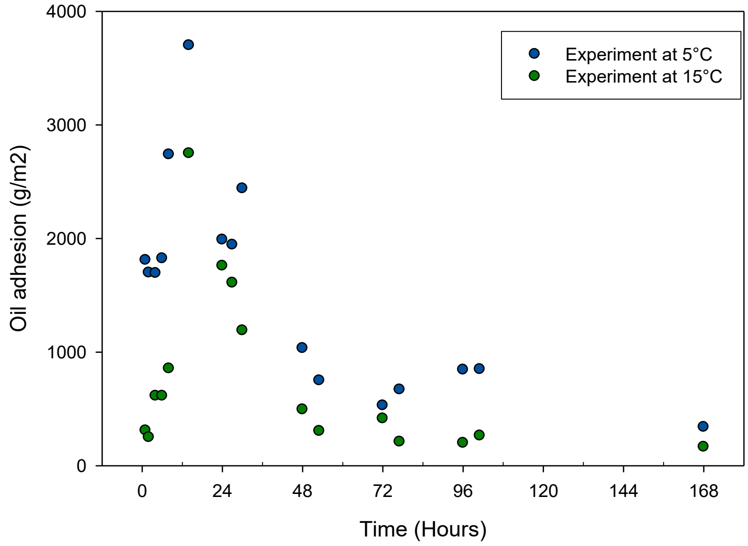
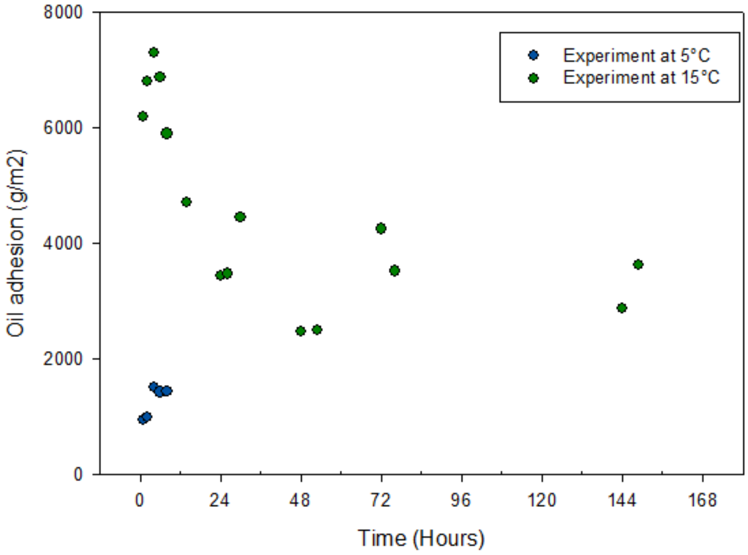
a) IM-5



b) IM-14



c) IM-15

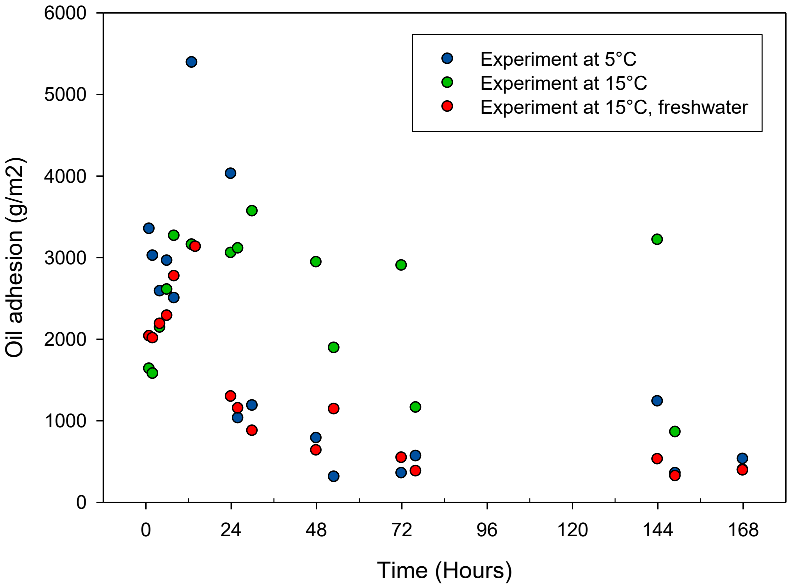


Figure 12 Evolution of the oil adhesion of a) IM-5, b) IM-14 and c) IM-15

8 OPERATIONAL GUIDELINES

8.1 Safety / flammability

In terms of safety, given the flash point of the 3 fresh VLSFOs (> 80-90°C), recovery operations from ships could be conducted directly following a spill at 5°C and 15°C.

8.2 Chemical dispersibility

The operational guidelines which resulted from this study are that this type of oils is not dispersible. Some oils (IM-5) may exhibit a potential for dispersibility when fresh but this dispersibility seems to rapidly decrease with the weathering time.

This response option seems thus not to be the most appropriate to treat a spill involving VLSFO.

8.3 Recovery

Considering the evolution of the oil adhesion, oleophilic skimmers could be appropriate for spills involving fresh and moderate weathered oils. Uncertainties remain considering weathered oils and this option might become challenging.

The maximum viscosity of some oils (IM-15) can be very high (> 200 000 mPa.s at 5 °C). Moreover, due to photo-oxidation processes, incorporation of fine mineral particles…those values are liable to be slightly greater in real conditions. For such products, viscosity could be a limiting factor for recovery and pumping operations. Additionally, it should be noted that some oils could exhibit a very sticky behaviour (fresh IM-15).

This response option is studied in a specific Task (task 4.1), in the frame of the WP 4.

The storage capacities will be a key parameter as the pollutant volume could be about 9 times greater than it was initially (IM-5: loss of around ~5% by evaporation but great increase of the volume due to more than 80% water uptake).

APPENDIX

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APPENDIX 1

Polludrome® description

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Cedre’s hydraulic canal: the *Polludrome®*

The weathering of crude oils is complex as different processes (evaporation, dispersion, emulsification, photo-oxidation…) take place simultaneously. Laboratory methodologies exist to simulate each of these different processes. For example, evaporation can be simulated by a simple topping (distillation) per evaporation or rotary evaporation. Concerning the oil emulsification the modified Mackay-Zagorsky method using rotary funnels can be used. An alternative method consists in adding progressively sea water to the oil; in this case the mixing energy is provided by a rotating stirrer.

However, no laboratory method exists to consider all the parameters simultaneously and to simulate the whole weathering process. In order to simulate these various phenomena realistically, *Cedre* has equipped its facilities with a hydraulic canal in which different marine (as well as inland) water conditions can be recreated, such as wind, waves and UV lights. This canal consists of a loop in which the water can be circulated. Large windows located along the canal allow observations at the surface and in the water column. The canal is set in an air-conditioned room and is equipped with a wave beater (adjustable period), current and wind generators, and UV lights (2 x 2000 W). With this equipment, it is possible to weather samples of a specific oil under a variety of climatic conditions.

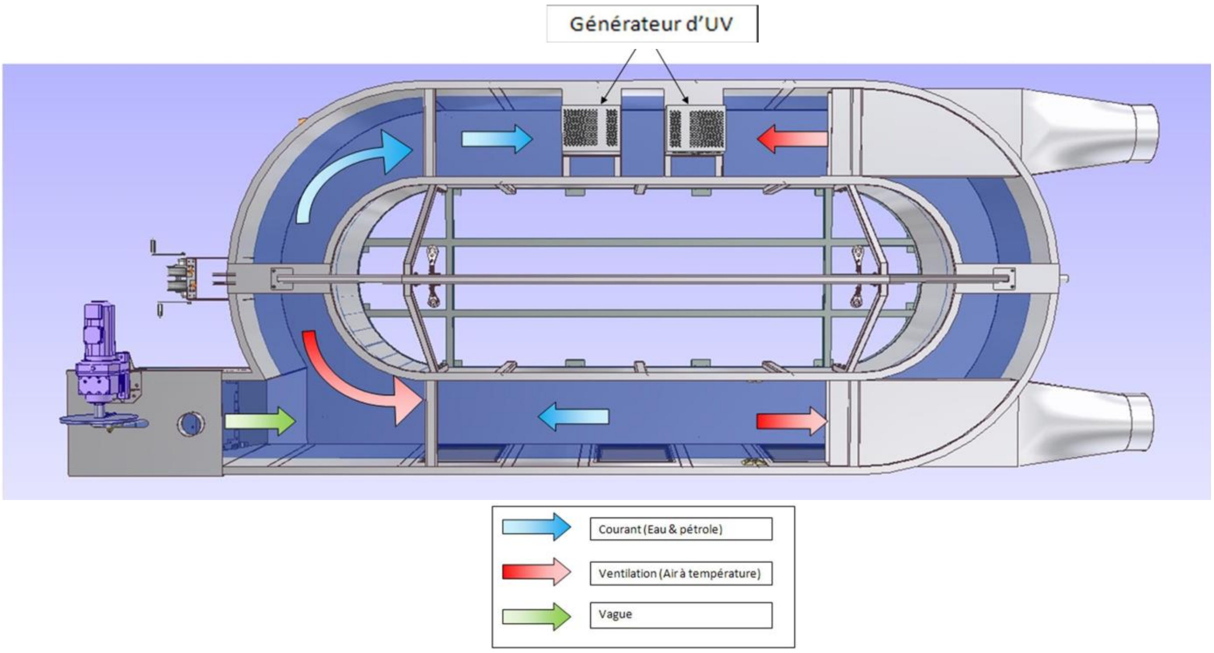

Figure 1 *The Polludrome®*

The general characteristics of the canal are:
- Canal dimensions: width: 0.6 m; wall height: 1.4 m; average water depth: 0.9 m.
- Waves typical characteristics: period 3 seconds, amplitude ± 0.1 m.
- Climate room: from 1 to 30°C.

All tests were run assuming a moderate situation (sea state 3. which corresponds to wave heights between 0.5 and 1.25 m). The corresponding parameters for the *Polludrome®* were:
- wave height: 20 cm
- mean period: 3 s
- current speed (water): 40 cm/s
- wind velocity: 5 m/s
- volume of seawater (salinity of 33): 7 m^3

The solar energy was recreated by the use of one of the two UV lights.

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APPENDIX 2

Test protocol

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Sampling procedure

The oil volume poured onto the water surface at the beginning of the test was set at 20 L to ensure an extensive sampling even in case of high evaporation rates and to account for oil that sticks on the tank walls. During the first 12 hours, one sample was collected at least every 2 hours; after that period, the intervals could be increased to 4 to 6 hours, and finally, remaining oil was sampled twice a day until the weathering time reached one week (*table 1*).

Table 1 *Sampling times* [1]

Sample reference	T0	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16
Time (hours)	0	1	2	4	6	8	14	22	26	30	48	53	72	77	96	101	168

[1] these sampling times correspond to typical values. As the objective of the study is to get a temporal evolution of the physical-chemical parameters and taking into account the inherent constrains of laboratory work organisation. the effective sampling times are liable to be different from the times mentioned in table 1.

Samples were collected by using a large funnel equipped with a tap after the oil had been gathered with a little boom set in the canal in order to form temporarily a thick slick. Natural dispersion can be observed, generally during the first hours of weathering for the tested oils, and is then assessed by collecting samples at a depth of 30 cm after 1 hour.

Polludrome® settings

Table 2 *Settings according to the weathering time*

Day	Sample	Time	Weathering time (hours)	Current	Wind	Waves
Monday	T_0	8h00	**0**	-	2	4
	T_1	9h00	**1**	-	2	4
	T_2	10h00	**2**	-	2	4.5
	T_3	12h00	**4**	-	2	4.5
	T_4	14h00	**6**	-	2	5
	T_5	16h00	**8**	-	2	5
	T_6	22h00	**14**	-	2	5
Tuesday	T_7	8h00	**24**	-	2	5
	T_8	10h00	**26**	-	2	5
	T_9	14h00	**30**	-	2	5
Wednesday	T_{10}	8h00	**48**	-	2	5
	T_{11}	13h00	**53**	-	2	5
Thursday	T_{12}	8h00	**72**	-	2	5
	T_{13}	13h00	**77**	-	2	5
Friday	T_{14}	8h00	**96**	-	2	5
	T_{15}	13h00	**101**	-	2	5
Monday	T_{16}	8h00	**168**	-	2	5

These settings are specific to the device which equips the *Polludrome®*

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APPENDIX 3

Methods of measurements

Methods of measurements

Evaporation

Evaporation – method 1

The saturate and aromatic fractions were analysed using gas chromatography. Chromatograms of these volatile compounds at different weathering times show the evolution of their distribution. The lighter molecules disappear progressively and the quantitative analysis of samples compared to the initial oil can give the evaporation rate. These analyses performed at various weathering times provide an assessment of the kinetics of evaporation. Considering the low rate of dissolution and natural dispersion compared to evaporation, water soluble fractions were not taken into account to assess the proportion of oil that evaporated.

To assess the evaporation rate of the whole oil, a calibration was established in the laboratory. Different samples of the initial oil were artificially evaporated and then analysed (*table 1*). This qualitative determination led to the calculation of a Weathering Index (WI), was proposed by Wang and Fingas (1994), which was plotted versus the evaporation rate. The calibration curve established that way was then applied to real samples to get their evaporation rates.

The Weathering Index is defined in the general following equation:

$$WI = \frac{L_1 + L_2 + L_3 + L_4}{H_1 + H_2 + H_3 + H_4}$$

L_1, L_2, L_3 and L_4 represent components that volatilize while H_1, H_2, H_3 and H_4 represent the non-volatile compounds in the oil (the choice of these target compounds depends on the initial composition of the oil; in our case, the light compounds were the linear alkanes $n\text{C}_{11}$ to $n\text{C}_{14}$, while the heavy molecules were $n\text{C}_{25}$ to $n\text{C}_{28}$). Consequently, as the oil evaporates, the Weathering Index decreases and a calibration curve similar to the one presented *figure 1* can be obtained:

Table 1 *Example of characterization of distilled samples of one crude oil*

	Sample 1	Sample 2	Sample 3
Distillation temperature (°C)	150	200	250
Evaporation rate (%)	12.1	20.7	29.7
Density @ 1°C / 10°C	0.908 / 0.901	0.921 / 0.913	0.933 / 0.925
Weathering Index	-	-	-

The calculation of the maximum evaporation rate can also be checked by comparing the oil density at its final weathering state with samples obtained in the laboratory and characterized by their evaporation rate (measured by gravimetry).

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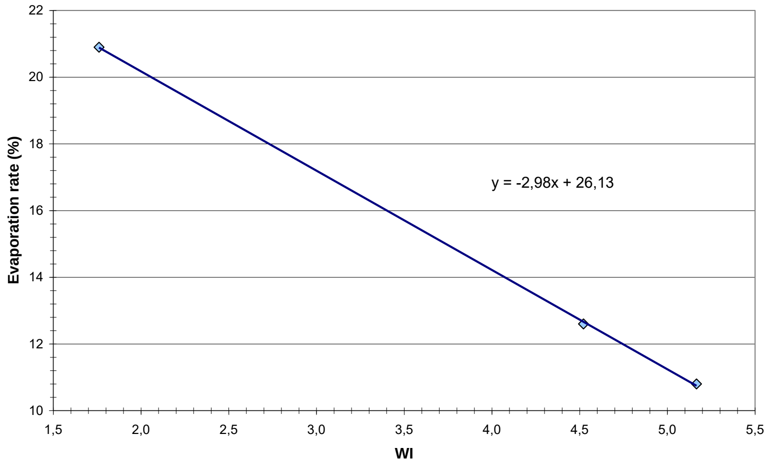

Figure 1 *Calibration curve established to measure the evaporation rate of weathered oils*

Evaporation – method 2

The analysis of weathered samples collected in the flume was performed by high-temperature gas chromatography equipped with a flame ionisation detector (HT-GC/FID). The total area was calculated and compared to the initial oil, hence the assessment of losses by evaporation. Results were also checked by the analysis of the artificially evaporated samples characterized by known evaporation rates. These calibration samples also enable the conversion of the evaporation rates from volumes to weight, and vice versa.

IFP Dispersibility

The chemical dispersibility of the surface oil was measured using the IFP test method (NF 90-345 French Standard) at the test temperatures (5°C and 15°C) and with a reference dispersant (*MODEL*). Tests were performed on samples collected during the weathering experiments in the flume or on oils artificially weathered at the laboratory scale.

In order to calibrate the experimental design, additional dispersibility tests were carried out with a model dispersant using the French procedure for dispersant approval (test performed at 20°C; reference oil : FOREF, mixture of Heavy Fuel Oil and Arabian Light topped at 110°C, viscosity of 1000 mPa.s at 20°C). Under these conditions, the reference value is 76% ± 3 and the results of the calibration have to be within this range.

Oil was extracted using dichloromethane and the concentration was measured by UV spectrophotometry at 580 nm.

Table 2 *Composition of the model dispersant*

Denomination	% weight
Dipropylene-glycol-n-butyl-ether	18.5
Span-80	6.5
Tween-80	12.9
Tween-85	19.1
Aerosol-OT-75 (14/05/14)	27.8
Exxsol-D80	15.2
Total	100.0

MNS Dispersibility

The chemical dispersibility of the surface oil was measured using the MNS test method according to test conditions described by Mackay and Szeto (1981)[6]. The test was calibrated using an asphaltenic oil and the level of energy chosen for the test corresponded, using the calibrated orifice plate, to a pressure drop of 25 mm H_2O.

Oil Adhesion

The evolution of the oil adhesion was measured by weighing the amount of oil that sticks to a given oleophilic plate (plate made of Teflon, 10 x 10 cm). These data will help to document the efficiency of oleophilic skimmers over time.

Oil Composition – Quantification of Individual Components (PAHs. n-alkanes)

The PAHs and *n*-alkanes concentrations were measured on the crude oil in its initial state.
10 mg of the oil sample were spiked with internal standards (perdeutarated PAHs and eicosane). Compounds were then analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). The GC was an HP 7890 series II (Hewlett-Packard. Palo Alto. CA. USA) equipped with a Multi Mode Injector (MMI) used in the pulsed splitless mode (Pulse Splitless time: 1 min. Pulse Pressure: 15 psi). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 320°C (20 min) at 3°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a HP 5-ms (Hewlett-Packard.Palo Alto. CA. USA): 50 m x 0.25 mm ID x 0.25 µm film thickness. The GC was coupled to a HP 7000 triple quadripole used in the Electronic Impact mode (Electronic Impact: 70 eV. voltage: 2000V). PAHs and *n*-alkanes quantifications were done using Single Ion Monitoring mode with respectively the molecular ion of each compound and a common fragment (generally m/z = 57) at a minimum of 2 cycles/s.

PAHs and *n*-alkanes were quantified relatively to the perdeuterated PAHs and eicosane introduced at the beginning of the sample preparation procedure.

Oil Composition – Quantification of Individual Components (COVs)

10 mg of the oil sample and 10 mL of reverse-osmosis purified water are added in a 20 mL flask. which is then spiked with 50 µL of the methanolic solution of internal standards (6 perdeuterated alkanes, from C_5 to C_{10}, and C_0 to C_4- perdeuterated benzenes). The flask is then closed with a cap.

<u>*Headspace (HS) parameters*</u>
Following an incubation time of 5 minutes at 60°C (stirring at 500 rpm with a 1 second break every 60 seconds), 1000 µL of the air is sampled and injected in the GC-MS system.

<u>*GC-MS analysis*</u>
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 Cooled Injection System CIS-4 (Gerstel. Switzerland). The injection was performed in splitless mode (CIS temperature: 225°C). The GC temperature program was: from 35°C (5 min) to 80°C (0 min) at 11°C/min, then 250°C (0 min) at 16°C/min. The carrier gas was helium at a constant flow of 1 mL/min. The capillary column used was a RXi-624 Sil MS (Restek.

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[6] Donald Mackay and Foon Szeto (*1981*) THE LABORATORY DETERMINATION OF DISPERSANT EFFECTIVENESS: METHOD DEVELOPMENT AND RESULTS. International Oil Spill Conference Proceedings: March 1981, Vol. 1981, No. 1, pp. 11-17.

Bellefonte. PA. USA): 30 m x 0.25 mm ID x 1.4 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 230°C. Alkanes and monoaromatics quantifications were done using Single Ion Monitoring mode at a minimum of 2 cycles/s.

Monoaromatics and and alkanes were quantified relatively to the perdeuterated linear alkanes, benzene and alkylated benzenes introduced at the beginning of the sample preparation procedure.

Oil Composition – Distribution according to the number of carbon atoms

10 mg of the oil were solubilized by 10 mL of CS_2. No purification was performed prior to the analysis.
The analysis was performed by high temperature gas chromatography coupled to a flame ionization detector (HTGC-FID). The GC was an HP 7890N (Hewlett-Packard. Palo Alto. CA. USA) equipped with an “on-column” injector. The injector program was: from 50°C to 400°C at 6°C/s. The oven temperature program: from 50°C (1 min) to 420°C (10 min) at 15°C/min. The carrier gas was hydrogen at a constant flow (15 mL/min). The capillary column used was a DB-HT Simdist (100% diméthylsiloxanne): 5 m x 0.53 mm x 0.15 µm film thickness. The chromatograph was coupled to a FID detector maintained at 425°C. The volume injected was 1 µL.

APPENDIX 4

Results of dispersibility tests on samples weathered at the laboratory scale

(***Model Dispersant***)

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IM-5

*Results of **IFP tests** performed on the fresh oil and emulsified residues*
At 5°C:

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	54	51						
50%			12	18				
75%					0	0		
Max							0	0

	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*
0%	3051	53	6									
50%				6816	15	40						
75%							24488	0				
Max										42007	0	

At 15°C

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	54	57						
50%			34	39				
75%					0	0		
Max							0	0

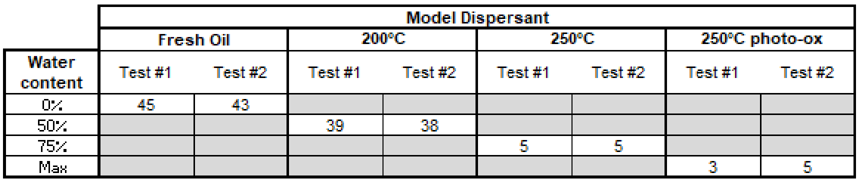
	15°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*
0%	507	56	5									
50%				2545	37	14						
75%							17007	0				
Max										33257	0	

*Results of **MNS tests** performed on the fresh oil and emulsified residues*
At 5°C:

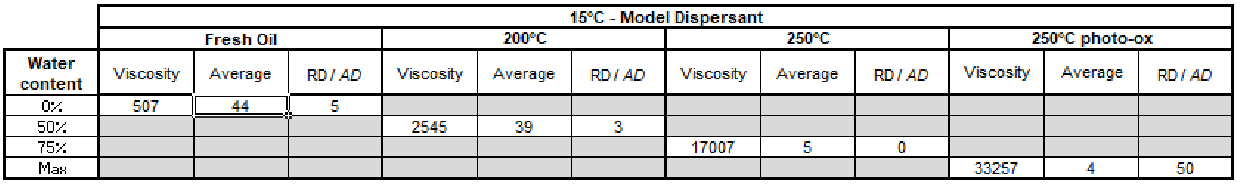
	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	62	70						
50%			23	22				
75%					13	9		
Max							2	2

	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*
0%	3051	66	12									
50%				6816	23	4						
75%							24488	11	36			
Max										42007	2	0

At 15°C:



	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	45	43						
50%			39	38				
75%					5	5		
Max							3	5



	15°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*	Viscosity	Average	RD / *AD*
0%	507	44	5									
50%				2545	39	3						
75%							17007	5	0			
Max										33257	4	50

RD (Relative Difference) is calculated as the ratio between the Absolute Difference (between two duplicates) and the average. It has to be lower than 14% for efficiencies greater than 40%:

$$RD = \frac{abs(E1 - E2)}{mean(E1.E2)} < 14$$

For efficiencies lower than 40%, the Absolute Difference has to be lower than 6%:

$$AD = abs(E1 - E2) < 6$$

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IM-14

*Results of **IFP tests** performed on the fresh oil and emulsified residues*
At 5°C:

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	0	nd						
50%			nd	nd				
75%					-	-		
Max							-	-

	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	21007	0	-									
50%				-	-	-						
75%							-	-	-			
Max										-	-	-

At 15°C

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	0	0						
50%			nd	nd				
75%					0	nd		
Max							-	-

	15°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	5347	0	-									
50%				-	-	-						
75%							28277	0	-			
Max										-	-	-

*Results of **MNS tests** performed on the fresh oil and emulsified residues*
At 5°C:

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	0	nd						
50%			nd	nd				
75%					-	-		
Max							-	-

	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	21007	0	-									
50%				-	-	-						
75%							-	-	-			
Max										-	-	-

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At 15°C:

	Model Dispersant							
	Fresh Oil		**200°C**		**250°C**		**250°C photo-ox**	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	0	nd						
50%			nd	nd				
75%					0	nd		
Max							-	-

	15°C - Model Dispersant											
	Fresh Oil			**200°C**			**250°C**			**250°C photo-ox**		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	5347	0	-									
50%				-	-	-						
75%							28277	0	-			
Max										-	-	-

RD (Relative Difference) is calculated as the ratio between the Absolute Difference (between two duplicates) and the average. It has to be lower than 14% for efficiencies greater than 40%:

$$RD = \frac{abs(E1 - E2)}{mean(E1.E2)} < 14$$

For efficiencies lower than 40%, the Absolute Difference has to be lower than 6%:

$$AD = abs(E1 - E2) < 6$$

IM-15

*Results of **IFP tests** performed on the fresh oil and emulsified residues*
At 5°C:

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	8	16						
50%			3	5				
75%					0	nd		
Max							nd	nd

	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	15032	12	67									
50%				31215	4	50						
75%							-	0	-			
Max										-	-	-

At 15°C

	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	42	nd						
50%			6	16				
75%					nd	nd		
Max							nd	nd

	15°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	4137	42	-									
50%				24046	11	91						
75%							-	-	-			
Max										nd	-	-

*Results of **MNS tests** performed on the fresh oil and emulsified residues*
At 5°C:

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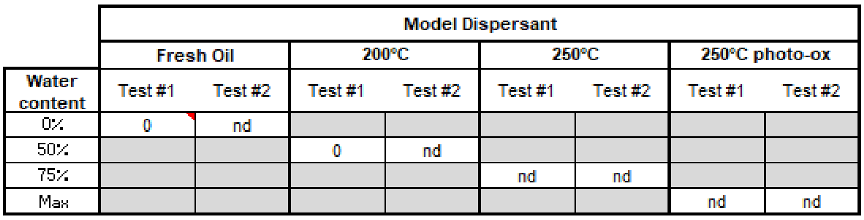
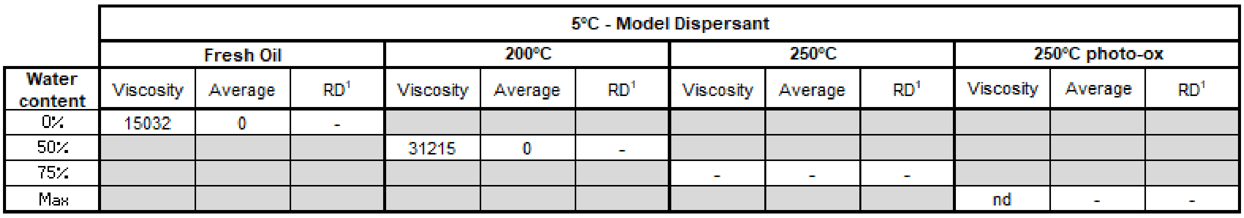
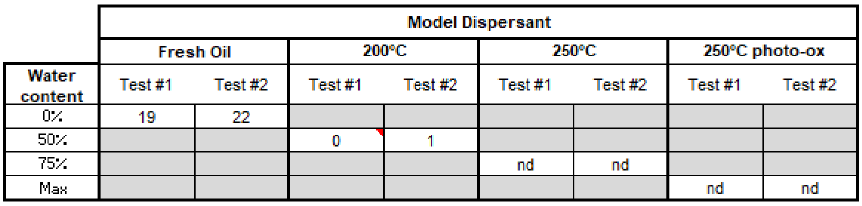


	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	0	nd						
50%			0	nd				
75%					nd	nd		
Max							nd	nd

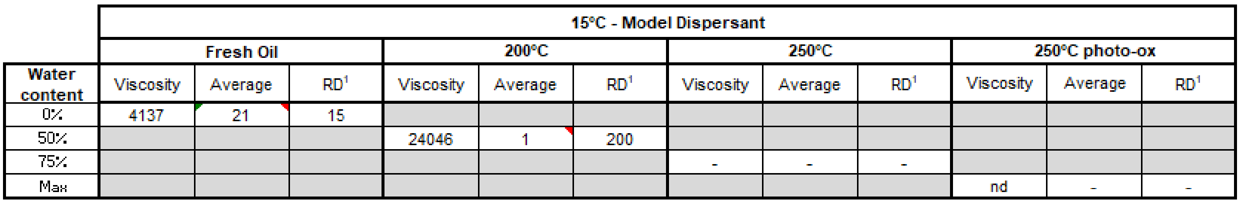


	5°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	15032	0	-									
50%				31215	0	-						
75%							-	-	-			
Max										nd	-	-

At 15°C:



	Model Dispersant							
	Fresh Oil		200°C		250°C		250°C photo-ox	
Water content	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
0%	19	22						
50%			0	1				
75%					nd	nd		
Max							nd	nd



	15°C - Model Dispersant											
	Fresh Oil			200°C			250°C			250°C photo-ox		
Water content	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]	Viscosity	Average	RD[1]
0%	4137	21	15									
50%				24046	1	200						
75%							-	-	-			
Max										nd	-	-

RD (Relative Difference) is calculated as the ratio between the Absolute Difference (between two duplicates) and the average. It has to be lower than 14% for efficiencies greater than 40%:

$$RD = \frac{abs(E1 - E2)}{mean(E1. E2)} < 14$$

For efficiencies lower than 40%, the Absolute Difference has to be lower than 6%:

$$AD = abs(E1 - E2) < 6$$

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APPENDIX 5

Comparison of dispersants efficiency
IFP test protocols

(Model Dipsersant, Dasic Slickgone NS, Finasol OSR 52, Corexit 9500)

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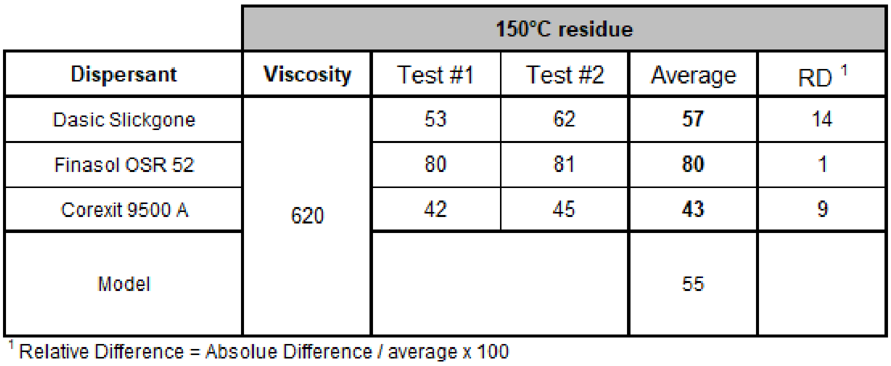
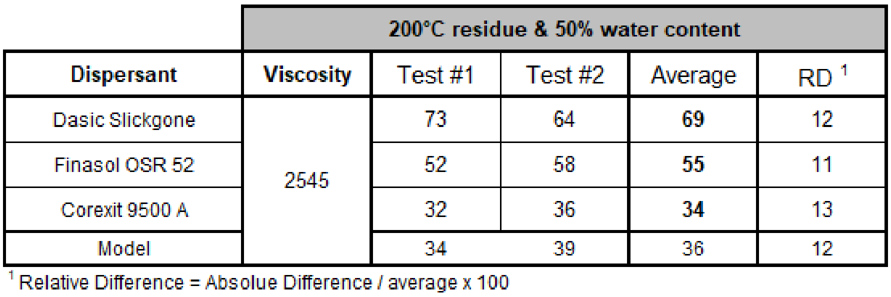
IM-5

Table 1 *IFP Experiments at 15°C*



	150°C residue				
Dispersant	**Viscosity**	Test #1	Test #2	Average	RD [1]
Dasic Slickgone	620	53	62	**57**	14
Finasol OSR 52		80	81	**80**	1
Corexit 9500 A		42	45	**43**	9
Model				55	

[1] Relative Difference = Absolue Difference / average x 100



	200°C residue & 50% water content				
Dispersant	**Viscosity**	Test #1	Test #2	Average	RD [1]
Dasic Slickgone	2545	73	64	**69**	12
Finasol OSR 52		52	58	**55**	11
Corexit 9500 A		32	36	**34**	13
Model		34	39	36	12

[1] Relative Difference = Absolue Difference / average x 100

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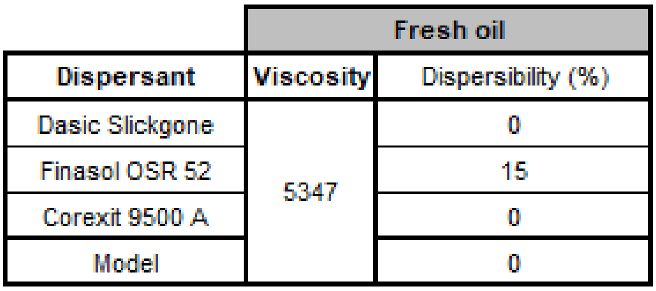
IM-14

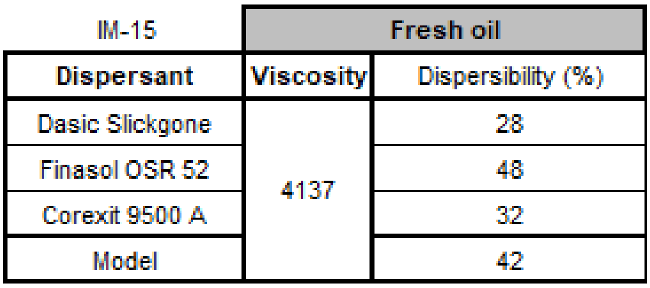
Table 2 *IFP Experiments at 15°C*



	Fresh oil	
Dispersant	**Viscosity**	Dispersibility (%)
Dasic Slickgone	5347	0
Finasol OSR 52		15
Corexit 9500 A		0
Model		0

IM-15

Table 3 *IFP Experiments at 15°C*



IM-15	Fresh oil	
Dispersant	**Viscosity**	Dispersibility (%)
Dasic Slickgone	4137	28
Finasol OSR 52		48
Corexit 9500 A		32
Model		42

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APPENDIX 6

OSCAR composition of the oils

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IM-5

***Table 1** Results of the OSCAR characterization of the fresh IM-5 sample (data from Task 3.1)*

Composition (% weight)	Individuals compounds
C_1-C_4 (dissolved gas)	0.08
C_5-saturates (n-/iso-/cyclo)	0.00
C_6- saturates (n-/iso-/cyclo)	0.00
C_7- saturates (n-/iso-/cyclo)	0.00
C_8- saturates (n-/iso-/cyclo)	0.00
C_9- saturates (n-/iso-/cyclo)	0.02
Benzene	0.00
C_1-Benzene	0.00
C_2-Benzenes	0.00
C_3-Benzenes	0.02
C_4 & C_5-Benzenes	0.00
C_{10}- saturates (n-/iso-/cyclo)	2.09
C_{11}-C_{12} (total saturates + aromatics)	3.88
C_{13}-C_{14} (total saturates + aromatics)	5.32
C_{15}-C_{16} (total saturates + aromatics)	5.31
C_{17}-C_{18} (total saturates + aromatics)	4.97
C_{19}-C_{20} (total saturates + aromatics)	4.04
C_{21}-C_{25} (total saturates + aromatics)	8.86
C_{25}+ (total)	63.02
Naphthalenes 1 (C_0-C_1 alkylated)	0.17
Naphthalenes 2 (C_2-C_3 alkylated)	0.22
PAHs 1 (medium solubility)	0.29
PAHs 2 (low solubility)	0.54
Phenols (C_0-C_4)	-

⬜ High dissolution potential

🟦 Medium dissolution potential

🟧 Low dissolution potential

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IM-14

Table 2 *Results of the OSCAR characterization of the fresh IM-14 sample*

Composition (% weight)	Individuals compounds
C_1-C_4 (dissolved gas)	0.07
C_5-saturates (n-/iso-/cyclo)	0,00
C_6- saturates (n-/iso-/cyclo)	0,00
C_7- saturates (n-/iso-/cyclo)	0,00
C_8- saturates (n-/iso-/cyclo)	0,00
C_9- saturates (n-/iso-/cyclo)	0,00
Benzene	0,00
C_1-Benzene	0,00
C_2-Benzenes	0,00
C_3-Benzenes	0,00
C_4 & C_5-Benzenes	0,00
C_{10}- saturates (n-/iso-/cyclo)	0,00
C_{11}-C_{12} (total saturates + aromatics)	1.11
C_{13}-C_{14} (total saturates + aromatics)	0.92
C_{15}-C_{16} (total saturates + aromatics)	1.12
C_{17}-C_{18} (total saturates + aromatics)	1.35
C_{19}-C_{20} (total saturates + aromatics)	2.36
C_{21}-C_{25} (total saturates + aromatics)	9.65
C_{25}+ (total)	82.74
Naphthalenes 1 (C_0-C_1 alkylated)	0.02
Naphthalenes 2 (C_2-C_3 alkylated)	0.10
PAHs 1 (medium solubility)	0.14
PAHs 2 (low solubility)	0.42
Phenols (C_0-C_4)	-

⬜ High dissolution potential

🟦 Medium dissolution potential

🟧 Low dissolution potential

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IM-15

Table 3 *Results of the OSCAR characterization of the fresh IM-15 sample*

Composition (% weight)	Individuals compounds
C_1-C_4 (dissolved gas)	0.03
C_5-saturates (n-/iso-/cyclo)	0.00
C_6- saturates (n-/iso-/cyclo)	0.00
C_7- saturates (n-/iso-/cyclo)	0.00
C_8- saturates (n-/iso-/cyclo)	0.00
C_9- saturates (n-/iso-/cyclo)	0.01
Benzene	0.00
C_1-Benzene	0.00
C_2-Benzenes	0.00
C_3-Benzenes	0.02
C_4 & C_5-Benzenes	0.00
C_{10}- saturates (n-/iso-/cyclo)	0.00
C_{11}-C_{12} (total saturates + aromatics)	4.01
C_{13}-C_{14} (total saturates + aromatics)	4.36
C_{15}-C_{16} (total saturates + aromatics)	4.47
C_{17}-C_{18} (total saturates + aromatics)	3.29
C_{19}-C_{20} (total saturates + aromatics)	3.33
C_{21}-C_{25} (total saturates + aromatics)	5.94
C_{25}+ (total)	71.66
Naphthalenes 1 (C_0-C_1 alkylated)	0.64
Naphthalenes 2 (C_2-C_3 alkylated)	0.40
PAHs 1 (medium solubility)	0.46
PAHs 2 (low solubility)	1.38
Phenols (C_0-C_4)	-

⬜ High dissolution potential

🟦 Medium dissolution potential

🟧 Low dissolution potential

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APPENDIX 7

HAP quantification (in µg/g)

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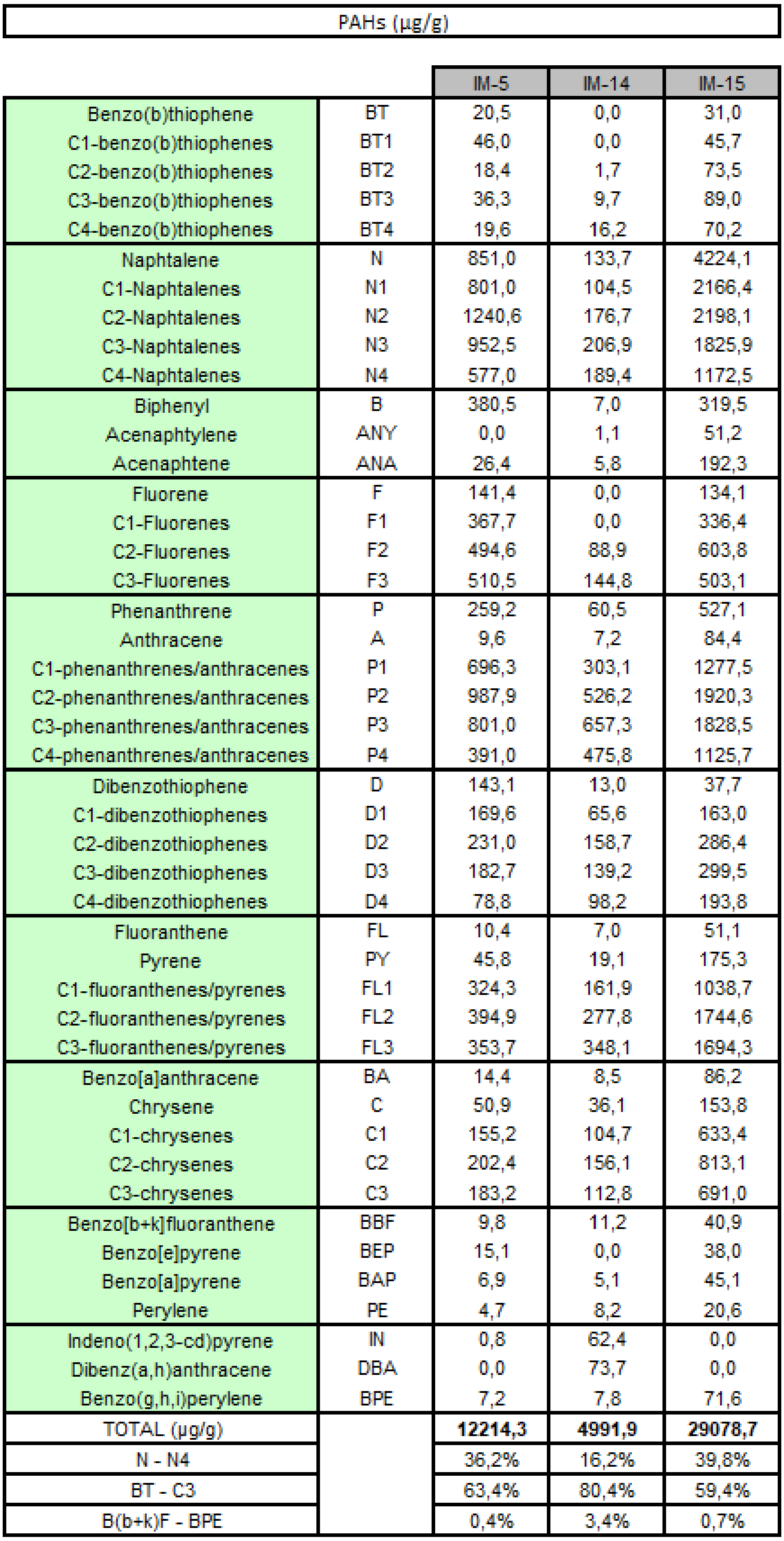

PAHs (µg/g)

		IM-5	IM-14	IM-15
Benzo(b)thiophene	BT	20,5	0,0	31,0
C1-benzo(b)thiophenes	BT1	46,0	0,0	45,7
C2-benzo(b)thiophenes	BT2	18,4	1,7	73,5
C3-benzo(b)thiophenes	BT3	36,3	9,7	89,0
C4-benzo(b)thiophenes	BT4	19,6	16,2	70,2
Naphtalene	N	851,0	133,7	4224,1
C1-Naphtalenes	N1	801,0	104,5	2166,4
C2-Naphtalenes	N2	1240,6	176,7	2198,1
C3-Naphtalenes	N3	952,5	206,9	1825,9
C4-Naphtalenes	N4	577,0	189,4	1172,5
Biphenyl	B	380,5	7,0	319,5
Acenaphtylene	ANY	0,0	1,1	51,2
Acenaphtene	ANA	26,4	5,8	192,3
Fluorene	F	141,4	0,0	134,1
C1-Fluorenes	F1	367,7	0,0	336,4
C2-Fluorenes	F2	494,6	88,9	603,8
C3-Fluorenes	F3	510,5	144,8	503,1
Phenanthrene	P	259,2	60,5	527,1
Anthracene	A	9,6	7,2	84,4
C1-phenanthrenes/anthracenes	P1	696,3	303,1	1277,5
C2-phenanthrenes/anthracenes	P2	987,9	526,2	1920,3
C3-phenanthrenes/anthracenes	P3	801,0	657,3	1828,5
C4-phenanthrenes/anthracenes	P4	391,0	475,8	1125,7
Dibenzothiophene	D	143,1	13,0	37,7
C1-dibenzothiophenes	D1	169,6	65,6	163,0
C2-dibenzothiophenes	D2	231,0	158,7	286,4
C3-dibenzothiophenes	D3	182,7	139,2	299,5
C4-dibenzothiophenes	D4	78,8	98,2	193,8
Fluoranthene	FL	10,4	7,0	51,1
Pyrene	PY	45,8	19,1	175,3
C1-fluoranthenes/pyrenes	FL1	324,3	161,9	1038,7
C2-fluoranthenes/pyrenes	FL2	394,9	277,8	1744,6
C3-fluoranthenes/pyrenes	FL3	353,7	348,1	1694,3
Benzo[a]anthracene	BA	14,4	8,5	86,2
Chrysene	C	50,9	36,1	153,8
C1-chrysenes	C1	155,2	104,7	633,4
C2-chrysenes	C2	202,4	156,1	813,1
C3-chrysenes	C3	183,2	112,8	691,0
Benzo[b+k]fluoranthene	BBF	9,8	11,2	40,9
Benzo[e]pyrene	BEP	15,1	0,0	38,0
Benzo[a]pyrene	BAP	6,9	5,1	45,1
Perylene	PE	4,7	8,2	20,6
Indeno(1,2,3-cd)pyrene	IN	0,8	62,4	0,0
Dibenz(a,h)anthracene	DBA	0,0	73,7	0,0
Benzo(g,h,i)perylene	BPE	7,2	7,8	71,6
TOTAL (µg/g)		**12214,3**	**4991,9**	**29078,7**
N - N4		36,2%	16,2%	39,8%
BT - C3		63,4%	80,4%	59,4%
B(b+k)F - BPE		0,4%	3,4%	0,7%

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APPENDIX 8

Results of the flume test experiments at 5 °C and 15 °C

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Table 1 *IM-5* – Results of experiment in the canal at 5 °C

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time (hours)	Viscosity (mPa.s)	Density	Water content (%)	Evaporation (% vol.)	Flash Point (°C)	Emulsions Stability Ratio	Oil Adhesion (g/m^2)	IFP disp. (%)	MNS disp. (%)
0	3967	0.920	0	-	91.0	-	-	64.0	53.0
1	5003	0.923	12.5	0.8	90.0	1.00	1810		
2	3944	0.923	10.0	0.5	92.0	1.00	1700		
4	3752	0.920	18.2	0.4	92.0	1.00	1695		
6	4762	0.926	31.9	0.5	95.5	1.00	1825		
8	7677	0.926	53.8	nd	> 100	1.00	2740		
14	11392	0.943	69.3	0.9	> 100	0.85	3700		
24	14671	0.958	76.4	0	> 100	0.60	1990	0.0	0.0
27	14640	0.950	76.5	0	> 100	0.67	1945		
30	16099	0.953	86.8	0.1	> 100	0.85	2440		
48	20300	0.975	77.3	1.5	> 100	0.80	1035	0.0	0.0
53	21312	0.963	79.4	1.3	> 100	0.81	750		
72	21483	0.963	80.6	2.9	> 100	0.85	530	nd	nd
77	21807	0.980	80.7	2.7	> 100	0.84	670		
96	25441	0.981	82.7	2.5	> 100	0.88	845		
101	24259	0.981	83.9	2.4	> 100	0.88	850		
168	31666	0.987	82.2	3.0	> 100	0.90	340	nd	nd

- : not significant

nd: not determined
NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

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Table 2 *IM-5* – Results of experiment in the canal at 15 °C

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time (hours)	Viscosity (mPa.s)	Density	Water content (%)	Evaporation (% vol.)	Flash Point (°C)	Emulsions Stability Ratio	Oil Adhesion (g/m²)	IFP disp. (%)	MNS disp. (%)
0	542	0.912	0	-	91.0	-	-	56	44
1	617	0.913	2.4	0	91.5	1.00	310		
2	605	0.914	3.6	0	94.0	1.00	250		
4	617	0.922	2.7	0	97.5	1.00	615		
6	688	0.922	5.8	0	> 100	1.00	615		
8	1134	0.940	26.0	0	> 100	0.13	855		
14	6317	0.967	76.4	0.4	> 100	0.20	2750		
24	8111	0.972	84.0	1.0	> 100	0.46	1760	6	13
27	7738	0.981	85.2	1.4	> 100	0.58	1610		
30	8455	0.992	83.1	1.5	> 100	0.48	1190		
48	11476	0.992	85.3	2.0	> 100	0.51	495	9	9
53	10813	0.996	85.1	3.3	> 100	0.52	305		
72	10767	0.993	86.0	4.6	> 100	0.60	415	nd	nd
77	12075	0.996	87.3	3.6	> 100	0.82	210		
96	9427	0.997	85.9	5.4	> 100	0.82	200		
101	8557	0.997	87.3	4.7	> 100	0.87	265		
168	19401	0.997	86.6	7.7	> 100	0.78	165	nd	nd

\- : not significant

nd: not determined

NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

Table 3 ***IM-14*** **– Results of experiment in the canal at 5 °C**

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time	Viscosity	Density	Water content	Evaporation	Flash Point	Emulsions	Oil Adhesion	IFP disp.	MNS disp.
(hours)	(mPa.s)		(%)	(% vol.)	(°C)	Stability Ratio	(g/m²)	(%)	(%)
0	71747	0.9448	-	-	> 100	-	-	0	0
1	55826	0.8560	3.2	0.8	> 100	1.000	940		
2	nm	0.8708	3.8	0.4	> 100	1.000	990		
4	56088	0.8749	4.5	0	> 100	1.000	1505		
6	63461	0.9007	8.8	0.7	> 100	1.000	1425		
8	53255	0.8832	5.5	3.4	> 100	1.000	1435		
14	61001	nm	16.4	0.8	> 100	1.000	nm		
25	59474	0.8810	8.1	2.3	> 100	1.000	nm	0	0
30	56323	0.8824	20.6	1.4	> 100	1.000	nm		
48	63342	0.8670	22.6	1.4	> 100	1.000	nm	nd	nd

- : not significant

nm: not measurable
nd: not determined
NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

Table 4 ***IM-14* – Results of experiment in the canal at 15 °C**

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time	**Viscosity**	**Density**	**Water content**	**Evaporation**	**Flash Point**	**Emulsions**	**Oil Adhesion**	**IFP disp.**	**MNS disp.**
(hours)	(mPa.s)		(%)	(% vol.)	(°C)	Stability Ratio	(g/m²)	(%)	(%)
0	17122	0.9372	-		> 100	-	-	0	0
1	18369	0.9261	6.4	3.4	> 100	1.000	6200		
2	22272	0.9114	5.0	0.1	> 100	1.000	6810		
4	21694	0.8912	8.2	2.1	> 100	1.000	7305		
6	22452	0.9124	11.1	1.3	> 100	1.000	6865		
8	21816	0.9112	14.9	1.8	> 100	1.000	5900		
14	20179	0.8650	23.2	1.1	> 100	1.000	4710		
24	19485	0.8220	47.9	0.5	> 100	0.744	3440	2	9
26	19465	0.8175	47.3	0	> 100	0.794	3475		
30	19877	0.8187	50.7	0	> 100	0.752	4455		
48	19931	0.8537	58.2	0.0	> 100	0.824	2480	2	6
53	22247	0.8456	59.6	0	> 100	0.834	2495		
72	22833	0.8529	61.0	0	> 100	0.851	4250	1	4
76	23610	0.8937	57.9	1.7	> 100	0.814	3520		
144	35709	0.9192	64.8	0	> 100	0.851	2870	nd	nd
149	32948	0.9220	62.6	0.5	> 100	0.755	3620		

- : not significant

nd: not determined
NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

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Table 5 *IM-15*– Results of experiment in the canal at 5 °C

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time	Viscosity	Density	Water content	Evaporation	Flash Point	Emulsions	Oil Adhesion	IFP disp.	MNS disp.
(hours)	(mPa.s)		(%)	(% vol.)	(°C)	Stability Ratio	(g/m²)	(%)	(%)
0	19406	0.9582	-	-	86.5	-	-	12	0
1	18537	0.9596	10.6	7.2	88.0	1.000	3350		
2	17513	0.9650	18.9	1.8	90.5	1.000	3020		
4	20354	0.9607	30.1	3.5	92.0	0.899	2585		
6	23488	0.9684	39.2	5.5	94.0	0.689	2960		
8	26344	0.9655	45.5	0	94.0	0.601	2500		
13	46394	0.9744	49.0	0	97.0	0.884	5390		
24	75504	0.9746	55.5	6.9	> 100	0.856	4025	0	0
26	64820	0.9760	55.2	8.6	> 100	0.858	1030		
30	77128	0.9879	nm	9.3	> 100	nd	1185		
48	111457	0.9870	61.9	7.8	> 100	0.879	785	0	0
53	121801	0.9864	64.2	14.5	> 100	0.890	310		
72	138781	1.0045	62.7	12.3	> 100	0.888	355	nd	nd
76	117453	0.9983	65.8	10.6	> 100	0.867	565		
144	202298	1.0049	66.2	9.7	> 100	0.926	1235		
149	199859	0.9979	68.5	10.2	> 100	0.885	355		
168	222613	1.0031	67.9	12.2	> 100	0.916	530	nd	nd

- : not significant

nd: not determined
NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

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Table 6 *IM-15* – Results of experiment in the canal at 15 °C

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time (hours)	**Viscosity** (mPa.s)	**Density**	**Water content** (%)	**Evaporation** (% vol.)	**Flash Point** (°C)	**Emulsions** Stability Ratio	**Oil Adhesion** (g/m²)	**IFP disp.** (%)	**MNS disp.** (%)
0	4402	0.9496	-	-	94.5	-	-	42	27
1	4918	0.9623	12.4	0	98.5	0.867	1635		
2	5688	0.9632	24.7	0.9	99.5	0.887	1575		
4	6837	0.9755	30.0	0	> 100	nm	2140		
6	10842	0.9877	59.1	0	> 100	0.622	2605		
8	nm	0.9883	61.0	0	> 100	0.391	3265		
14	17825	0.9723	66.8	3.1	> 100	0.470	3155		
24	26973	0.9847	70.0	3.0	> 100	0.666	3055	1	2
26	30303	0.9783	70.7	5.4	> 100	0.685	3110		
30	32365	0.9740	70.5	2.1	> 100	0.689	3565		
48	46842	0.9835	79.1	6.8	> 100	0.817	2940	1	1
53	48448	0.9801	70.1	5.4	> 100	0.705	1890		
72	60454	0.9900	68.3	5.0	> 100	0.699	2900	0	0
76	55666	0.9864	73.6	0	> 100	0.801	1160		
144	72174	0.9882	73.8	18.4	> 100	0.818	3215		
149	75046	0.9846	72.0	18.8	> 100	0.825	860		
168	107214	0.9903	63.8	12.5	> 100	0.831	395	0	0

- : not significant

nd: not determined
NB: given the very low evaporation rate of the product, some values were negative and were thus set to 0 in the table

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Table 7 *IM-15* – Results of experiment in the canal at 15 °C, in freshwater

	Physical properties				Safety	Response techniques			
						Recovery		Chemical dispersion	
Weathering time	Viscosity	Density	Water content	Evaporation	Flash Point	Emulsions	Oil Adhesion	IFP disp.	MNS disp.
(hours)	(mPa.s)		(%)	(% vol.)	(°C)	Stability Ratio	(g/m²)	(%)	(%)
0	4410	0,9496	-	-	94.5	-	-	0	0
1	6768	0,9506	12.3	nd	nd	0.858	2035		
2	7074	0,9514	19.4	nd	nd	0.922	2010		
4	8443	0,9558	31.6	nd	nd	1.000	2185		
6	8193	0,9598	48.0	nd	nd	0.755	2285		
8	12381	0,9635	51.9	nd	nd	0.655	2770		
14	13279	0,9562	56.8	nd	nd	0.632	3130		
24	26156	0,9658	66.9	nd	nd	0.802	1295	nd	nd
26	27306	0,9702	63.2	nd	nd	0.740	1150		
30	26925	0,9161	68.2	nd	nd	0.814	875		
48	40107	0,9684	69.6	nd	nd	0.789	635	nd	nd
53	44508	0,9657	71.1	nd	nd	0.804	1140		
72	48208	0,9759	66.9	nd	nd	0.802	545	nd	nd
76	52035	0,9620	71.9	nd	nd	0.880	380		
144	62458	0,9695	72.4	nd	nd	0.855	525		
149	64351	0,9414	69.0	nd	nd	0.874	320		
168	86346	0,0000	68.5	nd	nd	0.918	390	nd	nd

- : not significant

nd: not determined

APPENDIX 9

True Boiling Point (TBP) curve

Combination of laboratory data (up to 250°C) and simulated distillation (from 200 to 520°C)

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IM-5 (data from from Task 3.1 for this sample)

Table 1 *Results of laboratory and simulated distillation of the fresh IM-5 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
21	0.0	200	5.0
21	0.1	210	6.3
22	0.1	220	7.5
22	0.1	230	9.1
23	0.1	240	10.5
25	0.1	250	12.7
30	0.1	260	14.6
40	0.1	270	16.5
50	0.1	280	18.5
65	0.1	290	19.9
75	0.1	300	22.0
80	0.1	310	23.7
90	0.1	320	25.0
95	0.2	330	26.8
99	0.5	340	28.5
100	1.1	350	30.2
105	1.2	360	31.9
115	1.2	370	33.5
120	1.3	380	35.1
130	1.6	390	36.8
140	1.7	400	38.7
150	1.8	410	40.5
160	1.9	420	42.3
170	1.9	430	43.9
180	2.1	440	45.4
190	2.2	450	46.6
195	2.3	460	47.5
200	2.4	470	48.2
205	2.7	480	48.7
210	3.3	490	49.1
215	3.6	500	49.4
220	4.4	510	49.6
226	5.6	520	49.8
230	6.4		
235	7.7		
240	8.5		
245	9.3		
250	10.5		

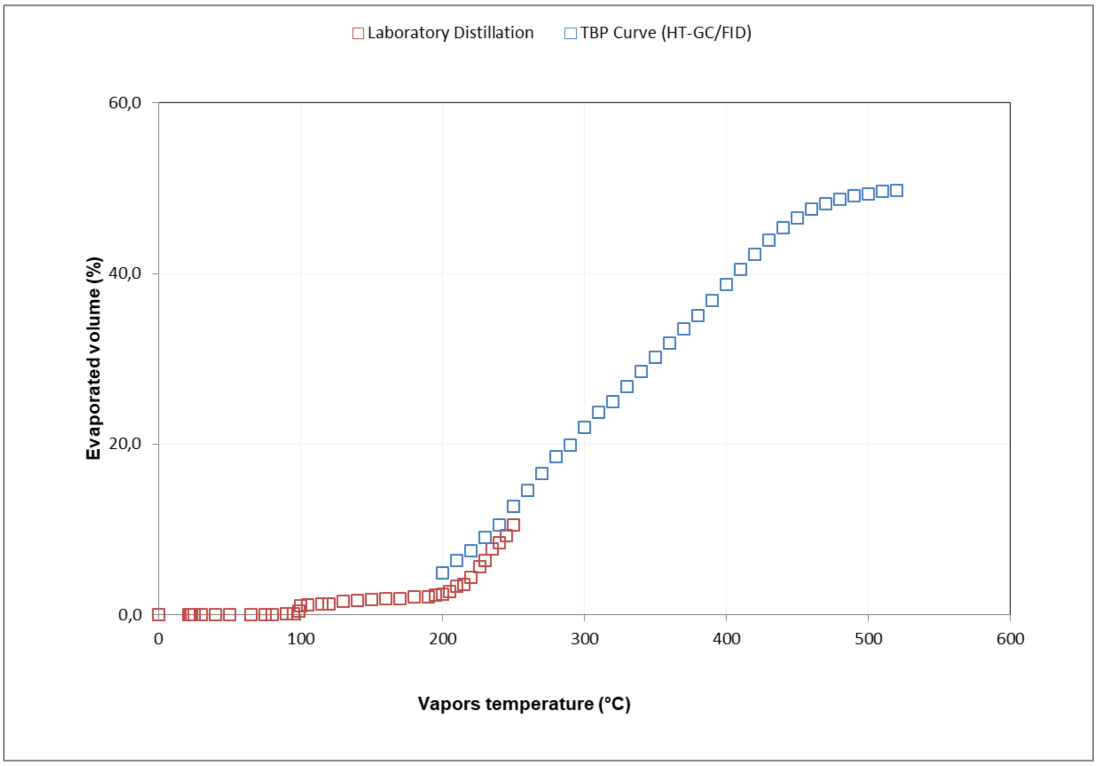

Figure 1 *Combination of results obtained for the laboratory and simulated distillation of the fresh Wakashio oil (IM-5 sample from Task 3.1)*

IM-14

Table 1 *Results of laboratory and simulated distillation of the IM-14 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
18	0.0	200	0.3
21	0.0	210	0.4
31	0.0	220	0.5
32	0.0	230	0.6
38	0.0	240	0.7
43	0.0	250	0.9
46	0.0	260	1.0
52	0.0	270	1.2
85	0.0	280	1.4
100	0.0	290	1.5
120	0.0	300	1.8
130	0.0	310	2.1
140	0.0	320	2.4
150	0.0	330	2.8
160	0.1	340	3.3
170	0.1	350	3.8
180	0.2	360	4.4
190	0.2	370	5.1
205	0.3	380	5.9
211	0.3	390	6.8
220	0.4	400	7.8
230	0.5	410	8.9
240	0.7	420	10.3
250	1.0	430	11.7
		440	12.9
		450	14.0
		460	14.9
		470	15.7
		480	16.5
		490	17.1
		500	17.6
		510	18.1
		520	18.6

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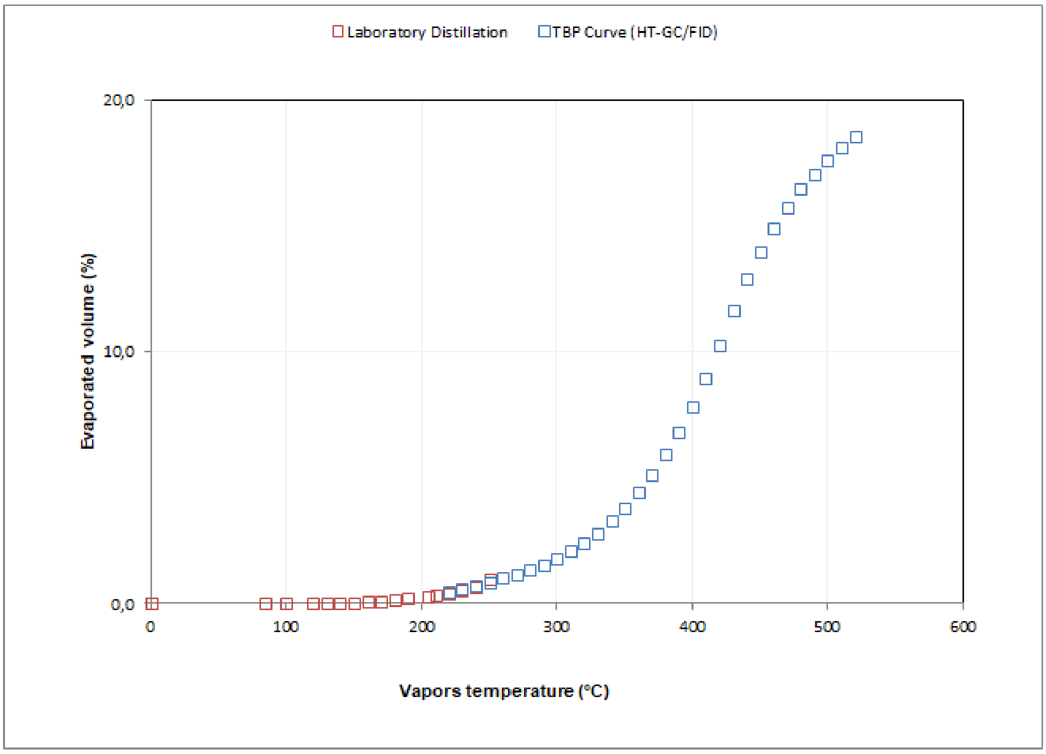

Figure 1 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-14 sample*

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IM-15

Table 1 *Results of laboratory and simulated distillation of the fresh IM-15 sample*

Vapor temperature (°C)	Evaporated vol. (%) Laboratory data	Vapor temperature (°C)	Evaporated vol. (%) SIMDIST data
23	0.0	200	1.3
26	0.0	210	3.0
27	0.0	220	4.2
30	0.0	230	5.9
32	0.0	240	7.3
33	0.0	250	9.1
31	0.0	260	10.8
33	0.0	270	12.5
35	0.0	280	14.2
40	0.0	290	15.6
46	0.0	300	17.4
48	0.0	310	19.0
50	0.0	320	20.3
55	0.0	330	21.8
65	0.0	340	23.1
90	0.0	350	24.4
95	0.0	360	25.6
100	0.0	370	26.7
120	0.0	380	27.8
126	0.1	390	28.8
150	0.2	400	29.8
175	0.2	410	30.8
180	0.2	420	31.8
185	0.3	430	33.0
190	0.4	440	34.1
195	1.1	450	34.9
200	1.4	460	35.7
205	1.8	470	36.4
212	2.1	480	37.0
217	2.7	490	37.6
220	3.7	500	38.1
225	4.9	510	38.7
230	5.7	520	39.2
234	6.9		
240	6.9		
245	8.4		
250	9.6		

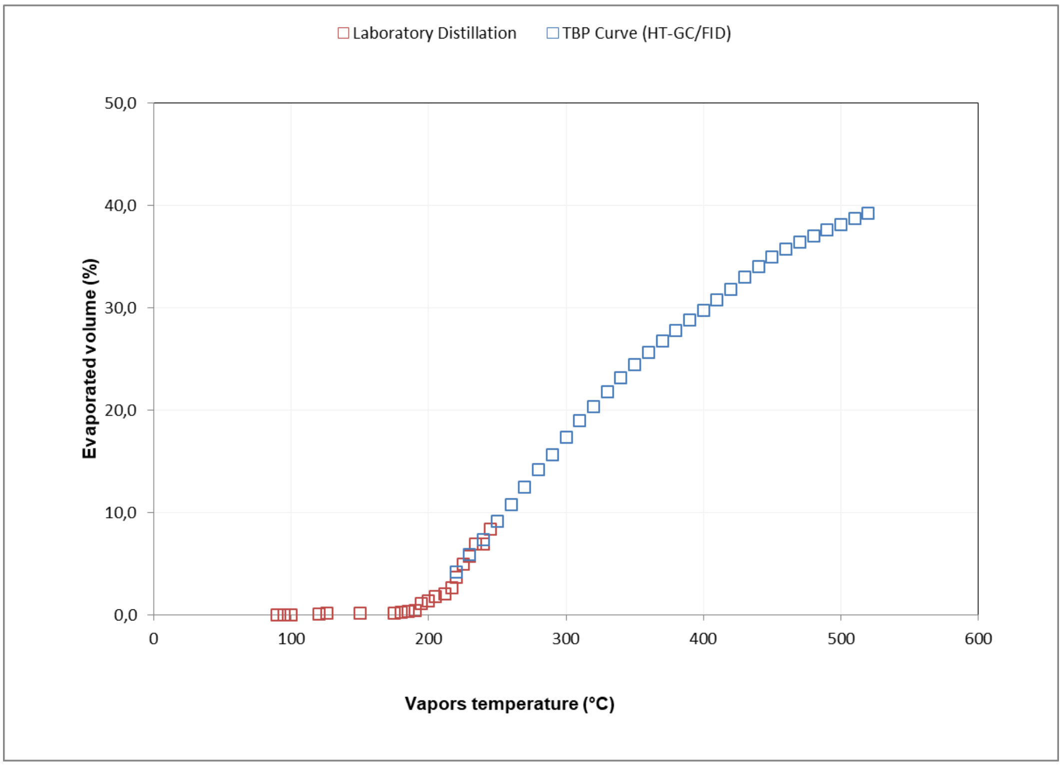

Figure 1 *Combination of results obtained for the laboratory and simulated distillation of the fresh IM-15 sample*

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APPENDIX 10

Pictures of the VLSFOs in the polludrome, at 5 and 15°

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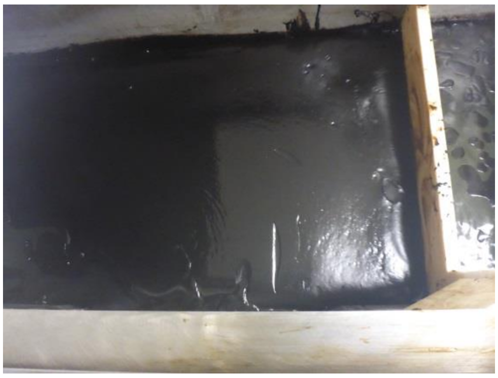
IM-5

T0

T2

T5



T7

T9

T11

T13

T16

Pictures taken from the top of the Polludrome® during the IM-5 sample weathering at 5°C

T0

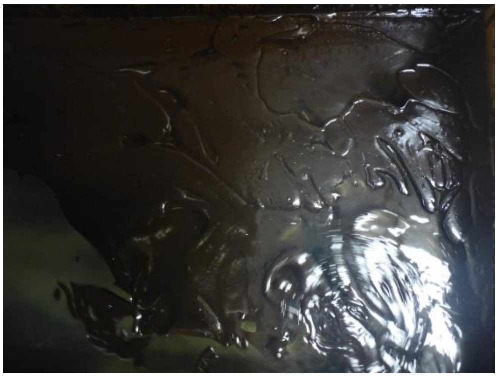
T2

T6

T7

T9

T11



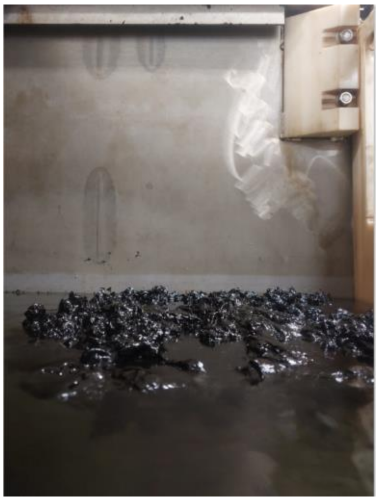
T13

T16

Pictures taken from the top of the Polludrome® during the IM-5 sample weathering at 15°C

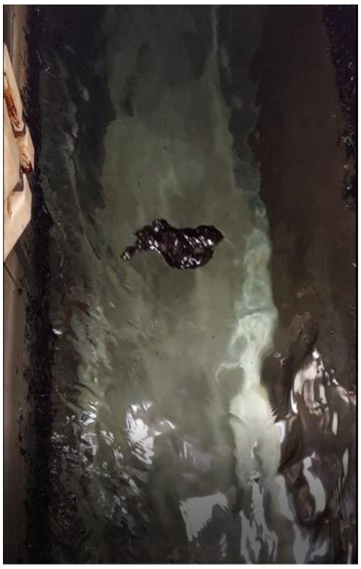
IM-14

T0



T1 (side view)

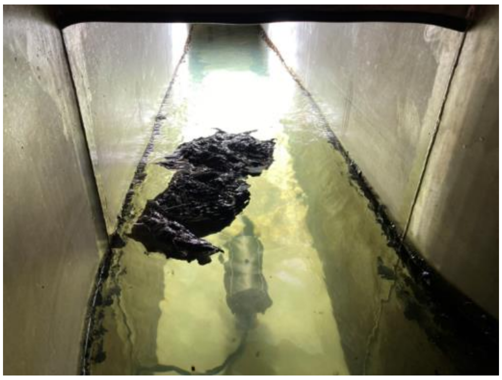
T6



T6

Pictures taken from the top of the Polludrome® during the IM-14 sample weathering at 5°C

T0



T1

T15

T15

Pictures taken from the top of the Polludrome® during the IM-14 sample weathering at 15°C

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IM-15

T0

T2

T16

T16

Pictures taken from the top of the Polludrome® during the IM-15 sample weathering at 5°C

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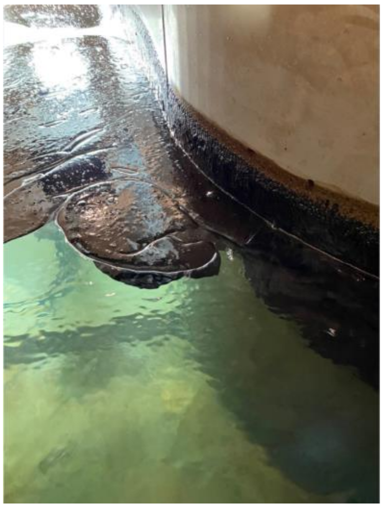
T0

T4

T16



T16

Pictures taken from the top of the Polludrome® during the IM-15 sample weathering at 15°C

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APPENDIX 3

Task 3.3 – Ecotoxicity

WP3

DELIVERABLE D3.2

TASK 3.3: ECOTOXICITY

FINAL REPORT

Co-funded by the European Union

Executive summary

In the frame of the Task 3.3 of the EU co-funded IMAROS project, ecotoxicity tests were performed on 3 marine organisms: the marine algae *Phaeodactylum tricornatum*, the marine copepod *Acartia tonsa* and the amphipod *Corophium sp*.

The tests were conducted in accordance with the "Harmonised Offshore Chemical Notification Format" (OSPARCOM).

Three VLSFO (IM-5, IM-14 and IM-15), tested at different concentrations, served as tested substances. The algae and the copepods were exposed to the soluble fraction of the oils collected thanks to WAF (Water Accommodated Fraction) preparations. Amphipods were exposed to direct contact with the oils.

Algal growth inhibition (for algae) and average mortality (for copepods and amphipods) was calculated in order to determine EC_{50} (effective concentration, for algae) or LC_{50} (lethal concentration, for copepods and amphipods), respectively resulting in 50 % inhibition of growth rate or in the loss of 50 % of the population studied.

The study led to the following conclusions:

- Marine algal growth inhibition test: even for the highest PAH concentration tested, the growth rate was still very close to the one of the control. EC_{50} at 72 hours could not be determined for the 3 VLSFO tested.

  No toxicity was observed on *Phaeodactylum tricornatum* by testing those 3 VLSFO.

- Determination of acute lethal toxicity to marine copepods: for the 3 VLSFO tested, LC_{50} was below the lowest PAH concentration tested (i.e. the lowest PAH concentration tested led already to a mortality higher than 50 %), **demonstrating to a high sensibility of those organisms. However, the sensitivity observed may be explained by a stress (potentially induced by the transport time) of the tested organisms**.
- Sediment bioassay using the amphipod *Corphium sp.:* **an impact of the oil on the mortality rate was observed.** The determination of LC_{50} seems related to the PAH quantification in the 3 oils, with the lowest LC_{50} calculated for IM-15.

Additionally, PAH quantification for the three VLSFO tested are in the same range as traditional fuel oils already analysed at Cedre. In addition, WAF toxicity measured by SINTEF on the thirteen LSFO collected in the frame of the Task 3.1 (Faksness and Daling, 2022[1]) is also in the same range as traditional fuel oils. **The toxicity of the LSFO tested seems thus to be in the same range as the one observed for traditional fuel oils.**

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[1] Chemical composition of fuel oils : Faksness and Daling, SINTEF report n° 2022:00383 - Unrestricted

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1 – MARINE ALGAL GROWTH INHIBITION TEST

The objective of the study is to conduct a marine algae toxicity test in accordance with the "Harmonised Offshore Chemical Notification Format" (OSPARCOM).

1 – 1 Materials and methods

1 – 1 - 1 Test method

This procedure is based on the ISO 10253: 2016 standard (Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornatum)* to which certain technical adjustments have been made.

1 – 1 - 2 Test item

Test substances: 3 VLSFO :IM-5, IM-14 and IM-15.

1 – 1 - 3 Reference item

Reference/positive substance: potassium dichromate ($K_2Cr_2O_7$).

1 – 1 - 4 Test system

An algal kit (Algaltoxkit) containing the test species *Phaeodactylum tricornatum* is used for the trials. Test organisms are incorporated in the kits in a "resting" or "immobilized" form, from which they can be activated "on demand" prior to the performance of the toxicity test. The transfer of the algal inoculum in an adequate growth medium reactivates the microalgae leading, within 3 days, to a culture in the exponential growth phase ready for the bioassay.

WAF diluted series were prepared from each VLSFO (IM-5, IM-14 and IM-15) and were mixed with algal culturing medium and algae at the concentration of ~1.10^4 cell/mL, leading to the following dissolved PAH concentrations:

- IM-5: from 1.6 to 25.6 µg .L^{-1} dissolved PAHs;
- IM-14: from 0.8 to 12.9 µg .L^{-1} dissolved PAHs;
- IM-15: from 9.9 to 156.1 µg .L^{-1} dissolved PAHs.

PAH quantifications in the WAF are presented in Appendix 1. Controls containing only algal culturing medium and algae at ~1.10^4 cell/mL were prepared in triplicate for each VLSFO tested.

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A reference/positive test was also carried out with $K_2Cr_2O_7$ in triplicate. The dilution series prepared for the reference test ranged from 3.2 to 31.7 mg/L.

Algae were incubated for 3 days in an incubator at 20°C (+/- 2 °C) with a constant uniform illumination supplied by cool white fluorescent lamps (10000 lux sideway illumination).

Optical density (OD at 670 nm) was used to measure the biomass evolution, and consequently to calculate the algal growth inhibition, with measurements every 24h. The EC_{50} (Effective Concentration) values are defined as the concentration resulting in 50 % inhibition of growth rate. The tests were performed in disposable spectrophotometric cells of 10 cm path-length (= “long cells”) as test vials, which allows for direct and rapid scoring of the OD in any spectrophotometer equipped with a holder for 10 cm cells. Optical density measurements of the algal suspensions at 670 nm wavelength in 10 cm long cells correlate very well with algal numbers and are hence in accordance with the prescription of ISO Guideline 10253 and other standard methods for determination of algal densities.

1 – 1 - 5 Test details

Growth medium

Synthetic seawater is prepared for algal culturing medium by mixing deionized water to salts and nutrients provided in the algal kit.

Preparation of test solutions

A WAF solution was prepared by adding a certain mass (amount necessary to cover the totality of the water surface) of each VLSFO to 1.7 L of filtered seawater (18.9 g for IM-5, 93.3 g for IM-14 and 107 g for IM-15), leading to a quantity of oil of 10.9 g/L, 53.7 g/L and 61.6 g/L, respectively) (*Figure 1*). The water was gently mixed for 24 in the dark and the WAF (i.e. soluble fraction) were then collected using the tap located at the bottom of the flask.

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Figure 1 *Example of WAF preparation (IM-15)*

This “100 % WAF” (with nutrients addition) was then diluted with the algal growth medium at 50 % (i.e , 50 % of WAF and 50 % algal growth medium), 25 %, 12.5% and 6.25% to obtain a range of PAHs concentrations. Nutrients and silica solutions were added to those WAFs. PAHs concentration of the “100% WAF” solution was determined by SBSE-TD-GC/MS analyses and the calculated concentration was then divided accordingly to the dilution factor. By doing so, the « 100% WAF » represents the maximum amount of oil added to the experimental system.

Experimental set-up

Algal inoculum were poured in 10 cm cells (final concentration ~1.10^4 cell/mL in growing stage), filled with WAFs or with the growth medium for the controls, in triplicate for each condition.

Three replicates of reference substance ($K_2Cr_2O_7$), from 3.2 to 31.7 mg.L^{-1}, served as positive control. $K_2Cr_2O_7$ was dissolved and diluted in algal culturing medium.

Incubation

Algae were incubated for 3 days in an incubator with a constant uniform illumination supplied by cool white fluorescent lamps (10000 lux sideway illumination), at 20°C (+/- 2 °C).

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***Figure 2** Incubation of the algae*

Measurements

The test was run for 72 ± 2 hours and the algal growth inhibition was determined based on by optical density measurements.

Calculations

Optical Density (OD) was determined in each cell after (after shaking of the cell) after 24h, 48h and 72h incubation. Mean daily OD values were calculated for the 3 replicate cells and algal growth inhibitions were determined for each test concentration. EC_{50} at 72h was calculated according to internationally accepted procedures (e.g. ISO 8692 or OECD Guideline 201). Regtox programme for automatic data treatment was used to determine the EC_{50}.

Test acceptance criteria

For a test to be valid, the following conditions should be fulfilled:

- The average growth rate in the control replicates shall be at least 1,4 d^{-1}. This growth rate corresponds to an increase in cell density by a factor of 67 in 72 h.

- The variation coefficient of the growth rate in the control replicates shall not exceed 5 %.

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1 - 2 Results and discussion

Percentages of inhibition were calculated following the ISO 10253 standard, by calculating first the average specific growth rate μ, for each test culture, using the following equation:

$$\mu = \frac{\ln(N_1) - \ln(N_0)}{t_1 - t_0} \qquad \text{(Eq. 1)}$$

with μ the **specific growth rate** (in d^{-1}), N_x the number of cell at the time x, and $t1 - t0$ the number of days between t_1 and t_0 . Growth rates are presented in *Tables 1-4*.

Table 1 *Growth rate (d-1) obtained with the positive substance* $K_2Cr_2O_7$

K2Cr2O7 - Specific growth rate μ (d-1)					
T = 24h					
Concentration (mg/L)	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
Control	1,41	0,95	1,17	1,18	19,36
3,17	1,24	0,66	1,15	1,02	30,77
5,56	0,55	0,00	0,48	0,34	87,32
9,92	0,22	0,00	0,15	0,12	91,82
17,86	0,00	0,00	0,00	0,00	-
31,74	0,00	0,00	0,00	0,00	-
T = 48h					
Concentration (mg/L)	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
Control	1,56	1,49	1,53	1,53	2,28
3,17	1,43	1,41	1,47	1,44	2,33
5,56	1,37	1,29	1,38	1,35	3,73
9,92	1,11	1,04	1,10	1,08	3,16
17,86	0,72	0,72	0,85	0,76	10,00
31,74	0,40	0,39	0,12	0,30	51,77
T = 72h					
Concentration (mg/L)	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
Control	1,50	1,50	1,49	1,50	0,38
3,17	1,40	1,40	1,40	1,40	0,29
5,56	1,31	1,32	1,30	1,31	0,50
9,92	1,14	1,12	1,16	1,14	1,70
17,86	0,92	0,93	0,91	0,92	0,83
31,74	0,50	0,51	0,48	0,50	2,94

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Table 2 *Growth rate (d-1) obtained with IM-5*

		IM-5 - Specific growth rate μ (d^{-1})				
T = 24h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,14	1,14	1,12	1,13	1,29
6,25% WAF	**1,6**	1,57	1,62	2,11	1,77	16,80
12,5% WAF	**3,3**	1,71	1,56	1,84	1,71	8,25
25% WAF	**6,5**	1,49	1,59	1,47	1,52	4,31
50% WAF	**13,0**	1,76	1,35	1,36	1,49	15,43
100% WAF	**25,6**	1,91	1,65	1,85	1,80	7,48
T = 48h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,55	1,60	1,66	1,60	3,47
6,25% WAF	**1,6**	1,62	1,62	1,78	1,67	5,68
12,5% WAF	**3,3**	1,65	1,64	1,63	1,64	0,64
25% WAF	**6,5**	1,66	1,66	1,63	1,65	1,17
50% WAF	**13,0**	1,65	1,61	1,62	1,63	1,35
100% WAF	**25,6**	1,60	1,55	1,61	1,59	1,89
T = 72h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,49	1,50	1,50	1,50	0,69
6,25% WAF	**1,6**	1,52	1,54	1,53	1,53	0,48
12,5% WAF	**3,3**	1,54	1,53	1,53	1,53	0,34
25% WAF	**6,5**	1,54	1,53	1,52	1,53	0,42
50% WAF	**13,0**	1,53	1,51	1,53	1,52	0,61
100% WAF	**25,6**	1,47	1,49	1,52	1,49	1,53

Table 3 *Growth rate (d-1) obtained with IM-14*

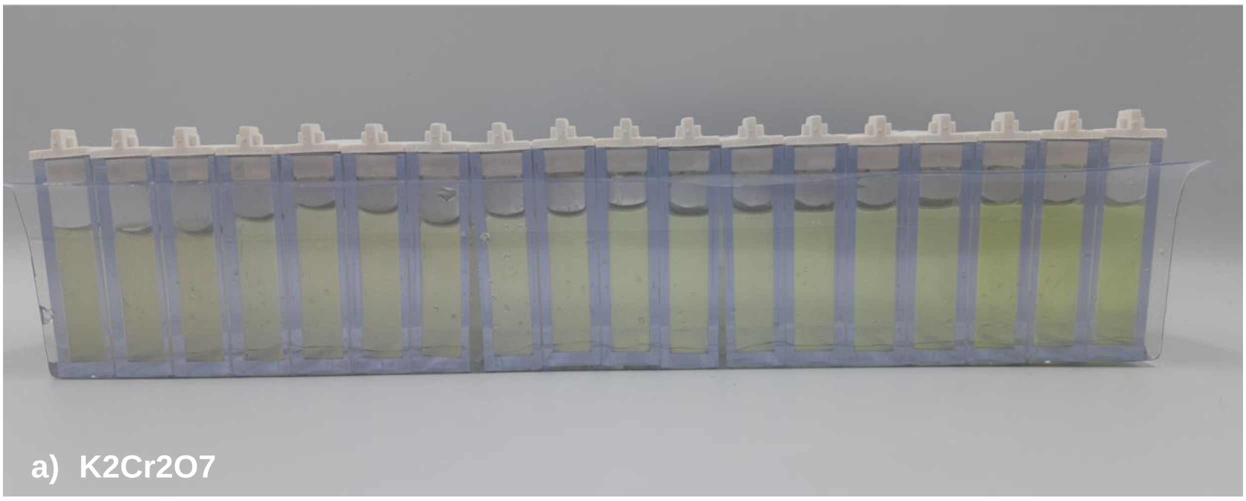
		IM-14 - Specific growth rate (d^{-1})				
T = 24h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	0,96	0,58	0,84	0,79	24,92
6,25% WAF	**0,8**	1,27	1,41	1,26	1,31	6,47
12,5% WAF	**1,6**	1,45	1,26	1,41	1,37	7,47
25% WAF	**3,3**	1,17	1,34	1,29	1,27	6,85
50% WAF	**6,6**	1,14	0,84	1,46	1,15	26,83
100% WAF	**12,9**	0,82	1,00	0,85	0,89	10,64
T = 48h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,55	1,56	1,57	1,56	0,54
6,25% WAF	**0,8**	1,67	1,62	1,58	1,62	2,81
12,5% WAF	**1,6**	1,64	1,67	1,64	1,65	0,93
25% WAF	**3,3**	1,65	1,67	1,65	1,66	0,86
50% WAF	**6,6**	1,63	1,59	1,65	1,62	1,87
100% WAF	**12,9**	1,57	1,56	1,57	1,57	0,40
T = 72h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,51	1,50	1,49	1,50	0,42
6,25% WAF	**0,8**	1,53	1,51	1,52	1,52	0,41
12,5% WAF	**1,6**	1,53	1,53	1,52	1,53	0,38
25% WAF	**3,3**	1,52	1,53	1,53	1,53	0,30
50% WAF	**6,6**	1,52	1,52	1,53	1,52	0,57
100% WAF	**12,9**	1,49	1,50	1,51	1,50	0,60

Table 4 *Growth rate (d-1) obtained with IM-15*

		IM-15 - Specific growth rate (d^{-1})				
T = 24h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,54	1,34	1,39	1,42	7,30
6,25% WAF	**9,9**	1,72	1,82	2,01	1,85	7,85
12,5% WAF	**19,8**	1,11	1,46	1,58	1,38	17,66
25% WAF	**39,7**	1,39	1,59	1,44	1,47	7,17
50% WAF	**79,4**	1,11	1,33	1,08	1,18	11,62
100% WAF	**156,1**	0,19	0,67	0,88	0,58	61,21
T = 48h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,61	1,62	1,68	1,64	2,51
6,25% WAF	**9,9**	1,74	1,65	1,64	1,68	3,36
12,5% WAF	**19,8**	1,64	1,69	1,65	1,66	1,60
25% WAF	**39,7**	1,66	1,69	1,65	1,67	1,22
50% WAF	**79,4**	1,56	1,58	1,56	1,57	0,76
100% WAF	**156,1**	1,39	1,51	1,42	1,44	4,31
T = 72h						
Condition	**[HAP]diss. (µg/L)**	Replicate 1	Replicate 2	Replicate 3	Mean	CV %
0% WAF	**Control**	1,53	1,53	1,55	1,54	0,72
6,25% WAF	**9,9**	1,53	1,53	1,51	1,53	0,63
12,5% WAF	**19,8**	1,51	1,54	1,53	1,53	0,78
25% WAF	**39,7**	1,53	1,53	1,53	1,53	0,26
50% WAF	**79,4**	1,50	1,51	1,50	1,50	0,30
100% WAF	**156,1**	1,43	1,41	1,42	1,42	0,70

The average growth rates in the control replicates at 72h are all above 1.4 d^{-1} (between 1.50 and 1.54 d^{-1}). The variation coefficient of the growth rate in the control replicates are all below 5 % (between 0.38 and 0.72%). The two test acceptance criteria are thus fulfilled.

Pictures of the spectrophotometric cells at the end of the trials (T=72h) are shown on *Figure 2*. A change of color is observed only for the positive substance.



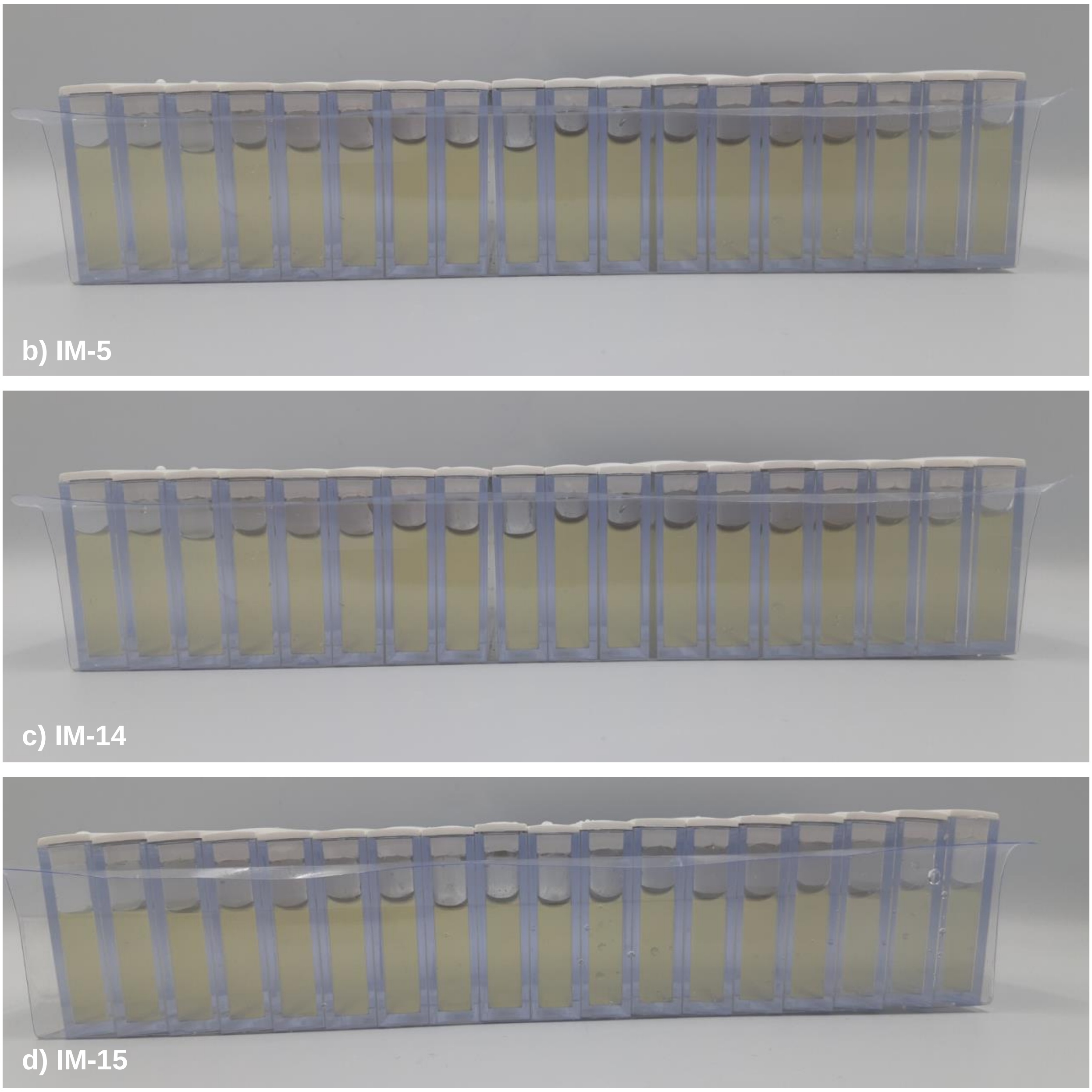


Figure 2 *Spectrophotometric cells at the end of the trials (T=72h). Controls are at the left part of the picture, highest concentration on the right part (side view of the 10 cm cells)*

Figure 3 presents the growth rate calculated for the 3 VLSFO, at 72h, for the different WAF conditions. WAF conditions, instead of HAP concentrations, were represented on the x-axis in order to compare the samples on the same graph. *Figure 4* presents the growth rate measured for the positive substance.

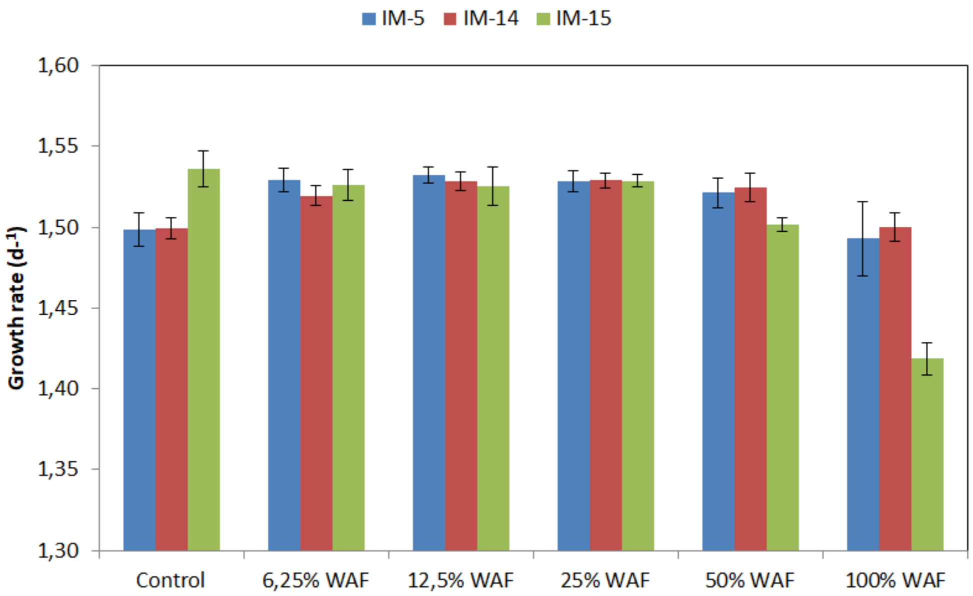


Figure 3 *Growth rates (d^{-1}), at 72h, of the diatom Phaeodactylum tricornutum exposed to the VLSFO IM-5, IM-14 and IM-15*

Figure 4 *Growth rates (d^{-1}), at 72h, of the diatom Phaeodactylum tricornutum exposed to the toxic of reference: $K_2Cr_2O_7$ (concentrations in mg/L)*

Growth rates in the control ranged from 1.50 ± 0.01 d^{-1} (IM-5, IM-14 and toxic of reference) to 1.54 ± 0.01 d^{-1} (IM-15). An inhibition was observed with the reference substance ($K_2Cr_2O_7$) (*Figure 4*), with specific growth rates decreasing from 1.50 ± 0.01 d^{-1} (control, without $K_2Cr_2O_7$) to 0.50 ± 0.01 d^{-1} (maximum concentration: 31.7 mg/L $K_2Cr_2O_7$), leading to an inhibition of 66 ± 1 %. Compared to this inhibition, no growth inhibition was clearly observed when the diatoms were exposed to dissolved compounds of the 3 VLSFO tested. Only the sample IM-15 exhibited a slight decrease for the 50% and 100% WAF, with a growth rate reaching 1.42 ± 0.01 d^{-1} for the 100% WAF condition, leading to an inhibition of 7.6 ± 0.6 %.

The percentage inhibition was then calculated from the mean value of μ for each test concentration and for control, from the following equation:

$$I_{\mu i} = \frac{\bar{\mu}_c - \bar{\mu}_i}{\bar{\mu}_c} \, x \, 100 \qquad \text{(Eq. 2)}$$

Where $I_{\mu i}$ is the percentage inhibition for the test concentration *i*, $\bar{\mu}_i$ is the mean growth rate for the concentration *i* and $\bar{\mu}_c$ is the mean growth rate for the control.

In order to determine EC_{50}, the normalized growth rate (100- $I_{\mu i}$) of each individual cell was calculated (*Table 5*). When possible (i.e. when a sufficient decrease of growth rate is calculated) data are plotted against the test concentrations and a non-linear model is fitted to the experimental data points by regression analysis, using the Regtox software, in order to determine the EC_{50}. Given the low impact of the 3 VLSFO on the growth rate (normalized growth rate close to 100% for all the conditions tested, see *Table 5*), the non-linear model could only be fitted for the toxic of reference $K_2Cr_2O_7$ (*Figure 5*).

Table 5 *Normalized growth rate calculated for the 3 VLSFO (IM-5, IM-14 and IM-15) and the positive substance* $K_2Cr_2O_7$

		$K_2Cr_2O_7$ - Normalized growth rate (%)		
	Concentrations (g/L)	Rep. 1	Rep. 2	Rep. 3
	0	100,17	100,27	99,56
	3,17	93,73	93,65	93,22
	5,56	87,52	87,99	87,11
	9,92	76,06	75,07	77,64
	17,86	61,14	61,96	61,03
	31,74	33,52	34,20	32,27
		IM-5 - Normalized growth rate (%)		
Condition	**[HAP]diss. (µg/L)**	Rep. 1	Rep. 2	Rep. 3
0% WAF	**Control**	99,20	100,43	100,37
6,25% WAF	**1,6**	101,60	102,57	102,00
12,5% WAF	**3,3**	102,62	102,19	101,95
25% WAF	**6,5**	102,46	101,94	101,61
50% WAF	**13,0**	101,95	100,81	101,82
100% WAF	**25,6**	98,14	99,59	101,19
		IM-14 - Normalized growth rate (%)		
Condition	**[HAP]diss. (µg/L)**	Rep. 1	Rep. 2	Rep. 3
0% WAF	**Control**	100,46	99,90	99,63
6,25% WAF	**0,8**	101,80	101,00	101,20
12,5% WAF	**1,6**	101,91	102,32	101,54
25% WAF	**3,3**	101,66	101,98	102,26
50% WAF	**6,6**	101,64	101,12	102,27
100% WAF	**12,9**	99,59	99,83	100,73
		IM-15 - Normalized growth rate (%)		
Condition	**[HAP]diss. (µg/L)**	Rep. 1	Rep. 2	Rep. 3
0% WAF	**Control**	99,34	99,88	100,77
6,25% WAF	**9,9**	99,65	99,73	98,61
12,5% WAF	**19,8**	98,46	99,99	99,42
25% WAF	**39,7**	99,80	99,41	99,31
50% WAF	**79,4**	97,44	98,02	97,80
100% WAF	**156,1**	92,86	91,63	92,58

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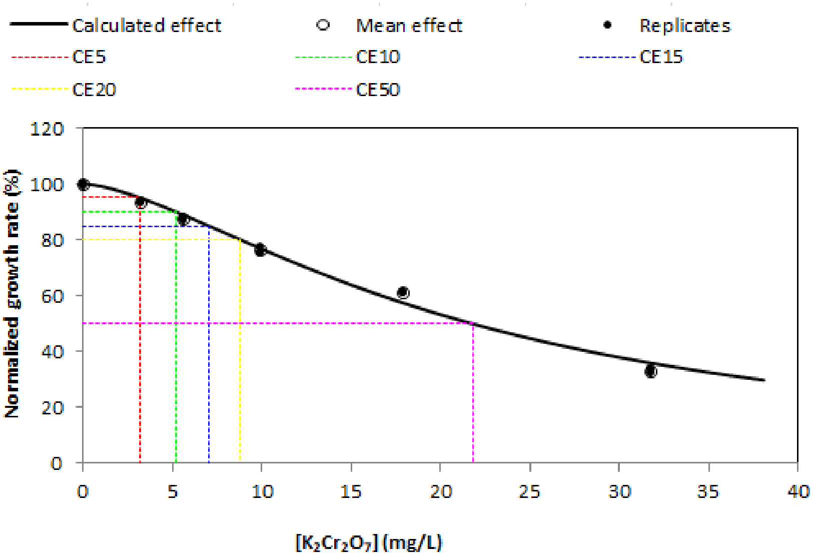

Figure 5 *Normalised growth rate (in d^{-1}) calculated with the positive substance $K_2Cr_2O_7$ and determination of the EC_{50} with the Regtox programme*

Regtox programme allowed thus only the calculation of a EC_{50} for the reference substance ($K_2Cr_2O_7$). This calculated concentration is 21.7 mg/L. Interlaboratory exercise (using *Phaedodactylum tricornutum* as algae and $K_2Cr_2O_7$ as positive control) based on the ISO 10253 standards was performed by 10 laboratories and led to the determination of an EC_{50} of 20.1 ± 5.3 mg/L (n = 7). The results obtain during this study are in accordance with those values.

1 - 3 Conclusion

The test acceptance criteria given are fulfilled:

- The average growth rate in the control replicates at 72h were all above 1.4 d^{-1} (between 1.50 and 1.54 d^{-1}).
- The variation coefficient of the growth rate in the control replicates were all below 5% (between 0.38 and 0.72%).

Even for the highest quantity of oil tested, EC_{50} at 72 hours could not be determined for the 3 VLSFO tested.

IM-5: For the highest quantity of oil tested (10.9 g.L^{-1}), leading to the dissolution of 25.6 µg.L^{1} PAHs, the average growth rate was 1.48 ± 0.02 d^{-1} (Control growth rate: 1.50 ± 0.01d^{-1}) and the EC50 at 72 hours could not be determined.

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IM-14: For the highest quantity of oil tested (53.7 g.L^{-1}), leading to the dissolution of 12.9 µg.L^{-1} PAHs, the average growth rate was 1.50 ± 0.01 d^{-1} (Control growth rate: 1.50 ± 0.01 d^{-1}) and the EC50 at 72 hours could not be determined.

IM-15: For the highest quantity of oil tested (61.6 g.L^{-1}), leading to the dissolution of 156.1 µg.L^{-1} PAHs, the average growth rate was 1.42 ± 0.01 d^{-1} (Control growth rate: 1.55 ± 0.01 d^{-1}) and the EC50 at 72 hours could not be determined.

2 – DETERMINATION OF ACUTE LETHAL TOXICITY TO MARINE COPEPODS

2 – 1 Materials and methods

2 – 1 – 1 Test method

The study was conducted with the marine copepod *Acartia tonsa.* The procedure was based on the ISO 14669: 2003 standard (Determination of acute lethal toxicity to marine copepods), to which certain technical adjustments have been made.

2 – 1 - 2 Test item

Test substances: VLSFO samples IM-5, IM-14 and IM-15.

2 – 1 - 3 Reference item

Reference substance: 3.5 Dichlorophenol (CAS: 591-35-5).

2 – 1 – 4 Test system

The marine copepods *Acartia tonsa* were used in this test. The copepods were obtained from the company GUERNSEY SEA FARM on 09/02/22, and were kept in acclimation tanks at 20°C. They were fed with mixed algae diet until 24 hours before the experimentation. The copepods were then exposed to the tested substances for a period of 48 hours. Mortalities were recorded at 24 and 48 hours and the concentration leading to the loss of 50 % of the population studied (LC_{50}) were determined.

2 – 1 - 5 Test details

Seawater

Natural seawater from an unpolluted site (Aquarium Oceanopolis, Brest) was used, after filtration on 0,45 µm filters.

Diet

The mixed algae diet was obtained from the company GUERNSEY SEA FARM.

Preparation of test solutions

Five Water Accomodaded Fractions (WAFs) were prepared, from a “100% WAF” characterized with an oil concentration of:

- 10.4 $g.L^{-1}$ for IM-5, corresponding to dissolved PAHs concentrations of 69.6 $µg.L^{-1}$.
- 53.0 $g.L^{-1}$ for IM-14, corresponding to dissolved PAHs concentrations of 12.0 $µg.L^{-1}$.

- 63.1 g.L^{-1} for IM-15, corresponding to dissolved PAHs concentrations of 162.9 µg.L^{-1}.

PAHs concentrations were determined by SBSE analyses.

Five Water Accomodaded Fractions (WAFs) were prepared, PAH concentrations varying between:

- 4.3 µg.L^{-1} and 69.6 µg.L^{-1} for IM-5;
- 0.75 µg.L^{-1} and 12.0 µg.L^{-1} for IM-14;
- 10.2 µg.L^{-1} and 162.9 µg.L^{-1} for IM-15.

PAH quantifications in the WAF are presented in Appendix 1.

Experimental set-up

5 mL solutions (seawater spiked or not with the reference and the test substances) were incubated in 6 mL flasks, in the number of 4 replicates for each concentration and 12 replicates for the blank. Five concentrations of the test substance were prepared in a geometric series. One concentration of reference substance was prepared, at 1.0 mg.L^{-1}, (4 replicates). 5 copepods were randomly distributed to each test vessel.

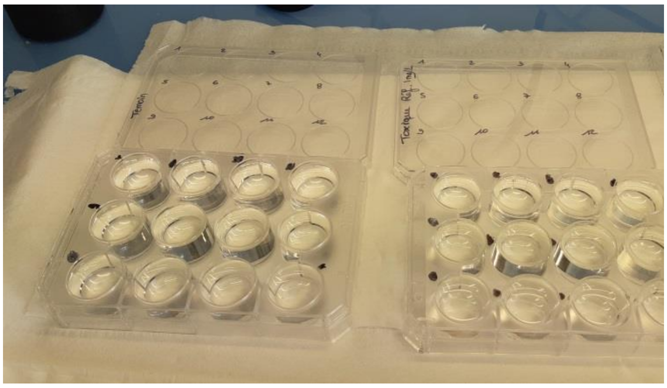

Figure 6 *Preparation of the control and the reference substance flasks*

Incubation

Tests were run under continuous light from fluorescent tubes of universal natural white type, at a temperature of 20°C ± 2 °C.

Measurements and observations

Tests were run for 48 ± 2 hours. The mortality was recorded each day.

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Figure 7 *Observation and counting of copepods*

Calculations

Final result was expressed as LC_{50} values.

Test acceptance criteria

A test can be considered acceptable if the following conditions are fulfilled:

- The oxygen saturation at the end of the test should be ≥ 4 $mg.L^{-1}$

- The mortality rate observed in the blanks should be ≤ 10 %

- The toxicity of the reference substance (3,5-dichlorophenol) should be in an acceptable range: 1$mg.L^{-1}$ >>> between 20% and 80% mortality.

Oxygen saturation could not be followed during those tests.

2 – 2 Results and discussion

Table 1-5 indicate the responses obtained for the controls (*Table 6*), the reference substance (3,5-Dichlorophenol) (*Table 7*) and the 3 VLSFO (IM-5, IM-14 and IM-15) (*Tables 8 – 10*).

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Table 6 *Mortality observed for the controls after 24 and 48 hours exposure period.*

Controls	Result 24h				
Concentration (mg.L^{-1})	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
0	12	5	0	0	7
		5	0	0	
		5	0	0	
		5	3	60	
		5	0	0	
		10	0	0	
		6	0	0	
		5	1	20	
		5	0	0	
		5	0	0	
		5	0	0	
		5	0	0	

Controls	Result 48h				
Concentration (mg.L^{-1})	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
0	12	5	0	0	21
		5	0	0	
		5	1	20	
		5	3	60	
		5	2	40	
		10	1	10	
		6	1	17	
		5	1	20	
		5	1	20	
		5	1	20	
		5	1	20	
		5	1	20	

Table 7 *Mortality observed for the reference substance (3,5- Dichlorophenol) after 24 and 48 hours exposure period.*

Controls REF TOX.	Result 24h				
Concentration (mg.L^{-1})	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
1,02	12	5	4	80	61
		4	4	100	
		5	4	80	
		5	4	80	
		5	3	60	
		5	2	40	
		1	0	0	
		5	4	80	
		6	3	50	
		5	2	40	
		6	3	50	
		6	4	67	

Controls REF TOX.	Result 48h				
Concentration (mg.L^{-1})	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
1,02	12	5	4	80	79
		4	4	100	
		5	4	80	
		5	4	80	
		5	4	80	
		5	4	80	
		1	1	100	
		5	4	80	
		6	3	50	
		5	5	100	
		6	3	50	
		6	4	67	

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Table 8 *Mortality observed for IM-5 after 24 and 48 hours exposure period.*

IM-5		Result 24h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**4,3**	4	5	2	40	10
			3	0	0	
			5	0	0	
			5	0	0	
12.5% WAF	**8,7**	4	5	1	20	14
			5	1	20	
			5	0	0	
			6	1	17	
25% WAF	**17,4**	4	4	1	25	16
			5	2	40	
			5	0	0	
			5	0	0	
50% WAF	**34,8**	4	5	2	40	35
			5	1	20	
			5	3	60	
			5	1	20	
100% WAF	**69,6**	4	4	1	25	16
			5	2	40	
			4	0	0	
			5	0	0	

IM-5		Result 48h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**4,3**	4	5	5	100	100
			3	3	100	
			5	5	100	
			5	5	100	
12.5% WAF	**8,7**	4	5	3	60	90
			5	5	100	
			5	5	100	
			6	6	100	
25% WAF	**17,4**	4	4	4	100	100
			5	5	100	
			5	5	100	
			5	5	100	
50% WAF	**34,8**	4	5	5	100	100
			5	5	100	
			5	5	100	
			5	5	100	
100% WAF	**69,6**	4	4	4	100	100
			5	5	100	
			4	4	100	
			5	5	100	

Table 9 *Mortality observed for IM-14 after 24 and 48 hours exposure period.*

IM-14		Result 24h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**0,8**	4	5	1	20	32
			5	2	40	
			5	0	0	
			3	2	67	
12.5% WAF	**1,5**	4	5	3	60	38
			5	1	20	
			6	2	33	
			5	2	40	
25% WAF	**3,0**	4	5	2	40	30
			5	1	20	
			5	1	20	
			5	2	40	
50% WAF	**6,0**	4	5	2	40	35
			5	2	40	
			5	1	20	
			5	2	40	
100% WAF	**12,0**	4	6	1	17	29
			5	0	0	
			5	3	60	
			5	2	40	
IM-14		Result 48h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**0,8**	4	5	3	60	70
			5	2	40	
			5	4	80	
			3	3	100	
12.5% WAF	**1,5**	4	5	4	80	71
			5	2	40	
			6	5	83	
			5	4	80	
25% WAF	**3,0**	4	5	4	80	60
			5	4	80	
			5	1	20	
			5	3	60	
50% WAF	**6,0**	4	5	2	40	55
			5	3	60	
			5	4	80	
			5	2	40	
100% WAF	**12,0**	4	6	5	83	96
			5	5	100	
			5	5	100	
			5	5	100	

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Table 10 *Mortality observed for IM-15 after 24 and 48 hours exposure period.*

IM-15		Result 24h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**10.2**	4	5	0	0	20
			5	2	40	
			5	0	0	
			5	2	40	
12.5% WAF	**20,4**	4	5	0	0	9
			5	1	20	
			5	0	0	
			6	1	17	
25% WAF	**40,7**	4	6	2	33	33
			5	1	20	
			5	0	0	
			5	4	80	
50% WAF	**81,4**	4	5	0	0	16
			5	0	0	
			4	1	25	
			5	2	40	
100% WAF	**162,9**	4	6	1	17	39
			5	2	40	
			5	2	40	
			5	3	60	
IM-15		Result 48h				
Condition	**[HAP] (µg.L^{-1})**	Replicates	Initial number of copepods	Number of dead copepods	% mortality	Average mortality (%)
6.25% WAF	**10.2**	4	5	4	80	90
			5	4	80	
			5	5	100	
			5	5	100	
12.5% WAF	**20,4**	4	5	4	80	80
			5	4	80	
			5	3	60	
			6	6	100	
25% WAF	**40,7**	4	6	4	67	82
			5	4	80	
			5	4	80	
			5	5	100	
50% WAF	**81,4**	4	5	5	100	90
			5	3	60	
			4	4	100	
			5	5	100	
100% WAF	**162,9**	4	6	6	100	100
			5	5	100	
			5	5	100	
			5	5	100	

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Considering the controls, the mean mortality increases from 7% after 24 hours to 21% after 48 hours, leading to mortality above the acceptable threshold value (10%) at the end of the test.

Considering the positive control, the mean mortality increases from 61% after 24 hours to 79% after 48 hours, leading to mortality at the upper range of the acceptable threshold value (80%) at the end of the test.

Those two observations highlight the sensitivity of the tested organisms. This sensitivity could be due to a stress induced by the transport time.

However when comparing the mortality rates between 24h and 48h, a clear impact of the VLSFOs is observed compared to the controls (*Figure 8*). For the three oils, controls represent a statistically different group (group a) than the other tested conditions (groups b or ab).

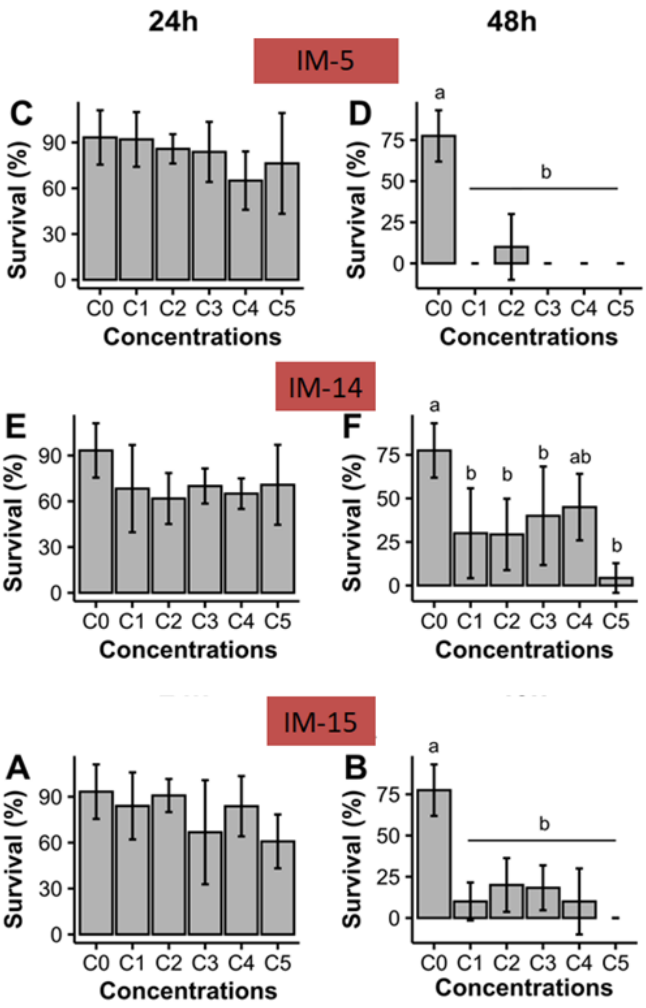

Figure 8 *Survival rate (%) in the controls (C0) and the 5 oil concentrations tested (increasing concentrations from C1 to C5) (a, b and ab represent statistically different groups)*

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Copepods exposed to dissolved compounds of the 3 VLSFO exhibited a mortality rate close to 100% at the first concentration level tested. Average mortalities are illustrated on *Figures 9, 10 and 11.*

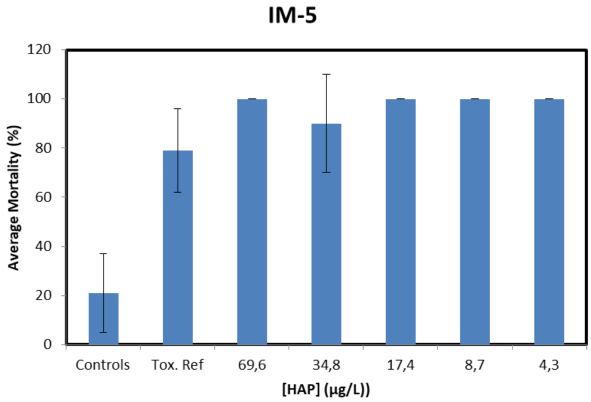

Figure 9 *Average mortality (%) of copepods exposed 48h to the dissolved compounds of IM-5 and to a toxic of reference (3,5-dichlorophenol)*

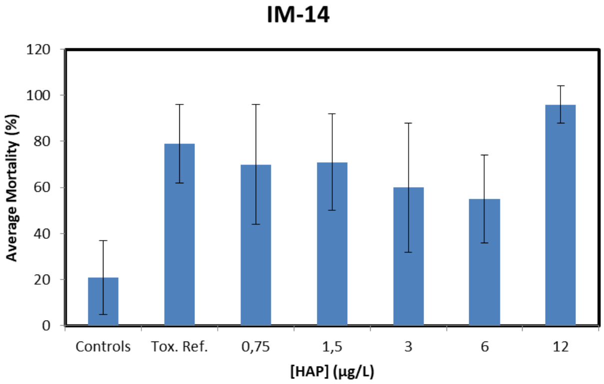

Figure 10 *Average mortality (%) of copepods exposed 48h to the dissolved compounds of IM-14 and to a toxic of reference (3,5-dichlorophenol)*

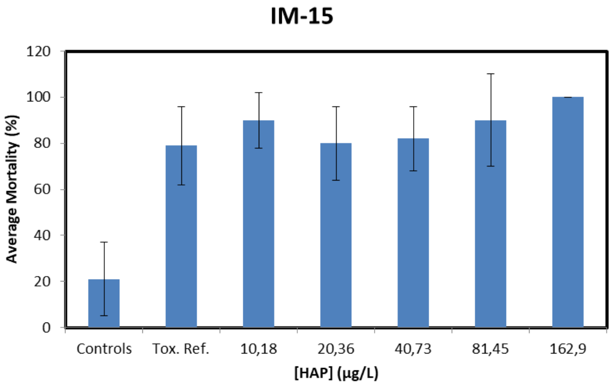

Figure 11 *Average mortality (%) of copepods exposed 48h to the dissolved compounds of IM-15 and to a toxic of reference (3,5-dichlorophenol)*

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2 – 3 Conclusion

The result with reference toxic was: 3,5-dichlorophenol; copepods were in an acceptable range of sensitivity, but at the upper range of the acceptable threshold value at the end of the test (80%). The blank control mortality was above the criteria for test acceptability (threshold at 10 %). The tested organisms exhibited a high sensitivity during the tests. However, given the mortality rates observed for the 3 tested products for all the WAF concentrations tested, an impact of the VLSFO on the survival rates was observed compared to the control.

For the 3 VLSFO tested**, LC_{50} is below the lowest PAH concentration tested** (i.e. the lowest PAH concentration tested led already to a mortality higher than 50 %). A stress induced during the transport of the tested organisms cannot be excluded and may explain the high mortality observed for the organisms in contact with the oil.

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3 – SEDIMENT BIOASSAY USING THE AMPHIPOD *CORPHIUM SP.*

3 - 1 Materials and methods

3 – 1 - 1 Test method

This procedure was based on the standard below, to which certain technical adjustments have been made:

OSPAR: Protocols on methods for the testing of chemicals used in the offshore oil industry. Part A: A Sediment Bioassay using an Amphipod *Corophium sp*.

3- 1 – 2 Test item

Test substances: VLSFO samples IM-5, IM-14 and IM-15

3 – 1 – 3 Reference item

The reference substance (positive control) was fluoranthene, CAS: 206-44-0, tested at 5 concentrations, ranging from 9.2 mg.kg^{-1} to 125.3 mg.kg^{-1}.

3 – 1 - 4 Test system

A marine amphipod was used in this test: *Corophium sp (Figure 12)*. These amphipods (4 - 5 mm) were obtained locally, from a natural area on the shoreline of Argenton (48.522773, -4.759978), and were stored in acclimation tanks at 15°C. They were not fed, but they were in the presence of sediments. The amphipods were exposed to the spiked sediment for a period of 10 days. Mortalities were recorded at the end of the test period and the concentration which kills 50 per cent of the amphipods (LC_{50}) was determined.

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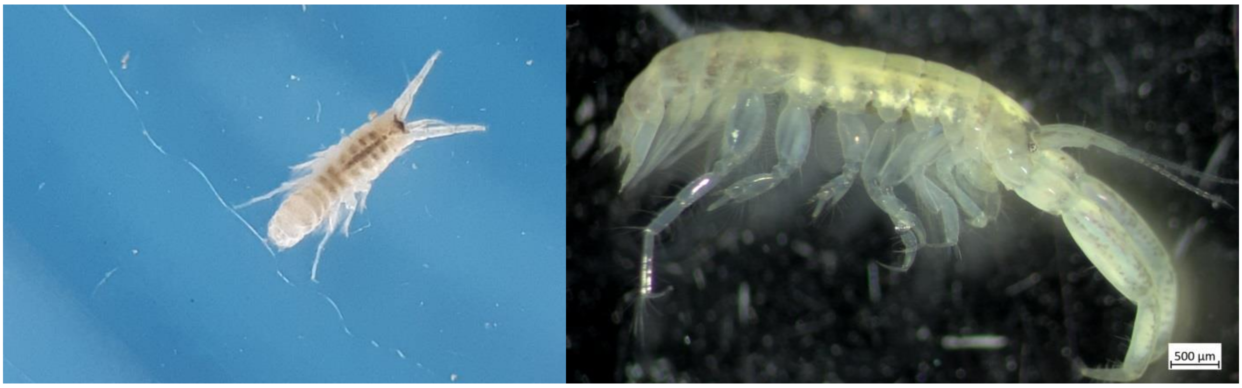

Figure 12 *Amphipods used in this study*

3 – 1 – 6 Test details

Seawater

Natural seawater (salinity: 34 $g.kg^{-1}$) from an unpolluted site (Aquarium Oceanopolis, Brest) was used.

Sediment

Natural sediment was collected from an unpolluted site, Argenton (48.522773, -4.759978), at the same area as the amphipods sampling.

Preparation of test sediment

Once the sediment has been sifted through a 500 µm sieve, it was rinsed and put in the oven in order to dry it. The tested substances (at different concentrations) were then mixed to dry sediment. Tests were carried out in triplicates:

- For the reference toxicant the triplicates separation was processed at the end of the preparation: fluoranthene (different masses were diluted in 6 mL of acetone) were added to 70 g of dry sediment and left for acetone evaporation. This preparation was added to 600 g of wet sediment, in plastic bottles. 100 mL of seawater was added to the preparations.
- For the VLSFO, given the high pour point and viscosity of some products, it was decided to prepare the triplicate at the beginning of the trials (to avoid differences between replicates due to heterogeneity of the mixture): Different oil masses were added to 23.3 g of dry sediment (*Figure 13*). Those mixtures were then added to 200 g of wet sediment and 35 mL of seawater was added to each of the 3 bottles.

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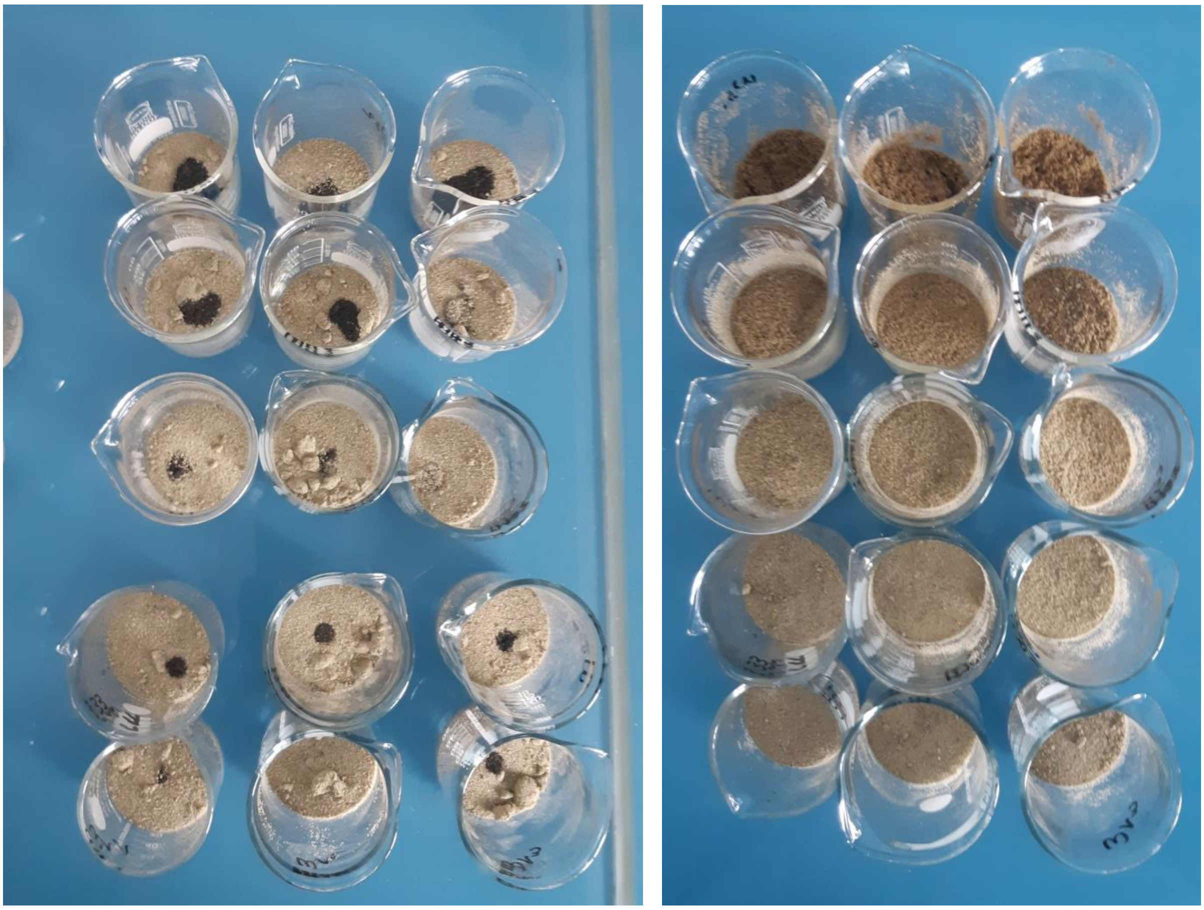

Figure 13 *Sediment preparation (before and after oil mixing)*

These mixtures were agitated using an orbital shaker for 20 hours at 150 rpm. Reference toxicant was then separated into three 1000 mL beakers and 700 mL seawater was added without disturbing the sediment. Bottles containing the tested products were also transferred to the beakers and 700 mL seawater was added as for the reference toxicant (*Figure 14*). The mixtures were left to settle overnight then the oxygenation of the water was started 2 hours before the start of the test.

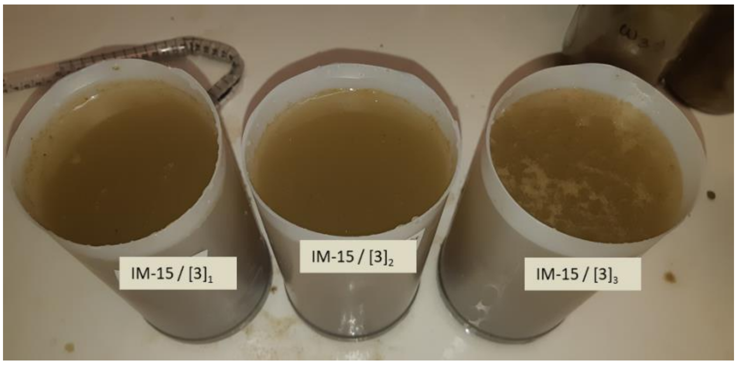

Figure 14 *Addition of seawater*

Experimental set-up

Beakers containing different oil concentrations (five concentrations in a geometric series for each VLSFO and for fluoranthene) were incubated, as well as 12 controls flasks (9 for control without any substance, 3 for acetone control). Twenty organisms were randomly distributed to each test vessel. Oil concentrations were determined using UV-spectrometry technique.

Incubation

The test preparations were incubated, at a temperature of 15°C ± 2°C and under continuous light (*Figure 15*).

Figure 15 *Incubation*

Measurements

The test was run for 10 days. Temperature, pH, salinity and oxygen concentration were monitored once a day. The mortality was recorded after 10 days, once the sediment has been sifted through a 500 µm sieve (*Figure 16*).

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Figure 16 *Mortality recording after 10 days experiment*

Calculations

The water content of the sediment was determined and the results were expressed in sediment dry weight (g.kg^{-1}).

The final results were expressed as LC$_{50}$ values. This result was calculated in accordance with the Regtox program.

Test acceptance criteria

According to OSPAR protocols, EN ISO 16712/2006 and other publications on the subject, for a test to be valid, the following conditions should be fulfilled:

- Organisms should be obtained a maximum of 14 days before t = 0
- The oxygen concentration during the test should be ≥ 85 %
- The mortality rate observed in the blanks should be ≤ 15 %
- The mortality rate observed in the individual blanks should be ≤ 40 %
- The toxicity of the reference substance (fluoranthene) should be within the range
19.9 ± 10.3 mg.kg^{-1} sediment dry weight.
- The test will use the same population of amphipods

3 – 2 Results and discussion

During the test, pH, temperature, salinity and oxygen were recorded every day, as indicated in *Table 11*. Evaporation was also visually controlled every day and was not noticed during the whole experiment. Oxygen concentration during the test is always higher than 85%, fulfilling one of the acceptance criteria.

Table 11 *Physico-chemical parameters monitored during the test*

Date	11/03/2022		14/03/2022				15/03/2022		17/03/2022				18/03/2022		21/03/2022			
Control	**J0**		**J3**				**J4**		**J6**				**J7**		**J10**			
Beaker	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**
Cont1 1	92,0	15,4	94,6	15,0	7,86	37	95,6	15,3	96,3	15,3	7,86	37	96,5	15,6	95,6	15,4	7,86	37
Cont1 2	93,5	15,2	95,6	15,3	7,87	37	95,4	15,6	95,5	15,2	7,89	37	95,9	15,8	95,8	15,6	7,86	37
Cont1 3	92,6	15,5	96,4	15,8	7,86	37	94,9	15,4	95,2	15,4	7,87	37	96,1	15,6	95,2	15,3	7,87	37
Cont2 1	93,5	15,6	95,7	15,8	7,87	37	94,2	15,6	95,8	15,6	7,86	37	96,4	15,9	95,3	15,4	7,86	37
Cont2 2	92,4	15,7	97,2	15,2	7,86	37	94,6	15,3	95,6	15,2	7,86	37	96,5	15,8	95,4	15,6	7,86	37
Cont2 3	91,8	15,4	95,2	15,3	7,87	37	94,2	15,6	95,8	15,8	7,84	37	98,1	15,6	94,8	15,4	7,87	37
Cont3 1	92,2	15,4	96,4	15,2	7,86	37	96,8	15,2	95,2	15,3	7,87	37	96,2	15,4	94,7	15,2	7,87	37
Cont3 2	93,1	15,2	95,5	15,4	7,86	37	95,8	15,4	95,3	15,2	7,86	37	96,8	15,2	95,8	15,4	7,86	37
Cont3 3	92,5	15,0	94,8	15,2	7,86	37	95,4	15,4	95,4	15,3	7,87	37	96,3	15,2	96,5	15,3	7,87	37
Cont+acetone1	93,2	15,3	94,7	15,2	7,86	37	95,7	15,2	95,7	15,2	7,87	37	96,5	15,3	94,8	15,2	7,87	37
Cont+acetone2	94,5	15,8	93,2	15,2	7,87	37	95,6	15,6	96,2	15,4	7,86	37	9,67	15,4	94,5	15,4	7,86	37
Cont+acetone3	94,8	15,8	94,6	15,6	7,86	37	95,6	15,3	94,9	15,2	7,87	37	96,8	15,5	94,8	15,3	7,87	37
FLU-[1] -1	92,1	15,2	94,6	15,2	7,89	37	95,8	15,3	94,8	15,4	7,89	37	95,9	15,4	94,5	15,4	7,89	37
FLU-[1] -2	94,3	15,3	93,7	15,6	7,87	37	96,8	15,4	95,2	15,2	7,87	37	96,5	15,6	95,2	15,3	7,89	37
FLU-[1] -3	94,5	15,2	94,1	15,7	7,86	37	95,3	15,6	95,8	15,4	7,86	37	96,8	15,3	95,3	15,2	7,86	37
FLU-[2] -1	92,6	15,4	93,0	15,4	7,86	37	95,1	15,3	94,8	15,3	7,86	37	96,7	15,2	95,8	15,2	7,87	37
FLU-[2] -2	93,1	15,2	95,1	15,3	7,84	37	95,2	15,4	94,7	15,4	7,84	37	96,9	15,5	96,5	15,2	7,89	37
FLU-[2] -3	92,1	15,2	92,9	15,2	7,87	37	95,6	15,6	95,8	15,4	7,87	37	95,9	15,8	94,8	15,6	7,89	37
FLU-[3] -1	92,1	15,2	93,9	15,3	7,86	37	95,6	15,2	96,5	15,3	7,86	37	96,1	15,6	94,5	15,2	7,87	37
FLU-[3] -2	94,1	15,6	92,9	15,4	7,84	37	95,8	15,3	94,8	15,4	7,87	37	95,9	15,8	98,5	15,4	7,86	37
FLU-[3] -3	94,1	15,2	93,6	15,4	7,85	37	95,7	15,6	94,5	15,4	7,89	37	96,1	15,6	96,7	15,2	7,87	37
FLU-[4] -1	93,7	15,3	95,2	15,4	7,87	37	95,8	15,2	98,5	15,4	7,89	37	96,4	15,9	96,7	15,4	7,89	37
FLU-[4] -2	94,7	15,2	92,7	15,2	7,86	37	95,6	15,4	96,7	15,2	7,87	37	96,5	15,8	96,2	15,0	7,87	37
FLU-[4] -3	94,4	15,3	94,5	15,2	7,86	37	95,8	15,4	97,6	15,4	7,86	37	98,1	15,6	94,9	15,3	7,86	37
FLU-[5] -1	94,3	15,4	94,0	15,2	7,87	37	95,3	15,3	95,2	15,2	7,86	37	96,2	15,4	94,8	15,4	7,86	37
FLU-[5] -2	94,2	15,2	93,9	15,6	7,87	37	95,6	15,3	95,3	15,4	7,84	37	96,8	15,2	95,2	15,4	7,87	37
FLU-[5] -3	94,9	15,3	92,5	15,2	7,86	37	95,8	15,9	95,4	15,3	7,87	37	95,9	15,4	95,8	15,3	7,87	37
IM-5-[1] -1	92,1	15,2	95,1	15,4	7,87	37	95,8	15,4	95,8	15,4	7,86	37	96,5	15,5	94,7	15,4	7,86	37
IM-5-[1] -2	93,5	15,2	94,5	15,2	7,85	37	97,4	15,6	96,5	15,3	7,87	37	96,8	15,4	95,8	15,4	7,87	37
IM-5-[1] -3	94,8	15,6	94,3	15,4	7,86	37	95,8	15,3	94,8	15,4	7,86	37	96,7	15,6	95,8	15,3	7,85	37
IM-5-[2] -1	93,5	15,4	94,2	15,0	7,87	37	96,8	15,2	94,5	15,4	7,87	37	95,9	15,5	96,8	15,4	7,85	37
IM-5-[2] -2	94,1	15,4	94,4	15,2	7,87	37	96,4	15,4	98,5	15,3	7,89	37	96,1	15,8	96,4	15,2	7,87	37
IM-5-[2] -3	93,7	15,2	94,5	15,0	7,86	37	95,8	15,4	96,7	15,4	7,89	37	96,4	15,6	95,8	15,4	7,86	37
IM-5-[3] -1	92,8	15,2	95,2	15,4	7,87	37	95,6	15,6	96,7	15,2	7,87	37	96,5	15,8	95,6	15,2	7,86	37
IM-5-[3] -2	95,2	15,2	92,7	15,3	7,86	37	95,7	15,6	97,6	15,4	7,86	37	98,1	15,6	95,7	15,4	7,84	37
IM-5-[3] -3	94,2	15,4	94,5	15,0	7,86	37	96,2	15,4	95,2	15,2	7,86	37	96,2	15,9	94,8	15,4	7,87	37
IM-5-[4] -1	93,8	15,6	94,0	15,3	7,85	37	96,5	15,4	95,3	15,4	7,86	37	96,8	15,8	93,5	15,4	7,86	37
IM-5-[4] -2	93,9	15,2	93,9	15,2	7,87	37	95,8	15,2	95,4	15,3	7,84	37	96,8	15,6	94,1	15,4	7,87	37
IM-5-[4] -3	92,6	15,4	92,5	15,3	7,87	37	95,6	15,3	95,8	15,4	7,87	37	96,7	15,4	93,7	15,2	7,86	37
IM-5-[5] -1	94,3	15,2	95,1	15,2	7,87	37	96,8	15,2	96,5	15,3	7,86	37	95,9	15,4	92,8	15,3	7,84	37
IM-5-[5] -2	95,1	15,3	94,5	15,3	7,86	37	94,9	15,4	95,7	15,4	7,87	37	96,1	15,6	95,2	15,2	7,87	37
IM-5-[5] -3	94,8	15,3	93,2	15,3	7,87	37	97,6	15,3	96,2	15,2	7,89	37	96,2	15,5	94,7	15,3	7,86	37

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Table 11 (cont.) *Physico-chemical parameters monitored during the test*

Date	11/03/2022		14/03/2022				15/03/2022		17/03/2022				18/03/2022		21/03/2022			
Control	**J0**		**J3**				**J4**		**J6**				**J7**		**J10**			
Beaker	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**	**O2 (%)**	**T (°C)**	**O2 (%)**	**T (°C)**	**pH**	**sal**
IM-15-[1] -1	92,1	15,4	94,6	15,3	7,89	37	97,8	15,4	94,8	15,2	7,87	37	96,8	15,9	94,3	15,4	7,89	37
IM-15-[1] -2	94,1	15,3	93,7	15,4	7,87	37	96,8	15,4	95,2	15,4	7,86	37	96,7	15,8	94,2	15,4	7,86	37
IM-15-[1] -3	94,1	15,6	94,1	15,2	7,86	37	95,7	15,4	95,8	15,3	7,87	37	96,1	15,6	95,4	15,2	7,87	37
IM-15-[2] -1	93,7	15,2	94,3	15,3	7,86	37	96,2	15,2	94,7	15,4	7,87	37	96,2	15,4	95,8	15,4	7,86	37
IM-15-[2] -2	94,7	15,6	94,2	15,3	7,89	37	96,5	15,3	95,8	15,4	7,86	37	96,2	15,4	96,5	15,2	7,86	37
IM-15-[2] -3	94,4	15,8	94,4	15,2	7,87	37	96,8	15,2	96,5	15,3	7,87	37	96,8	15,4	95,7	15,2	7,86	37
IM-15-[3] -1	94,3	15,4	94,5	15,4	7,87	37	94,9	15,3	94,8	15,4	7,89	37	95,9	15,5	96,2	15,2	7,87	37
IM-15-[3] -2	94,2	15,0	93,7	15,2	7,86	37	95,7	15,6	94,5	15,4	7,87	37	96,5	15,4	95,9	15,6	7,87	37
IM-15-[3] -3	94,9	15,2	94,1	15,2	7,87	37	96,2	15,4	98,5	15,4	7,86	37	96,8	15,6	96,5	15,2	7,86	37
IM-15-[4] -1	92,1	15,0	93,0	15,2	7,87	37	96,5	15,4	96,7	15,2	7,86	37	96,7	15,3	96,8	15,3	7,87	37
IM-15-[4] -2	93,5	15,3	95,1	15,6	7,86	37	96,8	15,6	95,3	15,8	7,84	37	96,7	15,2	96,7	15,2	7,86	37
IM-15-[4] -3	94,8	15,3	92,9	15,2	7,87	37	95,7	15,6	95,4	15,3	7,87	37	96,9	15,5	95,9	15,2	7,87	37
IM-15-[5] -1	93,5	15,4	93,9	15,3	7,86	37	96,2	15,3	95,8	15,2	7,86	37	95,9	15,3	96,1	15,4	7,86	37
IM-15-[5] -2	94,1	15,3	92,9	15,2	7,86	37	95,8	14,5	96,5	15,3	7,86	37	96,1	15,2	95,8	15,2	7,87	37
IM-15-[5] -3	95,2	15,0	93,6	15,3	7,84	37	95,8	15,3	94,8	15,2	7,87	37	95,9	15,5	96,5	15,3	7,89	37
IM-14-[1] -1	94,2	15,3	95,2	15,3	7,85	37	97,4	15,1	94,5	15,4	7,86	37	96,1	15,8	95,8	15,3	7,85	37
IM-14-[1] -2	93,8	15,2	92,5	15,3	7,82	37	95,8	15,1	98,5	15,2	7,87	37	96,8	15,6	94,7	15,3	7,87	37
IM-14-[1] -3	93,9	15,3	95,1	15,3	7,83	37	96,8	15,2	96,7	15,4	7,89	37	95,9	15,8	97,6	15,3	7,86	37
IM-14-[2] -1	92,4	15,3	94,5	15,2	7,85	37	96,4	15,6	96,7	15,2	7,89	37	96,5	15,6	95,8	15,2	7,86	37
IM-14-[2] -2	91,8	15,2	94,3	15,3	7,86	37	95,8	15,9	97,6	15,4	7,86	37	96,8	15,9	96,8	15,4	7,87	37
IM-14-[2] -3	92,2	15,3	94,2	15,3	7,82	37	95,8	15,9	95,2	15,3	7,84	37	96,8	15,3	96,4	15,2	7,87	37
IM-14-[3] -1	93,1	15,2	94,4	15,4	7,84	37	95,6	15,8	95,3	15,4	7,87	37	96,7	15,4	95,8	15,2	7,86	37
IM-14-[3] -2	92,5	15,3	94,3	15,2	7,86	37	95,7	15,7	95,4	15,4	7,86	37	96,7	15,8	95,8	15,2	7,87	37
IM-14-[3] -3	93,2	15,3	94,2	15,6	7,69	37	95,6	15,3	95,8	15,3	7,87	37	96,9	15,6	95,6	15,6	7,84	37
IM-14-[4] -1	92,5	15,2	94,4	15,2	7,89	37	96,8	15,1	96,5	15,4	7,89	37	95,9	15,4	95,6	15,2	7,87	37
IM-14-[4] -2	93,2	15,3	94,3	15,4	7,86	37	95,8	15,1	95,8	15,4	7,84	37	96,1	15,2	96,8	15,3	7,86	37
IM-14-[4] -3	94,5	15,3	94,2	15,3	7,85	37	96,4	15,4	94,7	15,4	7,87	37	95,9	15,2	94,5	15,3	7,86	37
IM-14-[5] -1	94,8	15,4	94,4	15,2	7,86	37	95,8	15,5	97,6	15,2	7,86	37	96,1	15,3	94,0	15,4	7,87	37
IM-14-[5] -2	93,5	15,2	94,3	15,3	7,89	37	95,6	15,6	95,2	15,4	7,87	37	96,8	15,4	93,9	15,2	7,86	37
IM-14-[5] -3	93,6	15,1	94,2	15,4	7,9	37	95,7	15,8	95,3	15,4	7,87	37	95,9	15,5	92,5	15,6	7,87	37
Time	16h00		9h00				9h00		9h00				9h00		7h45			

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Oil concentrations determined with UV-spectrometry are shown in *Table 2*, they varied from:

- 127.1 mg.kg^{-1} to 2456.5 mg.kg^{-1} for IM-5;
- 127.1 mg.kg^{-1} to 2387.2 mg.kg^{-1} for IM-14;
- 88.0 mg.kg^{-1} to 2405.2 mg.kg^{-1} for IM-15;

Table 12 also presents the mortality percentages obtained during the test, for all the conditions tested. It appeared that the control mortality was 5 %, fulfilling the acceptance criteria, whereas the amphipods mortality increased with the oil concentration to which they were exposed to. When exposed to VLSFO, mortality increased:

- from 8 to 100 % for IM-5;
- from 8 to 65 % for IM-14;
- from 13 to 100 % for IM-15.

Mortality was also observed for amphipods exposed to the fluoranthene. The lowest concentration tested (9.2 mg/kg) led to a mortality of 52 %.

Results are illustrated on *Figure 17*.

Table 12 *Mortality percentage obtained during the test.*

		Concentration mg.kg^{-1}	mortality replicate 1 (%)	mortality replicate 2 (%)	mortality replicate 3 (%)	Average mortality (%)
Controls		0	4,9			5,0
			3,3			
			5,7			
Controls acetone		-	3,33			3,3
Fluoranthene	Flu [1]	9,2	35,0	55,0	65,0	51,7
	Flu [2]	17,9	95,0	55,0	90,0	80,0
	Flu [3]	34,6	100,0	100,0	100,0	100,0
	Flu [4]	58,9	100,0	100,0	100,0	100,0
	Flu [5]	125,3	100,0	100,0	100,0	100,0
IM-5	[1]	127,05	10,0	5,0	10,0	8,3
	[2]	202,71	15,0	5,0	15,0	11,7
	[3]	476,95	45,0	60,0	30,0	45,0
	[4]	1047,15	90,0	80,0	90,0	86,7
	[5]	2456,51	100,0	100,0	100,0	100,0
IM-15	[1]	88,00	10,0	5,0	25,0	13,3
	[2]	204,34	25,0	30,0	25,0	26,7
	[3]	499,69	100,0	95,0	100,0	98,3
	[4]	1091,29	100,0	95,0	100,0	98,3
	[5]	2405,19	100,0	100,0	100,0	100,0
IM-14	[1]	127,14	10,0	10,0	5,0	8,3
	[2]	209,76	15,0	20,0	10,0	15,0
	[3]	554,56	5,0	45,0	20,0	23,3
	[4]	1035,98	55,0	40,0	35,0	43,3
	[5]	2387,23	60,0	60,0	75,0	65,0

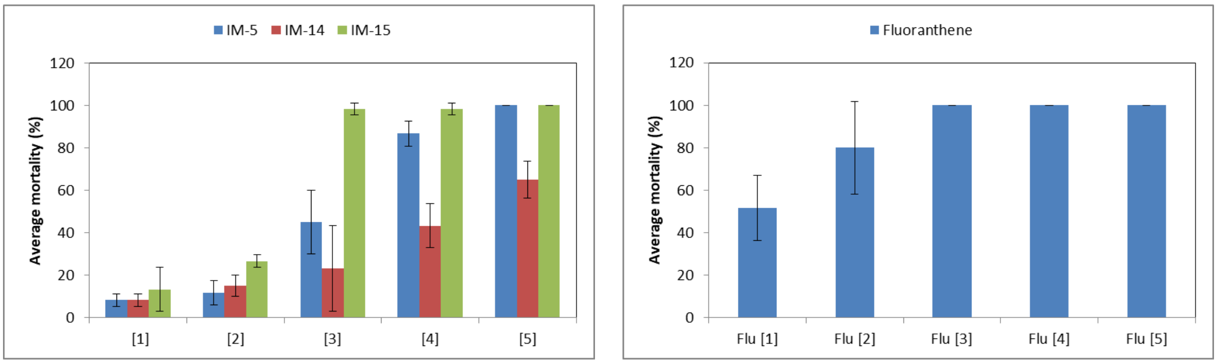
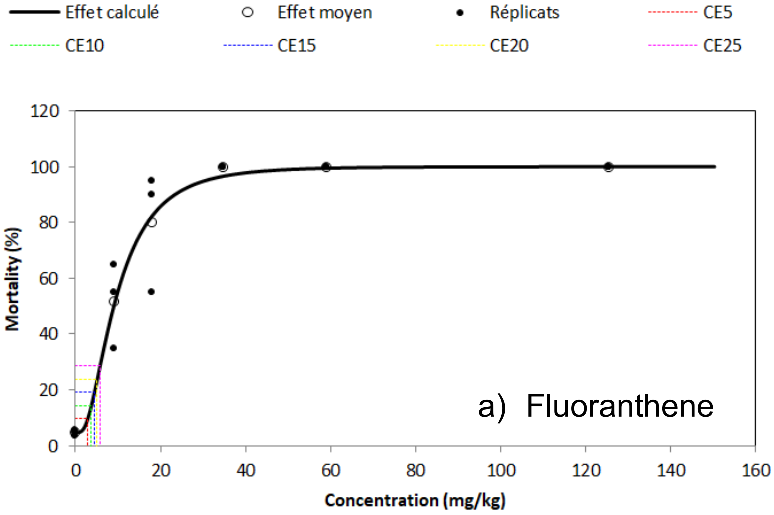


Figure 17 *Amphipods average morality observed after 10 days exposure to increasing concentrations of IM-5, IM-14, IM-15 and to the toxic of reference (fluoranthene)*

The RegTox software allows the exact calculation of the LC_{50}. *Figure 18* shows the evolution of the mortality (in %) in function of the oil concentration (in mg.kg^{-1}), for the 3 VLSFO tested and for the reference substance. From those graphs, the LC_{50} was calculated at 542 mg.kg^{-1} for IM-5, 2124 mg.kg^{-}1 for IM-14 and 266 mg.kg^{-1} for IM-15, whereas it is of 9.43 mg.kg^{-1} for fluoranthene.



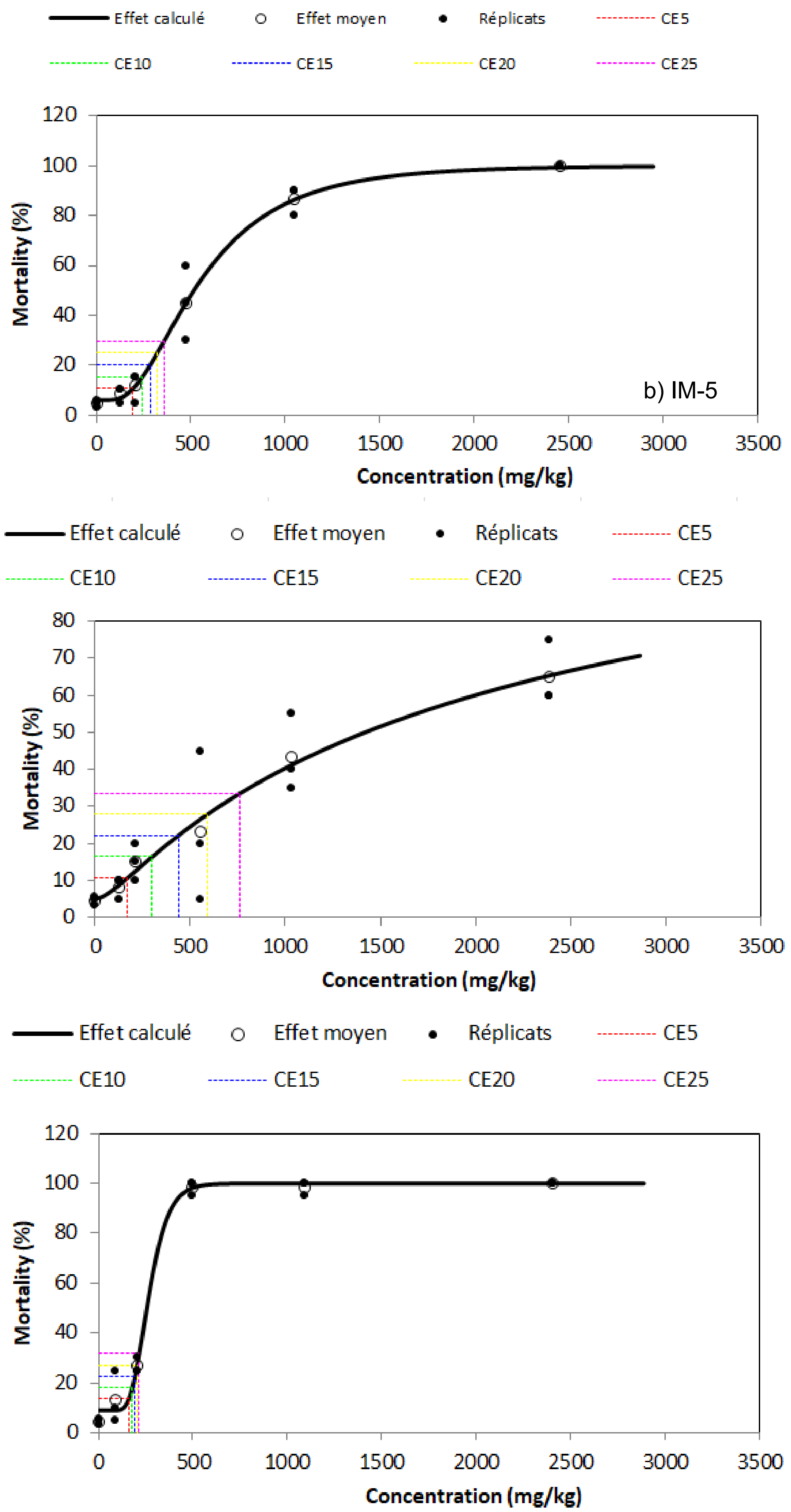


Figure 18 *Mortality (%) for the a) toxic of reference, b) IM-5, c) IM-14 and d) IM-15 concentrations tested (in mg.kg^{-1})*

3 – 3 Conclusion

The test acceptance criteria were fulfilled. Only toxicity of the reference substance (fluoranthene) was slightly below the minimum acceptable value (LC_{50} calculated at 9.4 mg $.kg^{-1}$.whereas the lower range of the acceptable value is 9.6 mg $.kg^{-1}$. This result could be due to the small size of the amhipods tested (4-5 mm). Usual size is around 5-10 mm and the difference may be related to the time of year when the organisms were collected (in February in the frame of this study).

VLSFO concentrations from 127.1 $mg.kg^{-1}$ to 2456.5 $mg.kg^{-1}$ for IM-5; from 127.1 $mg.kg^{-1}$ to 2387.2 $mg.kg^{-1}$ for IM-14; from 88.0 $mg.kg^{-1}$ to 2405.2 $mg.kg^{-1}$ for IM-15 were tested.
The test was run for 10 days under continue light, at a temperature of 15°C.
The result is expressed as the concentration of a product giving 50 % mortality, LC_{50}.

The conclusion of this test is as follows:

- IM-5: LC_{50} 10 days = 542 $mg.kg^{-1}$ (Confidence interval 5%: 481 – 615);
- IM-14: LC_{50} 10 days = 2124 $mg.kg^{-1}$ (Confidence interval 5%: 625 – 41548). The huge interval confidence calculated is due to the fact that the 100% mortality is not reached for this VLSFO;
- IM-15: LC_{50} 10 days = 266 $mg.kg^{-1}$ (Confidence interval 5%: 231 – 291).

It should be noticed that those results are in agreement with PAH quantification in the three oils. Results presented in Appendix 1 give PAH concentration of ~ 12 000 µg/g, ~ 5 000 µg/g and ~ 29 000 µg/g, respectively for IM-5, IM-14 and IM-15. The oil exhibiting the highest PAH concentration (IM-15) leads to the highest impact on amphipods, with the determination of the lowest LC_{50}.

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4 - CONCLUSION

The study led to the following conclusion:

- Marine algal growth inhibition test: even for the highest PAH concentration tested, the growth rate was still very close to the one of the control. EC_{50} at 72 hours could not be determined for the 3 VLSFO tested.
  No toxicity was observed on *Phaeodactylum tricornatum* by testing those 3 VLSFO.

- Determination of acute lethal toxicity to marine copepods: for the 3 VLSFO tested, LC_{50} was below the lowest PAH concentration tested (i.e. the lowest PAH concentration tested led already to a mortality higher than 50 %), **demonstrating to a high sensibility of those organisms. However, the sensitivity observed may be explained by a stress (potentially induced by the transport time) of the tested organisms**.
- Sediment bioassay using the amphipod *Corphium sp.:* **an impact of the oil on the mortality rate was observed.** The determination of LC_{50} seems related to the PAH quantification in the 3 oils, with the lowest LC_{50} calculated for IM-15.

Additionally, PAH quantification for the three VLSFO tested are in the same range as traditional fuel oils already analysed at Cedre. In addition, WAF toxicity measured by SINTEF on the thirteen LSFO collected in the frame of the Task 3.1 (Faksness and Daling, 2022[2]) is also in the same range as traditional fuel oils. **The toxicity of the LSFO tested seems thus to be in the same range as the one observed for traditional fuel oils.**

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[2] Chemical composition of fuel oils : Faksness and Daling, SINTEF report n° 2022:00383 - Unrestricted

APPENDIX

Appendix 1

PAH quantification

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Table 1 *PAH quantification in the fresh oils*

		IM-5	IM-14	IM-15
Benzo(b)thiophene	BT	20,5	0,0	31,0
C1-benzo(b)thiophenes	BT1	46,0	0,0	45,7
C2-benzo(b)thiophenes	BT2	18,4	1,7	73,5
C3-benzo(b)thiophenes	BT3	36,3	9,7	89,0
C4-benzo(b)thiophenes	BT4	19,6	16,2	70,2
Naphtalene	N	851,0	133,7	4224,1
C1-Naphtalenes	N1	801,0	104,5	2166,4
C2-Naphtalenes	N2	1240,6	176,7	2198,1
C3-Naphtalenes	N3	952,5	206,9	1825,9
C4-Naphtalenes	N4	577,0	189,4	1172,5
Biphenyl	B	380,5	7,0	319,5
Acenaphtylene	ANY	0,0	1,1	51,2
Acenaphtene	ANA	26,4	5,8	192,3
Fluorene	F	141,4	0,0	134,1
C1-Fluorenes	F1	367,7	0,0	336,4
C2-Fluorenes	F2	494,6	88,9	603,8
C3-Fluorenes	F3	510,5	144,8	503,1
Phenanthrene	P	259,2	60,5	527,1
Anthracene	A	9,6	7,2	84,4
C1-phenanthrenes/anthracenes	P1	696,3	303,1	1277,5
C2-phenanthrenes/anthracenes	P2	987,9	526,2	1920,3
C3-phenanthrenes/anthracenes	P3	801,0	657,3	1828,5
C4-phenanthrenes/anthracenes	P4	391,0	475,8	1125,7
Dibenzothiophene	D	143,1	13,0	37,7
C1-dibenzothiophenes	D1	169,6	65,6	163,0
C2-dibenzothiophenes	D2	231,0	158,7	286,4
C3-dibenzothiophenes	D3	182,7	139,2	299,5
C4-dibenzothiophenes	D4	78,8	98,2	193,8
Fluoranthene	FL	10,4	7,0	51,1
Pyrene	PY	45,8	19,1	175,3
C1-fluoranthenes/pyrenes	FL1	324,3	161,9	1038,7
C2-fluoranthenes/pyrenes	FL2	394,9	277,8	1744,6
C3-fluoranthenes/pyrenes	FL3	353,7	348,1	1694,3
Benzo[a]anthracene	BA	14,4	8,5	86,2
Chrysene	C	50,9	36,1	153,8
C1-chrysenes	C1	155,2	104,7	633,4
C2-chrysenes	C2	202,4	156,1	813,1
C3-chrysenes	C3	183,2	112,8	691,0
Benzo[b+k]fluoranthene	BBF	9,8	11,2	40,9
Benzo[e]pyrene	BEP	15,1	0,0	38,0
Benzo[a]pyrene	BAP	6,9	5,1	45,1
Perylene	PE	4,7	8,2	20,6
Indeno(1,2,3-cd)pyrene	IN	0,8	62,4	0,0
Dibenz(a,h)anthracene	DBA	0,0	73,7	0,0
Benzo(g,h,i)perylene	BPE	7,2	7,8	71,6
TOTAL (µg/g)		**12214,3**	**4991,9**	**29078,7**
N - N4		36,2%	16,2%	39,8%
BT - C3		63,4%	80,4%	59,4%
B(b+k)F - BPE		0,4%	3,4%	0,7%

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Table 2 *PAH quantification in the WAF*

Concentration en ng/L		IM-15 (WAF algae)	IM-5 (WAF algae)	IM-14 (WAF algae)	IM-15 (WAF copepods)	IM-5 (WAF copepods)	IM-14 (WAF copepods)
Naphtalène	N1	65 813	2 868	2 694	77 099	12 189	2 634
C1-Naphtalène	N2	22 359	3 120	1 351	20 479	12 374	1 241
C2-Naphtalène	N3	20 910	7 481	1 690	19 123	15 212	1 423
C3-Naphtalène	BT	9 159	2 669	1 404	8 222	5 797	976
Benzothiophène	BT1	10	18	19	10	63	29
C1-Benzothiophène	BT2	9 417	240	258	8 418	1 185	231
C2-Benzothiophène	BT3	5 131	509	335	4 731	1 248	317
C3-Benzothiophène	B	2 257	524	699	2 009	1 203	508
Biphényl	ANY	7 198	4 039	423	7 136	8 858	388
Acénaphtylène	ANA	454	<LQ	16	333	180	15
Acénaphtène	F1	3 446	469	160	3 109	1 058	136
Fluorène	F2	4 019	1 318	447	3 731	2 587	360
C1-Fluorène	F2	2 691	1 070	465	2 396	2 670	401
C2-Fluorène	F3	1 176	433	298	1 108	1 166	257
C3-Fluorène	P	381	150	152	389	410	130
Phenanthrene	A	1 419	344	586	1 311	802	683
Anthracene	P1	168	8	32	156	20	31
C1-Phenan/anthra	P2	1 511	337	847	1 394	907	946
C2-Phenan/anthra	P3	693	163	418	628	457	442
C3-Phenan/anthra	DBT	227	52	169	204	147	170
Dibenzothiophène	DBT1	180	246	149	164	596	170
C1-Dibenzothiophène	DBT2	193	78	190	175	219	198
C2-Dibenzothiophène	DBT3	85	25	98	75	74	101
C3-Dibenzothiophène	FL	22	8	44	20	22	44
Fluoranthène	PY	36	<LQ	10	31	7	12
Pyrène	FL1	103	11	27	93	30	27
C1-Fluoranthènes/Pyrènes	FL2	217	21	96	183	67	89
C2-Fluoranthènes/Pyrènes	FL3	134	9	43	113	29	42
C3-Fluoranthènes/Pyrènes	BaA	54	<LQ	14	31	9	12
Benzo[a]anthracène	C	8	1	2	8	2	2
Chrysène	C1	16	1	13	14	6	14
C1-Chrysènes	C2	17	2	13	16	6	13
C2-Chrysènes	C3	5	1	7	5	3	6
C3-Chrysènes	BBF	1,2	<LD	<LD	1,1	<LQ	<LQ
Benzo[b+k]fluoranthène	BEP	<LD	<LD	<LD	<LD	<LD	<LD
Benzo[e]pyrène	BAP	<LD	<LD	<LD	<LD	<LD	<LD
Benzo[a]pyrène	PE	<LD	<LD	<LD	<LD	<LD	<LD
Pérylène	IN	<LD	<LD	<LD	<LD	<LD	<LD
Indéno(1,2,3-cd)pyrène	DBA	<LD	<LD	<LD	<LD	<LD	<LD
Dibenzo(a,h)anthracène	BPE	<LD	<LD	<LD	<LD	<LD	<LD
Benzo(g,h,i)pérylène	BPE	<LD	<LD	<LD	<LD	<LD	<LD
Somme HAPs (ng/L)		159 511	26 215	13 168	162 914	69 603	12 048

Somme HAPs (µg/L)	160	26	13	163	70	12