

Modelling Low Sulphur Fuel Oil Weathering

IMAROS project, deliverable D3.4

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1 Introduction

1.1 General introduction to the IMAROS project

A ship incident such as a collision or grounding may result in an oil spill, causing a time consuming and costly response. Successful oil spill response may reduce the impacts on the marine environment, including impacts on the life in the water column, marine mammals, and sea birds. Furthermore, it may prevent severe impacts on the shoreline environment and socio-economic impacts on the affected coastal communities.

Knowledge and adequate response equipment are among the key factors to conduct a successful oil spill response operation. Diverse types of oil products spilt at sea may behave in quite diverse ways, resulting in diverging challenges for responders and a range of several environmental concerns. For instance, a spill of light diesel fuel quickly dissolves in the water column while a spill of heavy fuel oil becomes sticky and highly viscous and persists on the sea surface and on the shoreline for a long time.

In recent years, new IMO- and EU-regulations to limit the Sulphur emissions and to establish “Sulphur Emission Control Areas” (aka SECA-zones) had considerable impacts on the marine fuel markets. Following IMO MARPOL Annex VI, the global limit of Sulphur content in marine fuel oils has decreased from 3.5 % to 0.5 % from 2020 onwards, leading to the emergence of a new generation of fuel oils referred as hybrid fuel oils, ECA fuels, Ultra Low Sulphur Fuel Oils (ULSFO, $S < 0.1\%$) or Very Low Sulphur Fuel Oils (VLSFO, $S < 0.5\%$).

Initial laboratory and basin testing revealed a substantial diversity in the physical and chemical properties of these new fuel oils complicating the response options and influencing potential environmental impacts following an accidental spill. Large variations related to emulsification, weathering, water-solubility, toxicity etc. were also reported (e.g. (Hellstrøm, 2017; Holt et al., 2017), etc.).

The IMAROS project aimed at further investigating the challenges raised by these new fuel oils on oil spill response strategies. Three axes have been followed:

- IMAROS WP2 aimed at improving the understanding of the rapid changes in the oil market from 2019 to 2022 in terms of new fuel oil products entering the market, in terms of new fuel oils volume traded or in terms of geographical distribution patterns. More generally, WP2 aimed at providing an overall risk picture regarding the new generation fuel oils.
- IMAROS WP3 aimed at giving valuable insight into the chemical and physical properties of the new fuel oils, which are crucial to both predict and understand the behavior of the spilled oil. Among the different WP3 tasks, chemical characterization has been performed at lab scale, weathering experiments were carried out at meso-scale. These two tasks provided useful information for the modelling task presented in this report.
- Finally, IMAROS WP4 tested the efficiency of several response strategies to recover new fuel oil spill at seas or to clean shorelines.

1.2 Objectives and general methodology of the IMAROS modelling task

The main objective of the IMAROS task 3.5 “modelling the weathering of low Sulphur fuel oil” was to demonstrate the ability or the inability of the existing oil weathering parameterizations to predict the weathering of the new fuel oil types. In case the current parameterizations turn out to be inaccurate, new parametrizations had to be suggested. Finally, since each European countries operate their own oil spill drift, fate and behavior model, the findings and conclusions of this task had to be reported independently of these models but as best practices that could be implemented in the different national models.

To achieve all these objectives, a 3-step methodology was followed. First, a literature review has been performed to identify the state-of-the-art oil weathering parametrizations. Then, the selected weathering parameterizations were implemented in a so-called “toy model” (i.e., a light OD oil weathering model whose only purpose was to play with the implemented weathering parameterizations). Finally, the toy model results were validated / invalidated against observations from several experiments carried out at CEDRE’s polludrome (tank filled with water able to simulate the weathering of oil at sea).

The present reports strictly follow this 3-step approach. In section 2 , we define the concept of oil weathering and give a comprehensive introduction to the concept of weathering model and weathering process parametrizations. Interested readers shall find the equations of the weathering processes parametrizations in Annex I. In section 3, we present the physicochemical characteristics of the LSFO oils tested in the framework of the IMAROS project. 13 oils referred as IM1 to IM13 have been initially tested in Lab. Their properties were quite diverse, for instance with a pour point ranging between -27°C and +30°C. In a second step, weathering of 3 VLSFO oils have been tested at pilot scale (flume tank). This report focuses on these 3 oils referenced as IM-5, IM-14, and IM-15. In section 4, we present the numerical experiences we performed with our toy model to simulate the oil weathering as in CEDRE’s flume tank. In section 5, we compare and discuss the model simulation results with the observation in CEDRE’s flume tank. Finally, in section 6, we draw some conclusions and present some recommendations in the form of best practices.

2 Modelling oil weathering

The behavior of an oil spill at sea is complex due to multiple processes occurring simultaneously. To be able to predict what is the most likely outcome, they must all be considered. Models are needed to compute the rate of the processes shown in Figure 1.

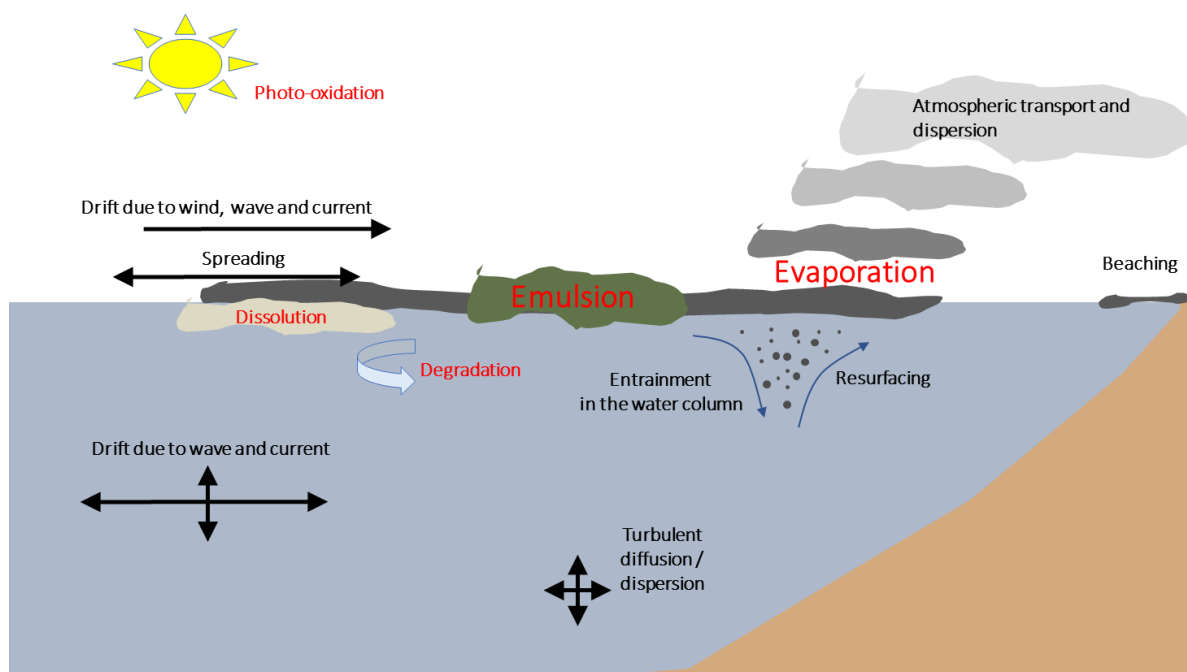


Figure 1 Processes occurring on an oil slick at sea, the ones in red are the processes of weathering

The processes which are the most visible are the drift due to the wind, waves and currents, the turbulent diffusion and dispersion, the entrainment in the water column, the resurfacing, and the

beaching. In order to be described accurately, physicochemical properties of the oil should be provided. However, as soon as oil is spilled at sea, several other processes will begin to affect the chemical composition of it: they are the “weathering” processes. They will impact the oil's physical properties, with the evaporation of the lightest molecules, the uptake of seawater forming a water-in-oil emulsion and the photooxidation.

All of this can have a high impact on the crisis management strategy, for instance an oil photo-oxidized for several hours will be less affected by chemical dispersant (Ward et al., 2018), the water incorporated in the oil with the emulsification process will increase the volume of pollutant to be recovered by the response teams on the field and can cause issue with the recovery equipment due to change of viscosity and density.

Authorities do take better response decisions when they can anticipate the fate and behavior of an oil spill at sea. For that, models predicting oil weathering are needed, more specifically models predicting time evolution of oil properties such as viscosity and density. These models use mathematical representation of the processes, called parametrization.

Weathering parametrizations describe the evolution of the amount of a compound in each state (evaporated, dissolved, emulsified...) as a function of time, its physicochemical properties, and the environmental conditions (aka met-ocean forcing). More specifically, these parametrizations describe the mass transfer and the mass transfer rate from the fresh oil compound fraction to the weathered oil compound fractions. They can also describe the time evolution of the oil viscosity and density as a function of the weathered fractions and the water content. The oil weathering parameterizations are sometimes empirical formulas (functions) but are most often differential equations. There are three categories of parametrizations:

- Empirical formula
- Differential equations applicable on the entire oil
- Differential equations applicable on each oil (pseudo-)component

Parametrizations based on empirical formula are usually directly derived from lab observations. They are fully accurate, if they are applied within the range of tested oil and lab conditions. Parametrizations based on differential equations are usually more generic, even if their calibration coefficients are oil-dependent; a drawback that parametrizations based on oil-pseudo components has not.

Table 1 gives an overview of the most used parametrizations for evaporation, dissolution, emulsion, volatilization, biodegradation and photooxidation as well as for viscosity and density. Some of these parametrizations have been conceived for oil, some for chemicals in general. The process with the largest amount of attention in the scientific community is evaporation. The evaporation parametrization hypothesized a limitation factor in the process which dictate the rate. There are two main factors of limitation, the wind speed (the evaporation is limited by the concentration in the air layer just above the slick) and the diffusion through the slick. In the first case, the wind velocity and the vapor pressure of the compound are both important whereas in the second case it is more related to the thickness of the slick.

For dissolution, oil compounds solubility is the important property, and the volatilization (going from dissolved to evaporated) needs both the solubility and the vapor pressure. This is the case because most of the parametrizations are put to a zero flux if the compound is not volatile (vapor pressure near zero) or dissolution (solubility near zero).

The emulsification process is parametrized as a function of the sea state (waves) or the wind.

Biodegradation relies on species which varies with location, but simple half-life can be used even if more complex parametrizations are available.

Photooxidation is the least documented weathering process. Although it is a complex process that involves chemical reactions, parametrizations are often limited to compute the rate of production of a “photo-oxidized oil fraction” - based on a half-life relation (Vaz et al., 2021).

Annex 1 to get the parametrizations equations. All these parametrizations have been implemented in a stand-alone “OD” python module whose only purpose was to play with the different parametrizations. For this reason, we called this model a toy model. This toy-model code is available on GitHub: https://github.com/naturalsciences/weathering_module_4_marine_pollution.

Table 1: parametrization ready to use in the python toy model, the parametrization by default is written in blue

Evaporation	• Parametrization derived from (Jones, 1997) and used in OILTRANS (Berry et al., 2012) • Parametrization derived from (Brighton P.W.M., 1985) and used in ALOHA (Jones et al., 2013) • Parametrization of (M. F. Fingas, 2015)
Dissolution	• Parametrization described in (Hines and Maddox, 1985; Legrand et al., 2017; MacKay and Leinonen, 1977)
Emulsion	• Parametrization described in (Scory, 2005) • Mackay parametrization, described in (Fingas, 1995)
Volatilization	• Parametrization of (Lyman et al., 1990)
Biodegradation and photooxidation	• Simple half-life (Vaz et al., 2021)
Viscosity	• Viscosity estimation from (Betancour et al., 2005; Lehr et al., 2002)
Density	• Sum of the fraction’s density and the water content

3 Experimental data

When doing modeling, the use of experimental data cannot be avoided for validation purposes, for calibration of empirical parameters, or simply for the model initial conditions. In this work, we have used two sets of data, from laboratory testing and from a mesoscale flume tank testing, also known as polludrome (CEDRE, 2022b). All the data we have used will be described in this section. Most of the parameters have been measured at 5°C and at 15°C for all the oil, but only IM-5, IM-14 and IM-15 have been fully tested in the polludrome, therefore the discussion only focuses on these 3 low Sulphur fuel oils.

3.1 Data from the laboratory

The data from the laboratory are physicochemical properties of fresh oil, but also from simulated weathering. Evaporation is simulated by heating the oil at several temperatures, then water can be mixed with the oil to simulate emulsion. The viscosity of the oil is measured at a shear rate of 10s^{-1} by default.

Table 2: Lab characterization of oils from CEDRE, multiple value means that the parameter value varies in the range with the evaporated simulation temperature

	IM-5		IM-14		IM-15	
Temperature [°C]	5	15	5	15	5	15
Density fresh [kg/m³]	919	911	945	937	958	951
Viscosity fresh (10s^{-1}) [mPa s]	3051	507	71747	17121	19406	4305
Viscosity fresh (100s^{-1}) [mPa s]	/	/	21007	5347	15032	4137
Maximum water content [%]	62-71	67-81	/	19-50	32-50	49-70
Pour point fresh [°C]	15		27		0	
Pour point weathered [°C]	3-24		/		/	

The model uses a list of “pseudo-component” for modelling oils, and weather them independently. The initial repartition of the oil in each of these pseudo-components must be provided as input to the model. In this project, two different pseudo-component approaches have been used, the boiling point curve and the OSCAR characterization, respectively.

The boiling point curve is a curve which compares the amount evaporated as a function of temperature at which the oil is heated (cf. Figure 2, Figure 3 and Figure 4). In this approach, a pseudo-component is created by subtracting the amount remaining at two different temperatures (or equivalently, the volume evaporated between these two temperatures). The boiling point of this pseudo-component is the upper temperature. When both data from laboratory and from FID were available at the same temperature, the values from laboratory were used.

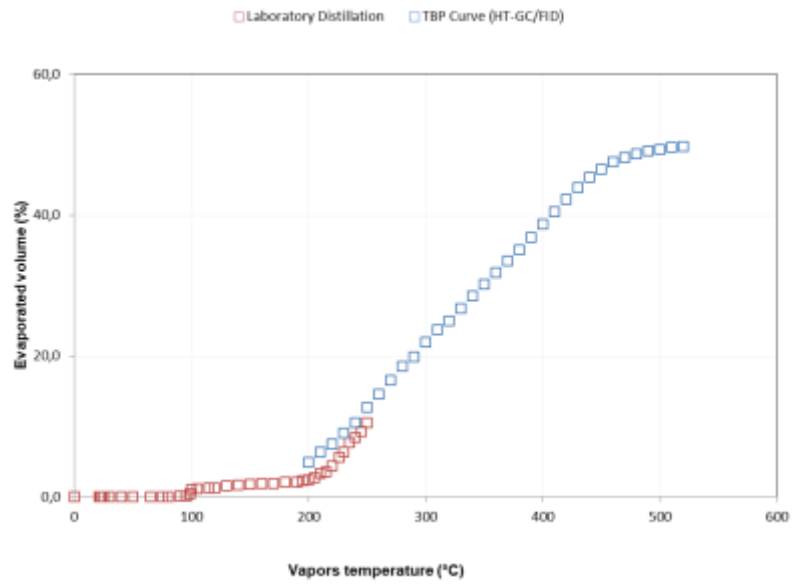


Figure 2: Boiling point curve for IM-5

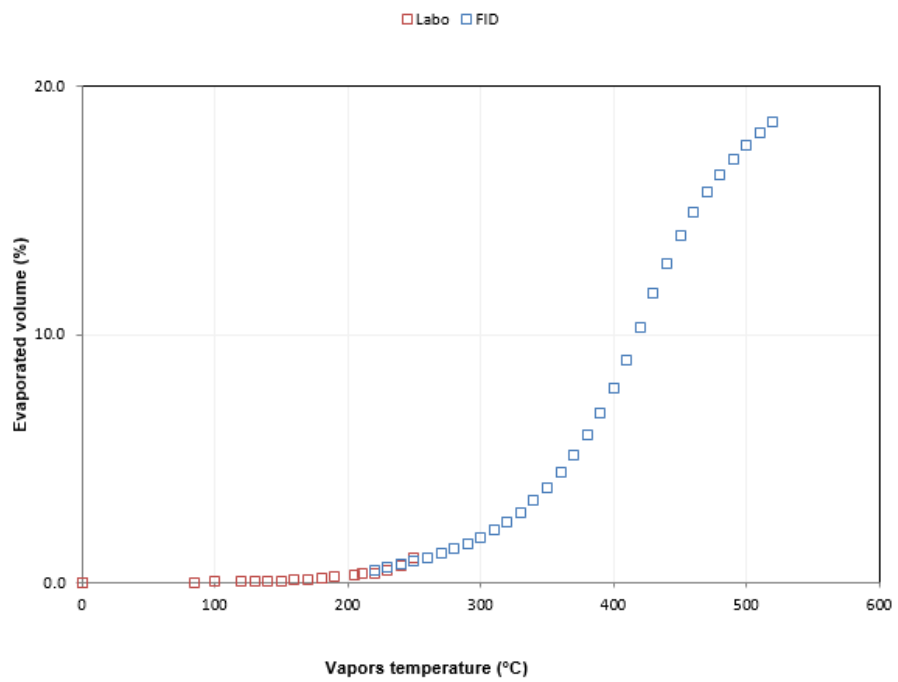


Figure 3: Boiling point curve for IM-14

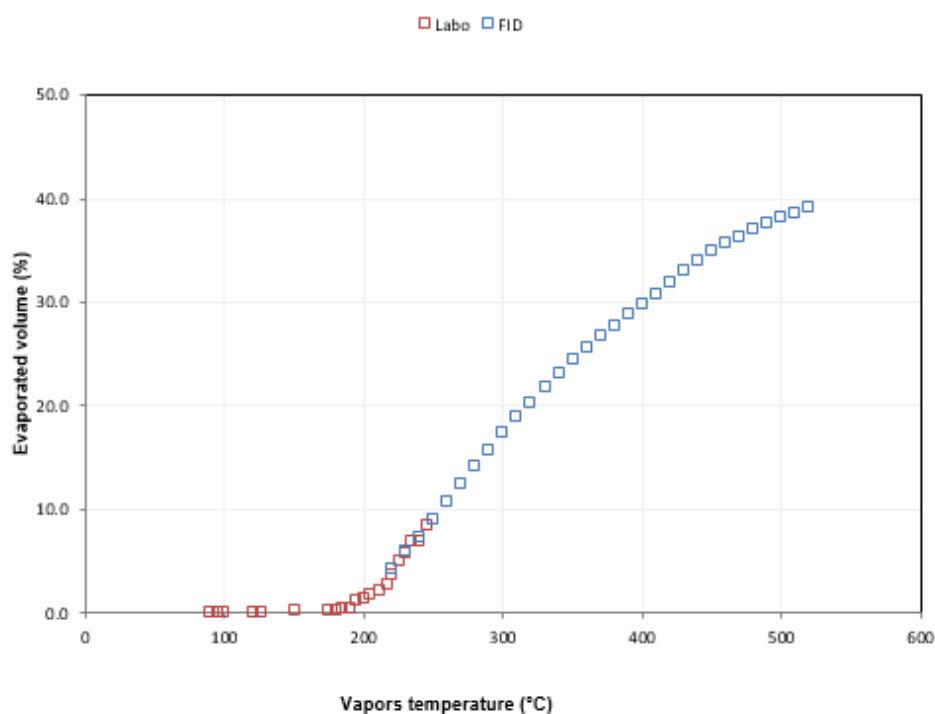


Figure 4: Boiling point curve for IM-15

The OSCAR characterization is created using the boiling point curves, GC/MS and GC/FID analysis (CEDRE, 2022a). It extends the boiling point curve approach by adding a distribution of pseudo components in 23+1 bulk chemical category (Table 3). This allows us to estimate the solubility and then to simulate the dissolution of the compounds, giving information about the oil chemical composition through time.

As an important remark, both pseudo-component approaches only discriminate the light molecules present in the oil mixture. The residual oil (heavier molecules) is not considered in the true boiling point curve approach; they do not evaporate. In the OSCAR characterization, this residual oil fraction is called C25+. This C25+ fraction encompasses a wide variety of heavy molecules so that no physicochemical properties can be associated to this oil pseudo-component a priori.

Table 3: OSCAR characterizations

Individual compounds	Composition (% weight) IM-5	Composition (% weight) IM-14	Composition (% weight) IM-15
C ₁ -C ₄ (dissolved gas)	0.08	0.07	0.03
C ₅ -saturates (n-/iso-/cyclo)	0	0.00	0.00
C ₆ - saturates (n-/iso-/cyclo)	0	0.00	0.00
C ₇ - saturates (n-/iso-/cyclo)	0	0.00	0.00
C ₈ - saturates (n-/iso-/cyclo)	0	0.00	0.00
C ₉ - saturates (n-/iso-/cyclo)	0.02	0.00	0.01
Benzene	0	0.00	0.00
C ₁ -Benzene	0	0.00	0.00
C ₂ -Benzenes	0	0.00	0.00
C ₃ -Benzenes	0.02	0.00	0.02
C ₄ & C ₅ -Benzenes	0	0.00	0.00
C ₁₀ - saturates (n-/iso-/cyclo)	2.09	0.00	0.00
C ₁₁ -C ₁₂ (total saturates + aromatics)	3.88	1.11	4.01
C ₁₃ -C ₁₄ (total saturates + aromatics)	5.32	0.92	4.36
C ₁₅ -C ₁₆ (total saturates + aromatics)	5.31	1.12	4.47
C ₁₇ -C ₁₈ (total saturates + aromatics)	4.97	1.35	3.29
C ₁₉ -C ₂₀ (total saturates + aromatics)	4.04	2.36	3.33
C ₂₁ -C ₂₅ (total saturates + aromatics)	8.86	9.65	5.94
C ₂₅ + (total)	63.02	82.74	71.66
Naphthalenes 1 (C ₀ -C ₁ alkylated)	0.17	0.02	0.64
Naphthalenes 2 (C ₂ -C ₃ alkylated)	0.22	0.10	0.40
PAHs 1 (medium solubility)	0.29	0.14	0.46
PAHs 2 (low solubility)	0.54	0.42	1.38
Phenols (C ₀ -C ₄)	-	-	-

3.2 Data from the polludrome

The polludrome is CEDRE's flume tank used to simulate oil weathering at a pilot scale under controlled environmental conditions (air and water temperature, water current, wind, sunlight and wave height, and period).

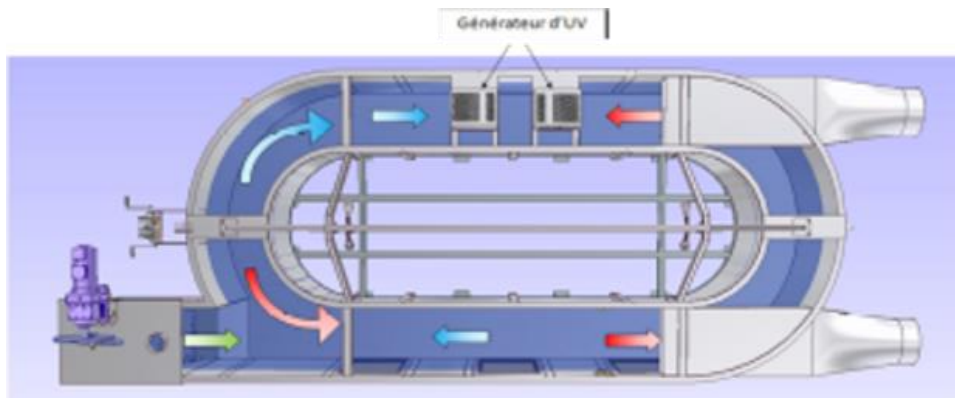


Figure 5: Top view from the polludrome



Figure 6: Picture of the polludrome, picture from CEDRE

For the IMAROS experiment, the polludrome was filled with 7m³ of seawater, with a water depth of 0.9m. The wind was set to 5m/s, the water currents at 0.4m/s, the waves height at 0.75m and the temperature at 5 or 15°C.

For each experiment, 20 liters (0.02m³) of oil was spilled in the polludrome. The oil kept turning in the polludrome for 7 days. Periodically, oil samples have been taken and basic analyses were performed on them to get information about viscosity, density, water content and evaporated fraction.

The selection of the tested LSFOs should have been based on a first screening of 13 oil samples (referred as IM-1 to IM-13) for which the physicochemical have been analyzed in lab (CEDRE, 2022a). Following the IMAROS 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 tanker, 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 low pour point (-27°C)

When starting the purchase process for getting the oils in large quantities (3 m³) for weathering and recovery tests, 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 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 (pour point +27°C).
- VLSFO from Malta: The identification IM-6 related to the task 3.1 has been changed to IM-15 for task 3.2 (pour point 0°C).

Each oil has been tested in the polludrome at 2 temperatures (5°C and 15°C); each experiment leading to quite diverse weathering behaviors.

The measurements of the polludrome experiments for viscosity, density, evaporated fraction, and water content are presented on Figure 7, Figure 8, Figure 9 and Figure 10, respectively. These measurements are summarized in **Error! Reference source not found.**. In particular, the maximal water content observed in the Lab is systematically underestimated (up to 15%) with respect to the maximal water content observed in the polludrome.

If the polludrome experiments normally happened for IM-5, some comments must be made for the experiments on IM-14 and IM-15.

The pour point of **IM-14** being much higher than the experiment temperature, this oil instantaneously froze/crystallized in a kind of 'granita' when it was poured in the polludrome. This 'granita' is a heterogenous slick, in which air bubbles and water droplets has been trapped. At 5°C, this 'granita' could hardly form water-in-oil emulsion. This experiment had to be stopped after 48 hours because all the oil was stuck on the polludrome walls; no free oil could be sampled anymore. At 15°C, emulsion took place. However, the heterogeneous and patchy nature of this slick led to inconsistent measurements, especially for density and evaporation (Figure 8, Figure 9).

Although the pour point of IM-15 was well below the experiment temperature, this viscous oil did not form a continuous and uniform slick but formed a series of oil lumps of diverse sizes (up to 10 cm long) and thicknesses that were floating at the seawater surface of the polludrome. The external shell of the oil lumps tended to solidify.

Table 4 : Summary of the main results of the 6 polludrome experiments for IM-5, IM-14, and IM-15 oils at 5°C and 15°C

	IM-5				IM-14				IM-15			
Temperature [°C]	5		15		5		15		5		15	
Average water content after 20h [%]	80.65		85.58		17.1		56.67		63.1		71.19	
Maximum water content from the lab [%]	71		81		0		50		50		70	
Evaporated fraction at the end of experiment	3		7.7		1.4		0.5		12.2		12.5	
Time [h]	0	168	0	168	0	48	0	149	0	168	0	168
Density [kg/m ³]	920	987	912	997	945	867	940	922	958	1000	950	990
Viscosity [mPa s]	3967	31666	542	19401	71747	63342	17122	32948	19406	222613	4402	107214

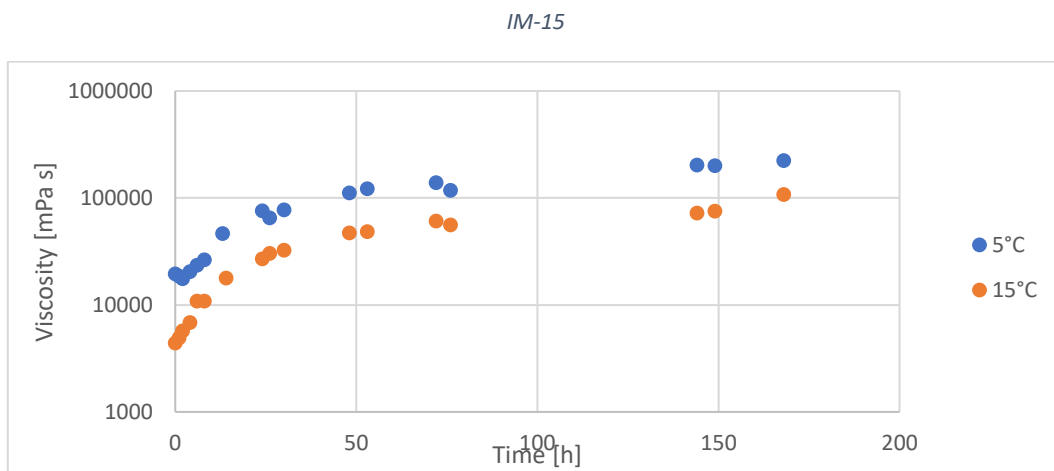
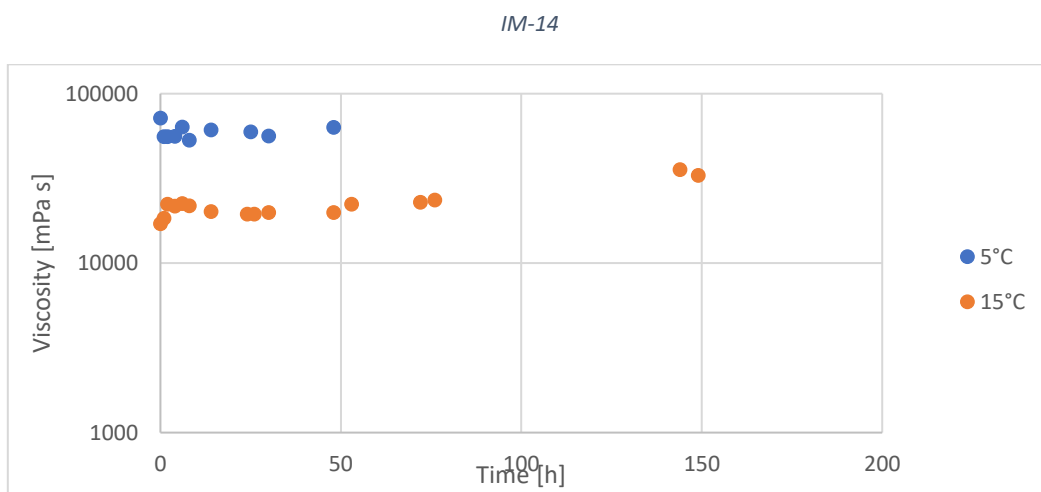
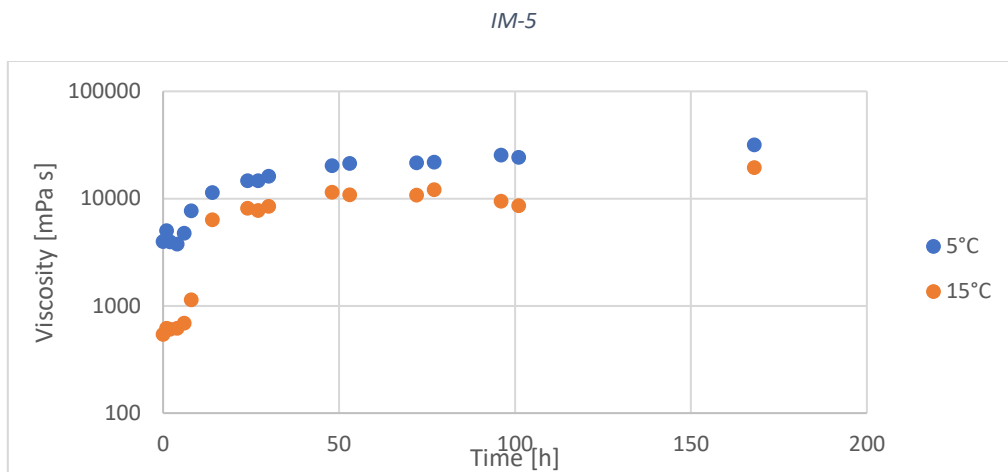
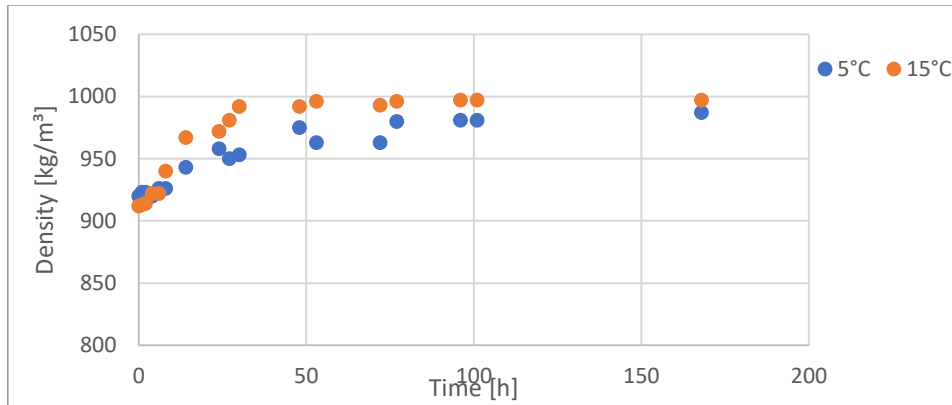
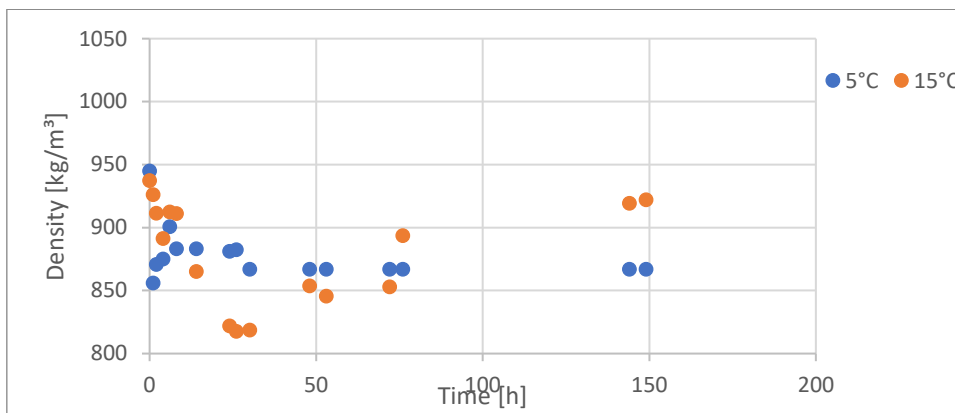


Figure 7: Time evolution of the oil viscosity as observed in the polludrome for IM-5 (top), IM-14 (middle) and IM-15 (bottom) at 5°C and 15°C.

IM-5



IM-14



IM-15

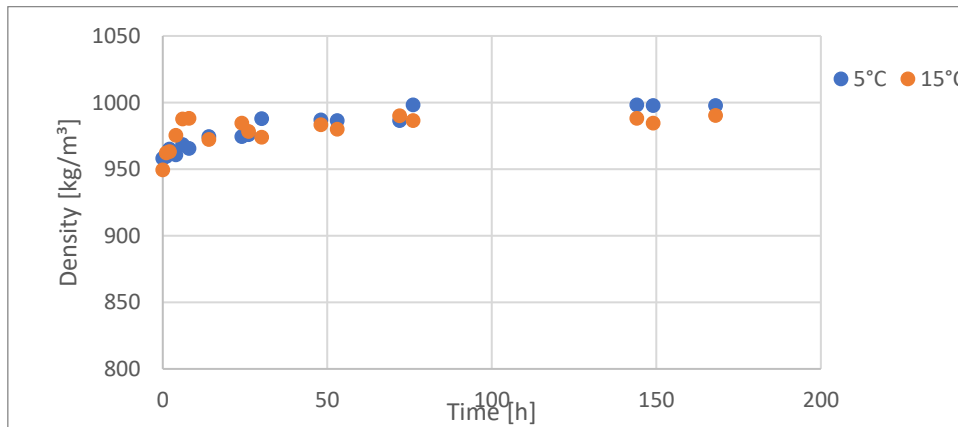


Figure 8: Time evolution of the oil density as observed in the polludrome for IM-5 (top), IM-14 (middle) and IM-15 (bottom) at 5°C and 15°C.

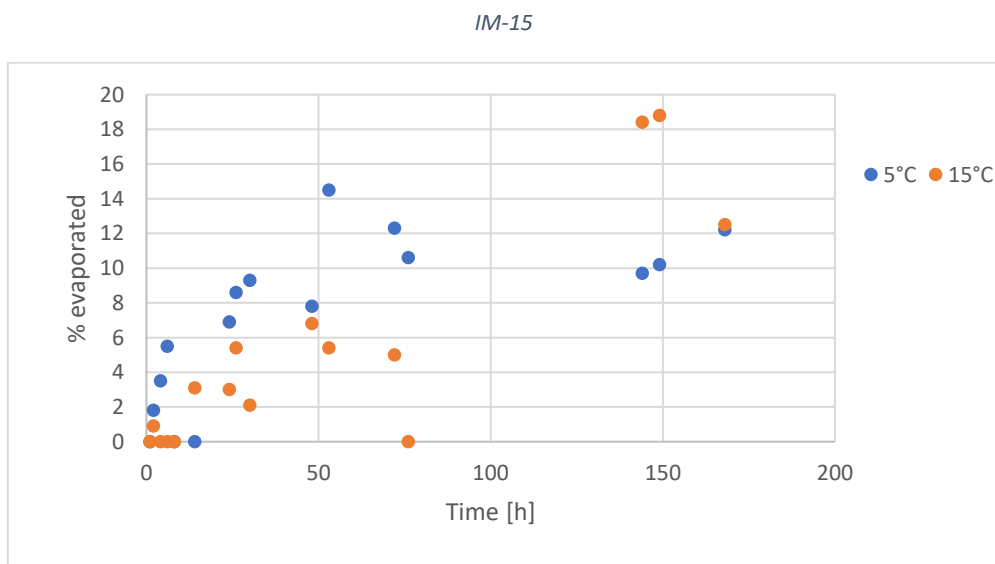
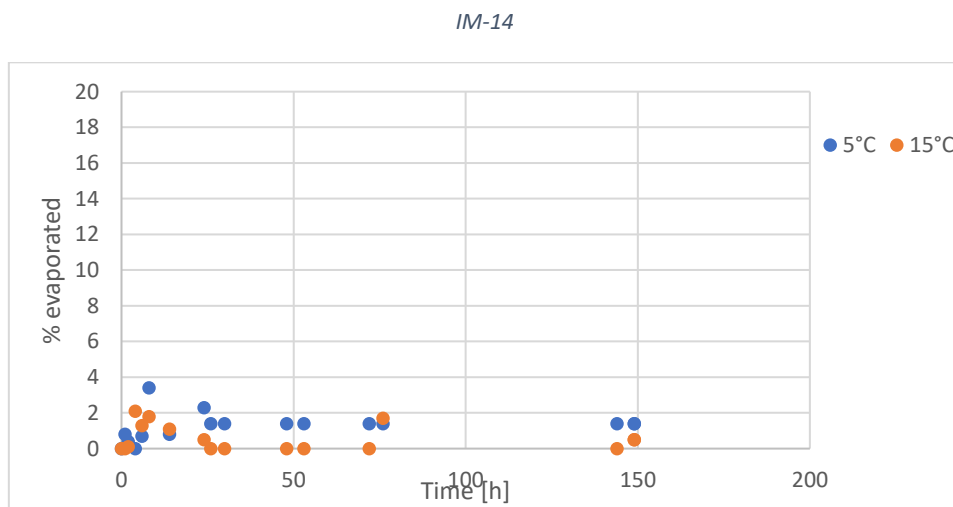
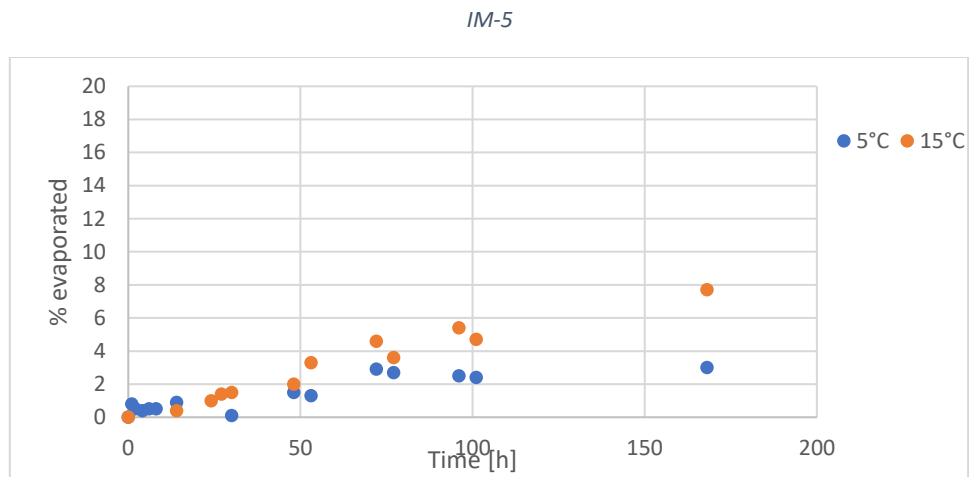


Figure 9: Time evolution of the evaporated fraction as observed in the polludrome for IM-5 (top), IM-14 (middle) and IM-15 (bottom) at 5°C and 15°C.

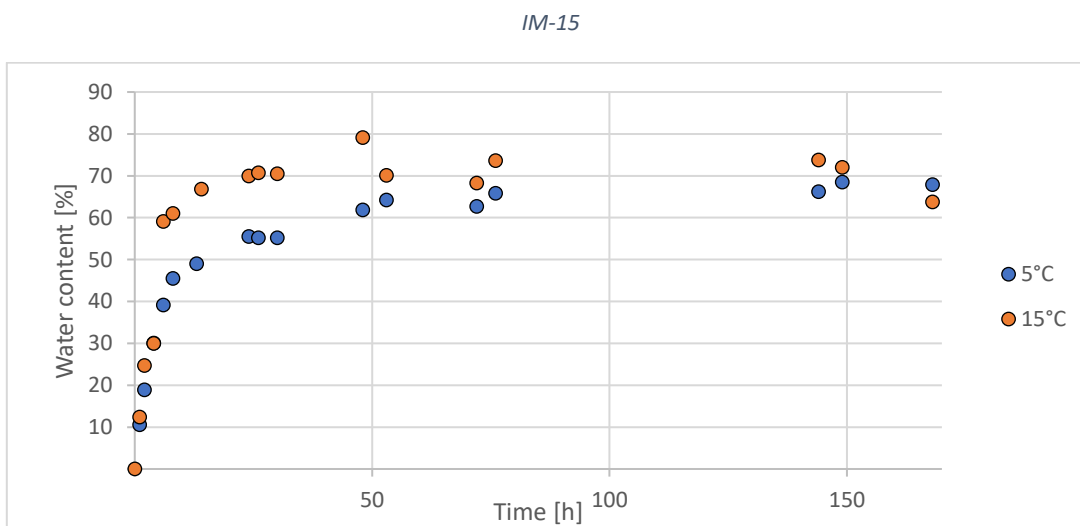
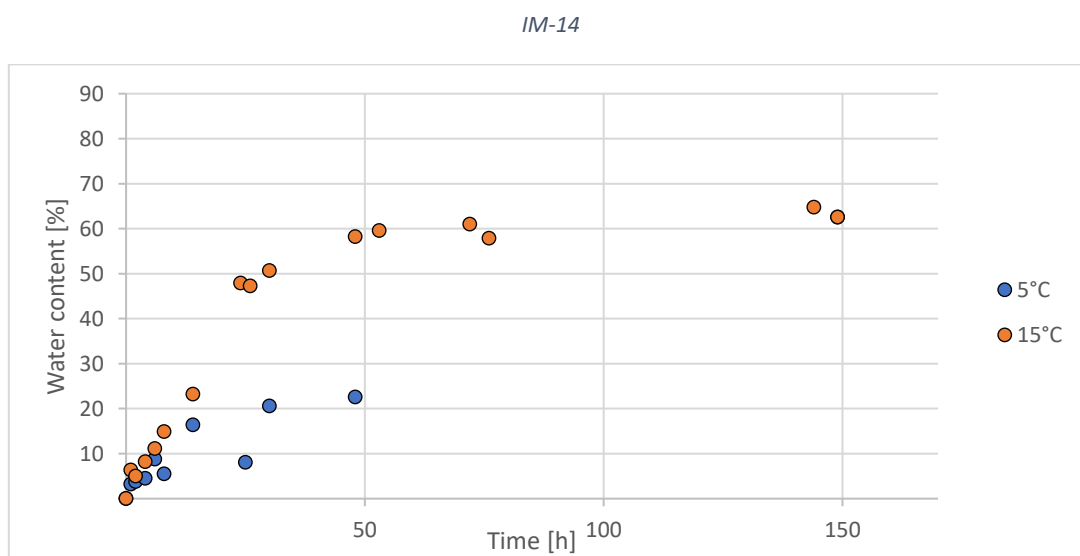
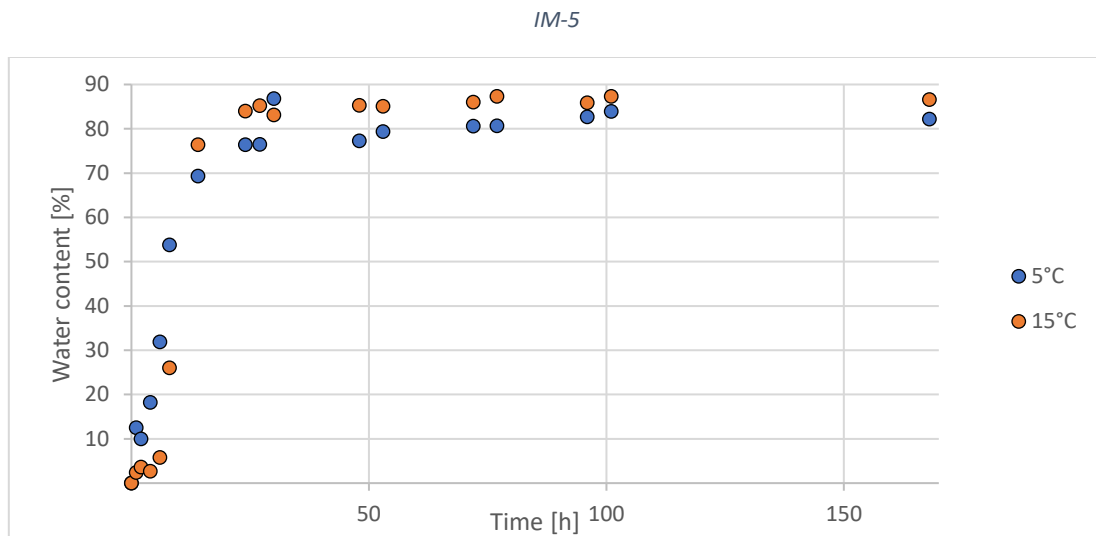


Figure 10: Time evolution of the water content as observed in the polludrome for IM-5 (top), IM-14 (middle) and IM-15 (bottom) at 5°C and 15°C.

4 Numerical experiment

For this task, the 6 polludrome experiments have been numerically simulated with the help of the toy model presented in section 2 and Annex I.

The model set-up was as follows:

- Polludrome volume: 7m³
- Polludrome depth: 0.9m
- Polludrome surface: 7.78m²
- Wind speed: 5m/s
- Current speed: 0.4 m/s
- Air temperature: 5°C or 15°C
- Seawater temperature: 5°C or 15°C
- Seawater density: 1025 kg/m³ (default value, no temperature or salinity dependency)
- Initial oil volume: 20 liters

For each oil and each temperature tested in the polludrome, 4 simulations have been performed to respectively test the model sensitivity against the 2 pseudo-components oil characterization (true boiling point vs OSCAR) and 2 commonly used evaporation parametrizations (Brighton and Jones).

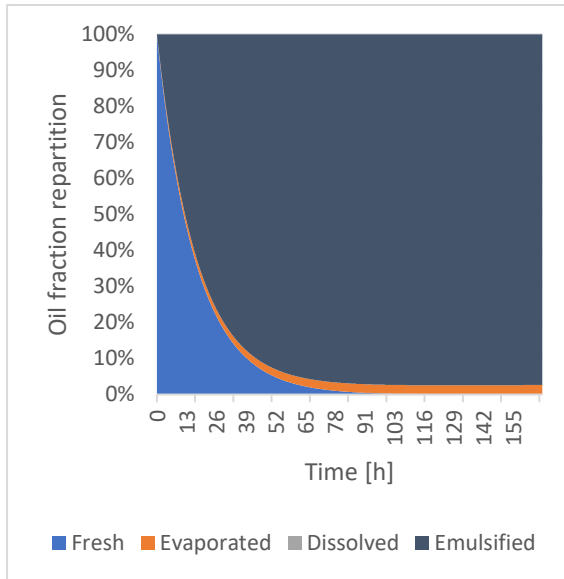
The other weathering parametrizations used were common to all simulations: Scory for emulsion, Hines and Maddox for dissolution, and Lyman for volatilization. Biodegradation and photooxidation were not considered in the numerical experiments.

Unless otherwise specified, the oil physicochemical properties come from the lab characterizations (section 3.1).

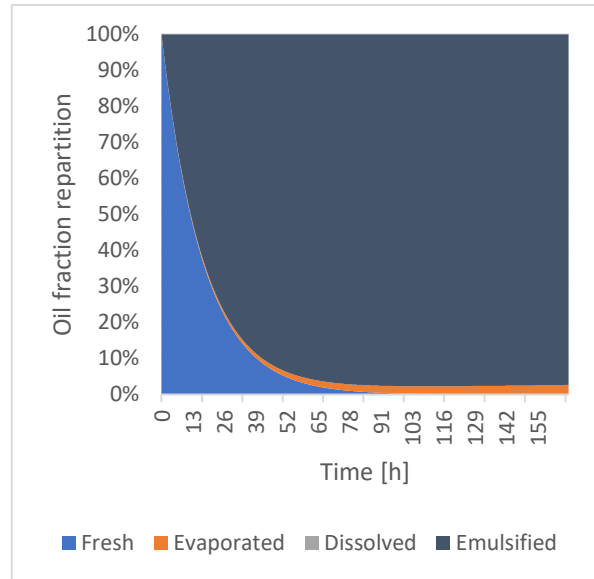
The results of the 6 numerical experiments are shown in Figure 11 to Figure 16. From these figures, we may conclude that the weathering models remain consistent whatever the used pseudo-component approach or the used evaporation parametrizations. For all the tested oils, the oil fraction dissolved in the seawater is 3 orders of magnitude smaller than for the evaporation and can therefore not be seen on the figures.

IM-5, IM-14 and IM-15 being not fully representative of the VLSFO diversity, model results for IM-1 to IM-13 are displayed in Annex II.

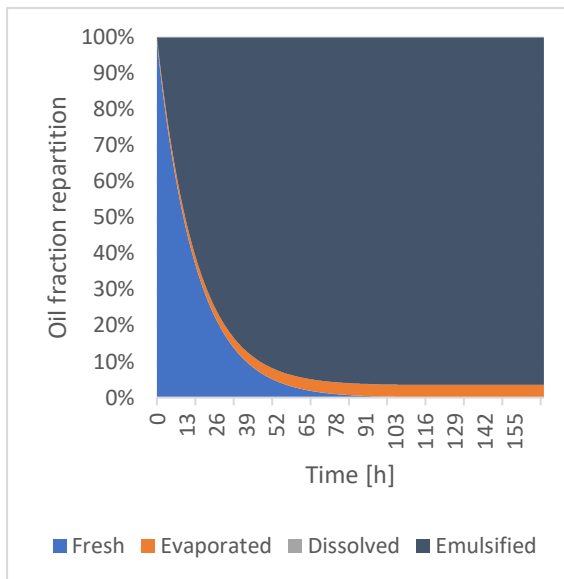
IM-5 – 5°C – true boiling point curve – Jones evap



IM-5 – 5°C – OSCAR – Jones evap



IM-5 – 5°C – true boiling point curve – Brighton evap



IM-5 – 5°C – OSCAR – Brighton evap

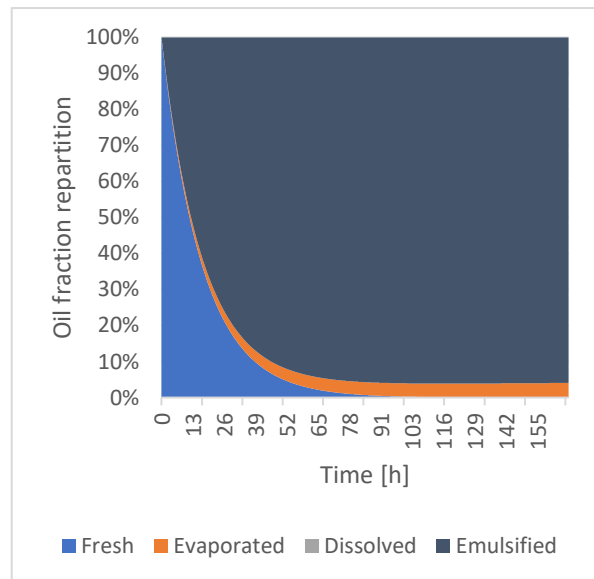
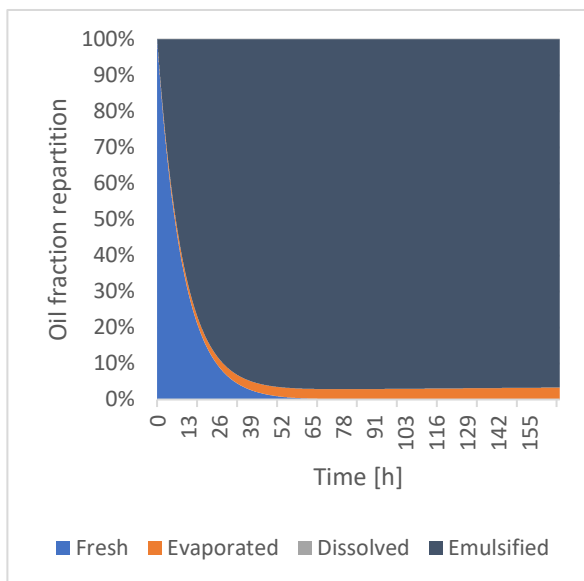
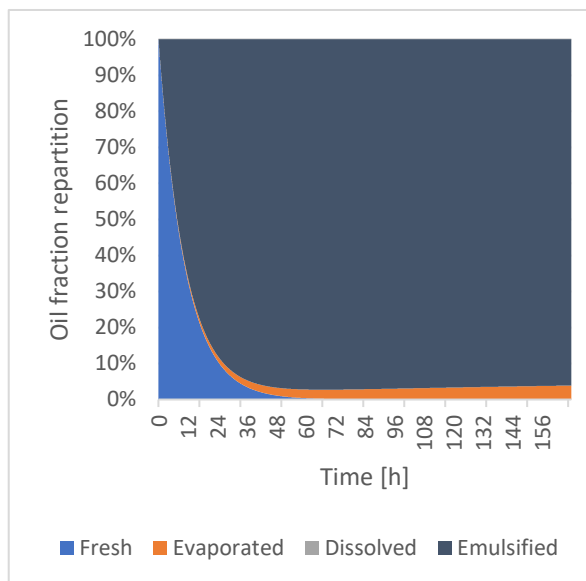


Figure 11 : Comparison of weathering simulations of IM-5 at 5°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation.

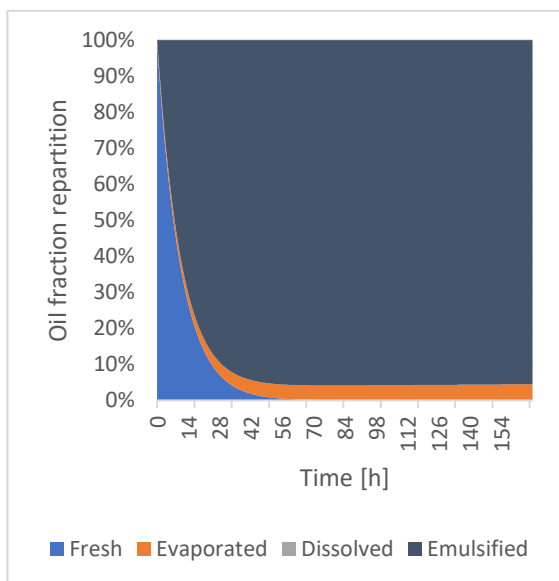
IM-5 – 15°C – true boiling point curve – Jones evap



IM-5 – 15°C – OSCAR – Jones evap



IM-5 – 15°C – true boiling point curve – Brighton evap



IM-5 – 15°C – OSCAR – Brighton evap

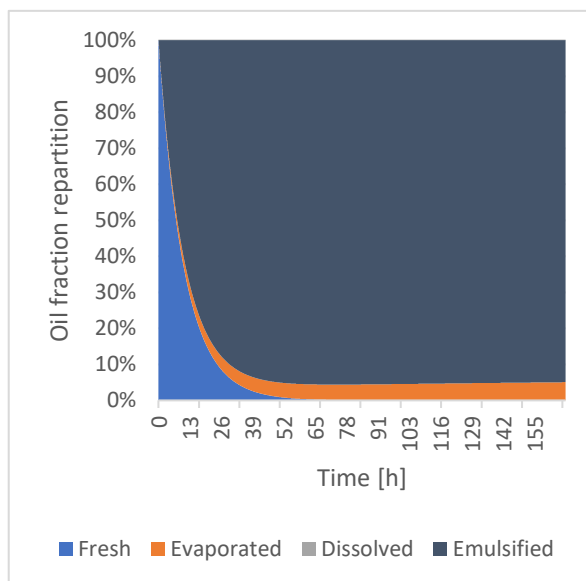
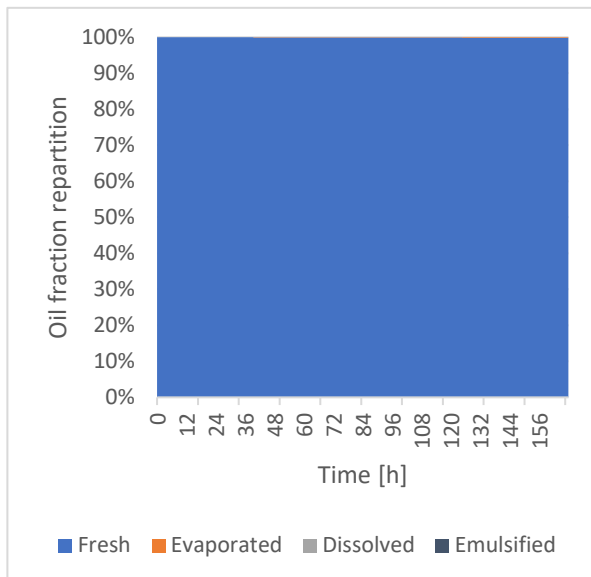
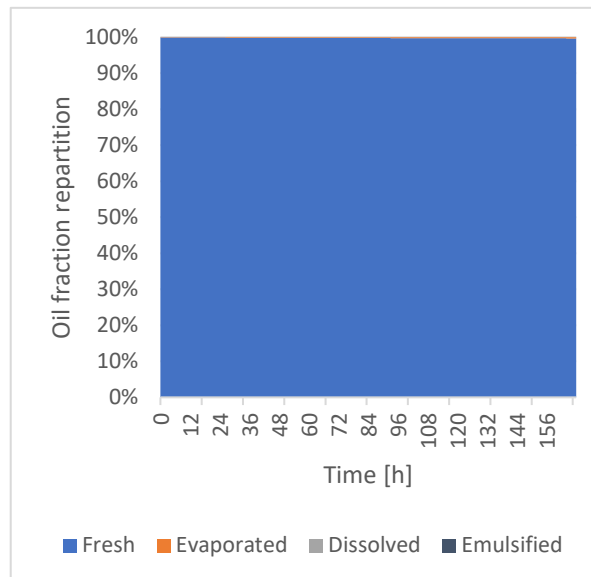


Figure 12 : Comparison of weathering simulations of IM-5 at 15°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation.

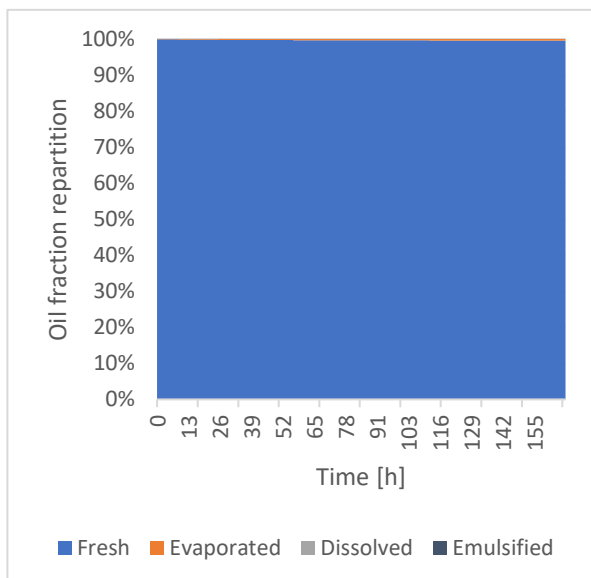
IM-14 – 5°C – true boiling point curve – Jones evap



IM-14 – 5°C – OSCAR – Jones evap



IM-14 – 5°C – true boiling point curve – Brighton evap



IM-14 – 5°C – OSCAR – Brighton evap

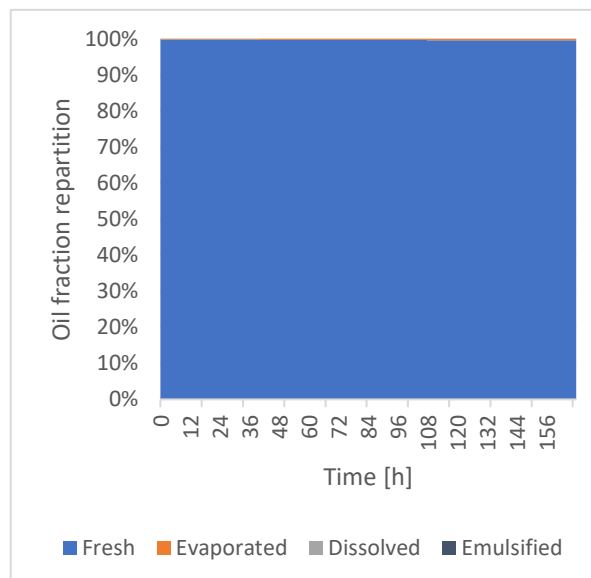
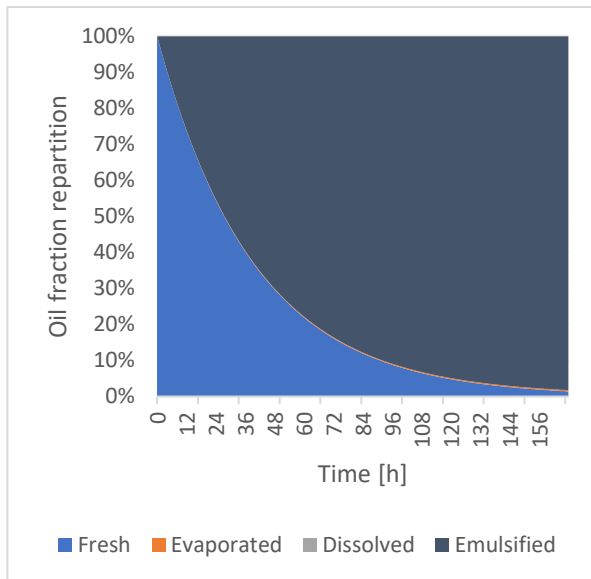
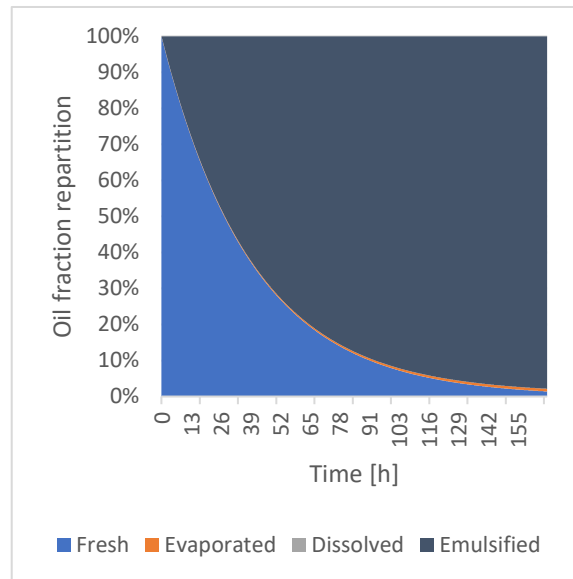


Figure 13 : Comparison of weathering simulations of IM-14 at 5°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation.

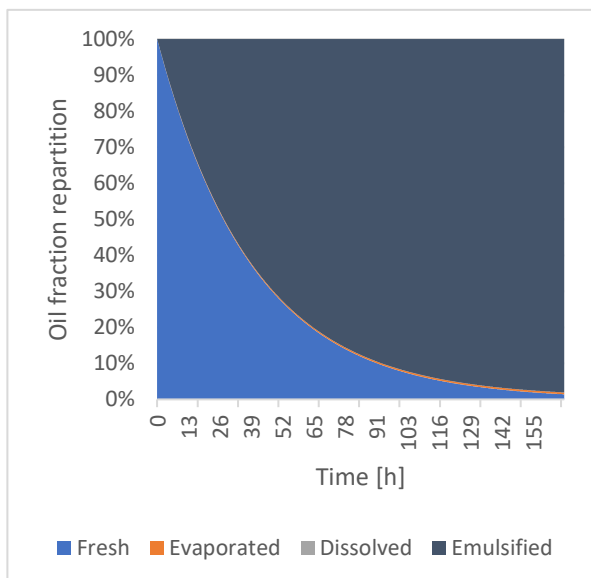
IM-14 – 15°C – true boiling point curve – Jones evap



IM-14 – 15°C – OSCAR – Jones evap



IM-14 – 15°C – true boiling point curve – Brighton evap



IM-14 – 15°C – OSCAR – Brighton evap

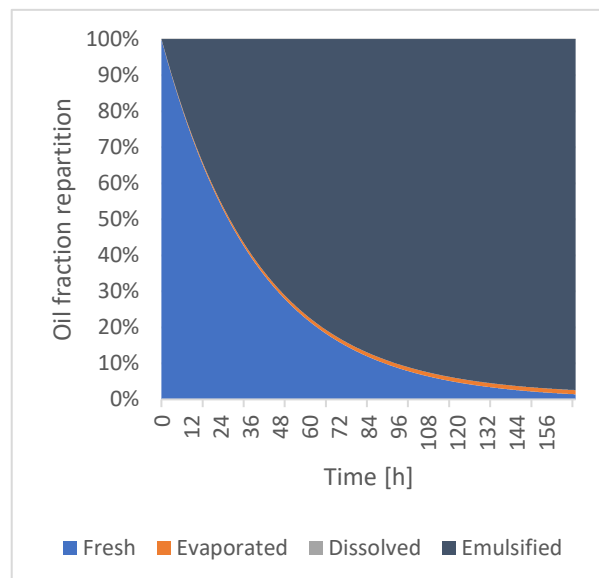
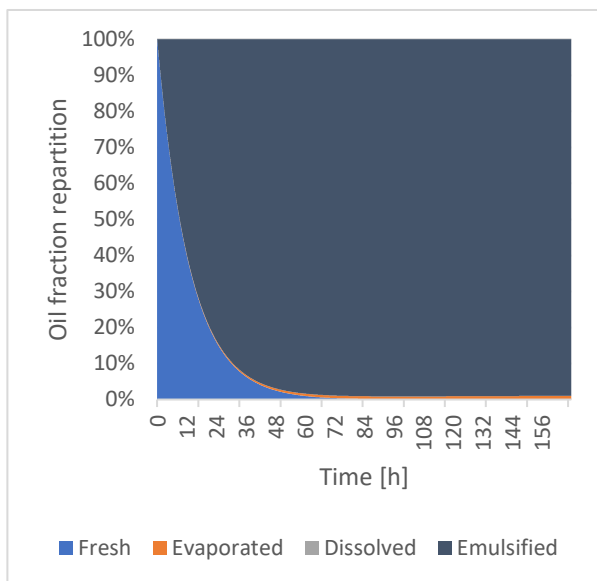
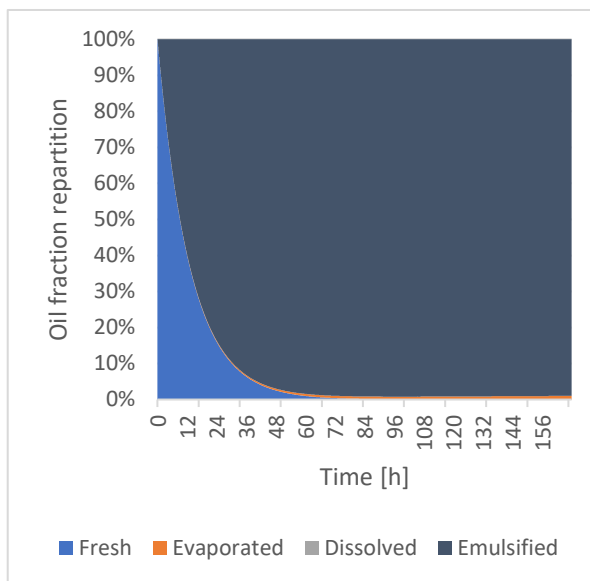


Figure 14 : Comparison of weathering simulations of IM-14 at 15°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation

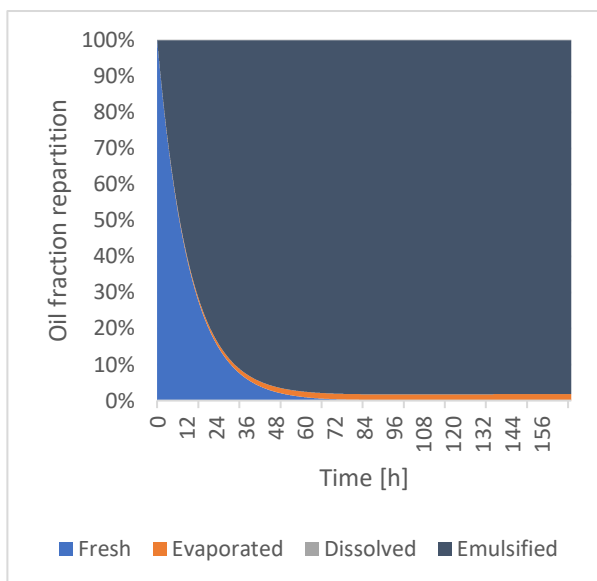
IM-15 – 5°C – true boiling point curve – Jones evap



IM-15 – 5°C – OSCAR – Jones evap



IM-15 – 5°C – true boiling point curve – Brighton evap



IM-15 – 5°C – OSCAR – Brighton evap

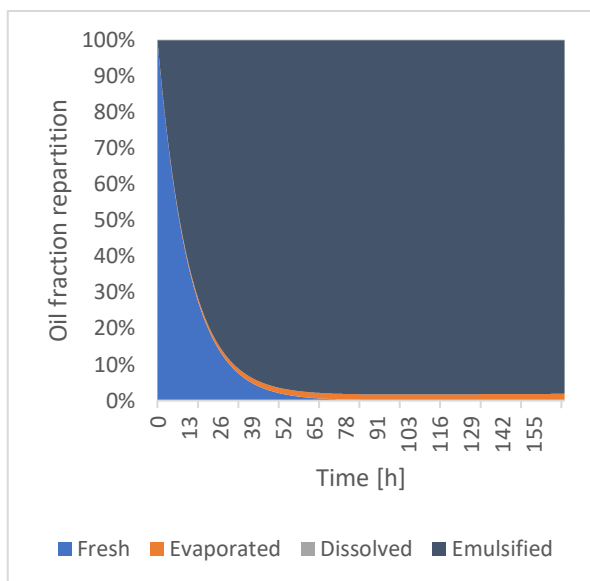
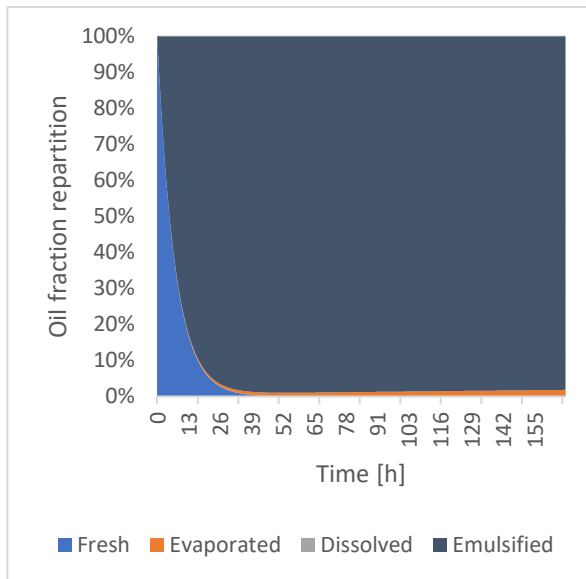
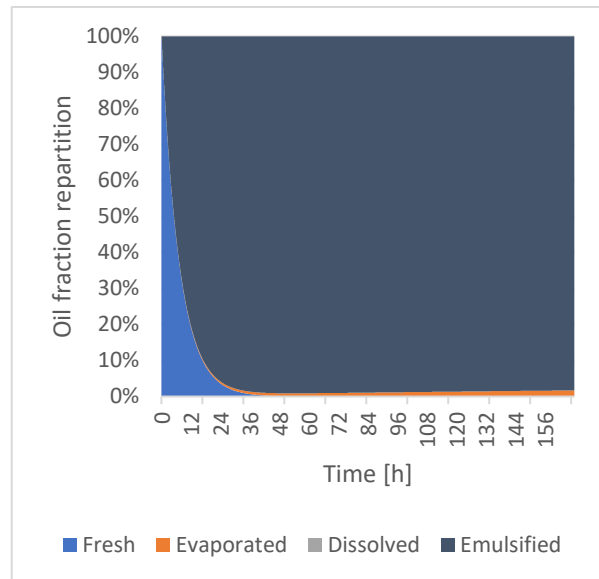


Figure 15 : Comparison of weathering simulations of IM-15 at 5°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation.

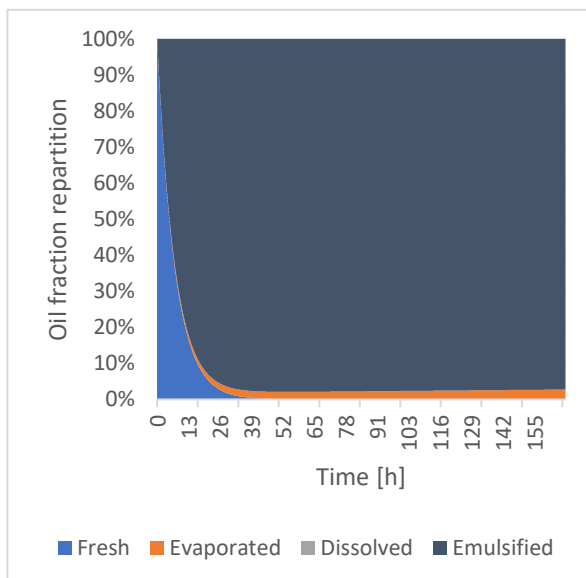
IM-15 – 15°C – true boiling point curve – Jones evap



IM-15 – 15°C – OSCAR – Jones evap



IM-15 – 15°C – true boiling point curve – Brighton evap



IM-15 – 15°C – OSCAR – Brighton evap

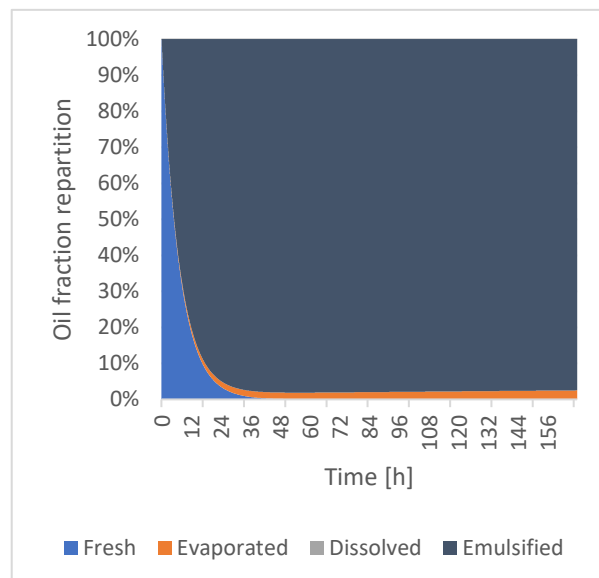


Figure 16 : Comparison of weathering simulations of IM-15 at 15°C for 2 different pseudo-components approach and 2 different parametrizations of evaporation

5 Validating oil weathering parametrizations

The main purpose of the IMAROS modelling task is to perform an in-depth validation of the toy model results against the polludrome observations. Polludrome observations providing information about the water content uptake, evaporation, oil density and oil viscosity, the validation exercise will focus on these 4 parameters. However, we will also show how the OSCAR characterization helps us to tell something about the evolution of the oil composition and even about the oil ecotoxicity.

More specifically we will in this section, we will answer the following questions

- Can models reproduce the water uptake rate in the water-in-oil emulsion for VLSFO?
- Are models able to represent VLSFO evaporation?
- What can models tell about the VLSFO slick composition?
- What can models tell about VLSFO ecotoxicity?
- Can models foresee VLSFO density?
- Can models foresee VLSFO viscosity?

5.1 Can models reproduce the water uptake rate in water-in-oil emulsion?

5.1.1 Calibration of the Scory's parametrization

The parametrization describing the emulsification process (Scory, 2005) (Annex I.4) computes the mass transfer between the fresh oil fraction remaining at the sea surface $V_f(t)$ and a fully emulsified oil fraction $V_{em}(t)$, *what* provides an estimate of the water content evolution. This Scory parametrization assumes that the emulsion process follows an exponential dynamic with a half-life $t_{1/2}$ of

$$t_{1/2} = \ln 2 \frac{1 - C_{18}}{C_{18}} \frac{C_{15}}{K_{em} H_s} C_{18} \quad (1)$$

H_s : Significant wave height [m], in the polludrome 0.75 m is used.

C_{15} : an empirical scaling coefficient, equal to 2000000 [m]

C_{18} : Maximum water content []

K_{em} : Kinetic coefficient of water uptake in the emulsion (0-120) [s^{-1}]

In this equation, both the maximal water content C_{18} and the kinetic coefficient K_{em} are oil-dependent parameters. If the maximum water content might be estimated from lab experiment (Table 2), the kinetic coefficient must be determined from the emulsion dynamics as observed in the polludrome experiments. For this purpose, the time-evolution of the normalized water content¹ is plotted in a base2 logarithmic scale (Figure 17 to Figure 22); the slope on this logarithmic graph is related to the half-life of an exponential function:

$$\frac{1}{slope} = \ln 2 \frac{1 - C_{18}}{C_{18}} \frac{C_{15}}{K_{em} H_s} C_{18} \quad (2)$$

¹ The normalized water content is the water content divided by the maximal water content.

$$K_{em} = \ln 2 \frac{1 - C_{18}}{C_{18}} \frac{C_{15}}{H_s} C_{18} \text{ slope} \quad (3)$$

After some trivial processing (Figure 17 to Figure 22 and Table 5), we have determined that the kinetic coefficient K_{em} was around 12 for IM-5, 13 for IM-14 and between 30 and 39 for IM-15. It is important to note that, since no formation of water-in-oil emulsion has been observed for IM-14 at 5°C, the value of K_{em} for this experiment (around 138.4) is not reliable.

Table 5: Determination of the K_{em} from the slope of the regression of the water content for the first 20 hours in the polludrome.

Oil	T° [°C]	slope [h ⁻¹]	Max water content from polludrome (C_{18})	$t_{1/2}$ [s]	$\frac{C_{18}}{1 - C_{18}} \frac{H_s}{C_{15}}$	$K_{em} = \frac{\ln 2}{t_{1/2} \frac{C_{18}}{1 - C_{18}} \frac{H_s}{C_{15}}}$
IM-5	5	0.1559	0.868	23091.73	2.47E-06	12.17
	15	0.1484	0.873	24258.76	2.58E-06	11.08
IM-14	5	0.0787	0.226	45743.33	1.09E-07	138.4
	15	0.0465	0.648	77419.35	6.90E-07	12.97
IM-15	5	0.1656	0.685	21739.13	8.15E-07	39.10
	15	0.2227	0.791	16165.24	1.42E-06	30.21

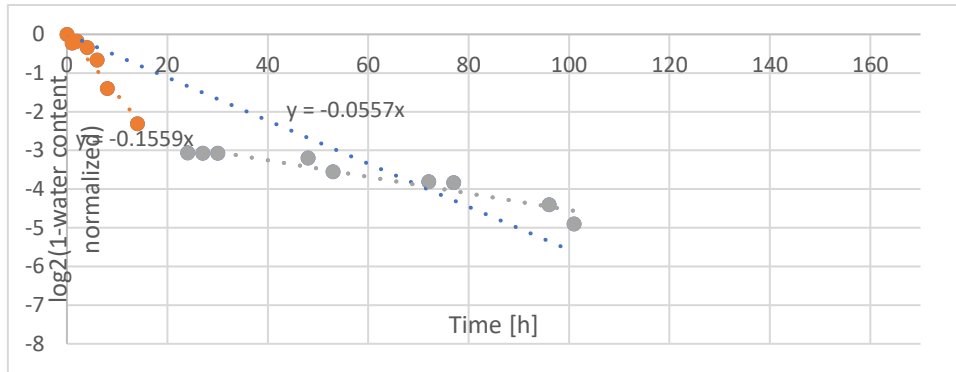


Figure 17: log base 2 of 1-Water content normalized as time function **for IM-5°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil. The slope of the regression curves blue and orange are shown on the plot.

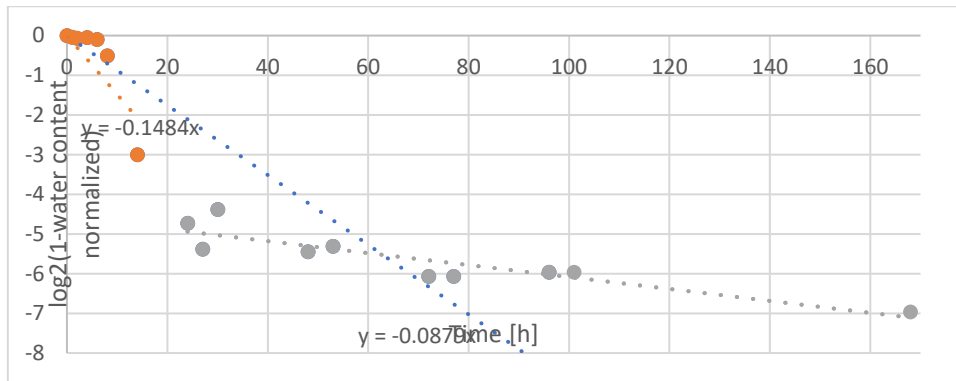


Figure 18: log base 2 of 1-Water content normalized as time function **for IM-5 15°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil. The slope of the regression curves blue and orange are shown on the plot.

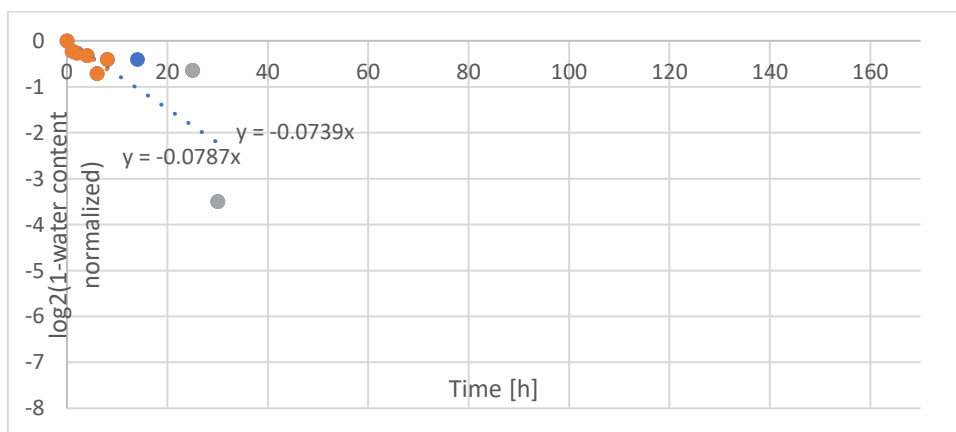


Figure 19: log base 2 of 1-Water content normalized as time function **for IM-14 5°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil. The slope of the regression curves blue and orange are shown on the plot. The regression curve has not been computed for the gray point because the experiment has been stopped early.

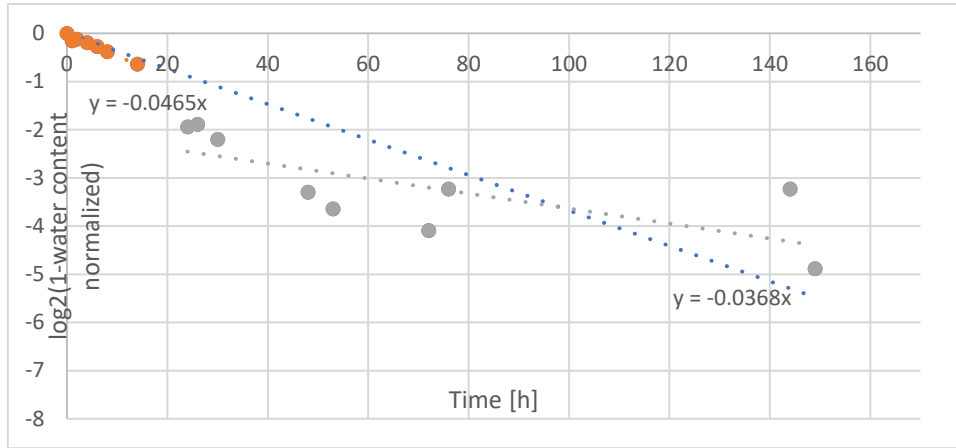


Figure 20: log base 2 of 1-Water content normalized as time function **for IM-14 15°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil. The slope of the regression curves blue and orange are shown on the plot.

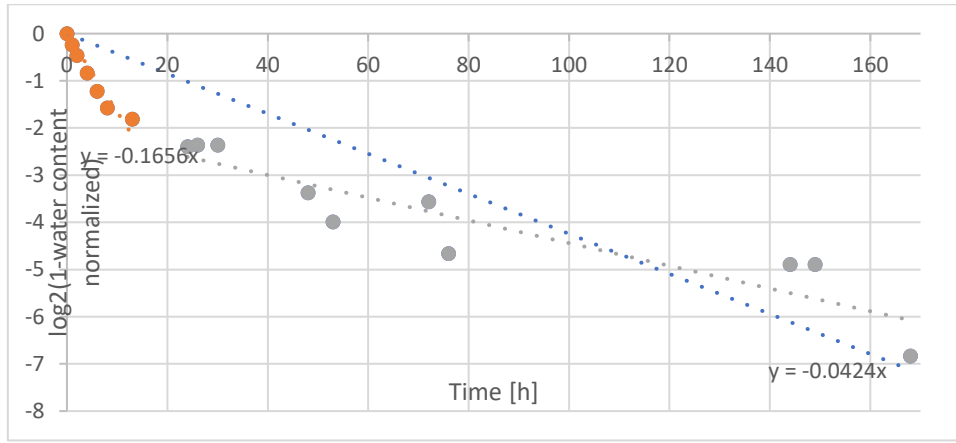


Figure 21: log base 2 of 1-Water content normalized as time function **for IM-15 5°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil. The slope of the regression curves blue and orange are shown on the plot.

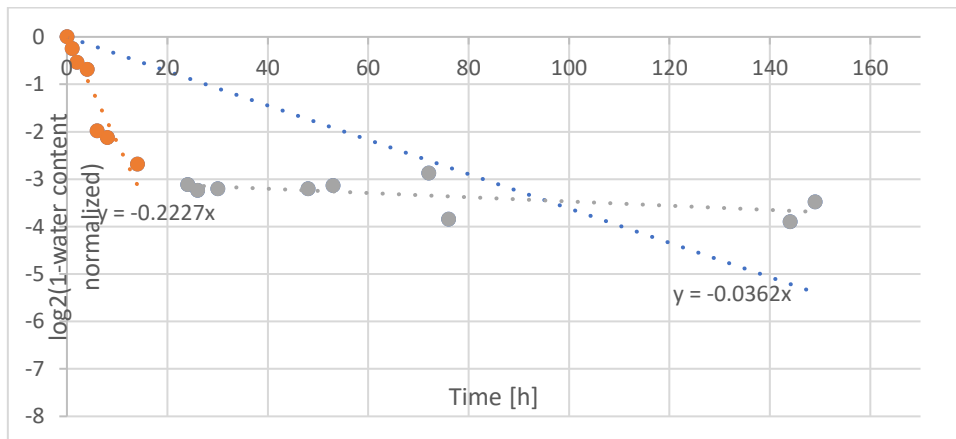


Figure 22: log base 2 of 1-Water content normalized as time function **for IM-15 15°C** in the polludrome. There are three regressions, one (orange) on the point before 20h and forced at (0,0), one gray on the point after 20h and one blue for a regression on all the points and forced at (0,0). The time needed to go down of one unit is the same as the half-life of the non-emulsified oil.

5.1.2 Are models able to reproduce the water uptake rate in water-in-oil emulsion?

Figure 23, Figure 24 and Figure 25 show a direct comparison between the water content observed in the polludrome experiments and the water content from the numerical experiments for IM-5, IM-14, and IM-15, respectively. Each Figure displays 4 curves. The continuous lines represent the simulation results with the maximal water content from the lab characterization (Table 2), while the dashed lines represent the simulation results with the maximal water content estimated from the polludrome experiments (**Error! Reference source not found.**).

From these Figures, we may conclude that, once calibrated, the Scory parametrization is able to perfectly reproduce the time-evolution of the water content in the water-in-oil emulsion for VLSFO oils. For instance, we clearly see the impact of the temperature on the water content.

However, the Figures also show that this emulsion parametrization is extremely sensitive to the parameters C_{18} , the maximal water content and the kinetic coefficient K_{em} . For instance, an underestimation of 10% of the maximum water content (as it can easily be done in Lab, cf. IM-5 at 5°C) will directly lead to an underestimation of the simulated water content but also to an underestimation of the water uptake dynamic.

In case of a real oil spill event for which none of these two values are known, we advise to perform a sensitivity analysis, with values for the water content ranging between 40 and 80% and values for K_{em} ranging between 0 and 120; the range of possible values will be refined as function of field observations become available.

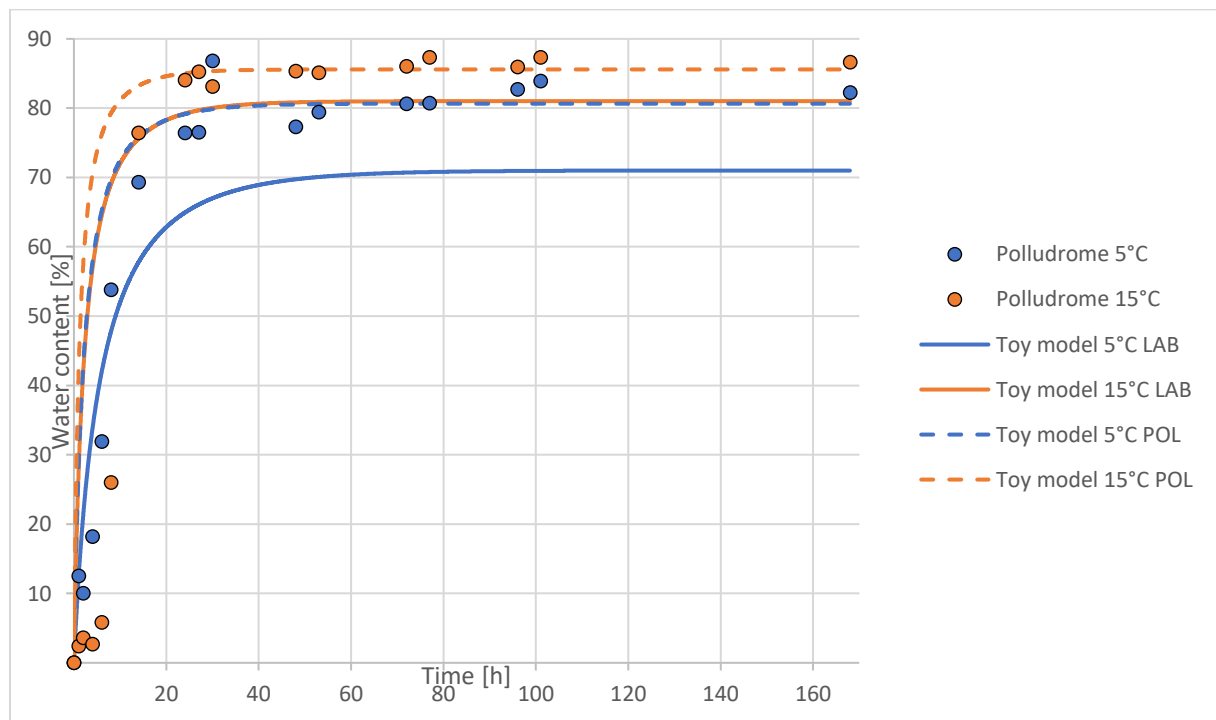


Figure 23: Water content of the IM-5 as a function of time. The “polludrome” points are experimental data, the “toy model LAB” uses the max water content from the laboratory and the “toy model POL” uses the average of the water content data after 20 hours from the polludrome. All data are at 5°C and 15°C.

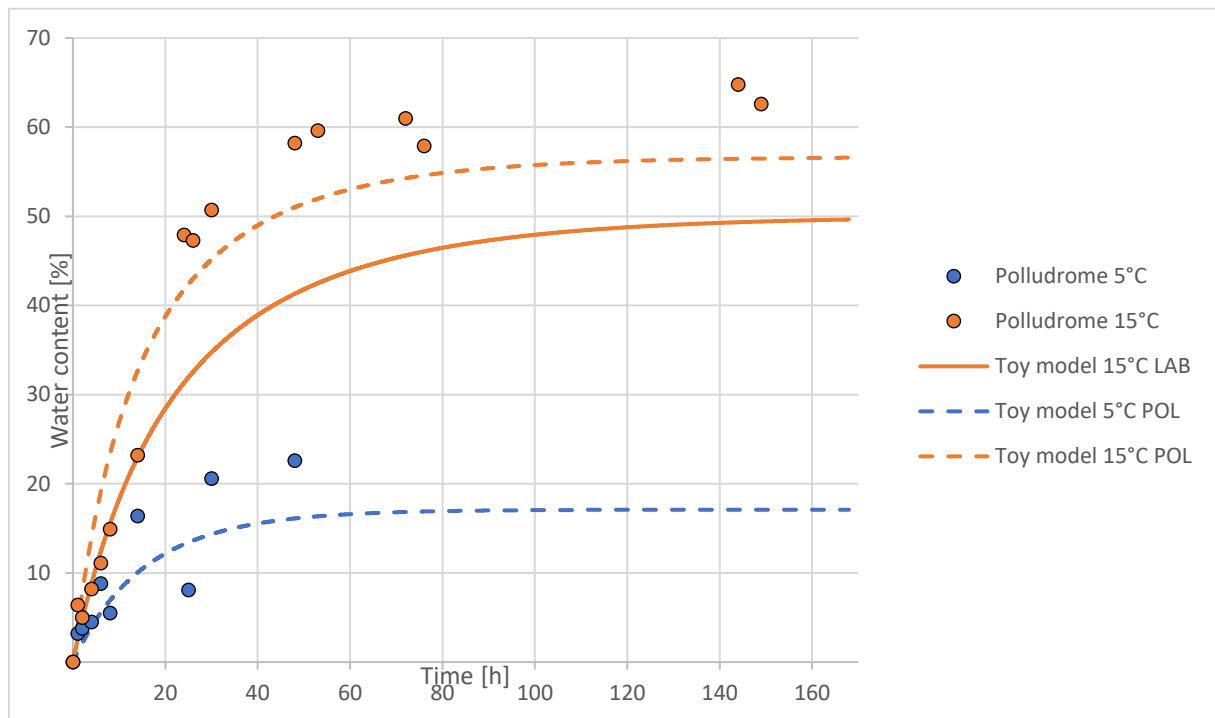


Figure 24: Water content of the IM-14 as a function of time. The “polludrome” points are experimental data, the “toy model LAB” uses the max water content from the laboratory and the “toy model POL” uses the average of the water content data after 20 hours from the polludrome. All data are at 5°C and 15°C, but the water content was not available at the laboratory for 5°C and thus the model will estimate a water constant of 0.

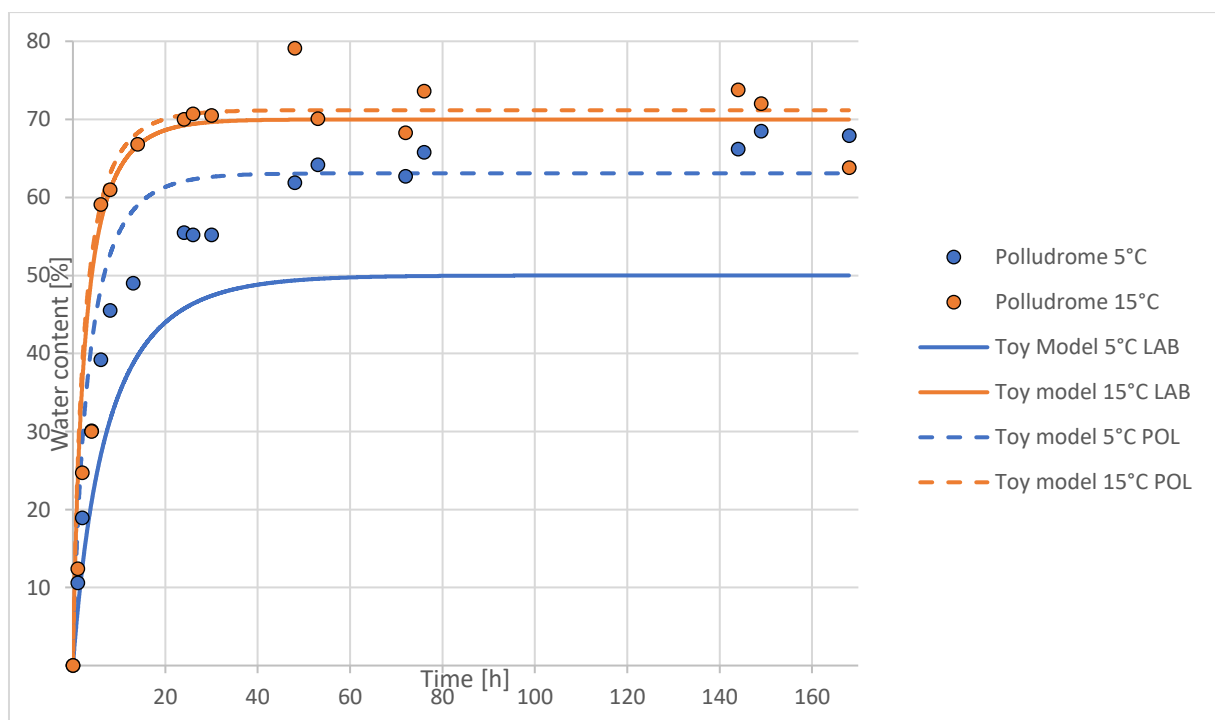


Figure 25: Water content of the IM-15 as a function of time. The “polludrome” points are experimental data, the “toy model LAB” uses the max water content from the laboratory and the “toy model POL” uses the average of the water content data after 20 hours from the polludrome. All data are at 5°C and 15°C.

5.2 Are models able to simulate the evaporation rate?

Evaporation is surely the main process explaining the changes in oil composition, the lightest compounds evaporating faster than the heaviest. In this study, the two main evaporation parametrizations (Jones, 1997) and (Brighton P.W.M., 1985) have been tested for two different pseudo-component characterizations: the true boiling point curve and the OSCAR characterization (section 3.1). This leads to 4 different simulations for each polludrome experiment, presented in Figure 34 to Figure 38. All the processes (evaporation, emulsification...) are used, but only the evaporated amount is showed. There are four lines for each oil, because each characterization has been tested for two different parametrizations for the evaporation.

Surprisingly, all the curves are always close to each other for each simulation. This means that the model is not sensitive to the parametrization of the evaporation or to the way the oil is characterized, meaning that it has some robustness here.

For IM-5, the model stays close to the data for most of the simulation duration and the small difference with the data could be explained by the uncertainty of the measurements. This is not the case with IM-15 where the data from the polludrome shows significantly more evaporation than the simulation of the model. However, the model predicted the other parameters (water content, density...) for this oil in the right order of magnitude, and the true boiling point curve or the OSCAR characterization does not have a large amount of volatile compounds. This, and the high dispersion of the data point could indicate that the data from the polludrome for this oil are highly uncertain. One hypothesis is that the crust formed by this oil could have a very high evaporation rate compared to the bulk of the oil, causing a heterogeneity which can be hard to take into account with the experimental data collection setup.

For IM-14, the measurements of the evaporated fractions in the polludrome experiment are scattered because they are smaller than the measurement error. Thus, they cannot be used to evaluate the predictions of the model apart from implying that the evaporated amount is very small. The evaporated amount as predicted by the model is very small too (around 1% or less) and is then probably close to reality.

From this comparison, we conclude that the two parametrizations can predict the amount evaporated at least in the right order of magnitude regardless of the characterization used on the oil. It could be interesting to have more experiments to better evaluate the parametrization and the characterizations, especially if it is possible to have data with less spreading.

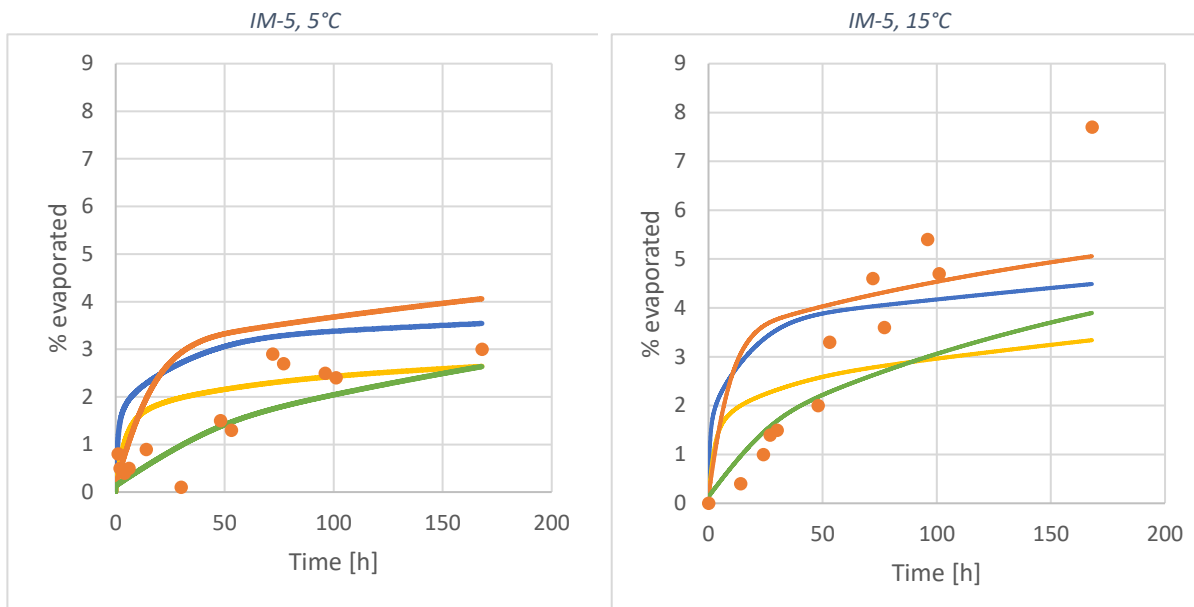


Figure 26: IM-5. Comparison of the polludrome evaporation rate data (orange dots) with the results from the toy model with the true boiling point approach and the Brighton evaporation (blue line), with the boiling point approach and the Jones evaporation (yellow line), with the OSCAR characterization and the Brighton evaporation (orange line) and with the OSCAR characterization and the Jones evaporation (green line).

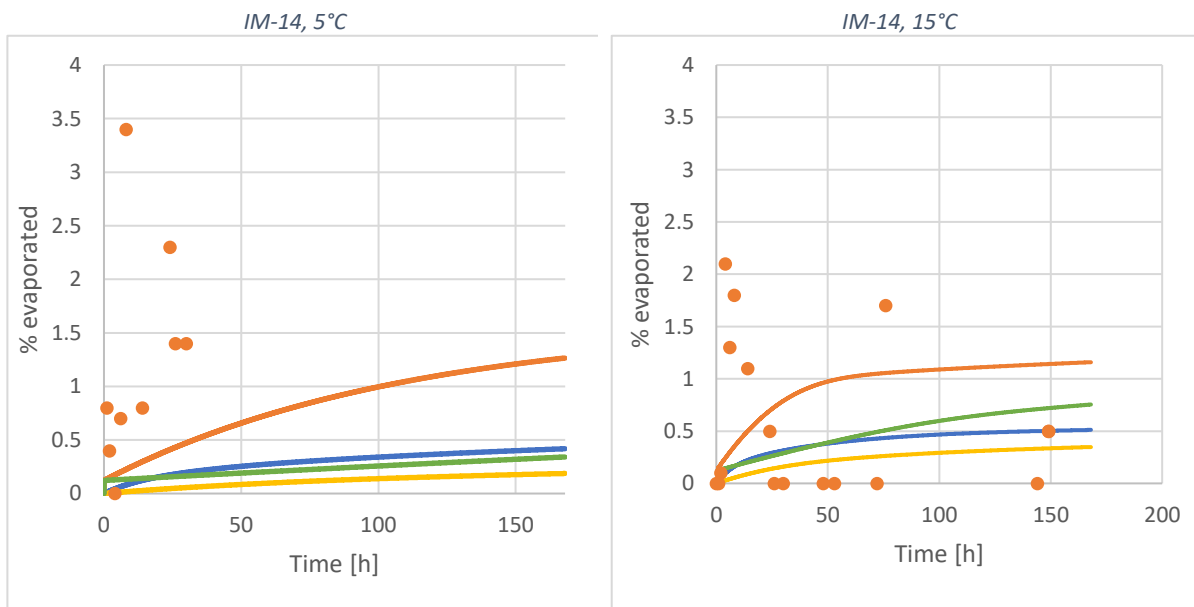


Figure 27: IM-14. Comparison of the polludrome evaporation rate data (orange dots) with the results from the toy model with the true boiling point approach and the Brighton evaporation (blue line), with the boiling point approach and the Jones evaporation (yellow line), with the OSCAR characterization and the Brighton evaporation (orange line) and with the OSCAR characterization and the Jones evaporation (green line).

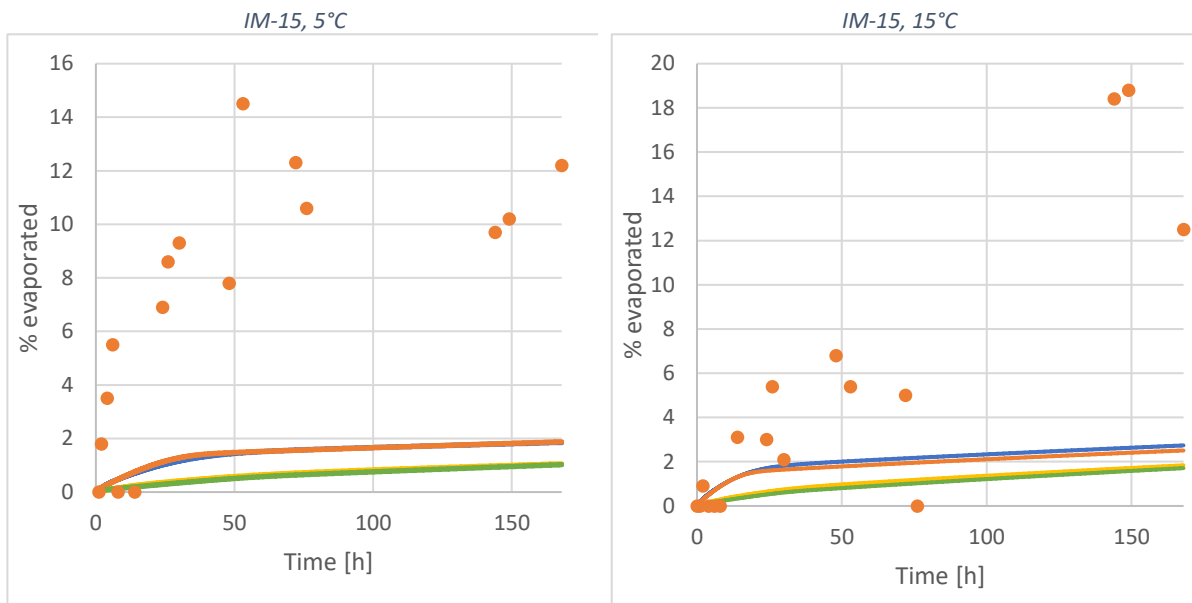


Figure 28: IM-15. Comparison of the polludrome evaporation rate data (orange dots) with the results from the toy model with the true boiling point approach and the Brighton evaporation (blue line), with the boiling point approach and the Jones evaporation (yellow line), with the OSCAR characterization and the Brighton evaporation (orange line) and with the OSCAR characterization and the Jones evaporation (green line).

5.3 What can models tell about the evolution of the oil chemical composition?

In the toy model, two pseudo-component approaches have been implemented: the true boiling point characterization and the OSCAR characterization. The OSCAR characterization sorts the light components of the oil mixture into 23 groups of homogeneous chemical compounds.

With respect to the true boiling point approach, the OSCAR characterization has two main advantages:

- The toy model can track the weathering of each chemical compound group individually.
- Since a solubility value can be associated to each group of chemical compounds, the toy model can simulate dissolution and volatilization processes.

Consequently, when the OSCAR characterization is available, a detailed analysis of the toy model results allows to get information about the evolution of the chemical composition of the surface slick (Figure 29, Figure 30 and Figure 31 for IM-5, IM-14, and IM-15 experiments at 15°C). As the evaporation is the main process driving the composition change, the OSCAR pseudo components are sorted as a function of their vapor pressure, starting with the most volatile compounds i.e., the group that will change the most. Unfortunately, the OSCAR characterization has not been performed on the polludrome samples, what prevent us validating the graphs at the end of the simulation.

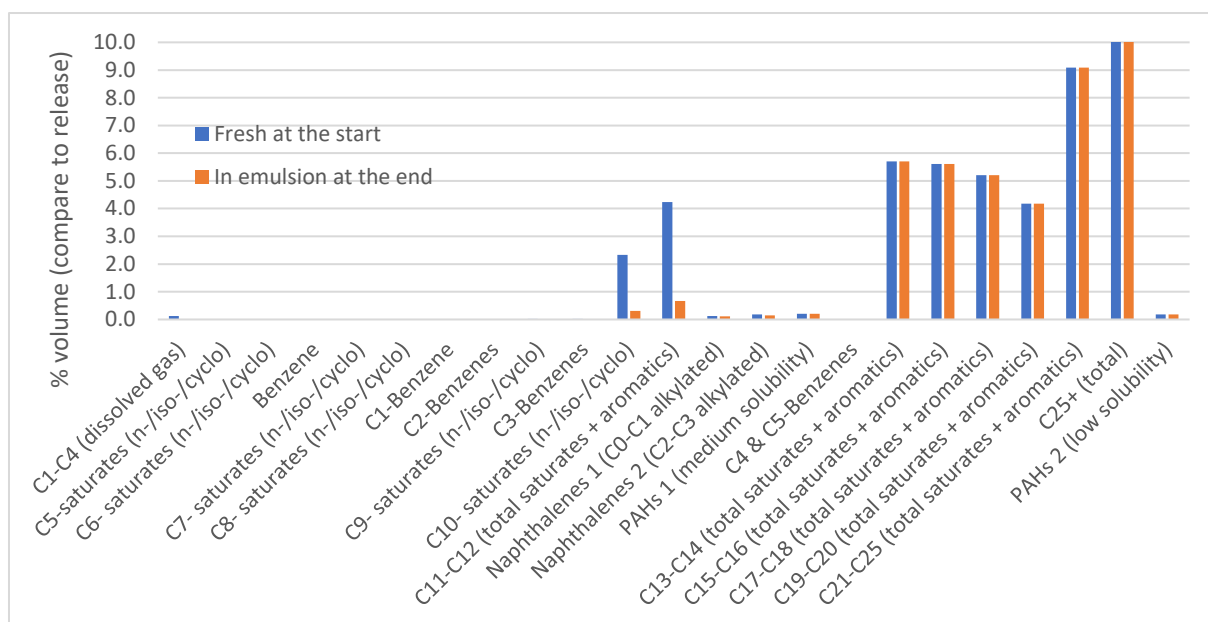


Figure 29: Evolution of the OSCAR pseudo component from the fresh at the start to the emulsion at the end for IM-5 at 15°C, there is no difference for the C25+ fraction between the start and the end, the value is well above 10%

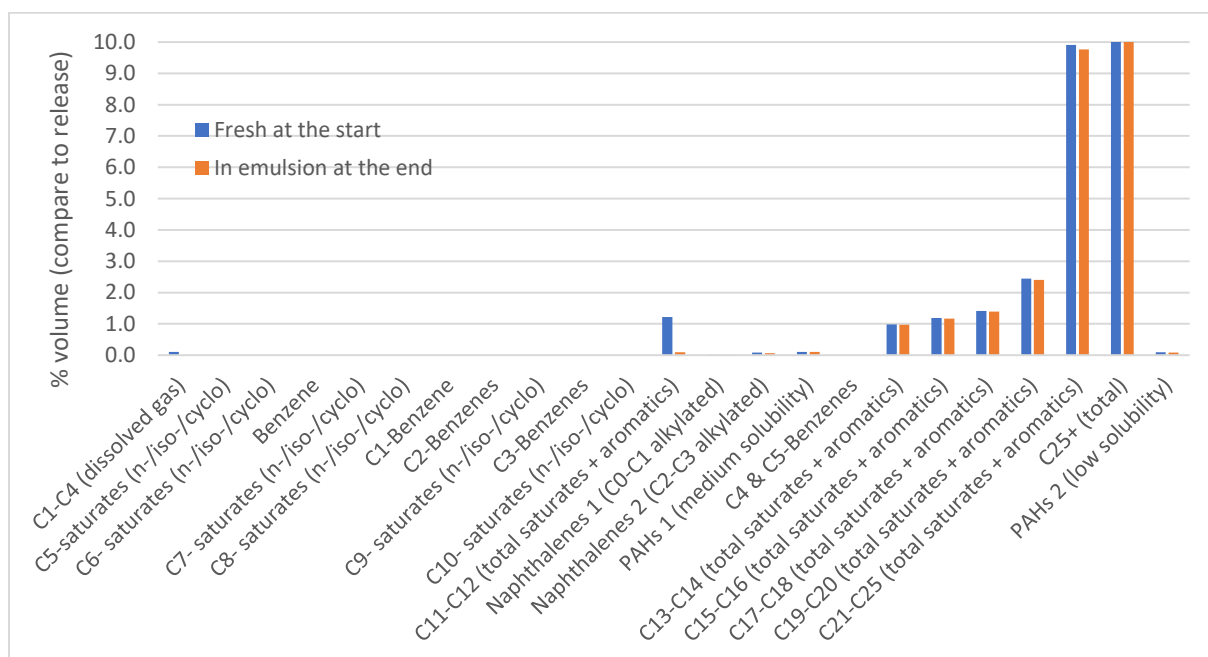


Figure 30 : Evolution of the OSCAR pseudo component from the fresh at the start to the emulsion at the end for IM-5 at 15°C, the value of C25+ is well above 10%. There is a decrease in some heavy compounds because they did not have the time to be fully emulsified.

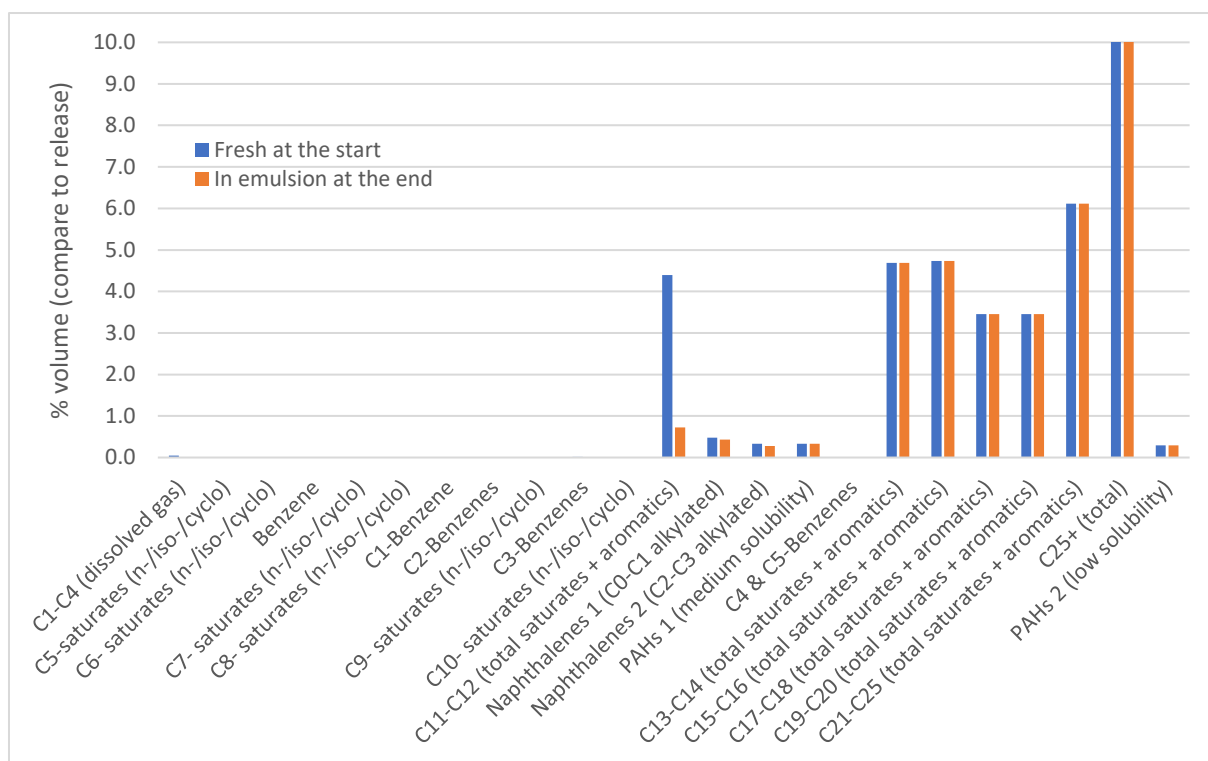


Figure 31: Evolution of the OSCAR pseudo component from the fresh at the start to the emulsion at the end for IM-5 at 15°C, there is no difference for the C25+ fraction between the start and the end and their value are well above 10%

5.4 Can models tell something about ecotoxicity?

The second advantage of the OSCAR characterizations is that it allows to compute dissolution and volatilization on the 23 chemical compounds groups. The simulations with the toy model suggest that for IM-5, IM-14 and IM-15, dissolution is 3 orders of magnitude smaller than evaporation (a factor 1000 between evaporation and dissolution).

Although such a difference cannot be displayed on Figure 11 to Figure 16, the interpretation of the dissolution fraction allows us to tell something about oil ecotoxicity. When performing such an analysis, we advise performing model simulations with volatilization process, as this process significantly changes the concentration of the dissolved fraction. Figure 32 and Figure 33 illustrates this constatation on the IM-5 case at 15°C: from the model simulation without volatilization (Figure 32), we might conclude that the largest fraction of the dissolved oil is made of C11-C12 aromatics while the simulation with volatilization (Figure 33) shows that the most abundant dissolved compounds are toxic PAH (Figure 33).

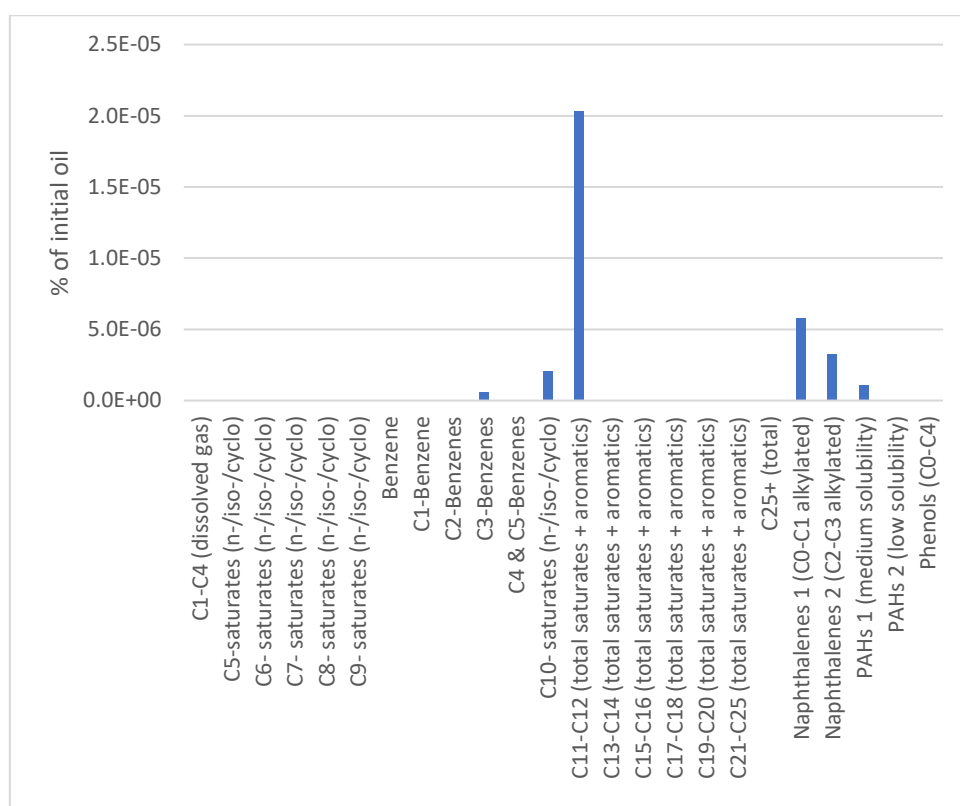


Figure 32: Composition of the water fraction of IM-5 at 15°C at the end of the simulation when there is dissolution but no volatilization, in % relative to the initial volume of oil

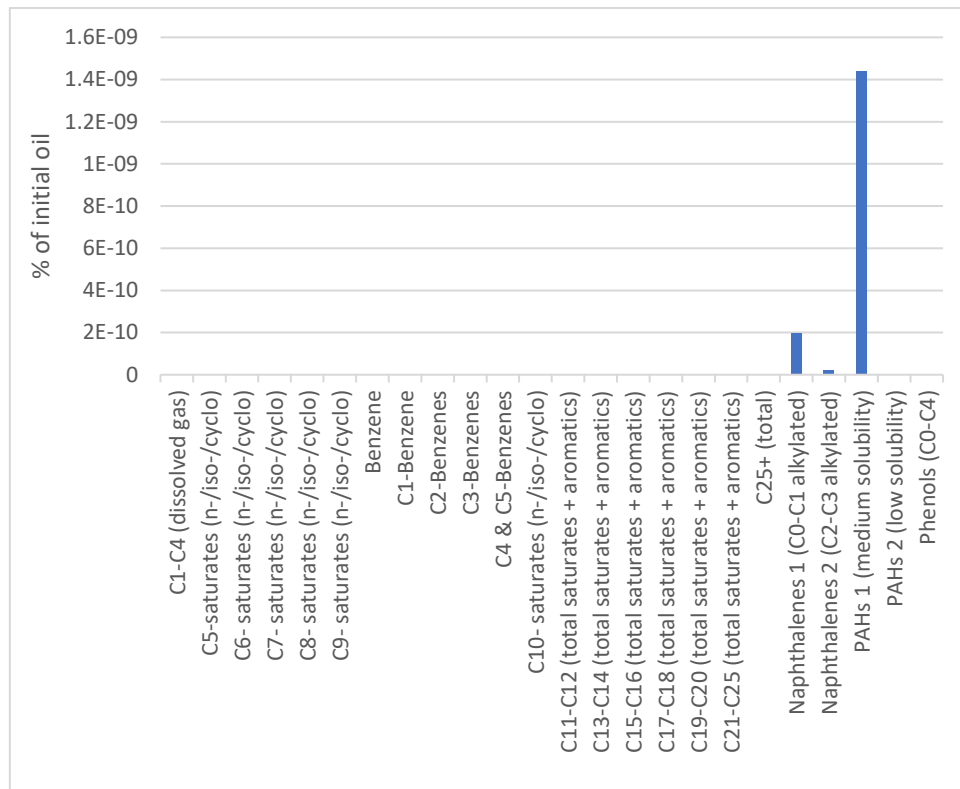


Figure 33 : Composition of the water fraction of IM-5 at 15°C at the end of the simulation with volatilization and dissolution, in % relative to the initial volume of oil

5.5 Are models able to predict the evolution of density?

Density is a key parameter to predict the evolution of the oil spilled at sea, even more for LSFO which can have a density close to the seawater density, causing oil to sink. It is then critically important to accurately predict the evolution of the oil slick density.

In the Figure 60 to the Figure 62, the prediction of the model is compared to the data from the polludrome, at 5°C and 15°C. Using the maximum water content determined by the laboratory or on the polludrome data can lead to significant variation in the results because the water have a high impact on the density of the emulsion. For IM-5 and IM-15, the model correctly predicts the density even if it slightly overestimates it. For IM-14, the data are heavily scattered, and a diminution of the density occurs. This could be caused by the incorporation of air bubbles inside the oil when it is spilled in the water, making it very heterogenous and causing high variability on the measurements.

The parametrization used can predict the density in the right order of magnitude if the water content and the evaporation are estimated accurately. The model can be closer to the empirical data if the maximum water content is determined very accurately. Phenomenon causing heterogeneity in the oil are not considered for now, because they are very unpredictable and can depend on the way the oil is spilled, making hard the comparison with empirical data.

From this analysis, we conclude that the weathering models can accurately predict density of weathered and emulsified VLSFO slicks, at least for conditions in which oil remains fluid (so for temperature higher than the pour point)

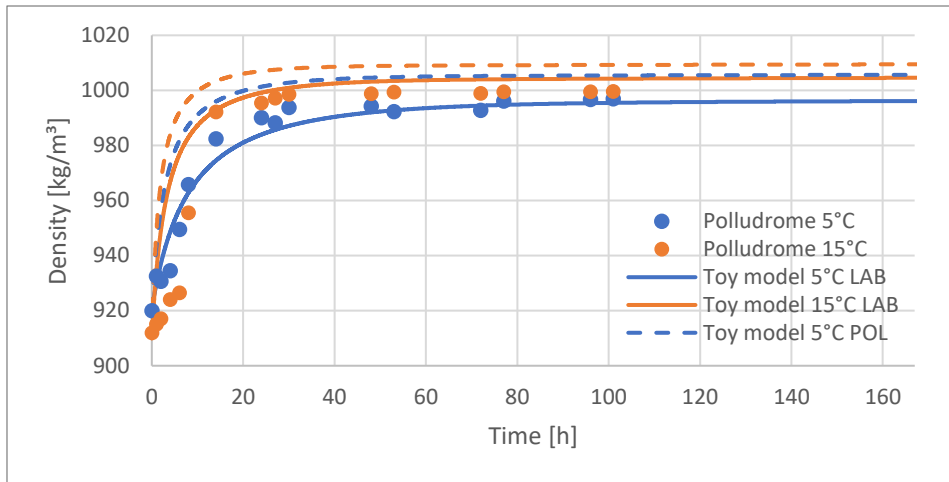


Figure 34 : Evolution of the density of IM-5 in the polludrome and simulated (toy model) at 5 and 15°C. LAB means that the max water content is from the laboratory data and POL means the max water content is from the polludrome data.

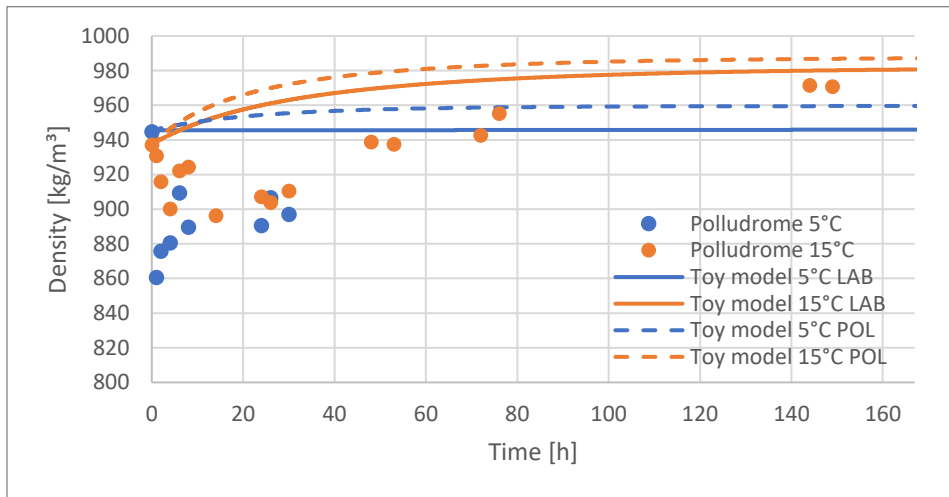


Figure 35 : Evolution of the density of IM-14 in the polludrome and simulated (toy model) at 5 and 15°C. LAB means that the max water content is from the laboratory data and POL means the max water content is from the polludrome data.

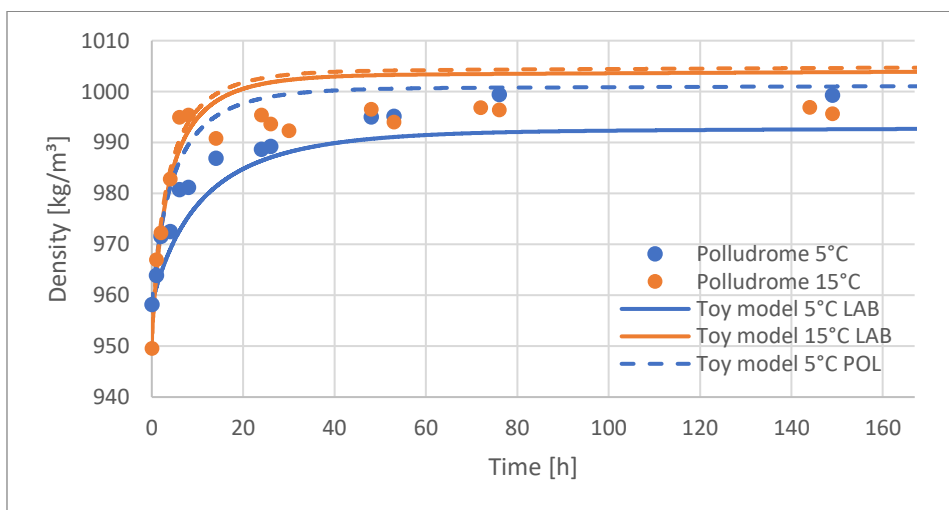


Figure 36 : Evolution of the density of IM-15 in the polludrome and simulated (toy model) at 5 and 15°C. LAB means that the max water content is from the laboratory data and POL means the max water content is from the polludrome data.

5.6 Are models able to simulate viscosity?

Viscosity is a complex parameter. At a macroscopic scale, it measures the resistance of a fluid to deformation at a given rate. At microscopic scale, it is related to intermolecular interactions and more precisely to momentum exchange between interacting molecules or between weakly bonded clusters of molecules. Such clusters are typically formed when temperature approaches the freezing/crystallizing point or for oil when temperature approaches the pour point (Riazi and Al-Otaibi, 2001). Viscosity is highly dependent on temperature. For complex fluid, viscosity can even span several orders of magnitude, explaining why it is usually plotted on a logarithmic scale.

Because of its complex nature, viscosity must be measured with ad hoc devices. In Lab, oil viscosity can be continuously measured as a function of the temperature and presented in the so-called viscosity sweep graph.

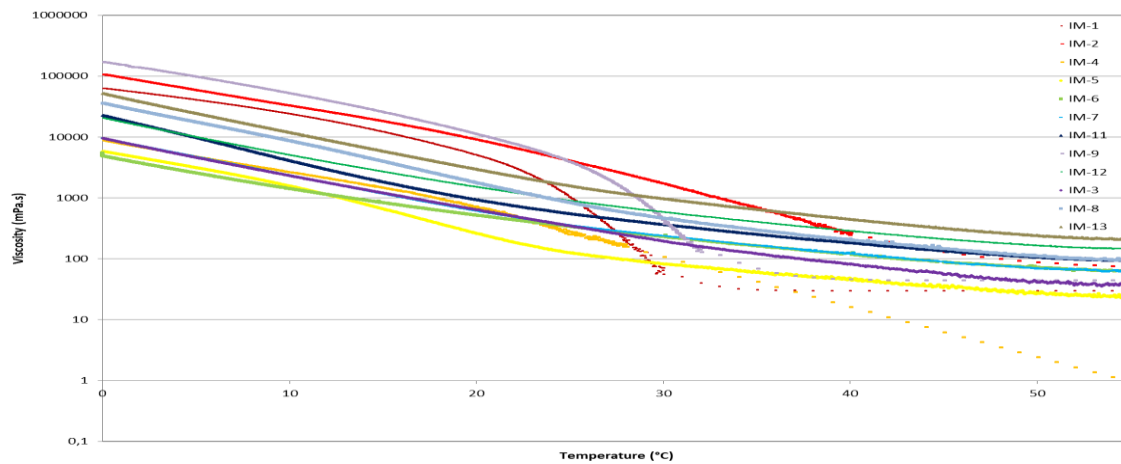


Figure 37 : Viscosity sweep graph for IM-1 to IM-13 (CEDRE, 2022a)

In absence of any viscosity sweep graph, a parametrization exists to estimate the oil viscosity from a few observations (Lehr et al., 2002) :

$$v_{oil} = v_{ref} \exp \left(C_{Temp} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) + C_{Evap} F_{Evap} \right) \quad (4)$$

v_{oil} : Kinematic viscosity of the oil [cSt]

v_{ref} : Kinematic viscosity at the reference temperature [cSt]

T_{ref} : Reference temperature [K]

T : Temperature [K]

C_{Temp} : Constant for each oil type [K], can be estimated to 5000 according to (Berry et al., 2012)

C_{Evap} : Constant for an oil type (Lehr et al., 2002), can be equal to 10 according to (Berry et al., 2012)

F_{Evap} : Fraction of oil evaporated from the slick [], (volume evaporated divided by volume spilled)

In addition to temperature, the water content is another important parameter to estimate the viscosity of an emulsified slick. For instance, (Betancour et al., 2005) suggest the following formula to compute the viscosity of an emulsified slick:

$$v_{slick} = v_{oil} \exp\left(\frac{C_{emul1}Y}{1 - C_{emul2}Y}\right) \quad (5)$$

Y : Water content of the emulsion []

C_{emul1}, C_{emul2} : Constants depending on the oil (2.5 and 0.65 respectively)

Combining the two formulas, in absence of any viscosity sweep graph, we can estimate the viscosity of an oil slick in this way (more details are available in annex I):

$$v_{oil} = v_{ref} \exp\left(C_{Temp}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) + C_{Evap} F_{Evap} + \frac{C_{emul1}Y}{1 - C_{emul2}Y}\right) \quad (6)$$

v_{oil} : Kinematic viscosity of the oil [cSt]

v_{ref} : Kinematic viscosity at the reference temperature [cSt]

T_{ref} : Reference temperature [K]

T : Temperature [K]

C_{Temp} : Constant for each oil type [K], can be estimated to 5000 according to (Berry et al., 2012)

C_{Evap} : Constant for an oil type (Lehr et al., 2002), can be equal to 10 according to (Berry et al., 2012)

F_{Evap} : Fraction of oil evaporated from the slick [], (volume evaporated divided by volume spilled)

Y : Water content of the emulsion []

C_{emul1}, C_{emul2} : Constants depending on the oil (0.25 and 0.65 respectively (Betancour et al., 2005))

The purpose of this section is twofold:

- Investigating if the default value for the empirical coefficients C_{Temp} , C_{emul1} and C_{emul2} can be used for VLSFOs.
- Investigating if the general viscosity formula can be used to make prediction of the viscosity evolution as observed in the polludrome experiments.

5.6.1 Calibration of the viscosity parametrization

5.6.1.1 Calibration of the C_{Temp} parameter

The value of C_{Temp} is estimated by (Berry et al., 2012) at 5000 [K].

Because CEDRE has performed a full characterization of IM-5 (Table 7), IM-14 (Table 8), and IM-15 (Table 9) at 5 and 15°C, we have been able to estimate the parameter C_{Temp} for various weathering and emulsion state:

$$C_{Temp} = \frac{\ln \frac{v_b}{v_a}}{\left(\frac{1}{T_b} - \frac{1}{T_a}\right)} \quad (7)$$

v_a, v_b : Kinematic viscosity of the oil [cSt] at the temperature T_a [K] and T_b [K] respectively.

The result of this analysis is presented in **Error! Not a valid bookmark self-reference..**

The average value of C_{Temp} is 8857 so a value relatively close to the default value 5000. The value of C_{Temp} parameter is the highest for pure/non-emulsified oil (around 12000) and tends to increase with the weathering stage. On the contrary, the value of the C_{Temp} parameter tends to decrease when the water content increases in the emulsion.

From this analysis, we cannot advise using a constant value of 5000 for the C_{Temp} for VLSFOs. A value of 12000 seems more appropriate. However, other formulas could easily be developed, for instance based on Bezier curves.

Table 6: Value of C_{Temp} [K] at several temperatures of distillation and water content from the laboratory. The empty cells are the cells means there was no measurement. * is when there is photooxidation too.

	IM-5					IM-14					IM-15				
Wat. cont./max wat cont. Dist. temp.	Fresh	150°C	200°C	250°C	250°C*	Fresh	150°C	200°C	250°C	250°C*	Fresh	150°C	200°C	250°C	250°C*
0%	14384	8457	10318	11624	13463	11484	13720	16272	13333	14798	12069	10413	11908	14941	/
50%	/	7082	7896	9164	3662	/	/	/	/	/	/	-1516	2091	/	/
75%	/	5327	4253	2922	4776	/	/	/	/	/	/	-1340	-245	/	/
100%	/	2915	4815	5237	-748	/	/	/	/	/	/	1820	/	/	/

5.6.1.2 Calibration of the parameters C_{emul1} and C_{emul2}

In this section, we investigate whether the default value for the parameters C_{emul1} (2.5) and C_{emul2} (0.65) can also be safely used for VLSFOs in general and IM-5, IM-14, and IM-15 in particular.

To this purpose, the viscosity of IM-5, IM-14 and IM-15 measured by CEDRE for various weathering conditions and emulsion state (Table 7, Table 8, Table 9) is compared with the viscosity curves predicted by Betancour formula (Figure 38 to Figure 41). For all the tested weathering conditions, the Betancour formula with the default values of the parameter produces good prediction of the emulsified slick viscosity for IM-5 and IM-14 but tends to overestimate the viscosity of IM-15. However, for fully weathered and emulsified slick (large value of Y on Figure 41), the Betancour formula overestimates the slick viscosity of IM-5 and IM-15 up to a factor 5, suggesting that the C_{emul2} is overestimated for these conditions.

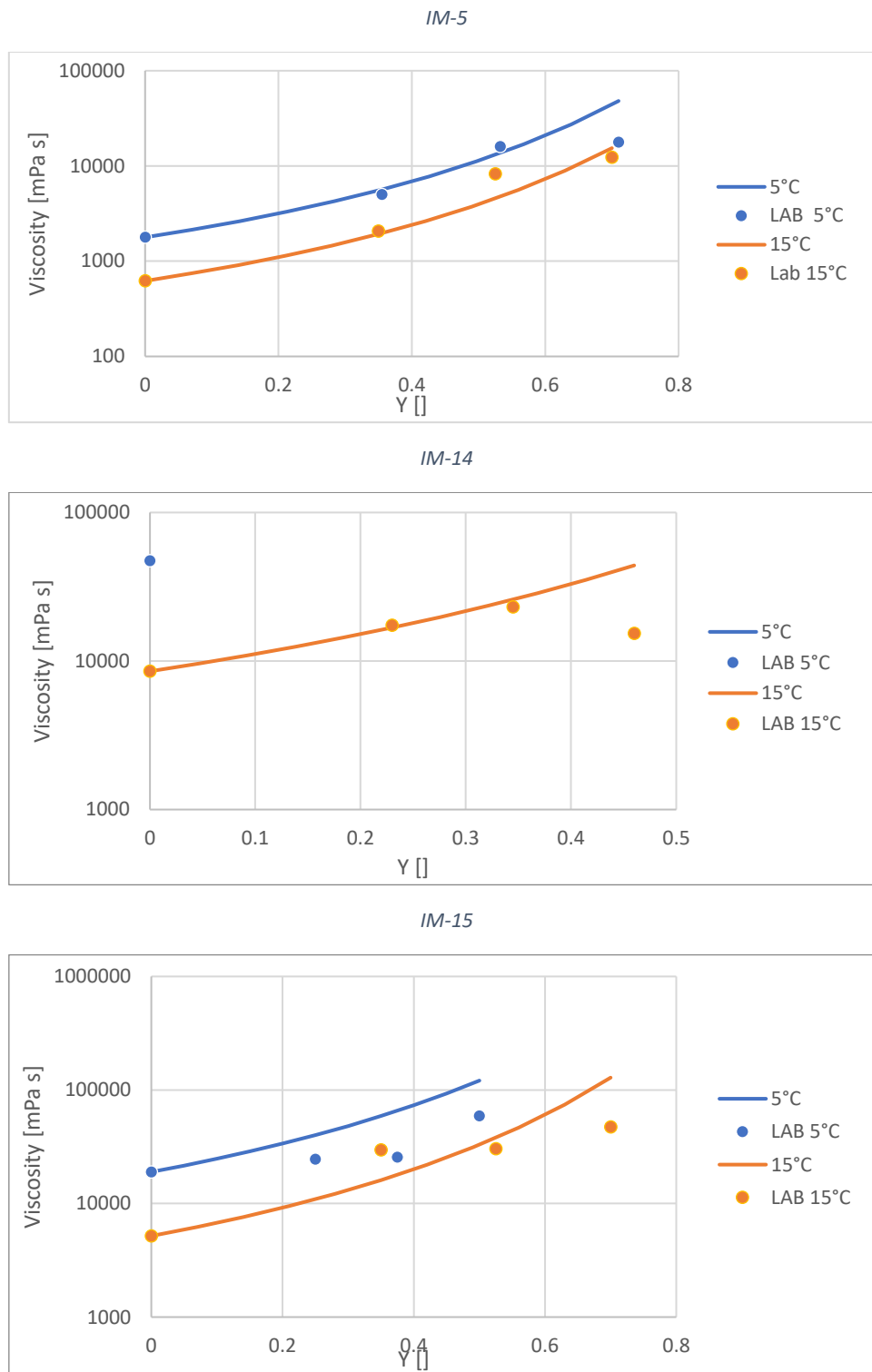


Figure 38 : Viscosity as a function of water content for IM-5, IM-14, and IM-15 after a heating at 150°C, the line are the values predicted from the initial viscosity and the water content and the point are value from the laboratory. The blue is for the measurements and simulation at 5°C and the orange for the measurements at 15°C.

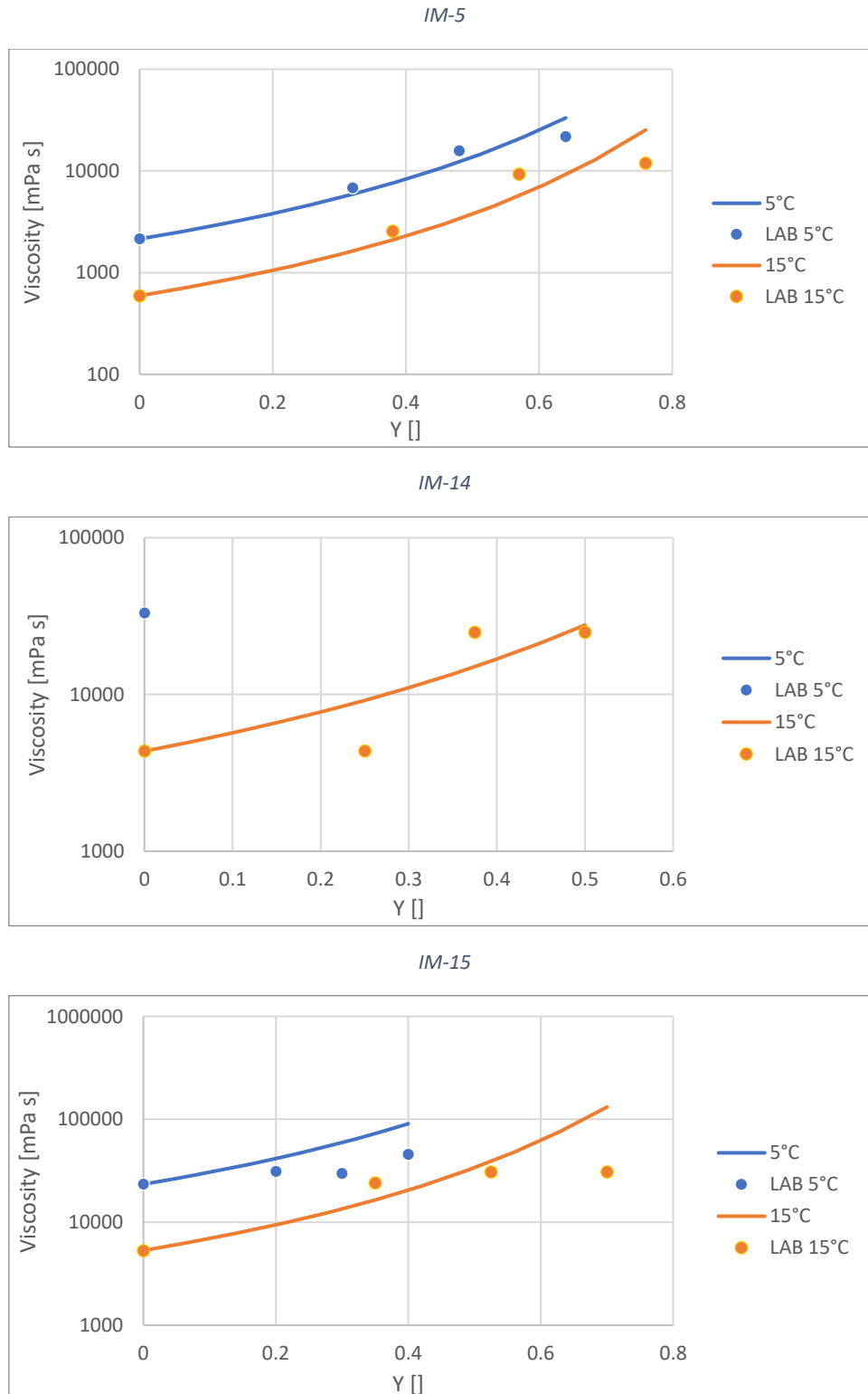


Figure 39 : Viscosity as a function of water content for IM-5, IM-14, and IM-15 after a heating at 200°C, the line are the values predicted from the initial viscosity and the water content and the point are value from the laboratory. The blue is for the measurements and simulation at 5°C and the orange for the measurements at 15°C.

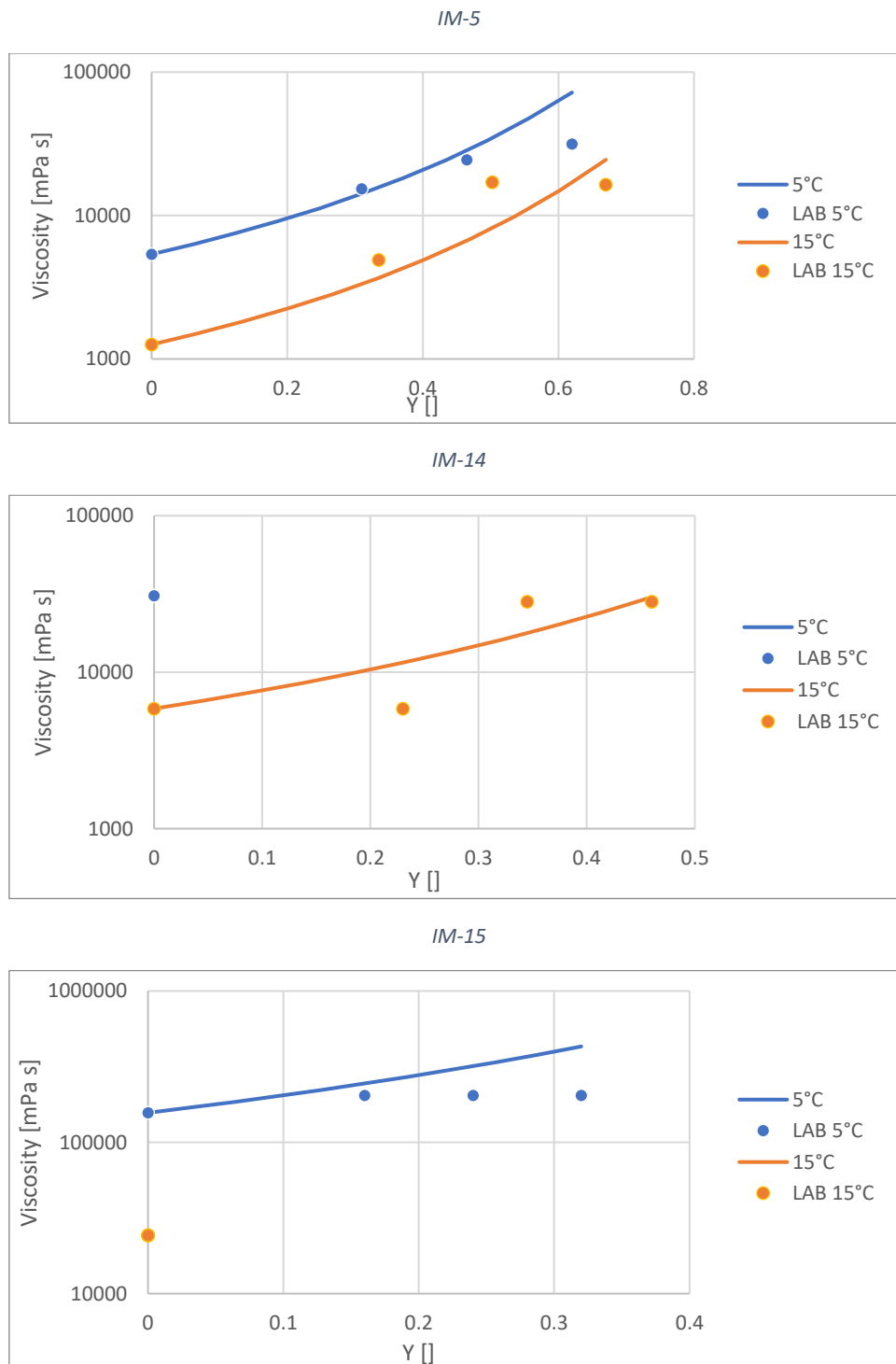


Figure 40 : Viscosity as a function of water content for IM-5, IM-14, and IM-15 after a heating at 250°C, the line are the values predicted from the initial viscosity and the water content and the point are value from the laboratory. The blue is for the measurements and simulation at 5°C and the orange for the measurements at 15°C.

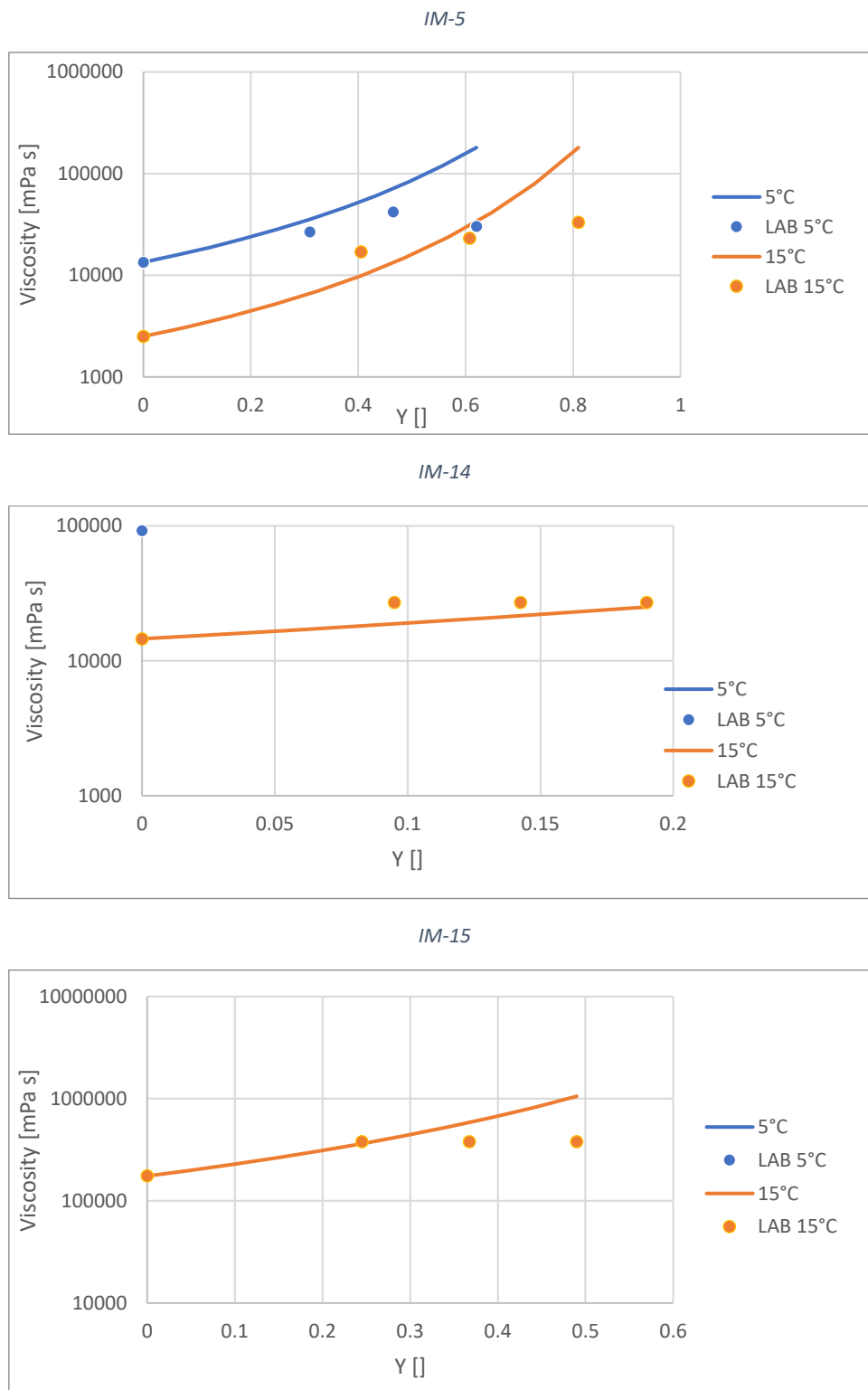


Figure 41 : Viscosity as a function of water content for IM-5, IM-14, and IM-15 after a heating at 250°C and a photooxidation, the line are the values predicted from the initial viscosity and the water content and the point are value from the laboratory. The blue is for the measurements and simulation at 5°C and the orange for the measurements at 15°C.

5.6.2 Can models correctly predict slick viscosity?

To answer this question, Figure 42 compares the viscosity values observed in the polludrome experiments against the viscosity values forecasted by the general formula with the default parameters:

$$\nu_{oil} = \nu_{ref} \exp \left(C_{Temp} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) + C_{Evap} F_{Evap} + \frac{C_{emul1} Y}{1 - C_{emul2} Y} \right)$$

The oil viscosity measured in Lab at $T_{ref} = 5^\circ\text{C}$ and $T_{ref} = 15^\circ\text{C}$ (Table 2) has been used as reference viscosity for experiments at 5°C and 15°C , respectively. This means that uncertainty on the C_{Temp} has no impact on the model result for viscosity.

The prediction of the viscosity for the experiment IM-15 at 5°C is excellent. However, although the toy model accurately computes the water content for all the other experiments (section 5.1.2), the predicted viscosity is overestimated up to a factor 5. This overestimation is consistent with the overestimation observed for the fully weathered and emulsified oil (Figure 41). This suggests that the default value of C_{emul2} is overestimated.

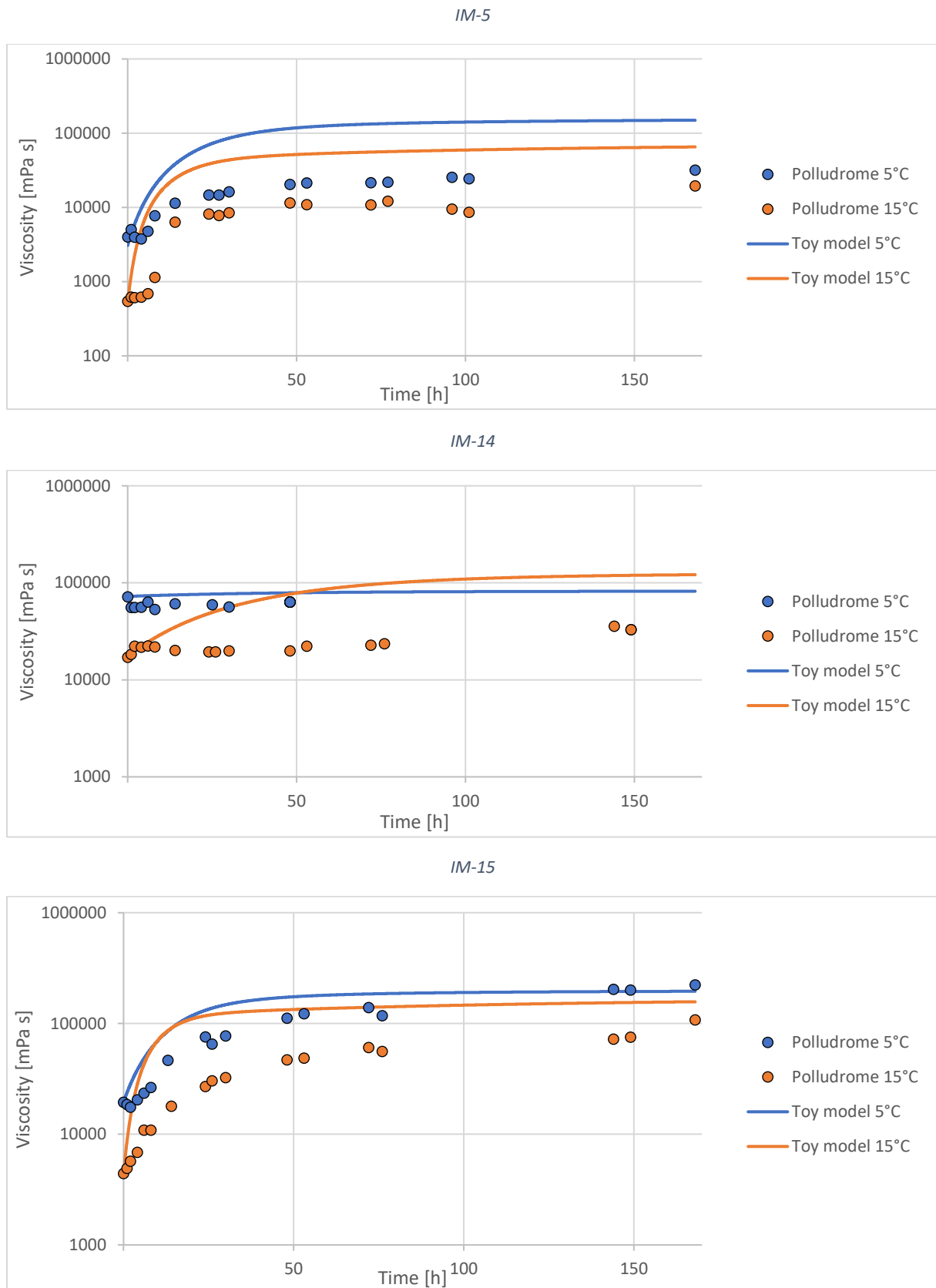


Figure 42: Viscosity as a function of time for IM-5, IM-14, and IM-15 at 5°C and 15°C. "Polludrome" is experimental data and "Toy model" is from the simulation.

6 Discussion and conclusion

The main endeavor of the IMAROS modelling task was to answer the following legitimate question:

“Should maritime Authorities continue to trust the results of oil weathering model simulation when they shape scientifically sounded response strategy during maritime pollution event involving new generation low Sulphur fuel oils?”

Otherwise stated, the main objective of the IMAROS modelling task was to demonstrate that the weathering parametrizations implemented in the different oil drift and fate models used by maritime Authorities continue producing trustful information for the new VLSFO fuels. The different national maritime Authorities using different models, the answer to this question had to be independent from the existing models and be formulated as best practices.

To this purpose, a review of the literature has been conducted to identify the most used weathering parametrizations in the oil drift and fate models and a selection of popular or relevant parametrizations have been implemented into a so-called OD toy model specifically implemented for this project. its source code has been uploaded on GitHub: https://github.com/naturalsciences/weathering_module_4_marine_pollution.

The physicochemical properties of the new generation low Sulphur fuel oils are remarkably diverse. To handle this diversity, the IMAROS consortium has selected 3 oils based on their respective physicochemical properties (Table 2):

- IM-5, a VLSFO with a relatively high pour point (15°C) but with a relatively low viscosity;
- IM-14, a sticky VLSFO with a very high pour point (27°C);
- IM-15, a highly viscous VLSFO with a relatively low pour point (0°C).

These weathering of these three oils have been observed in CEDRE polludrome at 5°C and 15°C. Surprisingly, the behavior of these 3 in the polludrome were also remarkably different:

- Despite a relatively high pour point (15°C), IM-5 formed a uniformed slick which behaved as a traditional oil slick;
- IM-14 instantaneously ‘froze’ when poured in the polludrome, forming a heterogeneous ‘granita’ slick in which seawater droplets and air bubbles have been trapped. At 5°C, the IM-14 ‘granita’ slick was unusually sticky, and no water-in-oil emulsion has been observed. At 15°C, the IM-14 ‘granita’ slick has been able to form some water-in-oil emulsion.
- Despite a low pour point (0°C), the highly viscous IM-15 oil formed discontinuous oil lumps that were also able to emulsify. However, the fact that the lump's outer shell has different physical properties than the lump's inner oil, indicates differences between the oil composition of the outer shell and the oil composition in the bulk.

To test the ability of the existing parametrizations to simulate VLSFO weathering, the 6 experiments in the polludrome have been numerically reproduced in the toy model. The validation of the model results against the polludrome measurements is globally positive in the sense that, after some calibration (K_{em} , C_{temp} , C_{emul1} , C_{emul2} , etc.), the model parametrizations simulate the observed weathering processes with the right timescale and the right order of magnitude, independently that the oil forms continuous slick, a ‘granita’ slick or discrete oil lumps.

We would like to formulate some lessons learned and the best practices drawn from this task:

1. As for traditional fuel oil, weathering parametrizations may only produce reliable weathering forecast if the oil physicochemical characteristics are known. To be able to run simulation, the

model weathering parametrizations must at least get information about the fresh oil density and viscosity at one or preferably two reference temperatures, information about the maximal water content, pour point, etc. and, if possible, to get access to the oil true boiling point curve or to the OSCAR oil characterization. Usually, these data are unknown in the early stage of the pollution event. However, at the difference of traditional oil, the diversity in the VLSFO prevents defining a generic VLSFO oil that could be used in the meantime.

Advise 1: The list of parameters available on the fuel oil safety sheet should be extended; oil bunkering companies should be made responsible and liable for the completeness and accuracy of the oil safety sheet they deliver.

Advise 2: In a future project, one should develop a VLSFO classification based on their physicochemical properties and behavior at sea. For each classification, a generic oil should be defined.

2. To accurately simulate the emulsion process, two key parameters are the maximum water content and the kinetic coefficient K_{em} . We have seen that the maximum water content estimated in the Lab can be underestimated by up to 15%. Such error has a direct impact on the prediction of the total volume of the oil slick and therefore on the slick density. We have also seen that the kinetic coefficient can be estimated from the half-life of the emulsion dynamic. This half-life is an empirical parameter estimated from a short flume tank experiment (short means half a day, at least).

Advise: If no accurate values exist for the oil maximum water content and the kinetic coefficient K_{em} , we advise to perform model sensitivity test by increasing the maximum water content up to 15% and by randomly selecting K_{em} values between 0 and 120. The range of values will be narrowed down once on-scene observations are reported to modellers.

3. For all the tested VLSFO, both with the Brighton parametrization or the Jones simulation accurately simulate evaporation. Both parametrizations support the true boiling point and the OSCAR characterization.

Advise 1: If we can choose between the true boiling point and the OSCAR characterization, we have a clear preference for the OSCAR characterization because it allows us to get additional information on the changes in oil composition and in the possible oil ecotoxicity.

Advise 2: The adequation between model and observation was not perfect for IM-15. We advise performing additional research to see which are the impacts of the lump formation on the evaporation.

4. Once the emulsion parametrization is correctly calibrated, the model predictions for slick density are reliable. This is an important constatation, since polludrome experiments with IM-14 and IM-15 showed that these slicks could be briefly submerged.
5. The study showed that we should be careful when using the viscosity formula with the default value of the calibration coefficients C_{temp} , C_{emul1} , and C_{emul2} . For the tested VLSFO, the default parameters lead to an overestimation by a factor 5 of the slick viscosity. The calibration exercise showed that
 - a. for the tested VLSFO, the C_{temp} coefficient should be taken twice larger than the default value (12000 instead of 5000).
 - b. the value of the C_{temp} coefficient must exponentially decrease when the water content increases.
 - c. The values of the parameters C_{emul1} and C_{emul2} seem adjusted whether the slick is homogeneous, heterogenous ('granita') or form oil lumps. For the latter two cases, the parameters C_{emul1} and C_{emul2} seem to be overestimated. However, it is too early to draw any conclusions.

Advice: Additional research is needed to study the relationship between the slick type and the values of the parameters C_{emul1} , and C_{emul2} .

6. The weathering parametrizations cannot predict whether the VLSFO slick will be homogeneous, heterogenous ('granita') or form oil lumps.

Advice 1: We therefore to highly advise maritime authorities to ask for an interpretation of the raw model results by an expert (a chemist or a modeler).

Advice 2: The current parametrizations assume that the oil slick spreads as a viscous fluid. However, this assumption is wrong for the heterogeneous/'granita' slicks and the oil lumps. Some additional research is therefore needed to develop a brittle visco-elastic parametrization of the slick spreading.

The general conclusion of the IMAROS modelling task is that, yes, the existing oil weathering models can simulate VLSFO processes. However, accurate simulation results are only possible if reliable information about the oil physicochemical properties and composition are available. This can only be achieved if a dialogue between maritime Authorities, chemists, and modelers is established.

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I. Annex: parametrizations implemented in the toy model

Several parametrizations have been implemented in the toy model.

I.1 Evaporation

Schmidt number

The Schmidt number is often used in the parametrizations for the evaporation. It is defined as follows:

$$Sc = \frac{\nu}{\kappa_c} \quad (8)$$

ν : Molecular kinematic viscosity of air [m²/s]

κ_c : Molecular diffusivity of pollutant in air [m²/s]

It can be estimated as (Lehr et al., 2002):

$$Sc = 1.3676 \sqrt{\frac{0.018}{MW}} \quad (9)$$

MW : molar mass [kg mol⁻¹]

Or with this relation (*CHEMMAP technical User's manual 6.10, 2014*):

$$D_{air} = D_{ref} \sqrt{\frac{MW_{ref}}{MW}} \quad (10)$$

D_{ref} : diffusivity of a reference chemical in air [cm²/sec]

MW_{ref} : molecular weight (g/mole) of reference chemical

The reference chemical is cumene for $MW > 100$ g/mole ($D_{air} = 0.0556$, $MW_{ref} = 120$)

and pentane for $MW < 100$ g/mole ($D_{air} = 0.071$, $MW_{ref} = 72.15$)

Mackay and Matsugu parametrization (Mackay and Matsugu, 1973)

First developed to quantify the evaporation of one pure hydrocarbon at a time, into a pool. The model has the assumption that the evaporation process is controlled by the boundary layer of the gas right above the slick. The model considers oil as a pure substance and the wind as turbulent.

The authors want to describe the evaporation rate of a certain oil as a function of temperature, wind-speed, atmospheric condition, radiation, ground/sea condition (roughness), dimension of the spill and the volatility and the diffusion of the oil. As said before, the model assumed that the limiting factor is the transfer coefficient from the interface to the atmosphere. The model is calibrated with cumene.

$$N = k_m \times \frac{P - P_\infty}{RT_p} \quad (11)$$

N : Evaporation rate [mol/m² h]

P : Vapor pressure of the hydrocarbon at the surface [Pa]

T_p : Temperature of the water [K]

P_∞ : Vapor pressure of the hydrocarbon at the bulk of the atmosphere (assumed 0) [Pa]

R : Perfect gas constant [J/mol K]

k_m : Mass transfer coefficient [m/h]

The k_m is described in the following equation. The n is depending on the “ground roughness” and the atmospheric temperature profile and the equation is made for average atmospheric conditions when $n = 0.25$ (typical values are between 0.25 and 1) (Mackay and Matsugu, 1973).

$$k_m = C U^{\frac{2-n}{2+n}} X^{\frac{-n}{2+n}} \quad (12)$$

$$U = U_1 Z^{\frac{n}{2-n}} \quad (13)$$

If $n = 0.25$, and the wind follows the velocity profile described in the previous equation.

$$k_m = C U^{0.78} X^{-0.11} \quad (14)$$

U_1 : Wind speed at 1 meter from the surface [m/h]

U : Wind speed, by convention taken at 10 meters from the surface [m/h]

Z : Height [m]

X : Pool diameter [m]

C : Constant depending on the oil [], 0.015 for cumene, for other:

$$C = 0.0292 Sc^{-0.47} \quad (15)$$

Sc : Schmidt number, detailed earlier []

The exponent on pool size is only valid for pool not too small (>0.1 meter) and the exponent on wind speed is near the 0.8 from Reynold number in turbulent flow.

Parametrization derived from (Jones, 1997) and used in OILTRANS

These parametrizations apply on multiple pseudo components i .

$$\frac{dV_i}{dt} = \frac{K_i A P_i \bar{V}_i X_i}{RT} \quad (16)$$

V_i : Volume of the compound i evaporated [m³]

A : Area of the quadtree leaf [m²]

R : Gas constant [J/mol K]

T : Temperature [K]

K_i : Mass transfer coefficient [m/s]

$\bar{V}_i$: Molar volume of i [m³/mol]

P_i : Vapour pressure of i [Pa]

X_i : Mole fraction of i []

$$K_i = 0.0048 U_{wind}^{7/9} X^{-1/9} Sc^{-2/3} \quad (17)$$

X : Downwind length of the oil slick axis [m]

U_{wind} : Wind speed [m/s]

$$X_i = \frac{\frac{V_i}{\bar{V}_i}}{\sum_{j=1}^{i_{max}} \frac{V_j}{\bar{V}_j}} \quad (18)$$

Parametrization from Stiver and Mackay (Stiver and Mackay, 1984)

Improvement from Mackay and Matsugu. Still consider oil as a pure substance, and only for substances with approximatively linear true boiling point curves(Keramea et al., 2021).

$$H = \frac{Pv}{RT} \quad (19)$$

H : Henry constant [].

P : Vapor pressure of the bulk liquid [Pa]

T : Temperature [K]

R : Perfect gas constant [J/mol K]

v : liquid molar volume [m³/mol]

$$d\theta = \frac{KA}{V_0} dt \quad (20)$$

K : Mass transfer coefficient under the wind [m/s]

A : Area [m²]

V_0 : Initial volume of spilled liquid [m³]

$$dF_v = H d\theta \quad (21)$$

F_v : volume fraction evaporated []

θ : evaporative exposure []

If A, K, T are constant and if the liquid is pure (F_v is independent of H), the integration gives:

$$F_v = H\theta \quad (22)$$

This equation cannot be used for oil modelling and the following one has been found from laboratory empirical data.

$$F_v = \left(\frac{T}{K_1}\right) \ln\left(1 + \frac{K_1\theta}{T}\right) \exp\left(K_2 - \frac{K_3}{T}\right) \quad (23)$$

$K_{1,2,3}$ are empirical constants, the model considers the oil as one pure substance. K_1 is obtained from the slope of F_v vs $\log \theta$. If $\theta > 10^4$, $K_1 \cong \frac{2.3T}{slope}$. $K_{2,3}$ can be found by measuring F_v at two different temperatures. The authors tested the model with multiples crudes oils.

The links between the ebullition temperature and the Henry constant has been found following the formula:

$$\ln H = 6.3 - 10.3 \frac{T_B}{T} \quad (24)$$

T_B : Ebullition temperature [K]

The model seems to overpredict the evaporation of substances with a boiling point above 280°C.

Modifications described in (Mishra and Kumar, 2015)

Considers the boiling oil temperature directly by rearranging the equation described above.

$$k_{evp} = 2.5 \cdot 10^{-3} W_{s10}^{0.78} \quad (25)$$

k_{evp} : Mass transfer coefficient [m/s]

W_{s10} : Wind speed at 10 meters above the sea [m/s]

$$T_0 = 532.98 - 3.125 API \quad (26)$$

T_0 : Initial boiling temperature of oil [K]

API : American Petroleum Institute gravity scale (relation with density)

$$T_g = 985.62 - 13.597 API \quad (27)$$

T_g : Gradient of oil distribution curve [K]

$$\frac{dF_e}{dt} = \frac{k_{evp}A}{V_0} e^{\left(a - \frac{b(T_0 + T_g F_e)}{T_{oil}}\right)} \quad (28)$$

F_e : Volume fraction evaporated [.]

A : Area [m²]

T_{oil} : Temperature of the oil spilled [K]

a and b are evaporation constant (6.3 and 10.3).(Mishra and Kumar, 2015)

Parametrization derived from (Brighton P.W.M., 1985) and used in ALOHA

This parametrization considers the pollutant (not only oil) as a whole but can be adapted to work on pseudo component. The evaporation mass flux is computed from the following equation:

$$E_{(x,t)} = C_s U_* j_{(x)} \quad (29)$$

$E_{(x,t)}$: Evaporative mass flux depending on distance and time [$\text{kg m}^{-2} \text{s}^{-1}$]

$j_{(x)}$: Mass transfer coefficient []

U_* : friction velocity of the air [m s^{-1}]

C_s : Chemical's vapor-phase saturation concentration [kg m^{-3}]

$$C_s = \frac{M_v P_v}{RT} \quad (30)$$

M_v : Molecular weight of the vapor

P_v : vapor pressure of the puddle [Pa]

Because $j_{(x)}$ depends on the position along the axis oriented parallel to the wind direction, it can be integrated over the whole area.

$$\bar{j} = \frac{1}{D_p} \int_0^{D_p} j_{(x)} dx \quad (31)$$

D_p : Diameter of a uniform circular puddle [m]

The main equation becomes:

$$E_{(t)} = C_s U_* \bar{j}_c \quad (32)$$

For the friction velocity of air:

$$U_* = 0.03U \left(\frac{10}{z} \right)^n \quad (33)$$

U : wind speed [m s^{-1}]

z : height of specified wind speed [m]

n : value depending on the wind speed profile, as in Table 1

Table 1 : Values of n

Pasquill Stability Class	n
A	0.108
B	0.112
C	0.120
D	0.142
E	0.203
F	0.253

The average mass transfer coefficient can be expressed as:

$$\bar{j} \approx \frac{k}{Sc_T} (1 + n) \left[\frac{1}{2} - \frac{1}{\pi} \tan^{-1} \left(\frac{e^\Lambda X_l}{\pi} \right) + \frac{1 - \gamma_e}{\ln^2(e^\Lambda X_l) + \pi^2} + \frac{\left(1 + (1 - \gamma_e)^2 + \frac{1}{6} \pi^2 \right) \ln(e^\Lambda X_l)}{(\ln^2(e^\Lambda X_l) + \pi^2)^2} \right] \quad (34)$$

γ_e : Euler constant (equals 0.577)

X_l : Dimensionless distance evaluated at the downwind edge []

$$X_l = \frac{nk^2 D_p}{Sc_T z_0 e^{\frac{1}{n}}} \quad (35)$$

z_0 : Surface roughness length [m]

k : von Karman constant (equals 0.4)

Λ : Measure of the ratio of the scalar roughness length of the puddle and the momentum roughness length of the terrain

$$\Lambda = \frac{1}{n} + 1 + 2 \ln(1 + n) - 2\gamma_e + \frac{k}{Sc_T} (1 + n) f_{(sc)} \quad (36)$$

$$f_{(Sc)} = \begin{cases} \left(3.85 Sc^{\frac{1}{3}} - 1.3\right)^2 + \frac{Sc_T}{k} \ln(0.13 Sc) & \text{for } Re_0 < 0.13 \\ \text{for } 0.13 \leq Re_0 \leq 2 : \text{interpolation between 0.13 and 2} \\ 7.3 Re_0^{\frac{1}{4}} \sqrt{Sc} - 5Sc_T & \text{for } Re_0 > 2 \end{cases} \quad (37)$$

Sc_T : Turbulent Schmidt number (equals 0.85)

Re_0 : Roughness Reynolds number

$$Re_0 = \frac{U_* z_0}{\nu} \quad (38)$$

ν : Kinematic viscosity of air [$m^2 s^{-1}$]

Parametrization of (M. F. Fingas, 2015)

The idea behind Fingas parametrization is that the evaporation rate is not limited by the air boundary layer but by diffusion through the oil mass. This is not valid for light oils (kerosene, diesel...) for which a square root is needed. The model only works for oil tested in a laboratory. The -15 does not seem to be useful when the C is given.

$$\% \text{ evaporated} = [C + 0.045(T - 15)] \ln(t) \quad (39)$$

T : Temperature [$^{\circ}C$]

t : time [min]

C : constant, can be corrected if the thickness of the slick is different than 1.5mm, and not needed if oil goes quickly under 1.5mm.

$$C' = C + 1 - 0.78\sqrt{\text{thickness}} \quad (40)$$

C can be approximated with the percentage distilled by weight at 180°C, (%D):

$$\% \text{ evaporated} = [0.0165(\%D) + 0.045(T - 15)] \ln(t) \quad (41)$$

This parametrization cannot be used with a pseudo component approach easily.

1.2 Dissolution

Parametrization described in (Hines and Maddox, 1985; Legrand et al., 2017; MacKay and Leinonen, 1977)

The dissolution process describes the transfer from the slick to the aqueous phase.

$$\frac{dn_{i,d}}{dt} = K (x_i C_i^S - C_i^w) A \quad (42)$$

$n_{i,d}$: Number of dissolved moles [mol]

A : Area [m²]

x_i : Mole fraction of component i []

C_i^S : Pure component i solubility [mol m⁻³]

C_i^w : Concentration of component i in water [mol m⁻³]

K : Mass transfer coefficient [m s⁻¹]

Re_L : Reynolds number []

$$Re_L = \frac{C_w L}{v_w} \quad (43)$$

v_w : Kinematic viscosity of water [m s]

C_w : current speed [m s⁻¹]

Sc : Schmidt number in water []

$$Sc = \frac{\nu}{\kappa_c} \quad (44)$$

ν : Molecular kinematic viscosity of water [m² s⁻¹]

κ_c : Molecular diffusivity of pollutant in water [m² s⁻¹]

For the diffusion coefficient, Hayduk and Laudie (1974) (in cm²/s):

$$D_c = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \nu_l^{0.589}} \quad (45)$$

μ : Dynamic viscosity [cP]

ν_l : Molar volume [cm³/mol]

For the molar volume, « Le Bas » estimation M_w : molecular weight [g/mol] and ν_l [m³/mol]

- Organic:

$$\nu_l = 4.9807 \times M_w^{0.6963} \quad (46)$$

- Inorganic:

$$\nu_l = 2.8047 \times M_w^{0.651}$$

For a slick

$$K_s = \frac{ShD_c}{L} \quad (47)$$

K_s : Mass transfer coefficient for a slick [m s^{-1}]

L : diameter of the slick [m]

D_c : diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]

Sh : Sherwood number []

$$Sh = 0.578 Sc^{1/3} Re_L^{1/2} \quad (48)$$

For a subsurface droplet

$$K_d = \frac{ShD_c}{d} \quad (49)$$

K_s : Mass transfer coefficient for a droplet [m s^{-1}]

d : Droplet diameter [m]

$$Sh = 2 + 0.347 Sc^{0.31} Re_d^{0.62} \quad (50)$$

$$Re_d = \frac{W_d d}{v_w} \quad (51)$$

W_d : Resultant velocity action on the droplet [m/s]

Mass transfer coefficient from (Fernandez, 2013)

This work assumes oil as a pure substance.

$$k_w = \frac{\dot{m}_{sol}}{\rho_w(w_s - w_\infty)} \quad (52)$$

k_w : Mass transfer coefficient across the pool water interface [m/s]

$\dot{m}_{sol}$: Mass flux of the chemical dissolved in water [$\text{kg/m}^2\text{s}$]

ρ_w : Water density [kg/m^3]

w_s : Mass fraction of the chemical in water at the interface []

w_∞ : Mass fraction of the chemical in bulk water (equals 0) []

Correction in case of high mass transfer rates:

$$m_{sol}'' = k_w \rho_w \ln \left(\frac{1}{1 - w_s} \right) \quad (53)$$

For open and coastal waters:

$$k_w = 10 \frac{u_w^*}{\frac{\sigma \ln(\delta_+)}{\varphi} + \beta_w + 2.35} \quad (54)$$

δ_+ : Height of the boundary layer between the pool and water surface [m]

β_w : Empirical function depending on the roughness []

φ : Von Karman constant (equals 0.47) []

σ : Turbulent Schmidt number (equals 0.8) []

$$\delta_+ = \frac{10 u_w^* \rho_w}{\mu_w} \quad (55)$$

ρ_w : Water density [kg/m³]

μ_w : Water viscosity [Pa s]

$$\beta_w = \begin{cases} 12.55 Sc_w^{0.667} + \frac{\sigma \ln(Sc_w)}{\varphi} - 5.3 & u_{(z=10m)} < 5m/s \\ 0.55 h_w^{0.5} (Sc_w^{0.667} - 0.2) - \frac{\sigma \ln(Sc_w)}{\varphi} + 11.2\sigma & u_{(z=10m)} \geq 5m/s \end{cases} \quad (56)$$

h_w : Wave height [m]

Sc_w : Schmidt number []

$$h_w = 0.01384 \frac{u_{(z=10m)} u_w^* \rho_w}{\mu_w} \quad (57)$$

$u_{(z=10m)}$: Wind speed 10 meters above the pool [m/s]

$$u_w^* = u_{(z=10m)} \left(\frac{\rho_a}{\rho_w} \right)^{\frac{1}{2}} \left(\frac{1}{2} C_f \right)^{\frac{1}{2}} \quad (58)$$

C_f : Friction coefficient at the water-pool interface []

$$\frac{1}{2}C_f = \begin{cases} 1.98 \times 10^{-3} & u_{(z=10m)} < 0.1 \text{ m/s} \\ 1.25 \times 10^{-3} [u_{(z=10m)}]^{-0.2} & 0.1 < u_{(z=10m)} < 3.06 \text{ m/s} \\ [0.8 + 0.65u_{(z=10m)}] \times 10^{-3} & 3.06 < u_{(z=10m)} < 22.3 \text{ m/s} \\ 2.25 \times 10^{-3} & 22.3 \text{ m/s} < u_{(z=10m)} \end{cases} \quad (59)$$

Parametrization from (Cohen et al., 1980)

(Cohen et al., 1980) proposed a model after studying phenol dissolution in water into the laboratory, with a wind between 0-9 m/s. The authors said that phenol dissolution is controlled by the oil phase transfer coefficient and not by the water phase transfer coefficient, which is the case for less soluble substances. This model can be used for each substance of the oil mixture if all the properties and the relative abundance of each of these substances is known.

$$N = K_w H_l C_0 \quad (60)$$

N : Mass flux [g/m²h]

C_0 : Phenol concentration in oil phase [g/m³]

H_l : Partition coefficient ratio of concentration of phenol in oil to water [(g/cm³)/(g/cm³)]

K_w : Water phase mass transfer coefficient, oil/water [m/h]

The model is then reused by (Shen et al., 1993), in a study over pollution in fresh water, but it considers the slick as only one substance, and does not consider the amount of oil directly. It changes the partition coefficient ratio by the oil solubility.

$$N = K A_s S \quad (61)$$

N : Mass flux [g/ h]

S : oil solubility[g/m³]

A_s : Area of the slick [m²]

K : dissolution mass transfer coefficient (assumed to be 0.01) [m/h]

The solubility can vary through time in the following formula:

$$S = S_0 e^{-0.1t} \quad (62)$$

S : solubility [kg/m³]

S_0 : initial solubility of oil in water [kg/m³]

t : time [hour]

These formulas are then reused by (Mishra and Kumar, 2015) with some modifications, but they still consider the oil as a whole.

$$S = S_0 \exp(-12F_e) \quad (63)$$

S : solubility [kg/m³]

S_0 : initial solubility of oil in water [kg/m³]

F_e : volume fraction evaporated [].

The model uses the fraction of evaporated content instead of the time to decrease the solubility.

$$\frac{dF_d}{dt} = K_{diss} A \left(\frac{S}{\rho_{oil}} \right) \quad (64)$$

A : area [m²]

K_{diss} : mass transfer coefficient of dissolution [m/s]

ρ_{oil} : density of the oil (only if the massic fraction is needed) [kg/m³]

F_d : volume fraction of oil dissolve in sea water []

1.3 Volatilization

Volatilization is the process for the transfer of the pollutant from the dissolved fraction to the evaporated one.

Parametrization of (Lyman et al., 1990)

This parametrization was created for pure chemical compounds.

Henry law constant

$$H = \frac{P_{vp}}{S} \quad (65)$$

H : Henry law constant [atm m³/mol]

P_{vp} : vapor pressure of the compound [atm]

S : solubility [mol m⁻³]

If $H < 3 \times 10^{-7}$, volatilization is ignored.

H' : nondimensional Henry constant:

$$H' = \frac{H}{RT} \quad (66)$$

R : 8.2×10^{-5} [atm m³ mol⁻¹ K⁻¹]

T : temperature [K]

Compute the liquid phase exchange coefficient

If $M < 65$ (g/mol)

$$k_l = 20 \sqrt{\frac{44}{M}} \quad (67)$$

M : molar mass [g mol⁻¹]

k_l : liquid phase exchange coefficient [cm h⁻¹]

Else (approximative), if windspeed < 3 m/s:

$$k_l = 2.5$$

if windspeed < 6 m/s

$$k_l = 10$$

if windspeed < 10 m/s

$$k_l = 23$$

if windspeed > 10 m/s

$$k_l = 50$$

Compute the gas phase exchange coefficient

If $M < 65$:

$$k_g = 3000 \sqrt{\frac{18}{M}} \quad (68)$$

k_g : gas phase exchange coefficient [cm h⁻¹]

If the molar mass is greater than 65:

$$k_g = 1137.5(V_{wind} + V_{curr}) \sqrt{\frac{18}{M}} \quad (69)$$

V_{wind} : wind speed [m s^{-1}]

V_{curr} : current speed [m s^{-1}]

Compute the overall liquid phase mass transfer coefficient

$$K_L = \frac{H' k_g k_l}{H' k_g + k_l} \quad (70)$$

K_L : mass transfert coefficient [cm hr^{-1}]

Compute the flux

$$N = K_L \left(C - \frac{P}{H} \right) \quad (71)$$

N : flux [$\text{g cm}^{-2} \text{s}^{-1}$]

C : concentration [g cm^{-3}]

P : vapor pressure of the compound [atm]

H : henry law constant [$\text{atm cm}^3 \text{g}^{-1}$]

1.4 Emulsification

Fingas stability model(M. Fingas, 2015)

Water can be found into oil in 5 ways:

- Water dissolution in oil (max 1%).
- Entrainment: drop mixed into the oil when the sea energy is high.
- Instable emulsion: like entrainment but the droplets are stabilized during several minutes or few hours and then disappears when sea energy diminishes.
- Mesostable emulsion: the water is stabilized up to several days by the viscosity and surface tension, changing the oil physical properties.
- Stable emulsion: like mesostable emulsion but can stay for a long time.

A “stability value” can be given to any oil.

Table 2 : oil properties corresponding to stability value, d is density, μ is viscosity and AR is the maximum between asphaltene and resin content.

Water in oil type	Starting properties	Minimum	Maximum
Entrained	$d > 0.94$ and $\mu > 6000$	-20	3
Unstable	$d > 1$ or $d < 0.85$, $\mu > 800\,000$ or $\mu < 100$ and Asphaltene or Resine $< 1\%$	-4	-18

Mesostable	μ or d other than above	-10	5
Stable	μ or d other than above	4	29

d : Oil density []

μ : Viscosity [mPa)s]

Stability is computed as follows:

$$\begin{aligned}
 \text{Stability} = & -15.3 + 1010 \times \text{Den} - 3.66 \times \text{Visc} + 0.174 \times \text{Rst} - 0.579 \times \text{Ast} \\
 & + 34.4 \times A/R + 1.02 \times \exp(\text{Den}) - 7.91 \times \exp(A/R) \\
 & - 2740 \times \ln(\text{Den}) + 12.2 \times \ln(\text{Visc}) - 0.034 \\
 & \times \ln(\text{Sst}) - 3.17 \times \ln(\text{Rst}) + 0.99 \times \ln(\text{Ast}) - 2.29 \times \ln(A/R)
 \end{aligned} \quad (72)$$

Den : exponential of the density

Visc : natural log of the viscosity

Rst : If resin content (1-90%) < 10, = 10-resin content. If resin content > 10, = resin content -10. If resin content is 0, = 20

Ast : If asphaltene content (1-90%) < 4, = 4- asphaltene content. If asphaltene content > 4, = asphaltene content -40. If asphaltene content is 0, = 20

A/R : ratio asphaltene and resin

Sst : If saturate content (1-90%) < 45, = 45- saturate content. If saturate content > 45, = saturate content -45

The wind speed must be comprised between 0 and 20 m/s, or the wave height must be between 0 and 1 meter. The model uses a pseudo component approach (Asphaltene and resin are used separately). The stability has been computed using other experimental data (complex and elastic modulus). Some parameters can be computed from the stability as shown in Table 3 and Table 4. The values can be interpolated.

Table 3 : Viscosity increases from starting oil as a function of stability.

	First day	Week	Year
Entrained	1.9	1.9	2.1
Mesostable	7.2	11	32
Stable	405	1054	991
Unstable	0.99	1	1

Table 4 : Water content as a function of stability.

	First day	Week	Year
Entrained	44.5	27.5	6
Mesostable	64.3	30	6
Stable	81	78	70
Unstable	6.1	6	5

From a kinematic viewpoint, a relation has been made, the constants are in Table 5.

$$y = a + \frac{b}{x^{1.5}}$$

y : Time to emulsion formation [min]

x : Wave height [cm]

Table 5 : Values of a and b .

	a [min]	b [cm]	R^2
Entrained	27.1	7.520	0.51
Mesostable	47	49.100	0.95
Stable	30.8	18.3	0.94

Parametrization described in (Scory, 2005)

Pollutant will go from fresh to emulsified with the following parametrization. It is a parametrization designed for oil.

$$\frac{dV_{em}}{dt} = \frac{C_{18}}{1 - C_{18}} \frac{K_{em}}{C_{15}} V_r H_s \quad (73)$$

$$\frac{dV_{em}}{dt} = \frac{-dV_r}{dt} \quad (74)$$

$$V_{water} = \frac{C_{18}}{1 - C_{18}} V_{em} \quad (75)$$

$$V_{tot,em} = V_{em} + V_{water} = \frac{1}{1 - C_{18}} V_{em} \quad (76)$$

$$V_{tot} = V_r + V_{em} + V_{water} = V_r + \frac{1}{1 - C_{18}} V_{em} \quad (77)$$

$$Y = \frac{V_{water}}{V_{tot}} \quad (78)$$

V_{em} : Volume of oil in the emulsion [m³]

V_r : Oil volume remaining at the surface [m³]

V_{water} : Water volume in the emulsion [m³]

$V_{tot,em}$: Total volume of the emulsion [m³]

V_{tot} : Total volume of the surface slick [m³]

Y : water fraction in the surface slick [%]

H_s : Significant wave height [m]

C_{15} : 2000000 [m]

C_{18} : Maximum water content (by default 0.8) []

K_{em} : Kinetic coefficient of water uptake in the emulsion (0-120) [s⁻¹]

If we assume that evaporation and other weathering processes are negligible, that the significant waves height is constant in time and that the initial fresh oil volume is V_0 , an analytical solution exists to this emulsification model:

$$V_r(t) = V_0 e^{-\frac{C_{18}}{1-C_{18}} \frac{K_{em}}{C_{15}} H_s t} \quad (79)$$

$$V_{em}(t) = V_0 \left(1 - e^{-\frac{C_{18}}{1-C_{18}} \frac{K_{em}}{C_{15}} H_s t} \right) \quad (80)$$

$$Y(t) = C_{18} \frac{1 - e^{-\frac{C_{18}}{1-C_{18}} \frac{K_{em}}{C_{15}} H_s t}}{1 - C_{18} e^{-\frac{C_{18}}{1-C_{18}} \frac{K_{em}}{C_{15}} H_s t}} \quad (81)$$

The emulsion clearly follows an exponential dynamic with a half-life of

$$t_{1/2} = \ln 2 \frac{1 - C_{18}}{C_{18}} \frac{C_{15}}{K_{em} H_s} \quad (82)$$

Mackay parametrization, described in (Fingas, 1995)

Consider oil as a pure substance.

$$\frac{dF_{wc}}{dt} = C_1 (U_w + 1)^2 \left(1 - \frac{F_{wc}}{C_2} \right) \quad (83)$$

U_w : Wind speed [m/s]

C_1 : 2×10^{-5} (2×10^{-6} according to ("D-WAQ PART User Manual," n.d.)) []

C_2 : 0.25 for home heating oil ("D-WAQ PART User Manual," n.d.) and 0.7 for crude/heavy oil (maximum water content) []

F_{wc} : Water content []

Parametrization from (Eley et al., 1988)

The model assumes oil as a pure substance.

$$\frac{dS}{dt} = k_S \left(1 - \frac{S}{S_{max}} \right)$$

S : Interfacial area [m²/cm³]

S_{max} : Maximum interfacial area [m²/cm³]

k_S : Interfacial parameter (depends on wave energy) [s⁻¹]

And the integration gives:

$$S = S_{max} (1 - e^{-k_S t})$$

t : time [s]

k_S and S_{max} are found in an empirical way.

The water fraction can be computed as follows:

$$Y = \frac{S d_W}{6 + S d_W}$$

Y : Water fraction []

d_W : water droplet diameter [m]

1.5 Biodegradation and photooxidation

Both parametrizations are simple half-life equations, describing the amount remaining from the amount before the timestep. The amount can be in any amount units (mol, m³, kg...).

$$Q_{(t+dt)} = Q_{(t)} (1 - e^{-k dt}) \quad (84)$$

$Q_{(t)}$: amount remaining at time t

$Q_{(t+\Delta t)}$: amount remaining at time $t + \Delta t$

k : half-life constant [s⁻¹]

1.6 Density

The computation of the density from the OSCAR characterization is computed as described here, with the assumption that the C25+ are the residual fraction. If the density of the residual fraction is not known, it can be computed as follows:

$$\rho_r = \rho_0 - \sum_{\substack{i, \text{ non C25+} \\ \text{fractions}}} f_{i0} \rho_i \quad (85)$$

ρ_0 : oil initial density [kg/m³]

ρ_r : oil residual density (after 250°C+ distillation) [kg/m³]

ρ_i : density of the fraction i [kg/m³]

f_{i0} : initial fraction of the component i []

$$\rho_{(t)} = \rho_r + \sum_{\substack{i, \text{ non } c25+ \\ \text{fractions}}} f_{i(t)} \rho_i \quad (86)$$

$\rho_{(t)}$: oil density at time t [kg/m³]

$f_{i(t)}$: fraction of the component i at time t []

$$\rho_{tot(t)} = F_{wc(t)} \rho_w + (1 - F_{wc(t)}) \rho_{(t)} \quad (87)$$

$\rho_{tot(t)}$: density of the emulsion (oil and water) at time t [kg/m³]

$F_{wc(t)}$: water fraction in the emulsion at time t [kg/m³]

1.7 Density Alternative SL

The computation of the density from the OSCAR characterization is computed as described here, with the assumption that the C25+ are the residual fraction. Indeed, although the density of the residual fraction is not known a priori, it can easily be estimated from the fresh oil density ρ_0 :

$$\rho_{c25+} := \frac{1}{f_{c25+0}} \left[\rho_0 - \sum_{\substack{i, \text{ non } c25+ \\ \text{fractions}}} f_{i0} \rho_i \right] \quad (88)$$

ρ_0 : oil initial density [kg/m³]

ρ_i : density of the fraction i [kg/m³]

f_{i0} : initial fraction of the component i []

Once average residual oil density is known, the time evolution of the oil density reads

$$\rho_{(t)} = \sum_i f_{i(t)} \rho_i \quad (89)$$

$\rho_{(t)}$: oil density at time t [kg/m³]

$f_{i(t)}$: fraction of the component i at time t []

$$\rho_{tot(t)} = F_{wc(t)}\rho_w + (1 - F_{wc(t)})\rho_o \quad (90)$$

$\rho_{tot(t)}$: density of the emulsion (oil and water) at time t [kg/m³]

$F_{wc(t)}$: water fraction in the emulsion at time t [kg/m³]

1.8 Viscosity

The viscosity can be decomposed into 3 exponentials depending on temperature, evaporation, and emulsification. It considers oil as a pure substance.

Andrade correlation

$$v_{oil} = v_{ref} \exp \left(C_{Temp} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (91)$$

v_{oil} : Kinematic viscosity of the oil [cSt]

v_{ref} : Kinematic viscosity at the reference temperature [cSt]

T_{ref} : Reference temperature [K]

T : Temperature [K]

C_{Temp} : Constant for each oil type [K], can be estimated to 5000 according to (Berry et al., 2012)

Formula for considering evaporation

$$v_{oil} = v_{ref} \exp(C_{Evap} F_{Evap}) \quad (92)$$

C_{Evap} : Constant for an oil type (Lehr et al., 2002), can be equal to 10 according to (Berry et al., 2012)

F_{Evap} : Fraction of oil evaporated from the slick [], (volume evaporated divided by volume spilled)

Formula for considering emulsification (Betancour et al., 2005)

$$v_{oil} = v_{ref} \exp \left(\frac{C_{emul1} Y}{1 - C_{emul2} Y} \right) \quad (93)$$

Y : Water content of the emulsion []

C_{emul1} , C_{emul2} : Constants depending on the oil (2.5 and 0.65 respectively)

Whole formula

$$v_{oil} = v_{ref} \exp \left(C_{Temp} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) + C_{Evap} F_{Evap} + \frac{C_{emul1} Y}{1 - C_{emul2} Y} \right) \quad (94)$$

It should be noted that the initial value of viscosity is needed.

II. Simulating the evolution of the fraction of the remaining oils

In the framework of the IMAROS project, 15 oils samples have been characterized. In the previous sections, results of multiple simulations for three VLSFOs (IM-5, IM-14, IM-15) were presented. In this section, weathering simulation results for IM-1 to IM-13 are presented for the conditions of the polludrome experiments, with the same parameters as the ones used for IM-5, IM-14, and IM-15. There is no experimental data to compare to these simulations because no polludrome experiments have been performed on them. The Kem will be at 20 for all the oils, the maximum water content and the OSCAR characterization is from (CEDRE, 2022a).

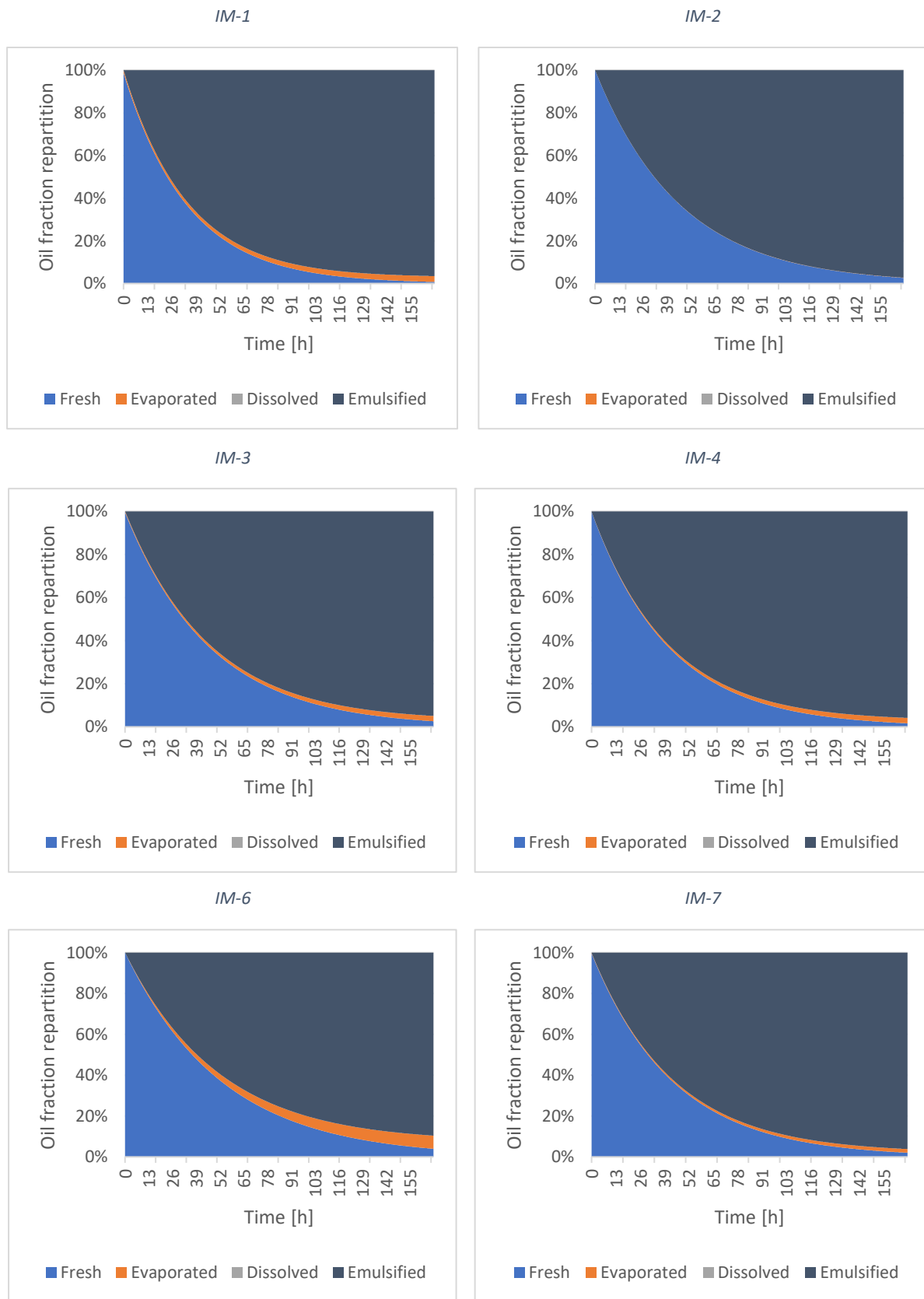


Figure 43: Evolution of the oil fraction repartition for IM-1 to IM-4 and IM-6 to IM-7 at 15°C

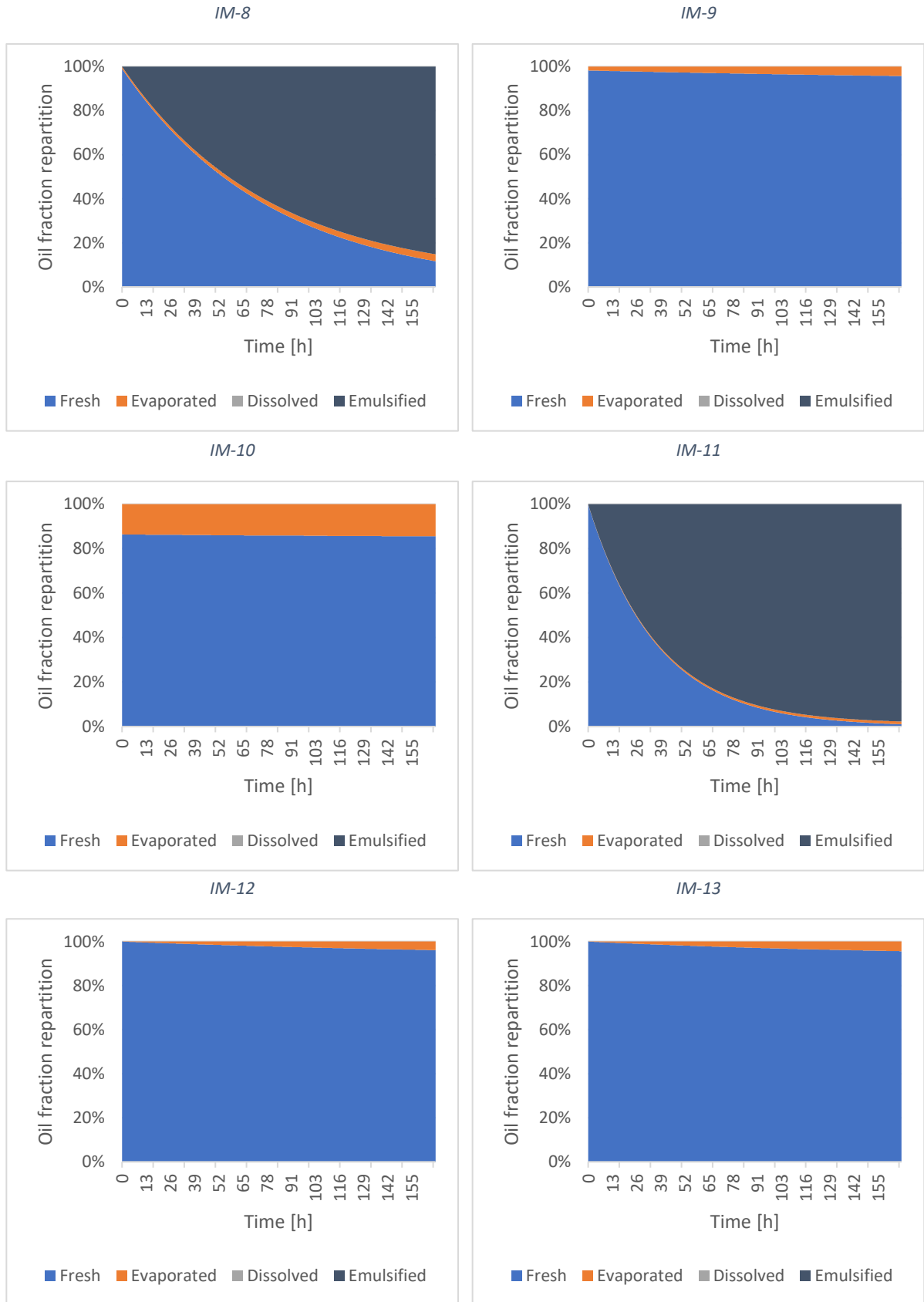


Figure 44 : Evolution of the oil fraction repartition for IM-8 to IM-13 at 15°C. It was not possible to form an emulsion with IM-9, IM-12, and IM-13, so there is no maximum water content and the one for IM-10 was not measured. These four oils will then not be emulsified in the simulation. IM-10 evaporates 10% instantaneously because it is composed of more than 8% in mass of C1-C4 fraction

III. Lab characterization of IM-5, IM-14, and IM-15

In the framework of task 3.2, CEDRE has performed a full characterization of the oil IM-5, IM-14, and IM-15. We reproduce here summary tables from (CEDRE, 2022b)

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

			Residues of distillation (Vapors temperatures)			
	Characterizations	Fresh				
			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

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

Characterizations		Fresh	Residues of distillation (Vapors 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

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

		Fresh	Residues of distillation (Vapors temperatures)			
	Characterizations		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	<i>Density</i>	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
	<i>Max. water content (%)</i>	-	50	40	32	/
Experiment at 15 °C	<i>Density</i>	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
	<i>Max. water content (%)</i>	-	70	70	/	49

Colophon



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