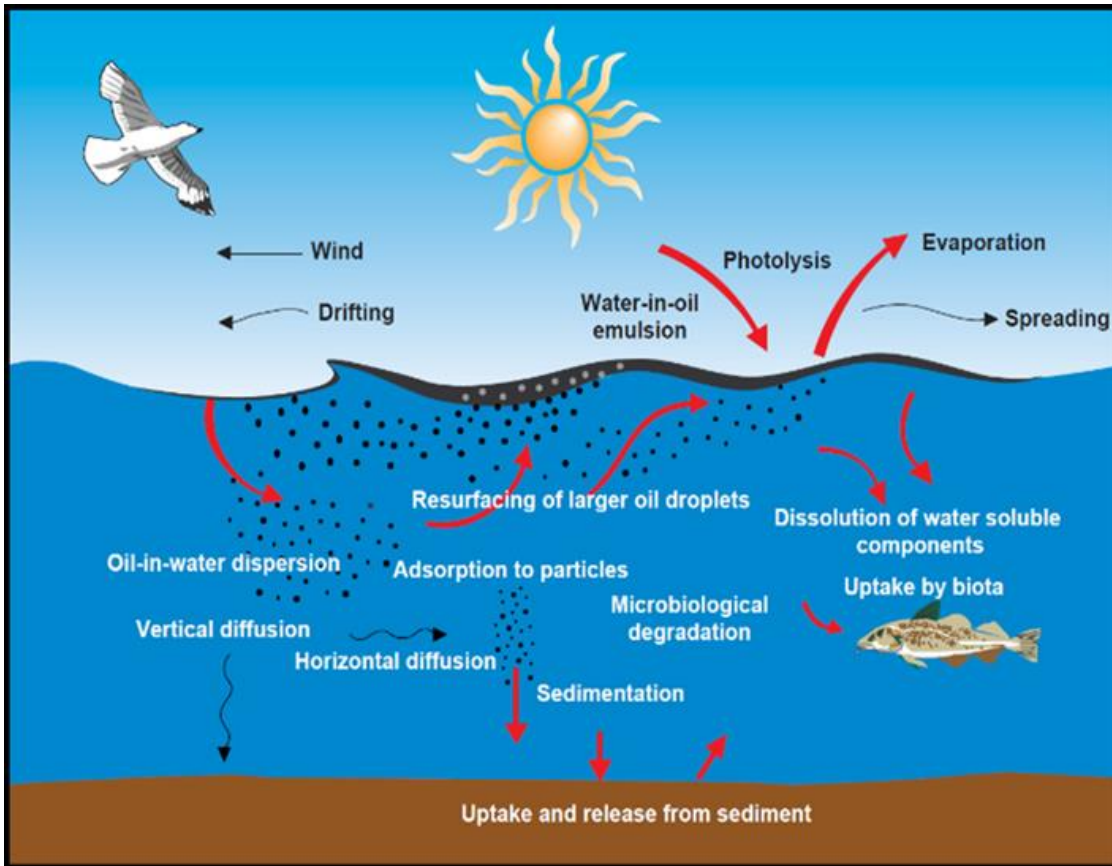




SINTEF



# Report

## Lille Prinsen – Weathering properties and behaviour at sea

In relation to oil spill response

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**SUMMARY**

A standardized bench-scale and meso-scale flume testing weathering study has been conducted on Lille Prinsen crude oil at 13 °C. The dispersibility testing on Lille Prinsen was included to estimate the viscosity limits and time window for dispersant use. The laboratory data were used as input to the SINTEF Oil Weathering Model (OWM) for weathering predictions from a surface release of Lille Prinsen at sea at 5 and 15°C. The weathering properties of Lille Prinsen are also discussed in relation to oil spill response.

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C	Input data to SINTEF Oil Weathering Model (OWM)
D	Chemical characterization – OSCAR composition file

## 1 Executive summary

In general, spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill preparedness. Oil weathering varies over time and with different environmental conditions. The lifetime of an oil spill at sea depends on the oil's properties, emulsification, release scenario, and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Input from the experimental weathering data is input to SINTEF Oil Weathering Model (OWM) to predict the properties of oils as weathered over time. The laboratory testing of Lille Prinsen was conducted at 13 °C, and OWM predictions were conducted at 5 and 15 °C, reflecting a span of winter and summer temperatures in the North Sea. The weathering study at 13 °C was considered sufficient to perform reliable predictions of Lille Prinsen at both temperatures, based on the properties of the oil.

Compared to many other Norwegian crude oils, the weathering study of Lille Prinsen shows the following properties relevant for the behaviour, if spilled at sea, with sufficient film thickness to emulsify (>0.1 mm):

- Lille Prinsen is a paraffinic crude oil with medium density (0.851 g/mL) with volatile compounds of 39 vol % at boiling points <250 °C, that cause a moderate degree of evaporative loss. E.g., after 12 hours the evaporative loss is in the range of 30-33 wt. % at 10 m/s wind speed.
- Due to the combination of medium wax (4.7 wt.%) and asphaltene (0.5 wt.%), and density, Lille Prinsen forms stable water-in-oil emulsions with high water uptake of 73-75 vol.% in winter and summer conditions
- The emulsion formed are expected to be persistent on the sea surface. E.g., the OWM predictions indicate a lifetime at 15 m/s wind speed of 2-3 days. In calmer weather conditions the lifetime is predicted to be >5 days.
- As much as 65-70% of the oil can remain on the sea surface in very calm weather conditions (2 m/s wind speed) after 5 days.
- The overall volume of the spilled oil can increase 1.5 times relative to the volume due to emulsification at summer and winter conditions
- The residue at sea may form semi-solid lumps/material particularly in calm sea conditions (<2-5 m/s wind speeds) due to the high pour points of +15 and +24 °C for the 150 and 250°C+ residues, expecting to be less pronounced in summer conditions than in colder seawater temperatures.

### Risk of fire /explosion hazard in oil spill response:

If free gas is not associated with an oil release (e.g., surface release of stabilized oil at 1 atm.), the flash point of the oil is the most important parameter when evaluating the potential for fire /explosion hazard. In such cases when the oil is spilled on the sea surface it assumes to reach the ambient water temperature within a short time. The fire hazard, based on the volatile components from the oil, may be high if the flash point of the oil is below the sea temperature.

For Lille Prinsen, the flash point is predicted to exceed the sea temperature within the first 15 minutes at wind speeds (2-15 m/s). However, for larger surface release rates, e.g., spill from a blowout or pipeline rupture, the time for the flash point to exceed the sea temperature can be extended. Moreover, some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Lille Prinsen reaches this limit (60 °C) in 3 hours after a spill at calm wind speed (2 m/s) at summer and 6 hours in winter conditions respective, and more rapidly at higher wind speeds. However, this limit is not considered as relevant for oil recovery vessels with A class certification for transport of liquids (Class I/II, flash point <60 °C).

A "safety" zone should be established early and downwind from the spill site before any response actions in case of an acute oil spill involving free gas. In a response operation, explosimeters should always be utilized to measure concentrations of free gas to minimize the risk for fire and explosion hazard at the spill site.



#### Effect of adding emulsion breaker:

The water in oil emulsions of Lille Prinsen were stable, but the emulsions were shown to easily release about 92-97 % of incorporated water when spiking a concentration of 2000 ppm by weight of the emulsion breaker (Aerosol OT-SE surfactant), and somewhat lower effect with the lower concentration of 500 ppm (66-94 %). Use of emulsion breaker may effectively be used during an oil spill operation to remove or reduce water from the recovered oil/emulsion which minimizes the storage volume. Emulsion breakers are normally injected at the skimmer head prior to transferring the collected oil/water to storage tanks.

#### Mechanical recovery :

The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous emulsions (lower than 1000 mPa.s) compared to emulsions that are more viscous. Boom leakage is also influenced by other factors such as operational speed and weather conditions. This study shows that the emulsion viscosities of Lille Prinsen surpassed 1000 mPa.s about 6-9 hours at 5 m/s wind speed (5 and 15 °C), and about 2-3 hours at 10 m/s wind speed at 5 and 15 °C. Moreover, viscosities larger than 20 000 mPa.s are known to reduce the flowability of the oil/emulsion and may reduce the recovery efficacy when using traditional weir skimmers. However, Lille Prinsen has predicted emulsion viscosities lower than this limit within 2-3 days weathering at summer and winter conditions at 10 m/s and >5 days for lower wind speeds.

#### Chemical dispersion:

Lille Prinsen is expected to have a good potential for chemical dispersion with use of Dasic Slickgone NS (DOR; dispersant-to-oil ratio 1:25) for viscosities <2500 mPa.s (low-energy test, IFP, and poorly dispersible for viscosities >12 000 mPa.s (high energy test, MNS). In the field, if the oil is reduced dispersible, additional energy e.g., thrusters, Fire Fighting (Fi-Fi) systems, higher DOR by repeated dispersant application may increase the efficacy of the dispersant treatment.

#### Solidification of residue at sea:

Increased weathering potentially increases the high pour points to the point of solidification (elastic properties) at the sea surface. Solidification typically arises in calm sea conditions (i.e., non-breaking waves) when the pour point of the oil is 5-15 °C above the seawater temperature. In such cases, if solidified (low emulsified /water free) lumps are observed on the sea surface, a lower dispersant effectiveness is likely.

#### High-capacity water flushing (mechanical dispersion):

The emulsification is the limiting factor for this strategy. The predicted film thicknesses >0.2-0.3 mm are the estimated upper limits for effective use of water flushing. Water flushing should therefore not be considered as a main response option for Lille Prinsen but could be a supplementary method in areas with thin oil films e.g., metallic /rainbow appearance in very calm weather conditions.

Monitoring and remote sensing: Monitoring and remote sensing should always be used as support in response operations for Lille Prinsen.

## 2 Introduction

New oil types, from heavy crude oil to light crude oils and condensates, are continuously coming into production worldwide, as well as on the Norwegian continental shelf. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. For example, the "Braer" accident at the Shetlands (1993) and the "Sea Empress" accident in Wales (1996) have demonstrated how different the fate and behaviour of the crude oils can be when spilled on the sea surface. For that reason, obtaining comprehensive knowledge about the expected behaviour of spilled oil at sea is of great importance. Moreover, the "Deepwater Horizon" incident in the Gulf of Mexico (2010) clearly showed how the efficacy of the different response techniques changed as the oil weathered and emulsified on the sea surface over a time after the release. These past experiences and other incidents shape the knowledge base and the subsequent refinement of future operative strategies in terms of where, when, and how the mitigation methods should operate during a response operation. Appendix A describes the general physical and chemical properties and weathering processes of oil spilled on the sea surface.

According to the Norwegian Environment Agency (NCA) and the Petroleum Safety Authority Norway (Ptil) regulations for petroleum activities (Aktivitetsforskriften §59), the characterization of oils with respect to their weathering properties and fate in the marine environment should be performed for all oils coming into production. SINTEF Ocean has performed a standardized small-scale weathering study, including dispersibility testing, and a supplementary meso-scale weathering study on Lille Prinsen at 13 °C. The obtained laboratory data have been used to predict the weathering properties of Lille Prinsen at 5 and 15 °C by use of the SINTEF Oil Weathering Model (OWM) reflecting winter and summer conditions. Such documentation gives an important basis for oil spill contingency planning and decision making during an oil spill operation. Information about the Lille Prinsen field is given, below (Figure 2-1).

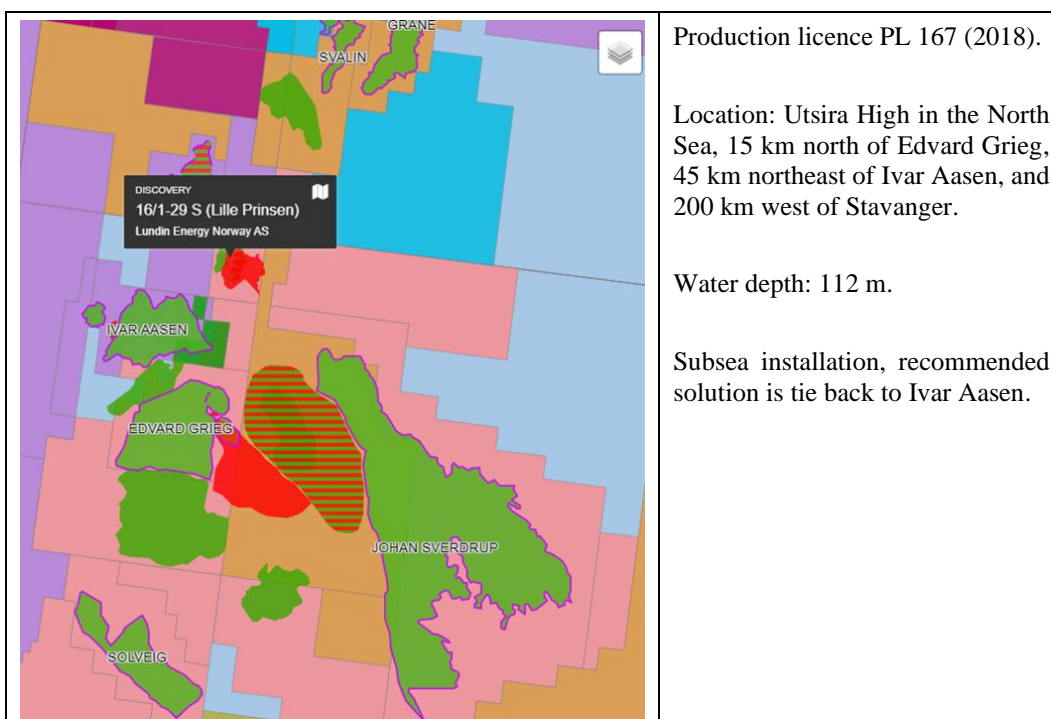


Figure 2-1 <https://www.norskipetroleum.no/fakta/funn/16-1-29-s/>



### 3 Small-scale laboratory testing

Description of the oil sample of Lille Prinsen for testing and the experimental setup for the small-scale and meso-scale weathering, and dispersibility methods are described in Appendix B.

Physico-chemical parameters and weathering properties of Lille Prinsen are also compared with previous weathering studies of Solveig, Edvard Grieg, Ivar Aasen, Johan Sverdrup, and Rolvsnes. These crude oils are produced on the neighboring fields at Utsira High and was selected in agreement with Lundin Energy Norway (see Table 3-1). Lille Prinsen is a subsea tie-back to Ivar Aasen. The first stage of the processing will occur at Ivar Aasen, before the oil and gas is transported to Edvard Grieg for final processing. Hence, the Lille Prinsen crude will be comingled with the Ivar Aasen crude at the Ivar Aasen platform and further with the crudes from Solveig, Edvard Grieg, and Rolvsnes at the Edvard Grieg platform. The blend is anticipated to exhibit similarities of the weathering properties as for the single paraffinic crude oil, included in the blend. Hence, an oil spill response of the blend is not expected to differ significantly from each of the paraffinic crude oils, selected for comparison. However, the heavier Johan Sverdrup is regarded as an asphaltenic crude oil, and the weathering properties are expecting to differ from the lighter paraffinic crude oils, herein.

Table 3-1 Crude oils compared with Lille Prinsen crude oil (SINTEF ID 2022-0178)

Oil type	SINTEF ID	Report no	Reference
Edvard Grieg <sup>a)</sup>	2010-0327	SINTEF A18427	Sørheim, 2011
Solveig <sup>b)</sup>	2013-0580	SINTEF A26115	Hellstrøm and Johnsen, 2014
Ivar Aasen <sup>c)</sup>	2011-0001	SINTEF A21165	Sørheim og Leirvik, 2011
Johan Sverdrup <sup>d)</sup>	2011-0444	SINTEF A22484	Sørheim, 2012
Rolvsnes	2021-6498	OC2021 A-117	Sørheim and Hellstrøm, 2022

a) Former Luno, b) Former Luno II, c) Former Draupne, d) Former Avaldsnes

#### 3.1 Gas chromatographic (GC/FID) characterization

The hydrocarbon profile of Lille Prinsen was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 3-1 illustrates the GC-FID outputs (gas chromatograms) of the fresh oil of Lille Prinsen and the corresponding evaporated residues at three different degrees of evaporative loss of volatiles with boiling points 150, 200 and 250°C+ (see Appendix E.2). The loss of low molecular weight (volatiles) compounds (shown towards the left of the chromatogram) at the three temperatures mimics that of natural weathering (evaporative loss at sea) corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.

The gas chromatograms show the n-alkenes as systematic narrow peaks and the peaks to the left in the chromatograms represent the components with the lowest boiling point. As can be seen in Figure 3-1, these components are gradually removed with higher distillation temperature. More complex components, such as resins and naphthenes, are not as easily separated as n-alkanes and form a broad and poorly defined bump below more pronounced peaks. The bump is often described as "Unresolved Complex Mixture", or UCM. Heavier compounds such as asphaltenes (>nC40) are not possible to analyse with this technique.

The gas chromatogram of fresh Lille Prinsen in comparison with Edvard Grieg, Solveig, Ivar Aasen, Johan Sverdrup, and Rolvsnes are shown in Figure 3-2. The crude oils exhibit similar paraffinic hydrocarbon profiles. The chromatograms also indicate medium amounts of wax/heavy paraffins compounds in the range of nC20-nC30.

Moreover, gas chromatography is an important tool for oil characterisation and for oil spill identification as an initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, are the nC17/Pristane and nC18/Phytane ratios. Table 3-2 shows the ratios of Lille Prinsen in comparison with the other oils in comparison. Ratios >1 are typically for non-biodegradable oils.

Table 3-2 Calculated ratios, average of fresh oil and weathered residues.

Oil	$nC_{17}/Pristane$	$nC_{18}/Phytane$
Lille Prinsen	1.7	2.1
Edvard Grieg	1.8	1.6
Solveig	1.0	1.8
Ivar Aasen	2.2	2.8
Johan Sverdrup	1.8	1.9
Rolvsnæs	1.2	2.0

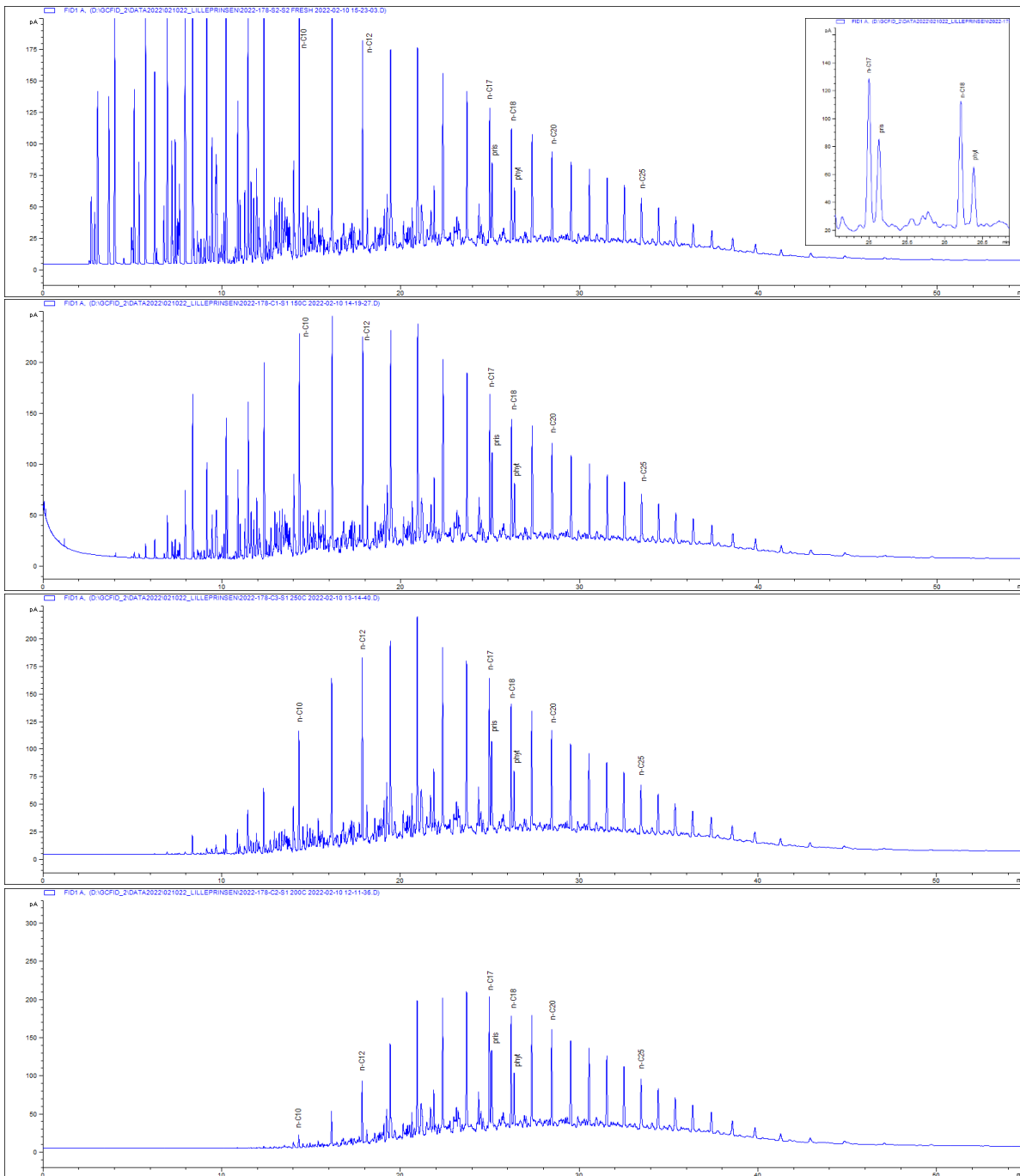
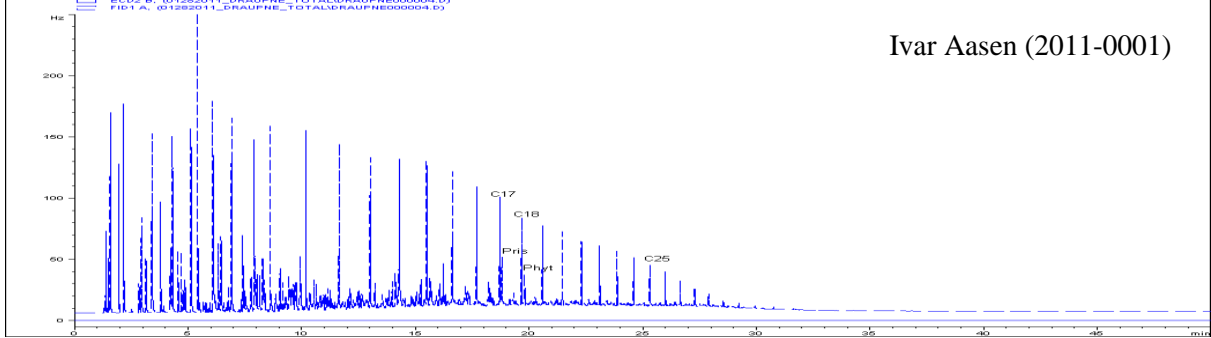
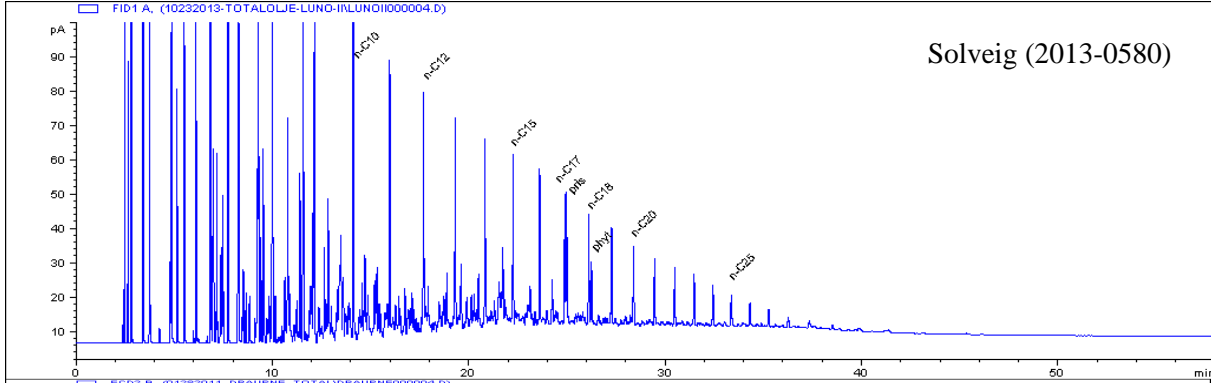
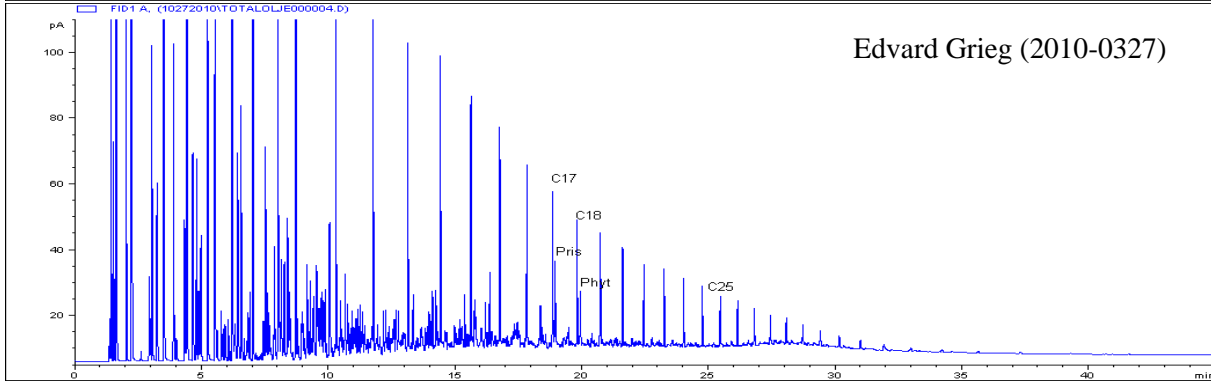
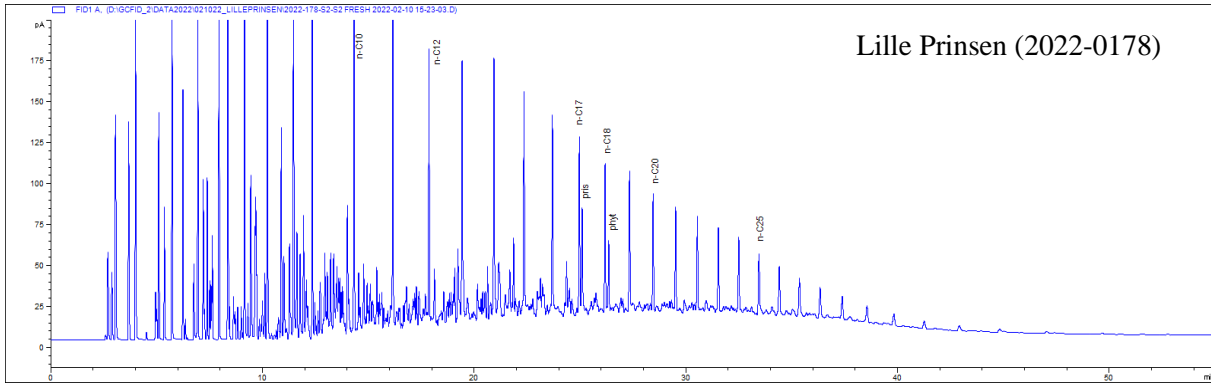


Figure 3-1 GC/FID chromatograms of fresh sample and evaporated residues of Fresh Lille Prinsen, and evaporated residues of 150°C+, 200°C+, 250°C+.



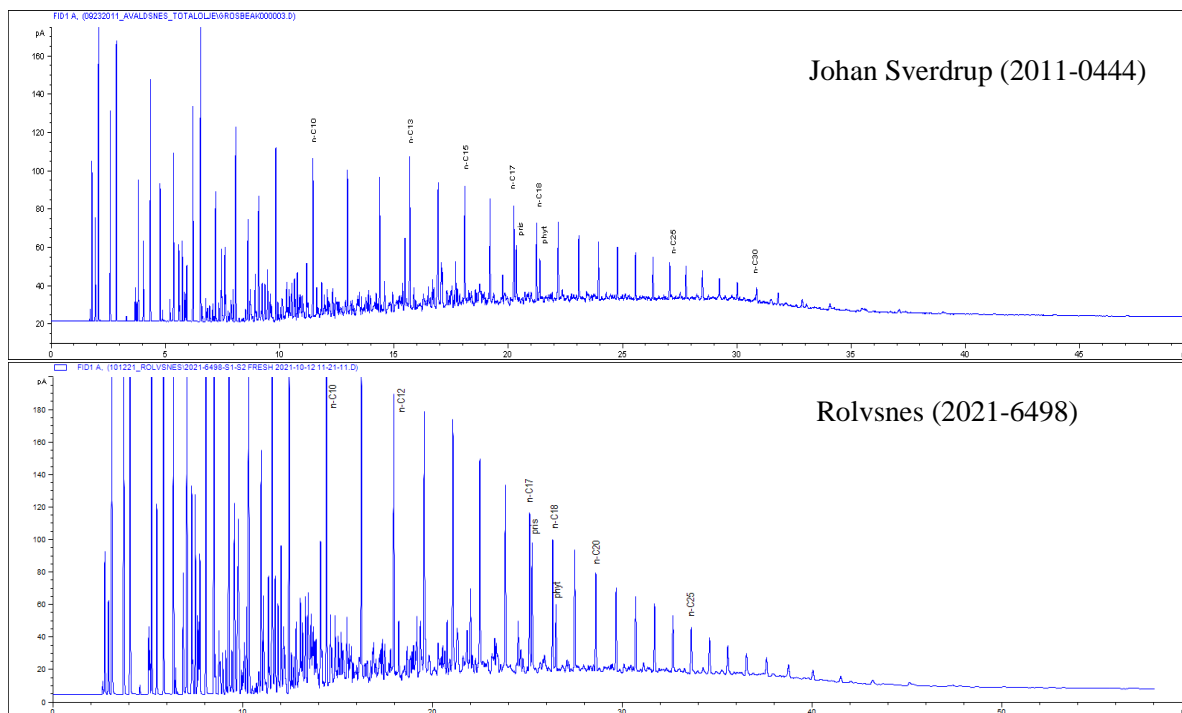


Figure 3-2 GD/FID chromatograms of fresh residues of Lille Prinsen, Edvard Grieg, Solveig, Ivar Aasen, Johan Sverdrup, and Rolvsnes. The retention times may differ between the chromatograms due to different temperature programs (relative comparison).

### 3.2 Chemical and physical properties

The chemical properties of asphaltene and wax content are given in Table 3-3 for Lille Prinsen in comparison with the Edvard Grieg, Solveig, Ivar Aasen, Johan Sverdrup and Rolvsnes. Lille Prinsen has a medium wax content (4-7 wt.%) and asphaltene content of 0.5 wt.% and the values are in the same range as the other oils in comparison, except from Johan Sverdrup that has a high asphaltene content of 1.8 wt %, which is regarded as high compared with crude oils on the Norwegian continental shelf.

The physical parameters of the fresh oil and residues of Lille Prinsen, in comparison with the other crude oils, are given in Table 3-4. Overall, the crude oils have many similarities in their physical properties. However, Johan Sverdrup is a heavier crude oil (0.891 g/mL) compared with the other oils, where Lille Prinsen, Solveig, Edvard Grieg, and Rolvsnes have medium densities in the range of 0.848-0.851, whilst Ivar Aasen has a slightly lower density of 0.838 g/mL. Lille Prinsen has an evaporative loss of the 250°C+ residue reflecting 39 vol. % and is very similar to Edvard Grieg and Ivar Aasen. Whilst Rolvsnes and Solveig have the highest evaporative loss of 47 and 45 vol. %, respectively, Johan Sverdrup has a significant lower evaporative loss of 26 vol. %.

The pour points of Lille Prinsen are in the same range as the other medium paraffinic crude oils herein, except for Johan Sverdrup that has somewhat lower pour points. The viscosities of fresh oil and residues at 13 °C (10s<sup>-1</sup>) of Lille Prinsen are in the same range as the other oils, except from Ivar Aasen that has lower viscosities. The same trends are also shown for viscosities at 5 °C.

Table 3-3 Asphaltene (“hard”) and wax content Lille Prinsen in comparison with other crude oils.

Oil	Residue	Asphaltenes "hard" (wt. %)	Wax (wt. %)
Lille Prinsen	Fresh	0.5	4.7
	150°C+	0.6	5.6
	200°C+	0.7	6.3
	250°C+	0.8	7.2
Solveig	Fresh	0.5	2.7
	150°C+	0.6	3.4
	200°C+	0.7	3.9
	250°C+	0.8	4.4
Edvard Grieg	Fresh	0.2	3.9
	150°C+	0.2	4.8
	200°C+	0.3	5.4
	250°C+	0.3	6.0
Ivar Aasen	Fresh	0.1	4.0
	150°C+	0.1	4.7
	200°C+	0.2	5.3
	250°C+	0.2	6.2
Johan Sverdrup	Fresh	1.8	2.9
	150°C+	1.9	3.2
	200°C+	2.1	3.4
	250°C+	2.2	3.7
Rolvsnæs	Fresh	0.4	3.6
	150°C+	-	-
	200°C+	0.5	5.2
	250°C+	0.6	6.3

Table 3-4 Physical properties of Lille Prinsen in comparison of other crude oils.

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/ml)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 5°C (10 s <sup>-1</sup> )	Visc. (mPa.s) 13°C (10 s <sup>-1</sup> )	IFT (mN/m)*
Lille Prinsen	Fresh	0	100	0.851	-	0	117	23	26
	150°C+	20	84	0.885	43	15	644	216	25
	200°C+	29	75	0.897	77	21	2301	697	28
	250°C+	39	65	0.911	114	24	6442	2582	26
Solveig	Fresh	0	100	0.851	-	-27	22	11	18
	150°C+	25	79	0.898	32	6	474	99	18
	200°C+	36	69	0.915	69	12	2689	569	21
	250°C+	45	61	0.931	108	18	10572	3165	20
Edvard Grieg	Fresh	0	100	0.850	-	6	138	30	-
	150°C+	22	82	0.883	46	15	955	207	-
	200°C+	32	72	0.897	85	21	5310	1150	-
	250°C+	40	64	0.908	112	27	9800	2350	-
Ivar Aasen	Fresh	0	100	0.838	-	-6	65	9	17
	150°C+	18	85	0.861	42	9	210	34	18
	200°C+	29	75	0.872	75	15	950	170	18
	250°C+	39	65	0.883	113	21	3810	770	-
Johan Sverdrup	Fresh	0	100	0.891	-	3	309	61	19
	150°C+	12	91	0.915	45	9	1243	281	19
	200°C+	18	85	0.924	76	6	2530	632	19
	250°C+	26	78	0.935	110	12	9449	2044	21
Rolvsnes	Fresh	0	100	0.848	-	0	-	12	-
	150°C+	-	-	-	-	-	-	-	-
	200°C+	35	70	0.901	-	18	-	449	-
	250°C+	47	57	0.921	-	24	-	2505	-

∴ No data available \*Initial interfacial tension

The True Boiling Point curve (TBP) of Lille Prinsen in comparison with the other crude oils is given in Figure 3-3. The TBPs reflects the evaporative loss of the 150, 200 and 250°C+ residue indicating the evaporative loss at sea. Overall, the TBPs show high similarities among the crude oils, except the heavier Johan Sverdrup that has a lower evaporative loss.

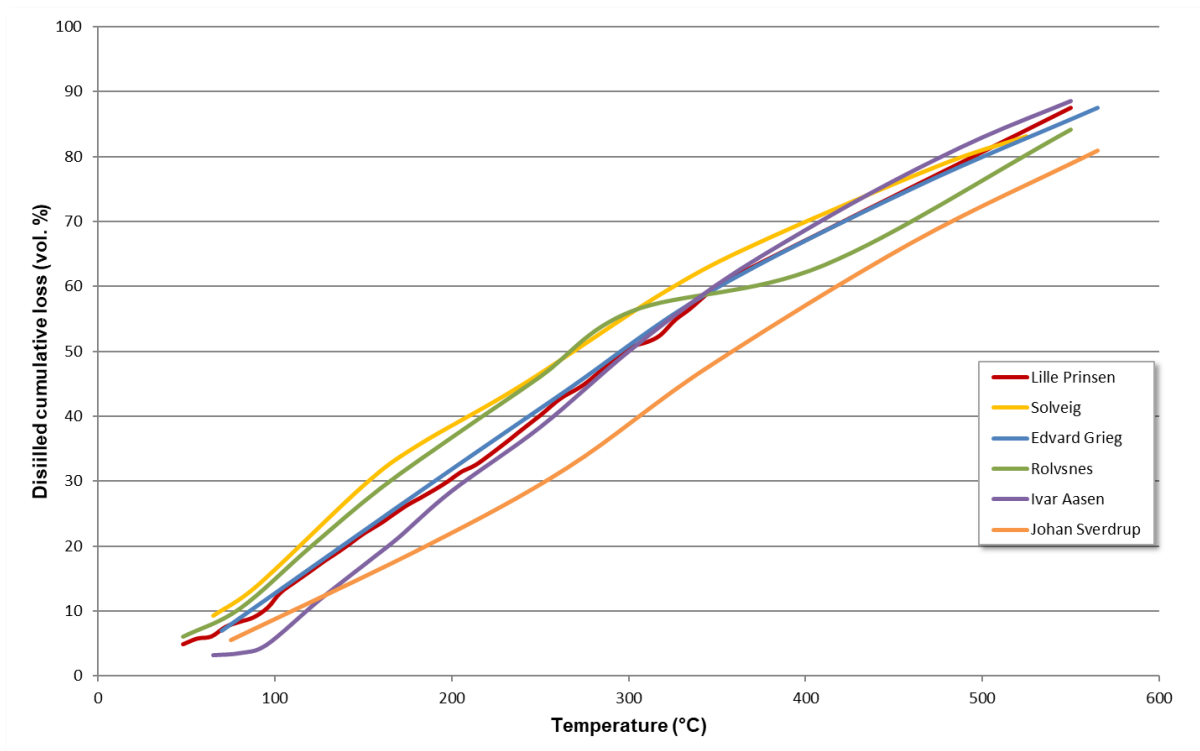


Figure 3-3 True boiling point (TBP) curves of Lille Prinsen compared with other crude oils.

## 3.2 Emulsifying properties

In general, oil-in water (o/w) emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion). The rotating cylinders method (Mackay and Zagroski, 1982) was used to study the emulsifying properties of Lille Prinsen, and the procedure for maximum water uptake is described in Hokstad et al. 1993 (Appendix B).

### 3.2.1 Emulsification

Emulsification testing of Lille Prinsen were conducted on the residues of 150°C+, 200°C+ and 250°C+ to produce data for stability, viscosity, maximum water uptake, kinetics of water uptake, and the effectiveness of the emulsion breaker application. Emulsions of maximum water content after 24 hours rotation are shown in Figure 3-4 at 13 °C. The figure shows from left to right emulsions prepared from the residues of 150°C+, 200°C+ and 250°C+, respectively.

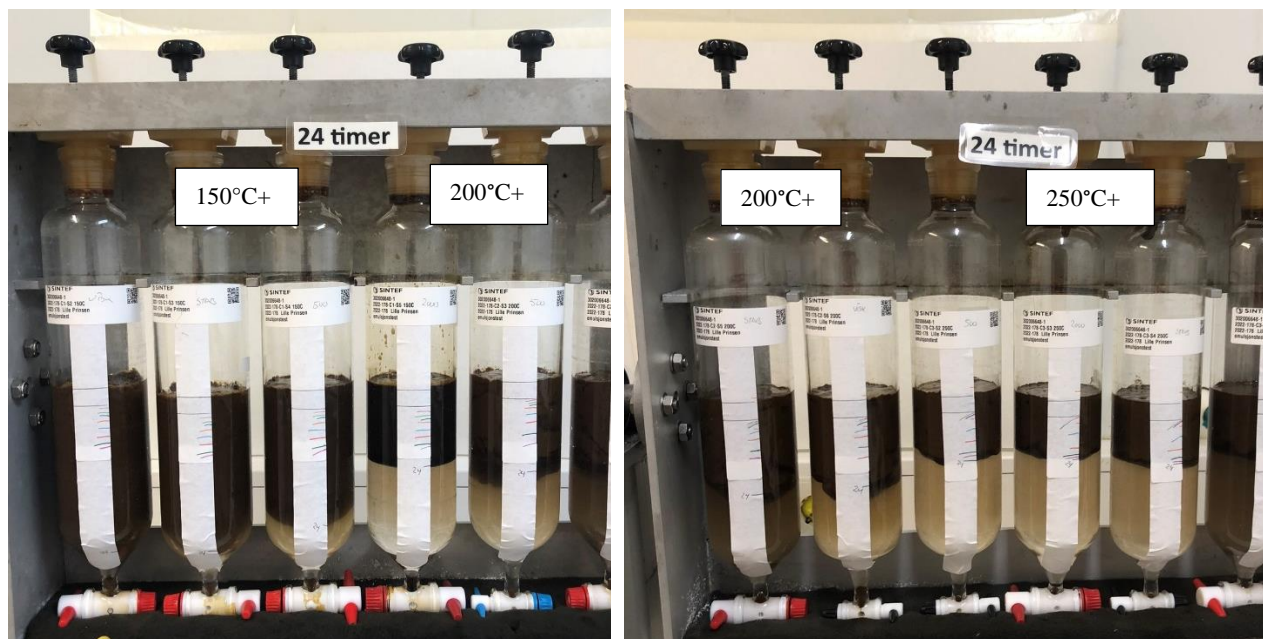


Figure 3-4 The rotating cylinders after 24 hours of rotation at 13 °C of Lille Prinsen.

### 3.2.2 Water uptake and maximum water content

The rate (kinetics) of water content in the water-in-oil (w/o) emulsions as a function of time is tabulated in Table 3-5.  $T_{1/2}$  is a constant defined as the time (hours) it takes to incorporate half of the maximum water uptake (vol. %) in 24 hours (rotating time) and is derived from the tabulated data for each residue.

Table 3-5 Water uptake for the evaporated residues of Lille Prinsen crude oil at 13 °C.

Mixing time	150°C + (Vol. % water)	200°C + (Vol. % water)	250°C + (Vol. % water)
Start	0	0	0
5 min	19	9	8
10 min	33	16	8
15 min	41	24	12
30 min	49	36	33
1 hour	59	46	53
2 hours	66	57	67
4 hours	71	67	73
6 hours	72	73	74
24 hours	87	82	75
$T_{1/2}$	0.40	0.84	0.64

\* Depending on weather situation and release rate, the residues are corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.

### 3.2.4 Efficiency of emulsion breaker and stability of emulsions

In mechanical recovery operations, separating water from oil-emulsion enables optimal use of available storage (i.e., facilities/tankers), and the efficiency of this separation can be enhanced by applying emulsion breakers. The effectiveness of the emulsion breaker Aerosol OT-SE surfactant was evaluated on different emulsified residues of Lille Prinsen at 13 °C. The choice of emulsion breaker was selected in agreement with Lundin Energy Norway AS.



The results show that the emulsified oil volume decreased after treatment with the emulsion breaker, as water was released from the emulsion as shown in Table 3-6 at 13 °C. Overall, adding 2000 ppm (0.2 ppm w.%) of the emulsion breaker relative to the oil were more efficient (92-97 %) to break the emulsion compared with a lower concentration of 500 ppm (66-94 %), particularly of the 250°C+ emulsion.

The emulsion stability was studied by quantifying the amount of volume fraction of water released from the emulsion after 24 hours settling time (after 24 hours rotation). Overall, Lille Prinsen forms stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first main row of Table 3-6 (no emulsion breaker added).

Table 3-6 Stability of emulsion and the effect of emulsion breaker at 13 °C on Lille Prinsen.

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 13 °C			% Effect. (released water)
		Reference	24 hours *	Stability ratio**	
150°C+	none	87	87	1.00	0
200°C+	none	82	82	1.00	0
250°C+	none	75	74	0.99	1
150°C+	OT-SE 500 ppm	87	30	0.06	94
200°C+	OT-SE 500 ppm	82	40	0.14	86
250°C+	OT-SE 500 ppm	75	51	0.34	66
150°C+	OT-SE 2000 ppm	87	17	0.03	97
200°C+	OT-SE 2000 ppm	82	17	0.04	96
250°C+	OT-SE 2000 ppm	75	19	0.08	92

ppm: parts per million, relative to oil fraction of emulsion

\*: w/o emulsion after 24 hours rotation and 24 hours settling

\*\* Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling; all the water is settled out for 24 hours settling. Stability ratio of 1 implies a totally stable emulsion

### 3.2.3 Viscosities and yield stress

Table 3-7 gives the viscosities of oil residue fractions of Lille Prinsen with different water content (water free, 50 vol. %, and 75 vol. % and maximum water) at 13 °C. The water free residues and the emulsions behave as *non-Newtonian* fluids due to the increasing degree of weathering (evaporation and water uptake), with higher viscosities at a lower shear rate ( $10s^{-1}$ ) compared to the viscosities measured at higher shear rate ( $100s^{-1}$ ). This decrease in viscosity with increasing shear rate is due to the shear thinning property of emulsion with increased mechanical force.

Yield stress is defined as the force that must be overcome so that an oil can spread / flow like a liquid on the sea (also known as the flow limit). This force is called the fluids "yield stress" or flow limit and is given the unit Pascal (Pa). Yield stress (flow limit) is measured with Physica MRC 300 rheometer. Many crude oils (particularly weathered residues and emulsions) are so-called *Bingham (pseudo) plastic* (semi-solid) fluids at sea temperature. This means that applied force must be exerted on the fluid to make it flow and hence spread, and this is mainly pronounced for *non-Newtonian* oils where the viscosities vary with the shear rate. The measurements were performed by applying a gradually increasing oscillating force to the sample where the deformation of the oil sample is measured. Results are given in Table 3-7. Lille Prinsen has for the emulsion of the 200 and 250°C+ residues relatively high yield stress and expect the oil to have reduced spreading after some hours at sea.

Table 3-7 Viscosity and yield stress of water-free and emulsions on Lille Prinsen.

Residue	Water content (vol. %)	Viscosity (mPa.s) 13 °C		Yield stress
		10 s <sup>-1</sup>	100 s <sup>-1</sup>	Pa
Fresh	0	23	17	ND
150°C+	0	216	103	ND
200°C+	0	697	247	0.52
250°C+	0	2582	651	2.45
150°C+	50	972	381	4.1
200°C+	50	1486	655	15.5
250°C+	50	4565	1235	28.2
150°C+	75	1903	581	9.65
200°C+	75	3934	1210	17.8
250°C+	75	21366	1523	68.8
150°C+	90	3213	253	18.5
200°C+	82	6687	1368	32.8
250°C+	74	13455	1134	-

ND: Not detected

### 3.3 Chemical dispersibility

The dispersibility testing on Lille Prinsen included:

- Dosage testing of relevant dispersant.
- Systematic testing on weathered /emulsified samples as a basis to predict the time-window for effective application of dispersant.

#### 3.3.1 Screening testing of dispersants

The screening testing on was performed using the low-energy IFP test (Institute Français du Pétrole), reflecting non-breaking waves (<5 m/s wind speed), in combination with the high-energy MNS test (Mackay-Nadeau-Szeto). Dispersants tested were Dasic Slickgone NS, Corexit 9500A, Finasol OSR-52, and Gamlen OD 4000. The screening testing was performed at 13 °C using the 200°C+ residue emulsified with 50 vol. % seawater. The results are presented in Table 3-8. All the dispersants tested were highly effective (100 %), using the high-energy MNS test, whilst Dasic Slickgone NS was most effective dispersant tested (51 %), using the low-energy IFP test.

Table 3-8 Screening testing on Lille Prinsen using the IFP-test and MNS-test at standard temperature of 13 °C.

Dispersant (DOR/DER =1:25)*	Efficiency dispersant (200°C+ /50 vol. % emulsion)*	Efficiency dispersant (200°C+ /50 vol. % emulsion)**
	IFP	MNS
Dasic NS	51	100
Corexit 9500A	18	100
Finasol OSR 52	29	100
Gamlen OD 4000	6	100

\*: DOR = Dispersant to oil ratio, DER= Dispersant to emulsion ratio

\*\* Emulsion viscosity: 1486 mPa.s (10s<sup>-1</sup>)

-: Not analysed

### 3.3.2 Dosage testing of dispersant

Dosage testing at 13 °C was performed using Dasic Slickgone NS on the Lille Prinsen emulsion (200°C+ / 50 vol. %). The dosage test helps to identify optimal design conditions for dispersant use and was performed with dispersant-to-emulsion ratio (DER) of 1:25, 1:50, 1:100 and 1:200, and with no dispersant added. The dosage testing was performed using the low-energy IFP test (Institut Français du Pétrole), reflecting non-breaking waves (<5 m/s wind speed), in combination with the high-energy MNS test (Mackay-Nadeau-Szeto). The results are presented in Table 3-8.

The dosage testing on Lille Prinsen showed high effects (96-100%) with use of the high-energy test (MNS). For the low-energy test (IFP), the results indicated low effect with declining DER. For DER 1:50 the effect of dispersant was reduced to 20 % vs. 51 % for DER 1:25 and showed very low effect of 5% for DER 1:100. This means that breaking waves (>5 m/s wind speeds) or artificial energy in non-breaking waves (<5 m/s wind speeds) will increase the dispersant effectiveness to disperse or break up surface emulsion of Lille Prinsen. No effect was observed with no dispersant added to the emulsion of Lille Prinsen, as shown in Table 3-9.

Table 3-9 Dosage rate testing on Lille Prinsen using the IFP-and MNS-test on the 200°C+ emulsion at 13 °C

Dispersant (Dosage rate)	Efficiency of dispersant on 200°C+/50 vol. % emulsion*	
	IFP	MNS
Dasic NS (1:25)	51	100
Dasic NS (1:50)	20	100
Dasic NS (1:100)	5	100
Dasic NS (1:200)	-	96
No dispersant	-	2

\* Emulsion viscosity: 1486-1611 mPa.s (10s<sup>-1</sup>)

-: Not quantified due negligible effect.

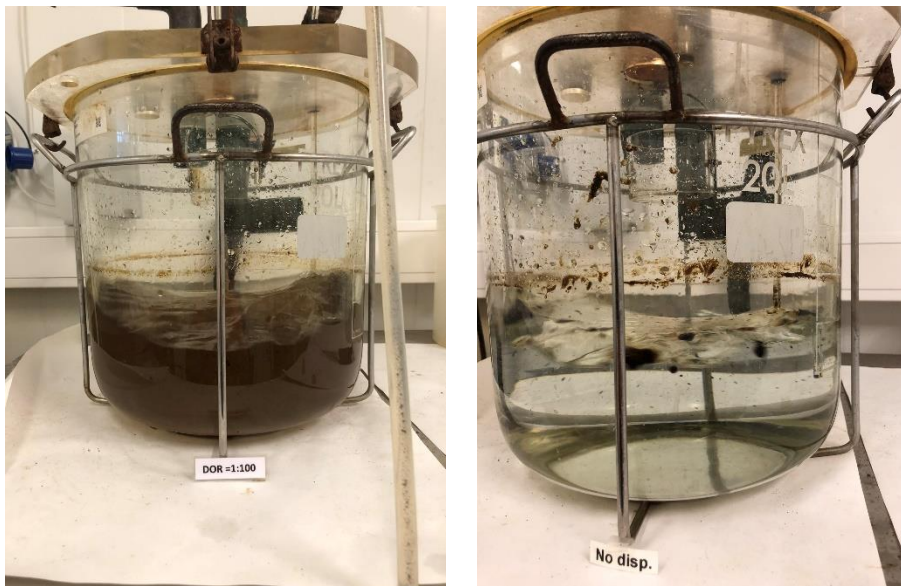


Figure 3-5 Example MNS (high-energy test) on 150°C+ 50% emulsion (Lille Prinsen). Left: After adding DOR/DER 1:100 Dasic Slickgone NS. Right: No dispersant added on the emulsion (no effect).

### 3.3.3 Systematic dispersant testing and dispersibility limits

A dispersant-to oil-dosage ratio of 1:25 (4 wt.%) is commonly used as the standard procedure to establish the time window for dispersant application. The results from the systematic dispersant testing at 13 °C is shown in Figure 3-6, and tabulated Table 3-10.

Table 3-10 Efficiency of dispersant on weathered Lille Prinsen oil/emulsions at 13 °C.

Residue	Water content (vol. %)	Viscosity (mPa·s) 10 s <sup>-1</sup>	Viscosity (mPa·s) 100 s <sup>-1</sup>	Efficiency (%)	
				IFP	MNS
150°C+	0	216	103	-	100
200°C+	0	697	247	-	100
250°C+	0	2582	651	-	22
150°C+	50	972	381	77	100
200°C+	50	1486	655	42	100
250°C+	50	4565	1235	3	25
150°C+	75	1903	581	61	96
200°C+	75	3934	1210	6	18
250°C+	75	21366	1523	-	-
150°C+	90	3213	253	50	91
200°C+	82	6687	1368	16	24
250°C+	74	13455	1134	3	4

-Not quantified

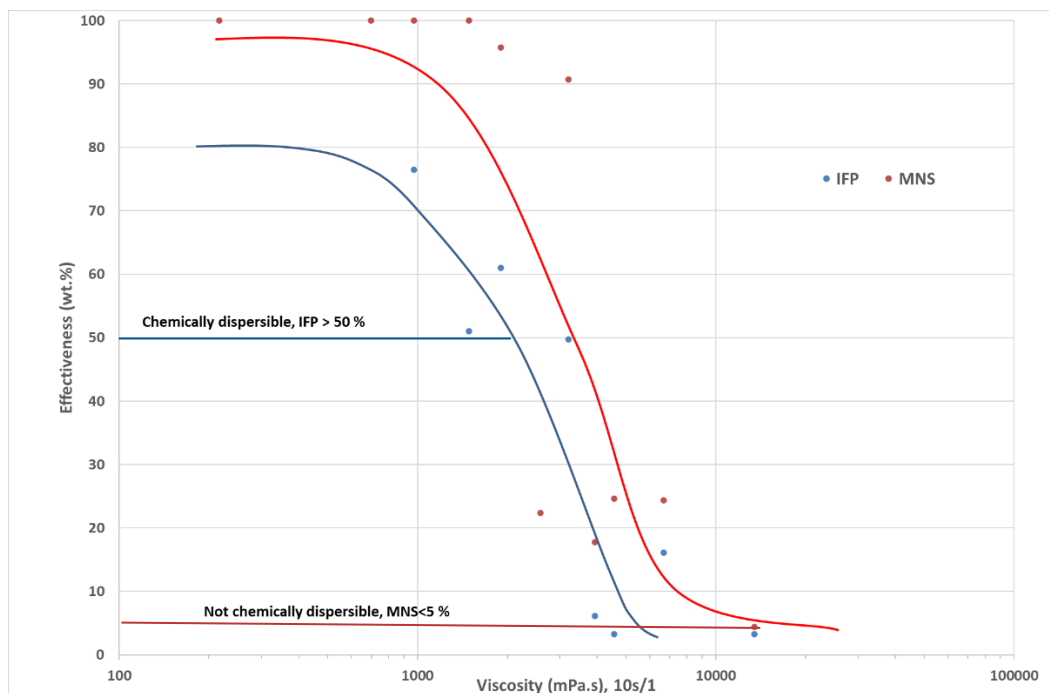


Figure 3-6 Dispersant effectiveness limits on Lille Prinsen.

Lille Prinsen was estimated to be good chemically dispersible for viscosities <2500 mPa.s (IFP-test, non-breaking waves, <5 m/s wind speeds) and found poorly (not) chemically dispersible >12 000 mPa.s based on the high energy MNS-test, reflecting breaking waves conditions (>5 m/s wind speeds) (Figure 3-6). Dispersibility of Lille Prinsen is estimated to be reduced for viscosities between 2500 and 12 000 mPa.s. Lille

Prinsen may require additional energy or higher dispersant dosage by multiple applications to enhance effective dispersion. The dispersibility limits are also summarised in Table 3-11.

*Table 3-11 Estimated viscosity limits for use of dispersants for emulsion of Lille Prinsen.*

<b>Dispersibility</b>	<b>Criteria (wt. %)</b>	<b>Dispersibility limits based on oil viscosities (mPa.s)</b>
Chemically dispersible	IFP efficiency >50%	2500
Reduced chemically dispersible		2500-12000
Poorly /not chemically dispersible	MNS efficiency <5 %	12000

## 4 Meso-scale laboratory testing

The weathering behaviour of Lille Prinsen was studied in the meso-scale flume basin. The weathering behaviour of the oil in the flume basin is a supplement to the small-scale laboratory testing (Chapter 3). A description of the meso-scale flume is given in Appendix B.3. This chapter provides an overview of the results from the flume testing, including the weathering properties, estimated mass balances and visual observations of Lille Prinsen. The results obtained give valuable operational information about the oil's behaviour. The experimental results obtained for Lille Prinsen are presented below.

A total of 9.2 litres of the fresh homogenized crude oil was applied carefully and evenly onto the seawater surface using a watering can. The seawater and air temperature for this experiment was 13 °C ( $\pm 2$  °C) due to sequence of the climate system. After application of the oil onto the seawater, the wind and wave energies were switched on. Artificial sunlight using a solar simulator was switched on after 60 minutes simulating photo-oxidation at summer conditions. The Lille Prinsen crude oil was weathered for 72 hours (3 days) before application of dispersant (Dasic Slickgone NS).

Table 4-1 shows the water content, evaporative loss, viscosity, and concentration of dispersed oil in the water column (naturally and chemically dispersed) at 13 °C at different time steps throughout the experiment.

Table 4-1 Summary results from the meso-scale flume testing of Lille Prinsen at 13 °C.

Sample nr.	Time (hours)	Water Content (vol%)	Evaporation (wt%)	Viscosity (mPa.s), 10 s <sup>-1</sup>	Oil-in- water ppm	Oil-in-water % of original amount
1	0.5	48	16	226	-	-
2	1	58	19	173	115	7.0
3	2	62	22	351	119	7.5
4	4	64	25	814	90	5.6
5	6	65	26	1384	61	3.6
7	24	76	31	4114	41	2.4
8	48	79	33	5883	30	1.7
9	72	80	34	6745	24	1.3
<b>1. Application of dispersant: 70.4g Dasic NS (DOR = 1.6 wt.%)</b>						
10 min. disp 1					57	3.0
30 min. disp 1		73		4784	59	3.3
<b>2. Application of dispersant: 63.0g Dasic NS (DOR= 1.5 wt.%)</b>						
10 min. disp 2					116	6.2
30 min. disp 2		46		3356	121	6.5
<b>3. Application of dispersant: 68.7g Dasic NS (DOR= 1.6 wt.%)</b>						
10 min. disp 3					157	9.2
30 min. disp 3					186	10.7
60 min. disp 3		34		3536	204	11.6

Total amount of dispersant: 202.1g (DOR= 4.7 wt.%) , ppm: parts per million.

### 4.1 Flume weathering data vs. predictions

The oil weathering from the meso-scale flume basin (maximum water uptake, evaporative loss, and emulsion viscosity) were compared with weathering predictions using the SINTEF Oil Weathering Model (OWM) with input data from the small-scale study at 13 °C. More information about the OWM is described in chapter 5.

Figure 4-1 shows the evaporative loss from the meso-scale testing compared to the predictions. The evaporative loss harmonizes well with the weathering predictions. For the water uptake (Figure 4-2), Lille Prinsen reached a maximum water uptake of approx. 80 vol. % within 24 hours, which regarded as in the same range as the prediction of ~ 75 vol. %. The higher water uptake within the first hours in the meso-scale flume

can be explained by formation of unstable emulsions in with large water droplets during the first hours of weathering, and this phenomenon has also been observed for other paraffinic crude oils from flume experiments, as well. The emulsion viscosities from the flume experiment did also support the predictions as shown in Figure 4-3.

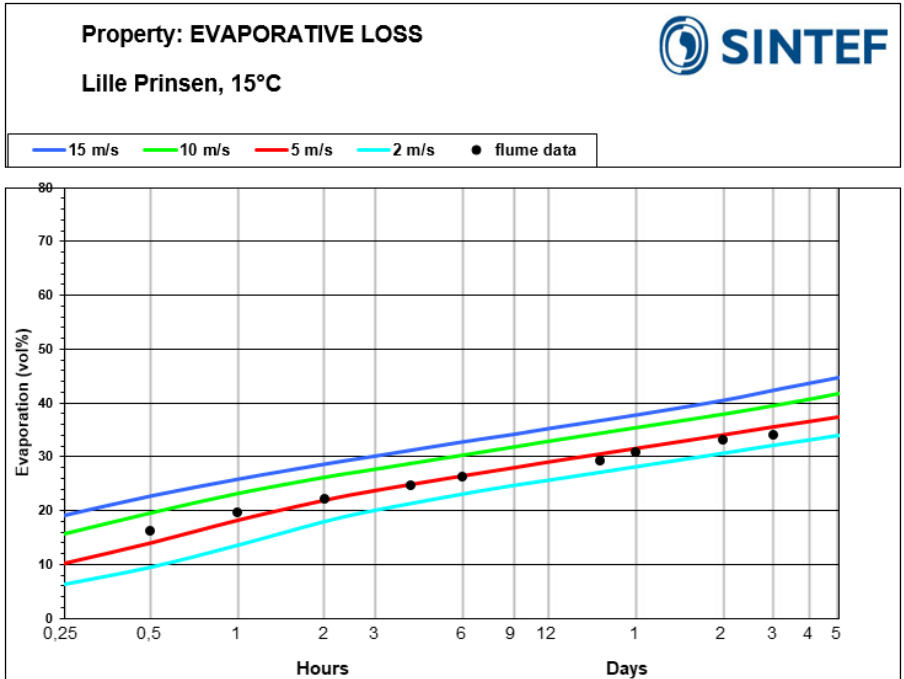


Figure 4-1 Predicted evaporative loss for Lille Prinsen. The dots represent the experimental data from the meso-scale flume testing at 13 °C.

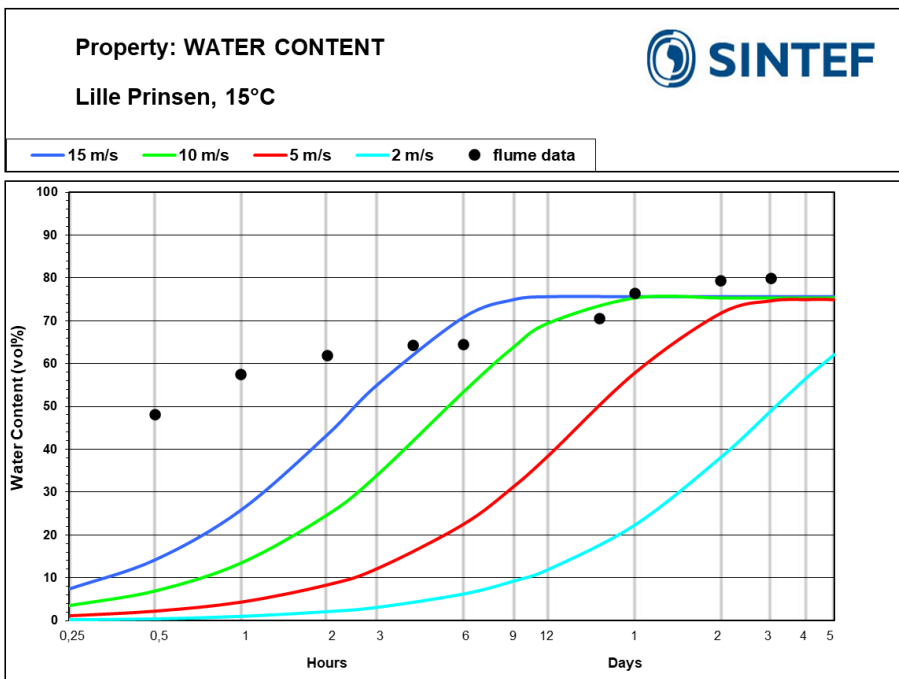


Figure 4-2 Predicted water uptake for Lille Prinsen. The dots represent the experimental data from the meso-scale flume testing at 13 °C.

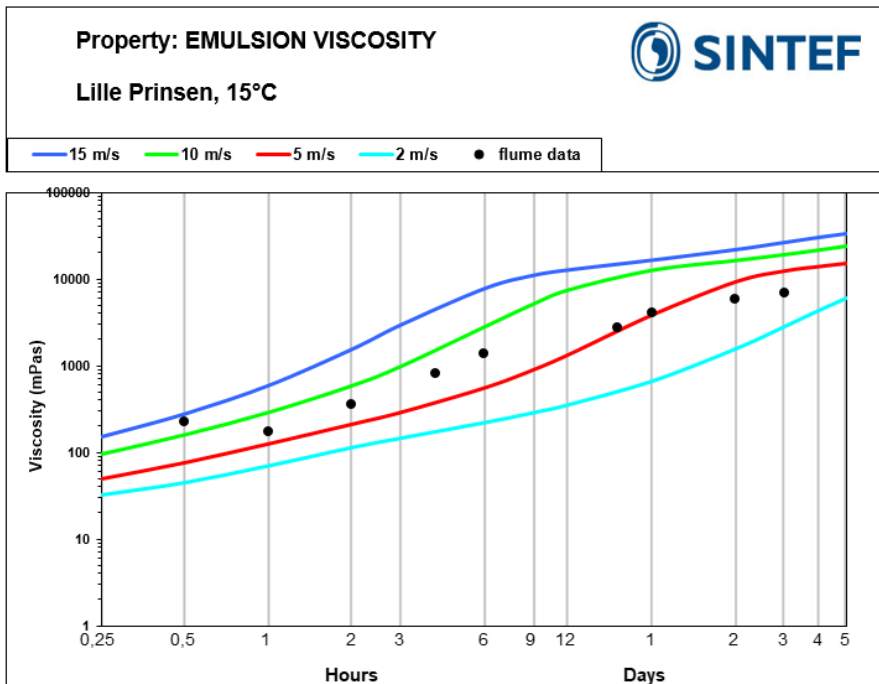


Figure 4-3 Predicted emulsion viscosities for Lille Prinsen. The dots represent the experimental data from the meso-scale flume testing at 13 °C.

## 4.2 Mass balances

The main elements in the mass balance for a crude oil spilled at sea are evaporative loss, the amount of oil on the surface, and the amount of oil dispersed. To conduct a mass balance, all oil must be accounted for. Therefore, in addition to the main elements, it was also necessary to consider each individual oil sample removed from the flume, the subsequent reduction in water volume, and the amount of oil absorbed to the flume wall.

The amount of oil evaporated, oil on surface, naturally dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated by weight. Table 4-2 shows the estimated results (by weight) of the mass balance after 24 hours of weathering time, whilst Figure 4-4 shows the mass balance before applying dispersant agent into the flume.

Table 4-2 Estimated mass balance of Lille Prinsen by weight.  
 Example after 24 hours weathering time in the meso-scale flume.

Properties	Mass balance (% of initial oil)
Evaporated	31
Oil on water surface	59
Dispersed/entrained oil	2.4
Sampled amount of oil	2.5
Oil adsorbed to the flume walls*	5

\*Estimated value from observations



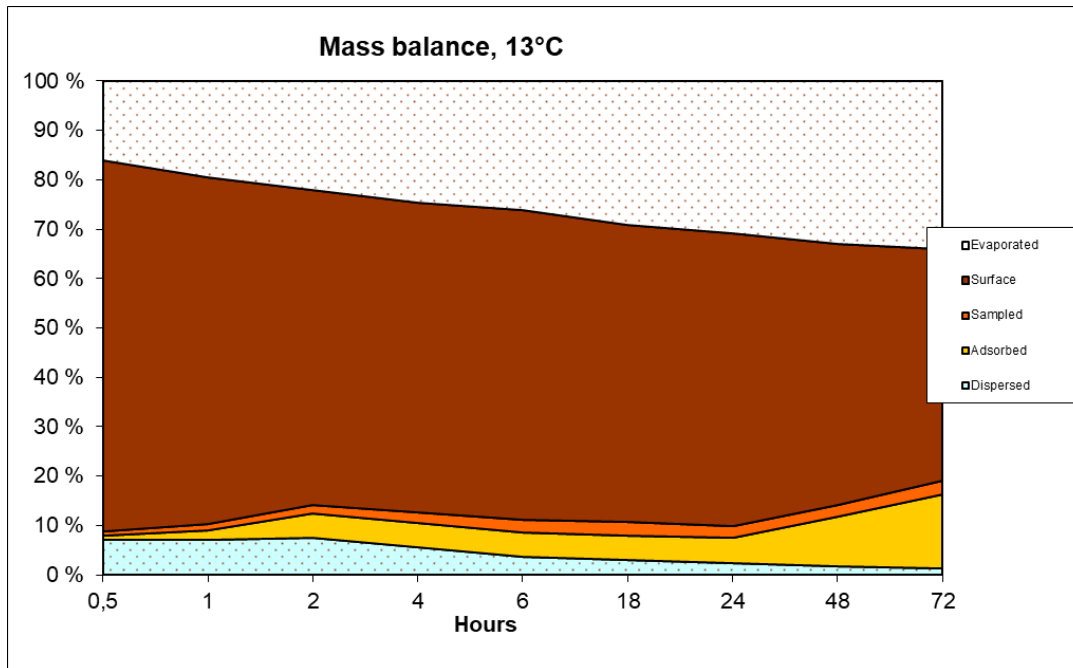


Figure 4-4 Mass balance for Lille Prinsen crude oil in the meso-scale flume basin at 13 °C, before dispersant application

### 4.3 In-situ chemical dispersion after 72 hours of weathering

After 72 hours of weathering, the dispersant Dasic Slickgone NS was sprayed successively 2 times on the remaining surface oil emulsion (*in-situ* application). The amount of application and dosage rates are summarized in Table 4-3. In addition, dispersed oil was sampled and quantified.

Table 4-3 Dispersant dosage on Lille Prinsen in the meso-scale flume basin (*in-situ* application).

Dispersant application (#)	Dasic NS application (g)	Dispersant -to -Oil Ratio (DOR)	Dispersant (wt. %)
1	70.4	1:63	<b>1.6</b>
2	63.0	1:67	<b>1.5</b>
3	68.7	1:63	<b>1.6</b>
1+2+3 cumulative	<b>202.1</b>	1:20*	<b>4.7</b>

\*Dispersant-to-emulsion Ratio (DER) 1:100

The efficiency of chemical dispersion (Figure 4-5) given as percentage (%) of the available oil after 72 hours of weathering (oil sample taken before application of dispersant) at 13 °C. This is different from the mass balances that show efficiency in % of originally applied amount of oil. The percentage of available oil dispersed or entrained oil droplets in the water phase are in the range of 20-25 % after the third round.

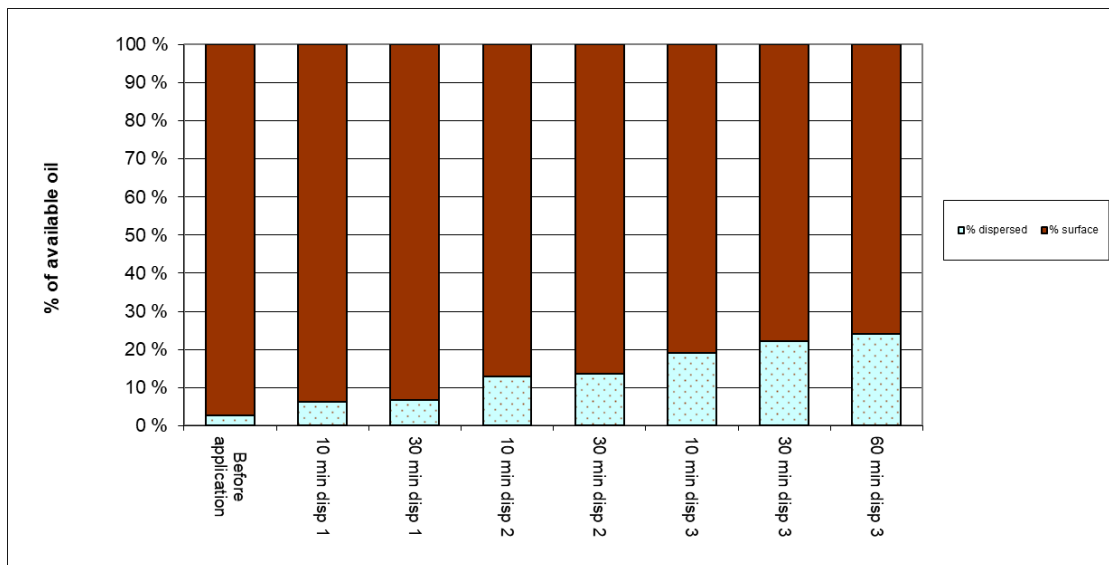


Figure 4-5 Mass balance of Lille Prinsen crude oil after application of Dasic Slickgone NS as percentage of available surface oil.

#### 4.4 Observations from the experiment

A selection of images taken during the flume experiment of Lille Prinsen are presented below. The apparent difference in colour among the pictures is due to the changing colour of the oil as evaporation and emulsification takes place.

Lille Prinsen crude oil was spread thinly when poured onto the seawater and started to emulsify within the first hour. Short time after application, large oil droplets in mm-size were entrained into the water column by the waves. After 30 minutes, the fresh oil reached a water-uptake of 48 % and 16 % of the lighter compounds had evaporated. The emulsion viscosity was measured to 226 mPa.s. The emulsion was highly unstable, however, during the experiment the oil emulsified to a thick, homogeneous, and light brownish emulsion.

After 24 hours of weathering the oil had turned into a viscous stable brownish emulsion with negligible amount of oil droplets observed in the water phase. The emulsion had a water-uptake of 76%, an evaporation of 31%, and a viscosity of 4114 mPa.s. From 48-72 hours of weathering, the emulsification continued and produced a more viscous emulsion with time, still with very small amount of entrained oil (droplets) in the water phase. After 72 hours of weathering, the viscosity increased from 226 mPa.s (0.5 hours) to 6745 mPa.s. Figure 4-6 shows an overview of pictures (time laps) from the weathering of Lille Prinsen after 30 min, 4 hours, 6 hours, 48 hours and 72 hours, respectively.

After 72 hours weathering the dispersant Dasic Slickgone NS was applied as an aerosol on the remaining emulsion (*in-situ* application) in three rounds (replicates). About 4 litres of the total volume of oil (9 litres) was available for chemical dispersion that corresponded to 22 litres of emulsion. The dispersant was applied three times on the surface oil/emulsion giving a cumulative dispersant-to-oil ratio (DOR) of 1:20, reflecting a dosage-to-emulsion ratio (DER) of 1:100.

In the first round, the dispersant slightly reduced the water-content from 80 to 73 vol. %, and the emulsion viscosity was reduced from 6745 to 4784 mPa.s. The second application of dispersant further reduced the water-content to 46 vol. % and reduced the emulsion viscosity to 3356 mPa.s. In addition, the water phase turned into a light brown colour that indicated formation of small oil droplets in  $\mu\text{m}$ -size. One hour after the third application, the water-content of emulsion was only slightly reduced to 34 vol. % with an emulsion viscosity of 3536 mPa.s, that was very similar to the emulsion viscosity from the second dispersion. Figure 4-7 to Figure 4-9 show images of the surface emulsion after treatment of dispersants.



*Figure 4-6 Weathering of Lille Prinsen (t= 0min, 30min, 1 hour, 2 hours, 4 hours, 6 hours, 24 hours, 48 hours and 72 hours). For the first 3 photos (0 to 1 hour) the sun lamp is not turned on. This effects the colour of the oil in the pictures.*



Figure 4-7 30 minutes after first application of Dasic Slickgone NS.



Figure 4-8 Emulsion 30 minutes after the second application of Dasic Slickgone NS.



Figure 4-9 Emulsion 30 minutes after the third application of Dasic Slickgone NS



#### 4.5 Concluding remarks from the meso-scale flume testing

The flume testing showed reduced dispersant effectiveness on Lille Prinsen when the weathered and emulsified oil had reached a viscosity of 6745 mPa.s (72 hours of weathering). The flume testing indicated that the oil/emulsion required 3 times application round of dispersant (cumulative DOR 1:20) to break up the "slick" into patches and disperse the oil (i.e., 20-25 % of available oil). Lille Prinsen crude oil may need replicative application or higher dosage to disperse the emulsion when it has reached such high viscosities with time. The third round of dispersant application also showed that the dispersant needed time, in combination of waves, to give an effect on the stable emulsions of Lille Prinsen.

However, it is expected that Lille Prinsen could be good dispersible <24 hours of weathering for viscosities lower than 2500 mPa.s, as the estimated limit from the small-scale study in non-breaking waves conditions (<5 m/s wind speed). The upper viscosity limit for dispersant use (i.e., no effect) was estimated to 12 000 mPa.s from the small-scale study. This corresponds to the observation from the meso-scale testing showing reduced dispersibility after 72 hours of weathering time in the flume.

## 5 Predictions SINTEF Oil Weathering Model (OWM)

### 5.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (Daling et al., 1990) was used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. Laboratory study of Lille Prinsen was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM). The experimental design for the study is described in Appendix B. The input data of Lille Prinsen to the SINTEF OWM are given in Appendix C.

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. The SINTEF OWM is schematically shown in Figure 5-1. The predictions obtained from the SINTEF OWM are useful tools in the oil spill contingency planning related to the expected behaviour of oil on the sea surface, and to evaluate the time window for operational response strategies in a spill operation. In this report, the presented predictions span a period from 15 minutes to 5 days after an oil spill has occurred. The SINTEF OWM is described in more detail in Johansen (1991), and in the user's guide for the model.

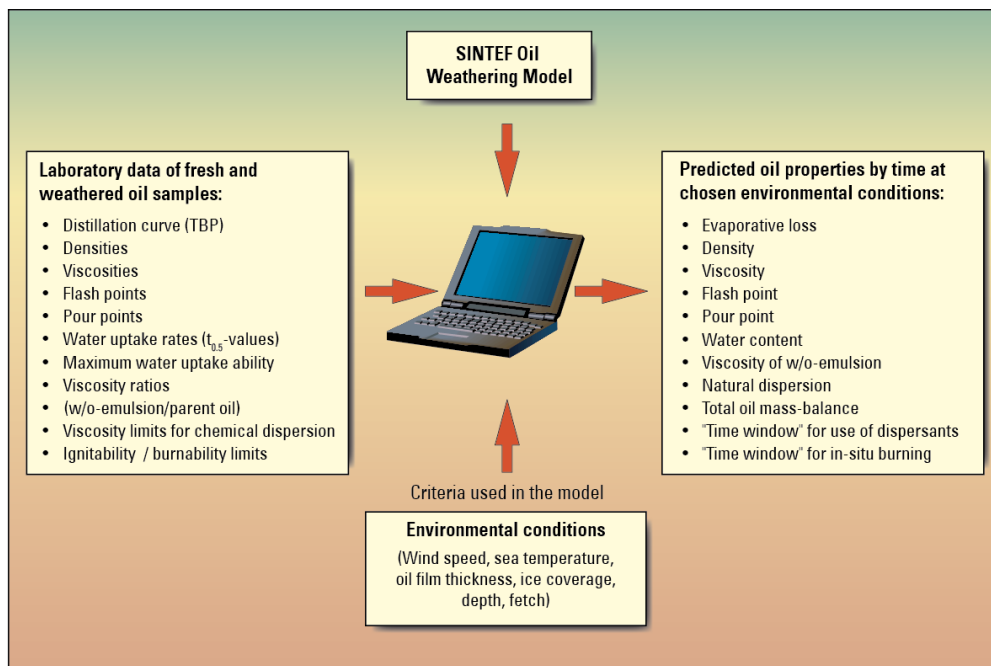


Figure 5-1 Schematic input data to the SINTEF OWM and the predicted output oil properties.

#### Oil film thickness

Oils in SINTEF OWM are categorized as condensate (non-emulsifying oil), low emulsifying oil/condensate, emulsifying oil, heavy bunker fuel or refined distillate. The categorization is based on the experimental results obtained in the laboratory. The terminal film thicknesses vary among these categories based on experimental (field) experience. Lille Prinsen is categorized as an emulsifying oil in OWM.

#### Seawater temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Due to the location of the oil field, the prediction seawater temperatures chosen for Lille Prinsen was 5 and 15 °C, reflecting typically winter and summer conditions.

## Wind speed

The relationship between the wind speed and significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 5-1.

Table 5-1 Relationship between wind speed and significant wave height used in the SINTEF OWM.

Wind speed [m/s]	Beaufort wind	Wind type	Wave height [m]
2	2	Light breeze	0.1 - 0.3
5	3	Gentle to moderate breeze	0.5 - 0.8
10	5	Fresh breeze	1.5 - 2.5
15	6 – 7	Strong breeze	3- 4

## 5.2 Predictions of Lille Prinsen weathering properties

A standard surface release was used as a spill scenario. The scenario chosen is not oil field specific but selected to give predictions of the expected weathering properties of the oil based on the experimental data and specified terminal oil film thickness. A standardized scenario will also more easily compare results of weathering properties with other oils.

### Input to SINTEF OWM

Oil type:	Crude oil
Geographical area:	North Sea
Terminal oil film thickness:	1 mm
Release rates:	1.33 metric tonnes per min. in 15 min, a total of 20 metric tonnes (80 m <sup>3</sup> /hour or 1900 m <sup>3</sup> /day)
Seawater temperatures:	5 and 15 °C
Wind speeds:	2 m/s, 5 m/s, 10 m/s and 15 m/s

### Predicted properties

- Evaporative loss
- Viscosity
- Flash point
- Pour point
- Mass balance

The predictions are based on 5 days weathering independently if there is not predicted any remaining oil within shorter time. The predictions are shown to indicate the weathering properties in cases there are patches or oil left on the surface up to 5 days.

### How to use the prediction charts: an example

If the oil has drifted on the sea surface, the following prediction charts could be used to determine the weathering properties of the oil/emulsion. Table 5-2 and Table 5-3 gives an example of predicted weathering properties for Lille Prinsen.

Table 5-2 Example of weathering properties of Lille Prinsen obtained from the OWM predictions after 12 hours of weathering at 2, 5 and 10 m/s wind speed at 15 °C.

<b>Weathering properties</b>	<b>12 hours 15 °C 2 m/s</b>	<b>12 hours 15 °C 5 m/s</b>	<b>12 hours 15 °C 10 m/s</b>	<b>12 hours 15 °C 15 m/s</b>
Evaporation, wt. %	25	29	33	35
Flash point, °C	78	90	107	117
Pour Point, °C	20	22	25	27
Water content, vol.%	13	37	70	75
Viscosity, mPa.s *	380	1300	8000	12000
Mass balance / Oil on surface wt.%	74	70	48	15

\*mPa.s = cP (mPa.s: SI-standard / cP: Industrial denotation)



Property: **EVAPORATIVE LOSS**  
 Oil Type: **LILLE PRINSEN**  
 Description: **Lille Prinsen 2022-178**  
 Data Source: **Sintef Ocean (2022), Weathering data used**



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0  
 Pred. date: May. 16, 2022

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- · · · Wind Speed (m/s): 5
- · · · · Wind Speed (m/s): 2

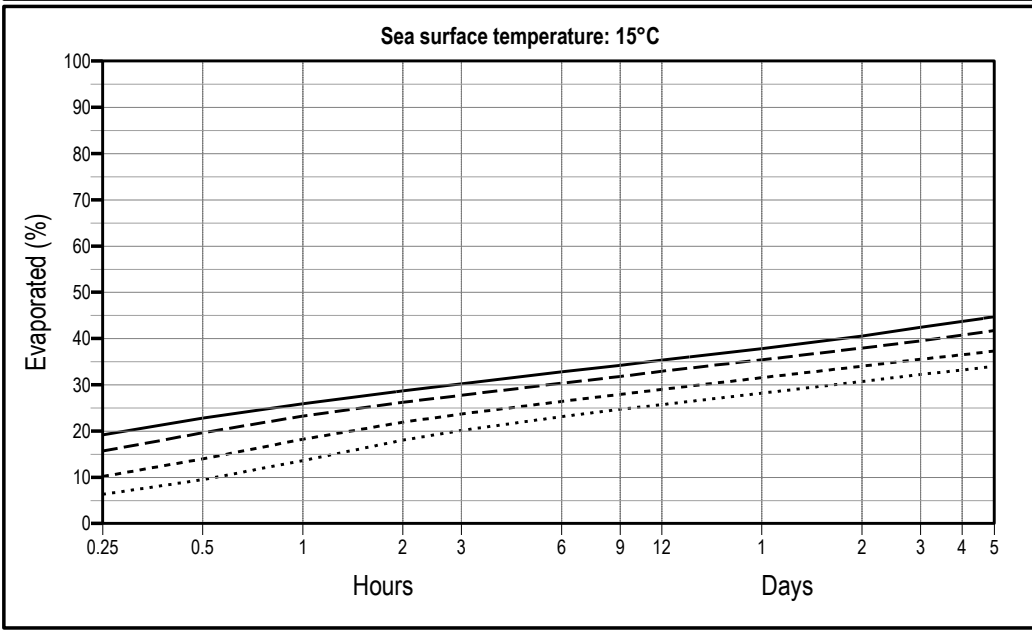
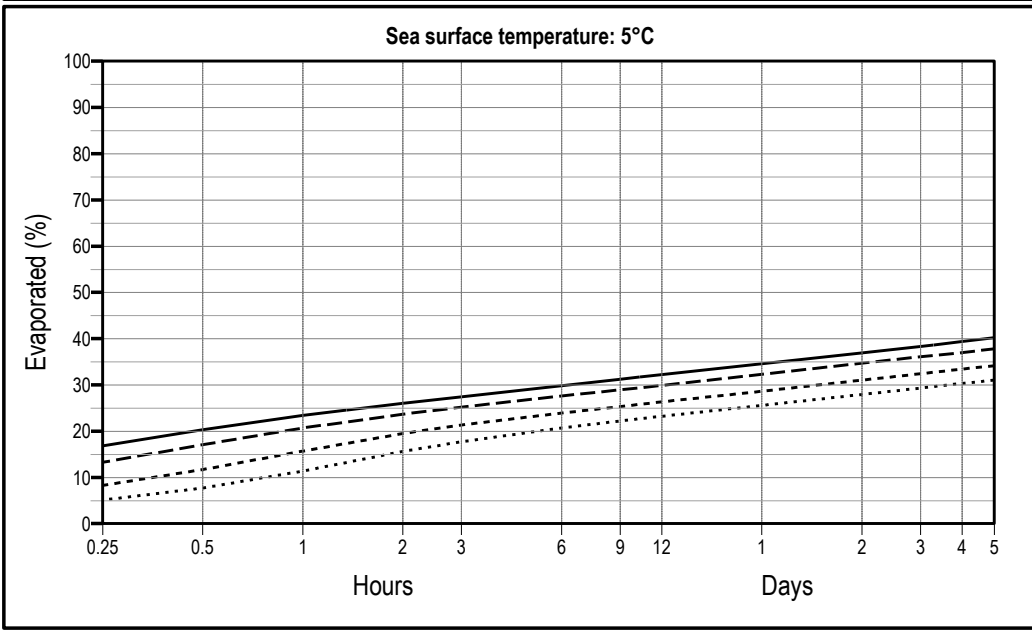


Figure 5-2 Evaporative loss of Lille Prinsen predicted at sea temperatures of 5 and 15 °C.

Property: FLASH POINT FOR WATER-FREE OIL  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0  
 Pred. date: May. 16, 2022

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- · - · Wind Speed (m/s): 5
- Wind Speed (m/s): 2
- No fire hazard
- Fire hazard in tannage (<60 °C)
- Fire hazard at sea surface (below sea temperature)

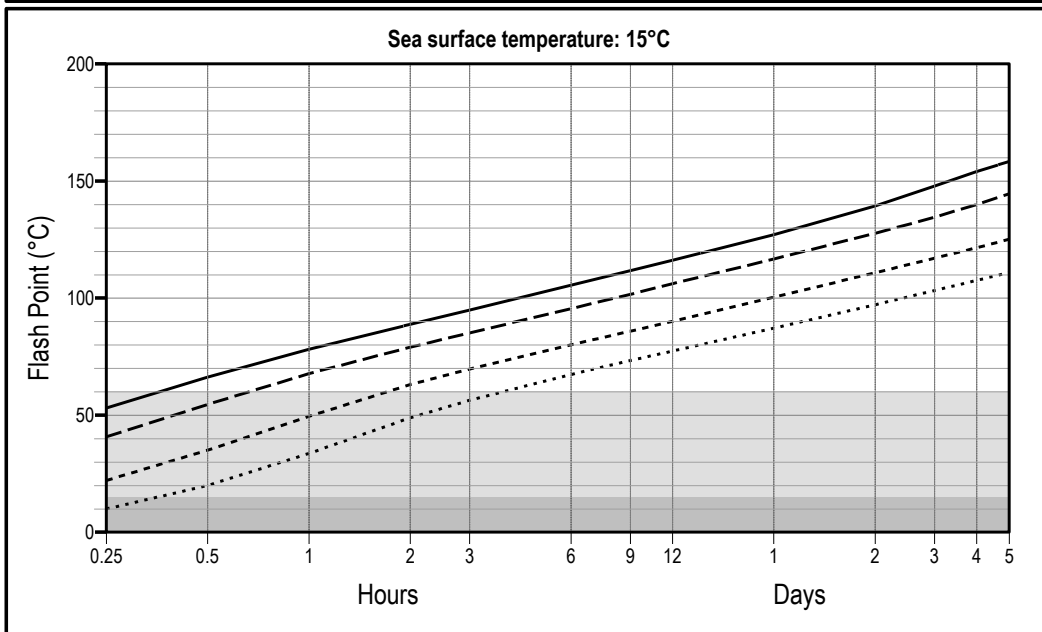
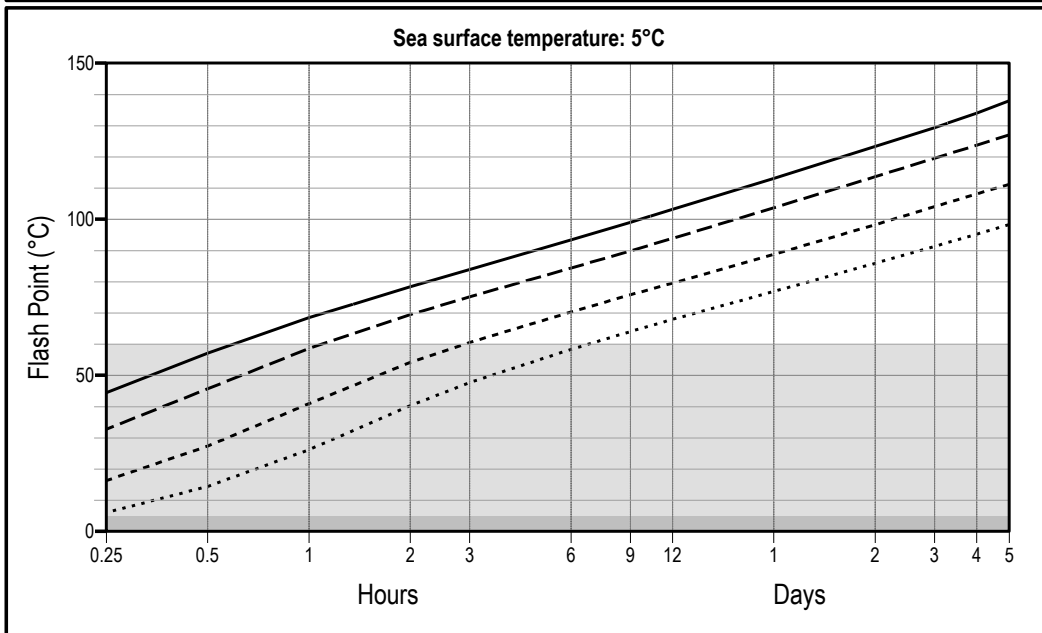


Figure 5-3 Flash point of water -free Lille Prinsen predicted at sea temperatures of 5 and 15 °C.

Property: POUR POINT FOR WATER-FREE OIL  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0  
 Pred. date: May. 16, 2022

— Wind Speed (m/s): 15	□ Chemically dispersible
- - - Wind Speed (m/s): 10	▒ Reduced chemical dispersibility
- · - · Wind Speed (m/s): 5	■ Poorly / slowly chemically dispersible
· · · · Wind Speed (m/s): 2	

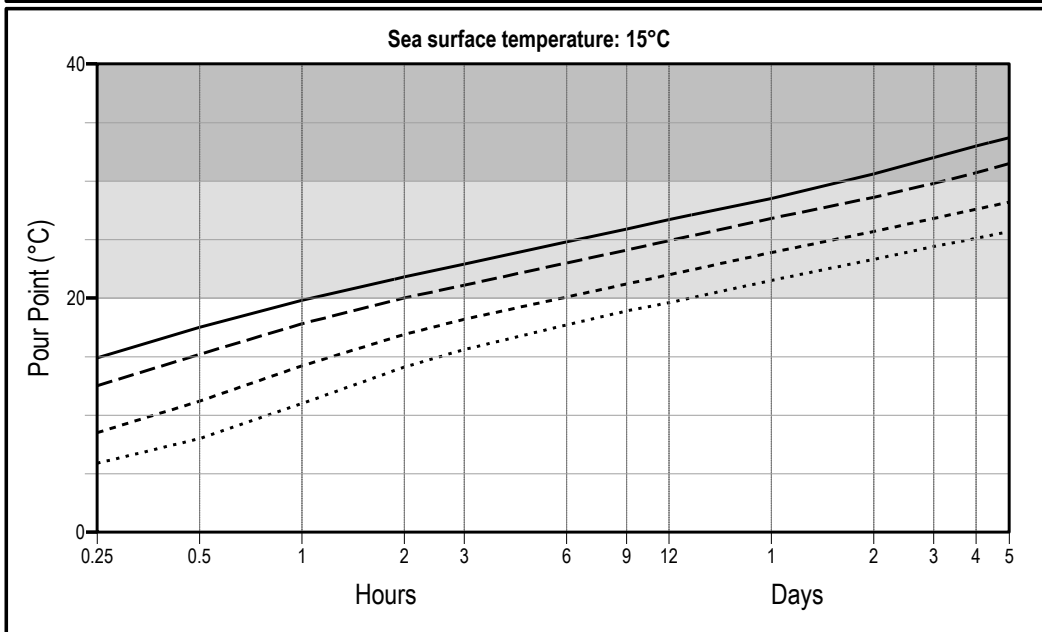
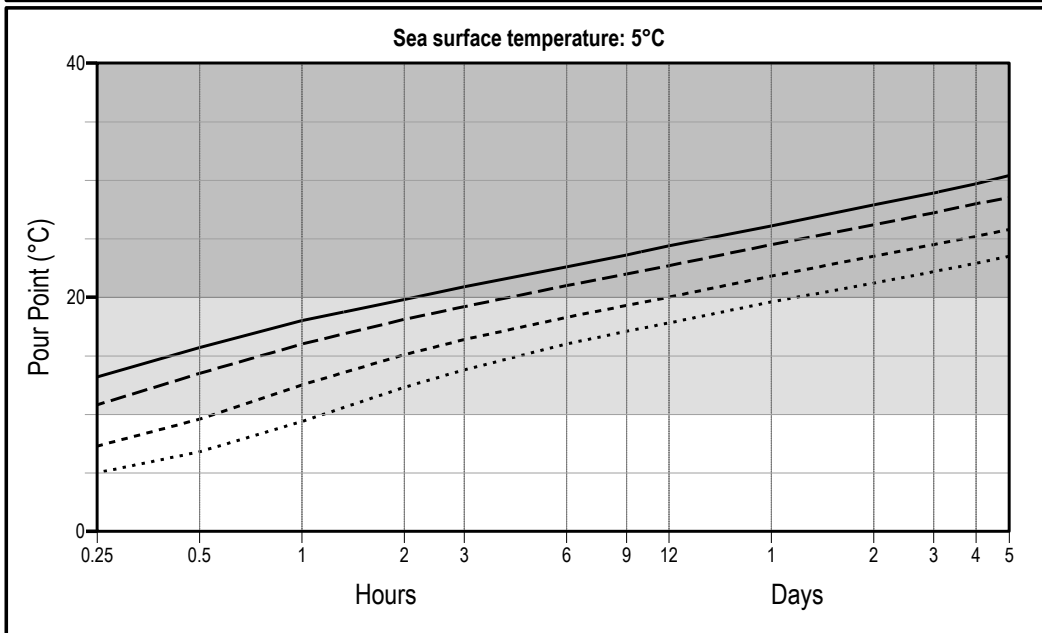


Figure 5-4 Pour point of water-free Lille Prinsen predicted at sea temperatures of 5 and 15 °C.

Property: WATER CONTENT  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0  
 Pred. date: May. 16, 2022

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- · · · Wind Speed (m/s): 5
- · · · · Wind Speed (m/s): 2

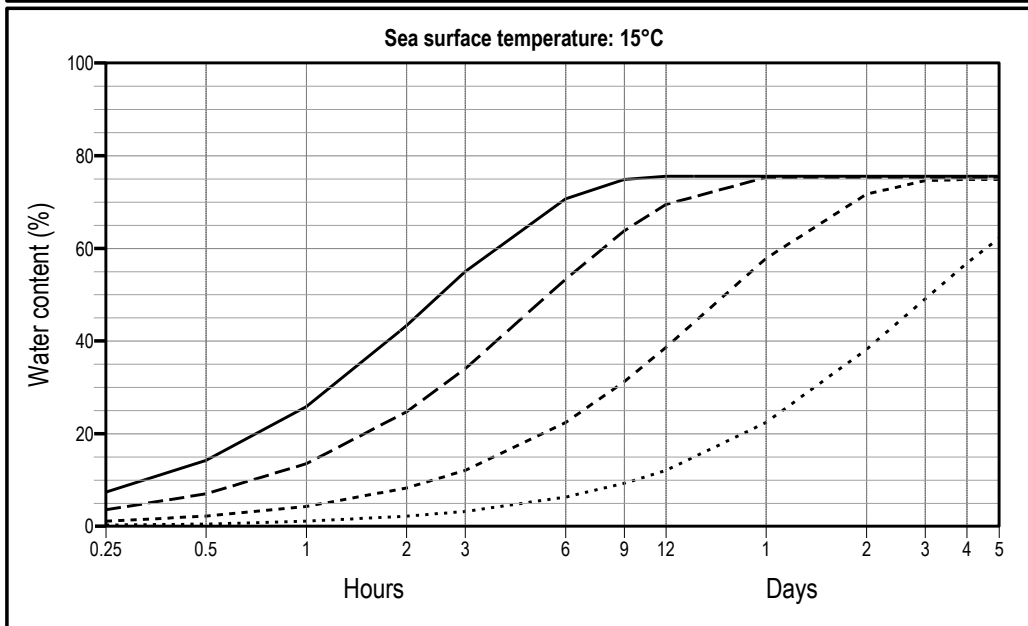
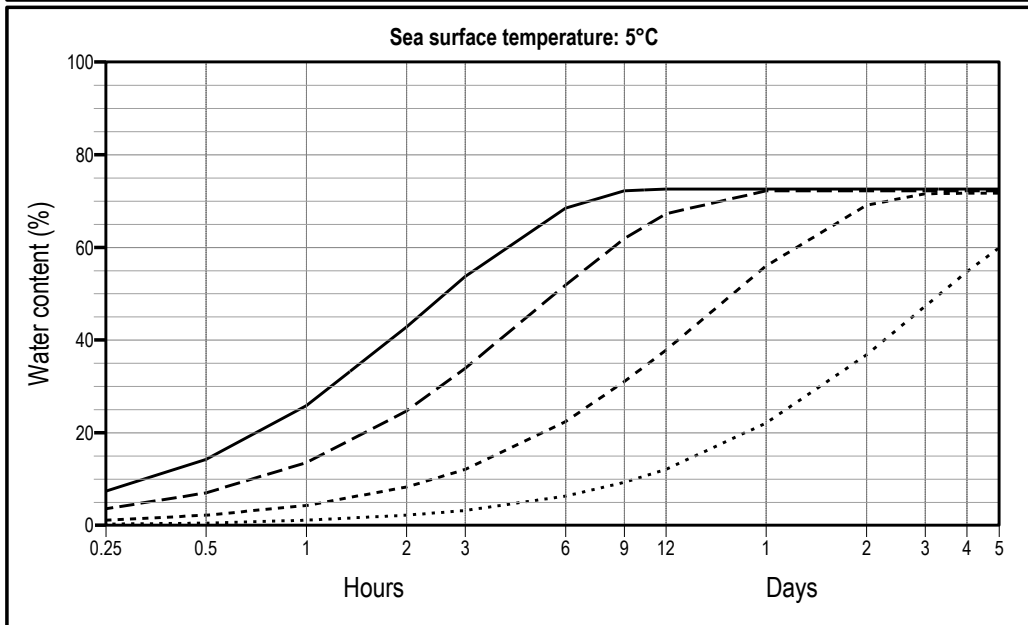


Figure 5-5 Water content of Lille Prinsen predicted at sea temperatures of 5 and 15 °C.

Property: VISCOSITY OF EMULSION  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0  
 Pred. date: May. 16, 2022

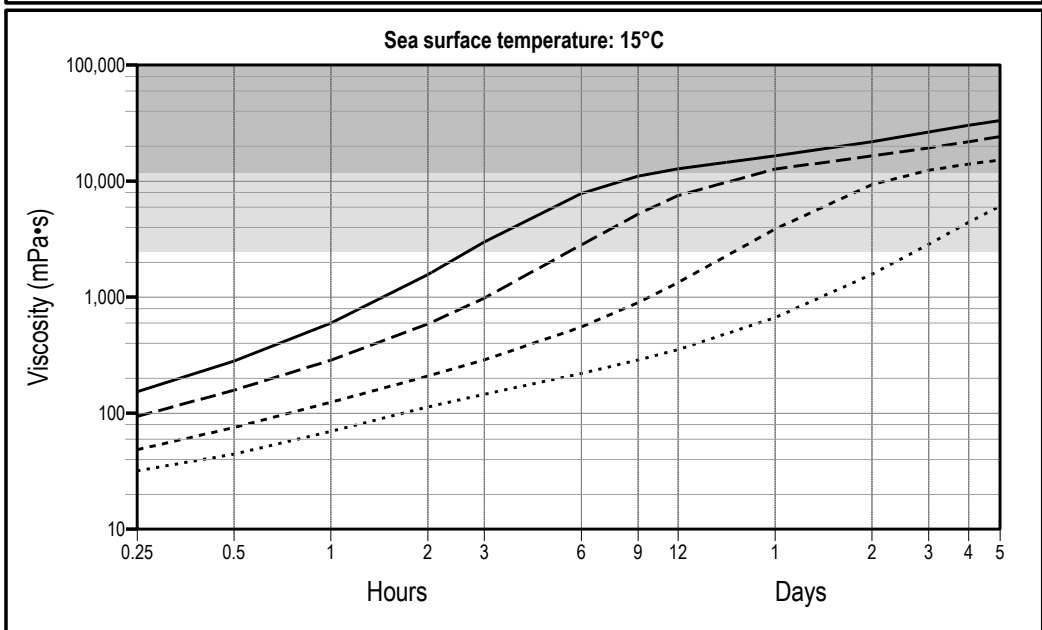
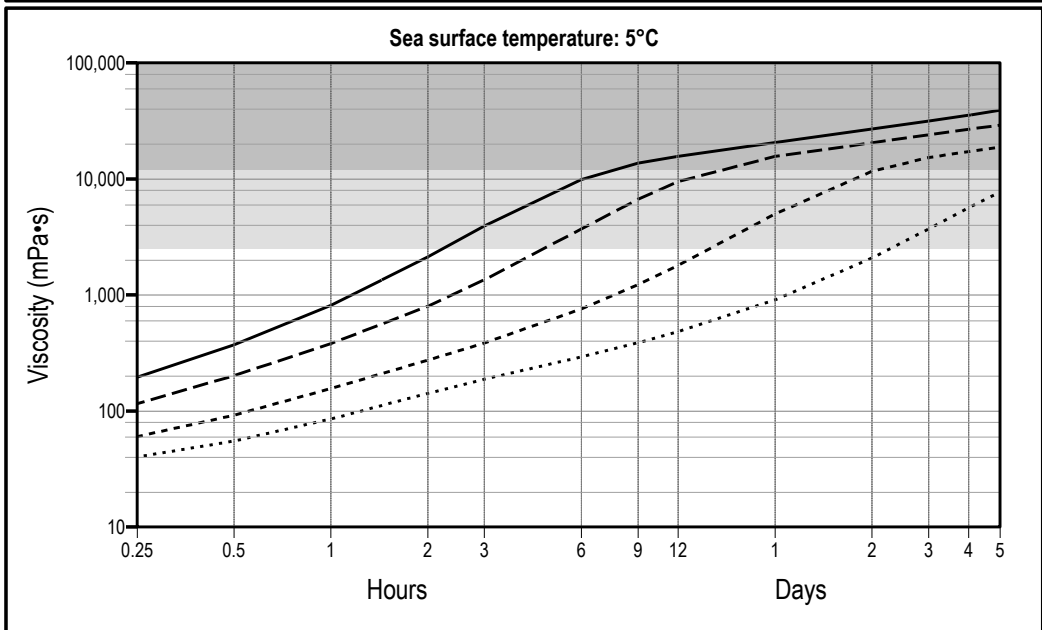
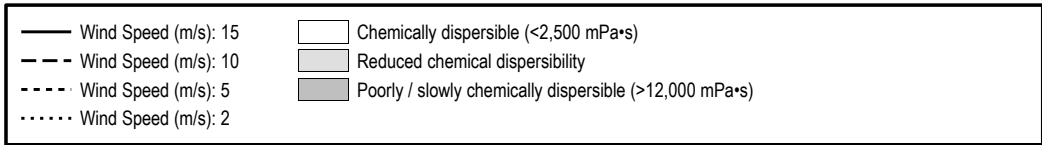


Figure 5-6 Viscosity of Lille Prinsen predicted at sea temperatures of 5 and 15 °C, shear rate 10 s<sup>-1</sup>.

Property: MASS BALANCE  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 16, 2022

Evaporated  
 Surface  
 Naturally dispersed

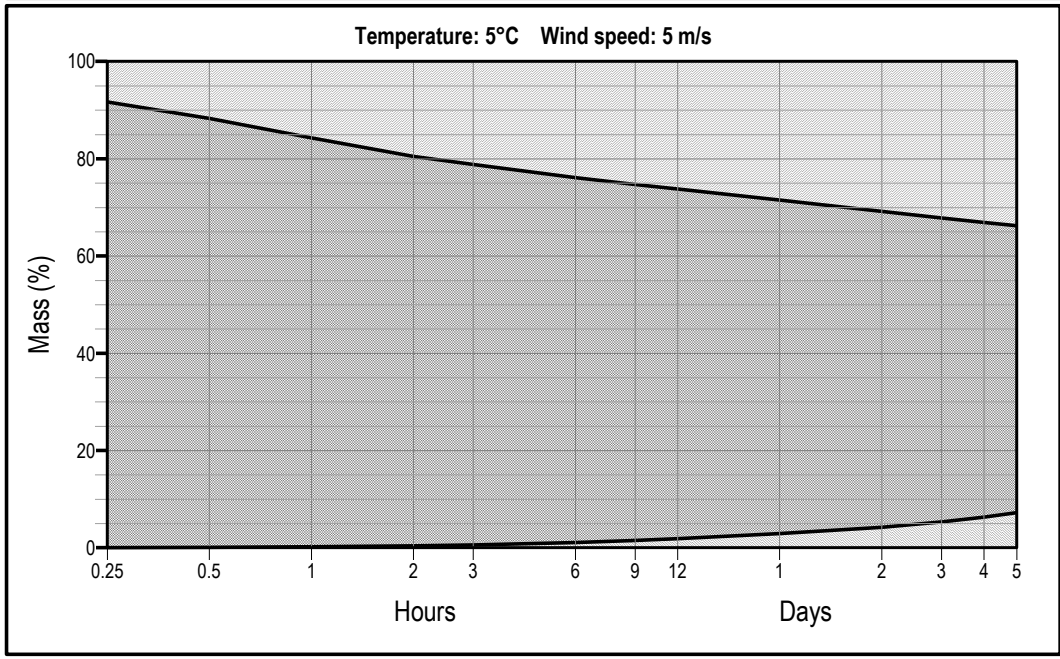
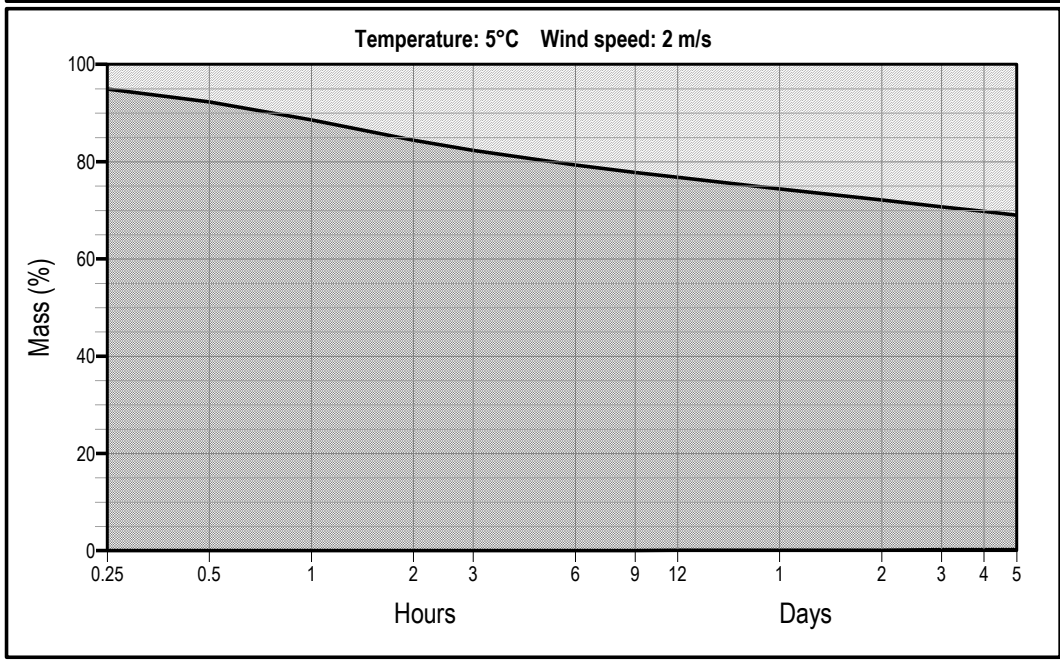


Figure 5-7 Predicted mass balance of Lille Prinsen predicted 5 °C, wind speeds of 2 and 5 m/s.

Property: MASS BALANCE  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May, 16, 2022

Evaporated  
 Surface  
 Naturally dispersed

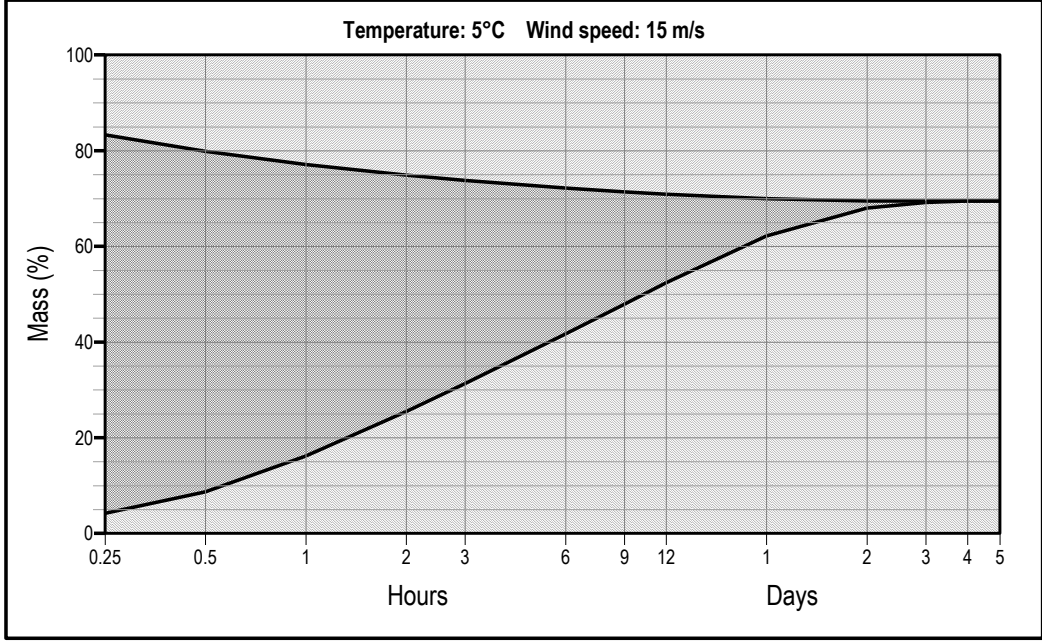
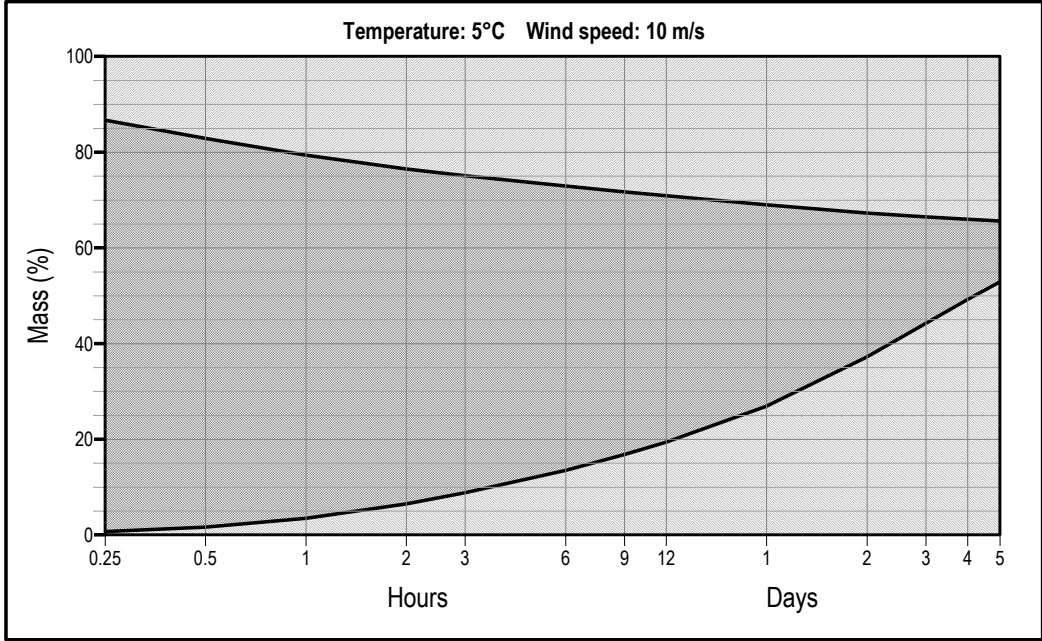


Figure 5-8 Predicted mass balance of Lille Prinsen predicted 5 °C, wind speeds of 10 and 15 m/s.

Property: MASS BALANCE  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 16, 2022

Evaporated  
 Surface  
 Naturally dispersed

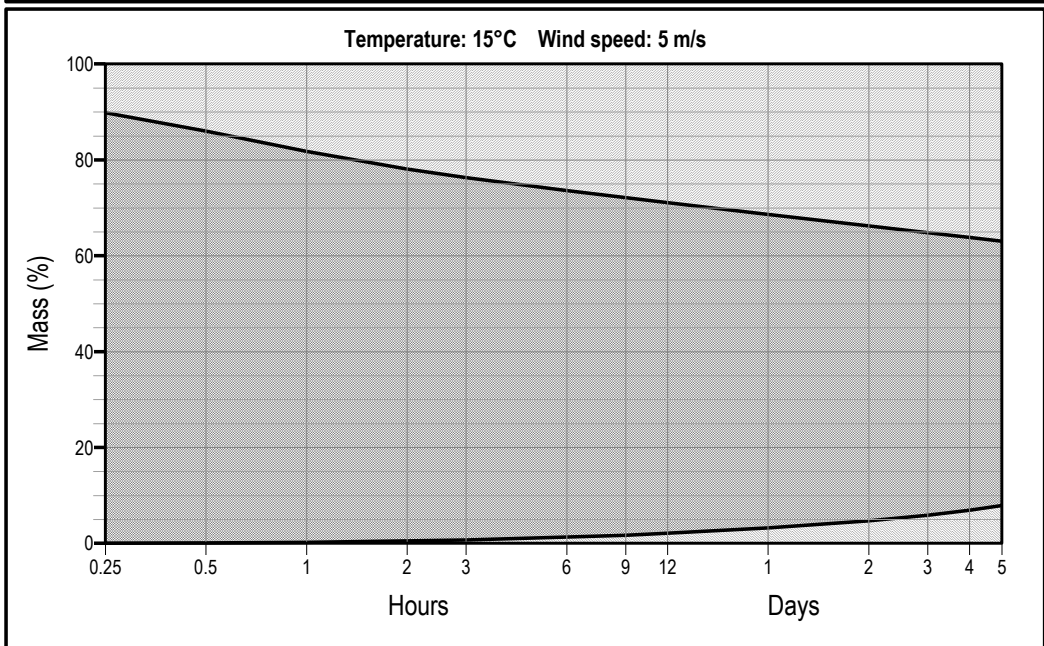
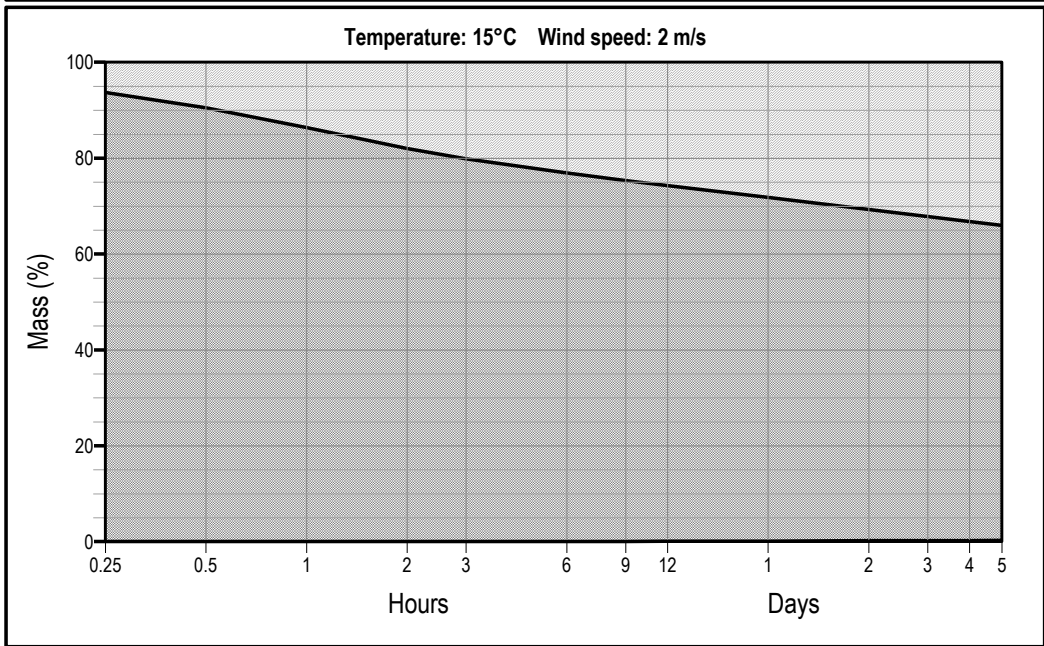


Figure 5-9 Predicted mass balance of Lille Prinsen predicted 15 °C, wind speeds of 2 and 5 m/s.



Property: MASS BALANCE  
 Oil Type: LILLE PRINSEN  
 Description: Lille Prinsen 2022-178  
 Data Source: Sintef Ocean (2022), Weathering data used



OWModel© 13.0

Surface release  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 16, 2022

Evaporated  
 Surface  
 Naturally dispersed

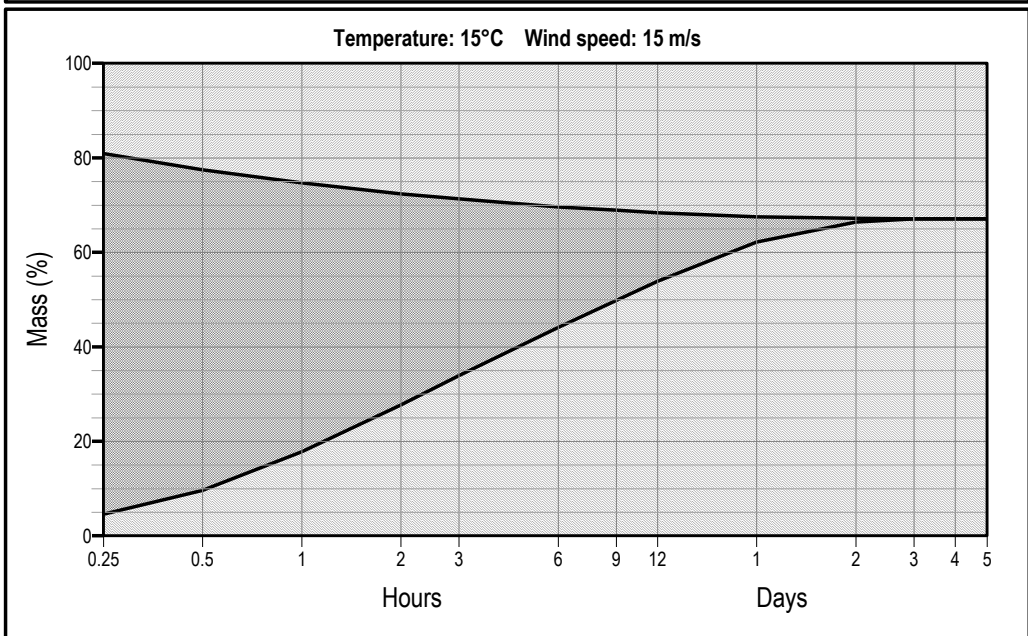
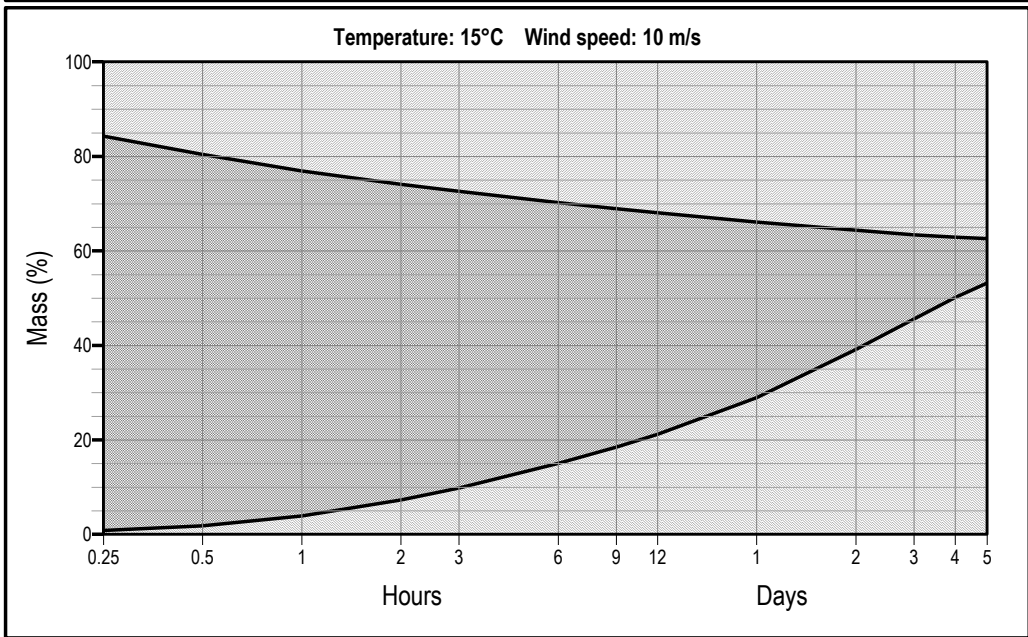


Figure 5-10 Predicted mass balance of Lille Prinsen predicted 15 °C, wind speeds of 10 and 15 m/s.

## 6 Comparison of OWM predictions

Weathering predictions from surface release scenario (80 m<sup>3</sup>/h) of Lille Prinsen were compared with predictions of Solveig, Edvard Grieg, Ivar Aasen, Johan Sverdrup, and Rolvsnes. The predictions for comparison are based on sea temperature of 15 °C and wind speed of and one selected wind speed (10 m/s).

### 6.1 Evaporative loss

Evaporation is one of the natural processes that helps removing spilled oil from the sea surface. Lille Prinsen exhibits most similarities with Edvard Grieg and Ivar Aasen (Figure 6-1). Solveig and Rolvsnes have the highest evaporative loss, whilst the heavier Johan Sverdrup has the lowest evaporative loss among these oils.

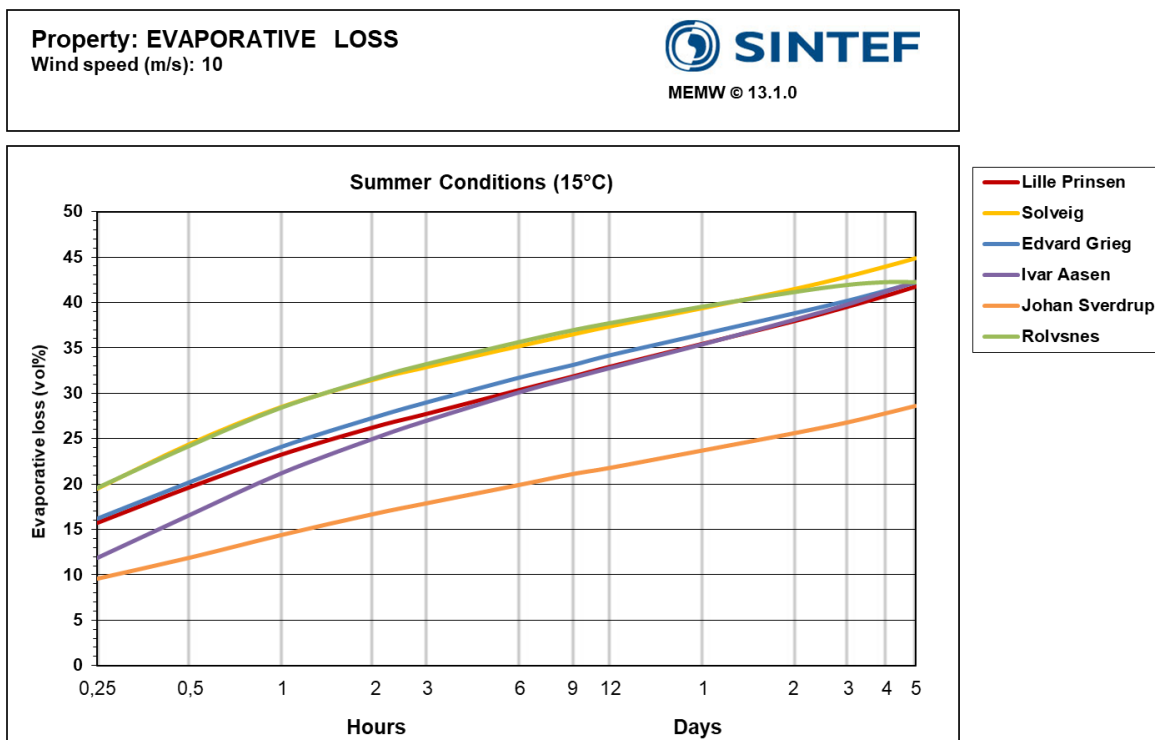


Figure 6-1 Predicted evaporative loss at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

## 6.2 Pour point

Lille Prinsen and Edvard Grieg have highest and the most similar pour points followed by Rolvsnes. Solidification typically arises at 10-15 °C above the sea temperature (see dotted line in Figure 6-2). Solveig and Ivar Aasen express similar and lower pour point during the first hours, and then increases due to evaporation. These paraffinic crude oils may have potential to solidify at sea after some days of weathering (water free residue). Johan Sverdrup on the other hand, has low predicted pour points reflecting both the low wax content and the high asphaltene contents, and solidification is not likely at sea after 5 days of weathering compared with the more paraffinic crude oils.

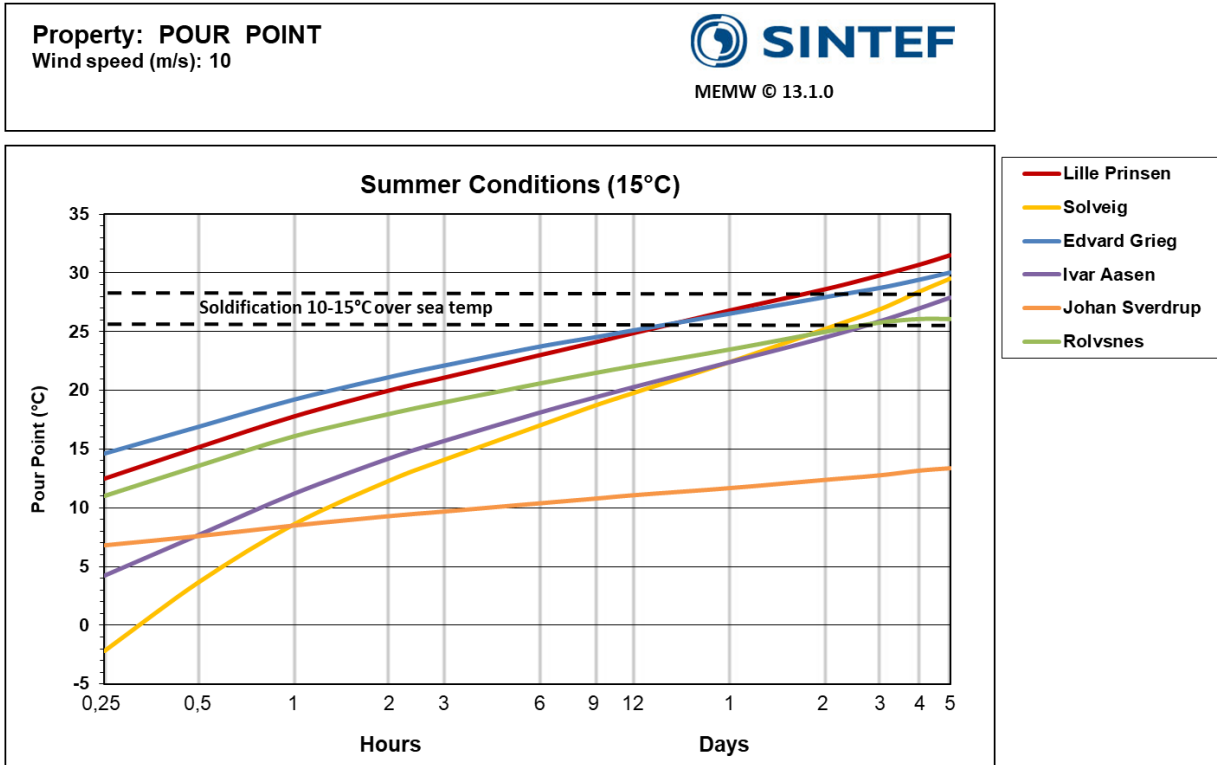


Figure 6-2 Predicted pour points at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

### 6.3 Flash point

The flash points of the crude oils in comparison are shown in Figure 6-3. The predictions show that none of the oils are expected to pose a fire hazard 15 minutes after release at 10 m/s wind speed for this scenario, where flash points are above the sea temperature of 15 °C. The flash point of Lille Prinsen is very similar as for the other oils in comparison. Johan Sverdrup has slightly higher flash point, whilst Solveig has slightly lower flash point among these oils. No flash point data obtained of Rolvsnes.

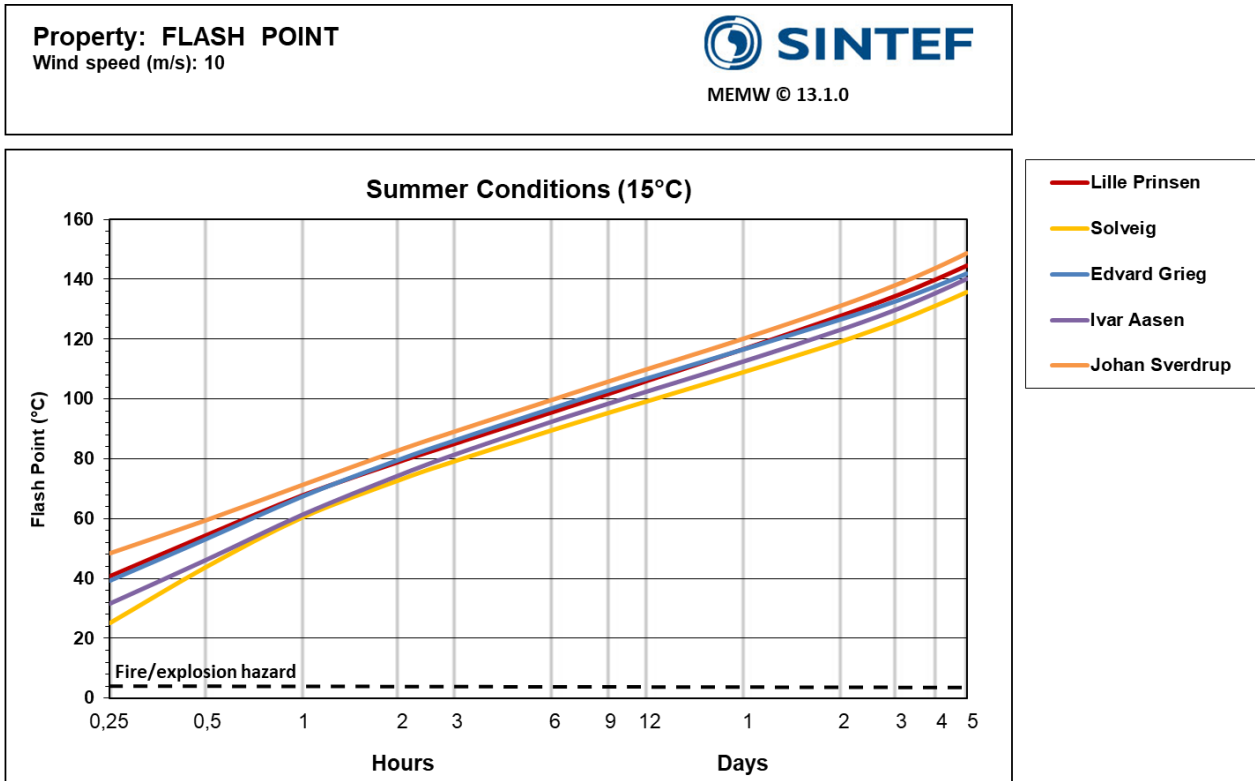


Figure 6-3 Predicted flash point at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

## 6.4 Water content

The maximum water uptake of Lille Prinsen in comparison with the other oils are shown in Figure 6-4. Lille Prinsen reaches a maximum water uptake of ~75 vol. %, slightly lower than for Edvard Grieg, Ivar Aasen, and Rolvsnes reaching 78-80 vol. %. Ivar Aasen exhibits the most rapid water uptake among these oils, whilst the heavier Johan Sverdrup has the slowest and lowest water uptake reaching a maximum water uptake just below 70 vol. %.

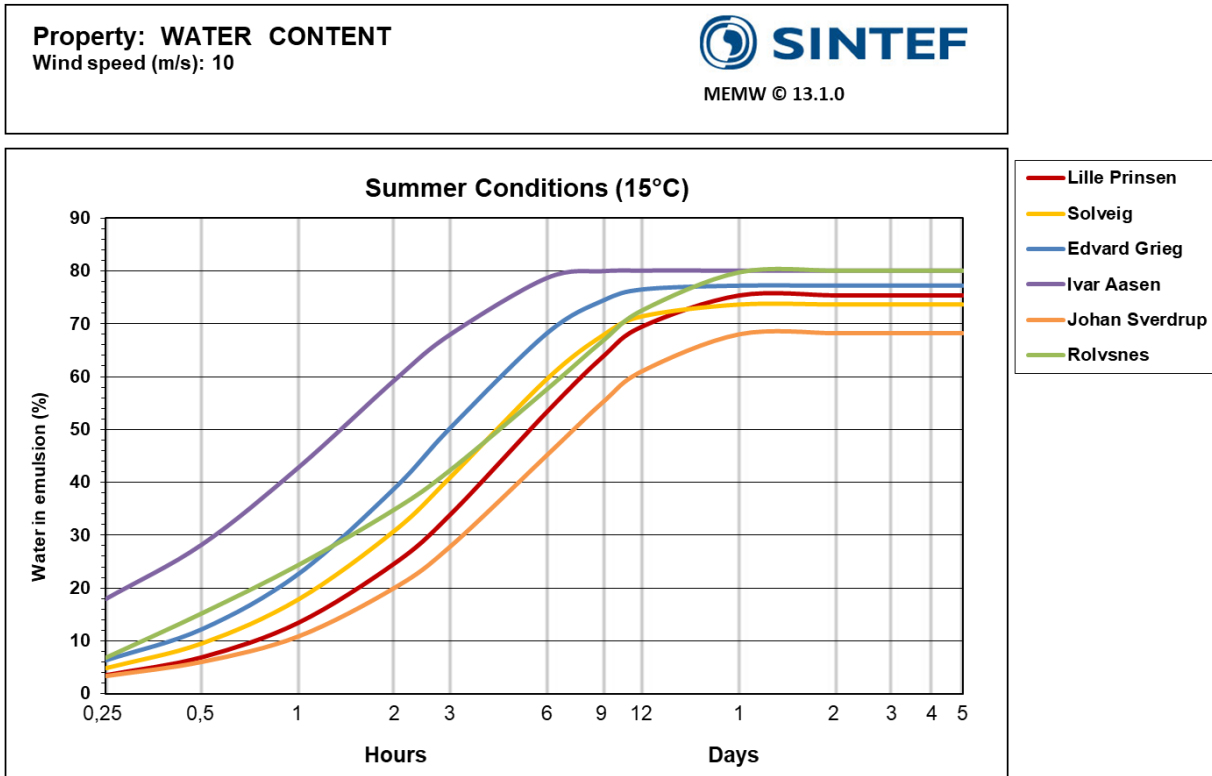


Figure 6-4 Predicted water content at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

## 6.5 Emulsion viscosity

Figure 6-5 shows the predicted (emulsion) viscosities of Lille Prinsen in comparison with the other oils. Lille Prinsen has an intermediate emulsion viscosity among these oils (not high, not low). Among these oils, Solveig reach the highest predicted emulsion viscosities, whilst Ivar Aasen reaches the lowest emulsion viscosity.

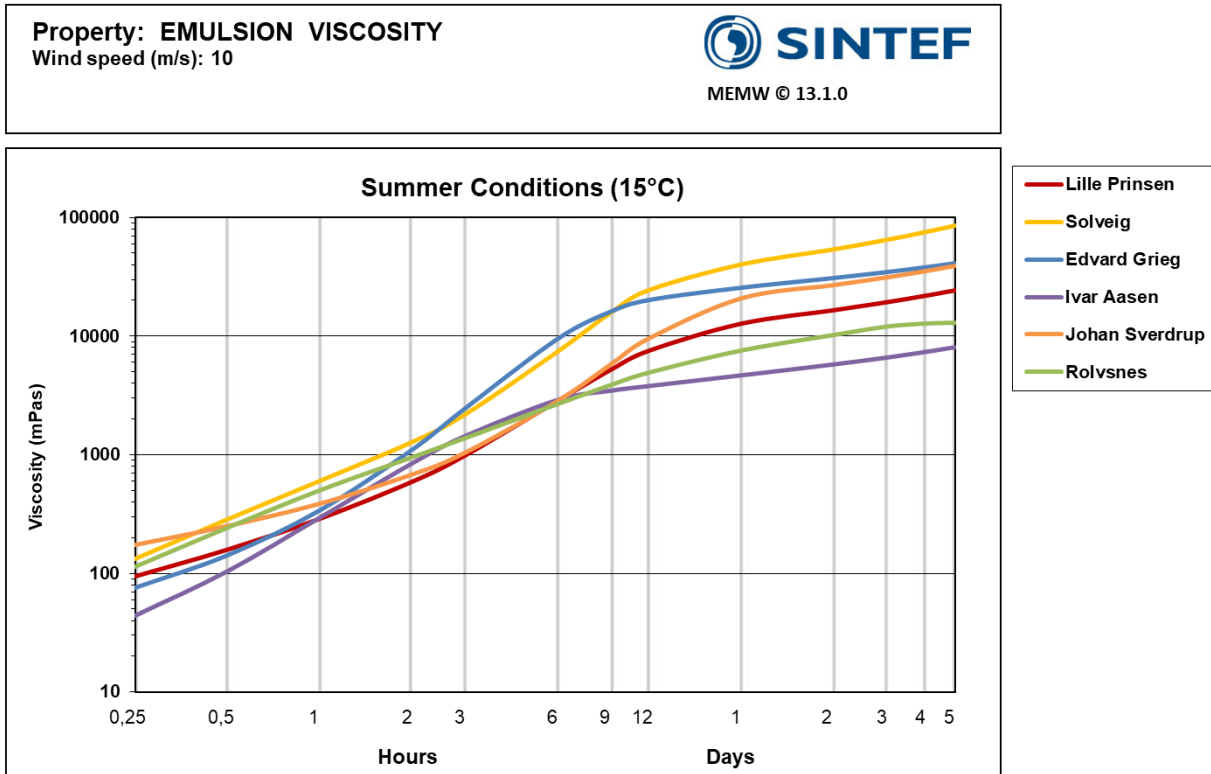


Figure 6-5 Predicted emulsion viscosity at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

## 6.6 Surface oil

Due to evaporative loss and natural dispersion, the oil on the sea surface will gradually be reduced. Figure 6-6 illustrates the predicted mass balance of Lille Prinsen in comparison with the other oils. Figure 6-6 shows that the oils in comparison are persistent on the sea surface with predicted lifetime >5 days for this scenario. Johan Sverdrup is however the most persisting oil, whilst Ivar Aasen and Rolvsnes have less amount of oil on the sea surface (< 10 %) after 5 days of weathering compared with the other oils.

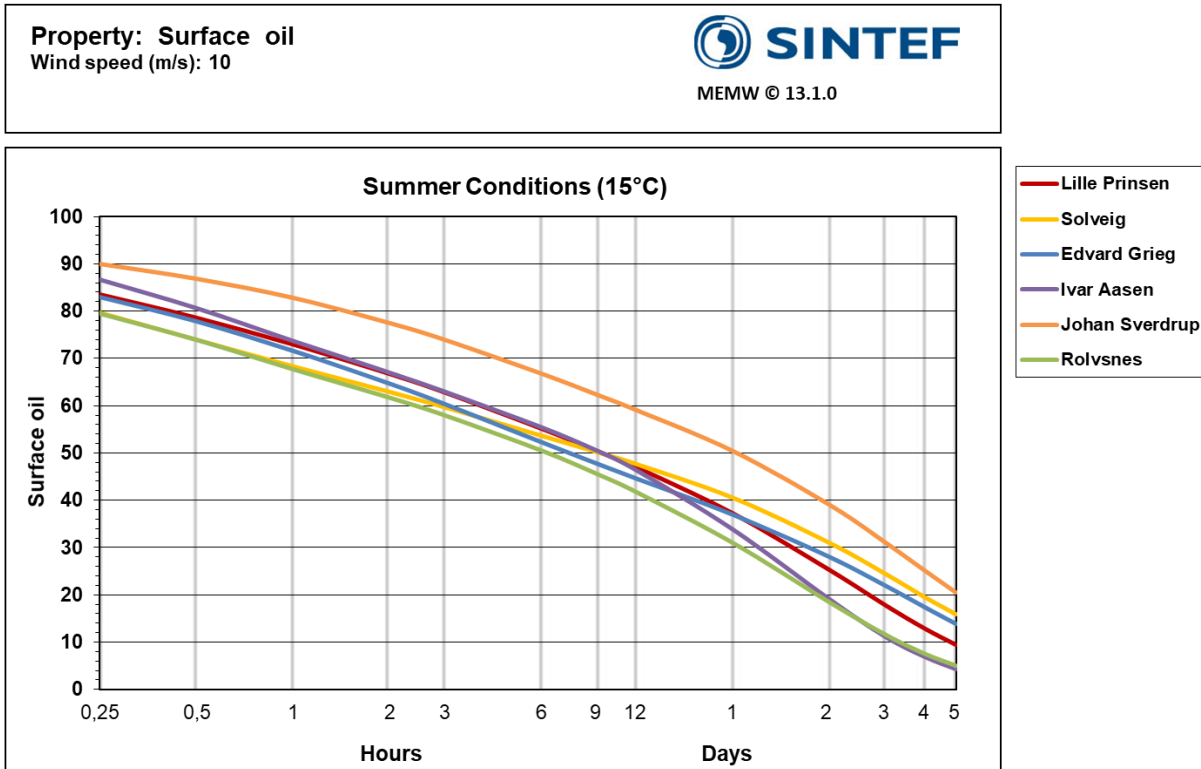


Figure 6-6 Predicted surface oil at 15 °C and 10 m/s for Lille Prinsen compared with a selection of other crude oils from neighboring fields. Release rate 80m<sup>3</sup>/h.

## 7 Weathering properties and response of Lille Prinsen

The relative content of heavy oil components within a spilled oil increases due to evaporation, and the physical and chemical properties of the oil will change over time. Knowledge about how the oil properties change during weathering is therefore important in the management of oil spill response. Currently, mechanical recovery and the use of oil spill dispersants are the main oil spill response options at sea in the Norwegian sector, today. The potential of using water-flushing (artificial energy) to disperse thin oil films mechanically is also discussed in this report.

### 7.1 Oil properties

The specific physico-chemical parameters of Lille Prinsen are input to SINTEF OWM. The physico-chemical analysis of the fresh and topped residues show that Lille Prinsen is a paraffinic crude oil with a medium density of 0.851 g/mL with a medium content of asphaltenes (0.5 wt. %) and a medium wax content of 4.7 wt. %. Lille Prinsen has a moderate evaporate loss of 39 vol. % of the 250°C+ residue. The fresh oil has a viscosity of 23 mPa.s at shear rate 10s<sup>-1</sup> (13 °C) and increases by evaporation to 2582 mPa.s (10s<sup>-1</sup>) for the waterfree 250°C+ residue. The fresh oil has a pour point of 0 °C, that increases significantly to +24 °C upon evaporation (250°C+). Moreover, Lille Prinsen forms stable water-in-oil emulsions with moderate to high viscosities that almost or partly breaks with application of emulsion breaker (Aerosol OT-SE surfactant).

### 7.2 Flash point – Fire/explosion hazard

Flash point refers to the lowest temperature at which an oil can vaporize to form an ignitable mixture in the air. In case of an oil spill on the sea surface, the (heated) oil rapidly will be cooled to the ambient seawater temperature within a short period of time. The potential for fire/explosion hazard will be at its greatest if the flash point of the oil is below the seawater temperature.

The flash points for Lille Prinsen are expected to surpass the sea temperature within 15 minutes at 5 and 15 °C, at wind speeds of 2 -15 m/s predicted with the standardized surface release (80 m<sup>3</sup>/h), as shown in Figure 5-3 and Figure 7-1. However, care should be taken during the first 0.5 hour, and use of explosimeter is recommended. Less than 1-hour delay time can be predicted related to fire/explosion hazard related to the flash point of the drifting oil itself. However, the release rate may influence on the rate of evaporation, and for considerably larger (batch) release rates e.g., 100 times higher (8000 m<sup>3</sup>/h), the rate of evaporative loss can thus be reduced particularly for the first hours after the release. Such high batch releases could be for example an incident scenario in connection to blowout or pipeline ruptures.

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C, e.g., towing vessels, smaller cargo, or other vessels available in the emergency. This means that fuels or oils with the flash point less than 60 °C, are for those type of vessels not permitted as cargo. However, this limit is not considered as relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flashpoints <60 °C), according to NFPA classification of Flammable and Combustible Liquids (<http://www.thetankshop.ca>). Refers to the flash point predictions in Figure 5-3 and Figure 5-1.

As a general recommendation after an acute oil spill involving free gas (e.g., from an oil/gas blowout), a "safety" zone typically 1-2 km from the source should be established early on and downwind from the spill site before response actions are initiated in open seaways. Prior to the initiation of spill response operations, an evaluation of fire/explosion hazard must always be conducted at the site. Explosimeters should be utilized continuously, and one should be aware of the possibility for varying release rates if "free" gas is involved.



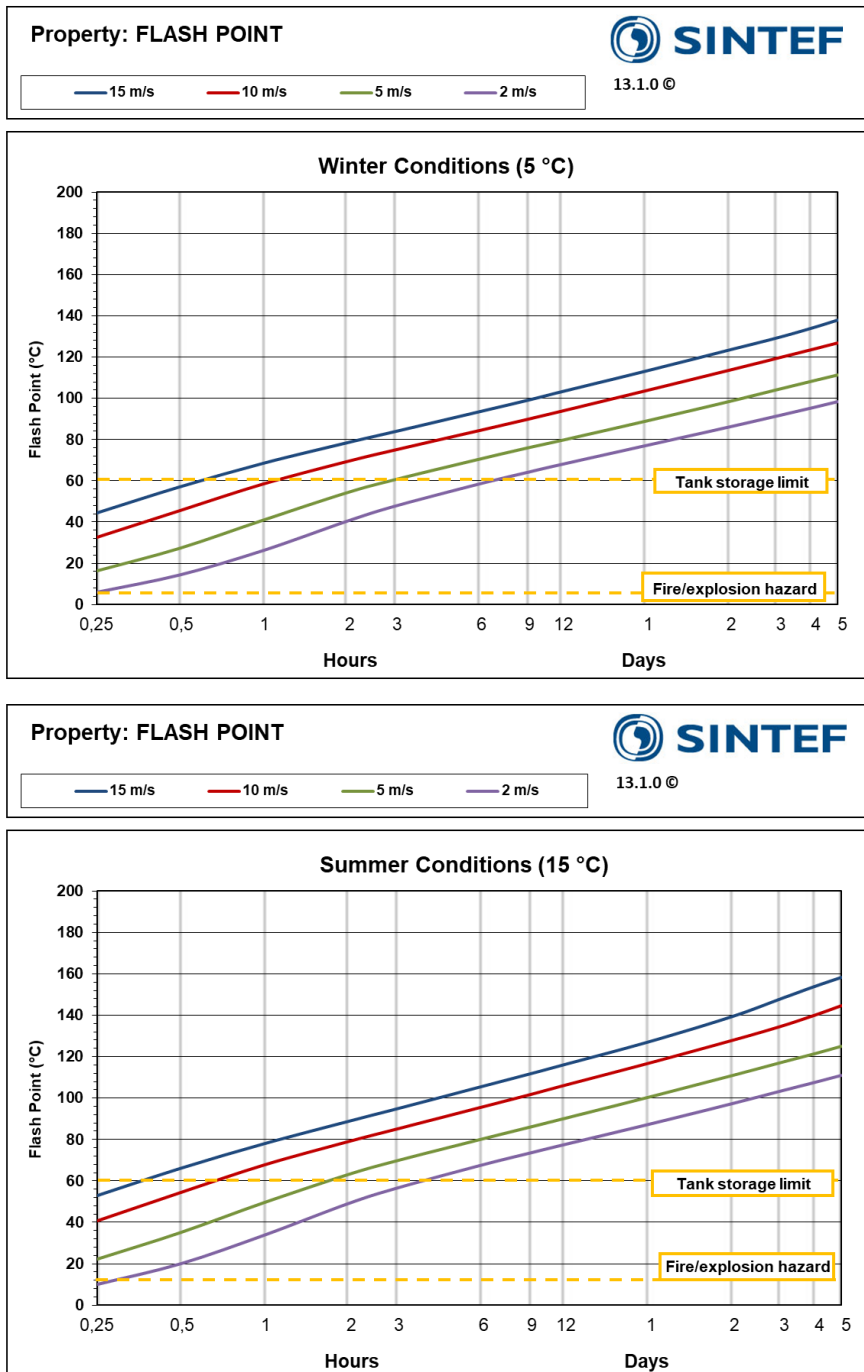


Figure 7-1 Flash point at different sea states for Lille Prinsen in winter and summer conditions (80 m<sup>3</sup> /h).

### 7.3 Solidification

Pour point depends on the oil's wax content and the amounts of light components that can keep the wax components dissolved in the oil phase. In addition, contents of asphaltenes may prevent or reduce precipitation and lattice formation and hence lowers the pour point. High pour points may prevent the dispersant to soak into the oil slick and influence the dispersant effectiveness and may also reduce the potential for flowability towards weir skimmers. In cases when high viscosities are not a limiting factor, high pour points may cause solidification (elastic properties) of semi-solid patches when oil is spilled on the sea surface. High pour point may therefore imply solidification on the sea surface immediately after the release, and this is most pronounced when the pour point of the fresh crude oil is typically 5-15 °C above the sea temperature, and in

cold seawater temperatures. Lille Prinsen has high pour points of its residues, and a remaining water-free residue at sea may therefore have a potential to solidify, particularly in winter condition as shown for the pour point prediction in Figure 5-4.

### 7.4 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion in the early stages of weathering. However, as water is mixed into the oil and emulsions are formed, the total volume will increase. Figure 7-2 shows the predicted mass balance of remaining surface emulsion and surface oil as a function of weathering of Lille Prinsen. The figure shows an increase in the volume of emulsion relative to the volume of released oil with a factor of about 1.5 at winter and summer conditions.

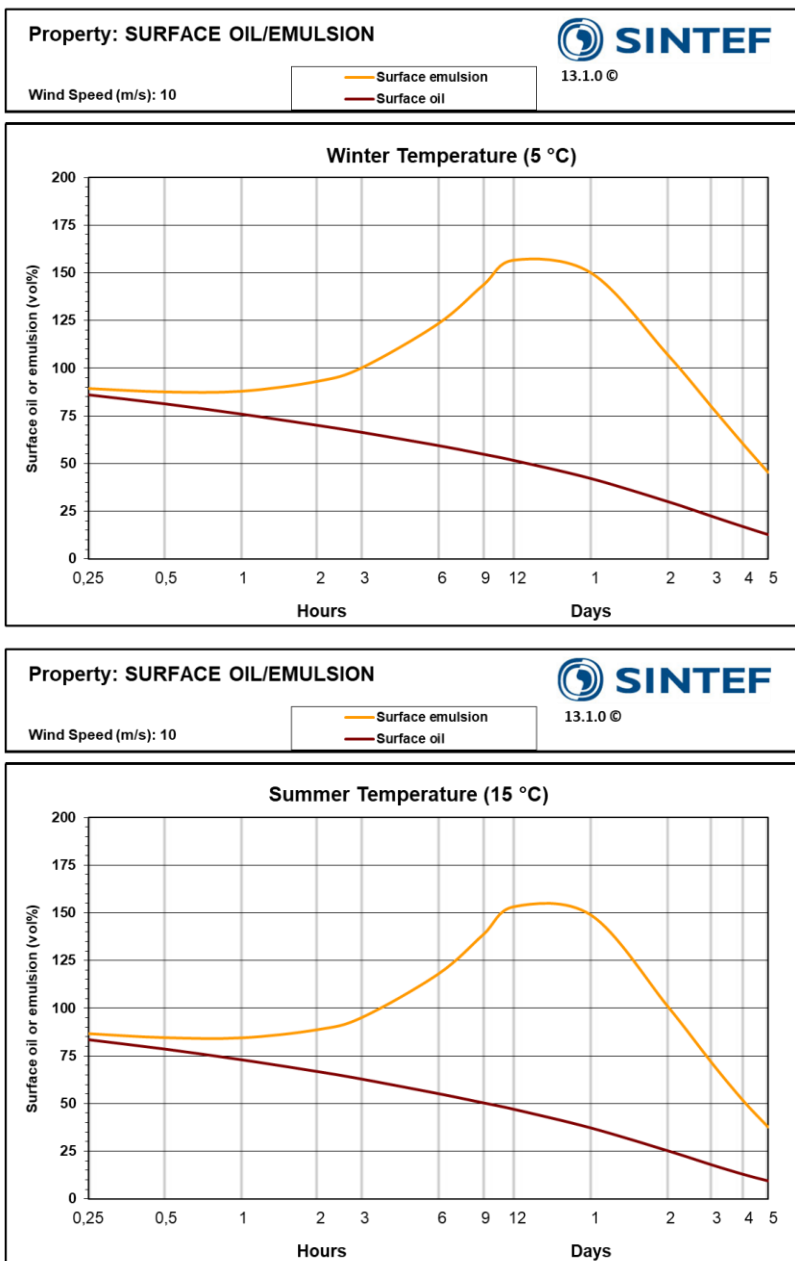


Figure 7-2 Difference in the total slick volume due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 °C and 15 °C. Release rate 80m<sup>3</sup>/h.

## 7.5 Submerged oil and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g., on the surface, underwater) and environmental conditions (temperature, wind, waves). Submerged oil (natural dispersion) and evaporation are the main weathering processes that remove an oil spill from the sea surface. The remaining surface oil after a release depends on the wind speeds and typically oils are more persistent on the sea surface with lower wind. Submerged oil /naturally dispersed oil may temporarily resurface when the wind calms down again.

Figure 7-3 shows the predicted remaining surface oil over time for different wind speeds and temperatures for Lille Prinsen. Only minor difference in lifetime between 5 and 15 °C for this oil. At high wind speeds of 15 m/s, no oil is predicted to remain on the sea surface after 2-3 days of weathering. Considerably larger spills are expected to produce longer lifetimes, and individual modelling may be necessary.

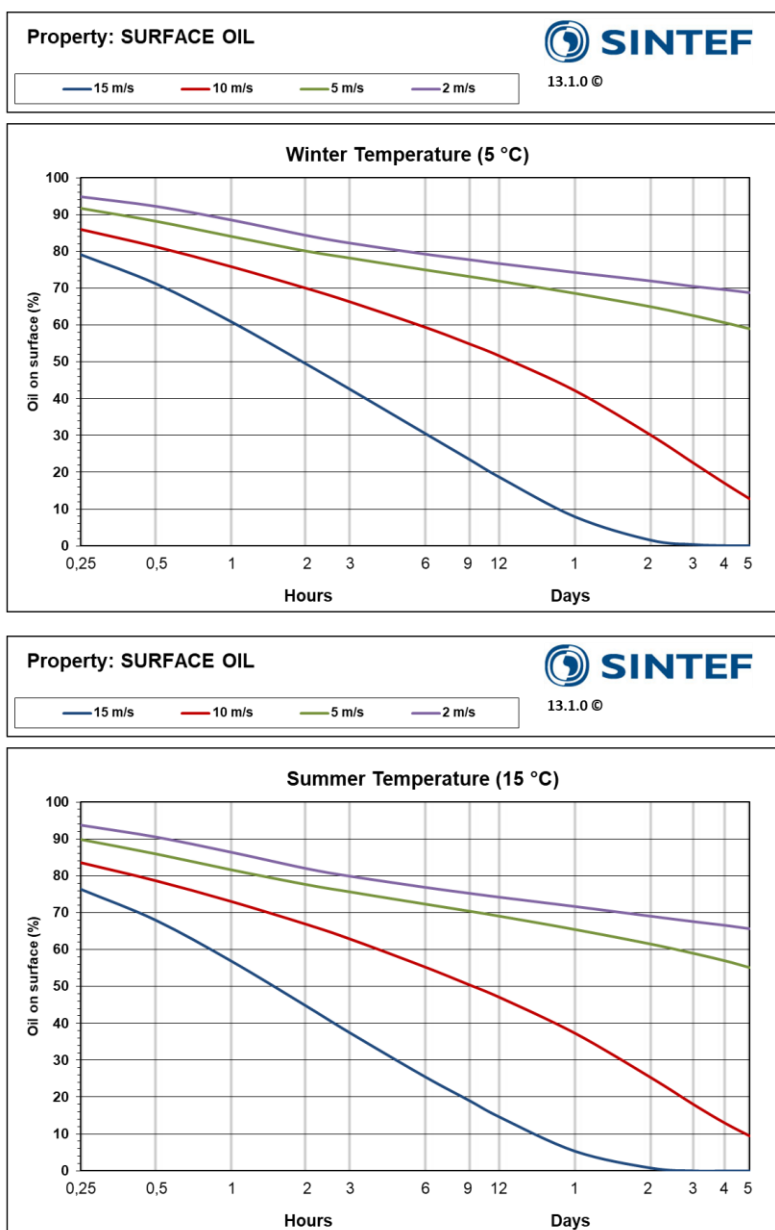


Figure 7-3 Remaining surface oil under different sea states for Lille Prinsen at 5 °C and 15 °C. Release rate 80m<sup>3</sup>/h.

## 7.6 Film thickness from surface release

In general, mechanical recovery requires normal minimum film thicknesses  $>0.1-0.2$  mm. Film thicknesses higher than  $0.05-0.1$  mm are considered for application of oil spill dispersants. Lower film thicknesses (e.g., metallic /rainbow) are likely to disperse naturally under breaking waves conditions and can be enhanced in non-breaking waves by mechanical dispersion (chapter 7.8). Figure 7-4 shows the predicted film thickness of Lille Prinsen for a surface release ( $80 \text{ m}^3/\text{h}$ ). The increase in film thickness after 1-3 hours is due to emulsification. Other factors like emulsion viscosities should also be considered when evaluate response options, as described in the next chapters.

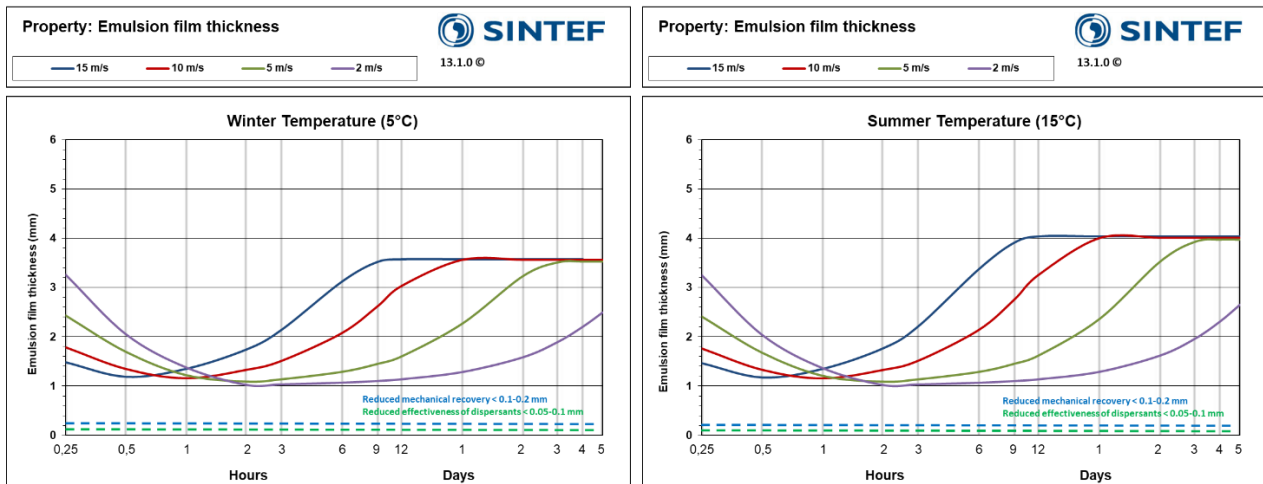


Figure 7-4 Predicted film thickness of Lille Prinsen from a surface (batch) release at 5 and 15 °C. Release rate  $80 \text{ m}^3/\text{h}$ .

## 7.7 Mechanical recovery

Experiences from Norwegian field trials with booms have demonstrated that the effectiveness of various mechanical clean-up operations may be reduced due to the high degree of leakage of the confined oil or emulsion from the oil recovery boom. Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than  $1000 \text{ mPa}\cdot\text{s}$  (Nordvik et al., 1992). However, other factors like the operational speed of recovery vessel and current weather conditions will also influence on the risk of boom leakage.

Weir skimmers may reduce recovery rates ( $\text{m}^3/\text{h}$ ) when skimming oils with viscosities in the range  $15-20\,000 \text{ mPa}\cdot\text{s}$  (Leirvik et al., 2001). NOFO is operating with viscosity limits for skimmer efficiency as followed: primary use of weir skimmers ( $<20\,000 \text{ mPa}\cdot\text{s}$ ), combination of weir and high-visc. skimmers ( $20-50\,000 \text{ mPa}\cdot\text{s}$ ), and primary high-visc. skimmer ( $>50\,000 \text{ mPa}\cdot\text{s}$ ).

The emulsion viscosities of Lille Prinsen are shown in Figure 7-5 at 5 and 15 °C. For boom leakage of confined oil, the emulsion viscosity exceeds  $1000 \text{ mPa}\cdot\text{s}$  after 2-4 hours at 10 m/s wind speed, but the time are stretched up to 1-2 days for very low wind speed (2 m/s). Overall, Lille Prinsen has a wide window of opportunity for traditional weir-skimmer head for viscosities  $<20\,000 \text{ mPa}\cdot\text{s}$  at summer and winter conditions.

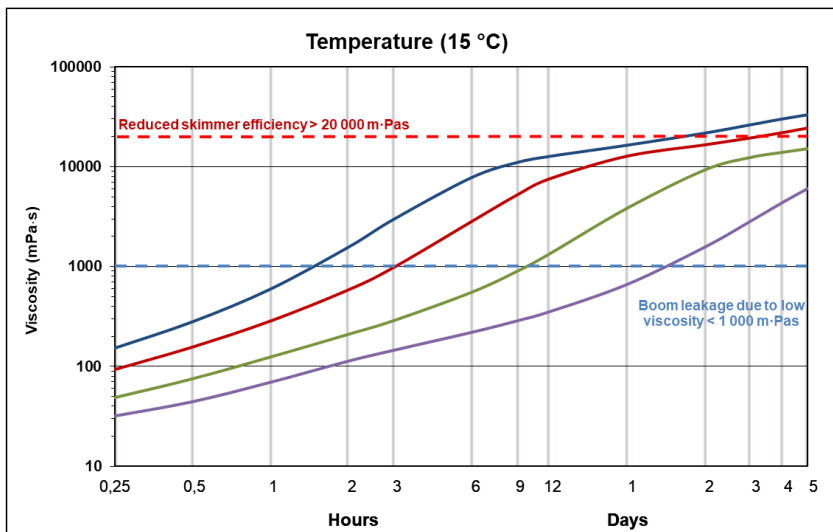
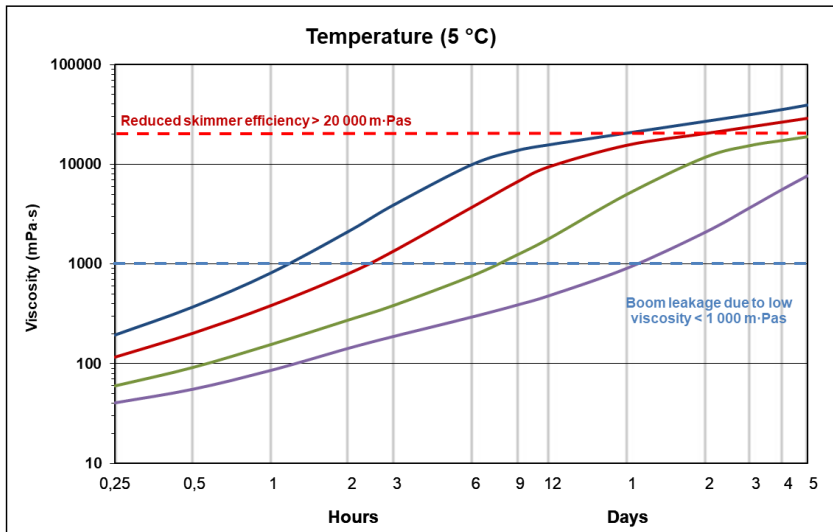
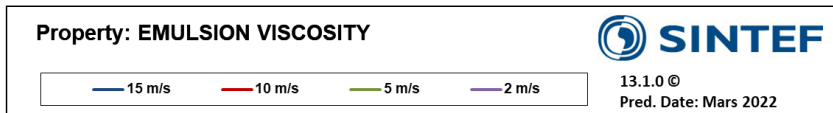


Figure 7-5 Predicted emulsion viscosity for Lille Prinsen at 5 °C and 15 °C compared with expected viscosity limits for boom leakage and poor flow to weir skimmers. Release rate 80m<sup>3</sup>/h.

## 7.8 Mechanical dispersion by high-capacity water flushing

In general, mechanical dispersion by high-capacity water flushing without using dispersants could have a potential for oil spill with thin (initial) film thickness up to 0.2-0.3 mm and viscosities <150-300 mPa.s. In such cases, water flushing from high-capacity water flush boom and/or fire-fighting (Fi-Fi) systems could possibly break up the oil/residue into smaller droplets and enhance the dispersion. Moreover, water flushing could also be used in combination with application of dispersant in calm weather condition to enhance dispersant efficiency with use of artificial energy some minutes after the dispersant treatment. This technology

was tested in a full-scale trial (NOFO Oil-on-Water trial) in 2016 and described by Daling et al., 2017 and Sørheim et al., 2017.


However, for Lille Prinsen mechanical dispersion by water flushing only is not considered as a strategy in oil spill response due to the formation of high emulsion film thicknesses (Figure 7-4) by emulsification, even the oil has low emulsion viscosities in the very early stage after an oil spill, as shown in Figure 7-5. The rapid emulsification of Lille Prinsen is the limiting factor for this strategy. However, use of water-flushing can be a supplementary method in "peripheral" areas with thin oil films, e.g., metallic /rainbow appearance.

## 7.9 Use of chemical dispersants

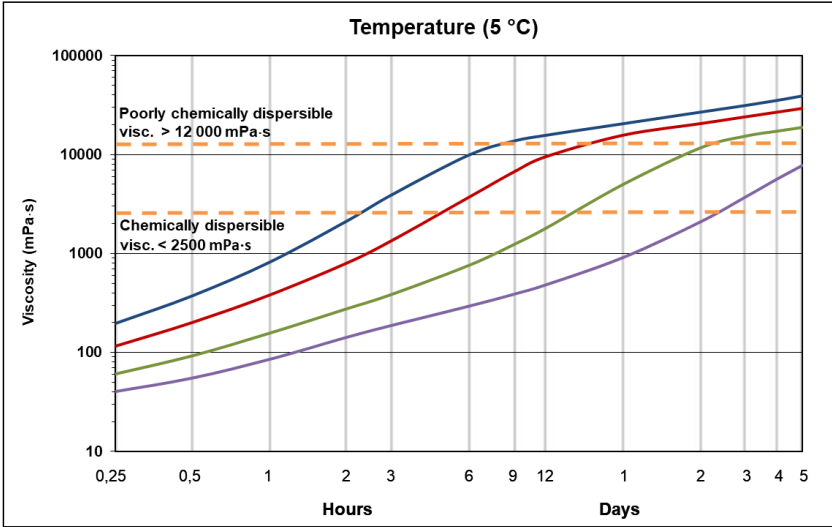
The viscosity limit for effective dispersant use was estimated to 2500 mPa.s, and the viscosity limit for when the emulsified oil is not or poorly dispersible was estimated to 12000 mPa.s. In cases where the oil (emulsion) is expected to be reduced dispersible, for viscosities between 2500-12000 mPa.s, additional energy or use of a higher dispersant dosage by repeated dispersant application is recommended to possibly enhance the dispersant efficiency. Providing additional energy through use of Fi-Fi systems or thrusters after dispersant application may increase the dispersion effectiveness in calm weather condition.


The window of opportunity for use of dispersant Dasic Slickgone NS is presented in Figure 7-6. The oil-emulsion is e.g., predicted to be (reduced) dispersible up to 2-3 days at summer and winter conditions, with wind speed of 5 m/s.

High pour points could reduce the dispersant effectiveness, where the dispersant droplets have a reduced ability to diffuse into the oil and may appear as droplets on the surface of solidified oil slick and be washed off the slick by wave activity. In certain weather conditions, low emulsification rate may enhance formation of solidified lumps, particularly at 5 °C. In a spill situation, the use of a simplified dispersibility testing kit is therefore recommended to assess the potential for chemical dispersion.

Property: EMULSION VISCOSITY  13.1.0 ©

15 m/s 10 m/s 5 m/s 2 m/s



Property: EMULSION VISCOSITY  13.1.0 ©

15 m/s 10 m/s 5 m/s 2 m/s

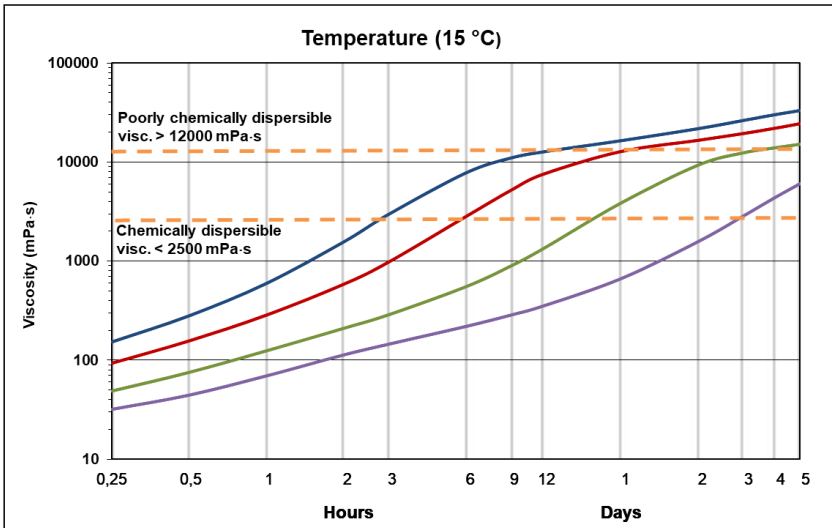


Figure 7-6 Predicted emulsion viscosity for Lille Prinsen at 5 °C and 15 °C including dispersibility limits. Release rate 80m<sup>3</sup>/h.

## 8 Summary of response options for Lille Prinsen

Lille Prinsen is a medium density paraffinic crude oil that forms stable water-in-oil (w/o) emulsion in scenarios where the (initial) film thickness  $>0.1$  mm, typically from surface releases. Certain scenarios from underwater releases depending on the water depth, gas to oil ratio (GOR), release rate, release rupture diameter etc. may also produce initial film thicknesses  $>0.1$  mm of surfaced oil, otherwise thinner initial oil films can be expected. An evaluation of a potential sub-surface release has however not been evaluated for Lille Prinsen.

High pour point of surface residue may cause solidification at sea, particularly in low temperature and calm sea conditions. High pour points typically prevent or reduce the dispersant efficiency.

### Mechanical recovery:

- Lille Prinsen has a wide window of opportunity for mechanical recovery with use of skimmers, such as the Transrec equipped with traditional weir-skimmer head for emulsion viscosities  $<20\,000$  mPa.s.
- Boom leakage and reduced recovery is a potential for viscosities  $<1000$  mPa.s.

### Use of chemical dispersants:

- Emulsions of Lille Prinsen is found to be dispersible with use of Dasic Slickgone NS for viscosities  $<2500$  mPa.s (DOR 1:25) in non-breaking waves, and not/poorly dispersible for viscosities  $>12000$  mPa.s assuming breaking waves conditions ( $>5$ m/s wind speeds).
- In the field, additional energy or higher DOR by repeated dispersant application may increase the dispersant effectiveness when the oil is reduced dispersible.

### High-capacity water flushing (mechanical dispersion):

- The emulsification is the limiting factor for this strategy.
- The predicted film thickness is  $>0.2-0.3$  mm which is the estimated upper limit for effective use of water flushing and is therefore not considered as a main response option for emulsions of Lille Prinsen.
- Mechanical dispersion be used a supplementary /secondary method on e.g., peripheral areas of thin oil films of metallic/rainbow appearances in calm weather conditions.
- Mechanical dispersion can be used after dispersant treatment under calm sea conditions.

### Monitoring and remote sensing:

- Monitoring and remote sensing should always be used as a support in response operation for Lille Prinsen.



## 9 Map categorization of Lille Prinsen

A semi-quantitative categorization has been developed by SINTEF to map crude oils into four main groups: Paraffinic, waxy, naphthenic, and asphaltenic oils, based on their typically physiochemical properties, as described below.

**Naphthenic oils** typically exhibit disrupted n-alkane (paraffins) patterns due to high degree of biodegradation of the oil in the reservoir. The content of paraffins is therefore normally low in for these oils and have low pour points (typically  $< -10$  °C) with corresponding low wax content. Such biodegraded crude oils may have high densities and a high degree of UCM (Unresolved Complex Mixture) consisting of a wide range of complex components, such as resins and naphthenes, but this is not true for all naphthenic oils.

**Paraffinic oils** are often characterized by low to medium density, which reflects high content of light and saturated components, such as paraffins (n-alkanes). Paraffinic crudes differ mainly from the waxy crudes with a lower wax content (typically  $< 6$  wt. %), hence the pour point of the fresh crude is often lower compared with waxy crude oils. Paraffinic crudes exhibit medium to high evaporation loss, with rapid and high-water uptake, and normally form stable emulsions.

**Asphaltenic oils** have high content of heavier components reflected by high densities (typically  $> 0.9$  g/mL) and low evaporation loss. The asphaltenic crudes often exhibit low pour points (typically  $> -4$  °C) due to the high asphaltene content ( $> 1$  wt. %) preventing wax precipitation and formation of a wax lattice structure. Compared with paraffinic and waxy crudes the asphaltenic crude oils usually have both a slower and a lower maximum water uptake. The asphaltenic crude oils form very stable, highly viscous, and persistent blackish emulsions with long expected lifetime on the sea surface. The high stability is caused by the stabilization by the polar components in the oil.

**Waxy oils** often exhibit high pour points due to large content of wax components (typically  $> 6$  wt. %). These oils tend to solidify producing elastic properties on the sea surface, particularly observed at low seawater temperatures. Solidification is typically pronounced if the seawater temperature is 5-15 °C below the pour point. Waxy crude oils typically exhibit a light to medium evaporative loss. The water uptake can vary extensively, whereas the emulsions can be very stable or even highly unstable depending on the content of stabilizing and polar surface-active components like the asphaltenes and resins.

The categorization of a selection of Norwegian crude oils including Lille Prinsen is given in Figure 9-1.

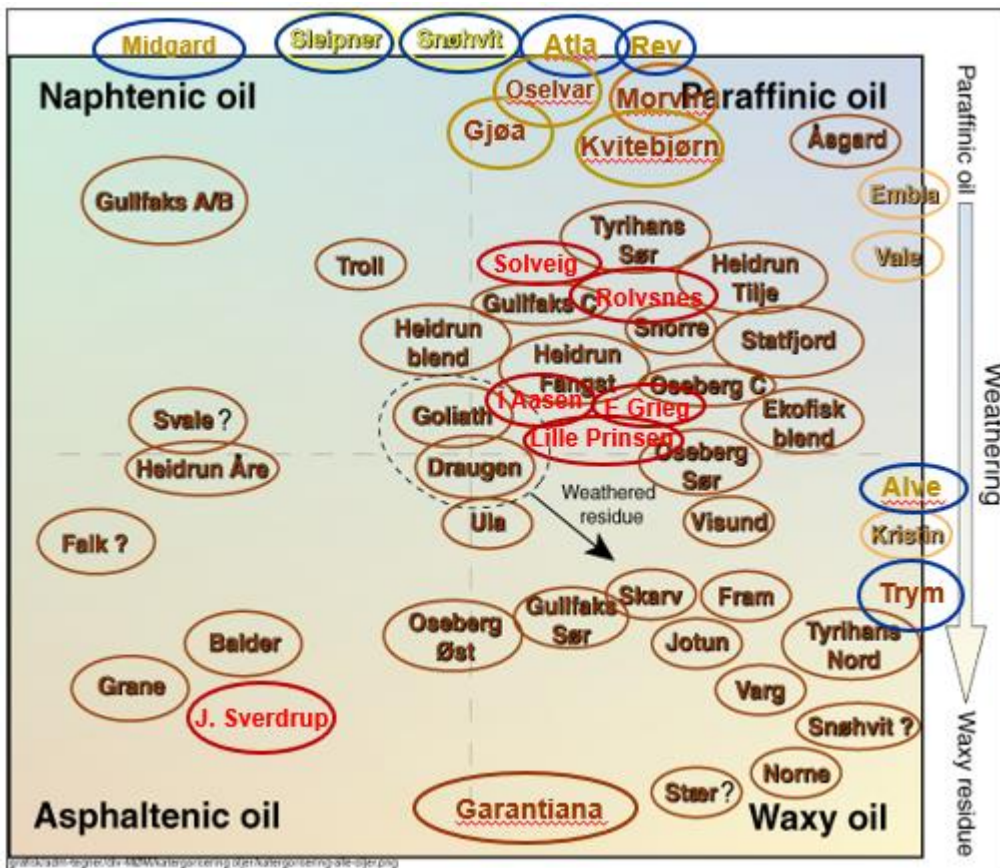


Figure 9-1 Categorization of a selection of Norwegian crude oils from previous studies including Lille Prinsen crude oil.

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## A Behaviour of oil on sea surface

### A.1 The chemical composition of crude oils and condensates

Crude oil is a complex mixture of thousands of chemical components. The relative compositions vary, giving rise to crude oils with different chemical and physical properties. The components found in crude oil are classified into two main chemical groups: hydrocarbons and non-hydrocarbons see Figure A-1

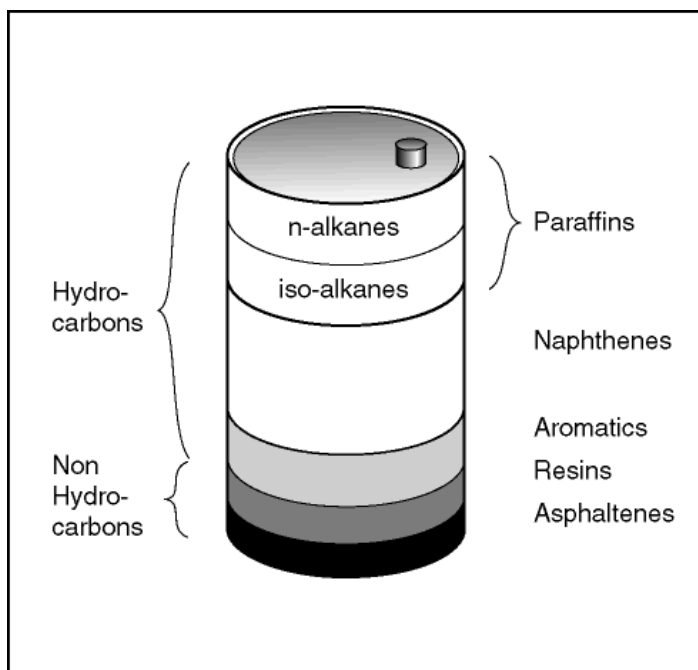


Figure A-1 The chemical composition of crude oils.

Most compounds in crude oils are hydrocarbons, which are composed of hydrogen (10-15 wt. %) and carbon (85-90 wt. %). These range from simple, volatile gases, such as methane with only one carbon atom to large, complex molecules with more than 100 carbon atoms. The hydrocarbons in crude oils include saturated and unsaturated molecules in linear, branched and cyclic configurations. Hydrocarbons are further classified into aliphatic and aromatic compounds. The two main groups of aliphatic compounds are paraffins and naphthenes.

#### Paraffins

Paraffins include *n*-alkane and *iso*-alkane aliphatic compounds. Waxes are an important subgroup of paraffins, containing more than 20 carbon atoms. The wax components of a crude oil will be present in a solution at elevated temperatures. At low temperatures, they may precipitate from the solution. These are principally *n*-alkanes. The wax content of crude oils can vary from 0.5 wt.% up to 40 or 50 wt.% in extreme cases, although most the world's crude oils have a wax content of 2-15 wt.%.

#### Naphthenes

This group includes cycloalkanes containing one or more saturated rings. Each ring may have one or more paraffinic side chains, which are chiefly five- and six-membered rings.

#### Aromatics

Aromatics are a specific type of unsaturated cyclic hydrocarbons. Benzene, toluene and xylenes are examples of mono-ring aromatics, naphthalenes are di-ring aromatics and polycyclic aromatic hydrocarbons (PAH) contain three or more aromatic rings.

## Non-hydrocarbons

In addition, hydrogen and carbon, some organic compounds in crude oils also contain small amounts of oxygen, nitrogen or sulphur, as well as some trace metals such as vanadium and nickel. These compounds are referred to as heteroatom organic compounds because they contain a heteroatom, which is any atom that is not carbon or hydrogen. The two most important groups of heteroatom organic compounds are resins and asphaltenes.

## Resins

Compared to the hydrocarbons, resins are relatively polar and often have surface-active properties. Resins have molecular weights ranging from 700-1000. Carboxylic acids (naphthenic acids), sulphoxides and phenol-like compounds can be found in this group as well.

## Asphaltenes

Asphaltenes are a complex group of poorly characterized chemical compounds that consist of condensed polycyclic aromatic compounds. They are large molecules with 6-20 aromatic rings and side chains (molecular weight 1,000-10,000). Asphaltenes may be classified as "hard" or "soft" based on the method of determination. Crude oils may contain up to 6 wt. % "hard" and 10 wt. % "soft" asphaltenes (Peregrino:13.4 wt.%)

## A.2 Main oil categories related to weathering

Different oil types can have extremely different compositions, which impact their physical properties and effect their behaviour after a spill at sea.

Oils that are subject to weathering can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

**Crude oils** contain relatively more of the heavier components than light oils or condensates. Crude oils can be weathered in the laboratory to mimic natural weathering that occurs on the sea surface. The laboratory weathered crude oil identified as 250°C+ residue, corresponds to 0.5 to 1 week after a spill at sea, and contains less than 50% of its original volume due to evaporation. The heavier components allow the formation of stable water-in-oil (w/o) emulsions, which reduces oil spreading at the sea surface. The final (terminal) film thickness of a crude oil depends on the emulsion's physical properties, and will be in the order of 1 mm.

**Light oils** and crude oils are not specifically differentiated in reservoir terminology. However, it is suitable to deal with the light oils as a separate category when referencing weathering properties. Light oils have a high content of low molecular weight hydrocarbons. When subjected to laboratory weathering, the 250°C+ residue of light oils may lose 50-70% of their total volume due to evaporation. In contrast to condensates, which only contain light components, light oils contain a mixture of light and heavy components. These heavy components may cause light crudes to emulsify in water, but these w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, with a final film thickness of approximately 0.5 mm.

**Condensates** only contain low molecular weight hydrocarbons and are considered extremely volatile. Laboratory weathered condensates, such as the 250°C+ residue, typically lose more than 70% of their initial volume. Condensates do not contain components such as asphaltenes or heavier waxes and will not emulsify significant amounts of water. The spreading of condensates is relatively fast, and can result in a final film thickness of approximately 0.05 mm.

## A.3 Physical properties of crude oils

The physical properties of specific oils are a result of their chemical composition. The most important physical properties in oil spill scenarios are discussed below.

## Density

The density of a crude oil is dependent on the density of all its components. The density of hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing larger amounts of high molecular weight aromatics, such as naphthenic and asphaltenic oils.

Specific gravity is defined as the oil density at 60°F (15.5°C) divided by water density at 60°F. In American literature, the density of the oil is often expressed as °API, where:

$$^{\circ}\text{API} = \frac{141.5}{\text{Specific gravity}} - 131.5$$

In the present study, the density of the oil is presented as specific gravity.

The density of fresh crude oils normally lies in the range 0.78 to 0.95 g/mL (50 to 10 °API).

### A.3.1 Rheological properties

The viscosity of crude oils expresses its resistance to flow and is of special interest when pumping oil. **Absolute viscosity** (also known as dynamic viscosity) is a measure of internal resistance. In the SI system, absolute viscosity has units of N s/m<sup>2</sup>, Pa s or kg/(m s), where 1 Pa s = 1 N s/m<sup>2</sup> = 1 kg/(m s). Absolute viscosity can also be expressed in the metric CGS (centimeter-gram-second) system as g/(cm s), dyne s/cm<sup>2</sup> or Poise, where 1 Poise = 1 dyne s/cm<sup>2</sup> = 1 g/(cm s) = 1/10 Pa s = 1/10 N s/m<sup>2</sup>. [https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d\\_412.html](https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.html) The industry often uses centipoise, as the *Poise* is normally too large, 1 Poise = 100 cP and 1 cP = 0.001 N s/m<sup>2</sup>. The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPa.s (cP) at ambient sea temperature. In comparison, water has an “absolute” viscosity of 1 cP and syrup's is 120 000 cP at 20°C.

**Kinematic viscosity** is absolute viscosity divided by density. 1 centistoke (cSt) = 1 cP / density. Because the density of weathered oils and emulsion are typically 0.9 – 1 g/mL, the units cSt and cP will often have similar values. Viscosity is temperature dependent. For liquids, the viscosity decreases with increasing temperatures. Viscous and waxy crude oils can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to, or below, their pour point. Water-in-oil (w/o) emulsions exhibits this non-Newtonian behaviour with shear thinning. In an oil spill situation, an emulsion may be liquid under turbulent conditions at sea, but can become much more viscous, or even semi-solid in calmer water conditions, or on beaches. Thus, the measurements of the viscosity of w/o-emulsions must be carried out under strictly controlled conditions (defined shear rates and thermal and mechanical history of the sample). At SINTEF, a shear rate of 10 s<sup>-1</sup> is routinely used for expressing viscosity data on w/o-emulsions.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al., 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa.s for fresh crude oils and several hundred/thousand mPa.s for their residues. Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.

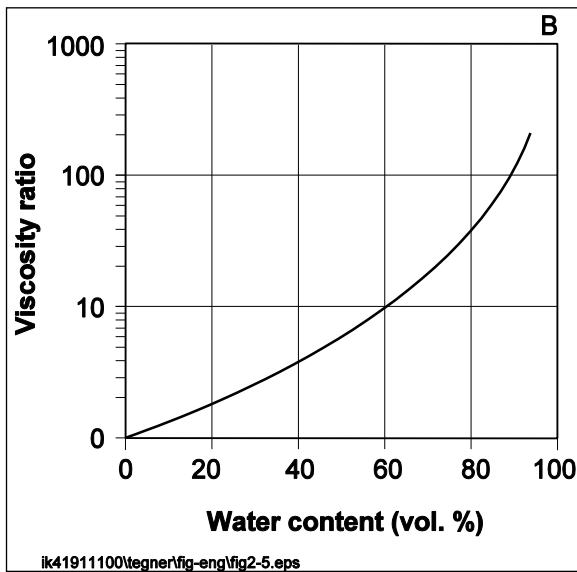


Figure A-2 Example of viscosity ratio as a function of water content.

### A.3.2 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point (ASTM-D97). The method accurately determines the temperature at which the oil become semi-solid under the specified laboratory conditions. Due to the movement at the sea surface, the oil may remain a liquid at sea at temperatures as low as 5 to 15°C lower than the pour point of the oil. The pour point of oil with high wax content will increase dramatically with evaporation as the lower weight molecules, which contribute to keeping the wax in solution, evaporate. The pour point for oils with high wax contents can reach 30°C, while low viscous naphthenic oils may have pour points as low as -40°C. In an oil spill clean-up situation, the pour point provides essential information for when determining the efficiency of various skimmers, pumping rates and the use of dispersing agents.

### A.3.3 Distillation curve

The distillation curve, which is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. The boiling point of a chemical component depends on its vapour pressure, which is a function of its molecular weight and chemical structure. Low molecular weight oil components have a higher vapour pressure, thus lower boiling points than higher molecular weight components of a similar type. Aromatic compounds boil at a higher temperature than paraffinic compounds of the same molecular weight, and *iso*-alkanes boil at a lower temperature than the equivalent *n*-alkanes. Hence, the distillation curve is an indicator of the relative amount of different chemical components, principally as a function of molecular weight, but also as determined by the chemical composition.

### A.3.4 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by the heating of oil will form an ignitable mixture in air. The flash point depends on the proportion of low molecular weight components. Fresh crude oils normally have a low flash point (from -40°C to 30°C). From a safety point of view, flash points are most significant at, or slightly above, the maximum temperature that may be encountered in storage or transport. The flash point is an approximate indicator of the relative fire and explosion hazard of oil.



**Rule of thumb:**

*In the presence of an oil slick at sea, a fire and/or explosion hazard exists when the oil's flash point is close to or lower than the sea temperature.*

Natural weathering processes such as evaporation and emulsion formation contribute to reducing the potential hazard by increasing the flash point. Thus, it will be a relatively short fire and/or explosion danger in the initial stages of oil spill. In the laboratory, the flash point is measured in a closed system with the components in the oil and gas equilibrated. In the field, however, the weather situation will influence the flammability of the air above the slick. The gas concentration will be high just above the oil film in calm weather and high temperatures, whereas the concentration will be low in cold and windy weather due to dilution and transport and a lower degree of evaporation.

**A.4 The behaviour of crude oil spilled at sea**

This chapter gives a general description of the main weathering processes when oil is spilled at sea. There are many natural processes that take place that change the volume and chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, spreading, sedimentation, oxidation and biodegradation. A common term for all these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacterial flora, etc.). Figure A-3 illustrates the various weathering processes, and Figure A-4 shows their relative importance over time.

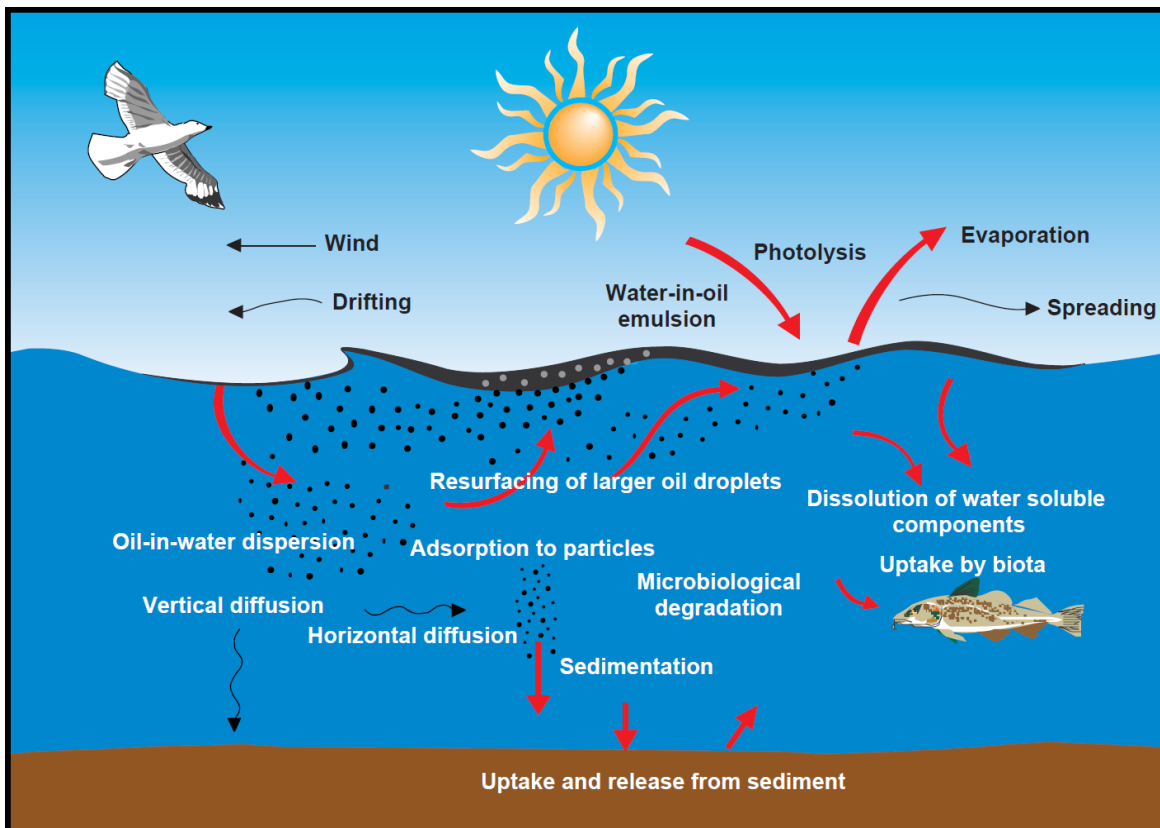


Figure A-3 Illustrating the weathering processes that take place when oil is spilled on the sea surface.

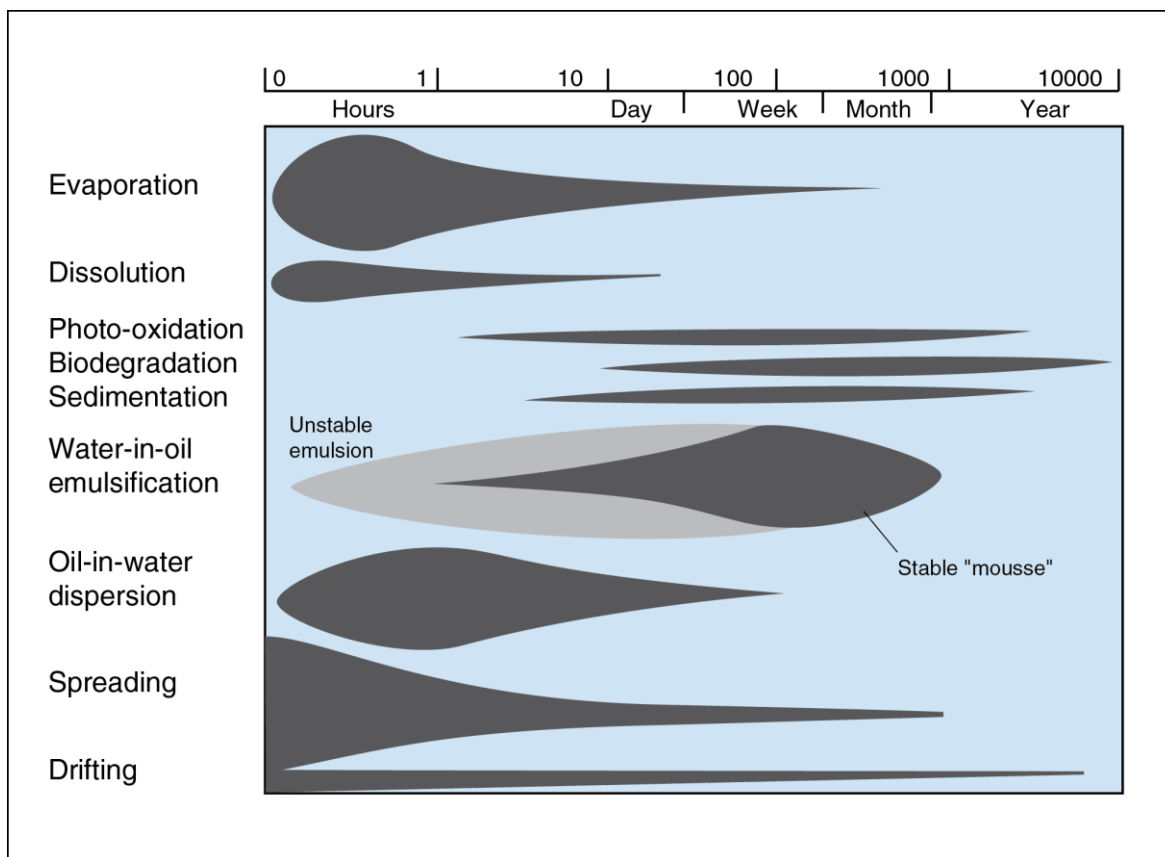


Figure A-4 Weathering processes' relative importance over time. Note: logarithmic scale.

#### A.4.1 Evaporation

Evaporation is one of the natural processes that support the removal of spilled oil from the sea surface. The evaporation process starts immediately after the oil is spilled, and the evaporation rate decreases exponentially throughout the duration of the oil spill. The evaporated amount depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and oil film thickness.

The rate of evaporation varies for different oil types. Light refinery products (e.g., gasoline and kerosene) may completely evaporate after a few hours/days on the sea surface. Condensates and lighter crude oils can lose 50% or more of their original volume during the first days after an oil spill. The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds, which increases the relative amounts of higher molecular weight compounds. With evaporations, the chemical and physical properties of the remaining oil will change. The density, viscosity, pour point and wax and asphaltene content, will all increase with increased evaporation.

#### A.4.2 Spreading

Oil spilled at sea will spread on the sea surface. Spreading is often the dominant process in the initial stages of an oil spill and decreases as the viscosity and density of the remaining oil increases. The spreading process is also reduced if the oil's pour point is 5-15°C below the sea temperature.

Oceanographic conditions (e.g., wind, waves and currents) affect the spreading process. The oil slick will be broken into "wind rows" aligned in the direction of the wind, see Figure A-5. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that most of the total oil slick area consists of a thin film (<1 mm oil thickness) that only contains 10% of the oil volume. Most of the oil

volume (~90%) is in small patches of w/o emulsions with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area.

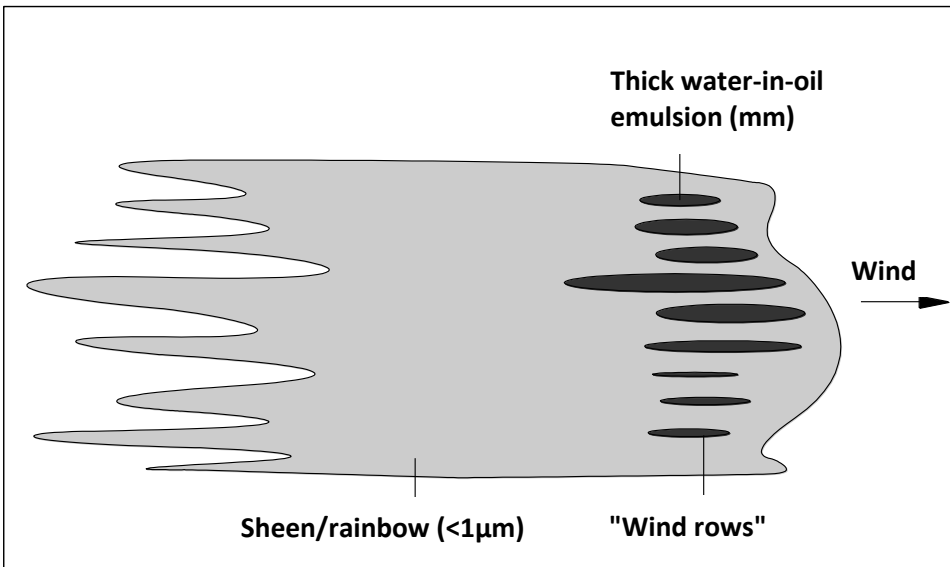


Figure A-5 The spreading of oil spilled on the sea surface and the distribution within the oil slick.

### A.4.3 Drift of an oil slick

The oil slick will drift as the weathering processes continue. The wind and current conditions cause the oil slick to drift, as illustrated in Figure A-6. Waves and wind create a current in the mass of water which amounts to approximately 3% of the wind speed at the sea surface. The influence of the wind decreases rapidly with the depth of the water below the surface. At 1 to 2 meters the current reduces to approximately 1% of the wind speed. This means that oil on the surface of the open sea, will move faster than the water below (e.g., Reed and Turner, 1991; Reed et al., 1994). In the absence of wind, the oil drift is governed by the prevailing (background) current.

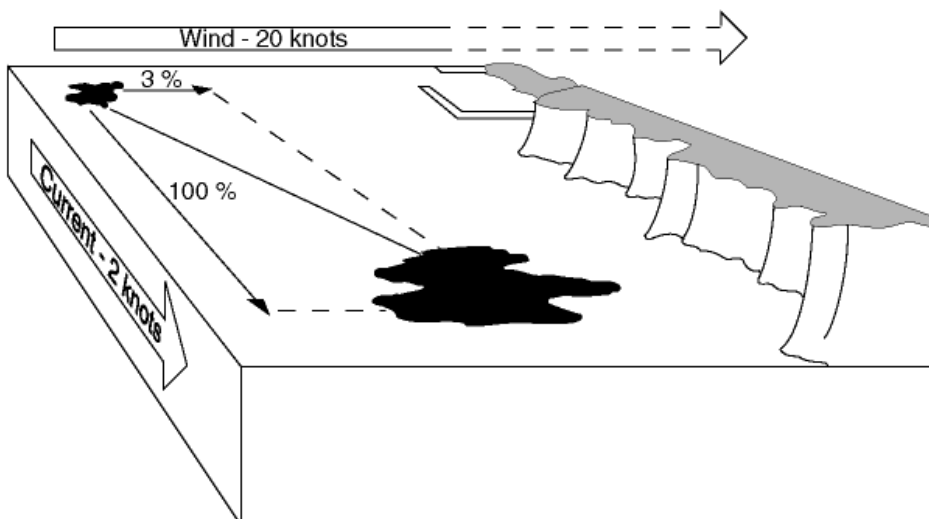


Figure A-6 An illustration showing how wind and current can influence the drifting of an oil slick.

#### A.4.4 Water-in-oil (w/o) emulsion

The formation of water-in-oil emulsions significantly affects the behaviour and clean-up of oil spilled at sea. Because of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion process. The minimum criterion for the formation of w/o emulsions is the presence of breaking waves (i.e., a wind speed of >5 m/s). Nonetheless, a slow water uptake can also take place during calmer weather. Figure A-7 shows how wind speed influences the w/o formation rate.

Surface active compounds present in crude oil will promote the formation of w/o emulsions and contribute to stabilizing the emulsion. These components contain both hydrophilic and hydrophobic groups. The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have revealed that the maximum water uptake is independent of the prevailing weather conditions if the lower energy barrier for the formation of w/o emulsions is exceeded. The rate, however, depends highly on the weather conditions. In the laboratory, the  $t_{1/2}$ -value is determined, which is the time in hours it takes before the oil has emulsified half of its maximum water content. The w/o emulsion formation rate depends on the oil's chemical composition, which varies for different oil types.

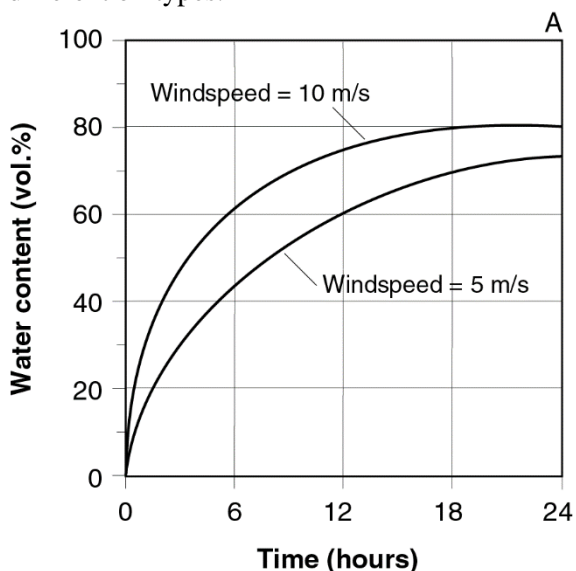


Figure A-7 Example of how weather conditions influence the w/o emulsion formation for typical oils.

The stability of the w/o emulsion depends on the water droplet size, since not all water droplets in the emulsion are stable. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of the slick due to wave action, whereas the largest droplets may coalesce and be squeezed out of the w/o emulsion. After a certain period, the emulsion may only contain small water droplets with diameters of 1 to 10  $\mu$ m, yielding a more stable emulsion.

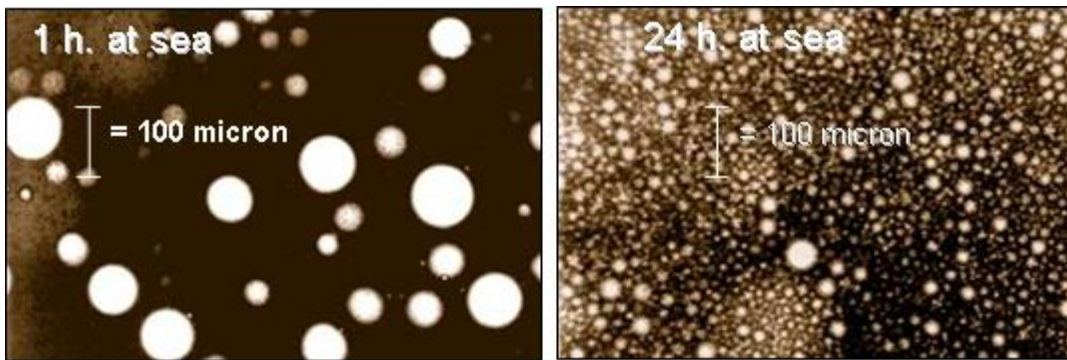


Figure A-8 Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder.

Thus, the formation of emulsions is the result of water retention by oil as an effect of both viscous and interfacial forces. The interfacial forces are the most important, and asphaltenes are largely responsible for this. Resins are similar compounds to asphaltenes and can stabilize an emulsion, but not to the same extent.

Resins and asphaltenes have both hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil, thereby forming a layer that stabilizes the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilizes the interfacial “skin” layer. The interfacial layer between the oil and water forms a physical barrier that hinders the coalescence of the water droplets and will stabilize the w/o emulsion. The stabilization of the water droplets by asphaltenes and wax is shown in Figure A-9.

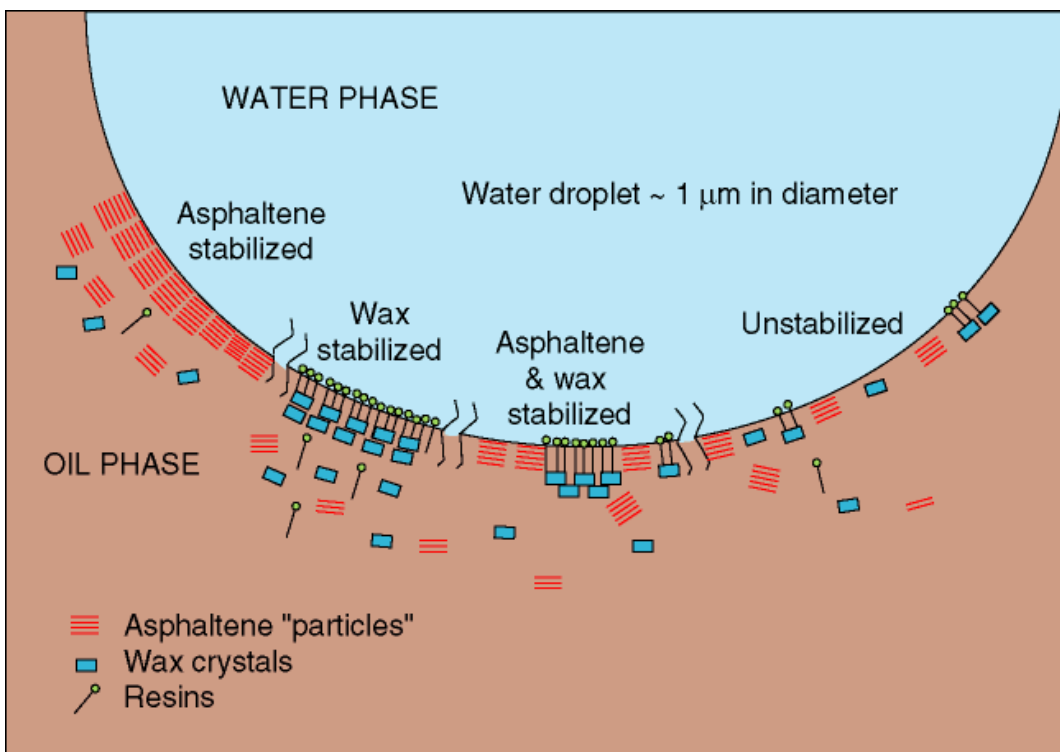


Figure A-9 Interfacial layer stabilized by wax and asphaltenes in w/o emulsion.

Oils that contain large amounts of wax and small amounts of asphaltenes can form w/o emulsions stabilized by a continuous phase’s rheological strength (viscosity and elasticity) due to wax structure formed by precipitated wax. Wax stabilized emulsions are characterized by large water droplets and are fairly stable when stored, although they may break down when stress is applied and/or when the emulsion is heated to, e.g. 40-50°C.

Crude oil and sea water interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to understand and control droplet formation in dispersant system is extremely important. Addition of dispersants reduces the interfacial tension between oil and water that subsequently promotes the formation of a larger number of small oil droplets when surface waves entrain oil into the water column. These small, submerged oil droplets are then subject to transport by subsurface currents and other natural removal processes, such as dissolution, volatilization from the water surface, biodegradation, and sedimentation resulting from interactions with suspended particulate material.

#### A.4.5 Oil-in-water (o/w) dispersion

Natural oil-in-water (o/w) dispersion will take place if there is sufficient energy on the sea surface, i.e. if there are breaking waves present. The waves will break the slick into small oil droplets (~1 mm - 1 mm in diameter), which are then mixed into the upper water column. The largest oil droplets will resurface and form a thin oil film (typically <50 µm). This thin oil film will be rapidly dispersed again by breaking waves as smaller droplets into the water column and will be available for rapid biodegradation.

The natural dispersion rate depends highly on oil type and can be one of the main processes that determine the lifetime of an oil slick on the sea surface. Natural o/w dispersion will gradually decrease with time since the evaporation of the lighter compounds will increase the viscosity of the remaining oil.

The purpose of applying chemical dispersing agents is to increase, or enhance, the natural dispersion rate. Dispersants reduce the interfacial tension between water and oil and thus promote natural o/w dispersion. When effective chemical dispersion is achieved, small oil droplets are formed, with typical diameters ranging from 5 to 100 µm. These are retained in the upper layers of the water column by the prevailing turbulence of wave action.

#### A.4.6 Water solubility

The water solubility of saturated hydrocarbons is generally very low, while lower molecular weight aromatic compounds are water-soluble to some extent; particularly aromatics, such as BTEX, 2-ring PAH and paraffin's up to C<sub>7</sub> have a potential to be dissolved in the water column (McAuliffe, 1987). Within the various types of hydrocarbons, the water solubility decreases from aromatics to naphthenes and from *iso*-alkanes to *n*-alkanes. In each series, the water solubility decreases with *increasing* molecular weight.

Evaporation and the release of oil components into the water mass are competitive processes since most of the water-soluble components are also volatile. The evaporation process is approximately 10 to 100 times faster than the release in the water column. The concentration of soluble oil components into the water column during an oil spill is quite low (< 1 mg/L), while the dissolution of oil components into the water column does not contribute to removing the oil from the sea surface. However, the water-soluble fraction is of great interest since it has a high bioavailability and thus the potential to cause acute toxic effects on marine organisms.

#### A.4.7 Photo-oxidation

Under the influence of sunlight, some of the oil components will slowly oxidize to resins and finally asphaltenes. The photo-oxidized components will stabilize the w/o emulsions and influence the oil's persistence on the sea surface. After a long period of weathering at sea, tar balls (mainly consisting of asphaltenes) may be formed. These tar balls break down very slowly, both at sea and on beaches.

#### A.4.8 Biodegradation

Seawater contains an abundance of microorganisms that can break down all types of oil components. Various microorganisms prefer specific oil components as their energy source. Bacteria prefer to degrade oil in contact with water and the rate of biodegradation depends on the water/oil interface area. The interface area increases as the oil is spread over the sea surface in a thin layer or by chemical or natural dispersion of oil into the water column. Important factors influencing the biodegradation rate are temperature, the concentration of available

nutrients (i.e. nitrogen and phosphorus), oxygen, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the high molecular weight/heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched *iso*-alkanes > cyclic alkanes > cyclic naphthenes > aromatics > resins > asphaltenes (Perry, 1984).

At sea, the formation of oil droplets by natural or chemical enhanced dispersion will increase the biodegradation rate in the water mass by 10 to >100 times compared to surface oil due to increased water/oil interfacial area. When immobilised on hydrophobic synthetic fabrics, *n*-alkanes biodegraded within 2-4 weeks at North Sea conditions (13°C; Brakstad and Lødeng, 2005). Some small PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000), but high molecular-weight oil compounds associated with particulate oil biodegrade more slowly and some very high molecular-weight compounds (equivalent to the heavy residues in crude oil that are used to make bitumen) may not biodegrade to any significant degree.

#### A.4.9 Sedimentation

Crude oil and oil residues rarely sink into the water mass since there are few oils that have a density higher than water, even after extreme weathering. Oil can sink by sticking to materials present in the water mass. W/o emulsions that have a higher density value (e.g. emulsified bunker fuel oils) can more easily stick to a material, particularly if coming to the shore, and can sink to the bottom if washed out again from the shore. In connection to sub-sea blowout at the sea bottom, it is assumed that some of the oil droplets generated in the plume may adsorb to suspended particles or encounter with the seabed sediment. This can cause some sedimentation of oil droplets to the seabed near the release. It is assumed that sub-sea dispersant treatment will reduce the potential for such sedimentation, due to lower adsorption /stickiness to sediment particles.

#### A.4.10 Deep water releases

Size distribution of the oil droplets formed during a subsurface release strongly influences the subsequent fate of the oil in the environment. Large droplets (typically larger than 5 mm) reach the surface after a couple of hours rise time from a depth of approximately 1000 m, while smaller droplets (down to 0.5 mm) may rise for up to a day before they will come to the surface. Fine droplets (below 100 microns) may stay in the water for weeks or even month before they eventually reach the surface. However, factors like vertical turbulence mixing in the water column, density stratification and cross flows will contribute to keep such fine small droplets submerged for even prolonged periods (Johansen et al., 2003). In case of deep-water releases, large droplets (mm range) will usually rise to the surface and form an oil layer with sufficient thickness to emulsify (form water-in-oil emulsions). This is usually caused by loss of buoyancy and more horizontal entrainment of the gas/oil/water plume due to dissolution of gas, possible hydrate formation, cross currents, and density layers. However, large droplets (mm range) will leave the entrained plume and rise to the surface, illustrated in Figure A-10. This was observed both during the "DeepSpill" experiments in 2000 (Figure A-11) and the DWH oil spill in 2010 (Figure A-12). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.

Thick surface oil slick

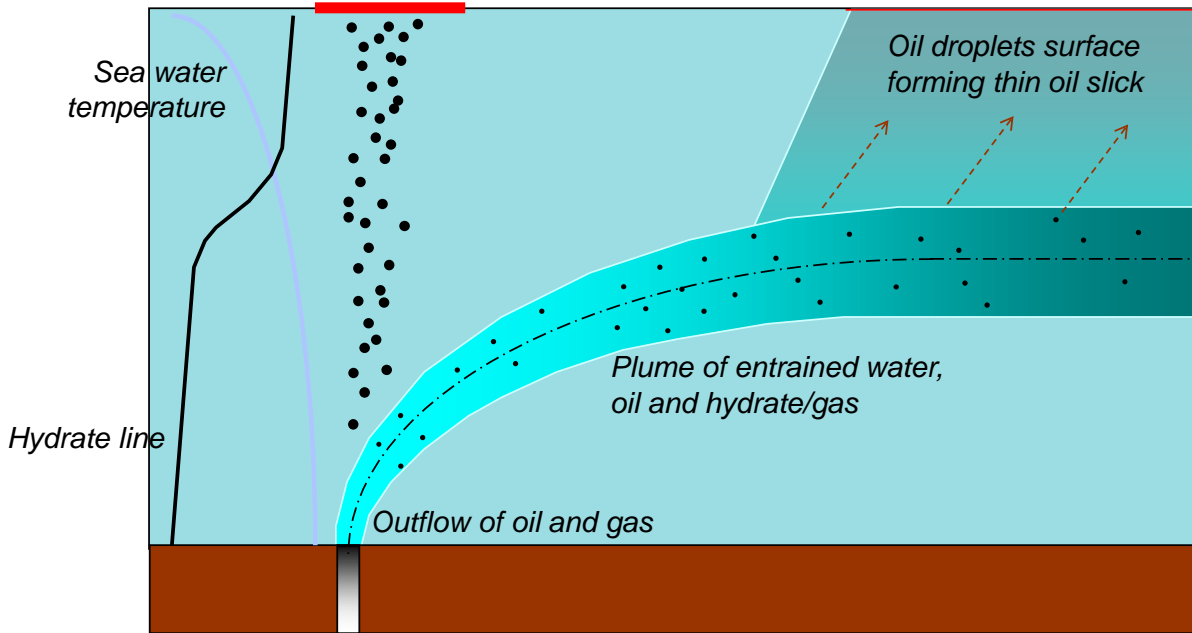
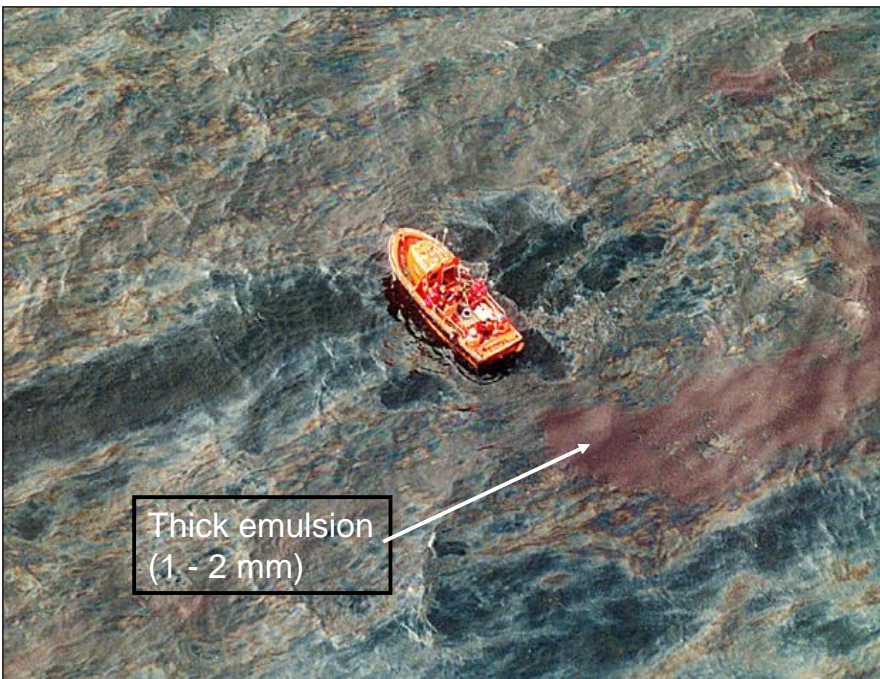


Figure A-10 Illustration of possible creation of thick surface oil slick ( $> 200 \mu\text{m}$ ) from deep-water release of oil.



Thick emulsion  
(1 - 2 mm)

Figure A-11 Surface oil slick (initial thickness  $> 200 \mu\text{m}$ ) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying like an oil slick from a surface batch release (from Leirvik et al., 2011).



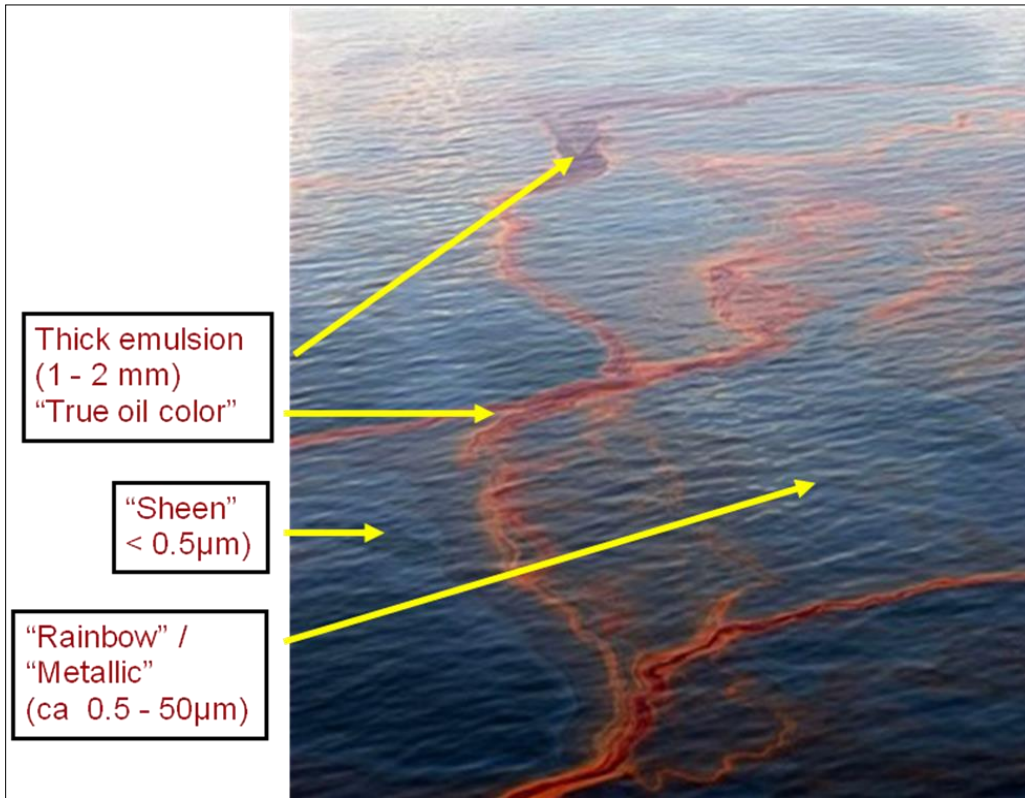


Figure A-12 Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release.

#### A.4.11 Shallow releases

In case of a sub-surface release of oil and gas in shallower water (<500 meter) the buoyancy of the rising water/gas/oil plume is usually sufficient to reach the surface. The gas will be released to the atmosphere, while the large volumes of water will set up a horizontal current that will create a wide and thin surface oil slick (see Figure A-13 and Figure A-14, Rye et al., 1997). This surface oil slick could be too thin to emulsify (< 200 microns), and evaporation and natural dispersion will be the predominant weathering processes.

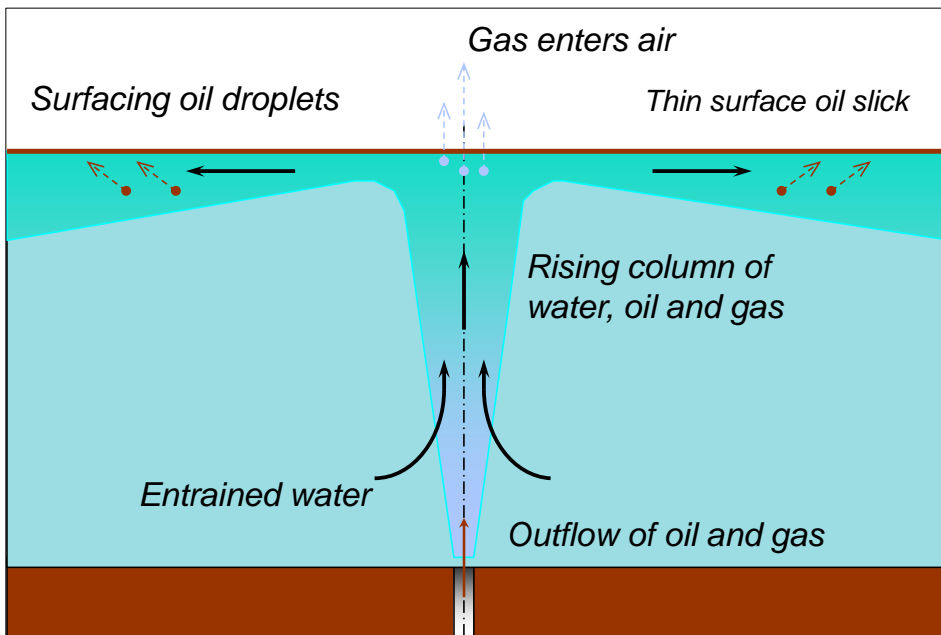


Figure A-13 Illustration of possible creation of thin surface oil slick ( $< 200 \mu\text{m}$ ) from a shallow subsurface release ( $< 500 \text{ m}$ ).

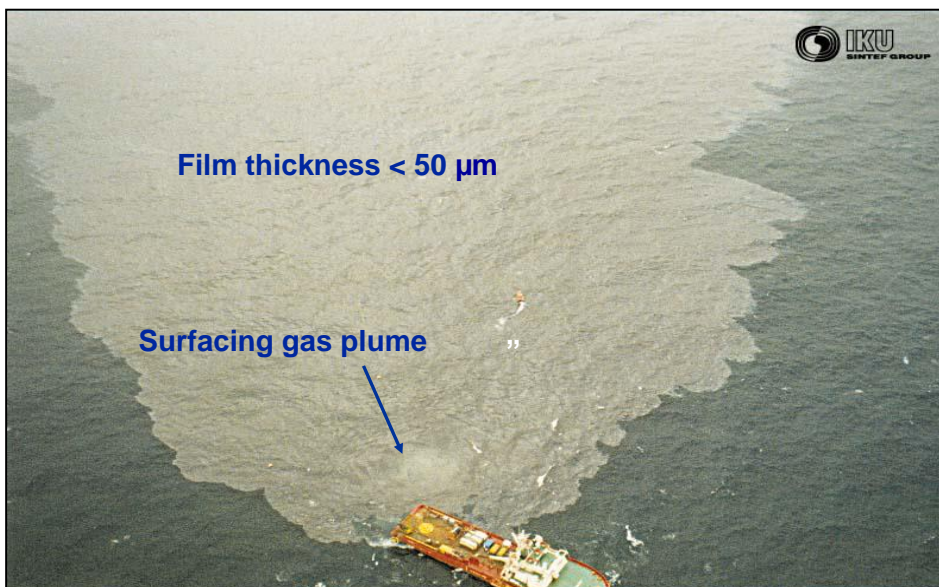


Figure A-14 Surface oil slick ( $< 50 \mu\text{m}$ ) from experimental subsurface release at 106 m in 1996. The surface oil did not emulsify and had a very limited lifetime (hours) due to the low film thickness and high rate of natural dispersion (even at  $< 10 \text{ m/s}$  wind).

## B Experimental setup

### B.1 Oil sample and test temperature

SINTEF Ocean received two 25L barrels of Lille Prinsen crude oil marked 16/1-34 A on January 13<sup>th</sup>, 2022 (Figure B-1). The shipment was sent by Stratum Reservoir. The oil sample was registered in LIMS and given SINTEF ID: 2022-178. Check of free-water in the cans and water content in the oil phase (Karl Fisher titration) was performed. A small amount, <20 mL, of free water was found in the bottom of the barrels. The water content of homogeneous samples of the oil was determined to 0.1-0.3 vol.%. Important for HSE and risk assessment prior to the topping/distillation step (limit <2 vol. %) to simulate evaporative loss at sea by topping/distillation. The weathering study (small-scale and meso-scale) was performed at 13 °C.



Figure B-1 2x25 L steel cans of Lille Prinsen

### B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the crude oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The general procedure is illustrated in Figure B-2.

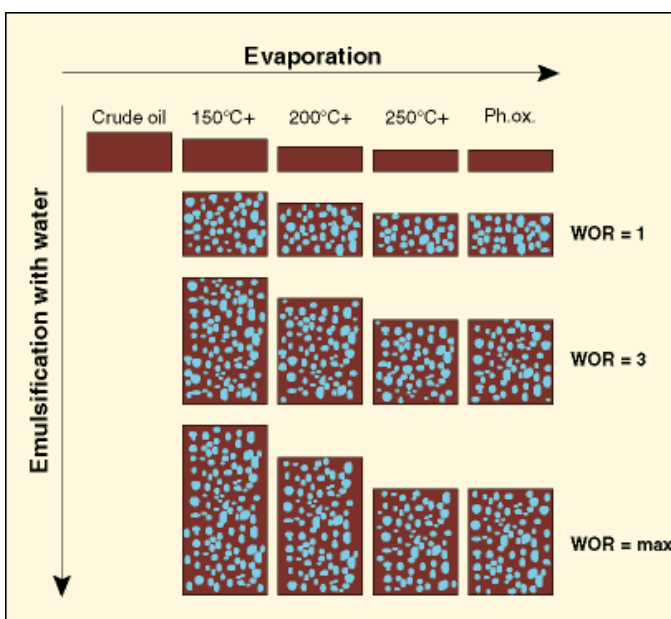


Figure B-2 Small-scale laboratory weathering flow chart of oil.

WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

### B.3 Evaporation

The evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh oil was carried out as a simple one-step distillation to vapour temperatures of 150 °C, 200 °C and 250 °C, which resulted in oil residues with an evaporation loss corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+, respectively.

### B.4 Physical and chemical analysis

The viscosity, density, pour point and flashpoint of the fresh and water-free residues was analysed. In addition, wax content and "hard" asphaltene was measured for the 250°C+ residue. Viscosity for all the w/o emulsions was determined. The analytical methods used are given in Table B-1 and Table B-2.

Table B-1 Analytical methods used to determine the physical properties.

Physical property	Analytical method	Instrument
Viscosity	McDonagh et al, 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour point	ASTM method D97	-
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR
Interfacial tension	In house	DSA100

Table B-2: Analytical methods used to determine the chemical properties.

Chemical property	Analytical method
Wax content	Bridiè et al, 1980
"Hard" asphaltene	IP 143/90

#### Chemical characterization by GC-FID and GC-MS

- The distribution of hydrocarbons (nC<sub>5</sub>-nC<sub>40</sub>) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC-FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols, and alkylated phenols (C<sub>0</sub>-C<sub>4</sub>) were completed using an Agilent 6890 Gas Chromatograph coupled with a, 5973 MSD detector (GC-MS) operating in SIM mode (Selected Ion Monitoring)

The volatile components were in the range of nC<sub>5</sub>-nC<sub>10</sub> and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode and using a modified version of the EPA 8260 analysis method).

### B.5 Emulsification properties

The w/o emulsification studies were performed by the rotating cylinders method developed by Mackay and Zagorski (1982), which is described in detail by Hokstad et al., 1993. The method includes the measuring of the following parameters:

- Relative water uptake (kinetics)
- Maximum water uptake
- Stability of the emulsion
- Effectiveness of emulsion breaker (Alcopol 60%)

The principle of the rotating cylinders method is illustrated in Figure B-3. Oil (30 mL) and seawater (300 mL) are mixed and rotated with a rotation speed of 30 rpm in separating funnels (0.5 L). The emulsification kinetics is mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.

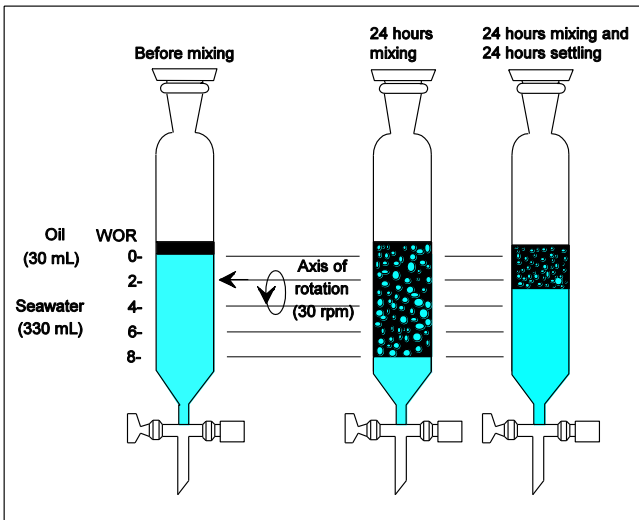


Figure B-3 Principle of the rotating cylinder method.

## B.6 Chemical dispersibility testing

There are several different tests for evaluating the effect of chemical dispersants. The energy input will differ in the different tests, and the obtained efficiency will be representative of different wave energies. At SINTEF, the IFP and MNS test is used in dispersibility testing. IFP and MNS test apparatus are shown in Figure B-4.

**IFP** (Institut Français du Pétrole test, Bocard *et al.*, 1984) is a low energy test estimated to represent low wave energies (2-5 m/s wind speed). A surge beating up and down in the test vessel at a given frequency, gives energy input to the seawater column. The water column is continuously diluted, which gives a more realistic approach to field conditions, compared to other tests.

**MNS** (Mackay-Nadeau-Szeto test, Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea state condition. The energy input in this system, applied by streaming air across the oil/water surface, produce a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min.

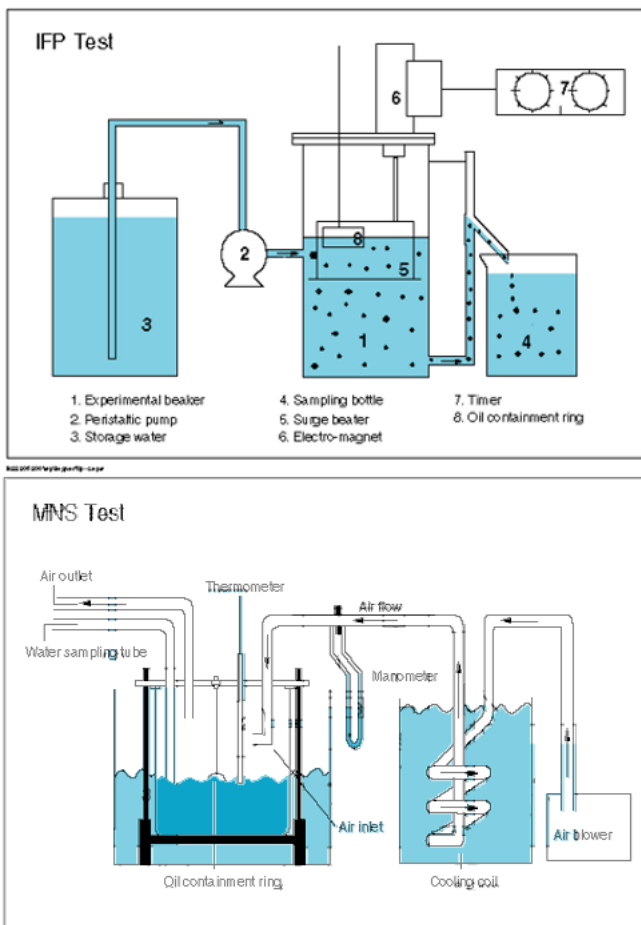


Figure B-4 Laboratory apparatus for effectiveness testing of dispersants.

## B.7 Meso-scale laboratory testing

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. In the small-scale laboratory testing, these processes are studied individually. By using the meso-scale flume, the weathering and effect of dispersants can be studied under more realistic conditions, having the weathering processes to occur at the same time, giving a better image of the behaviour of the oil at sea.

### B.7.1 Description of the flume basin

A meso-scale flume basin (Singsaas et al., 1993), located at SINTEF's Sealab, is routinely used to simultaneously study the weathering processes under controlled conditions. The meso-scale flume basin was rebuilt in 2006, having state of art instrumentation. A schematic drawing of the flume is given in Figure B-4.

Approximately 5m<sup>3</sup> seawater circulates in the 10 metres long flume. The flume basin is stored in a temperature-controlled room (0°C-20°C). Two fans are placed in a covered wind tunnel, controlling the wind speed. The fans are calibrated to simulate an evaporation rate corresponding to a wind speed of 5-10 m/s on the sea surface.

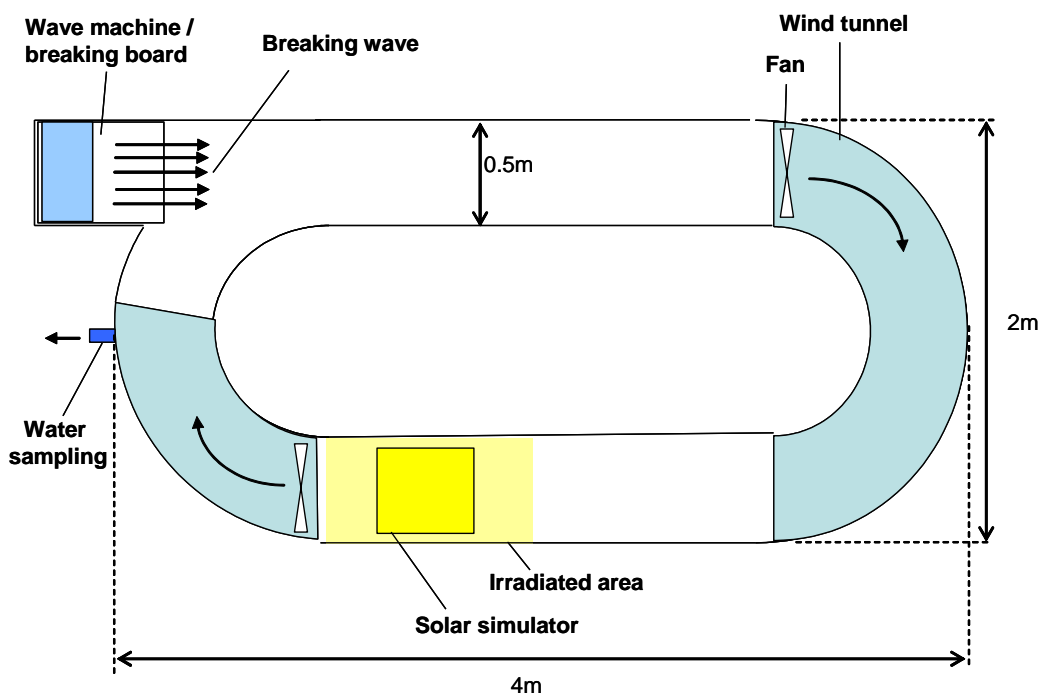


Figure B-4 Schematic drawing of the meso-scale flume.

### B.7.2 Oil weathering in the flume basin

In a meso-scale flume study, a standard volume sample (9 L) of the relevant oil is carefully released on the seawater surface under calm conditions. The wave machine and fans are then started, and the experiment begins. A reference water sample is collected before the beginning of the experiment. Both surface oil/emulsion and water column are sampled frequently the first 6 hours, then after 12 hours and subsequently every day.

After three days (72 hour) dispersant is applied to the surface emulsion. Water samples are then collected more frequently. The addition of dispersant may be repeated once or twice, in which case water samples are also collected.

#### **Analysis of surface oil/emulsion**

Samples of the surface oil/emulsion are collected using an aluminum tray and transferred to a 0.5 L separating funnel. The free water is removed after settling for 10 minutes in the climate room. The oil phase is further handled for an analysis of its physical properties.

The physical properties determined for all surface oil samples during the experiments are:

- Viscosity
- Water content
- Density
- Evaporative loss
- Emulsion stability

#### **Analysis of water samples**

Water samples are analysed for oil concentration in the water column (droplets and dissolved components). The samples are taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water is acidified with some droplets of 10% hydrochloride, HCl (pH < 2). The sampling position is shown in Figure B-4. Samples are then extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultraviolet (UV) spectrophotometry.

**Solar simulation in the meso-scale flume**

Sunlight is simulated with a solar simulator from Gmbh Steuernagel. The solar lamp (4 KW) emits a wavelength spectrum calibrated to fit natural sunlight at high noon and in the absence of clouds. Figure B-5 shows the measured spectrum from the solar simulator compared to one of the most widely used standard spectra for solar irradiance (CIE publication 85, 1989).

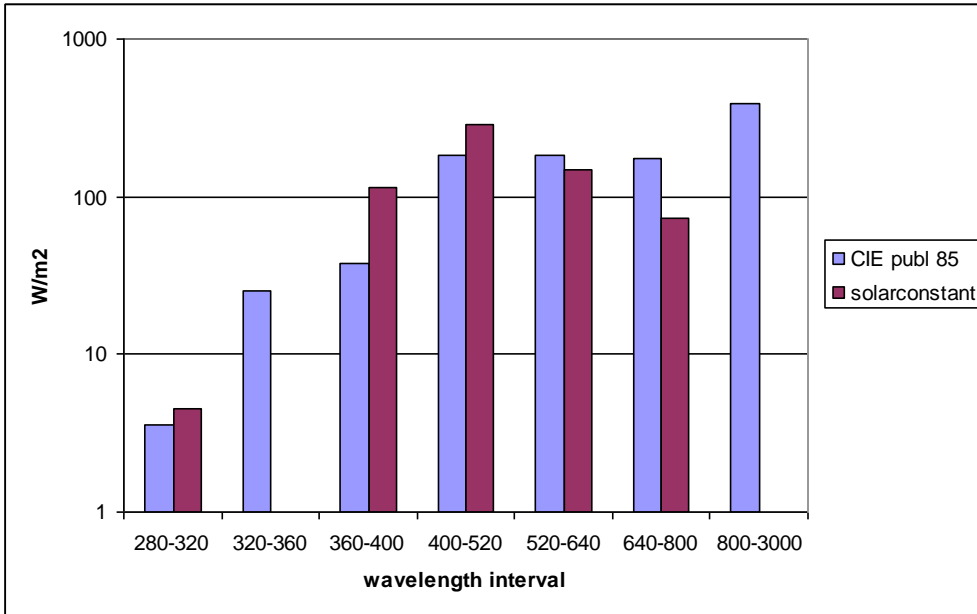


Figure B-5 Measured wavelength compared to standard spectrum suggested in CIE publication 85.

The exact exposure of solar irradiance on the oil in the meso-scale flume is somewhat difficult to calculate. Since the oil is moving, it will only be within the irradiated area periodically. The exposure will be highly dependent on the distribution of the oil in the flume and the thickness of the emulsion on the water surface. In Figure B-6 an estimated irradiation per day, using the solar simulator, is compared with the average irradiation per day for selected Norwegian cities.

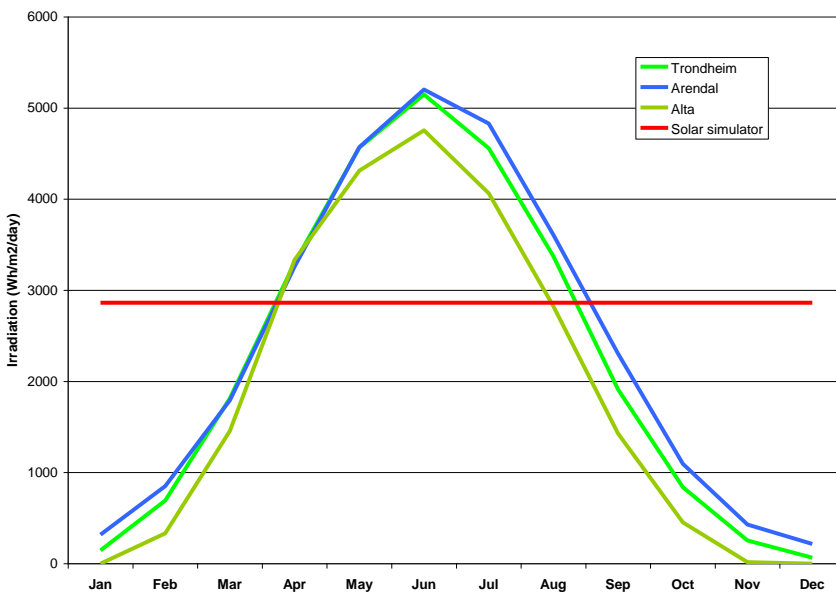


Figure B-6 Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume.



## C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Lille Prinsen are given in Table C-1 to Table C-3. The oil weathering predictions at 5 and 15 °C were based on the laboratory data at 13 °C.

Table C-1 Physical and chemical properties Lille Prinsen.

Properties of fresh oil	Values
Density (g/mL)	0.85089
Pour point (°C)	0
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	23
Flash point (°C)	-
Asphaltenes (wt. %)	0.53
Wax Content (wt. %)	4.71
Dispersible for visc. <	2500
Not dispersible for visc. >	1200
Max. water uptake vol.%	-

\* Measured at shear rate 100 s<sup>-1</sup>

-: Not analyzed /no data

Table C-2 True boiling point (TBP) curve of Lille Prinsen  
TBP based on "LP-Mini-Crude Assay (Intertek)

Temp. °C	Lille Prinsen Vol. %
48.0	4.92 %
56.0	5.80 %
64.0	6.12 %
72.0	7.60 %
80.0	8.38 %
88.0	9.08 %
96.0	10.60 %
103.0	12.85 %
112.0	14.64 %
120.0	16.17 %
128.0	17.75 %
136.0	19.18 %
144.0	20.74 %
150.0	21.93 %
160.0	23.59 %
165.0	24.54 %
174.0	26.21 %
182.0	27.43 %
190.0	28.68 %
198.0	30.05 %
205.2	31.44 %
213.3	32.51 %
222.0	34.20 %
230.6	35.99 %
239.2	37.87 %
250.0	40.17 %
261.2	42.71 %

271.0	44.26 %
277.0	45.39 %
285.5	47.32 %
294.0	49.09 %
302.4	50.76 %
310.8	51.49 %
317.9	52.52 %
326.3	54.86 %
334.6	56.56 %
344.1	58.83 %
350.0	60.25 %
550.0	87.51 %

Table C-3 Lab weathering data for Lille Prinsen, 13 °C.

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	199	251	304
Vol. Topped (%)	0	20	29	39
Weight Residue (wt. %)	100	84	75	65
Density (g/mL)	0.85089	0.88456	0.89739	0.91119
Pour point (°C)	0	15	21	24
Flash Point (°C)	-	43	77	114
*Viscosity of water-free residue (mPa.s = cP)	17	100	250	650
Viscosity of 50% emulsion (mPa.s = cP)**	-	970	1490	4570
Viscosity of 75% emulsion (mPa.s = cP)**	-	1900	3930	-
Viscosity of max water (mPa.s = cP)**	-	4680	8880	13950
Max. water cont. (vol. %)	-	90	83	75
(T1/2) Halftime for water uptake (hrs)	-	0.40	0.84	0.64
Stability ratio	-	1.00	1.00	0.99

\* Measured at shear rate  $100\text{ s}^{-1}$

\*\* Measured at shear rate  $10\text{ s}^{-1}$

- No data – not measured

## D Chemical characterization – OSCAR composition file

The method for generating oil profile as input for OSCAR is based on the quantification of semi-volatile organic hydrocarbons (SVOC) and volatile organic hydrocarbons (VOC) by GC-MS. The composition is divided into individual pseudo-component groups (OSCAR groups) representing the oil based on the TBP (True Boiling Point) and GC-MS analysis.

Table D-1 Chemical characterization of Lille Prinsen (fresh oil) from GC-MS analysis and TBP oil fraction.

Wt.%	Comp. group no.	Lille Prinsen SINTEF ID
3.000	1	C1-C4 gasses (dissolved in oil)
1.000	2	C5-saturates (n-/iso-/cyclo)
1.779	3	C6-saturates (n-/iso-/cyclo)
0.221	4	Benzene
3.200	5	C7-saturates (n-/iso-/cyclo)
0.968	6	C1-Benzene (Toluene) et. B
6.332	7	C8-saturates (n-/iso-/cyclo)
1.428	8	C2-Benzene (xylenes; using O-xylene)
2.625	9	C9-saturates (n-/iso-/cyclo)
0.947	10	C3-Benzene
3.100	11	C10-saturates (n-/iso-/cyclo)
0.079	12	C4 and C4 Benzenes
4.798	13	C11-C12 (total sat + aro)
0.023	14	Phenols (C0-C4 alkylated)
0.447	15	Naphthalenes 1 (C0-C1-alkylated)
8.053	16	C13-C14 (total sat + aro)
0.000	17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0
0.000	37	metabolite 1
0.000	38	metabolite 2
0.688	18	Naphthalenes 2 (C2-C3-alkylated)
5.012	19	C15-C16 (total sat + aro)
0.392	20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkyltd;<4 rings)
4.408	21	C17-C18 (total sat + aro)
7.500	22	C19-C20 (total sat + aro)
8.634	23	C21-C25 (total sat + aro)
0.366	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
35.000	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional Oil Spill Contingency And Response model system that calculates and records the distribution (as mass and concentrations) of contaminants on the water surface, on shore, in the water column and in sediments. The model allows multiple release sites, each with a specified beginning and end to the release. This allows time-variable releases at a given location, as well as throughout the study area. The model computes surface spreading, slick transport, entrainment into the water column, evaporation, emulsification and shore interactions to determine oil drift and fate at the surface. In the water column, horizontal and vertical transport by currents, dissolution, adsorption, settling and degradation are simulated. By modelling the fate of individual pseudo-components, changes in the oil composition due to evaporation, dissolution and degradation are accounted for.