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Report

Brasse crude oil – Properties and behaviour at sea

In relation to oil spill response

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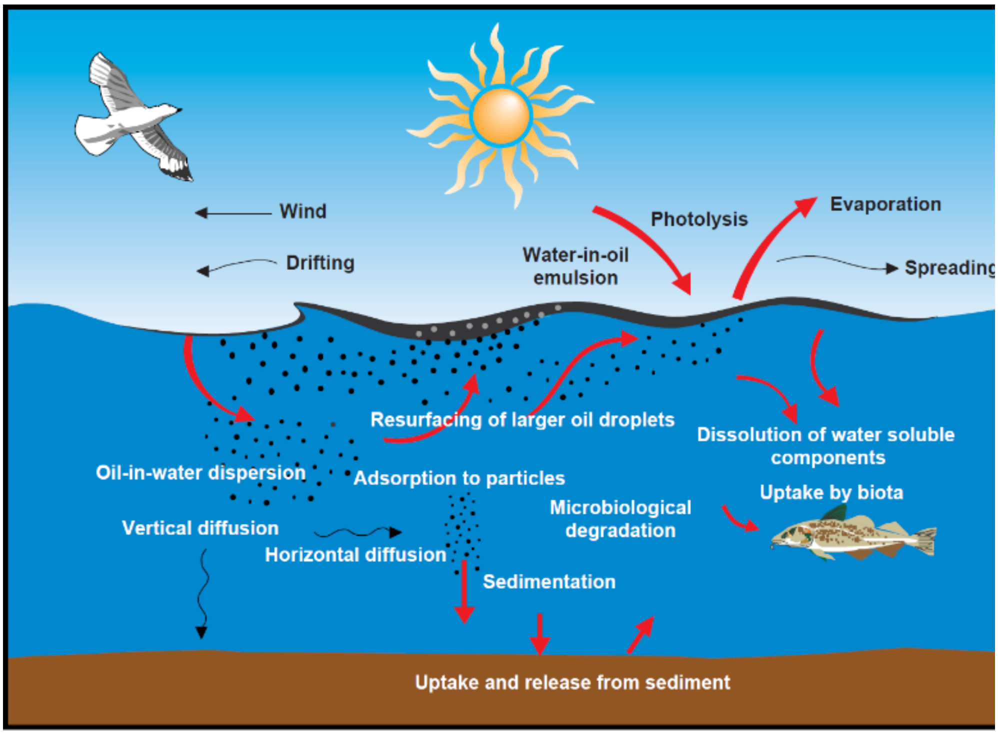

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Report

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ABSTRACT
A weathering study has been conducted on Brasse crude oil. This study included a small-scale laboratory study and a meso-scale flume basin experiment. In addition, standardized dispersibility tests was conducted on various dispersants and their efficiency was determined using the SINTEF Minitower to simulate an underwater dispersant injection. The SINTEF Oil Weathering Model (OWM) was used to predict the weathering properties of Brasse crude oil if spilled on the sea surface at 5 and 13 °C, reflecting winter and summer temperatures in the North Sea. The weathering properties are also discussed in relation to oil spill response by mechanical containment and recovery, and chemical dispersibility.

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Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill countermeasures. Oil weathering varies over time and with different environmental conditions. Based on input from the experimental weathering data, the SINTEF Oil Weathering Model (OWM) is used to predict the properties of oil as it weathered over time. 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). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Evaporation of the lightest compounds increases the relative amount of wax and asphaltenes and changes the physical properties on the residual oil. This summary gives a brief overview of the main changes predicted for Brasse crude oil when weathered on the sea surface.

Brasse is a paraffinic crude oil with a density of 0.847 g/mL with a low content of asphaltenes (0.16 wt. %), and a low to medium wax content (2.88 wt. %), compared with other Norwegian crude oils in the surrounding areas. The pour points of fresh Brasse oil and its residues ranges from -15 to + 24 °C.

We show here that Brasse can form high viscous water-in-oil (w/o) emulsions with a maximum water uptake of 75-80 vol. %. The emulsions formed were stable, but released water when adding different concentrations (500 and 2000 ppm by weight) of the emulsion breaker (Alcopol O 60 %). The highest concentration (2000 ppm) was shown to be the most effective and partly broke the emulsions. Emulsion breaker could effectively be used during an oil spill operation to remove or reduce water from the emulsion. Emulsion breakers are normally injected at the skimmer head prior to transferring the collected oil/water to storage tanks, which minimizes the storage volume.

The mass balance shows that oil is broken up and removed from the sea surface within 2 days in high wind speeds (15 m/s) at 5 and 15 °C, due to the high degree of evaporative loss and natural dispersion/entrainment. However, after 5 days with calm weather conditions (2 m/s wind speed) as much as ~ 65 % of the oil can remain on the sea surface.

In general, oil spilled on the sea surface assumes to reach the ambient water temperature within a short time period. The fire and explosion hazard will be high if the flash point of the oil is below the sea temperature. For Brasse surface spill, the flash point is predicted to exceed the sea temperature within the first 15-30 minutes at all wind speeds (2-15 m/s). Some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Brasse reaches this limit (60 °C) in 3-6 hours after a spill at calm wind speed (2 m/s) at summer and winter conditions, and more rapidly at higher wind speeds. However, as a general recommendation after an acute oil spill from a blowout release, a safety zone should be established early on and downwind from the spill site before response actions are initiated in cases of free gas reaches the surface.

The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous oils (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. Here we show that the emulsion viscosities of Brasse surpassed 1000 mPa.s after 2 hours at 5 m/s wind speed. In addition, viscosities > 15-20 000 mPa.s may reduce the flowability of the oil/emulsion when using traditional weir skimmers. Here we show, at the highest wind speeds (10-15 m/s), the oil/emulsion viscosities of Brasse exceeded this limit (15-20 000 mPa.s.) in 12 hours at 5 °C and in 1 day at 15 °C. Although, for lower wind speeds, sufficient flowability towards weir skimmers are expected within 5 days of weathering.

Brasse is expected to have a potential for chemical dispersion in both winter and summer conditions. The oil was estimated based on the dispersant testing to be easily dispersible with the dispersant Dasic NS, for viscosities < 2500 mPa.s. Our study showed, however, that Brasse has a potential to be reduced dispersible with Dasic NS at oil viscosities from 2500 mPa.s up to 15 000 mPa.s with a dispersant to oil ratio (DOR) 1:25. In the field, if the viscosity of Brasse is between 2500 mPa.s and 15 000 mPa.s after dispersant spraying, and thus has a reduced dispersibility, additional energy (e.g. thrusters, Fire Fighting (Fi-Fi) systems or MOB (Man over board) boats) or higher DOR and/or repeated dispersant application may increase dispersant effectiveness. It is expected that

Brasse, particularity in calm weather conditions, requires artificial energy and high DOR to enhance the dispersibility of the oil emulsions.

The effect of subsurface injection of dispersants was evaluated on Brasse. The tested dispersants produced a reduction in droplet size distribution with increasing DOR. Here Corexit 9500 shows the greatest decrease in the oil droplet size and most efficient at a DOR of 1:50. Dasic NS, found to be the most efficient dispersant for surface dispersion, produced the lowest droplet size reduction, and the reduced efficiency could be compensated using a higher DOR.

Increased weathering could potentially increase the pour point of Brasses to the point of solidification at the sea surface, especially at 5 °C. In such cases, if solidified (low emulsified /water free) lumps are observed on the sea surface, the use of a high-viscosity skimmer may be recommended, and lower dispersant effectiveness is likely.

Finally, the weathering properties of Brasse vs. Brage show similarities between the two oils, and Brage could therefore considered as an acceptable candidate as a reference crude oil in oil spill contingency analysis. The oils are not expected to give very different outputs from such analysis.

Short summary of the main findings from this project

- Compared with other Norwegian crude oils, Brasse is a medium density crude oil (0.847 g/mL) with a low to medium content of wax (2.88 wt. %), and a low content of asphaltene (0.16 wt. %)
- The flash points of Brasse will be above the sea temperature within 15-30 minutes at winter and summer temperature at 2 m/s, and earlier at higher wind speeds
- Brasse forms high viscous water-in-oil (w/o) emulsions with a maximum water uptake of 75-80 vol. %
- The emulsions formed were found to be stable, but released water when adding emulsion breaker (Alcopol O 60 %). The use of emulsion breaker could be considered for Brasse to increase the storage capacity when recovered
- A combined response of chemical dispersion and mechanical recovery could be applied to a Brasse oil spill, both under summer and winter conditions. The emulsion film thicknesses are not considered as limiting factor for either mechanical recovery or chemical dispersion from a surface release
- Wide window of opportunity for mechanical recovery with use of skimmers, such as the Transrec equipped with traditional weir-skimmer head
- The oil has a potential for solidification due to high pour points of the residues. In such cases, use of high-viscosity skimmer could be recommended, and lower dispersant effectiveness is likely
- Brasse is easily dispersible with the dispersant Dasic NS for viscosities < 2500 mPa.s, and found not dispersible for viscosities >15 000 mPa.s
- In the field, additional energy or higher DOR and/or repeated dispersant application may increase dispersant effectiveness if viscosities are between 2500 mPa.s and 15 000 mPa.s
- The effect of subsurface injection of dispersants showed that Corexit 9500 had the greatest decrease of the oil droplet size compared with the other dispersants, and found most efficient at DOR of 1:50

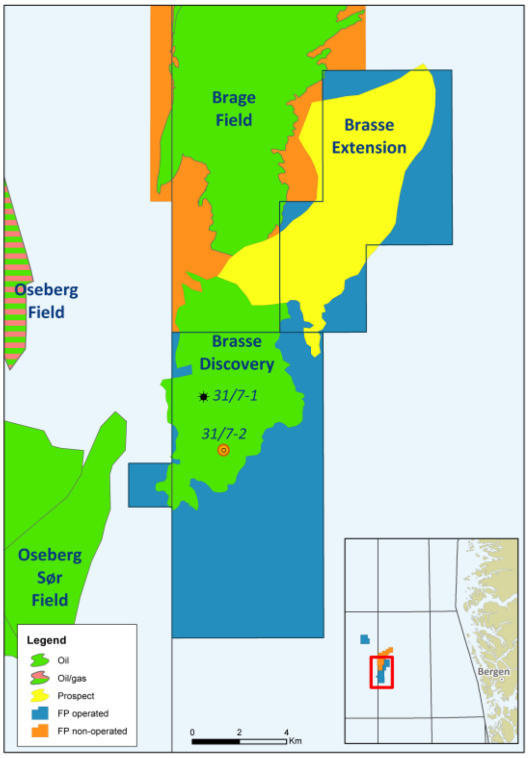
1 Introduction

New oil types (from heavy crude oil to light crude oils and condensates) are continuously coming into production worldwide. 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.

The Deepwater Horizon incident in the Gulf of Mexico (2010) clearly showed how dispersant application efficiency may change as oil is weathered and emulsified on the sea surface over a long period. These past experiences shape the knowledge base and the subsequent refinement of future operative strategies in terms of where, when and how dispersants may be effectively applied during a response operation.

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway 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 on all oils coming into production.

SINTEF Ocean, Dept. of Environment and New Recourses has performed a weathering study and dispersibility testing on Brasse crude oil based on a request from Faroe Petroleum. The weathering study was conducted at 13 °C The obtained weathering data were used to predict the weathering properties of the oil by use of the SINTEF Oil Weathering Model (OWM), if spilled at sea under different wind speeds (2,5,10 and 15 m/s) at sea temperatures of 5 and 13 °C.



The Brasse prospect is located in the Upper Jurassic Sognefjord formation. The Brasse field discovery was made by Faroe in 2016 and is located within tie-back distance to existing infrastructure: 13 kilometres to the south of the Wintershall-operated Brage field platform, in which the Company holds a 14.3% working interest and 13 kilometres to the south east of the Statoil-operated Oseberg Field Centre.

Key project milestones include the Final Concept Selection and the submission of a Plan for Development and Operations (PDO), both of which are planned for 2018. Water depth~118 m.

http://www.fp.fo/license/brasse/

Figure 1-1: Brasse field discovery (PL740 /PL740B) location in the North Sea (http://www.fp.fo/wp-content/uploads/2017/05/Brasse-.jpg)

2 Small-scale laboratory testing results

The methodology of small-scale testing is described in Appendix B. Physicochemical parameters and weathering properties of Brasse were also compared with other relevant crude oils from the North Sea region, including Brage, Veslefrikk, Oseberg A, and Oseberg Sør from the neighbouring fields (Table 2-1). The crude oils in comparison were selected in agreement with Faroe Petroleum. Brasse crude oil was given the SINTEF ID: 2017-5349.

Table 2-1: Oils compared with Brasse crude oil data in the report

Oil	SINTEF-ID	Report Number	Reference
Brage	2012-0246	SINTEF A24699	Farooq, 2013
Veslefrikk	2012-0004	SINTEF A23535	Strøm, 2012
Oseberg A	2012-0341	SINTEF A25226	Strøm, 2013
Oseberg Sør	2012-0245	SINTEF A24709	Sørheim and Vadla, 2013

2.1 Pre-handling and homogenization

Three barrels (25 L) of Brasse crude oil were measured for water content, density and hydrocarbon distribution on GC/FID (see chapter 2.2 for explanation) upon arrival. The oil samples had water contents lower than 2 vol. %, and no additional laboratory HSE precautions for distillation (topping) were therefore required. The samples were further heated and homogenized prior to physicochemical analysis according to SINTEF`s internal procedures for pre-handling of crude oils.

2.2 Chemical composition and physical properties

The chemical composition of the hydrocarbon profile of *n*-alkanes ($n\mathrm{C}_5$-$n\mathrm{C}_{36}$) of Brasse crude oil is shown in Figure 2-1. The wax and asphaltene contents are given in Table 2-3, and the physical properties of the crude oil are given Table 2-4. Appendix D shows the composition of OSCAR groups derived from the chemical characterization of the fresh crude oil based on GC-MS analysis and the boiling point fraction.

Gas chromatographic flame ionization detector (GC-FID) characterization

The hydrocarbon profile of the Brasse crude oil was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 2-1 illustrates the GC-FID output (i.e. gas chromatogram) of the fresh oil and its corresponding evaporated residues at three different temperatures (150, 200 and 200°C+). The loss of low molecular weight compounds (shown towards the left of the chromatogram) at the three temperatures mimics that of natural weathering, and provides support for the artificial evaporation of the crude oil by use of distillation (topping) in the laboratory.

The gas chromatograms show the *n*-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, are shown as a broad and poorly defined bump below the sharp peaks, and are often described as the “Unresolved Complex Mixture” (UCM). Brasse exhibits a relative high content of UCM compared to Brage, Veslefrikk and Oseberg Sør, whilst Oseberg A and Brasse are more comparable as shown in Figure 2-2. Heavier compounds such as asphaltenes ($> n\mathrm{C}_{40}$) are not possible to analyze with this technique. The GC characterization shows that Brasse crude oil is a paraffinic crude oil with a high content of light components.

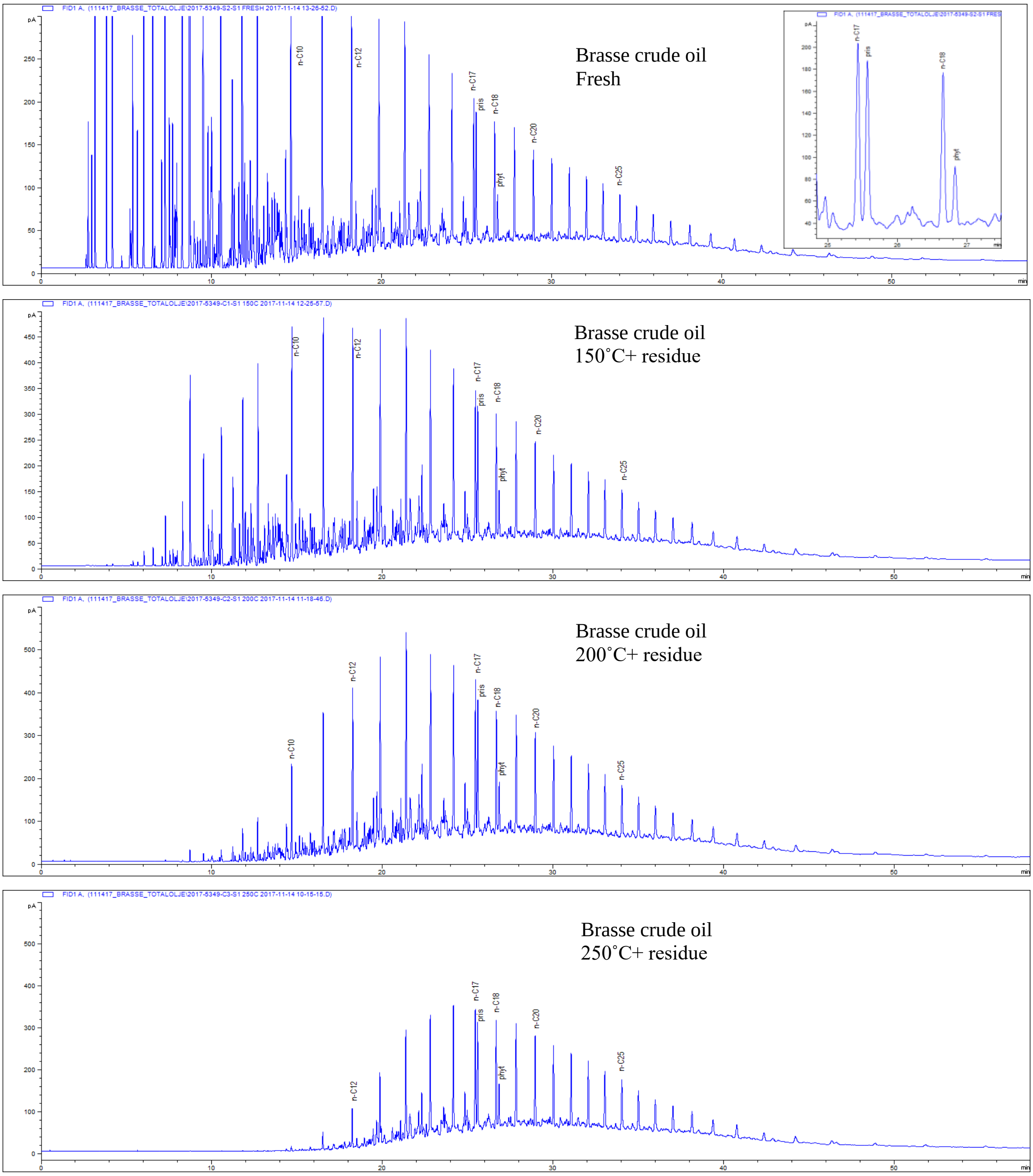


Figure 2-1: GC/FID chromatograms of fresh sample and evaporated residues of Brasse crude oil

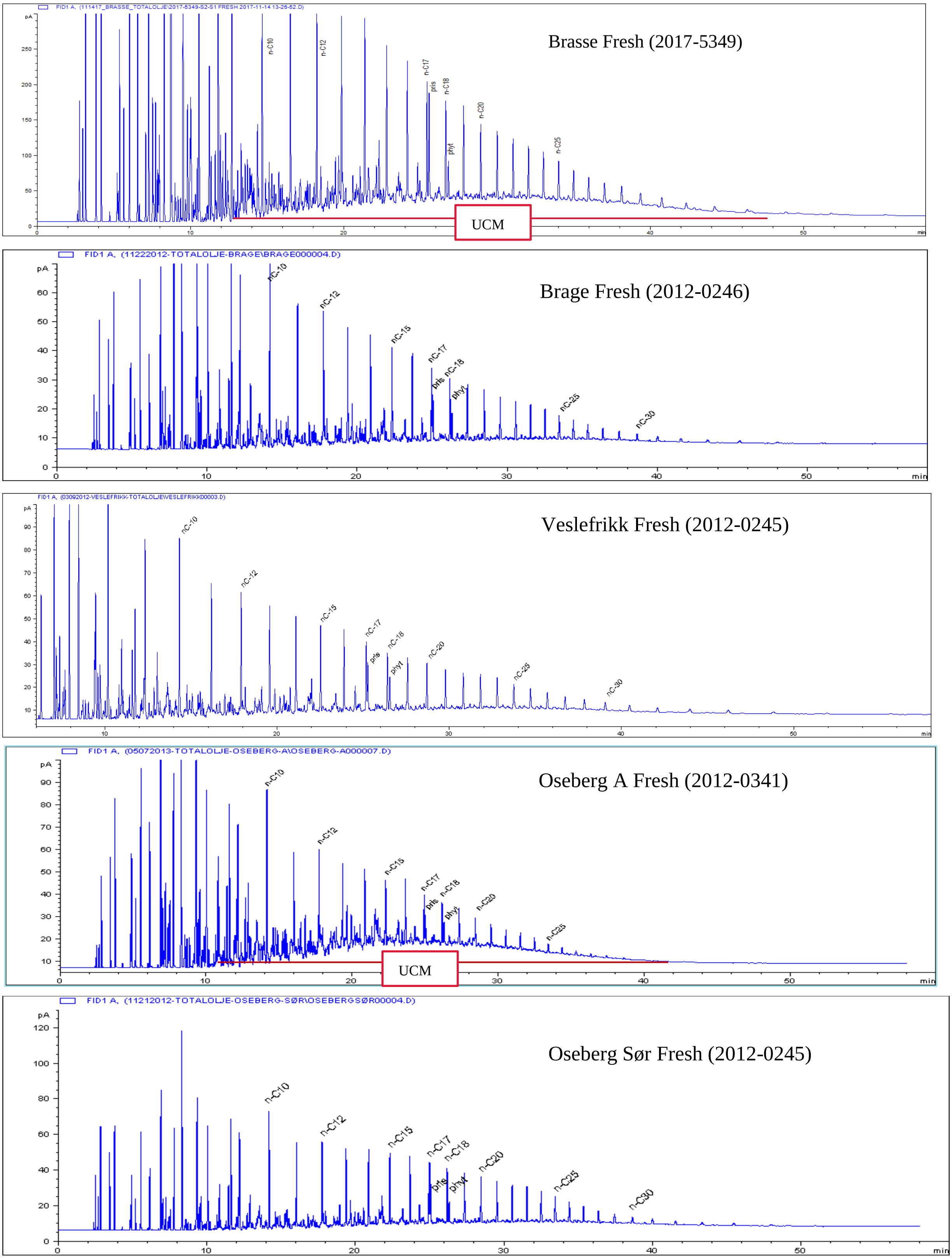


Figure 2-2: GC/FID chromatograms for fresh oils used for comparison (Brasse, Brage, Veslefrikk, Oseberg A and Oseberg Sør)

GC-FID is also a tool in oil spill identification, where common screening parameters are the $n\mathrm{C}_{17}$/pristane and $n\mathrm{C}_{18}$/phytane ratios. These ratios relate the more biodegradable *n*-alkanes to the more recalcitrant isoprenoids (pristane and phytane). Thus, the ratios of nC_{17}/pristane and $n\mathrm{C}_{18}$/phytane are reduced as biodegradation proceeds. These ratios for Brasse are compared to other crude oils in Table 2-2.

Table 2-2: nC_{17}/Pristane and nC_{18}/Phytane ratios

Oil	**$n\mathrm{C}_{17}$/Pristane**	**$n\mathrm{C}_{18}$/Phytane**
Brasse	1.1	2.6
Brage	1.7	2.4
Veslefrikk	1.5	1.8
Oseberg Sør	1.0	2.7
Oseberg A	1.7	2.0

Asphaltene and wax content for the fresh and weathered residues

The contents of asphaltene and wax are given in Table 2-3. Brasse has a low to medium content of wax (2.88 wt.%), whilst Brage, Veslefrikk and Oseberg Sør exhibit medium to high wax contents, compared with other Norwegian crude oils. Compared to the asphaltenic Oseberg A, fresh Brasse has a lower content of asphaltene (0.16 wt.%) and is in the same range as the other oils listed (except for Oseberg A). Oseberg A has a higher content of asphaltene (1.1 wt.%) compared with the other listed Norwegian crude oils from this region in the North Sea (Table 2-3).

Table 2-3: Asphaltene ("hard") and wax content for Brasse and other relevant crude oils for comparison

Oil type	**Residue**	**Asph. "hard" (wt. %)**	**Wax (wt. %)**
Brasse	Fresh	0.16	2.88
	150°C+	0.19	3.54
	200°C+	0.22	4.10
	250°C+	0.27	4.93
Brage	Fresh	0.1	4.7
	150°C+	0.2	5.6
	200°C+	0.2	6.5
	250°C+	0.2	8.0
Veslefrikk	Fresh	0.3	6.7
	150°C+	0.4	8.4
	200°C+	0.4	9.5
	250°C+	0.5	11.0
Oseberg A	Fresh	1.1	1.5
	150°C+	1.2	1.6
	200°C+	1.3	1.7
	250°C+	1.4	1.8
Oseberg Sør	Fresh	0.11	5.6
	150°C+	0.13	6.4
	200°C+	0.15	7.3
	250°C+	0.17	8.4

Physical properties for the fresh and weathered residues

The physical properties of the fresh and the water free residues of Brasse are listed in Table 2-4 and are compared to other crude oils. Brasse, Brage and Veslefrikk show similarities in their evaporative loss. The viscosities are lower for Brasse compared with Brage, Veslefrikk and Oseberg Sør due to its lower wax content. The weathered residues of the paraffinic oils (Brasse, Brage, Veslefrikk and Oseberg Sør) all exhibit high pour points. However, fresh Brasse has a much lower pour point due to a lower wax content. Oseberg A exhibits very low pour points for all its residues, which is caused by its high asphaltene content preventing precipitation and lattice formation of wax structures.

Figure 2-3 shows that the high initial and decay in IFT values of Brasse with respect to time is very significant for the fresh oil and its residues. The IFT values confirm that the surface-active components from the oil migrate towards the oil/water interface and hence decreases the IFT values with respect to time, which is valid for low asphaltenic crude oils.

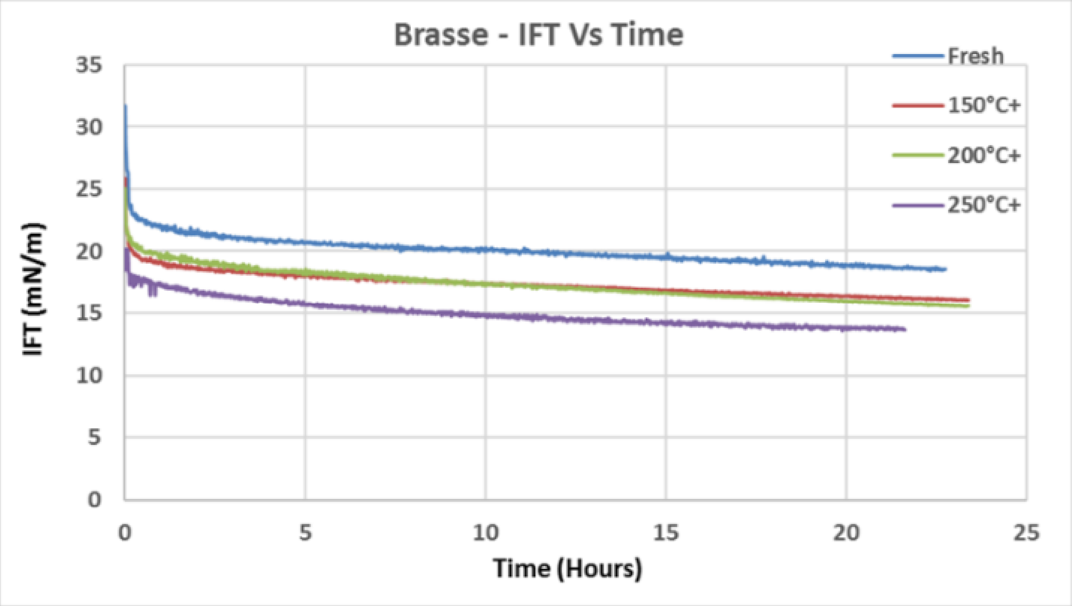


Figure 2-3: Interfacial tension decay of Brasse fresh crude oil and its residue with respect to time

Table 2-4: Physical parameters of Brasse crude oil, and other relevant oils for comparison

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 13 °C (10 s^{-1})	IFT (mN/m) ini.
Brasse	Fresh	0	100	0.847	-	-15	9	30
	150°C+	22	81	0.879	43	9	102	25
	200°C+	34	70	0.845	85	18	408	25
	250°C+	46	58	0.911	123	24	1964	18
Brage	Fresh	0	100	0.826	-	-6	40	30
	150°C+	19	84	0.849	37	15	231	29
	200°C+	31	72	0.861	72	24	872	24
	250°C+	45	59	0.875	116	27	5603	-
Veslefrikk	Fresh	0	100	0.825	-	3	7	-
	150°C+	23	80	0.860	47	18	259	-
	200°C+	33	71	0.872	77	21	969	-
	250°C+	43	61	0.884	113	24	4728	-
Oseberg A	Fresh	0	100	0.902	-	-21	53	27
	150°C+	7.6	94	0.915	42	-33	93	23
	200°C+	16	87	0.926	77	-27	215	24
	250°C+	26	77	0.939	118	-15	2006	19
Oseberg Sør	Fresh	0	100	0.839	-	9	98	28
	150°C+	16	86	0.862	38	15	459	26
	200°C+	27	76	0.873	77	24	1274	18
	250°C+	37	67	0.883	110	27	6931	-

-: *No data*

2.3 Emulsifying properties

Emulsification

In general, emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion), forming a weathered oil residue that often tends to be relatively resistant to other weathering processes such as evaporation, and increases the total volume of oil due to the uptake of water into the oil.

The emulsifying properties of Brasse crude oil were studied by use of rotating cylinders as described in Hokstad et al., 1993, see Appendix B. Experiments containing residues of 150°C+, 200°C+ and 250°C+ were made to produce data for stability, viscosity, maximum water uptake, kinetics, and the effectiveness of the emulsion breaker application. The emulsion containing the maximum water content after 24 hours rotation is shown in Figure 2-4, below. The figure shows from left to right emulsions prepared from the residues of 150°C+, 200°C+ and 250°C+, respectively.

Figure 2-4: Rotating cylinders of water-in-oil (w/o) emulsions of Brasse crude oil after 24 hours at 13 °C

Water uptake and maximum water content

The rate of water uptake (kinetics) was also studied by use of the rotating cylinders. The water content in the water-in-oil (w/o) emulsions as a function of time is tabulated in Table 2-5. The $t_{1/2}$ value is defined as the time (hours) it takes to incorporate half of the maximum water uptake (vol. %) in 24 hours (rotating time).

After 24 hours, Brasse expressed a rapid and high-water uptake for the residues 150°C+, 200°C+ and 250°C+, which ranged from 74 to84 vol. %, as shown in Table 2-5.

Table 2-5: Water uptake for the evaporated residues of Brasse 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	24	13	0
10 min	33	24	3
15 min	44	34	8
30 min	53	46	33
1 hour	63	57	62
2 hours	71	69	74
4 hours	86	83	75
6 hours	87	82	75
24 hours	84	81	74
$t_{1/2}$	0.28	0.37	0.49

** 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.*

Stability and efficiency of emulsion breaker

In mechanical recovery operations, separating oil from water enables optimal use of available storage (i.e. facilities/tankers) and the stability and efficiency of this separation can be enhanced by applying emulsion breakers. The effectiveness of the emulsion breaker Alcopol O 60% was evaluated on different residue fractions of emulsified Brasse crude oil. Our results shown that the emulsified oil volume decreased after treatment with the emulsion breaker in all residues, as water was released from the emulsion (Table 2-6).

The emulsion stability of Brasse was studied by quantifying the amount of water released from the emulsion after 24 hours settling time. The crude oil formed stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first row of Table 2-6. The emulsions were partly broken when adding the emulsion breaker (Alcopol O 60%). A concentration of 2000 ppm (0.2 wt. %) was shown to be most effective to break the emulsions.

Table 2-6: Stability of emulsion and the effectiveness of emulsion breaker at 13 °C of Brasse crude oil

Residue	**Emulsion breaker**	**Water-in-oil emulsion (vol. %) at 25 °C**		**Stability ratio****
		Reference	**24 hours ***	
150ºC+	none	84	84	1.00
200ºC+	none	81	81	1.00
250ºC+	none	74	74	1.00
150ºC+	Alc. O 60 % 500 ppm	84	58	0.30
200ºC+	Alc. O 60 % 500 ppm	81	60	0.29
250ºC+	Alc. O 60 % 500 ppm	74	63	0.81
150ºC+	Alc. O 60 % 2000 ppm	84	12	0.25
200ºC+	Alc. O 60 % 2000 ppm	81	19	0.29
250ºC+	Alc. O 60 % 2000 ppm	74	21	0.58

ppm: parts per million

**: 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*

-no data

Viscosities of water-free and emulsified residues

The viscosity of an oil describes the oils ability to resist gradual deformation by increasing shear, where viscosities of so-called *Newtonian* oils remains constant independent on the applied shear rate (s^{-1}) at a given temperature. When shear is applied on so-called *non-Newtonian* oils, the viscosity of such oils decreases.

The viscosities of the fresh oil, water-free residues and emulsified residues of Brasse crude oil at 13 °C are given in Table 2-7. The fresh oil behaves as a *Newtonian* fluid with shear rates of 10, 100 and 1000 s^{-1}. The water-free residues and 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 (10 s^{-1}) compared to the viscosities measured at higher shear rates (100 and 1000 s^{-1}). The yield stress, the force that must be applied to make the oil to begin to flow, is tabulated in Appendix E.

Table 2-7: Viscosity of fresh oil, residues and emulsions of Brasse at 13 °C

Residue	**Water content (vol. %)**	**Viscosity (mPa.s) 13 °C**		
		10 s^{-1}	**100 s^{-1}**	**1000 s^{-1}**
Fresh	0	9	9	9
150°C+	0	102	64	39
200°C+	0	408	197	97
250°C+	0	1964	676	273
150°C+	50	375	233	n.a.
200°C+	50	1426	567	n.a.
250°C+	50	6103	1238	n.a.
150°C+	75	1306	433	n.a.
200°C+	75	4161	1092	n.a.
250°C+	75	13129	2411	n.a.
150°C+	86	4332	793	n.a.
200°C+	81	8162	1490	n.a.
250°C+	75	15861	3513	n.a.

n.a: not applicable

2.4 Chemical dispersibility

The dispersibility testing of Brasse crude oil included:

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

Screening testing of dispersants

The screening testing was performed using the low energy test (IFP), reflecting non-breaking waves (< 5 m/s wind speed) according to the Norwegian dispersant testing regulations. In addition, due to the low effectiveness shown with IFP-test, dispersant effectiveness was also tested with use of the high energy MNS test (reflecting breaking waves; > 5m/s wind speed). The screening testing was performed at a standard temperature of 13 °C, using a 200°C+ residue emulsified with 50 vol. % seawater. The results are presented in Table 2-8. Dasic NS expressed the highest dispersibility effectiveness on IFP, with only a 14 wt. %. However, the MNS test showed that Dasic NS, Corexit 9500 and Finasol OSR 52 were 100 % effective when applied on the same emulsion. Radiagreen OSD is European Maritime Safety Agency (EMSA) "green" product, and is not included as a part of the dispersant stockpile in Norway.

Table 2-8: Screening testing on Brasse 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)* IFP	Efficiency dispersant (200°C+ /50 vol. % emulsion)** MNS
Dasic NS	14	100
Corexit 9500	8	100
Finasol OSR 52	8	100
Gamlen OD 4000	6	-
Radiagreen OSD	12	-

** Emulsion viscosity: 1426 mPa.s ($10s^{-1}$)*

*** Emulsion viscosity: 1708 mPa.s ($10s^{-1}$)*

-: Not analysed

Dosage testing of dispersants

Dosage testing with Dasic NS, Corexit 9500 and Finasol OSR 52 was performed at 13 °C, using a similar emulsion as for the screening test, as described above. The dosage test helps to identify optimal design conditions for dispersant use, and was performed with dispersant-to-oil/emulsion ratios (DOR /DER) of 1:25, 1:50, 1:100 and 1:200, and also with no dispersant added. The results are presented in Table 2-9. For the MNS-test, the results indicate high dispersibility of Brasse (200°C+) in breaking waves conditions (> 5 m/s wind speed), with results ranging from 80-100 wt.% for the different (DOR /DER). A relatively high effectiveness (33 wt. %) was also measured with no dispersant added. The IFP-test showed low effectiveness on DOR/DER 1:25, and further testing at lower dosages were therefore not performed.

Table 2-9: Dosage testing on Brasse at 13 °C

Dispersant (DOR/DER)	Effectiveness of dispersant on 200°C+/50 vol. % emulsion*	
	IFP	MNS
Dasic NS (1:25)	14	100
Corexit 9500 (1:25)	8	100
Finasol OSR 52 (1:25)	8	100
Dasic NS (1:50)	-	100
Corexit 9500 (1:50)	-	100
Finasol OSR 52 (1:50)	-	100
Dasic NS (1:100)	-	100
Corexit 9500 (1:100)	-	100
Finasol OSR 52 (1:100)	-	100
Dasic NS (1:200)	-	100
Corexit 9500 (1:200)	-	100
Finasol OSR 52 (1:200)	-	82
No dispersant	-	33

**The viscosity of the emulsion 1813 mPa.s ($10s^{-1}$)*

-: Not analysed due to low dispersant effectiveness

Systematic dispersant testing of the oil dispersibility at varying weathering

Dasic NS was chosen for the continued systematic testing of the oil dispersibility at varying weathering degrees to determine the time window for dispersant use. Dasic NS is the dispersant agent in NOFO's stockpile, and a dosage rate of 1:25 (4 wt.%) is commonly used as the standard procedure to establish the time window for dispersant application, and was also shown to be a good representative among the dispersants tested form this study.

Table 2-10 shows the tabulated results from this testing as basis to estimate the dispersibility limits expressed as a function of effectiveness and viscosities (see Figure 2-5). The dispersibility limits (viscosities) are further used as input to the SINTEF Oil Weathering Model (OWM) to predict the time-window for dispersant use.

Table 2-10: Effectiveness of dispersant on weathered Brasse oil/emulsions at 13 °C

Residue	Water content (vol. %)	Viscosity (mPa.s) 10 s^{-1}	Effectiveness (%)	Effectiveness (%)
			IFP	MNS
150°C+	0	102	68	100
200°C+	0	408	51	100
250°C+	0	1964	1	55
150°C+	50	375	81	95
200°C+	50	1426	14	100
250°C+	50	6103	3	50
150°C+	75	1306	75	78
200°C+	75	4161	12	66
250°C+	75	13129	4	10
150°C+	86	4332	68	33
200°C+	81	8162	14	9
250°C+	75	15861	3	4

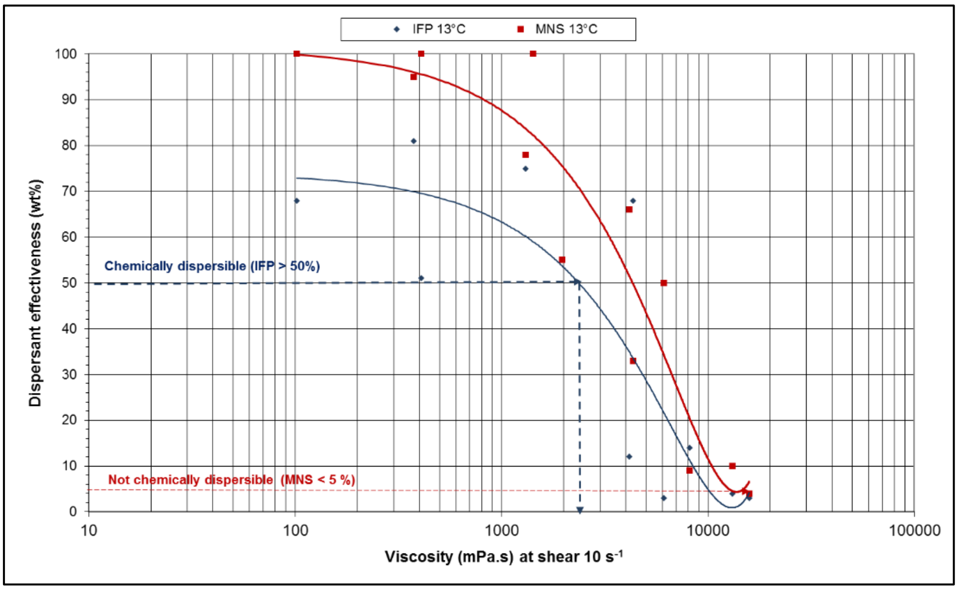


Figure 2-5: Dispersant effectiveness on oil/emulsion of Brasse crude oil at 13 °C

Brasse was found to be dispersible for viscosities lower than 2500 mPa.s, reflecting 50 % effectiveness by use of the IFP-test. Moreover, reduced dispersibility is expected with viscosities above 2500 mPa.s and up to 15 000 mPa.s. It should be emphasized that reduced dispersibility means that the oil/emulsion is still dispersible, but may require additional energy and/or higher dispersant dosage to enhance effective dispersion. The viscosity limit where Brasse is not dispersible, expressed with effectiveness lower than 5 % using the MNS-test, was estimated to 15 000 mPa.s. The dispersibility limits are also summarised in Table 2-11.

Table 2-11: Estimated viscosity limit for Brasse for use of dispersant and criteria for definition of time window

Dispersibility	**Criteria for effectiveness (wt. %)**	**Dispersibility limits based on oil/emulsion viscosity (mPa.s)**
Chemically dispersible	IFP > 50 %	2500
Not chemically dispersible	MNS < 5 %	15 000

3 Meso-scale flume laboratory testing results

The description of the meso-scale flume is given in Appendix B.3. This section provides an overview of the results from the flume testing, including the weathering properties, estimated mass balance and visual observations of the Brasse crude oil. The results obtained give valuable operational information about the oil's behaviour. The weathering behaviour in the flume basin was found to be an important supplement to the small-scale laboratory testing.

The experimental results obtained for Brasse in the meso-scale laboratory testing are presented below Table 3-1 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 points throughout the test.

Table 3-1: Results from the meso-scale flume laboratory testing of Brasse crude oil at 13 ºC

Sample no	Time (hours)	Water content (vol%)	Evaporative loss (wt%)	Viscosity (mPas), 10 s^{-1}	Oil-in-water ppm*
P1	0.5	70	19	201	-
P2	1	72	22	273	26
P3	2	75	24	403	-
P4	4	80	27	301	-
P5	6	80	30	493	10
P6	12	81	31	1006	-
P7	24	78	34	2955	5
P8	48	77	39	5603	6
P9	72	78	37	7119	6
1st application of dispersants: 67.2 g Dasic NS (DOR = 1.5 wt. %)					
10 min. disp 1	-	-	-	-	33
30 min. disp 1	-	36	-	3020	39
2nd Application of dispersants: 71.1 g Dasic NS (DOR= 1.6 wt. %)					
10 min. disp 2	-	-	-	-	119
30 min. disp 2	-	41	-	3111	157
3rd Application of dispersants: 68.9 g Dasic NS (DOR= 1.5 wt. %)					
10 min. disp 3	-	-	-	-	326
30 min. disp 3	-	-	-	-	383
60 min. disp 3	-	-	-	-	392
120 min. disp 3	-	42	-	3631	283

-: no measured data. **:ppm=parts per million*

The oil weathering results from the flume basin (maximum water uptake, evaporative loss and emulsion viscosity) were compared with the weathering prediction using the SINTEF Oil Weathering Model (OWM) derived from the small-scale study given in Figure 3-1, Figure 3-2 and Figure 3-3.

The evaporative loss (Figure 3-1) shows that the predicted and experimental flume data harmonized well. The emulsion water content from the flume experiment (Figure 3-2) indicated a higher water uptake in the first 2-3 hours compared with the predicted data. This is probably due to the unstable emulsion observed in the flume containing larger oil droplets. After 3 hours of weathering, the maximum water uptake from the flume and the predicted water uptake has reach the same level around 80 vol. %. The evolution of emulsion viscosities from the flume experiment also harmonized with the predicted data.

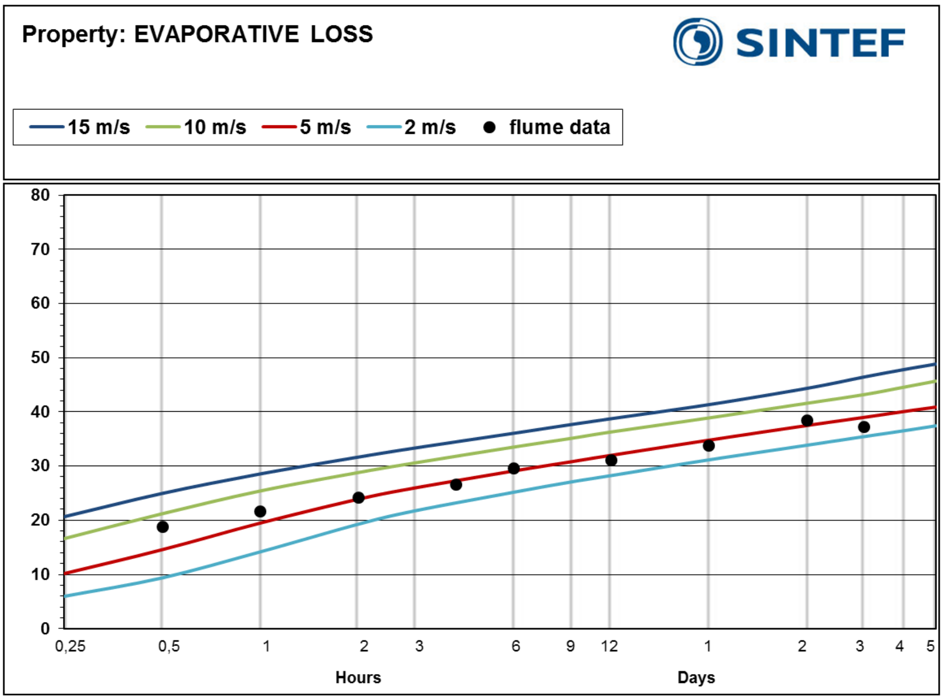


Figure 3-1: Predicted evaporative loss for Brasse crude oil. The dots represent the experimental data from the meso-scale flume testing

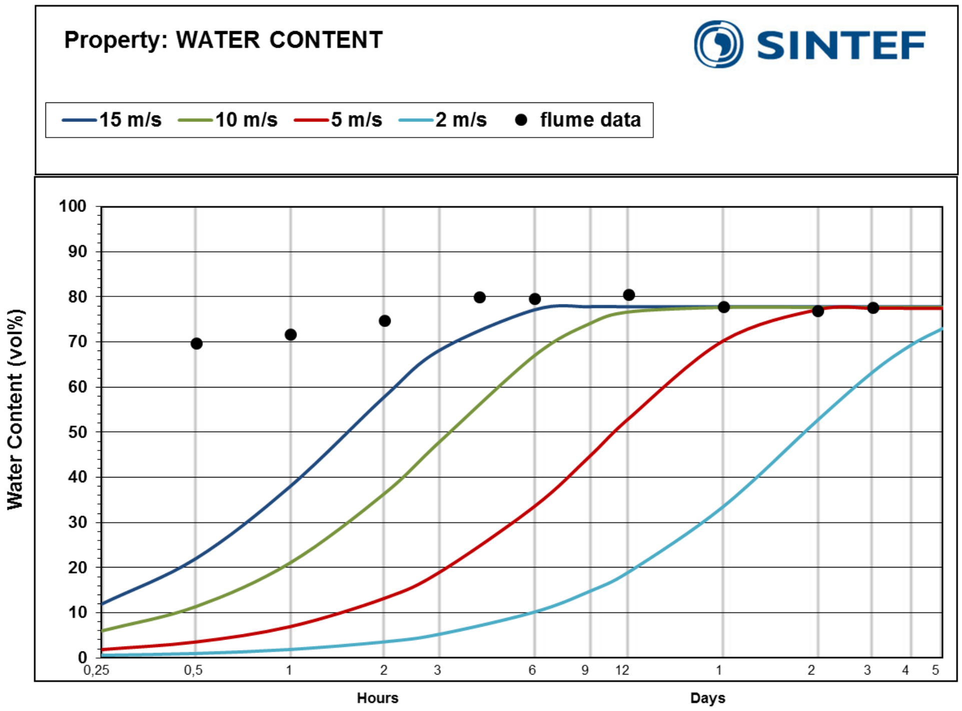


Figure 3-2: Predicted water uptake for Brasse crude oil. The dots represent the experimental data from the meso-scale flume testing.

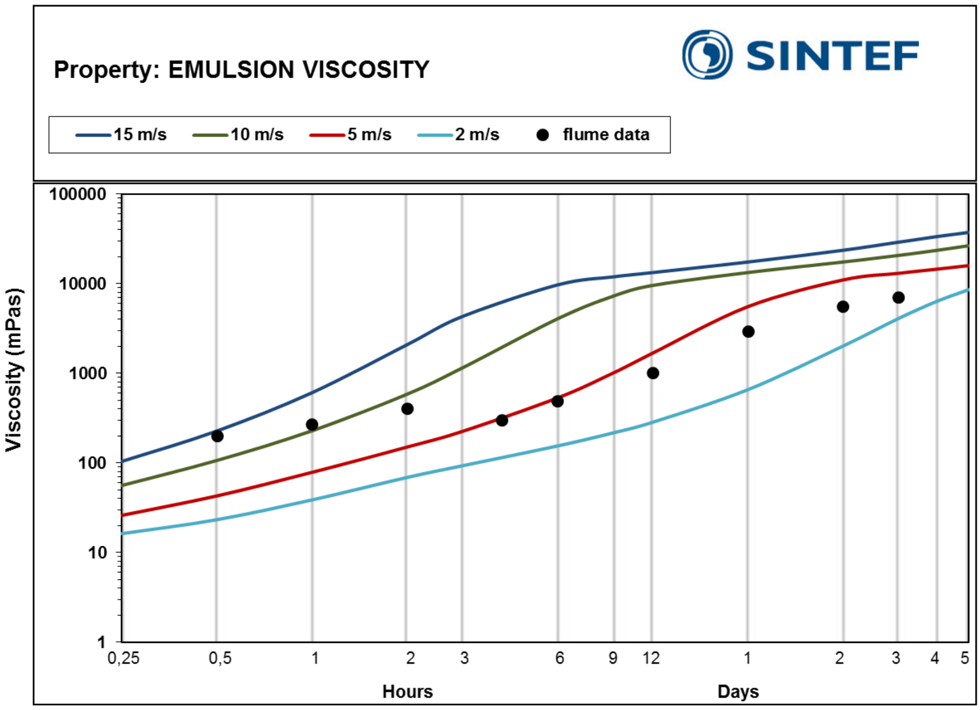


Figure 3-3: Predicted viscosity for Brasse crude oil. The dots represent the experimental data from the meso-scale flume testing.

Mass balance

The main elements in the mass balance for a crude oil spilled at sea are: evaporative loss, the amount of oil at the surface, and the amount of oil dispersed. In order 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. Figure 3-4 shows the mass balance before applying dispersant agent into the flume, whilst Table 3-2 shows the estimated results (by weight) of the mass balance after 24 hours of weathering time.

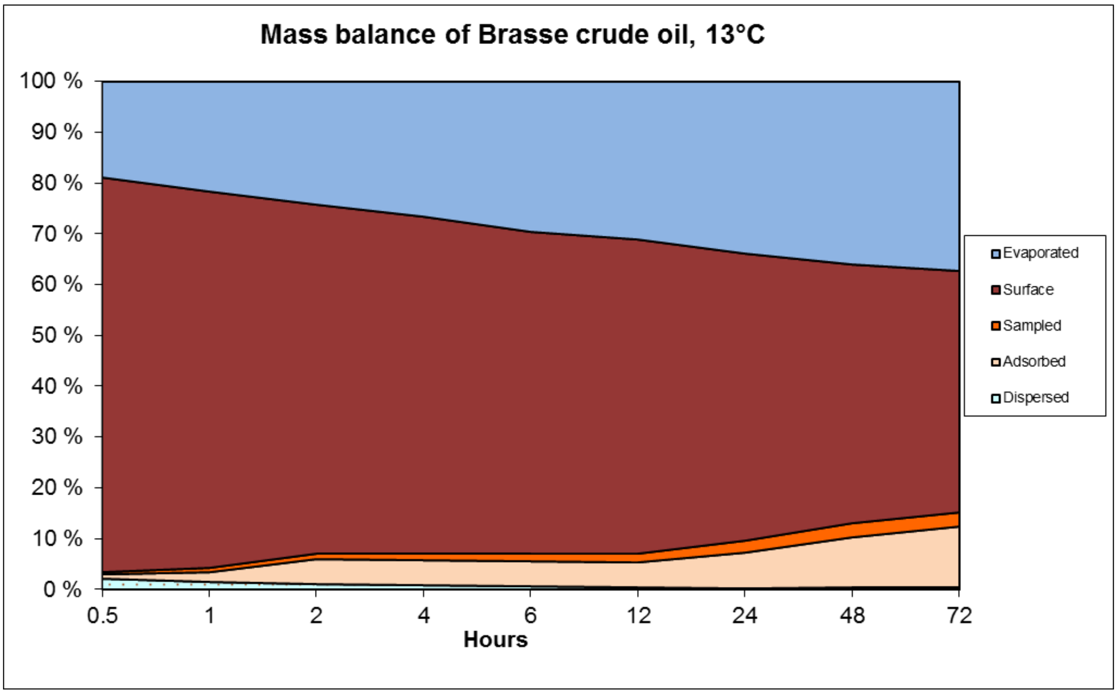


Figure 3-4: **Mass balance for Brasse crude oil in the meso-scale flume basin at 13 °C, before dispersant application**

Table 3-2: Tabulated values of the estimated mass balance of Brasse by weight. Example after 24 hours weathering time.

Properties	**Mass balance (% of initial oil)**
Evaporated	34
Oil on water surface	57
Dispersed oil	0
Sampled amount of oil	2
Oil adsorbed to the flume walls*	7

**Estimated value from observations*

In-situ chemical dispersion

After 72 hours of weathering, the dispersant Corexit 9500 was sprayed successively three times on the remaining surface oil emulsion (*in-situ* application). The amount of application and dosage rates are summarized in Table 3-3. In addition, dispersed oil was sampled and quantified as followed:

- 10 and 30 minutes; after first dispersant application
- 10 and 30 minutes; after second dispersant application
- 10, 30 and 120 minutes; after third dispersant application

*Table 3-3: Dispersant dosage rates on Brasse in the meso-scale flume basin (***in-situ** *application)*

Dispersant application (#)	Corexit 9500 application (g)	Dispersant -to -Oil Ratio (DOR)	Dispersant (wt. %)
1	62.6	1:67	1.5
2	71.1	1:63	1.6
3	68.9	1:67	1.5
1+2+3	207.2	1:20	4.6

Visual observations from the flume basin experiment of Brasse crude oil

A selection of pictures taken during the flume experiment is 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. Artificial sunlight simulated using a solar simulator was turned on during the experiments simulating photo-oxidation. Sample no is labelled as P0-P9, and visual observations are shown in Figure 3-5.

P0 – Application of oil: The oil was spread thinly when poured onto the water surface, and covered the entire surface after application. A significant amount of large oil droplets was observed in the water phase.

P1 – 0.5 hour: The oil was still evenly spread out as a thin slick on the water surface. An unstable emulsion started to form. Some adherence of oil to the flume walls was observed

P2 – 1 hour: The emulsion was still unstable and foam-like. Large oil droplets in the mm-range were observed in the water column

P3 – 2 hours: The emulsion became more stable. Large oil droplets were still observed in the water column, but these appeared to move slower than before (possibly due to the increased water content by emulsification)

P4 – 4 hours: The emulsion continued to thicken and became even more stable with time. The emulsion appeared light brown with streaks of darker brown. The slick did not longer cover the entire water surface. Fewer large oil droplets were now observed in the water column

P5 – 6 hours: The emulsification continued and produced a viscous and stable emulsion. Small pockets of water were observed on top of the oil/emulsion. Few oil droplets were observed in the water column. Some adherence of oil to the flume walls was observed

P6 – 12 hours: The emulsion continued to appear stable and homogeneous. Very few oil droplets were observed in the water column

P7–24 hours: No significant changes from 12 hours. The emulsion appeared thick and homogeneous.

P8 – 48 hours: The emulsion appeared even more thick and viscous, covering approximately half of the water surface in the flume. No oil droplets were visually observed in the water column

P9 – 72 hours: Similar as P8. When wave action was stopped, the emulsion spread to cover nearly the entire water surface of the flume.

In-situ chemical dispersion of Brasse

After 72 hours of weathering in the flume, the dispersant Dasic NS was sprayed on the remaining surface oil (in-*situ* application) using a Wagner paint sprayer. Approximately 48 wt.% of the total volume of oil (approx. 9.6 litres) was available for chemical dispersion, as shown in Figure 3-5. Dasic NS was applied three times on the surface giving a cumulative dispersant-to-oil ratio (DOR) of 1:20 reflecting a dosage-to-emulsion ratio (DER) of 1:100. The following is a summary of each Dasic NS dispersant application:

Dispersant application 1: The emulsions appeared to break and lose some structure. Streaks of darker oil were observed in the emulsion. Some oil dispersed into the water column as small droplets, but most of the oil remained on the surface. At close inspection the emulsion appeared somewhat grainy and coverage seemed patchy, but because of the large amount of oil on the surface the emulsion looked coherent (Figure 3-6).

Dispersant application 2: Very similar progression as with the first dispersant application was observed. More oil was dispersed into the water column (Figure 3-7).

Dispersant application 3: Very similar progression as with dispersant application 1 and 2. Some oil continued to be dispersed into the water column, while most of the oil remained on the surface. Approximately one hour after the third dispersant application, the emulsion started to appear more viscous and structured and some re-emulsification was taking place (Figure 3-8).

P0 – Application of Brasse in the meso-scale flume. Large oil droplets were observed in the water column

P1 – 30 minutes after oil application into the meso-scale flume

P3 – 2 hours

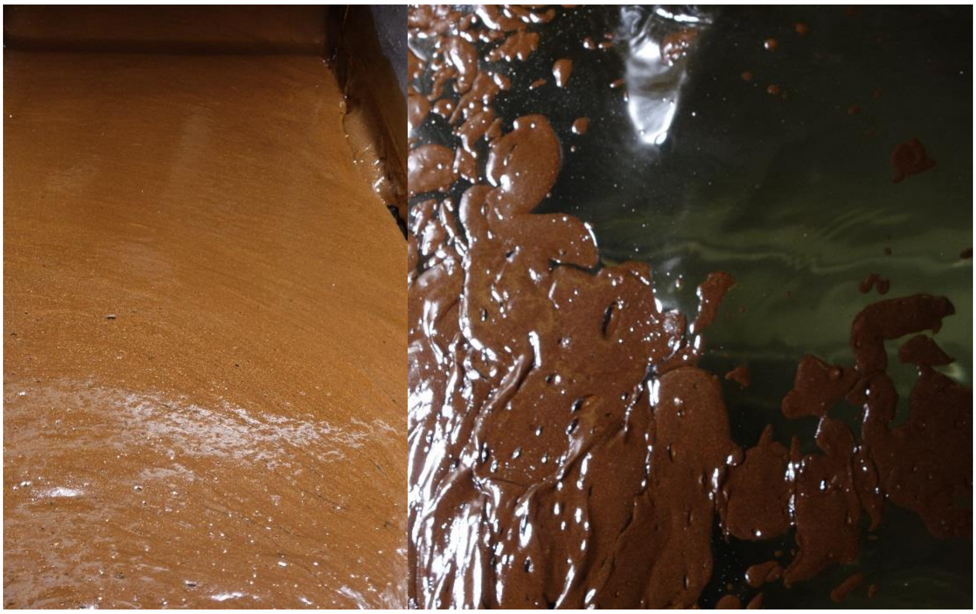
P4 – 4 hours

P5 – 6 hours

P6 – 12 hours

P7 – 24 hours

P8 – 48 hours and formation of stable emulsion



P9 – 72 hours. Emulsion is evident and its viscosity was 7119 mPa.s

Figure 3-5: Visual observation P0-P9 for 72 hours weathering

10 minutes after first dispersant application. The viscosity 30 minutes after the first dispersant was reduced to 3020 mPa.s. The surface emulsion was partly broken and loosing water.

Figure 3-6: 1st dispersant (Dasic NS) application on Brasse

10 minutes after second dispersant application. The viscosity of the broken emulsion: 3111 mPa.s samples 30 minutes after the second application.

Figure 3-7: 2nd dispersant (Dasic NS) application on Brasse

10 minutes after third dispersant application

60 minutes after third dispersant application

120 minutes after third dispersant application. The slick started to re-emulsify. Viscosity: 3631 mPa.s

Figure 3-8: 3^rd dispersant application (Dasic NS) on Brasse

Summary observation

After application of Brasse onto the water surface, the oil spread out and quickly covered nearly the entire water surface. Artificial sunlight simulated photo-oxidation. The oil initially appeared brown/green in colour. Significant amounts of large oil droplets were observed in the water column. The oil quickly started to emulsify, but the emulsion appeared to be foam-like and unstable. The appearance /colour was now a mix between light brown with darker streaks. During the first day the emulsion gradually became more viscous and stable as the lighter oil components evaporated, while the amount of oil droplets observed in the water column gradually decreased until no oil droplets were observed in the water after 24 hours. Minor changes were observed after the first 24 hours, the main change being the continued thickening and stabilization of the oil/ emulsion. The appearance of the emulsion changed from a light and dark brown mixture to a homogenous light brown.

After 72 hours, dispersant Dasic NS was applied to the remining surface oil. This resulted in reduced viscosity (7000 to around 3100-3600 mPa.s), and the emulsions appeared to flatten and lose some of its structure. Streaks of darker oil were also observed in the emulsion. A small amount of oil was observed to be dispersed into the water phase as small droplets, but most of the oil remained on the surface. Dispersant application was repeated twice, with 30-minute intervals, for a total of 3 rounds. The effects were similar each time, dispersing a small amount of oil while most of the oil remained on the surface. After the third round of dispersant application, the experiment continued for another 2 hours. Some re-emulsification was observed during this time. The emulsion was not very dispersible after 72 hours of weathering, and in an oil spill operation this oil/emulsion may require a combination of higher dosage and additional energy to increase the effectiveness for dispersant use.

4 Subsurface effectiveness screening of dispersants

4.1 Experimental Setup

SINTEF has constructed and built an experimental setup for small scale testing of underwater injection of dispersants. The experiments are performed in an 80-litre tank with a controlled flow through of seawater where the oil is injected through a nozzle at the bottom of the tank. In this study the dispersants were injected just prior to the oil release point. The test tank is shown schematically in Figure 4-1.

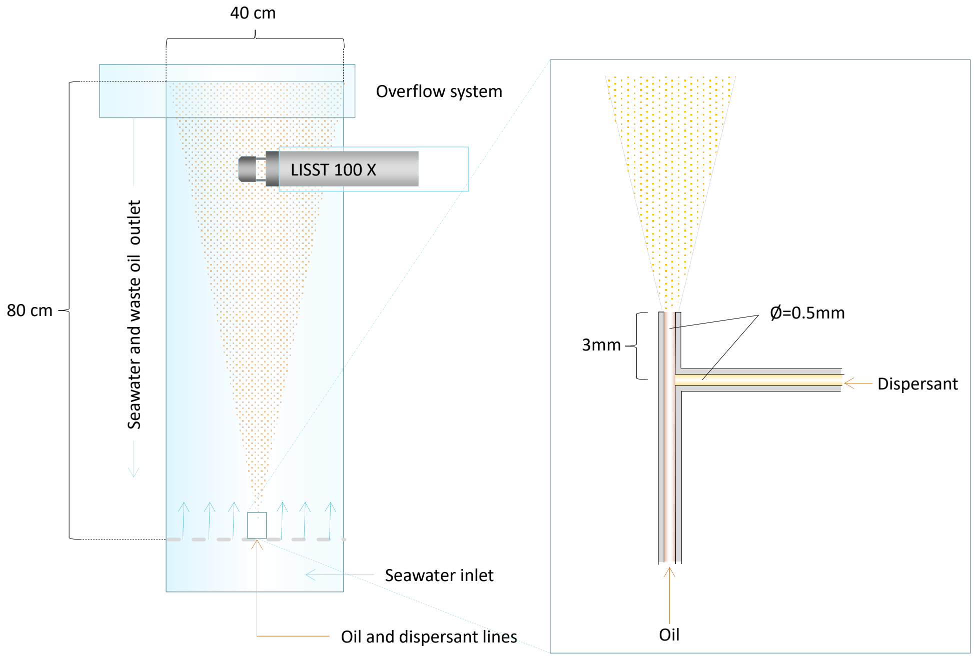


Figure 4-1: Schematic presentation of the SINTEF minitower for dispersant injection testing

Piston pumps were used for pumping both oil and dispersant to ensure pulse free flow. The oil was released through a 0.5 mm inner-diameter nozzle. An oil flow rate of 100 ml/min was used throughout this screening. Dispersants were injected at five Dispersant-to-Oil-Ratios (DOR): 1:1000, 1:500, 1:250, 1:100 and 1:50. The dispersants were injected into the oil line (see Figure 4-1), 3 mm prior to the oil outlet. Injecting dispersant prior to the release point simulates a filed scenario where a dispersant line is inserted down into the main release orifice. The dispersants tested in this screening were Corexit 9500, Dasic NS, Finasol OSR 5, Radiagreen OSD and Gamlen OD4000.

The size distribution of oil droplets formed in the flume was measured with a LISST100x (Sequoia Scientific Inc., Bellevue, Washington). The instrument protruded into the tank wall as shown in Figure 4-1, and the measurement cell was positioned in the centre of the tank. The instrument utilises laser scattering techniques for determining the droplet size distribution. The size distribution is reported as concentrations of droplets within 32 different size-bins (i.e. categories) ranging from 2.5 µm to 500 µm (logarithmically spaced). The instrument was placed 60 cm above the nozzle in order to measure droplets within the instrument's concentration range. The seawater flow through system enabled a controlled dilution of the plume prior to measurement, and an efficient removal of droplets between the dispersed oil releases.

4.2 Results and discussion

The dispersants Corexit 9500, Dasic NS, Finasol OSR 5 and Radiagreen OSD and Gamlen OD4000 were tested in the SINTEF minitower. The distribution of different droplet sizes and their concentrations are shown in Figure 4-2, with each line representing a different dispersant dosage.

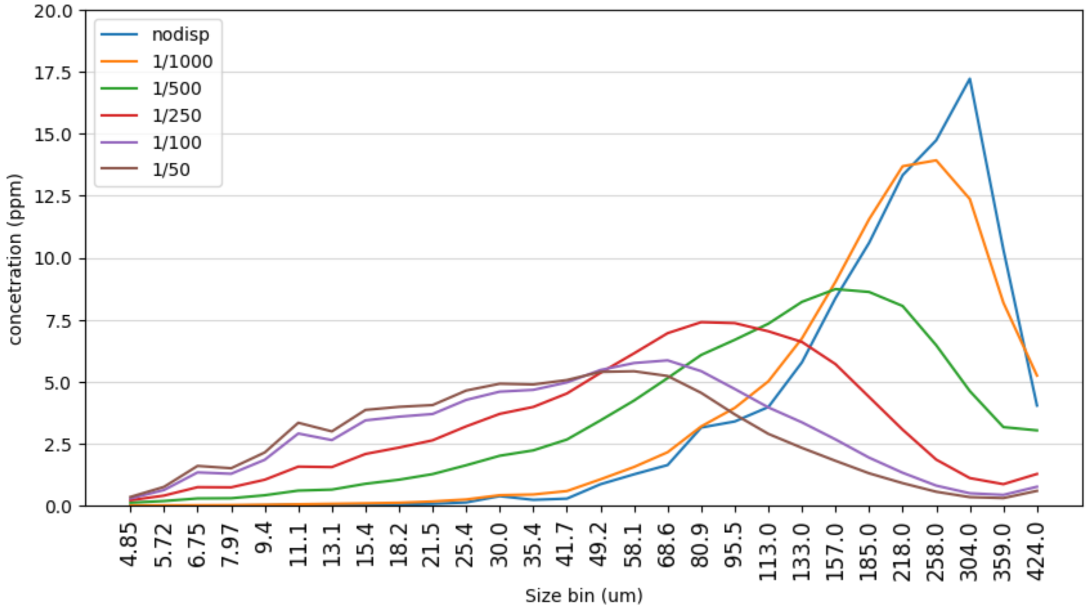


Figure 4-2: Droplet size distribution of the Brasse crude after treatment with increasing dosages of the dispersant Corexit 9500 in the SINTEF minitower

The droplet size distributions produced in the SINTEF minitower only indicate the efficiency of the tested dispersants at the given ratios. The droplet size distribution is strongly dependent on the release rate and diameter of the release orifice. Scaling can be applied to obtain theoretical droplet size distributions at given release scenarios with varying release rates and diameters. This type of scaling was not within the scope of this screening.

To assess the efficiency of the dispersants, the Median Volume Distribution (MVD) was calculated for all droplet size distributions. The Ratio (R) between the MVD from the untreated oil to the MVD for the treated oil with different products and concentrations was used as a measure of the effect of the dispersant at the given dosage ratio.

R=MVD (treated)/MVD (oil alone)

An example of the comparison of shifts in MVD for two of the dispersants at the same DOR (1:100) is shown in Figure 4-3, where treatment with Corexit 9500 and Dasic NS shifts the MVD down by a Ratio (R) of 0.2 and 0.5 respectively. The calculated Ratio of MVD (treated and untreated) is shown in Table 4-1 for all the dispersants from this screening study at the different DOR. The MVD for all droplet size distribution is shown in Table 4-2.

The results for screening of all dispersants are summarized in Figure 4-4.

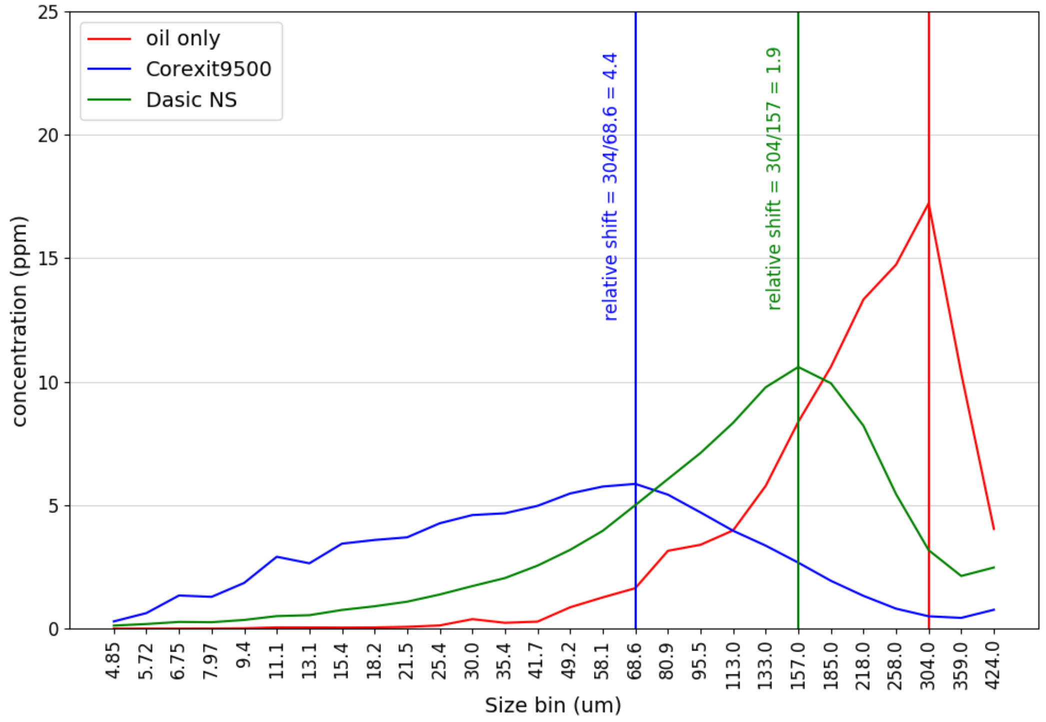


Figure 4-3*: *Droplet size distribution of untreated Brasse crude, compared to the distribution after treatment with two of the dispersants at a DOR of 1:50. The different shifts in Median Volume Distribution (MVD) for the two dispersant products are illustrated.

Table 4-1: Ratio of MVD (treated) and MVD (untreated) for all measurements

Dispersant /DOR	oil only	1:1000	1:500	1:250	1:100	1:50
Dasic NS	1.0	0.9	0.8	0.8	0.5	0.5
Corexit 9500	1.0	0.9	0.5	0.3	0.2	0.2
OSR 52	1.0	0.8	0.5	0.5	0.3	0.3
Radiagreen OSD	1.0	0.6	0.5	0.5	0.4	0.4
Gamlen OD4000	1.0	0.6	0.5	0.5	0.2	0.2

Table 4-2: Calculated MVD for all measurements

Dispersant /DOR	oil only	1:1000	1:500	1:250	1:100	1:50
Dasic NS	337	304	258	258	185	157
Corexit 9500	337	304	185	95.5	80.9	68.6
OSR 52	337	258	185	185	113	95.5
Radiagreen OSD	337	218	185	157	133	133
Gamlen OD4000	337	218	185	157	80.9	80.9

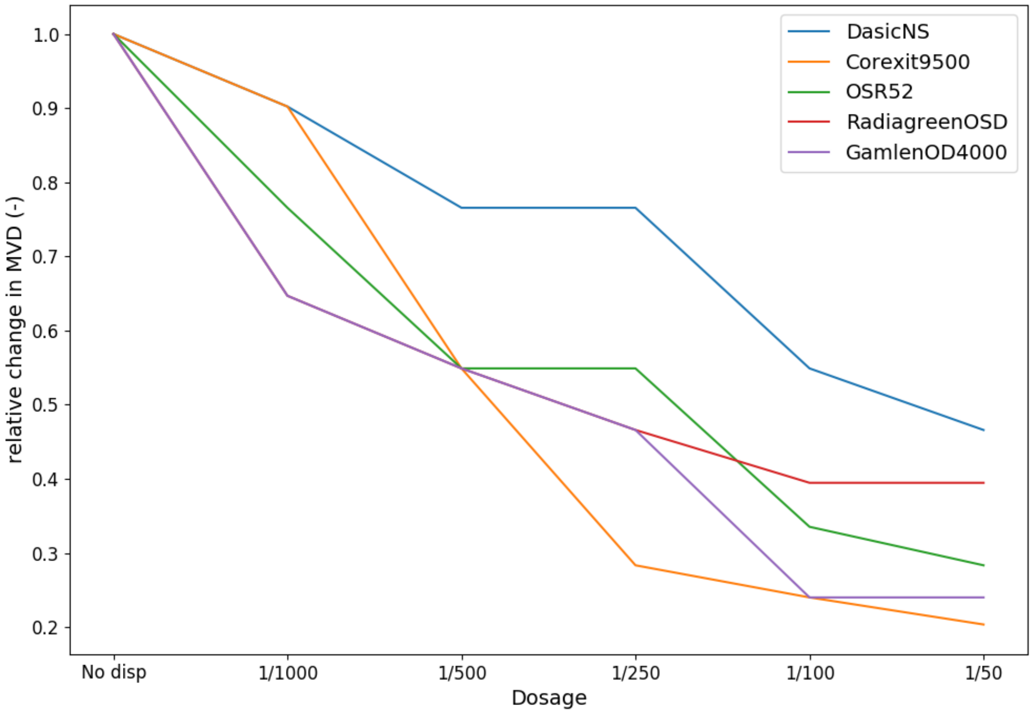


Figure 4-4: Relative change in MVD for the five dispersants summarized for all tested dispersant injection ratios.

Conclusion

The testing in the SINTEF minitower give a relative comparison between the effectiveness of dispersants. All dispersant tested in the SINTEF minitower experiments on Brasse fresh oil showed a decrease in the droplet size distribution for all DORs, compared to oil without dispersant added. Corexit 9500 showed the greatest decrease in the oil droplet size distribution from DOR 1:500 and higher. DOR 1:50 of Corexit 9500 caused the median droplet distribution to be 82 µm. Droplet sizes around 100 µm are expected to be retained in the water column for a noticeably long time and being bioavailable. The 1:50 DOR could therefore be considered as a possible dosage for subsea dispersant injection. However, it must be emphasized that in an operational situation, other parameters (water depth, release rate and nozzle diameter) would affect the droplet sizes significantly, and this may influence on the dispersant-to-oil ratio requirement.

Dasic NS was the dispersant with the lowest efficiency using this screening test, which may imply a need for an even higher DOR to achieve the same effectiveness as for e.g. Corexit 9500 and Finasol OSR52. The low efficiency of Dasic NS compared to the other dispersants has also been demonstrated on other crude oils such as Maria (Andreassen et al., 2013), Skarfjell (Ramstad et al., 2014), and Brynhild (Hellstrøm et al.,2015)) from a similar screening study.

5 Predictions with 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 the weathering properties of Brasse crude oil was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM) (version 4.0 beta). The experimental design for the study is described in Appendix B. The input data to the SINTEF OWM is 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.

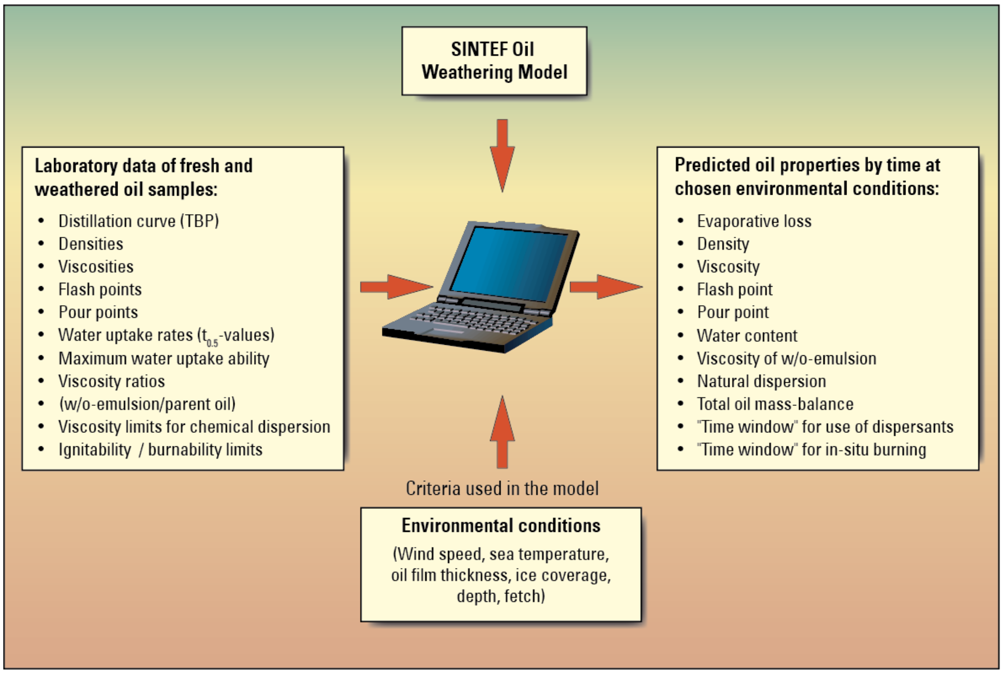


Figure 5-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

Spill scenario

A standard surface release from the OWM was used as the spill scenario (see section 5.2). 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.

Oil film thickness

The oils are categorized as condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate. The categorization of oil is also based on the experimental results obtained in the laboratory. The terminal film thicknesses vary among these categories based on experimental (field) experience. Brasse is categorized as an emulsifying (crude) oil with terminal oil film thicknesses of 1 mm.

Sea 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 temperature chosen for Brasse crude oil was 5 and 15 °C.

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 Brasse crude oil weathering properties

Input to the OWM

Oil type: Crude oil
Geographical area: North Sea
Terminal oil film thickness: 1 mm
Release rate: 1.33 metric tonnes/minute for 15 minutes; a total of 20 metric tonnes
Sea temperature: 5 and 13 °C
Wind speed: 2 m/s, 5 m/s, 10 m/s and 15 m/s

How to use the prediction charts: an example

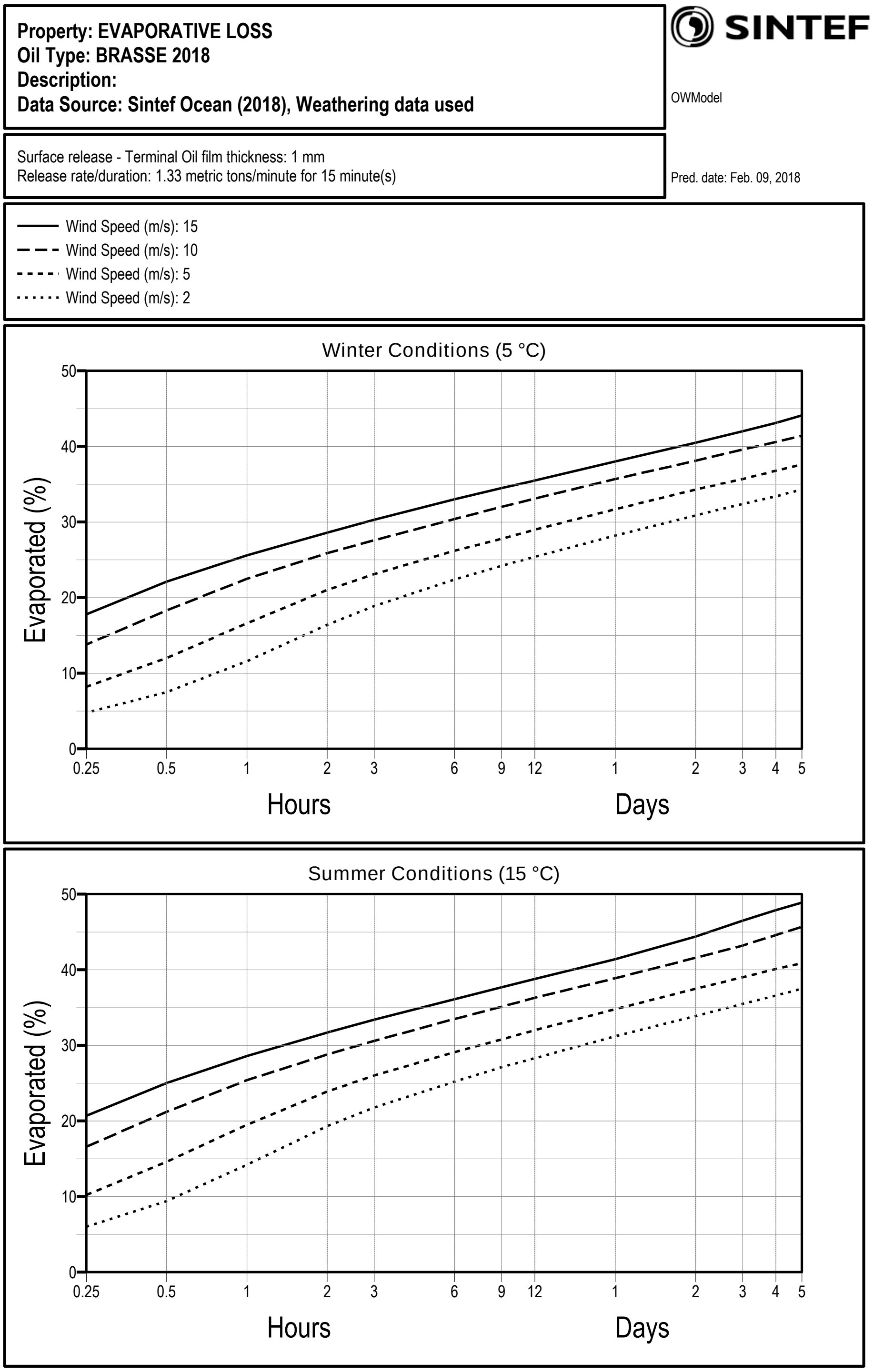
If the oil has drifted on the sea surface, the following prediction charts could be used to determine the weathering properties of the oil/emulsion. Table 5-2 gives examples for the following scenario:

- Drift time: 12 and 24 hours
- Sea temperature: 25 °C
- Wind speed: 10 m/s

Table 5-2: Example of weathering properties for Brasse crude oil obtained from the OWM predictions after 2, 24 and 72 hours of weathering at 10 m/s wind speed

Weathering property	**2 hours 5 ˚C 10 m/s**	**2 hours 15 ˚C 10 m/s**	**24 hours 5 ˚C 10 m/s**	**24 hours 15 ˚C 10 m/s**	**72 hours 5 ˚C 10 m/s**	**72 hours 15 ˚C 10 m/s**
Evaporation, wt. %	26	29	36	39	40	43
Water content, vol. %	36	36	75	78	75	78
Flash point, °C	68	78	102	114	117	131
Pour Point, °C	12	15	22	25	26	29
Viscosity, mPa.s *	750	580	16000	13000	24000	21000

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



Property: EVAPORATIVE LOSS
Oil Type: BRASSE 2018
Description:
Data Source: Sintef Ocean (2018), Weathering data used

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

OWModel

Pred. date: Feb. 09, 2018

Figure 5-2: Evaporative loss of Brasse crude oil predicted at sea temperatures of 5 and 15 °C

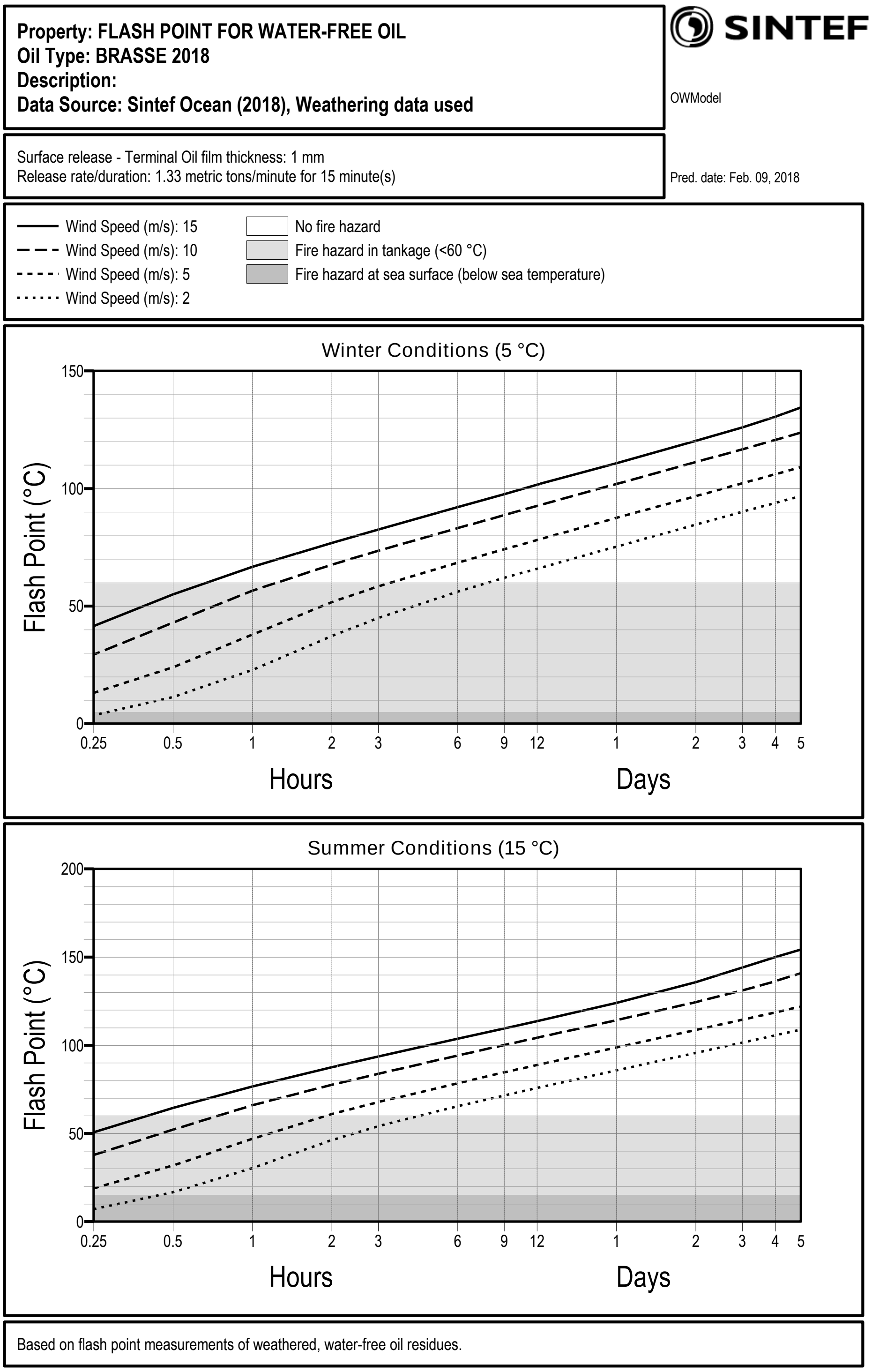


Figure 5-3: Flash point of Brasse crude oil predicted at sea temperatures of 5 and 15 °C

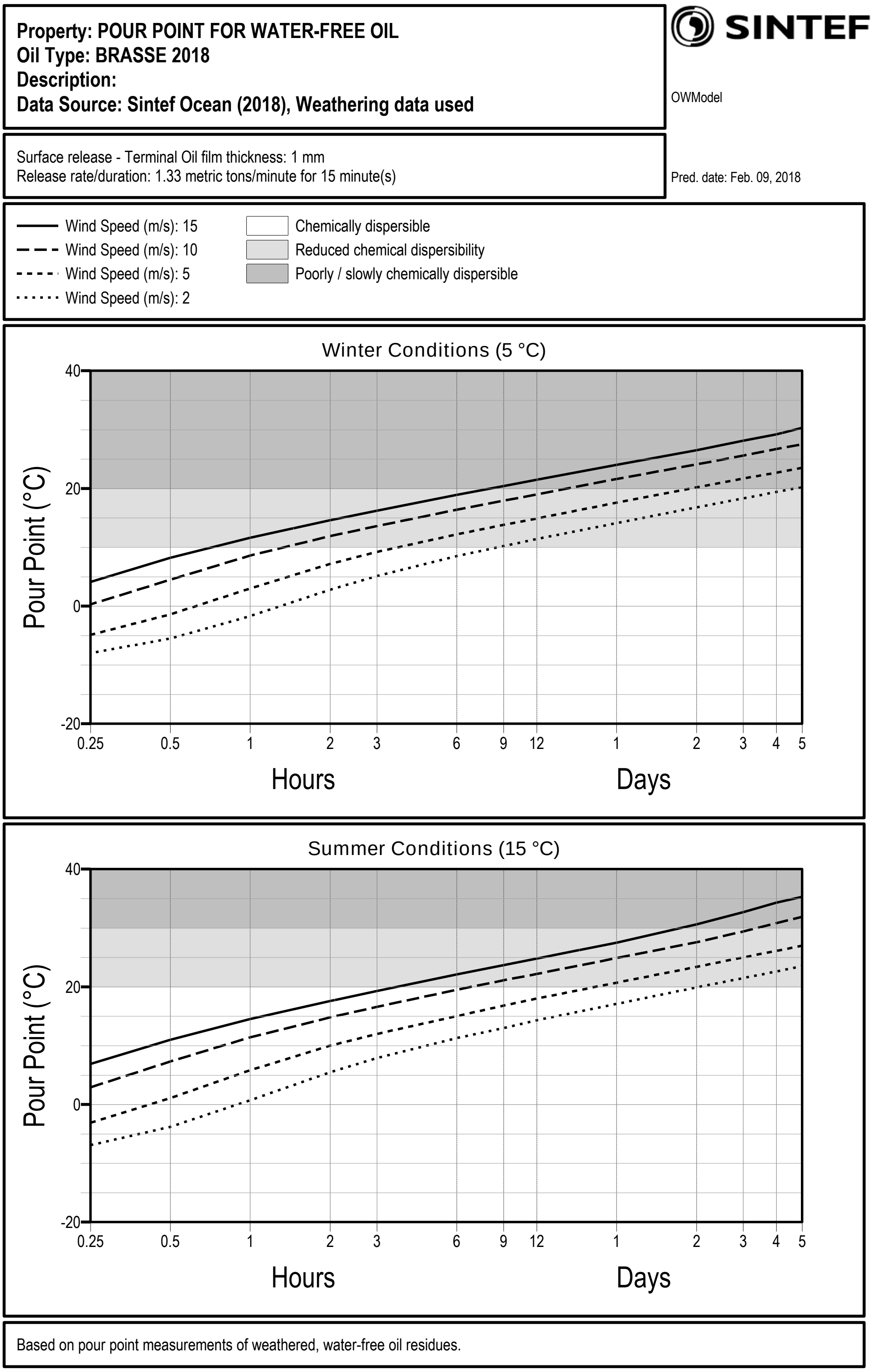


Figure 5-4: Pour point of Brasse crude oil predicted at sea temperatures of 5 and 15 °C

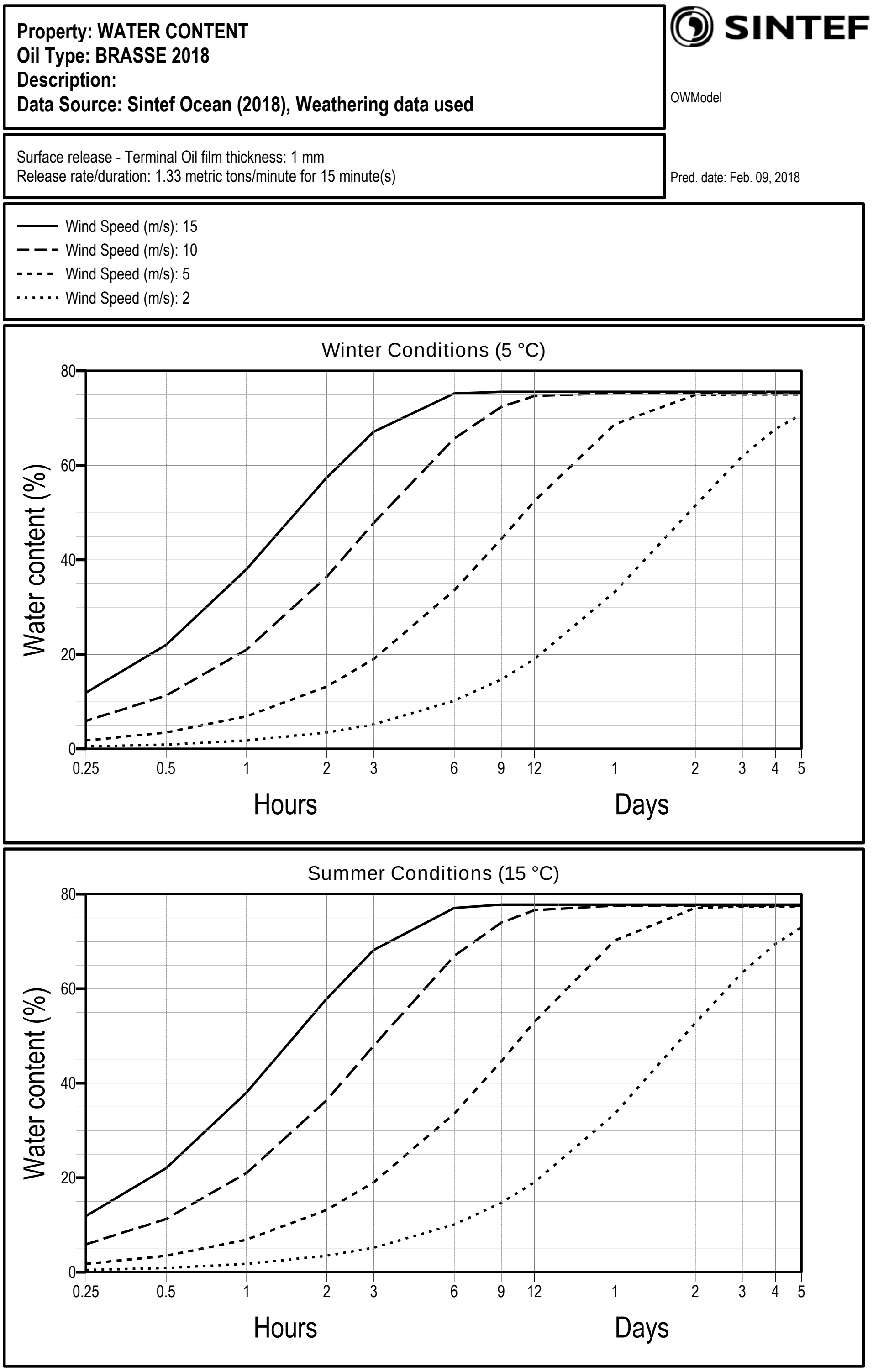
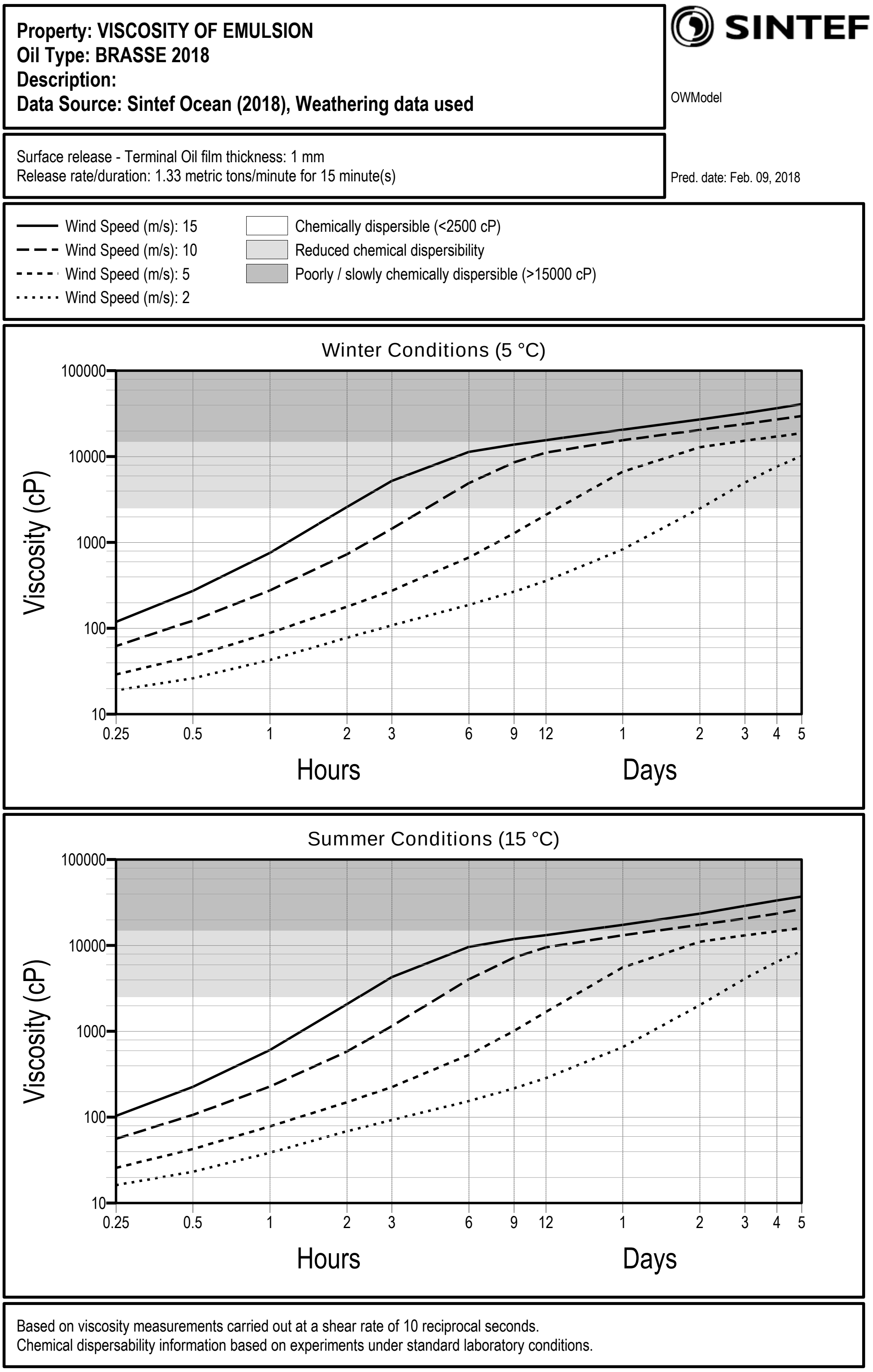


Figure 5-5: Water content of Brasse crude oil predicted at sea temperatures of 5 and 15 °C



Property: VISCOSITY OF EMULSION
Oil Type: BRASSE 2018
Description:
Data Source: Sintef Ocean (2018), Weathering data used

OWModel

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Feb. 09, 2018

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.
Chemical dispersability information based on experiments under standard laboratory conditions.

Figure 5-6: Viscosities of Brasse crude oil emulsions predicted at sea temperatures of 5 and 15 °C. Predictions are based on measurements of emulsions performed at a shear rate of 10 s^{-1}

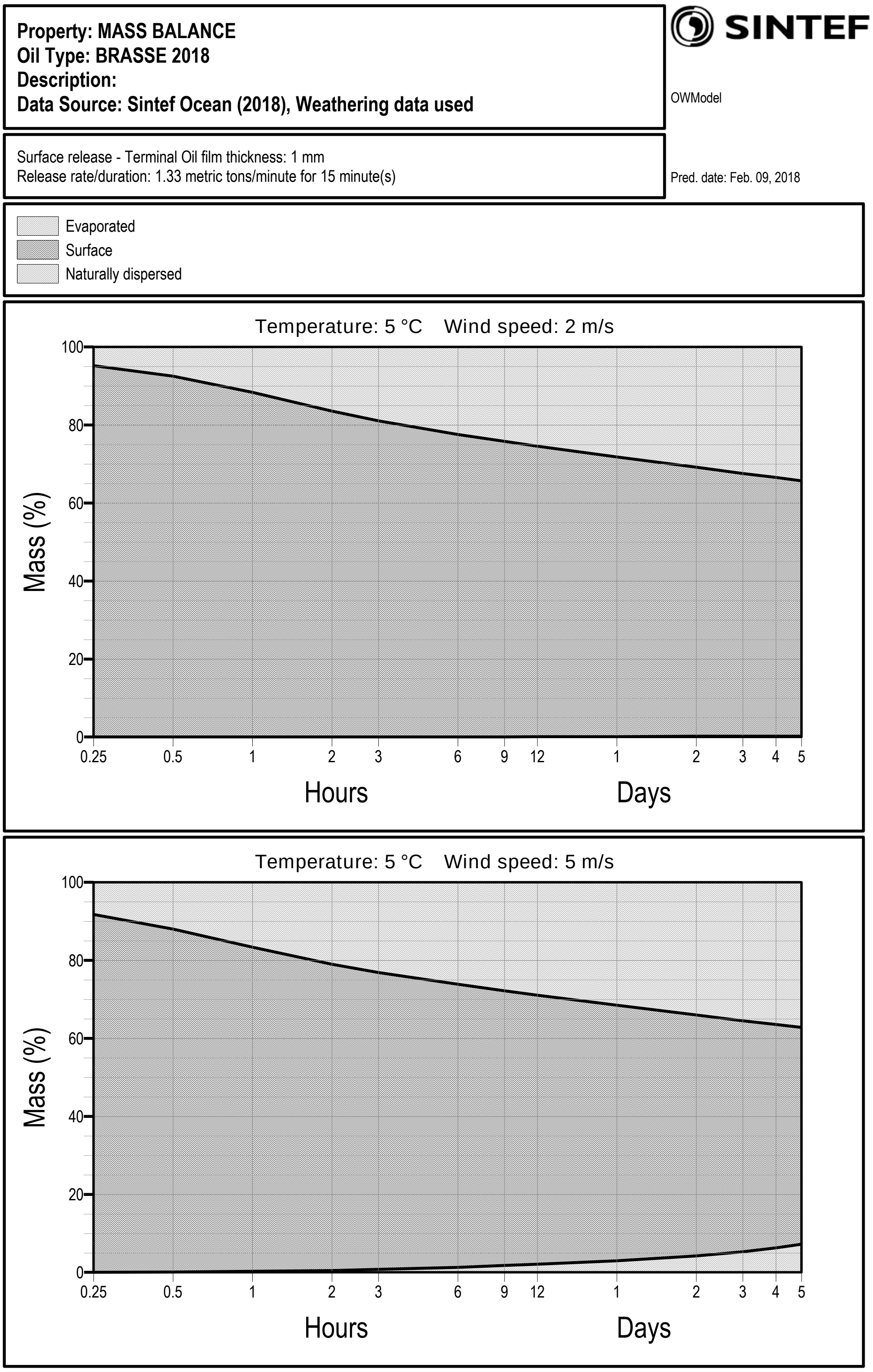


Figure 5-7: Predicted mass balance for Brasse crude oil at 5 °C and wind speeds of 2 and 5 m/s

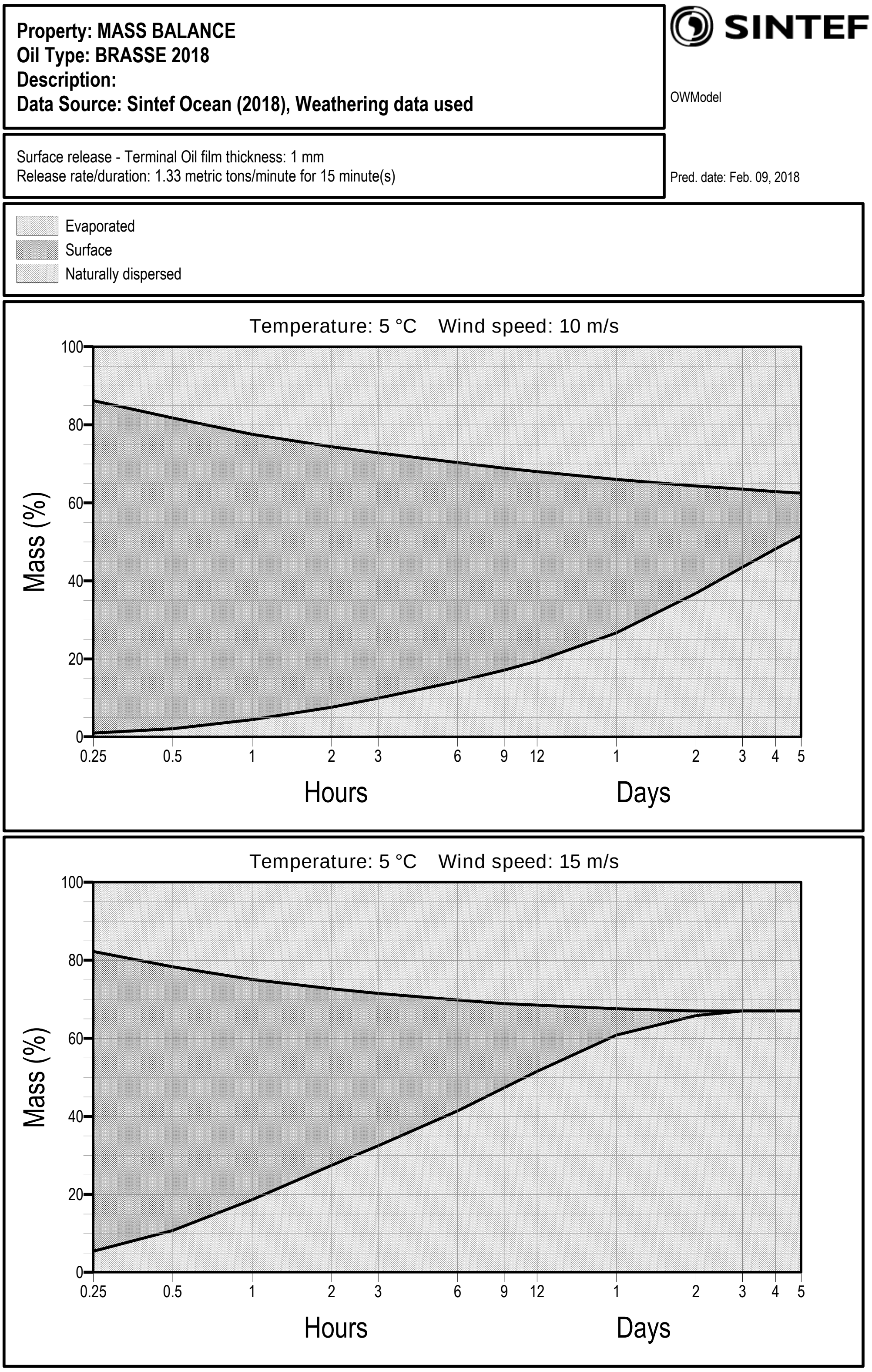
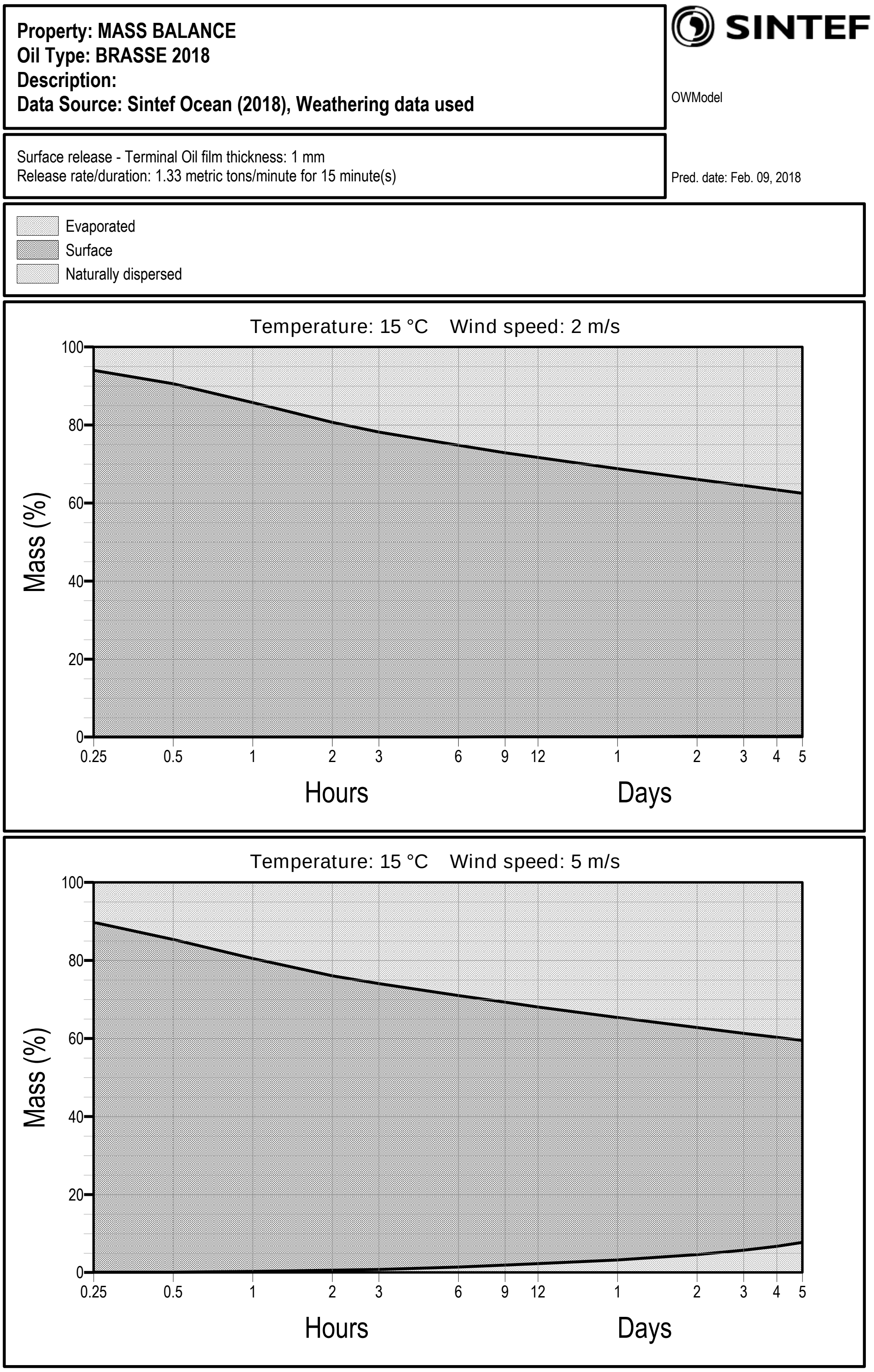


Figure 5-8: Predicted mass balance for Brasse crude oil at 5 °C and wind speeds of 10 and 15 m/s



Property: MASS BALANCE
Oil Type: BRASSE 2018
Description:
Data Source: Sintef Ocean (2018), Weathering data used

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Feb. 09, 2018

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Figure 5-9: Predicted mass balance for Brasse crude oil at 15 °C and wind speeds of 2 and 5 m/s

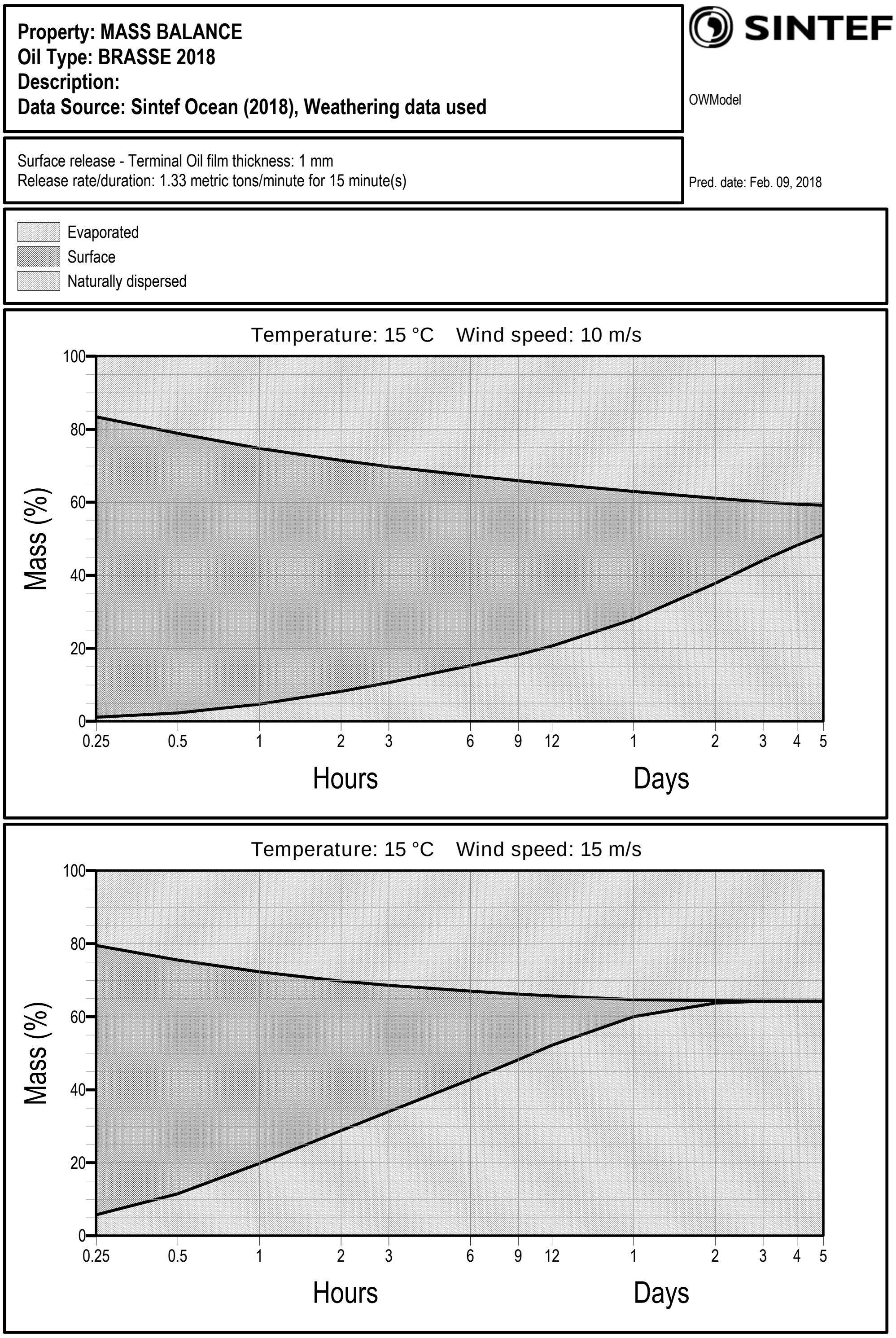


Figure 5-10: Predicted mass balance for Brasse crude oil at 15 °C and wind speeds of 10 and 15 m/s

6 OWM predictions - Comparison of Brasse with other crude oils

Weathering predictions of Brasse were compared to a selection of other crude oils. The presented comparisons given in the figures below are based on predictions at 15 °C and a wind speed of 10 m/s.

6.1 Evaporative loss

The evaporative loss of Brasse and the crude oils used for comparison are presented in

Figure ***6-1***, below. Brasse, Brage and Veslefrikk exhibit similarities in their evaporative loss (42-46 vol. %) after 5 days of weathering. Oseberg A shows the lowest evaporative loss compared with the other oils, and reaches about 28 vol. % loss after 5 days due to its high density and less content of the lighter components.

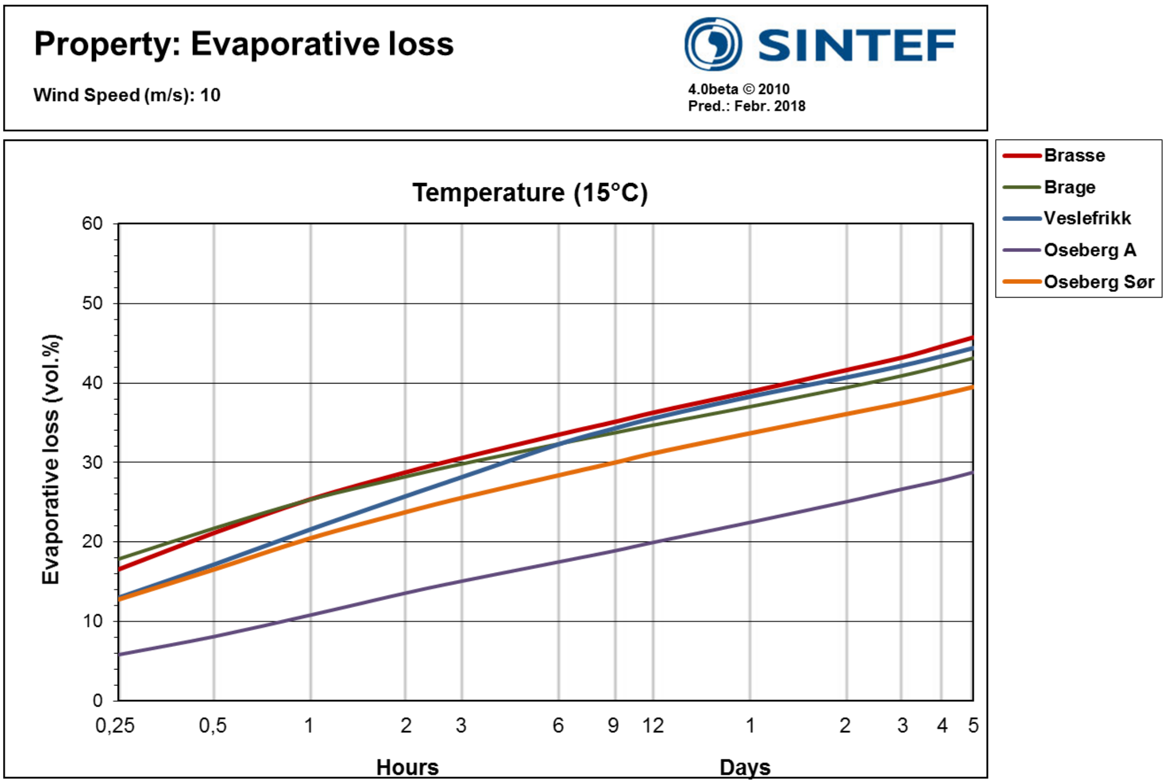


Figure 6-1: Predicted evaporative loss at 15 °C and 10 m/s for Brasse compared with other crude oils

6.2 Flash point

When oil is spilled on the sea surface, the oil will be cooled to the ambient water temperature within a short period. The probability of fire will be high as long as the flash point of the oil is below the sea temperature. Fire hazard is dependent upon the amount of volatile components in the oil and the potential for fire is usually over within the first few minutes of a spill due to the rapid evaporation of those components. The flash points of Brasse and other oils in comparison are shown in Figure 6-2. None of the oils show any fire or explosion hazard 15 minutes after release, the time at which the flash points are above the sea temperature of 15 °C.

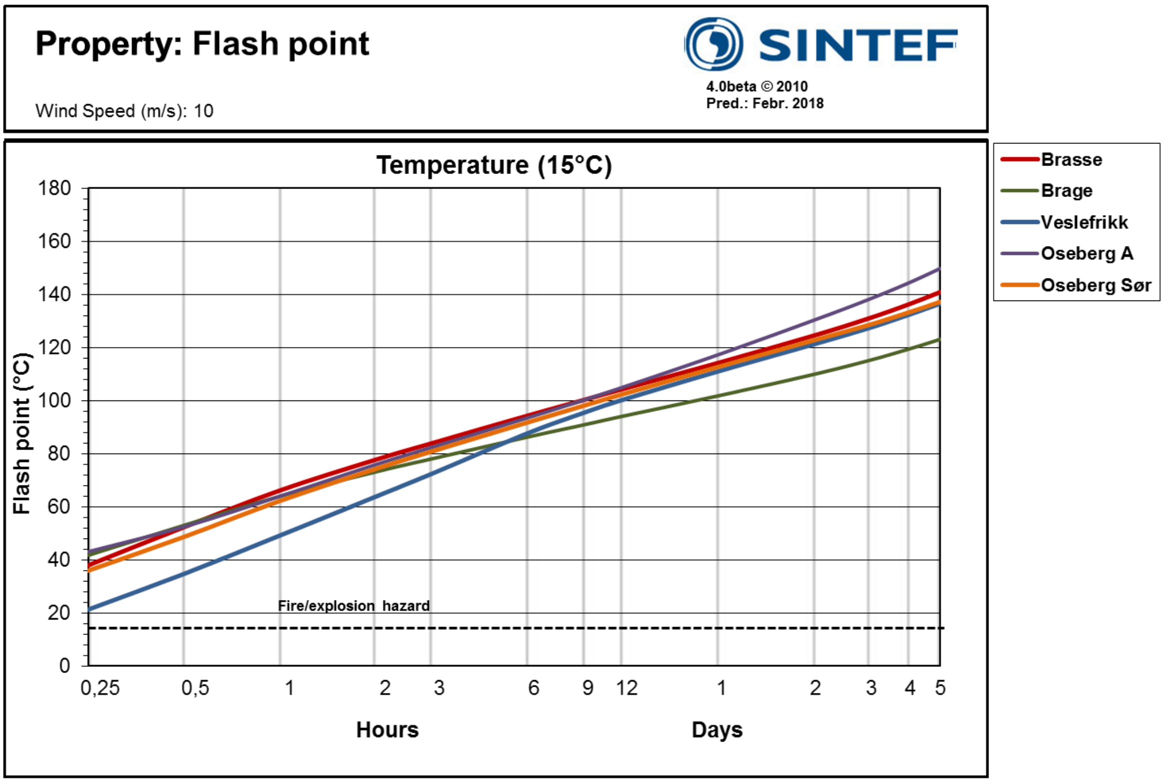


Figure 6-2: Predicted flash point at 15 °C and 10 m/s for Brasse compared to other oils

6.3 Pour point

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, high asphaltene content prevents 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. The pour points of Brasse and the other oils for comparison are given in Figure 6-3.

Solidification typically arises at 5-15 °C above sea temperature, see dotted line in Figure 6-3. Brasse and the other paraffinic crude oils (Brage, Veslefrikk and Oseberg Sør) have similar pour points of their water free residues. They have relatively high pour point development after some hours at sea and could potentially pose a challenge with solidification. The asphaltenic Oseberg A expresses low pour points and will not have a potential for solidification at sea.

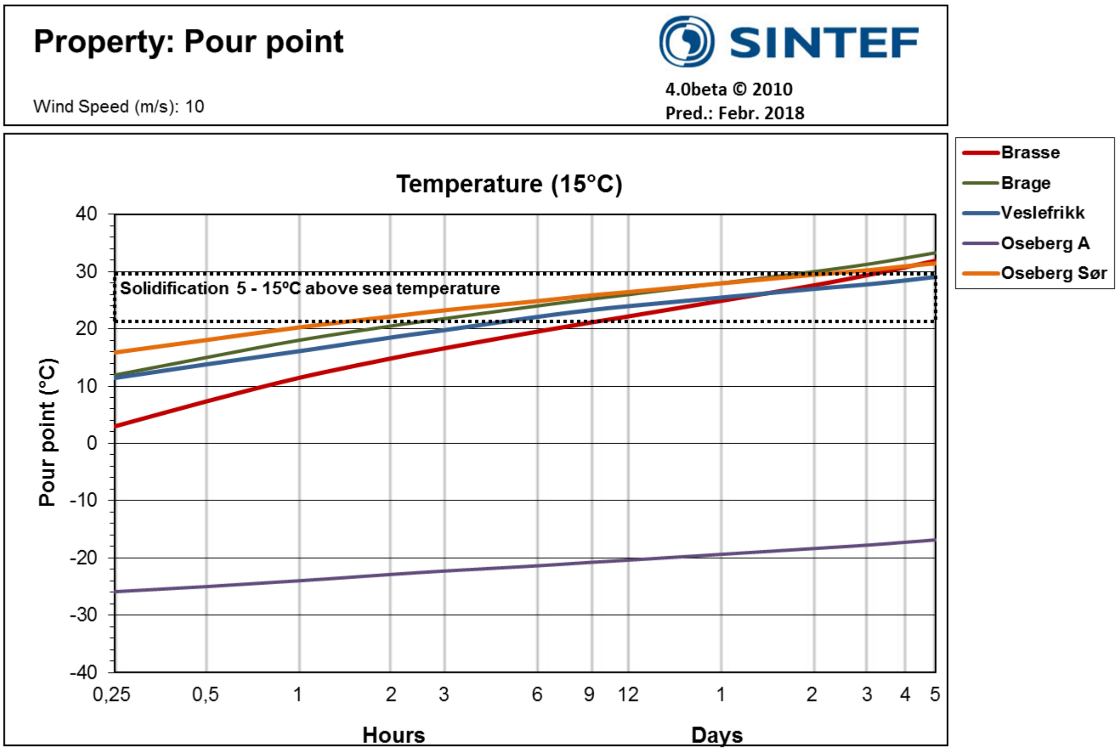


Figure 6-3: Predicted pour point at 15 °C and 10 m/s for Brasse compared to other oils

6.4 Water content

Water uptake and content for Brasse and the oils used for comparison are shown in Figure 6-4. The maximum water uptake of Brasse is in the same range for all the oils (77-80 vol. %). Oseberg A has the slower and slightly lower maximum water content, whilst Oseberg Sør shows the most rapid emulsification rate among these crude oils.

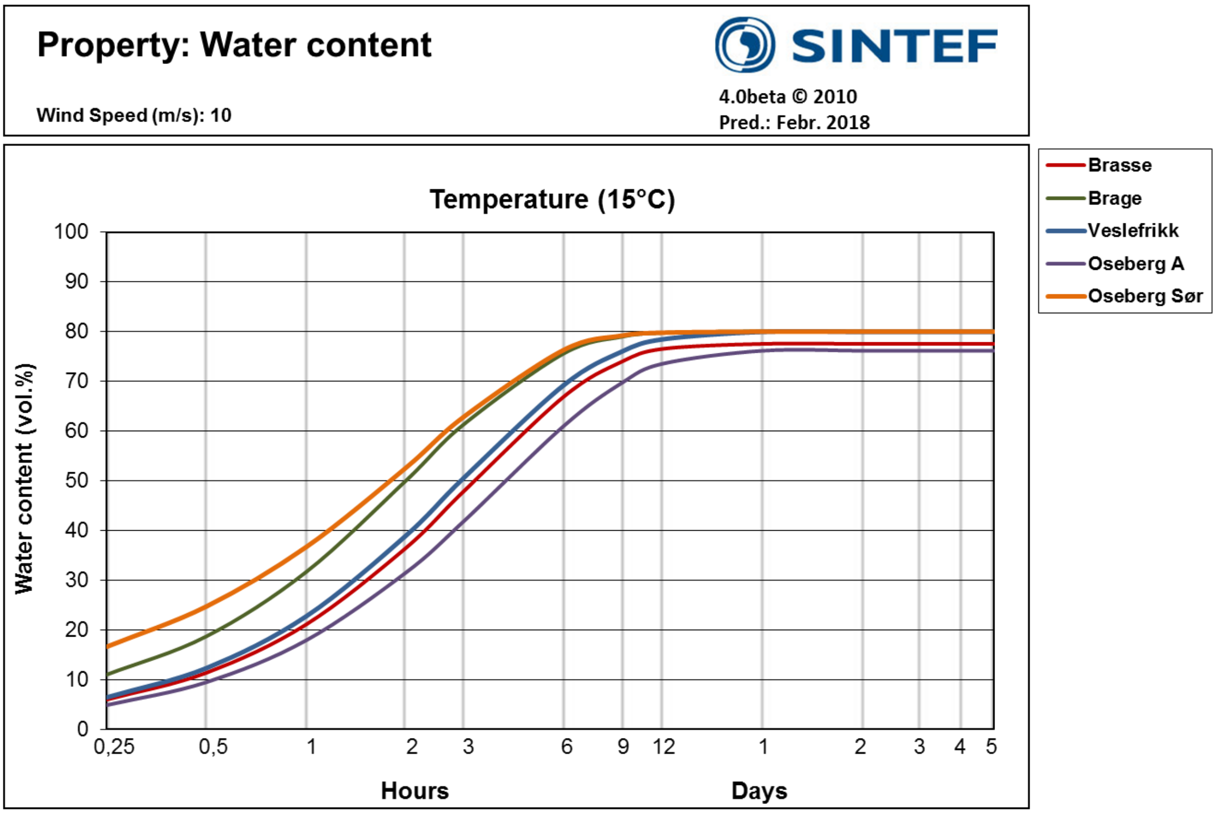


Figure 6-4: Predicted water content at 15 °C and 10 m/s for Brasse compared to other oils

6.5 Emulsion viscosity

Figure 6-5 shows the predicted emulsion viscosities of Brasse and the other oils in comparison. Brasse and Veslefrikk have fairly similar emulsion viscosity development, and reach around 20 000 mPa.s after 5 days of weathering. Oseberg A has the highest emulsion viscosities, whilst Brage ends up with the lowest emulsion viscosity.

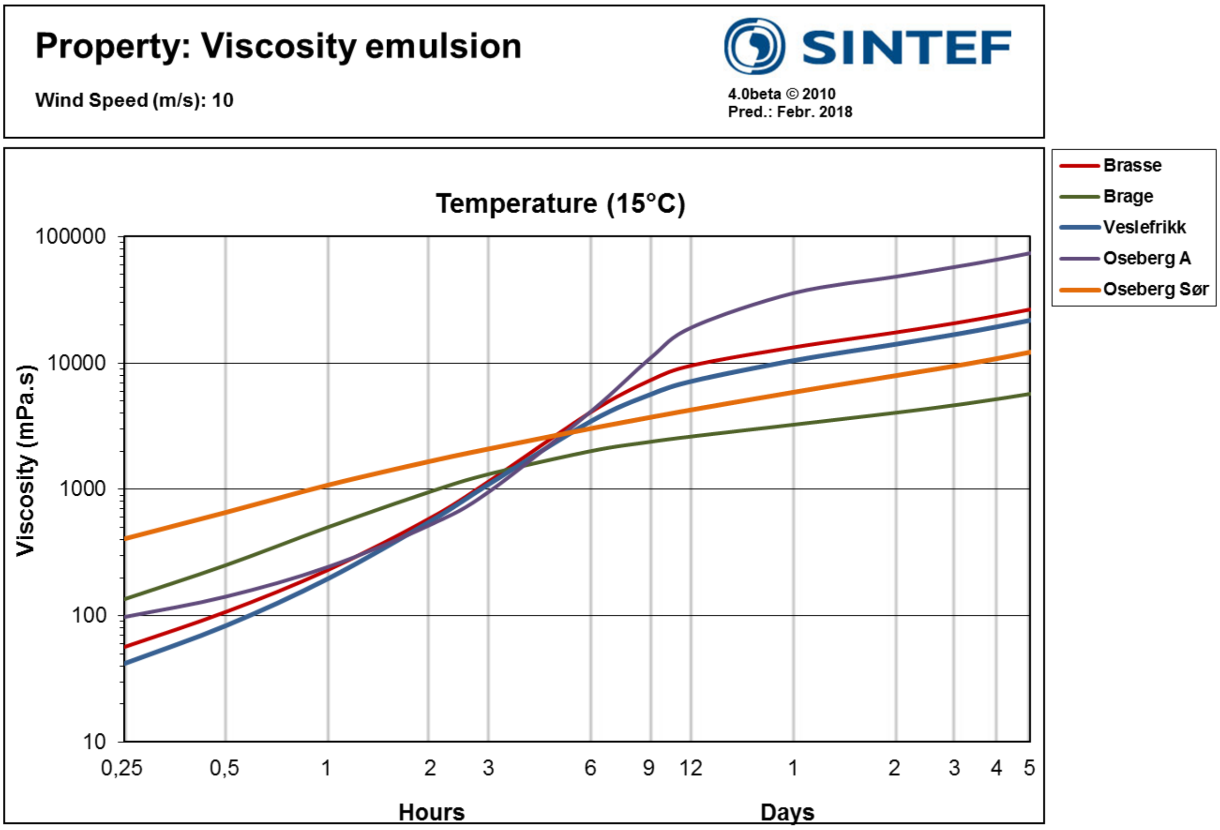


Figure 6-5: Predicted emulsion viscosity at 5 °C and 10 m/s for Brasse compared to other oils

6.6 Surface oil

Due to evaporative loss and natural dispersion/entrainment, the amount oil on the sea surface will gradually be reduced. Figure 6-6 illustrates the predicted mass balance of Brasse remaining as surface oil as a function of weathering compared to other oils. The paraffinic crude oils (Brasse, Brage, Veslefrikk and Oseberg Sør) have comparable amounts of remaining surface oil during 5 days of weathering. The heavier asphaltenic Oseberg A expresses a higher percentage of remaining surface oil and is more persistent on the sea surface.

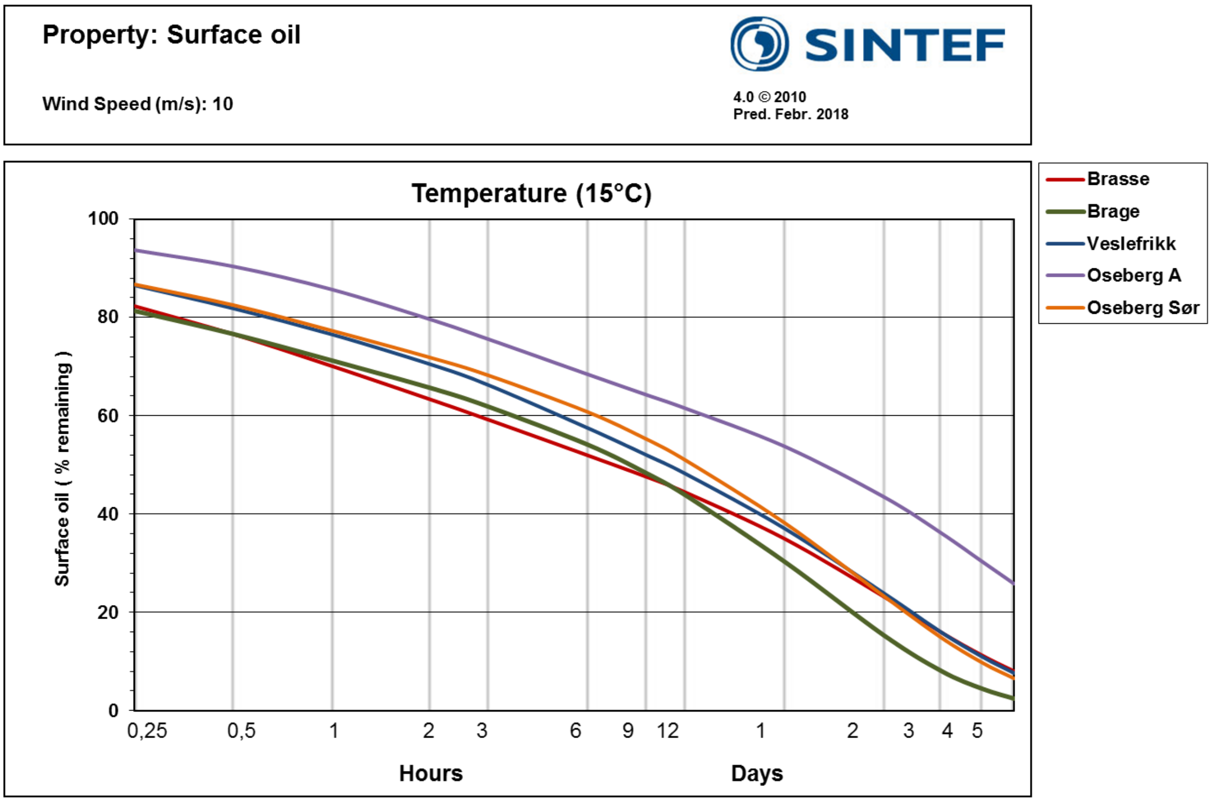


Figure 6-6: Predicted remaining surface oil at 15 °C and 10 m/s for Brasse compared to other oils

6.7 Surface emulsion

Predicted volumes of surface emulsion slicks are shown in Figure 6-7. The total surface slick is reduced, due to evaporation and natural dispersion (similar as shown in Figure 6-6) in the initial stages of weathering. However, the volume of water mixed into the oil increases the total volume of the surface emulsion considerably, as illustrated in the figure below. Increasing surface emulsions should be considered in a spill operation, for example, when evaluating skimmer capacity.

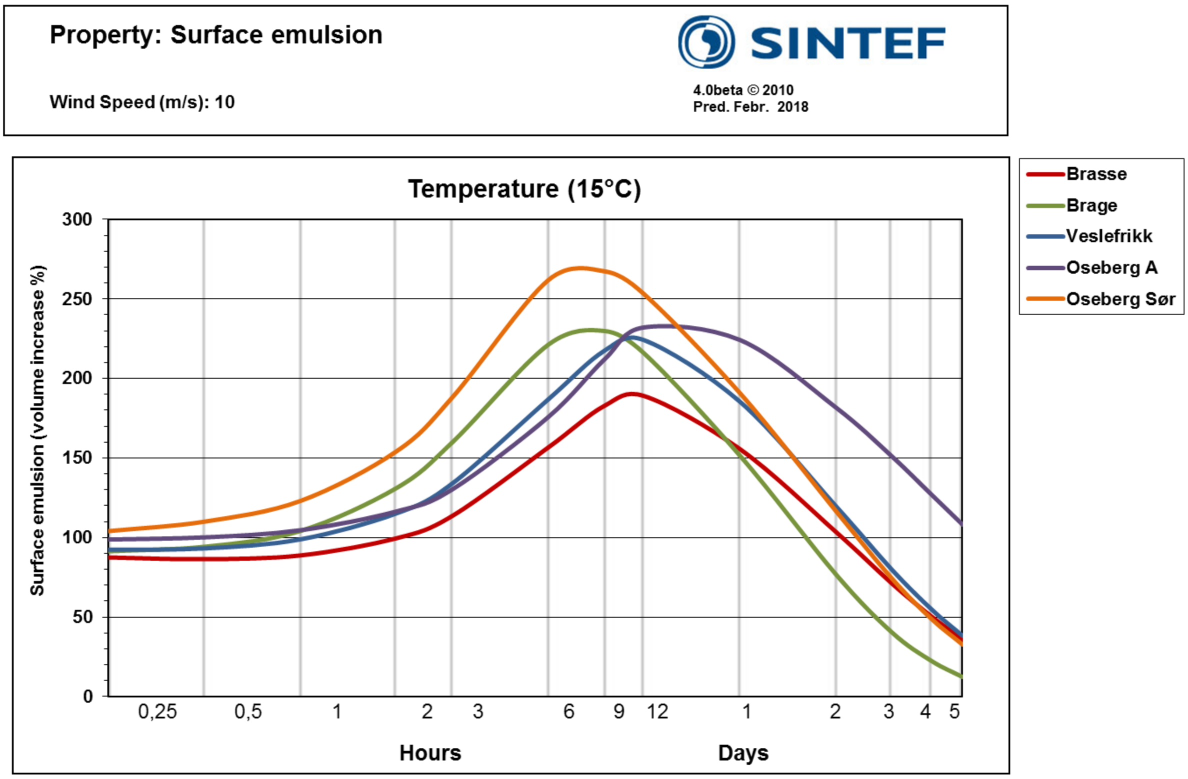


Figure 6-7: Predicted surface emulsion at 15 °C and 10 m/s for Brasse compared to other oils

7 Weathering properties of Brasse crude oil related to oil spills

The relative concentration of heavy oil components within a spilled oil increases due to weathering, and the physical and chemical properties of the oil will change over time. Knowledge about how the oil's 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. These response options are discussed for the Brasse oil and are related to its weathering properties (e.g. viscosity). The weathered oil is expected to have a window of opportunity for ignitibility / in-situ burning, but this response option has not been evaluated in this study.

7.1 Oil properties

Brasse is a medium density crude oil (0.847 g/mL), with a low to medium content of wax (2.88 wt. %), and a low content of asphaltene (0.16 wt. %), compared with other Norwegian crude oils. Fresh Brasse oil exhibits a low viscosity of 9 mPa.s at a shear rate 10s^{-1} (13 °C). Brasse is categorised as a paraffinic crude oil based on chromatographic characterization, where the hydrocarbon profile shows systematic typical peaks of *n*-alkanes (paraffins). The fresh crude oil has a low pour point of -15 °C that extends to +24 °C (250°C+ residue) with evaporation of the lightest compounds. Brasse forms stable water-in-oil (w/o) emulsions with a maximum water uptake of up to 80 vol. % with high emulsion viscosities.

7.2 Flash point – Fire/explosion hazard

Flash point refers to the lowest temperature at which a fuel or 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 fire/explosion hazard will be at its greatest if the flash point of the spilled oil is below the seawater temperature

The flash points for Brasse will be above the sea temperature within a few minutes at winter temperature (5 °C), and earlier at higher wind speeds. In summer condition (15 °C), at low wind speed of 2 m/s, the flash point takes a bit longer to reach the sea temperature, but will reach the sea temperature within 15-30 minutes. See Figure 7-1.

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. At a low wind speed (2 m/s) this limit is reached within 9 hours at 5 °C, and 6 hours 15 °C. The flash point limit will be reached considerably faster at higher wind speeds (Figure 5-1).

As a general recommendation after an acute oil spill involving free gas from subsea release, a "safety" zone should be established early on and downwind from the spill site before response actions are initiated. 1-hour drifting time of slick (from the source) has been suggested in Norway before oil spill response operations are initiated in open sea waters. Shorter waiting times have been predicted related to fire/explosion hazard. The following precautions should be taken:

- 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

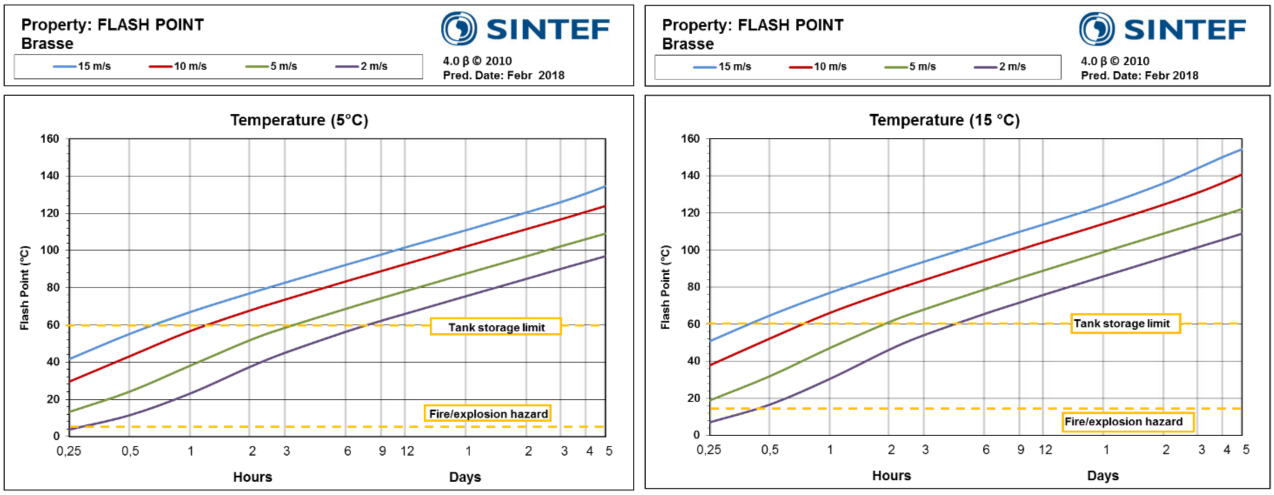


Figure 7-1: Predicted flash points at different wind speeds for Brasse crude oil at 5 and 15 °C

7.3 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion/entrainment in the early stage of weathering. However, as emulsion are formed and seawater is mixed into the oil, the total volume of the oil (emulsion) increases. Figure 7-2 illustrate this increase of volume relative to the volume of the remaining surface oil at 10 m/s wind and at 5 and 15 °C. The figure shows that the volume of the emulsion increases about 3.5 times at 12 hours weathering.

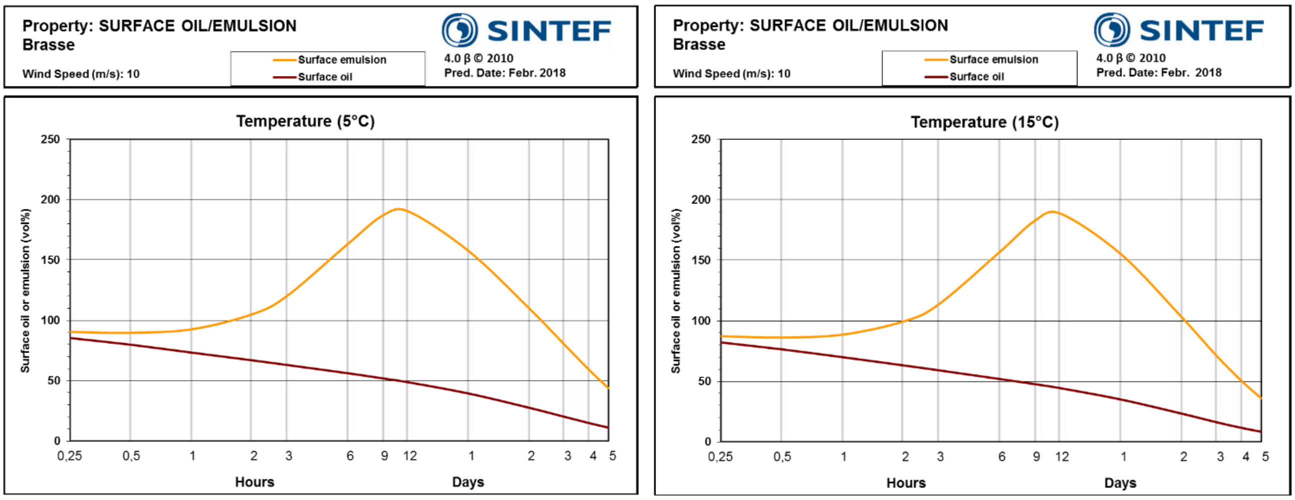


Figure 7-2: Difference in the total slick volume of Brasse crude oil due to emulsification (orange) compared to non-emulsified oil (brown). Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 and 15 °C

7.4 Addition of emulsion breaker

Emulsion breaker can be used during an oil spill operation to enhance the release of water from an emulsion. Emulsion breakers are normally injected at the skimmer head prior the entering to storage tank and are not added directly on the oil spill at open sea.

Figure 7-3 illustrates the relative volumetric composition of emulsion and free water, for the 250 and 250°C+ residue, reflecting approx. 0.5-1 hour and 0.5-1-week weathering with and without addition of emulsion breaker (Alcopol O 60 %; 500 and 2000 ppm by weight). The effectiveness of the emulsion breaker was found to be relative to the dosage applied, with effectiveness increasing with increasing concentration of emulsion breaker. The use of emulsion breaker could be considered for Brasse crude oil to increase the storage capacity when recovered.

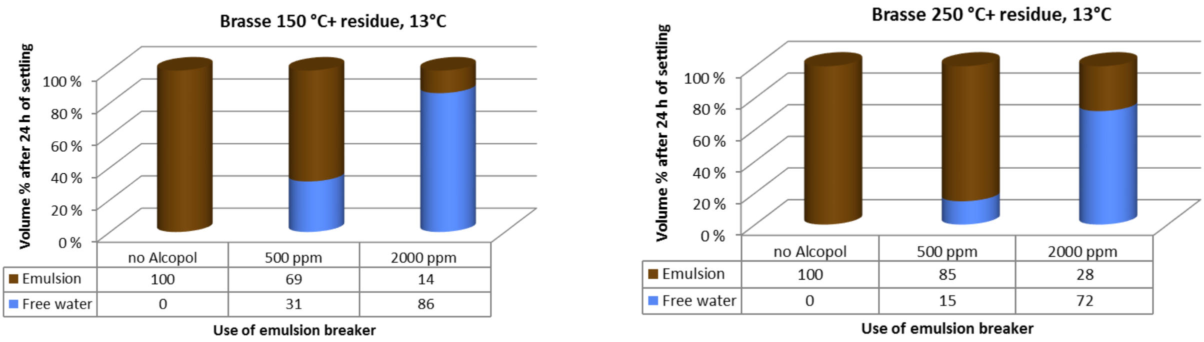


Figure 7-3: Relative volumetric composition of emulsion and free water after approximately 0.5 hour (left) and 1 week (right) of weathering of Brasse. The x-axis shows the dosage of emulsion breaker Alcopol O60% (500 ppm and 2000 ppm by weight) and no emulsion breaker

7.5 Lifetime at sea – Natural dispersion 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). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface. Figure 7-4 shows the remaining surface oil over time for different wind speeds and temperatures. Considerably larger spills may produce longer lifetimes, and individual predictions could be considered in such cases. At high wind speed of 15 m/s, no oil remained on the sea surface after 2-3 days of weathering at 5 and 15 °C. However, the variation is strongly dependent on the wind speed and more oil remained on the sea surface with lower wind.

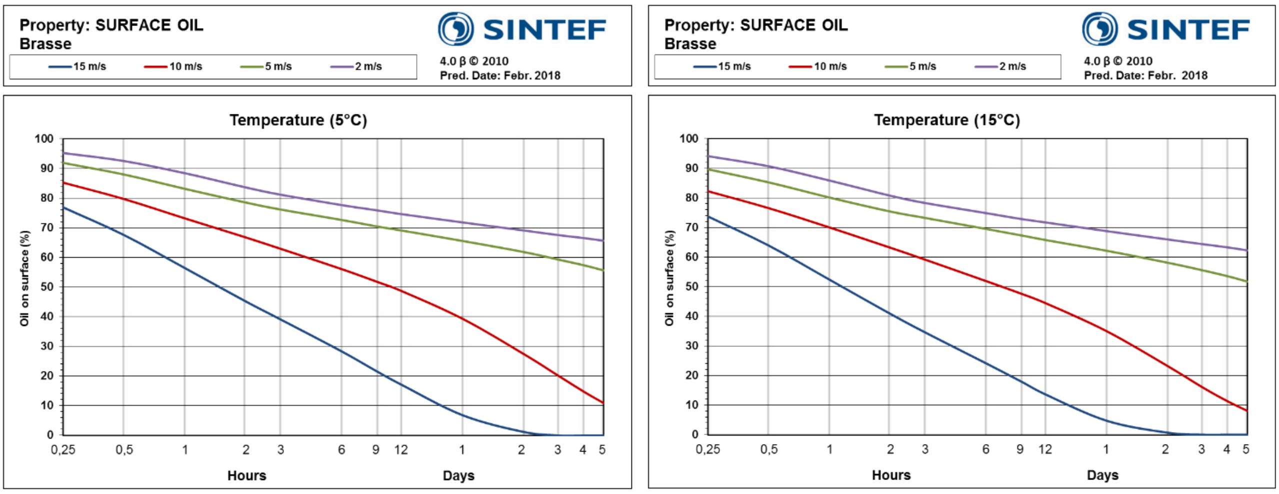


Figure 7-4: Remaining surface oil for Brasse crude oil at 5 and 15 °C

7.6 Emulsion film thickness

Mechanical recovery requires normal minimum film thicknesses > 0.1 mm – 0.2 mm. Film thicknesses > 0.05 mm – 0.1 mm are considered for application of oil spill dispersants, as lower film thicknesses are likely to disperse naturally. With surface releases, a combined response of chemical dispersion and mechanical recovery could be applied to a Brasse oil spill, both under summer and winter conditions, see Figure 7-5. The emulsion film thicknesses are not considered as limiting factor for either mechanical recovery or chemical dispersion from a surface release.

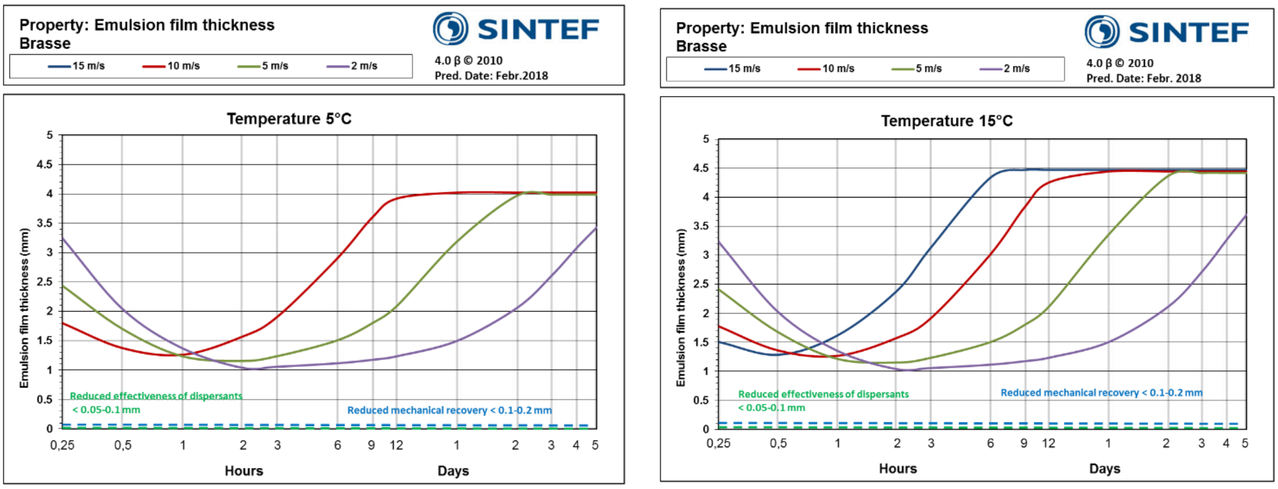


Figure 7-5: Expected time window for effective use by mechanical recovery and dispersants as a function of emulsion film thickness for Brasse at 5 and 15 °C (surface release)

7.7 Mechanical recovery by boom and skimmer

Experiences from Norwegian field trials with oil spill 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 spill boom.

Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 mPa.s (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been set at 1000 mPa.s in Figure 7-6. However, other factors like the operational speed of the recovery vessel and current weather conditions will also influence the risk of boom leakage. Therefore, it may be possible to recover oil/emulsion in calm weather conditions with viscosities lower than this limit (1000 mPa.s). Previously studies at SINTEF have shown that weir skimmers may reduce recovery rates (m^3/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001). It has been observed that the recovery rate of rope skimmer also varies among different categorizations of crudes oils (Singsaas et al., 2000).

The emulsion viscosities of Brasse are shown in Figure 7-6. For example, the emulsion viscosity exceeds 1000 mPa.s after about 2 hours at 5 m/s wind speed, and within 6 hours in calmer wind conditions (2 m/s). The emulsion viscosities may exceed 15-20 000 mPa.s within 1-2 days at wind speeds of 10 m/s, which decreases the efficiency of weir skimmers at 5 and 15 °C. Although, for lower wind speeds, sufficient flowability towards weir skimmers are expected for this oil within five days of weathering. Overall, this gives a relatively wide window of opportunity for mechanical recovery with use of skimmers, such as the Transrec equipped with traditional weir-skimmer head.

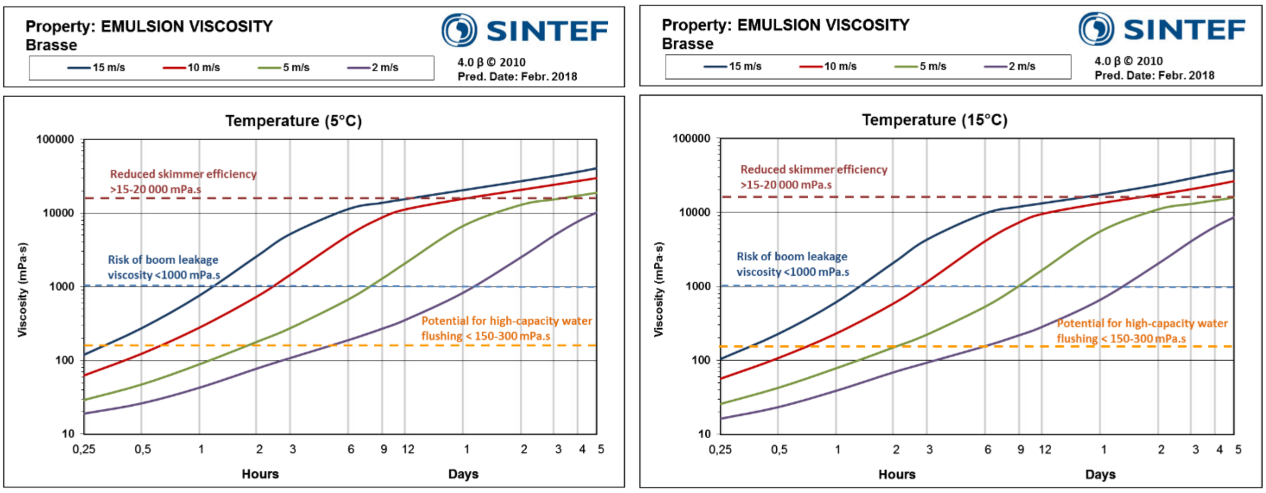


Figure 7-6: Expected time window for effective use of booms and weir skimmers, and high-capacity water flushing (see chapter 5.9) as a function of emulsion viscosity for Brasse at 5 and 15 ºC

7.8 Mechanical dispersion by high-capacity water flushing

Mechanical dispersion by high-capacity water flushing could have a potential in e.g. subsea oil spill scenarios with thin initial film thickness up to 0.2 - 0.3 mm and oil/emulsion viscosities < 150 - 300 mPa.s. In such cases, water flushing from high-capacity water flush boom or firefighting (Fi-Fi) systems could have a potential for breaking up the oil/emulsion into smaller droplets in a very early phase of a spill. 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. It should be emphasized that this technology has not been implemented as a part of the oil spill response in Norway today. However, mechanical dispersion by high-capacity water flushing could be a relevant response option in an early phase from an underwater blowout anticipating both low film thicknesses and low viscosities, and no formation of solidified lumps on the sea surface. The SINTEF OWM underwater module could be used to simulate the film thickness from a specified oil-gas subsea release scenario. Moreover, the film thicknesses are depending on the spill conditions as water depth, gas-to-oil ratio (GOR) and release rate. For a surface release, the high emulsion film thicknesses as shown in Figure 7-5 is a limiting factor even the viscosities are low in the initial phase of the spill (Figure 7-6).

7.9 Use of oil spill dispersant

Brasse has a potential for use of oil spill dispersant. The window of opportunity for use of the dispersant Dasic NS is presented in Figure 7-7. The viscosity limit for effective dispersant use for Brasse was estimated to be 2500 mPa.s (low energy IFP-test), and the limit for when the oil is not dispersible was estimated to be 15 000 mPa.s (high energy MNS-test).

Figure 7-7 shows a reduced dispersibility for Brasse after 12 hours at 5 m/s wind speed at 5 °C, whilst at 15 °C the time window was between 12 hours and 1-day weathering. When the oil/emulsion is expected to be reduced dispersible, an additional energy or use of a higher dispersant dosage and/or repeated dispersant application is recommended to increase the dispersant efficiency. Providing additional energy through use of Fi-Fi systems, thrusters or MOB boats after dispersant application may enhance the dispersion rate in calm weather conditions.

In cases when high viscosity of the oil /emulsion is not a limiting factor, high pour point may cause solidification (elastic properties) on the sea surface. Solidification typically arises at 5-15 °C above the sea temperature. 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 the solidified wax and be washed of by wave activity. In certain weather conditions, e.g. in very calm wind, the 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 of the oil/emulsion.

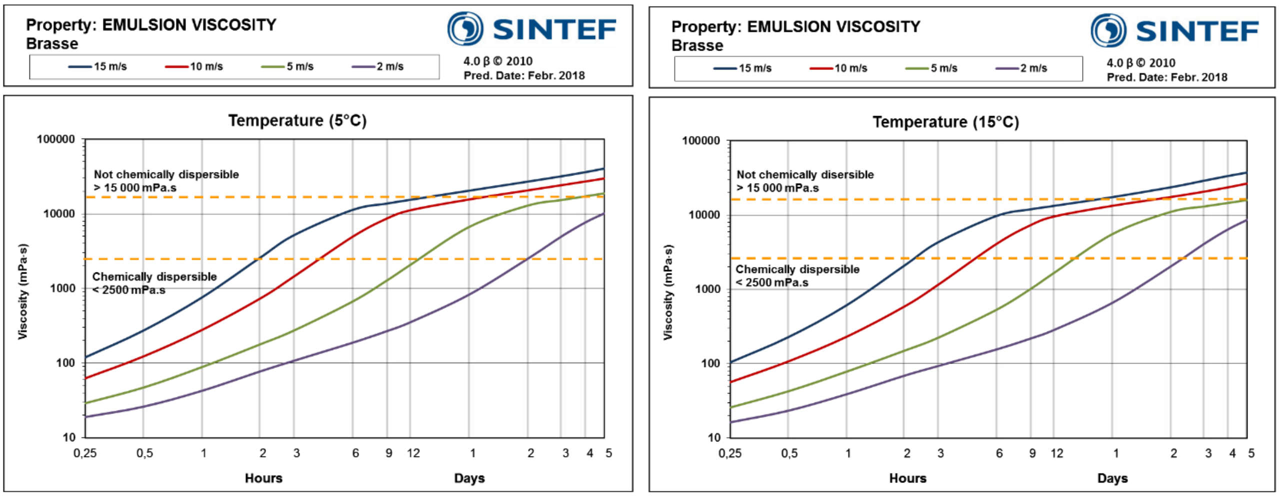


Figure 7-7: Time window for use of chemical dispersant as a function of emulsion viscosity for Brasse at 5 and 15 °C

Screening of dispersants (Dasic NS, Corexit 9500, OSR 52, Gamlen 4000 and Radiagreen OSD) on Brasse, simulating underwater dispersant injection from a subsea release, showed that Corexit 9500 had the highest effectiveness relative to the other dispersants, reflecting decrease in the droplet size distribution. This was mostly pronounced for DOR from 1:500 and higher. Dasic NS on the other hand showed the lowest effectiveness and less decrease in the droplet size distribution with increasing DOR, as also observed for other crude oils from similar testing.

7.10 Comparison of Brasse vs. Brage

Brage has been used as a reference oil for oil spill contingency analysis for the Brasse oil filed. The weathering properties of Brasse has been therefore been compared with Brage related to oil spill response, and summarized in Table 7-1.

Table 7-1: Comparison of weathering properties related to oil spill response

Comparison of weathering properties	Brasse	Brage
Physical and chemical properties	• Low content of asphaltenes (0.16 wt %) • Low /medium content of wax (2.88 wt %). • Medium density paraffinic crude oil (0.847 g/mL) • Pour point: -15ºC. The pour points of residues increase heavily (+9 to +24 ºC) • Evaporation loss 250C+: 46 vol.% High degree of similarities in physicochemical properties with Brage	• Low content of asphaltenes (0.1 wt %) • Medium content of wax (4.7 wt %) • Medium density paraffinic crude oil (0.826 g/mL) • Pour point: -6 ºC. The pour points of its residues increase heavily (+15 to +24 ºC). • Evaporation loss 250C+:45 vol. % High degree of similarities in physicochemical properties with Brasse
Water uptake	Brasse reached a water uptake of 75-80 vol. % at 5 and 15 °C. Brasse has a relatively rapid water uptake, although lower compared with Brage.	Brage has a rapid water uptake. The predicted max. water is 80 vol. % at 5 and 15 °C.
Stability of emulsion	Brasse forms stable emulsion. The emulsions partly break with addition of emulsion breaker (2000 ppm, Alcopol 60 %). 72 % free water was released for 250°C + emulsion at 13 °C.	The oil forms stable emulations Addition of emulsion breaker (2000 ppm, Alcopol 60 %) partly breaks the emulsion. 75 vol. % of free water was released for the 250°C+ at 13 °C
Mass balance	Brasse has slightly longer lifetime of oil at sea surface vs Brage Example: 2 days weathering at 15ºC and 10 m/s wind speed: Natural dispersion: 39 % Evaporation: 38 % Surface oil: 23%	Brasse has slightly longer lifetime of oil at sea surface vs Brage Example: 2 days weathering at 15ºC and10 m/s wind speed: Natural dispersion: 47 % Evaporation: 38 % Surface oil: 15%
Dispersibility	Brasse has a potential for chemical dispersion-several days at summer and winter conditions. Dispersible for viscosities <2500 mPa.s and not dispersible for viscosities >15000 mPa.s. Wide window of opportunity for dispersant use. E.g. 5 days at 2-5 m/s wind speeds, and 12 hours to 1 day at 10-15 m/s wind speeds.	Brage has a potential for chemical dispersion-several days at summer and winter conditions. Dispersible for viscosities <1500 mPa.s and not dispersible for viscosities >16000 mPa.s. Wide window of opportunity for dispersant use > 5 days
Mechanical recovery	Brasse forms relative high emulsion viscosities and reach > 15-20 000 mPa.s after 5 days of weathering at 10-15 m/s wind speeds. The risk of boom leakage should be considered for viscosities < 1000 mPa.s. E.g.	Brage forms emulsion viscosities < 10 000 mPa.s. The risk of boom leakage < 1000 mPa.s. E.g. 3-6 hours at 5 m/s wind speeds, and 1-2 hours at 10-15 m/s wind speeds

	2-3 hours at 5 m/s wind speed, and < 1 hour at 10-15 m/s	
Solidification	Brasse has a potential for solidification e.g. 9-12 hours at 10 m/s, 15 °C on the sea surface. This may reduce the dispersibility and use of high visc. skimmer could be considered in such cases.	Brage has a potential for solidification e.g. 2-3 hours at 10 m/s, 15°C on the sea surface. This may reduce the dispersibility and use of high visc. skimmer could be considered in such cases.

The weathering properties of Brasse vs. Brage show similarities between the two oils, and Brage could therefore considered as an acceptable candidate as a reference crude oil in oil spill contingency analysis. The oils are not expected to give very different outputs from such analysis.

8 Categorization of crude oils

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 are 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 10-15 ºC 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.

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A The behaviour of crude oil on the 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.

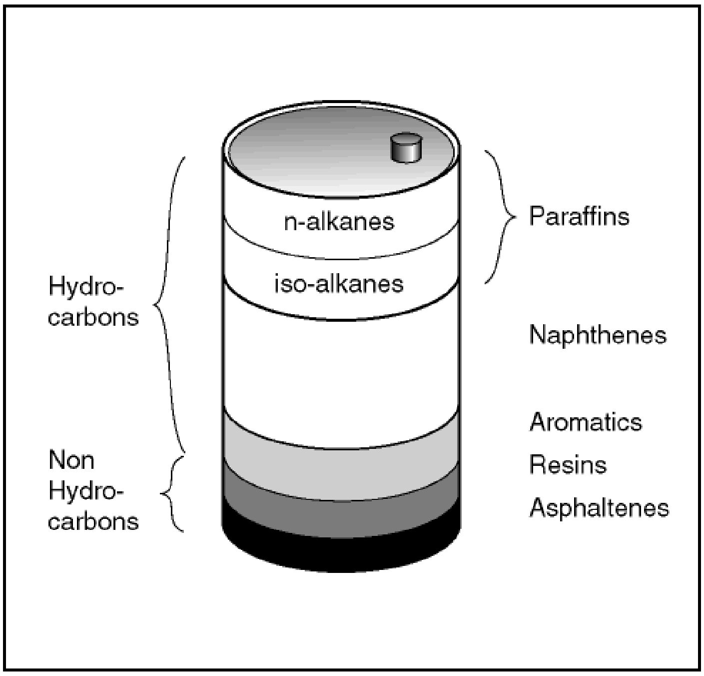


Figure A-1: The chemical composition of crude oils

A.1.1 Hydrocarbons

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 the majority of 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.

A.1.2 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 is 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.

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 of 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:

$$\boxed{°\text{API} = \frac{141.5}{Secific\ gravity} - 131.5}$$

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^2, Pa s or kg/(m s), where 1 Pa s = 1 N s/m^2 = 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^2 or Poise, where 1 Poise = 1 dyne s/cm^2 = 1 g/(cm s) = 1/10 Pa s = 1/10 N s/m^2. 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^2. 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^{-1} 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.

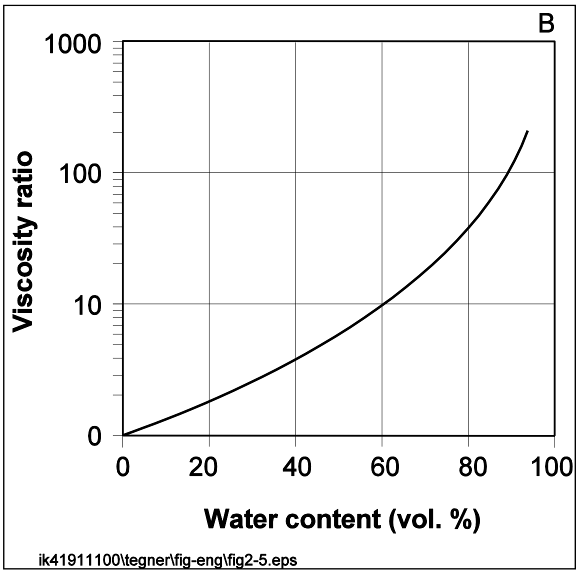


Figure A-2: Example of viscosity ratio as a function of water content

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 *10 to 15^{o}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 (True Boiling Point curve – TBP)

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.

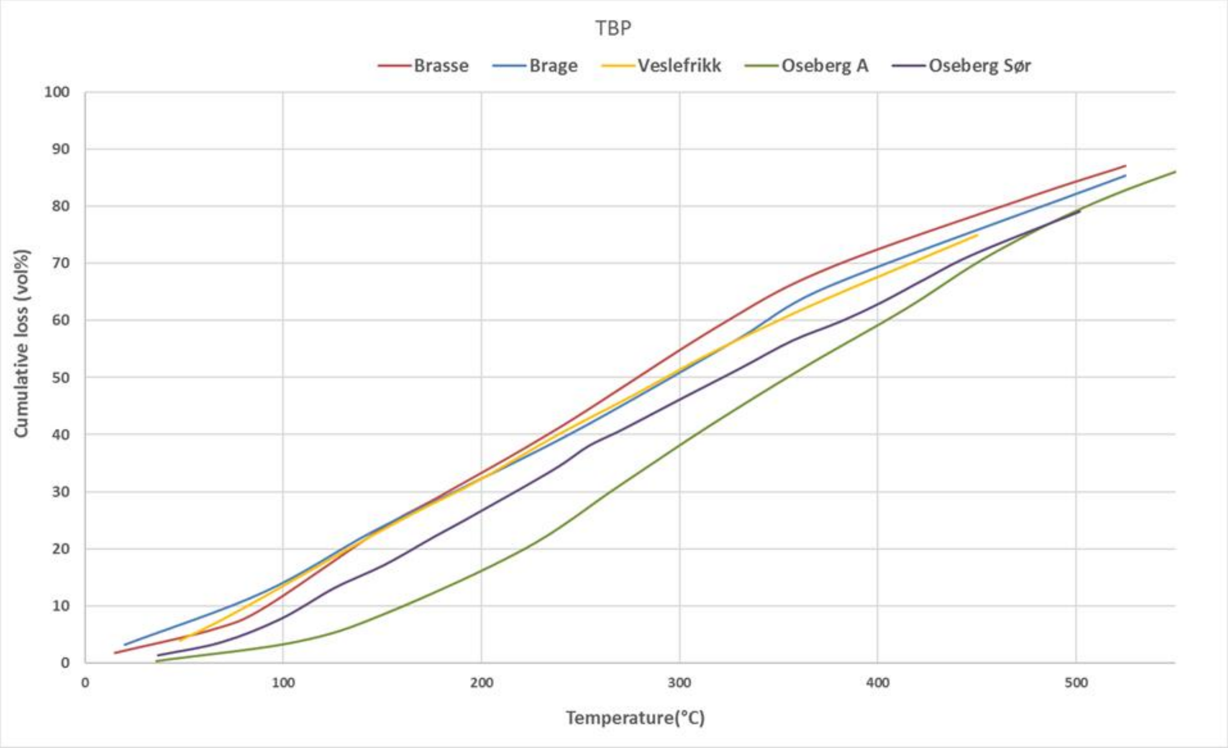


Figure A-3: Distillation curves from SINTEF OWM for Brasse crude oil in comparison with Brage, Veslefrikk, Oseberg A, and Oseberg Sør.

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 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-4 illustrates the various weathering processes, and Figure A-5 shows their relative importance over time.

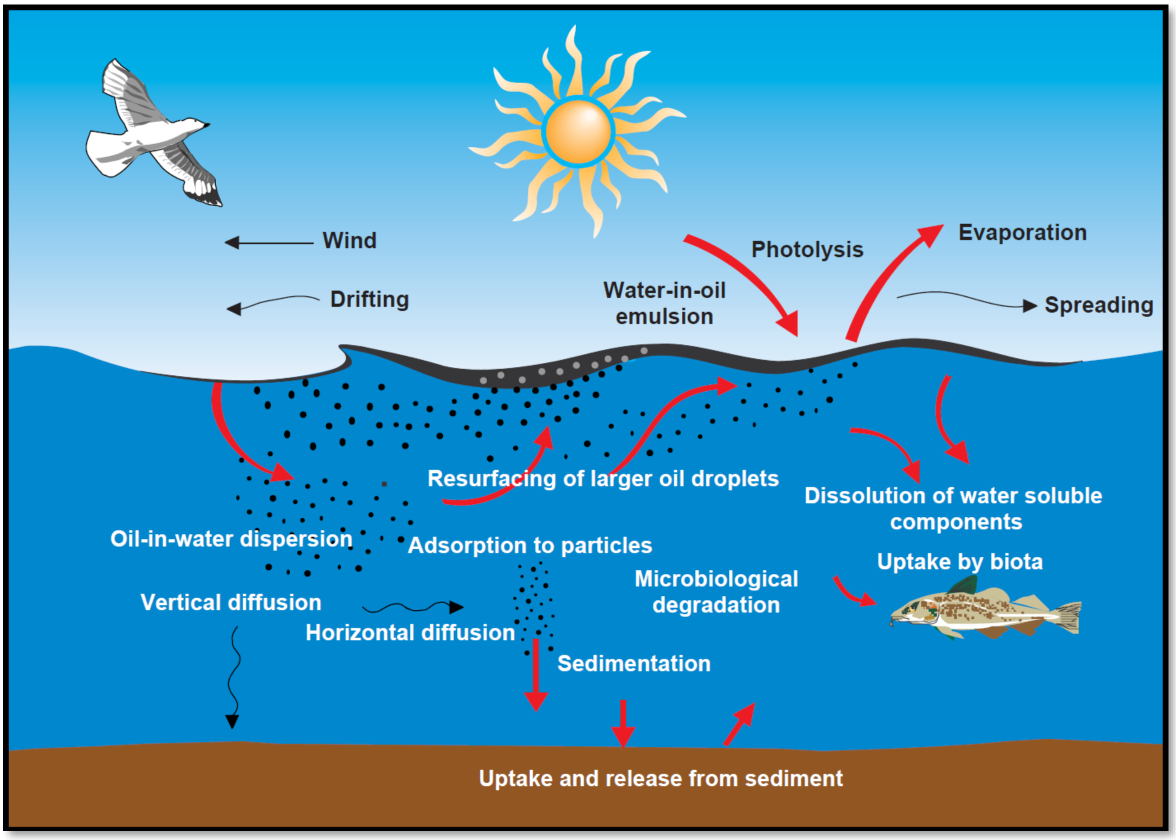


Figure A-4: Illustrating the weathering processes that take place when oil is spilled on the sea surface

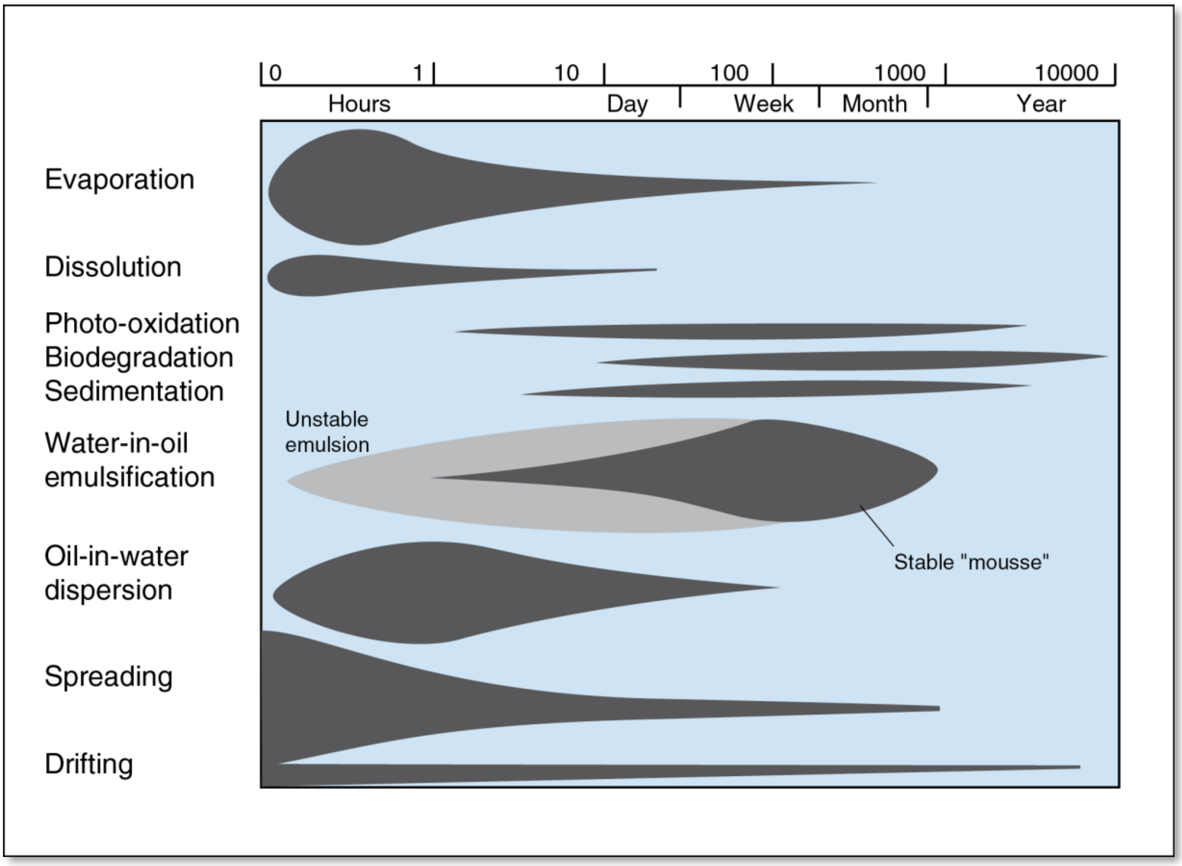


Figure A-5: Weathering processes' relative importance over time. Note: logarithmic scale

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-6. 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 µm oil thickness) that only contains 10% of the oil volume. Most of the oil volume (~90%) is located 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.

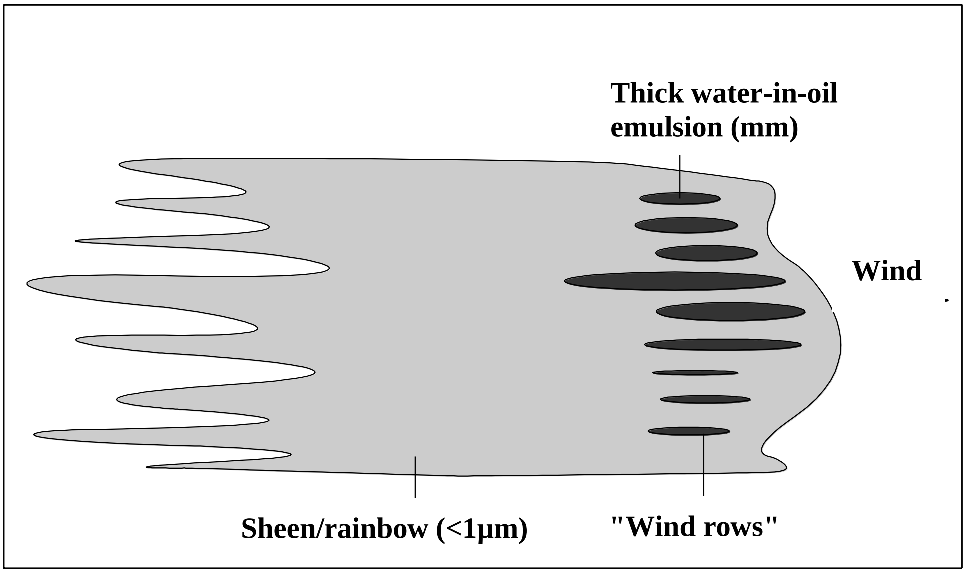


Figure A-6: The spreading of oil spilled on the sea surface and the distribution within the oil slick

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-7. 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.

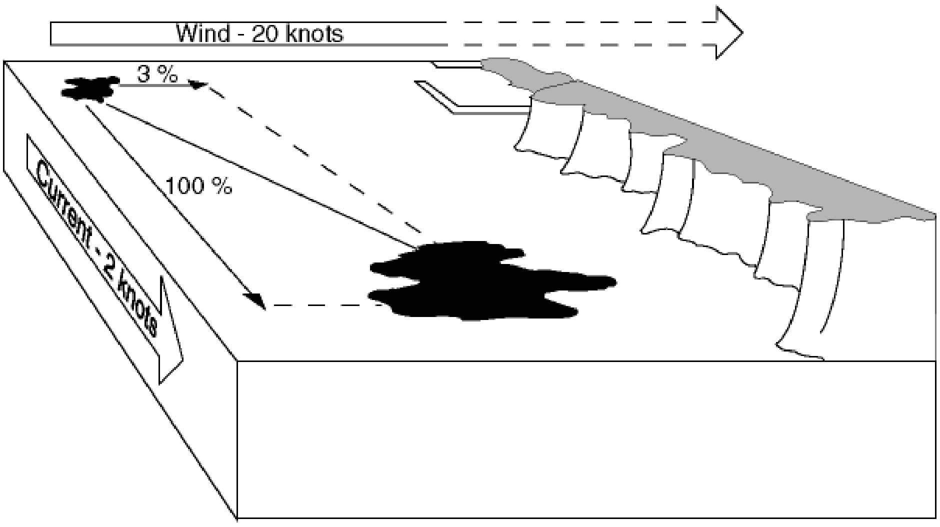


Figure A-7: An illustration showing how wind and current can influence the drifting of an oil slick

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-8 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.

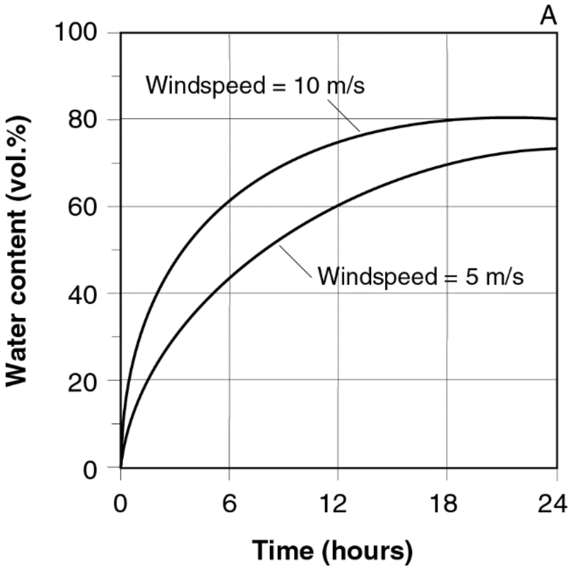


Figure A-8: Example of how weather conditions influence the w/o emulsion formation for typical oils

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 µm, yielding a more stable emulsion.

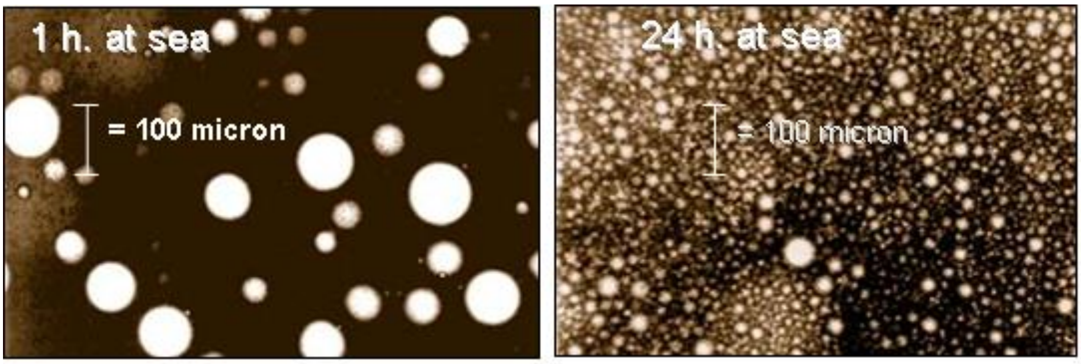


Figure A-9: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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-10.

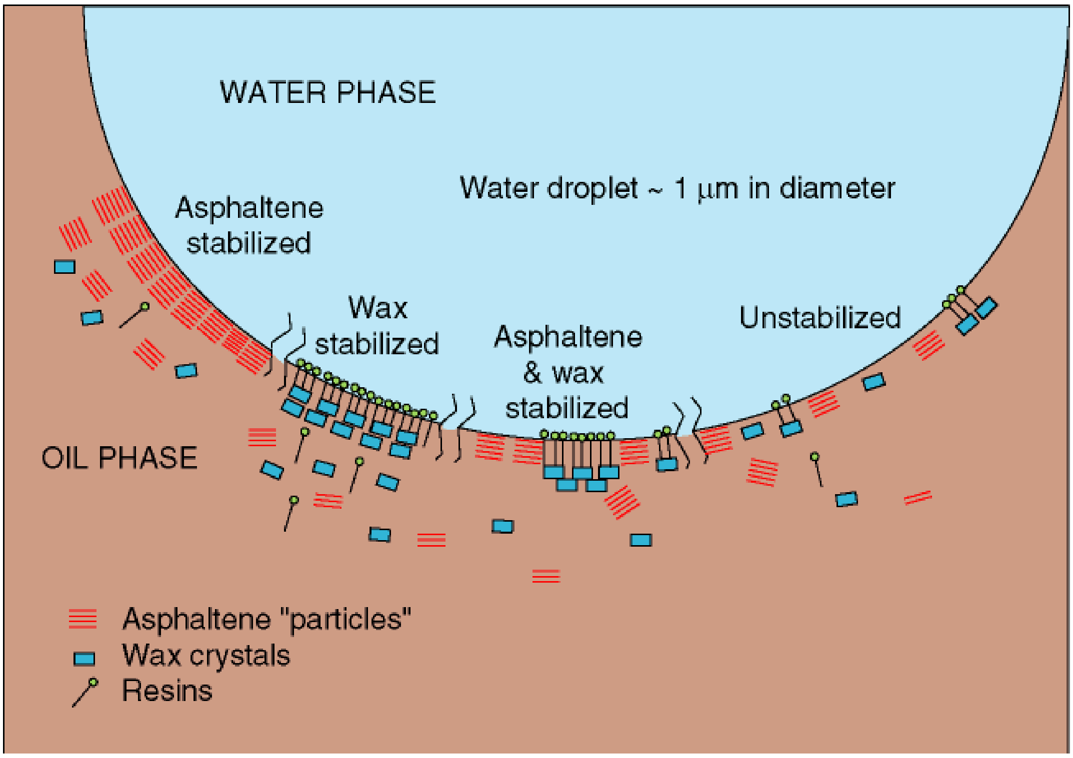


Figure A-10: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

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 both 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.

At SINTEFs laboratories we have the possibility to measure the ultra-low interfacial tension (IFT) values of oil/water/surfactant interfaces by the spinning drop apparatus. With our ultra-modern equipment, it is possible to measure the IFT in the range from $1 \cdot 10^{-6}$ to $2 \cdot 10^{3}$ mN/m.

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 µm - 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 reduces 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_7) 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.4.10Deep 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-11. This was observed both during the "DeepSpill" experiments in 2000 (Figure A-12) and the DWH oil spill in 2010 (Figure A-13). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.

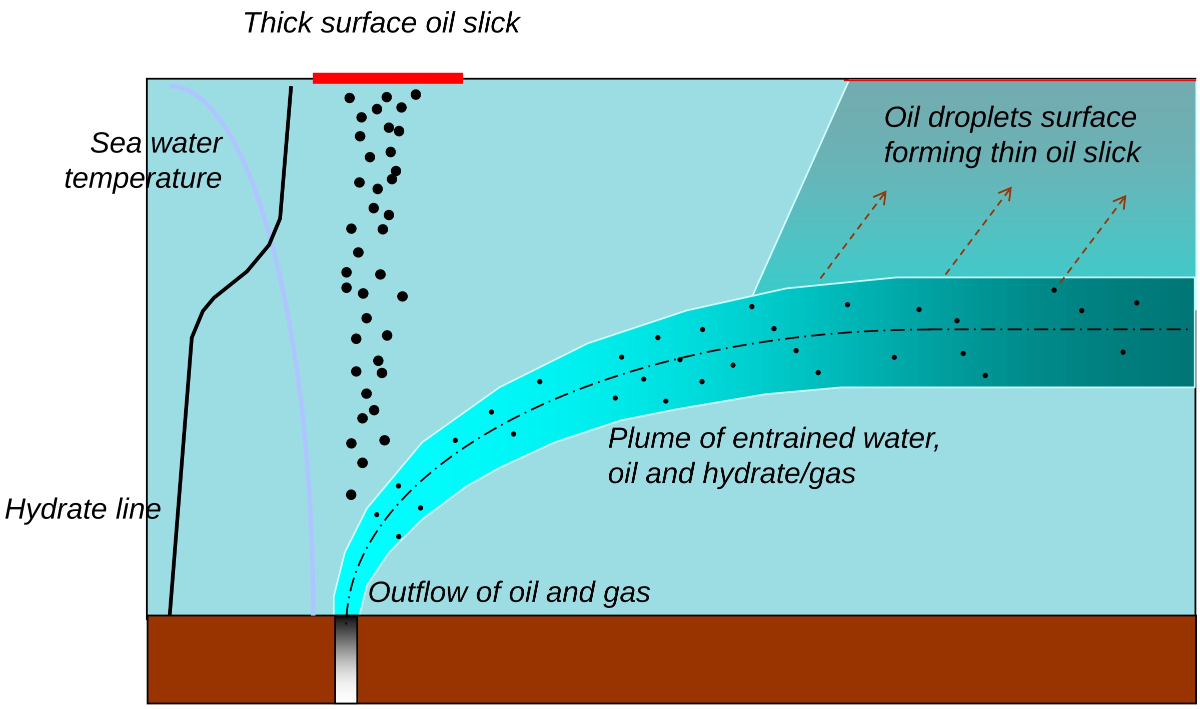


Figure A-11: Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil

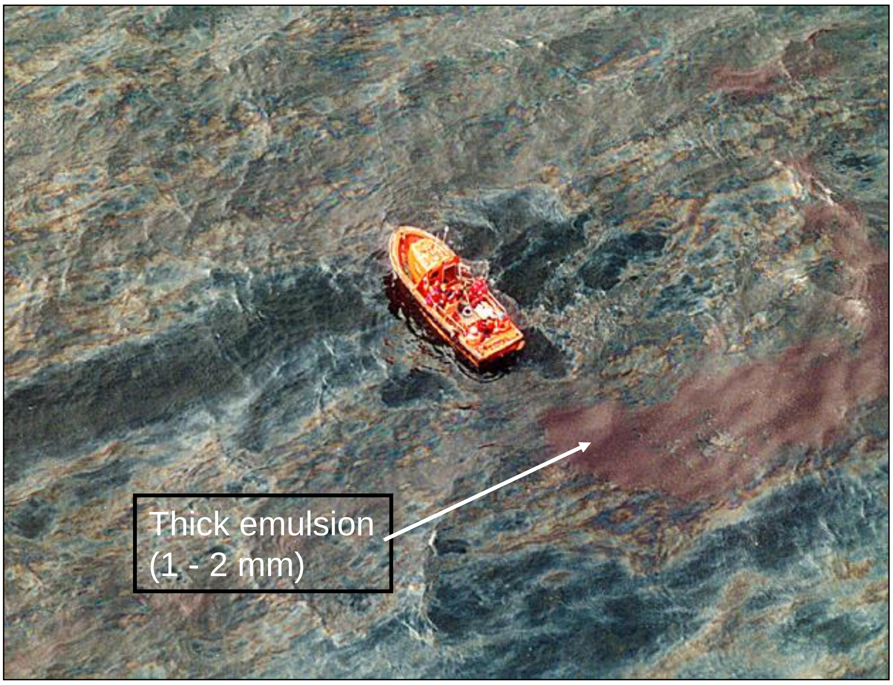


Figure A-12: Surface oil slick (initial thickness > 200 µm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)

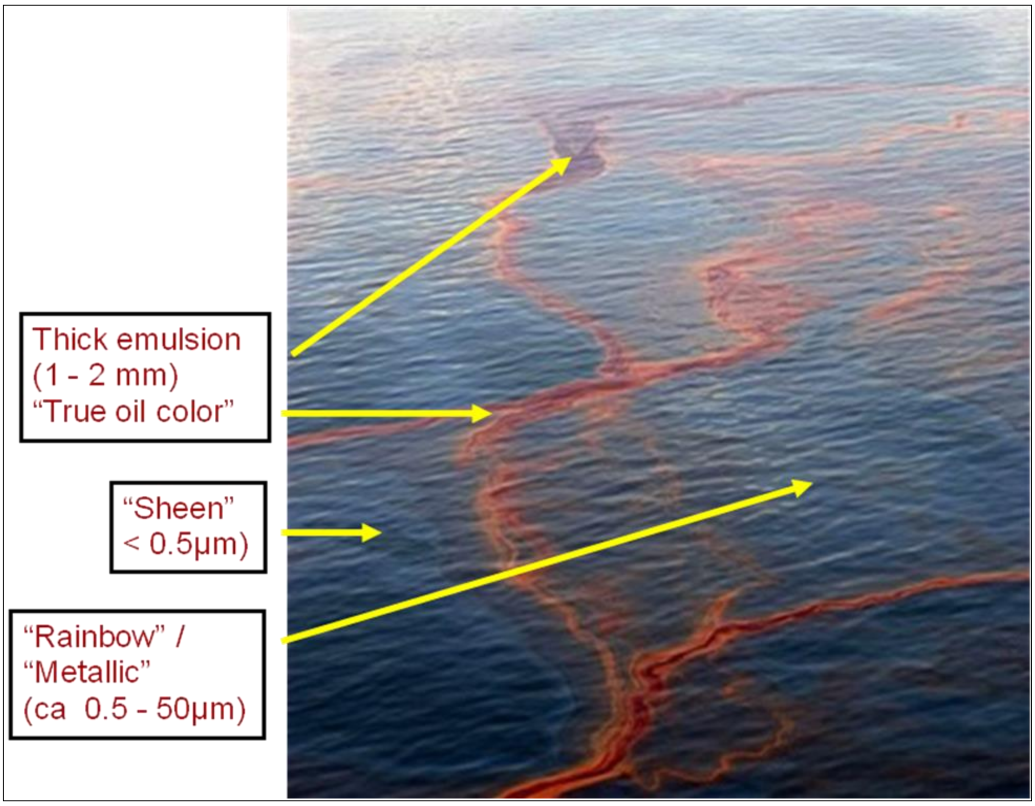


Figure A-13: Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying similar to an oil slick from a surface batch release

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-14, Figure A-15 and 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.

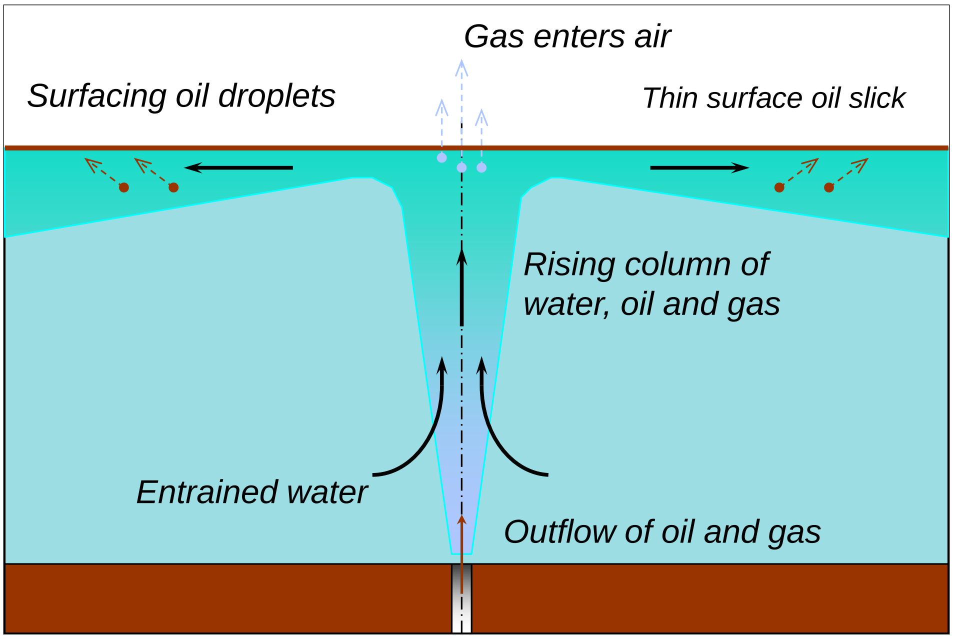


Figure A-14 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)

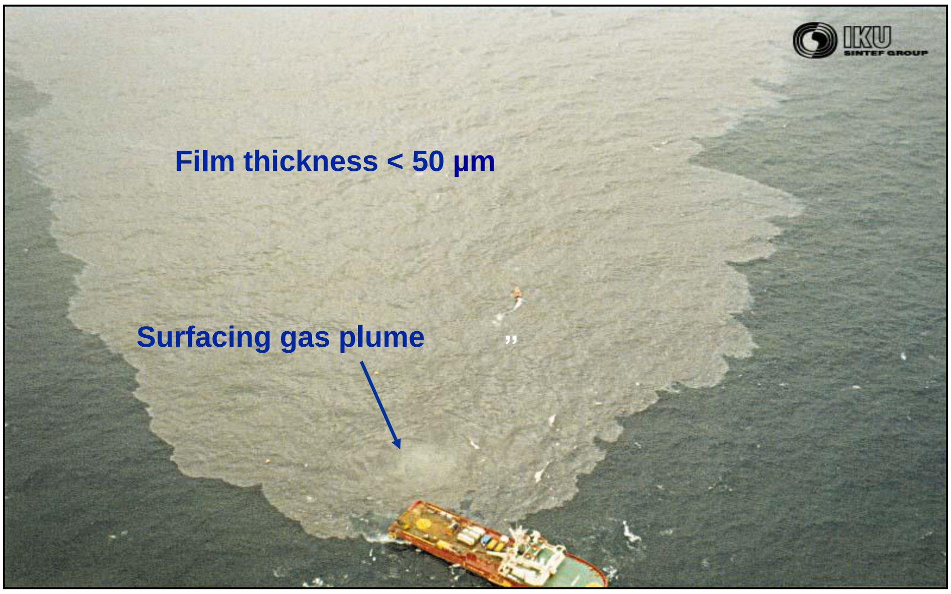


Figure A-15: Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

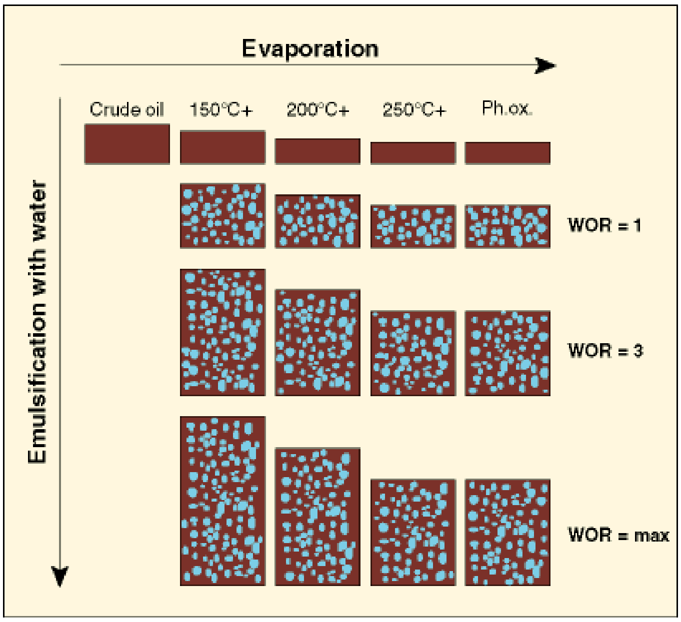
B.1 Oil samples and test temperature

Brasse crude oil (3 x 25 Litres) arrived at SINTEF Ocean AS 15.08.2017 (Figure B-1). The crude oil was given the unique SINTEF ID 2017-5349. The weathering and dispersibility study were performed at 13 °C.

Figure B-1: 3x 25 Litres barrels of Brasse crude oil arrived at SINTEF Ocean

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.



WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

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

B.2.1 Evaporation

The density of the oil was monitored during the degassing. This was performed before evaporation by standard procedure. 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.2.2 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" asphaltenes 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 (IFT)	Pendant drop method	Krüss DSA100 Drop Shape Analyser

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_5-nC_{40}) 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_0-C_4) 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_5-nC_{10} 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.2.3 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.

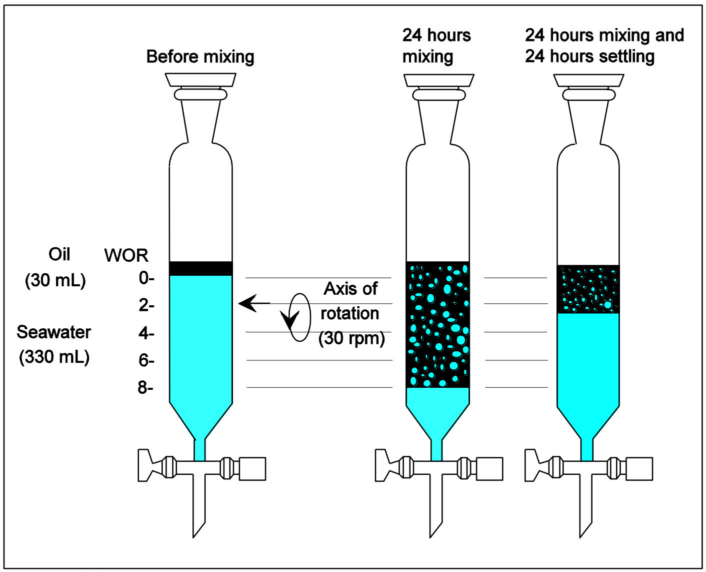


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Figure B-3: Principle of the rotating cylinder method

B.3 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.3.1 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 the art instrumentation. A schematic drawing of the flume is given in Figure B-4.

Approximately 5 m^3 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.

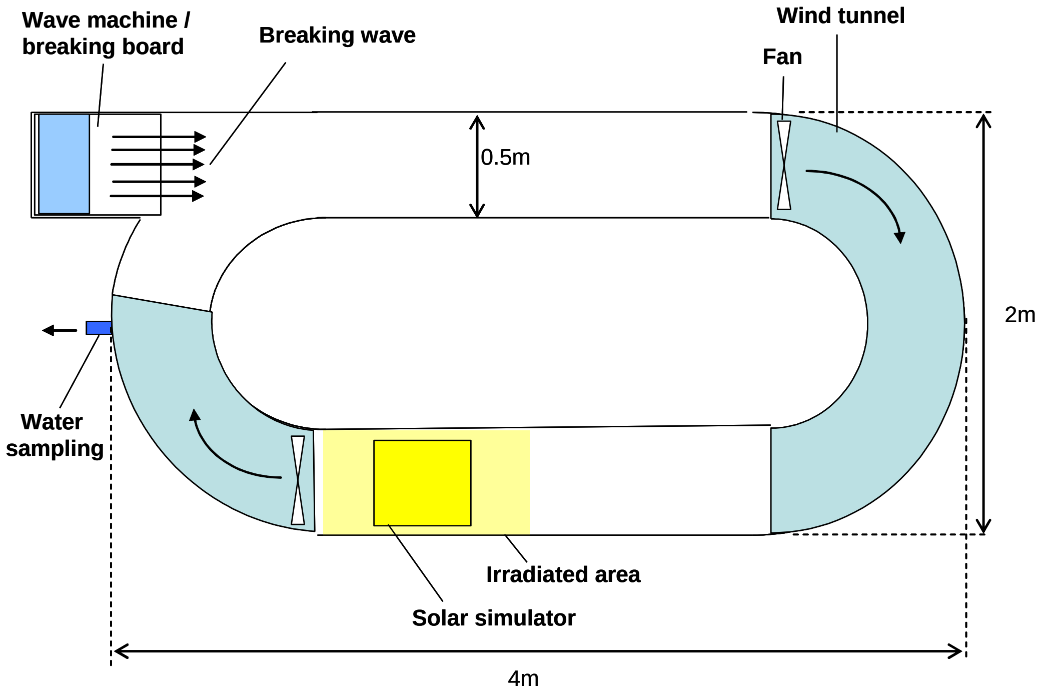

Figure B-4: Schematic drawing of the meso-scale flume

B.3.2 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% 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 Ultra Violet (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).

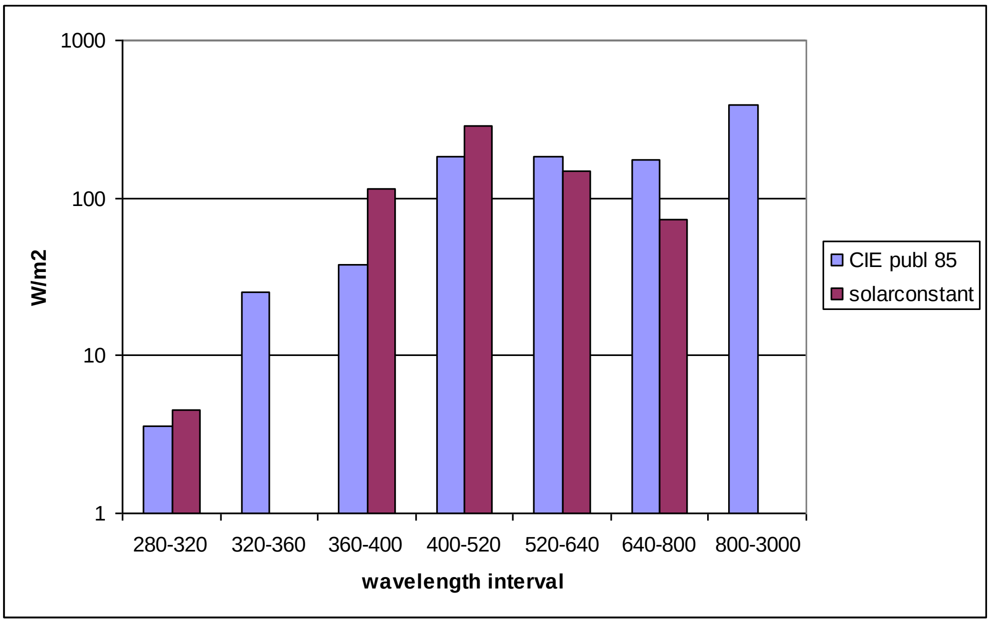

Figure B-5: Measured wavelength compared to standard spectrum suggested in CIE publication 85

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.

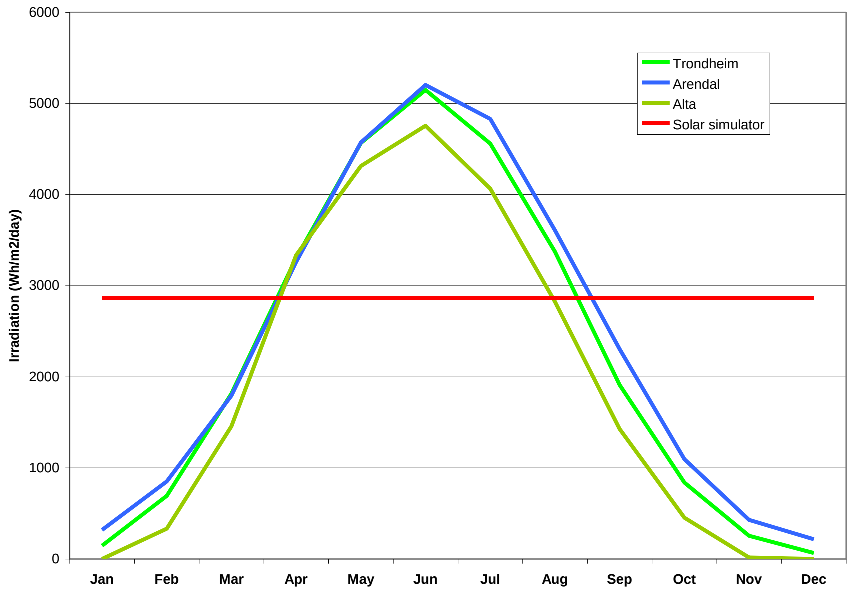

Figure B-6: Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume

The simulated irradiance seems to be the approximate average of the daily irradiance throughout the year. It should be noted, however, that the simulations are not considering clouds. The real irradiation will be lower than that predicted in Figure B-6.

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Brasse crude oil is given in Table C-1 to C-3.The oil weathering predictions were based on the laboratory data at 13 °C.

Table C-1: Physical and chemical properties for Brasse crude oil at 13 °C

Properties of fresh oil	Value
Density (g/mL)	0.8465
Pour point (°C)	-15
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	9
Asphaltenes (wt. %)	0.16
Wax Content (wt. %)	2.88
Dispersible for visc. <	2500
Not dispersible for visc. >	15000

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

Table C-2: True boiling point (TBP) curve for Brasse crude oil

Temp. (°C)	Cumulative loss (vol. %)
15	1.77
65	5.88
90	9.56
150	23.58
180	29.37
240	41.36
320	59.08
375	69.11
475	81.43
525	87.06

**TBP received from Faroe Petroleum Norge AS*
Crude Assay Report no: 12002/00022867/17

Table C-3: Lab weathering data for Brasse crude oil at 13 °C

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	202	260	317
Vol. Topped (%)	0	21.7	33.5	45.8
Weight Residue (wt. %)	100	81.3	70.3	58.4
Density (g/mL)	0.8465	0.8791	0.8948	0.9109
Pour point (°C)	-15	9	18	24
Flash Point (°C)	-	42.5	84.5	122.5
Viscosity of water-free residue (mPa.s =cP)	9	64	197	676
*Viscosity of 50% emulsion (mPa.s = cP)**	-	375	1426	6103
*Viscosity of 75% emulsion (mPa.s = cP)**	-	1306	4161	13129
*Viscosity of max water (mPa.s = cP)**	-	4332	8162	15861
Max. water cont. (vol. %)	-	86	81	75
(T1/2) Halftime for water uptake (hrs)	-	0.28	0.37	0.49
Stability ratio	-	1	1	1

** Measured at shear rate 100* s^{-1}
***Measured at shear rate 10* s^{-1}
- No data

D Chemical characterization of Brasse

Table D-1: Chemical characterization ("oil profile") of Brasse fresh oil derived from GC-MS analysis and TBP oil fraction

No	Description	Brasse crude oil wt.%
1	C1-C4 gasses (dissolved in oil)	2.000
2	C5-saturates (n-/iso-/cyclo)	2.000
3	C6-saturates (n-/iso-/cyclo)	1.731
4	Benzene	0.269
5	C7-saturates (n-/iso-/cyclo)	3.000
6	C1-Benzene (Toluene) et. B	1.056
7	C8-saturates (n-/iso-/cyclo)	7.944
8	C2-Benzene (xylenes; using O-xylene)	1.516
9	C9-saturates (n-/iso-/cyclo)	3.304
10	C3-Benzene	1.180
11	C10-saturates (n-/iso-/cyclo)	3.000
12	C4 and C4 Benzenes	0.069
13	C11-C12 (total sat + aro)	5.931
14	Phenols (C0-C4 alkylated)	0.000
15	Naphthalenes 1 (C0-C1-alkylated)	0.467
16	C13-C14 (total sat + aro)	7.533
17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0	NA
37	metabolite 1	NA
38	metabolite 2	NA
18	Naphthalenes 2 (C2-C3-alkylated)	0.696
19	C15-C16 (total sat + aro)	6.304
20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)	0.312
21	C17-C18 (total sat + aro)	6.688
22	C19-C20 (total sat + aro)	6.000
23	C21-C25 (total sat + aro)	7.776
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.224
25	C25+ (total)	31.000

NA – Not analysed

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

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. OSCAR may compute oil weathering from crude assay data, although the most reliable results are produced if the target oil has been through a standardized set of laboratory weathering procedures established by the SINTEF laboratories. Alternatively, the model may use oil-weathering properties from oils for which data already exist, selecting the oil in the oil database that most closely matches the composition of the oil of concern.

E Yield stress rheology

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). Many crude oils (and emulsions) are so-called Bingham-plastic fluids at sea temperature. This means that applied force must be exerted on the fluid to make it flow and hence spread, and is mainly pronounced for *non-Newtonian* oils where the viscosities varies with the shear rate. Yield stress can be utilized in modelling tool for modelling spreading of oil on the sea surface and for calculation of oil terminal film thicknesses.

The measurements were performed by applying a gradually increasing oscillating force to the sample. The instrument measure the sample's response to the exerted oscillating. The yield stress is derived from measurement of oscillation stress-sweep with increasing applied force on the sample where the deformation of the oil sample is measured. Results from the yield stress measurements of Brasse are tabulated in Table E-1, below.

Table E- 1 Yield stress (flow limit) measurements for Brasse at 13 °C measured with Physica MRC 300 rheometer

Residue	**Water Content (Vol%)**	**Yield stress (Flow limit) (Pa)**	**Deformation**
Fresh	0	ND	ND
150°C+	0	ND	ND
200°C+	0	ND	ND
250°C+	0	2.8	0.87
150°C+	50	ND	ND
200°C+	50	3.44	1.03
250°C+	50	5.62	1.31
150°C+	75	0.53	1.38
200°C+	75	8.76	-
250°C+	75	7.29	1.22
150°C+	86*	25.3	6.16
200°C+	*	20.9	4.88
250°C+	56*	9.18	1.21

*ND: No yield stress quantified *Maximum water*

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