

Report

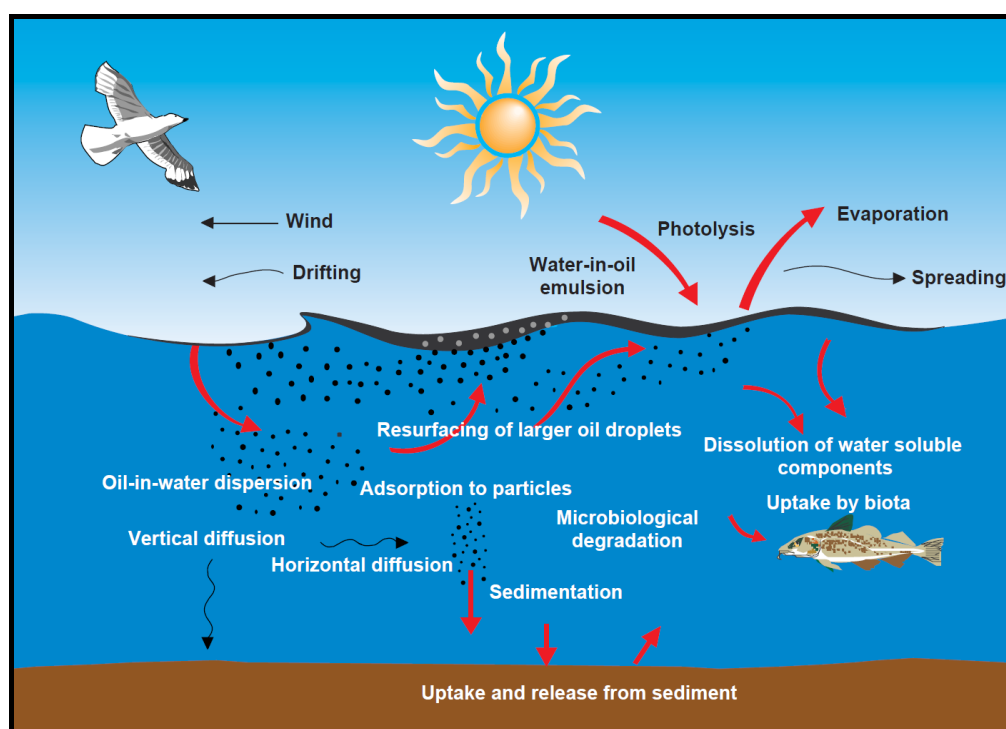
Luno II crude oil – properties and weathering at sea

Related to oil spill response

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Report

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ABSTRACT**Abstract heading**

A study of the weathering properties of Luno II has been performed using both small and meso-scale laboratory testing at two temperatures, 5°C and 13°C. The obtained data was used as input in the SINTEF Oil Weathering Model (OWM) to predict the fate and behaviour of Luno II in a spill situation at sea. The weathering properties are discussed in relation to oil spill response; mechanical recovery and chemical dispersion.

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Table of contents

1	Executive summary	5
2	Introduction	6
3	Experimental results.....	7
3.1	Small-scale laboratory testing results.....	7
3.1.1	Chemical composition and physical properties.....	7
3.1.2	Emulsifying properties of Luno II.....	13
3.1.3	Chemical dispersibility	19
3.2	Meso-scale laboratory testing results.....	25
3.2.1	Evaporation.....	28
3.2.2	Water uptake	29
3.2.3	Mass balance	31
3.2.4	<i>In situ</i> chemical dispersion	32
3.2.5	Visual observations.....	32
4	Predictions with SINTEF Oil Weathering Model (OWM)	40
4.1	Description of SINTEF OWM	40
4.2	Predictions of Luno II weathering properties	41
4.3	Comparison with other oils.....	51
5	Weathering properties of Luno II crude oil related to oil spill properties	57
5.1	Oil properties	57
5.2	Flash point - fire/explosion hazard	57
5.3	Emulsion formation.....	57
5.4	Breaking of emulsion with addition of emulsion breaker	58
5.5	Lifetime at sea - natural dispersion and evaporation	59
5.6	Oil spill response	60
5.6.1	Mechanical recovery.....	60
5.6.2	Use of chemical dispersants	62
6	Categorization of Luno II versus other Norwegian crudes.....	64
7	References	65
A	- The behaviour of crude oil on the sea surface.....	67
A.1	The chemical composition of crude oils	67
A.1.1	Hydrocarbons	67
A.1.2	Heteroatomic organics	68

A.2	Main oil categories - related to weathering	68
A.3	Physical properties of crude oils	69
A.3.1	Rheological properties.....	69
A.3.2	Pour point	70
A.3.3	Distillation curve (True Boiling Point curve-TBP).....	70
A.3.4	Flash point	71
A.4	The behaviour of crude oil spilled at sea	72
A.4.1	Evaporation.....	73
A.4.2	Spreading	73
A.4.3	Drift of an oil slick	74
A.4.4	Water-in-oil (w/o) emulsion	75
A.4.5	Oil-in-water (o/w) dispersion	77
A.4.6	Water solubility	78
A.4.7	Photo-oxidation	79
A.4.8	Biodegradation	79
A.4.9	Sedimentation	79
B	Experimental setup.....	80
B.1	Oil samples and test temperature	80
B.2	Small-scale laboratory testing.....	80
B.2.1	Evaporation.....	81
B.2.2	Physical and chemical analysis	81
B.2.3	Emulsification properties.....	82
B.2.3.1	Calculation of Emulsion Stability	82
B.2.4	Chemical dispersibility testing	83
B.3	Meso-scale laboratory testing	84
B.3.1	Description of the flume basin	84
B.3.2	Oil weathering in the flume basin	85
C	Input data to SINTEF Oil Weathering Model (OWM)	88
D	Chemical characterisation of the fresh oil on GC/MS	89

APPENDICES

[List appendices here]

1 Executive summary

When weathered on the sea surface, both oil and condensates will undergo changes that affect oil spill countermeasures in various ways, as a function of time and weather conditions. This summary gives a brief overview of the main changes to Luno II crude oil when weathered on the sea surface, and compares the changes to previously studied oils.

Luno II is a medium heavy paraffinic crude oil with a density of 0.851 g/ml, a medium asphaltene content of 0.5 wt. % and a low wax content of 2.7 wt. %. High initial evaporative loss will result in a relative increase of asphaltene and wax content, if the oil is spilled at sea. This relative increase of heavy end components will alter the chemical properties of the oil. Luno II rapidly forms stable water-in-oil (w/o) emulsions with relatively high viscosities in both summer and winter conditions. Luno II is predicted to have a long lifetime at sea except in very high sea states (wind =15 m/s), where the evaporative loss and natural dispersion combined will remove the oil from the sea surface within five days based on the mass balances.

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. For Luno II crude oil the flash point will be above the sea temperature within one hour in low wind (2m/s) in winter temperature, and faster in summer temperature and with higher wind speeds due to faster evaporation of lightest compounds. Some vessels engaged in oil recovery operations may not be classified to carry liquids with flash point lower than 60°C. Luno II will reach this limit in low wind conditions (2 m/s) after 12 hours at winter temperature and within six hours in summer temperature.

Luno II forms stable emulsions at both summer and winter temperatures. The maximum water contents of the emulsions are generally higher at 13°C compared to 5°C; maximum water content is 56 vol. % at 5°C compared to 71 vol. % at 13°C. The crude oil exhibits rather high emulsion viscosities, and the viscosities increase considerably with increasing water content.

As Luno II rather rapidly forms highly viscous emulsion, boom leakage will only be a problem for the first 12-14 hours in very calm conditions (2 m/s wind speed), when the emulsion viscosities are below 1000 mPas. However, as Luno II forms emulsions with high viscosities (20000 mPas) e.g. after 12 hours of weathering at 10 m/s wind speed, the oil is expected to have reduced flowability towards weir skimmers. The use of "high visc." skimmers could therefore be recommended.

In general Luno II has a potential for use of chemical dispersant. The oil is expected to be easily dispersed with viscosities lower than 3000 mPas, and has reduced chemical dispersibility up to viscosities of 25000 mPas. For optimal results the dispersants should be applied as quickly as possible; in strong wind (15m/s) the emulsion reaches the viscosity limit for dispersibility within six hours. Once the oil is expected to have reduced chemical dispersibility, additional energy or a higher dispersant dosage (DOR= dosage to oil ratio) should be applied. Repeated application of dispersant may also increase the effectiveness, especially in calmer sea states. Additional energy can be provided using firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application in order to enhance dispersant effectiveness.

2 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. 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 oils can be when spilled on the sea surface. For that reason, having good knowledge about the expected behaviour of oil at sea in case of an accidental spill is highly valuable.

Recent dispersibility studies of the oil spilled after the Deepwater Horizon incident in the Gulf of Mexico (2010) clearly showed how dispersant application efficiency may change as the oil is weathered and emulsified on the sea surface over a longer period. This may form important support for refining operative strategies in terms of where, when and how dispersants could be effectively applied during a response operation.

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway (Ptil) regulations for petroleum activities (Aktivitetsforskriften §59), the characterization of oils with respect to their weathering properties and fate in the marine environment should be performed for all oils coming into production.

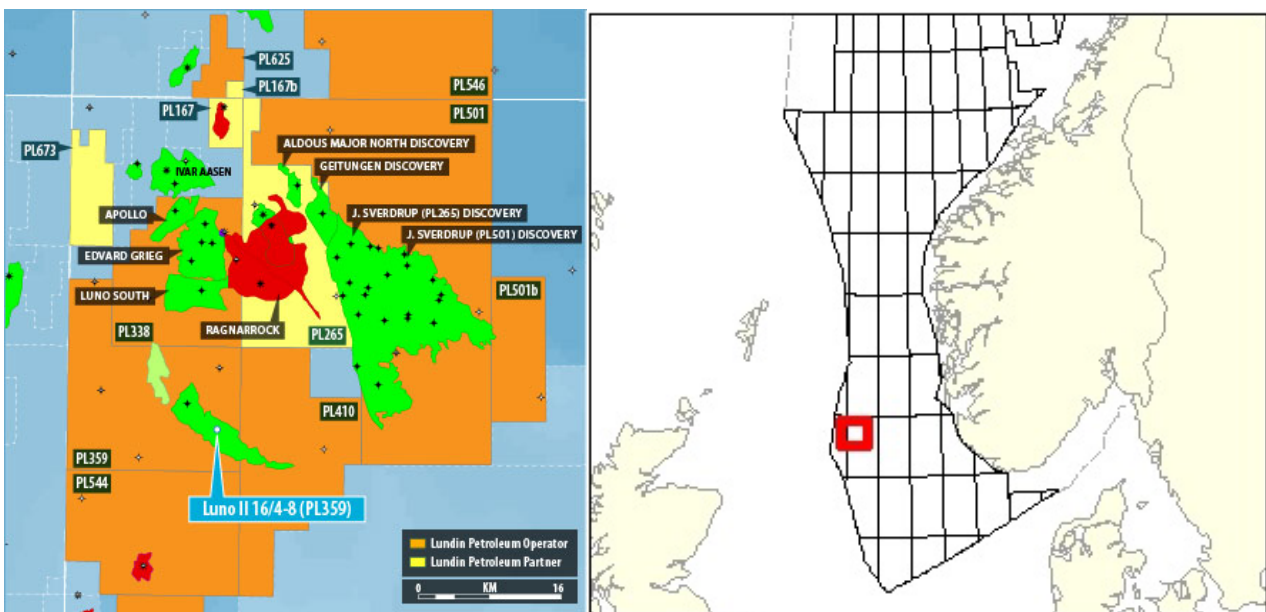


Figure 2-1: Location of Luno II oil field in the North Sea. (Sources: http://www.lundin-petroleum.com/eng/exploration_programme.php, http://www.npd.no/global/norsk/1-aktuelt/boretillatelser/b2013/16-4-6-s_ny.pdf)

Luno II is an oilfield located in the North Sea approximately 15 km south of Edvard Grieg and 200 km west of Stavanger. The reservoir is found in sandstone, 280 meters thick, from the Jurassic to Triassic epochs and is located at 1950 meters below sea surface.

On Lundin Norway's request, a full weathering study of Luno II crude oil at summer and winter temperature has been conducted. The study included small-scale laboratory testing and meso-scale flume tests at two temperatures, 5°C and 13°C. The obtained data were used in order to predict Luno II's fate and behaviour when spilled at sea, under different weather conditions. The results and predictions are discussed with regard to oil spill response operations.

3 Experimental results

3.1 Small-scale laboratory testing results

The small-scale weathering results of Luno II are compared with similar data of other Norwegian oils, listed in Table 3-1. The oils are primarily selected based on their variety in properties and behaviour and in agreement with Lundin Norway.

Table 3-1: Oils compared to Luno II data in the report

Oil	Previous name	SINTEF ID	Ref	Rapportnr.
Edvard Grieg	Luno	2010-0327	Sørheim, 2011	A18427
Ivar Aasen	Draupne	2011-0001	Sørheim og Leirvik, 2011	A21165
Johan Sverdrup	Avaldsnes	2011-0444	Sørheim, 2012	A22484
Grane		1997-0253	Strøm og Daling, 1997	STF66 F98038
Statfjord A		2000-0036	Moldestad et al., 2001	STF66 F00138

The Luno II crude oil used in this study was given SINTEF ID 2013-0580.

3.1.1 Chemical composition and physical properties

The chemical composition of Luno II and other crude oils are shown in Figure 3-1 and Figure 3-2 as GC/FID chromatograms. Appendix D shows the result of the chemical characterization of the fresh oil on GC/MS.

Gas chromatographic flame ionization detector (GC/FID) characterization

The chemical composition of Luno II, as characterized by gas chromatography (GC/FID), is shown in Figure 3-1. The same figure also present the gas chromatographic characterization of the corresponding residues (150°C+, 200°C+, and 250°C+), and verify the artificial evaporation of the oil by use of distillation (topping) in the laboratory.

The gas chromatograms show the *n*-alkenes as systematic narrow peaks and the peaks to the left in the chromatogram represent the components with the lowest boiling point. As can be seen in Figure 3-1, these components are gradually removed with higher distillation temperature. More complex components, such as resins and naphthenes, are not as easily separated as *n*-alkanes and form a broad and poorly defined bump below more pronounced peaks. The bump is often described as "Unresolved Complex Mixture", or UCM. Heavier compounds such as asphaltenes (> *n*C₄₀) are not possible to analyse with this technique.

The GC/FID characterization indicates that Luno II is a paraffinic crude oil reflecting a medium amount of wax/paraffinic compounds in the range of *n*C₂₀-*n*C₃₀ (Figure 3-1). Also the other crude oils in comparison, except Grane, exhibit hydrocarbon profiles with typically paraffinic features, as shown in Figure 3-2.

Gas chromatography (GC/FID) is an important tool for oil characterisation and for oil spill identification as an initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, are the *n*C₁₇/Pristane and *n*C₁₈/Phytane ratios. These parameters for Luno II and other Norwegian oils are given in Table 3-2. **Error! Reference source not found.**

Table 3-2: *n*C₁₇/Pristane and *n*C₁₈/Phytane ratios for Luno II fresh oil compared to other oils

Oil	<i>n</i> C ₁₇ /Pristane	<i>n</i> C ₁₈ /Phytane
Luno II	1.0	1.8
Edvard Grieg	1.8	1.6
Ivar Aasen	2.2	2.8
Johan Sverdrup	1.8	1.9
Grane	1.3	N.C.
Statfjord A	1.7	2.3

N.C.: Not Calculated

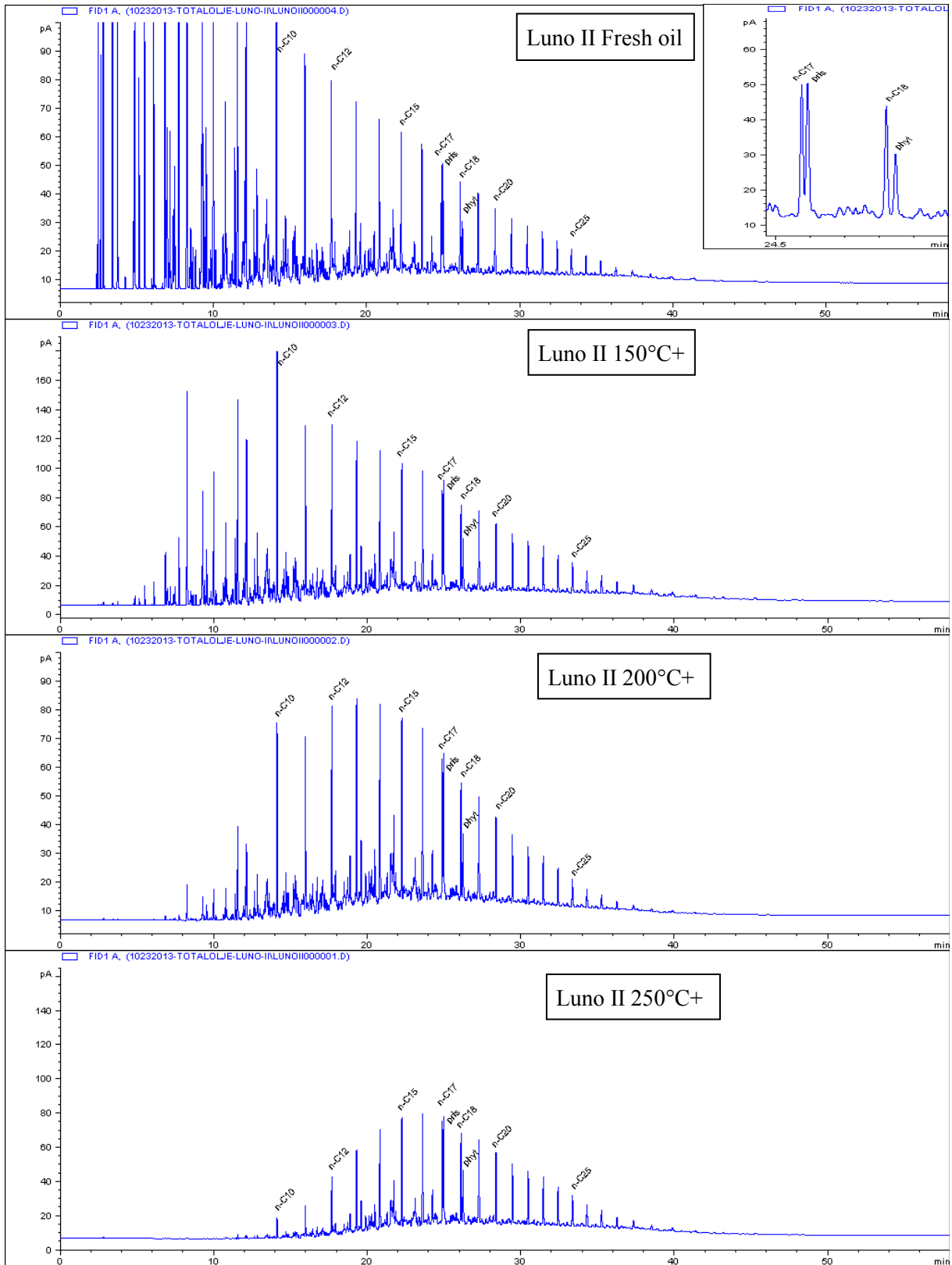
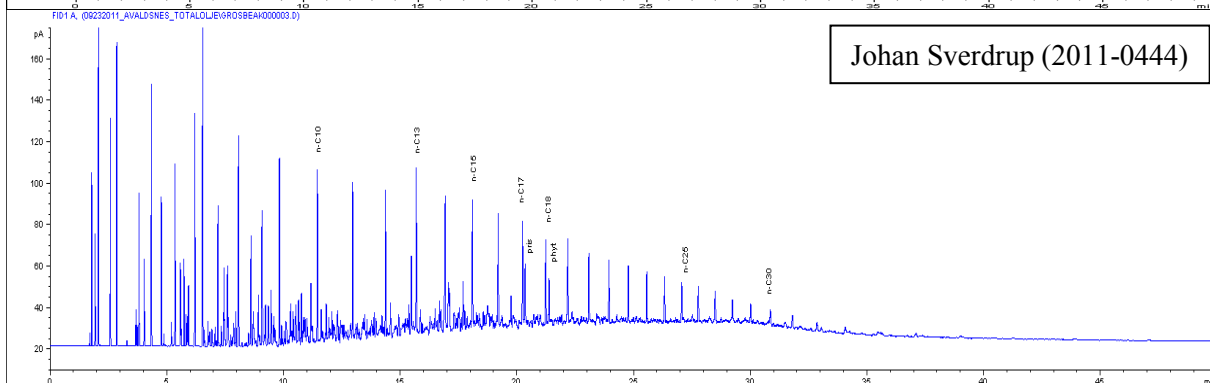
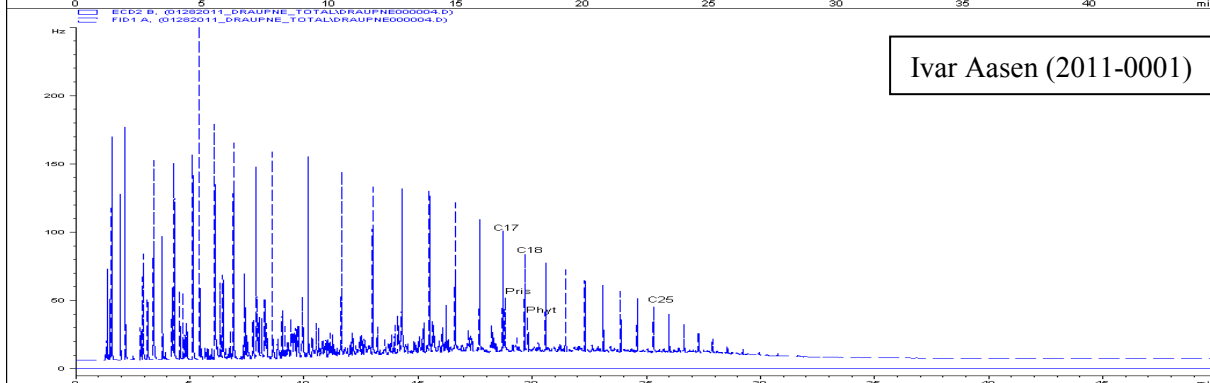
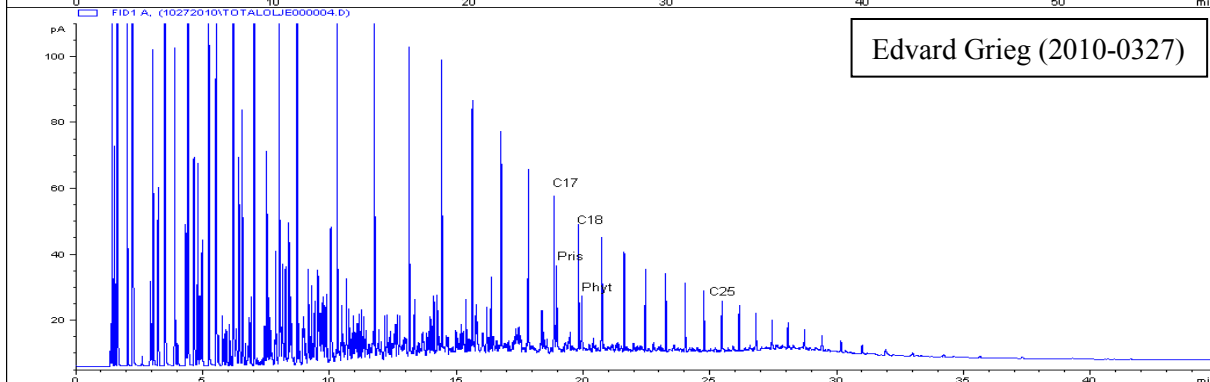
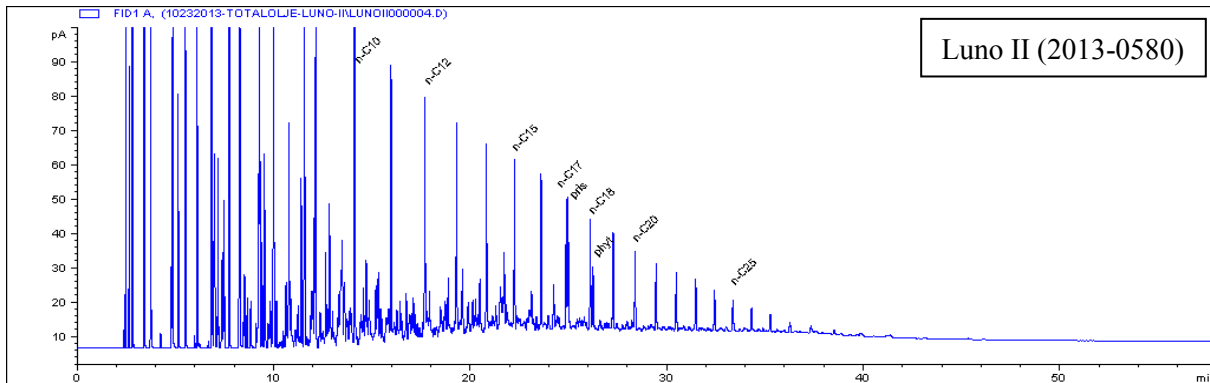


Figure 3-1: GC/FID chromatograms of the fresh and evaporated residues of Luno II crude oil



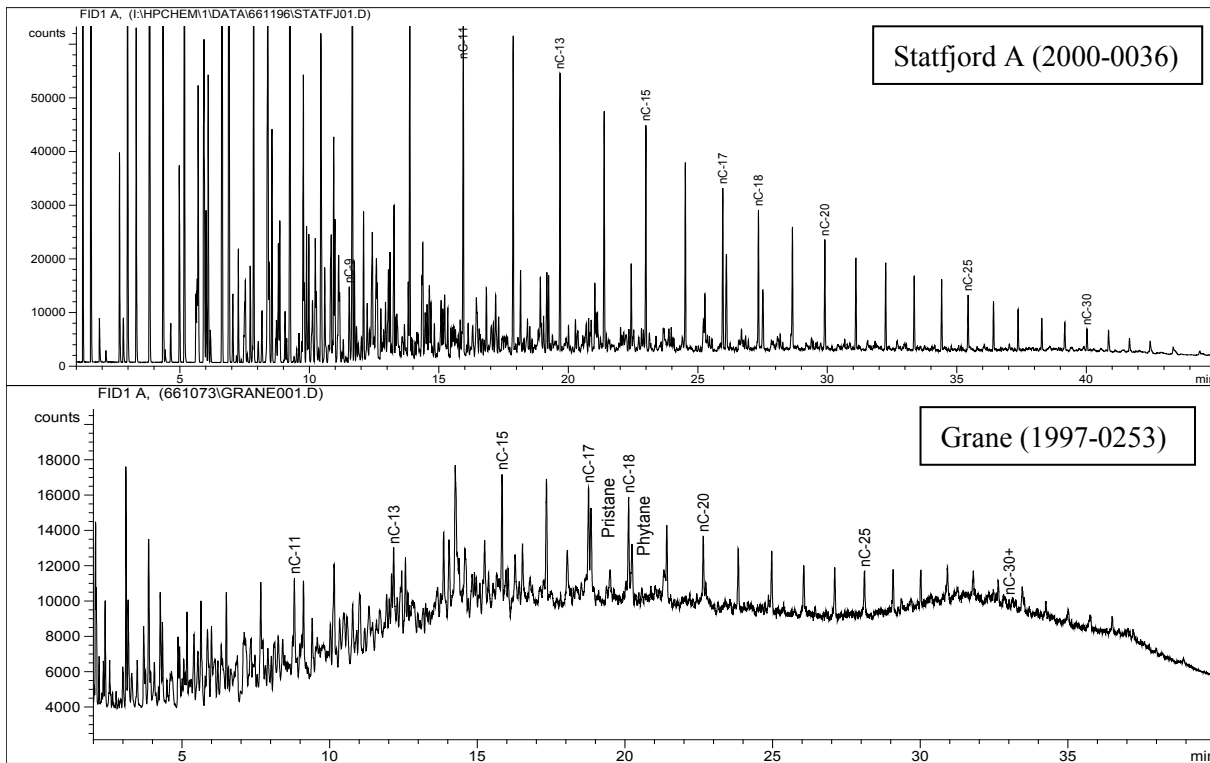


Figure 3-2: GC/FID chromatograms for fresh residues of other relevant crude oils

Asphaltene and wax content

The chemical properties of asphaltene and wax contents are given in Table 3-3. Luno II expresses low wax content comparable to Johan Sverdrup, and an intermediate content of asphaltenes compared to the chosen oils. Compared to other Norwegian crude oils, Luno II exhibits medium asphaltene content and low wax content.

Table 3-3: Asphaltene (“hard”) and wax content for different crude oils and evaporated fractions

Oil	Residue	Asphaltenes "hard" (wt. %)	Wax (wt. %)
Luno II	Fresh	0.5	2.7
	150°C+	0.6	3.4
	200°C+	0.7	3.9
	250°C+	0.8	4.4
Edvard Grieg	Fresh	0.2	3.9
	150°C+	0.2	4.8
	200°C+	0.3	5.4
	250°C+	0.3	6.0
Ivar Aasen	Fresh	0.1	4.0
	150°C+	0.1	4.7
	200°C+	0.2	5.3
	250°C+	0.2	6.2
Johan Sverdrup	Fresh	1.8	2.9
	150°C+	1.9	3.2
	200°C+	2.1	3.4
	250°C+	2.2	3.7
Grane	Fresh	1.4	3.5
	150°C+	1.4	3.9
	200°C+	1.4	4.3
	250°C+	1.5	4.8
Statfjord A	Fresh	0.1	4.3
	150°C+	0.1	5.5
	200°C+	0.1	6.4
	250°C+	0.1	8.3

Physical properties of fresh and weathered residues

Physical properties of Luno II and the other crude oils are listed in Table 3-4. Luno II has a slightly higher evaporative loss compared to Edvard Grieg, Ivar Aasen and Statfjord A, and the highest among the presented oils. The density of fresh Luno II is similar to Edvard Grieg while the 250°C+ residue of Luno II has a density similar to the 250°C+ residue of Johan Sverdrup.

Luno II flash points are in general lower compared to the other oils, likely due to higher content of the most volatile components. The pour points of Luno II are comparable to those of Ivar Aasen. The viscosities of the water free residues of Luno II are in the same range as Edvard Grieg, Johan Sverdrup and Statfjord A.

Table 3-4: Physical parameters of Luno II in comparison with other Norwegian crude oils

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/ml)	Flash point (°C)	Pour point (°C)	Visc. (mPas) 5°C (10 s ⁻¹)	Visc. (mPas) 13°C (10 s ⁻¹)	IFT (mN/m)
Luno II	Fresh	0	100	0.851	-	-27	22	11	18
	150°C+	25	79	0.898	32	6	474	99	18
	200°C+	36	69	0.915	69	12	2689	569	21
	250°C+	45	61	0.931	108	18	10572	3165	20
Edvard Grieg	Fresh	0	100	0.850	-	6	138	30	-
	150°C+	22	82	0.883	46	15	955	207	-
	200°C+	32	72	0.897	85	21	5310	1150	-
	250°C+	40	64	0.908	112	27	9800	2350	-
Ivar Aasen	Fresh	0	100	0.838	-	-6	65	9	17
	150°C+	18	85	0.861	42	9	210	34	18
	200°C+	29	75	0.872	75	15	950	170	18
	250°C+	39	65	0.883	113	21	3810	770	-
Johan Sverdrup	Fresh	0	100	0.891	-	3	309	61	19
	150°C+	12	91	0.915	45	9	1243	281	19
	200°C+	18	85	0.924	76	6	2530	632	19
	250°C+	26	78	0.935	110	12	9449	2044	21
Grane	Fresh	0	100	0.942	26	-24	1330	638	-
	150°C+	3	98	0.948	70	-18	1980	962	-
	200°C+	5	96	0.950	92	-15	2830	1084	-
	250°C+	13	89	0.960	139	-6	5970	3229	-
Statfjord A	Fresh	0	100	0.827	-	0	-	43	-
	150°C+	22	79	0.868	-	12	-	832	-
	200°C+	34	68	0.883	-	21	-	1697	-
	250°C+	42	52	0.896	-	27	-	2894	-

-: No data available

3.1.2 Emulsifying properties of Luno II

The emulsifying properties of Luno II were studied by use of the rotating cylinders (Hokstad *et al.*, 1993). Figure 3-3 and Figure 3-4 show examples of emulsions in the rotating cylinders at 13 °C and 5 °C, respectively. Luno II formed stable brownish emulsions at both temperatures and for all residues. The emulsions formed from 150°C+ and 200°C+ residues at 13 °C had a mousse-like appearance and consistency, and this was also true for the emulsions from the 150°C+ residue at 5 °C. The emulsions made from the heavier residues did not obtain this mousse consistency but formed a stable emulsion layer, as seen in the lower picture in Figure 3-3.



Four flasks on the left: Emulsions formed at 13 °C from the 150°C+ residue after 24 hours of rotation

Two flasks on the right: Emulsions formed at 13 °C from the 200°C+ residue after 24 hours of rotation

Two flasks on the left: Emulsions formed at 13 °C from the 200°C+ residue after 24 hours of rotation

Four flasks on the right: Emulsions formed at 13 °C from the 250°C+ residue after 24 hours of rotation

Figure 3-3: Emulsions formed after 24 hours at summer temperature (13 °C)



Four flasks on the left: Emulsions formed at 5 °C from the 150°C+ residue after 24 hours of rotation

Two flasks on the right: Emulsions formed at 5 °C from the 200°C+ residue after 24 hours of rotation

Two flasks on the left: Emulsions formed at 5 °C from the 200°C+ residue after 24 hours of rotation

Four flasks on the right: Emulsions formed at 5 °C from the 250°C+ residue after 24 hours of rotation

Figure 3-4: Emulsions formed after 24 hours at winter temperature (5 °C)

Water uptake and maximum water content

The parameters for kinetics (rate of water uptake) and maximum water uptake were studied by use of the rotation cylinders. The water contents in the water-in-oil emulsions as a function of time are shown in Table 3-5 and Table 3-6. The constant $T_{1/2}$, which is derived from the tabulated data, is defined as the time (hours) required to incorporate half the maximum water quantity, and is used as input to the Oil Weathering Model (OWM). The water uptake is slower at 5 °C than at 13 °C, as is expressed by the higher $T_{1/2}$ values for 5 °C. The maximum water uptake is overall higher at 13 °C, between 70-85 vol. %. At 5 °C maximum water uptake reached 56 vol. % for the 250°C+ residue.

Table 3-5: Water uptake of the evaporated residues of Luno II crude oil in rotating flasks at 13 °C

Mixing time	150°C + (Vol. % water)	200°C + (Vol. % water)	250°C + (Vol. % water)
Start	0	0	0
5 min	36	25	10
10 min	48	33	10
15 min	56	40	10
30 min	68	50	24
1 hour	75	59	40
2 hours	91	68	54
4 hours	87	76	63
6 hours	84	81	66
24 hours	83	80	71
T _{1/2}	0.14	0.29	0.93

Table 3-6: Water uptake of the evaporated residues of Luno II crude oil in rotating flasks at 5 °C

Mixing time	150°C + (Vol. % water)	200°C + (Vol. % water)	250°C + (Vol. % water)
Start	0	0	0
5 min	31	13	24
10 min	45	14	21
15 min	50	16	21
30 min	61	25	23
1 hour	69	43	2
2 hours	75	56	25
4 hours	84	65	43
6 hours	83	69	47
24 hours	82	75	56
T _{1/2}	0.18	0.88	2.00

Stability and efficiency of emulsion breaker

The stability of the emulsions from the weathered residues of Luno II crude oil was tested by quantifying the amount of water released from the emulsion during 24 hours of settling after 24 hours of rotation. In addition, the efficiency of emulsion breaker (Alcopol O 60 %) was evaluated. The results are given in

Table 3-7 for both 5 °C and 13 °C.

Luno II forms stable emulsions at both winter and summer temperatures. The application of emulsion breaker resulted in only partial dehydrations of the emulsions. The higher concentration (2000 ppm) of emulsion breaker was in general more effective than the lower concentration (500 ppm), at both temperatures.

Table 3-7: Stability of Luno II emulsions (no emulsion breaker) and efficiency of emulsion breaker at 5 °C and 13 °C

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 5 °C			Water-in-oil emulsion (vol. %) at 13 °C		
		Reference	24 hours *	Stability ratio**	Reference	24 hours *	Stability ratio**
150°C+	none	82	81	0.99	83	83	1.00
200°C+	none	75	76	1.00	80	80	1.00
250°C+	none	56	57	1.00	71	71	0.98
150°C+	Alc. O 60 % 500 ppm	82	75	0.67	83	74	0.60
200°C+	Alc. O 60 % 500 ppm	75	69	0.74	80	70	0.61
250°C+	Alc. O 60 % 500 ppm	56	57	1.00	71	62	0.65
150°C+	Alc. O 60 % 2000 ppm	82	54	0.26	83	46	0.18
200°C+	Alc. O 60 % 2000 ppm	75	35	0.18	80	42	0.19
250°C+	Alc. O 60 % 2000 ppm	56	45	0.66	71	67	0.82

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 during 24 hours settling. Stability ratio of 1 implies a totally stable emulsion.

Viscosity of water free residues and emulsified residues

Table 3-8 and

Table 3-9 give the viscosities of oil residue fractions with different water concentration (water free, 50 vol. %, 75 vol. % and max. water) at 5 °C and 13 °C, respectively. As a non-Newtonian fluid, the viscosities of Luno II oil and emulsions are dependent on the shear rate; the viscosities are higher at a lower share rate (10 s^{-1}) compared to higher shear rate (100 s^{-1}). This decrease in viscosity with increasing shear rate is likely caused by breaking up the wax lattice structure with increased mechanical force.

Table 3-8: Viscosity of Luno II water free residues and emulsified residues at 5 °C

Residue	Water content (vol. %)	Viscosity (mPas)	
		10 s^{-1}	100 s^{-1}
Fresh	0	22	20
150°C+	0	474	269
200°C+	0	2689	1052
250°C+	0	10572	3173
150°C+	50	1235	785
200°C+	50	5289	2282
250°C+	50	21369	3309
150°C+	75	5259	1711
200°C+	75	21944	3995
250°C+	75	_*	_*
150°C+	82	36215	3994
200°C+	75	20165	4029
250°C+	55**	25459	2388

*: The 250°C+ residue did not obtain 75 vol. % water-in-oil emulsion at 5 °C, max. water uptake was 55 vol. %.

Table 3-9: Viscosity of Luno II water free residues and emulsified residues at 13 °C

Residue	Water content (vol. %)	Viscosity (mPas)	
		10 s ⁻¹	100 s ⁻¹
Fresh	0	11	11
150°C+	0	99	76
200°C+	0	569	361
250°C+	0	3165	1392
150°C+	50	529	415
200°C+	50	1904	1074
250°C+	50	9615	3152
150°C+	75	2105	574
200°C+	75	6227	1637
250°C+	75	-	-
150°C+	83	20155	2648
200°C+	80	23888	4094
250°C+	71	24632	4208

*: The 250°C+ residue did not obtain 75 vol. % water-in-oil emulsion at 13 °C, max. water uptake was 71 vol. %

3.1.3 Chemical dispersibility

The dispersibility testing included:

- Screening of five different dispersants to find the best and relevant dispersant for the Luno II oil.
- Dosage testing of the best/relevant dispersant.
- Systematic dispersant study with the best dispersant at the optimal dosage rate (DOR - Dispersant to Oil Ratio), to determine the time window for effective dispersant use on the Luno II oil in a spill scenario.

Screening and dosage study of dispersants

A screening study was performed using the low energy test (IFP) to investigate the effectiveness of different dispersants and the optimal dose rate (DOR = Dispersant to Oil Rate, by weight).

The dosage testing was conducted at 13 °C with the 200°C+ residue emulsified with 50 vol. % water, and different DORs of 1:25, 1:50, 1:100, and 1:200. Results from the screening study are given in Table 3-10, while results from the dose rate testing are given in

Table 3-11. The dose rate testing was conducted using both the low energy test (IFP) and the high energy test (MNS).

Table 3-10: Screening test of dispersants on Luno II crude oil at 13 °C using the MNS & IFP tests

Dispersant (DOR 1:25)	IFP	MNS
	Efficiency dispersant 200°C+ /50 vol. %	Efficiency dispersant 200°C+ /50 vol. %
Corexit 9500	82	100
Dasic NS	66	100
Finasol OSR 62	54	-
Gamlen OD 4000	51	-
Superdispersant	33	-

- Not tested:

The viscosity for screening testing was 1904 mPas ($10s^{-1}$) at 13 °C for the 200°C+ 50 vol. % emulsion.

Table 3-11: Dosage rate testing of Dasic NS on Luno II crude oil at 13 °C

Dispersant (dosage rate)	Efficiency of dispersant on 200°C+/50 vol. % emulsion IFP	Efficiency of dispersant on 200°C+/50 vol. % emulsion MNS	Viscosity (mPas) 10 s⁻¹, 13°C
Dasic NS (1:25)	66	100	1904
Dasic NS (1:50)	45	100	1911
Dasic NS (1:100)	22	100	1911
Dasic NS (1:200)	8	94	1911

The results of the screening test showed that Corexit 9500 was the most effective dispersant in the low energy IFP-test. However, Dasic NS was chosen for further testing since this dispersant had promising effectiveness and is currently in use in Norway. Consequently, the dosage test and continued dispersibility testing were performed with Dasic NS.

As can be seen in

Table 3-11, the dosage rate test showed varied dispersibility effectiveness. The IFP-test is a low energy (non-breaking waves) test, while the MNS-test represents a high energy system (breaking waves). The additional energy in the MNS-test provides a higher degree of natural dispersion, thus explaining the higher effectiveness.

The dosage of 1:25 was the most effective as observed for the IFP-test, while the lower dosages gave decreasing effectiveness.

Window of opportunity for use of dispersant on Luno II crude oil

Dasic NS is the dispersant agent currently in the NOFO stock, and is considered to be the operational target agent when applying dispersant on a marine oil spill. A dosage rate of 1:25 (4 wt. %) is the standard procedure used to establish the time window for dispersant application.

Results from the systematic dispersibility study at 5 °C and 13 °C are given in Table 3-12 and Table 3-13, respectively.

Table 3-12: Efficiency of Dasic NS on weathered oil / emulsions of Luno II at 5 °C

Residue	Water content (vol. %)	Viscosity (mPas) 10 s ⁻¹	Viscosity (mPas) 100 s ⁻¹	IFP	MNS
				Efficiency (%)	Efficiency (%)
150°C+	0	474	269	77	100
200°C+	0	2689	1052	13	100
250°C+	0	10572	3173	0	32
150°C+	50	1235	785	66	100
200°C+	50	5289	2282	4	100
250°C+	50	21369	3309	2	-
150°C+	75	5259	1711	32	71
200°C+	75	21944	3995	3	52
250°C+	75	-	-	-	-
150°C+	82	36215	3994	4	51
200°C+	75	20165	4029	2	5
250°C+	55	25459	2388	1	1

Table 3-13: Efficiency of Dasic NS on weathered oil / emulsions of Luno II at 13 °C

Residue	Water content (vol. %)	Viscosity (mPas) 10 s ⁻¹	Viscosity (mPas) 100 s ⁻¹	IFP	MNS
				Efficiency (%)	Efficiency (%)
150°C+	0	99	76	80	100
200°C+	0	569	361	62	100
250°C+	0	3165	1392	10	100
150°C+	50	529	415	80	100
200°C+	50	1904	1074	66	100
250°C+	50	9615	3152	6	61
150°C+	75	2105	574	74	75
200°C+	75	6227	1637	30	47
250°C+	75	-	-	-	-
150°C+	83	20155	2648	23	21
200°C+	80	23888	4094	8	7
250°C+	71	24632	4208	3	5

The criteria for estimation of dispersibility effectiveness are listed in Table 3-14 along with the estimated viscosity limits for use of dispersants on Luno II emulsions. The viscosity limits are estimated from Figure 3-5.

Table 3-14: Estimated viscosity limits for use of dispersant for Luno II emulsion and the criteria for definition of time window

Dispersibility	Criteria (wt. %)	Dispersibility limits based on oil viscosities (mPas = cP)*
Chemically dispersible	IFP efficiency > 50 %	3000
Not chemically dispersible	MNS efficiency < 5 %	25000

* Estimated limits are based on the dispersibility data from both the low energy IFP-test and the high energy MNS-test

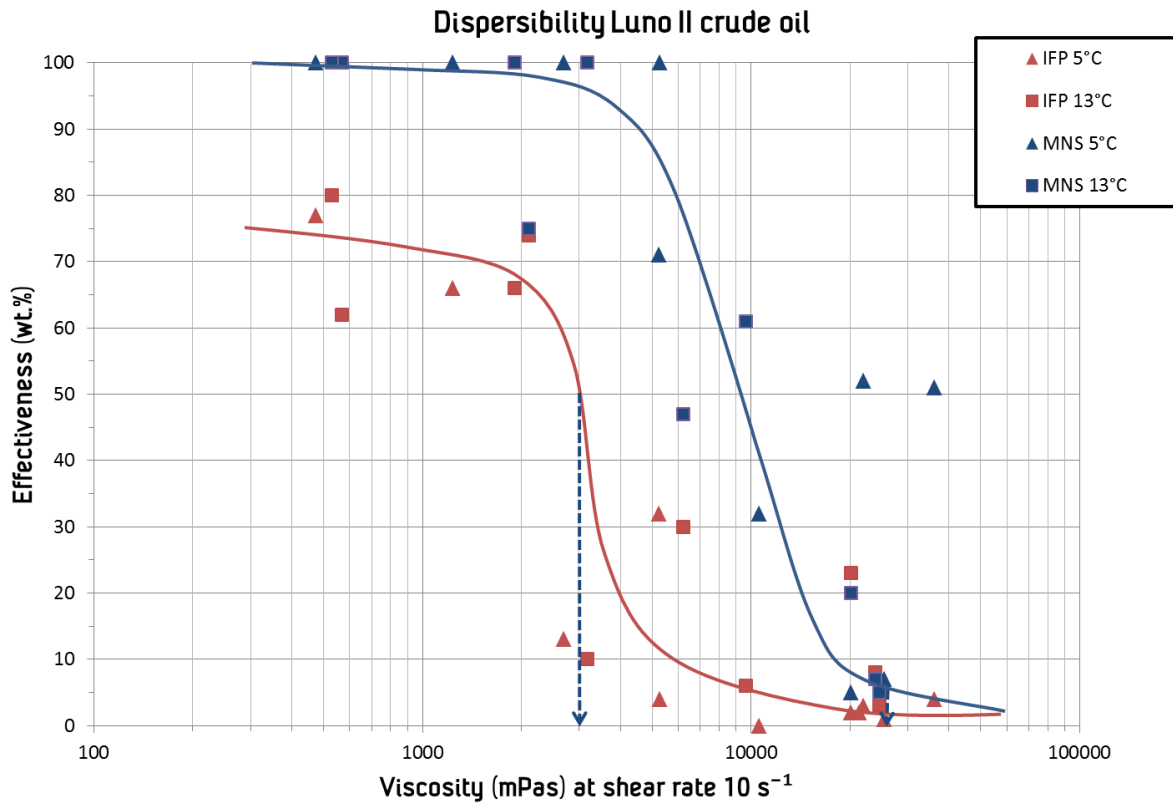


Figure 3-5: Dispersant effectiveness on Luno II crude oil and its weathered residues at 5 °C and 13 °C

3.2 Meso-scale laboratory testing results

The meso-scale testing gives valuable operational information about the oil's behaviour under more realistic conditions, and the flume-testing is therefore a supplement to the small-scale testing. The experimental results obtained for Luno II in the meso-scale laboratory test are presented below. Table 3-15 and

Table 3-16 show the results from the meso-scale experiments at 5°C and 13°C, respectively.

Table 3-15: Results from the meso-scale weathering experiment of Luno II at 5 °C

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPas), 10 s ⁻¹	Oil in water ppm*
1	0.5	77	18	243	57
2	1	75	21	539	59
3	2	74	24	2355	63
4	4	75	27	3573	62
5	6	74	29	4705	46
6	12	74	31	6997	31
7	24	75	33	12065	17
8	48	74	35	17655	11
9	72	74	36	21107	7
1st application of dispersants: 52 g Dasic NS (DOR = 1.1 wt. %)					
3 min. disp 1	-	-	-	-	13
10 min. disp 1	-	-	-	-	27
60 min. disp 1					
2nd Application of dispersants: 49 g Dasic NS (DOR= 1.1 wt. %)					
3 min. disp 2	-	-	-	11218	33
10 min. disp 2	-	-	-	-	62
30 min. disp 2	-	-	-	-	63
120 min. disp 2	-	-	-	-	75
240 min. disp 2	-	-	-	-	63

-.: no measured data.

*:ppm=parts per million

Table 3-16: Results from the meso-scale weathering experiment of Luno II at 13 °C

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPas), 10 s ⁻¹	Oil in water ppm*
1	0.5	68	22	279	76
2	1	74	25	428	86
3	2	75	29	1237	88
4	4	78	31	3204	73
5	6	82	32	5879	37
6	12	83	34	7786	36
7	24	80	36	11504	16
8	48	81	39	19670	9
9	72	79	40	23401	30
1st application of dispersants: 50 g Dasic NS (DOR = 1.1 wt. %)					
3 min. disp 1	-	-	-	-	22
10 min. disp 1	-	-	-	-	19
60 min. disp 1	-	-	-	-	-
2nd Application of dispersants: 50 g Dasic NS (DOR= 1.1 wt. %)					
3 min. disp 2	-	-	-	20648	27
10 min. disp 2	-	-	-	-	26
30 min. disp 2	-	-	-	-	29
120 min. disp 2	-	-	-	-	31

-: no measured data.

*:ppm=parts per million

3.2.1 Evaporation

Figure 3-6 shows the evaporative loss obtained in the meso-scale experiments compared to the values predicted by the SINTEF oil weathering model (OMW). The predictions correspond well with the measured evaporative loss.

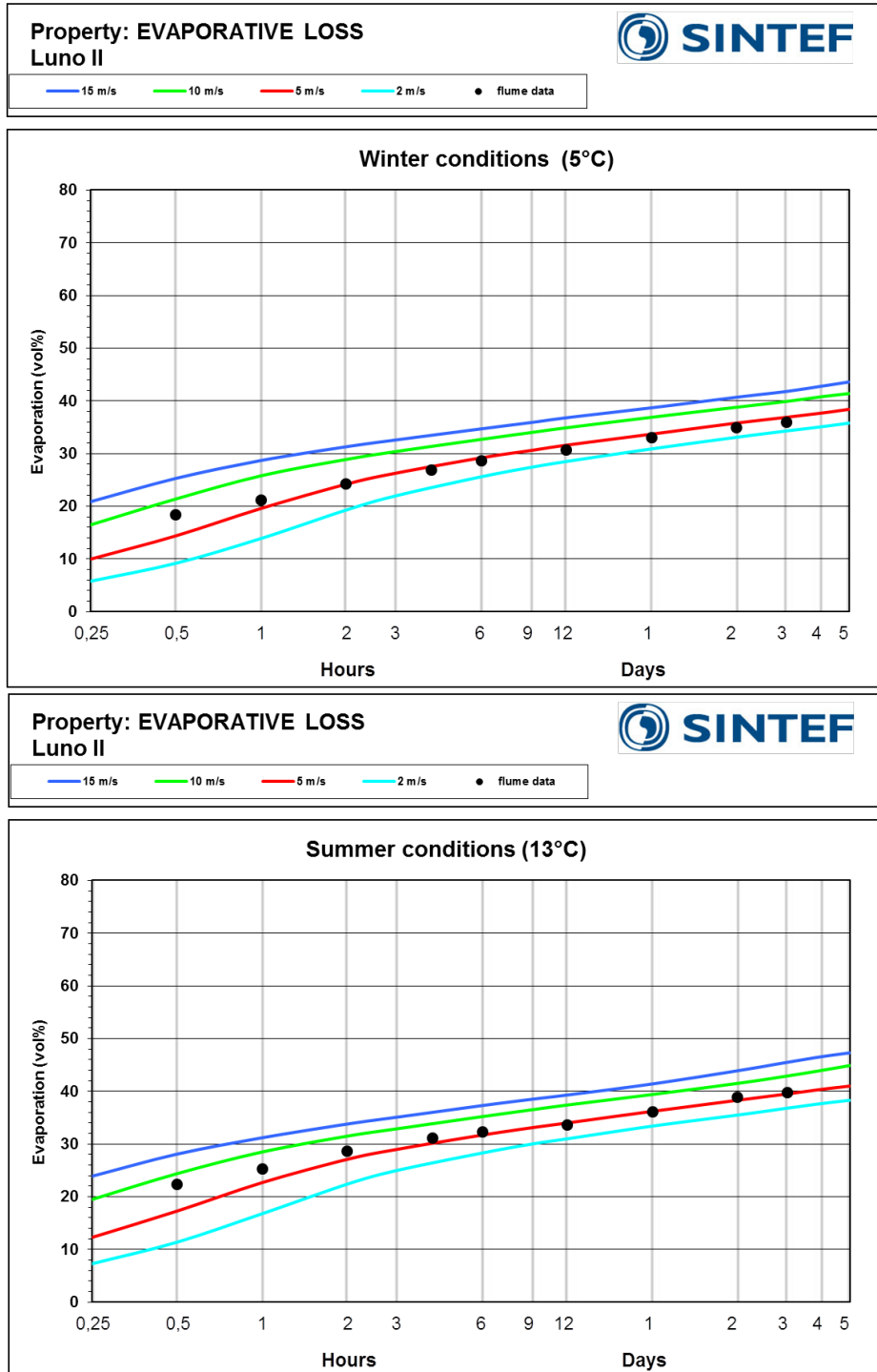


Figure 3-6: Predicted evaporative loss for Luno II with the results from the meso-scale experiments at 5 °C and 13 °C

3.2.2 Water uptake

In Figure 3-7 the water uptake predicted by SINTEF OWM is shown along with the measured water uptake from the flume experiments. As can be seen, the measured maximum water content was somewhat higher in both the experiments compared to the OWM predictions. As the emulsions were not stable with large water droplets during the first hours of weathering, the water content is more unreliable and explains why the flume experiments indicate a more rapid water uptake compared to the OWM predictions.

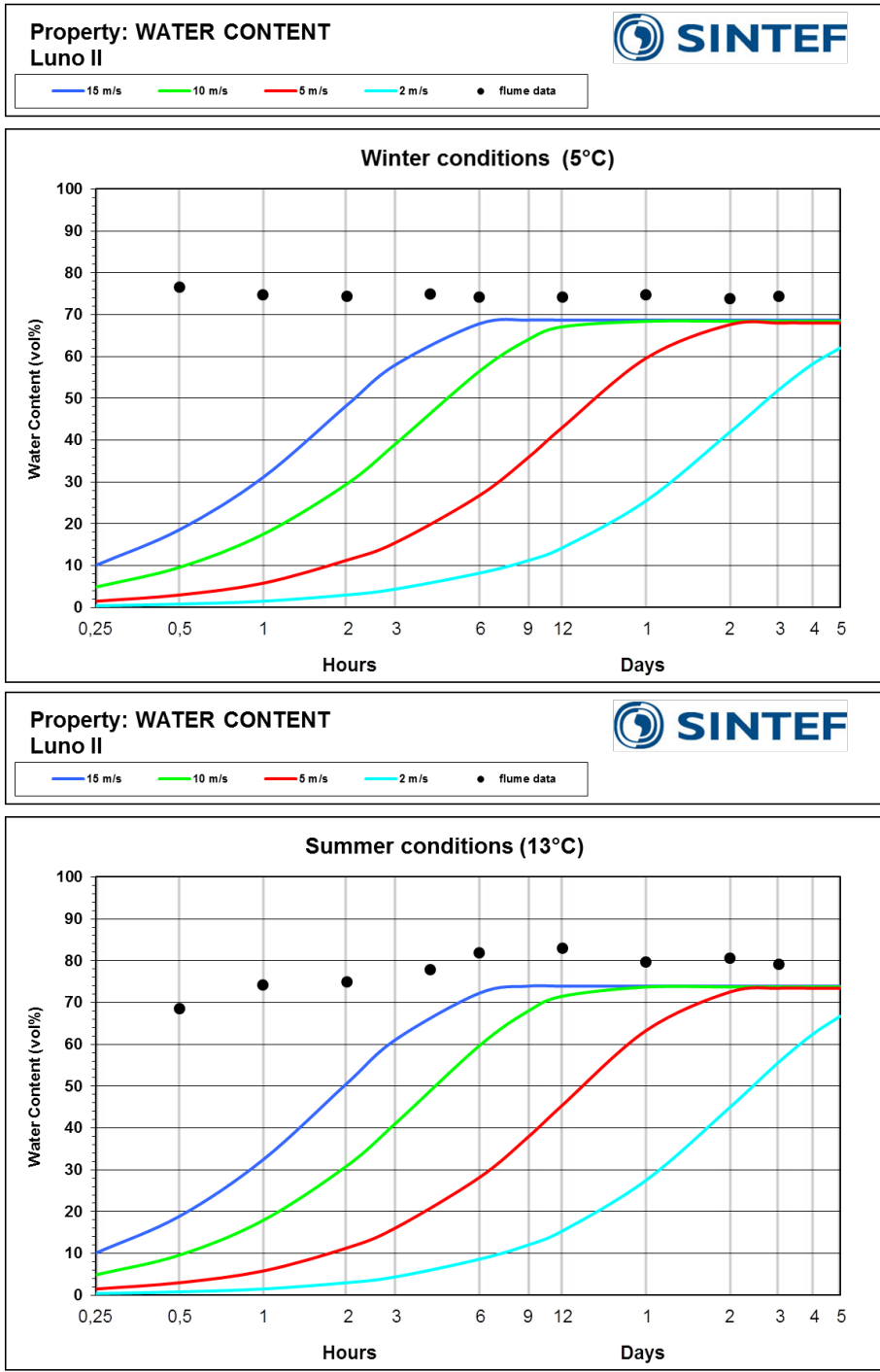


Figure 3-7: Predicted water uptake for Luno II and the results from the meso-scale experiments at 5 °C and 13 °C

The measured emulsion viscosities are presented in Figure 3-8 along with the predicted emulsion viscosities from SINTEF OWM. The predicted viscosities corresponded very well with the measured viscosities, at both test temperatures (5 °C and 13 °C).

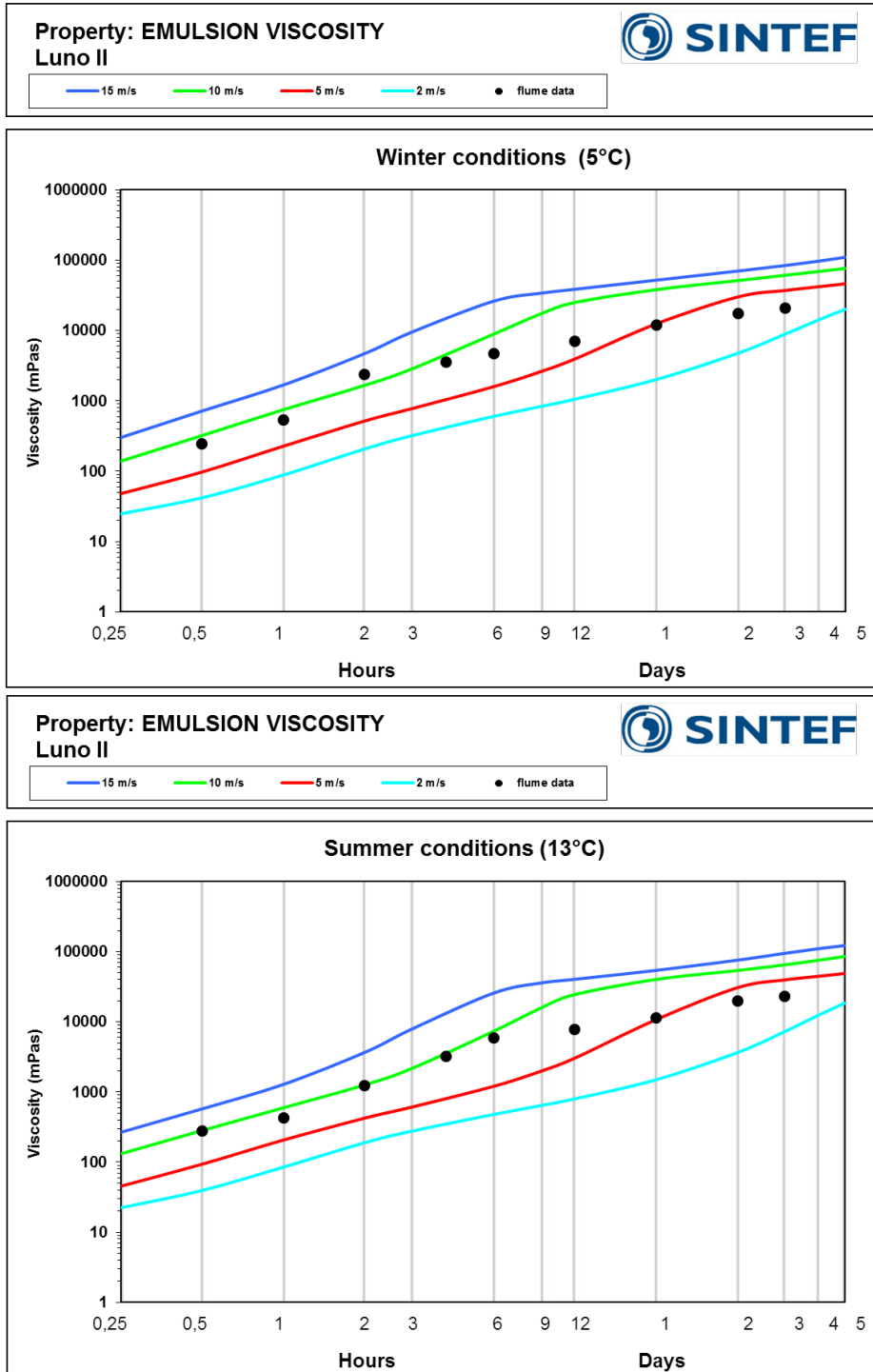


Figure 3-8: Predicted emulsion viscosities for Luno II with the results from the meso-scale experiments at 5 °C and 13 °C

3.2.3 Mass balance

The main elements in the mass balance for a crude oil spilled at sea are:

- evaporative loss
- surface oil
- dispersed oil

Because the initial oil sample and water volume in the flume are reduced throughout the test, the following parameters must be taken into consideration:

- amount of oil sampled
- amount of water sampled
- amount of oil sticking to the flume wall

The amount of oil evaporated, oil on surface, dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated. Table 3-17 shows values for the mass balance of Luno II during weathering in flume experiments after 24 hours.

Table 3-17: Mass balance for Luno II during the meso-scale laboratory tests at 5 °C and 13 °C (after 24 hours of weathering)

Mass balance (% of initial oil)	5°C	13°C
Evaporated	33	36
Oil on water surface	60	56
Dispersed oil	1	1
Sampled amount of oil	2	2
Oil adsorbed to the flume walls	4	5

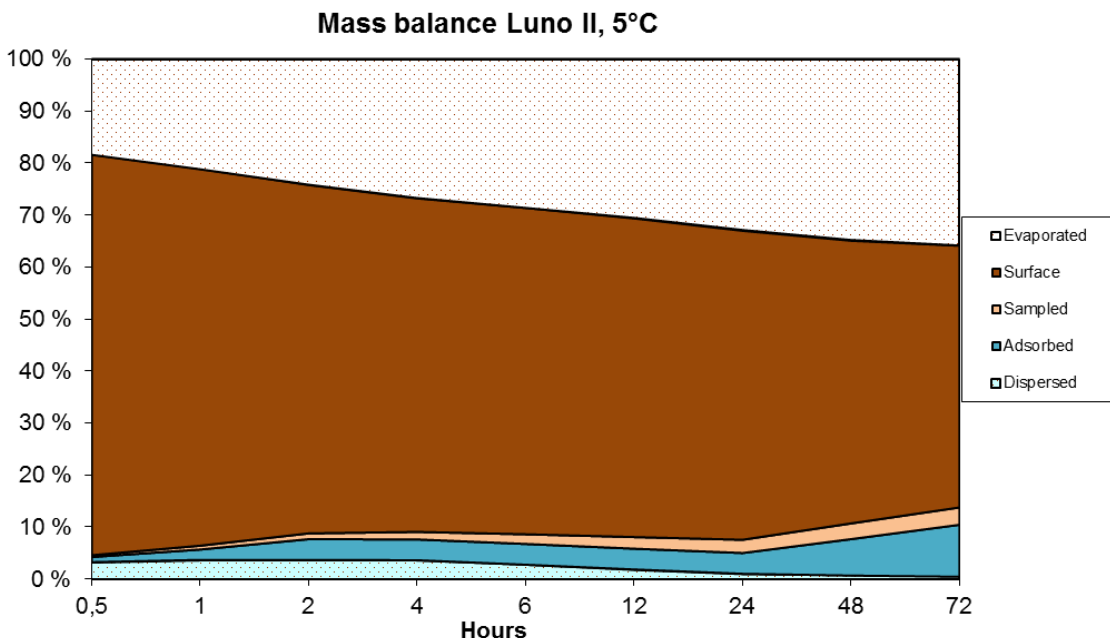


Figure 3-9: Mass balance of Luno II in the 5 °C meso-scale laboratory test before the application of dispersant

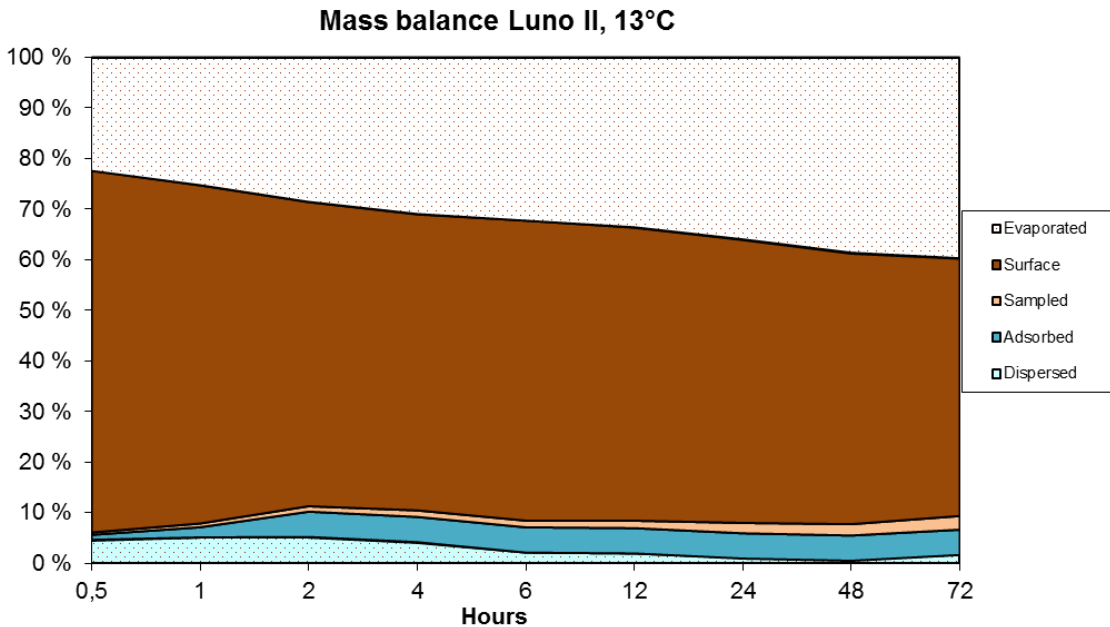


Figure 3-10: Mass balance of Luno II in the 13 °C meso-scale laboratory test before the application of dispersant

3.2.4 In situ chemical dispersion

After 72 hours of weathering, the chemical dispersant Dasic NS was applied by spraying it twice on the water-in-oil emulsion (*in situ* application). The dosage ratios are given in Table 3-18.

Table 3-18: Dispersant dosage rates used in Luno II meso-scale experiment (in situ application)

Test temperature (°C)	Dasic NS application (g)	Dispersant to Oil Ratio (DOR), wt. %	Dispersant to Emulsion Ratio (DER), wt. %
5	52	1.1	0.3
5	49	1.1	0.3
13	50	1.1	0.2
13	50	1.1	0.2

As the effect of the first application of dispersant was low, the dispersant was applied twice in each experiment. In both experiments water samples were taken at

- 3 and 10 minutes after the first application
- 3, 10, 30 and 120 minutes after the second application

An additional water sample was taken after 240 minutes in the 5 °C experiment.

3.2.5 Visual observations

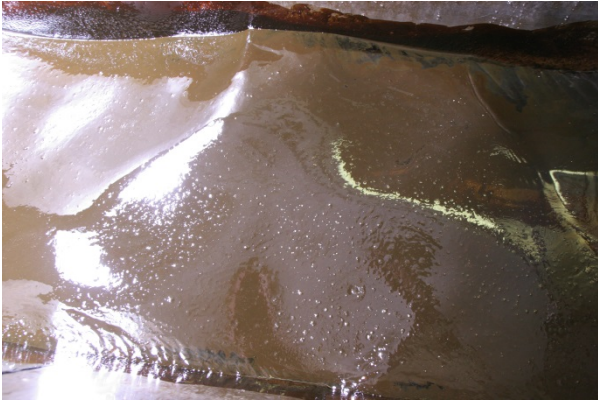
When released onto the sea water in the meso-scale flume, the Luno II crude oil rapidly formed unstable emulsions with large water droplets (free water). The emulsions became more stable during the first 24 hours of weathering in the flume. The colour of the emulsion turned from dark brown to a reddish brown colour during the first 24 hours of weathering, and became more light brownish after three days of weathering.

A relatively high amount of oil was available for chemical dispersion, as shown in the mass balance (Table 3-17). The oil dispersed poorly and a sizable slick remained on the surface throughout the whole experiment. The dispersant (Dasic NS) broke up the slick in to smaller lumps instead of the one continuous sheet of

emulsion observed during the first 3 days. However, in the 5 °C test these smaller lumps reformed a slick between two hours and four hours after dispersant application. The results indicated that a higher dosage could be applied on the slick in an oils spill situations at both temperatures.

A selection of pictures taken at the various sampling times from both tests, are presented below. The dissimilarities in colour within the same sample times are due to photographing at different angles; the pictures to the left were taken from a near vertical position relative to the flume surface while the pictures to the right were taken at an angle and depict the oil and emulsions lit by the artificial light. Pictures taken after addition of dispersant are all taken at an angle.

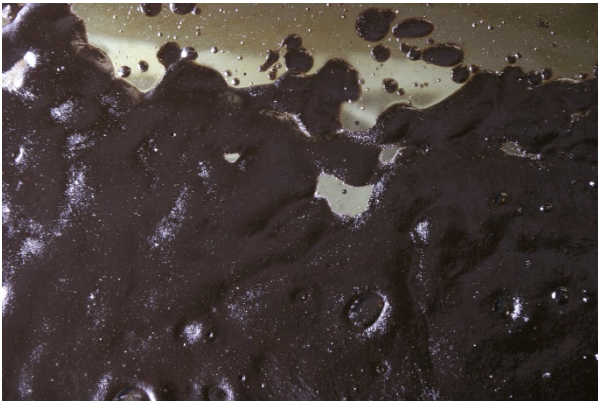
Pictures taken during the 5 °C experiment



Start (Time = 0)



1 hour after oil release



6 hours after oil release



24 hours after oil release



3 days after oil release

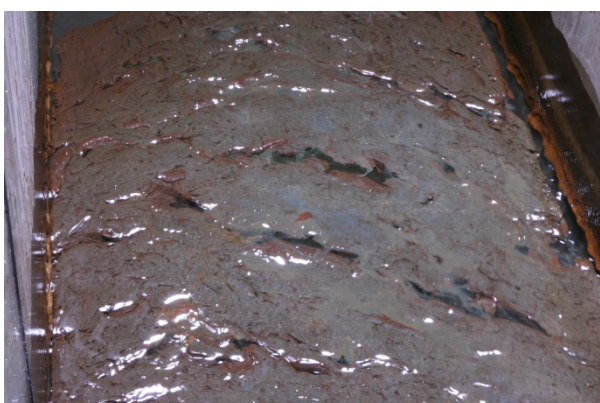
In situ application of dispersant (Dasic NS), 5 °C



0 minutes after 1st dispersant application



10 minutes after 1st dispersant application



0 minutes after 2nd dispersant application



30 minutes after 2nd dispersant application



120 minutes after 2nd dispersant application



240 minutes after 2nd dispersant application

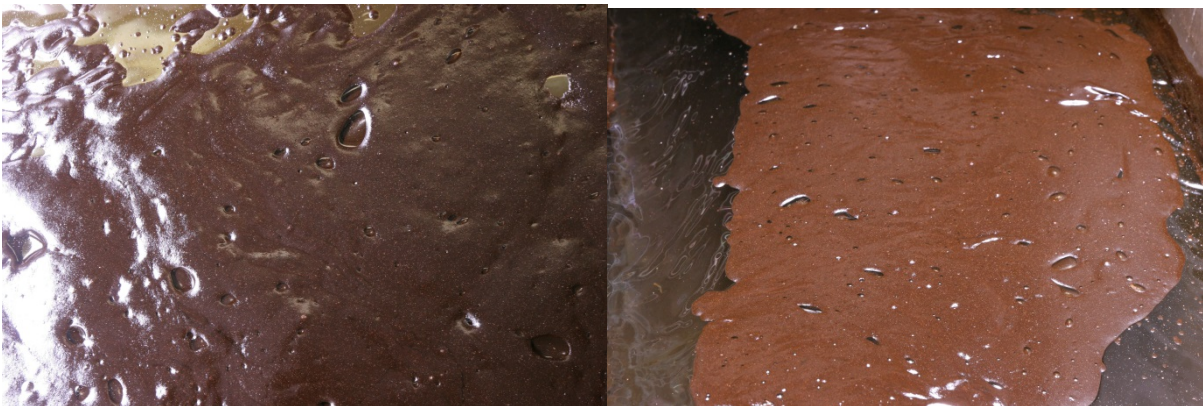
Pictures taken during the 13 °C experiment:



Start (Time = 0)



1 hour after oil release



6 hours after oil release



24 hours after oil release



3 days after oil release

In situ application of dispersant (Dasic NS), 13 °C



0 minutes after 1st dispersant application



10 minutes after 1st dispersant application



0 minutes after 2nd dispersant application



30 minutes after 2nd dispersant application

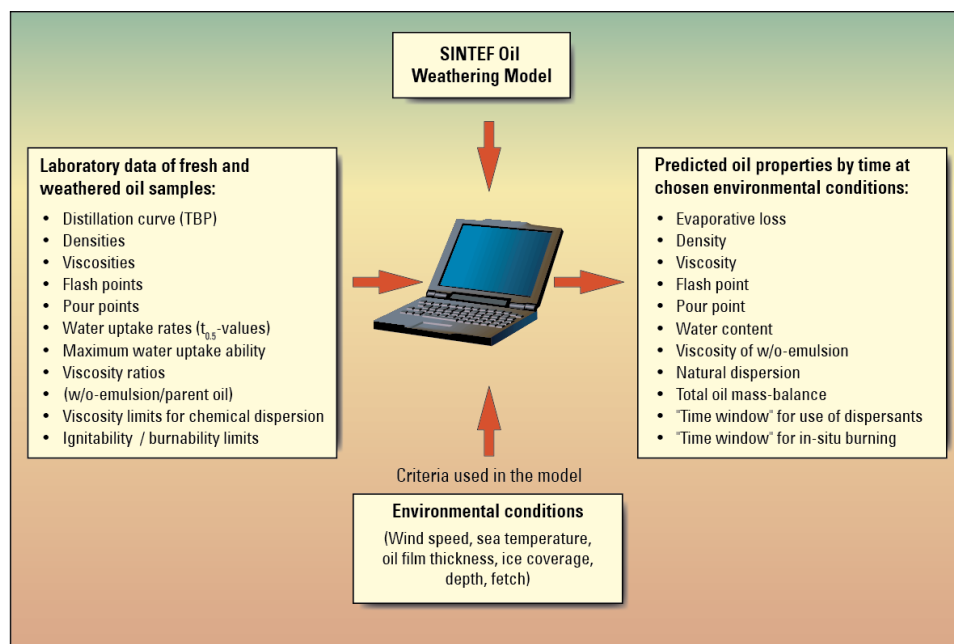


120 minutes after 2nd dispersant application

4 Predictions with SINTEF Oil Weathering Model (OWM)

4.1 Description of SINTEF OWM

A laboratory study of the weathering properties of Luno II at 5°C and 13°C has been conducted. The data are used as input to the SINTEF OWM (version 4.0 β). The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change rate of the oil's properties and behaviour on the sea surface. The SINTEF OWM is schematically shown in Figure 4-1.



handboker/grafisk/fig-eng/model-col-eng2.ai

Figure 4-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

The predictions obtained from the SINTEF OWM are useful tool 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 time 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.

In laboratory testing, a systematic stepwise procedure developed at SINTEF (Daling *et al.*, 1990) is used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. The experimental design for the study of Luno II is described in Appendix B, page 80, and the results are presented in detail in Chapter 3, page 7. The input data to the SINTEF OWM is given in Appendix C, page 88.

Spill scenario

In this project, a surface release at a standard rate of 1.33 metric tonnes per minute was chosen as the spill scenario.

Oil film thickness

In the SINTEF OWM, the oils are categorized into condensate, low emulsifying crude, emulsifying crude, heavy bunker fuel or refined distillate based on experimental results obtained in small-scale testing. The terminal film thickness varies among these categories based on experimental field experience. Luno II was categorized as an emulsifying crude oil.

Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one for average summer temperatures and one for average winter temperatures. The temperatures chosen for Luno II are 5 °C 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 4-1.

Table 4-1: 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

4.2 Predictions of Luno II weathering properties

The prediction charts and input to the OWM model are presented below. The detailed data used as input to SINTEF OWM for Luno II are given in Appendix C.

Input to SINTEF OWM

Oil type:	Crude
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 °C and 15 °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 Luno II has drifted on the sea surface, the following prediction charts can be used to determine the remaining oil/emulsion's chemical, physical and emulsifying properties.

Table 4-2 give an example for the following scenario:

- Drift time: 12 hours
- Sea temperature: 5 °C/15 °C
- Wind speed: 10 m/s

Table 4-2: Weathering properties for Luno II obtained from the prediction charts after 12 hours of weathering

Property	Winter temperature (5 °C, 10 m/s)	Summer temperature (15 °C, 10 m/s)
Evaporation, vol. %	35	37
Water content, vol. %	67	71
Flash point, °C	87	100
Pour Point, °C	17	20
Viscosity, mPas*	25000	25000

*mPas = cP (mPas: SI-standard/cP: Industrial denotation)

Property: EVAPORATIVE LOSS
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

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

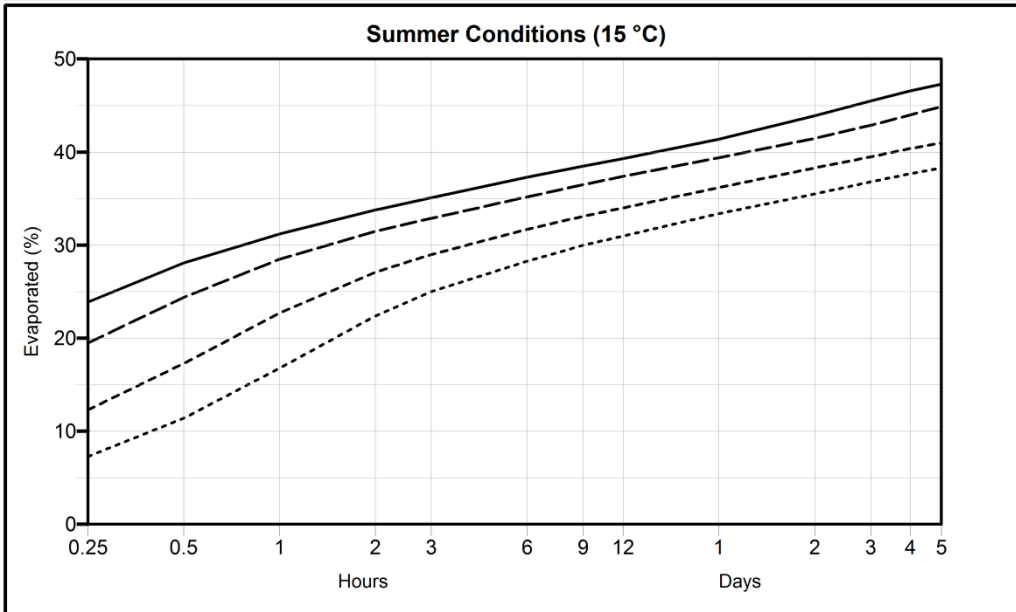
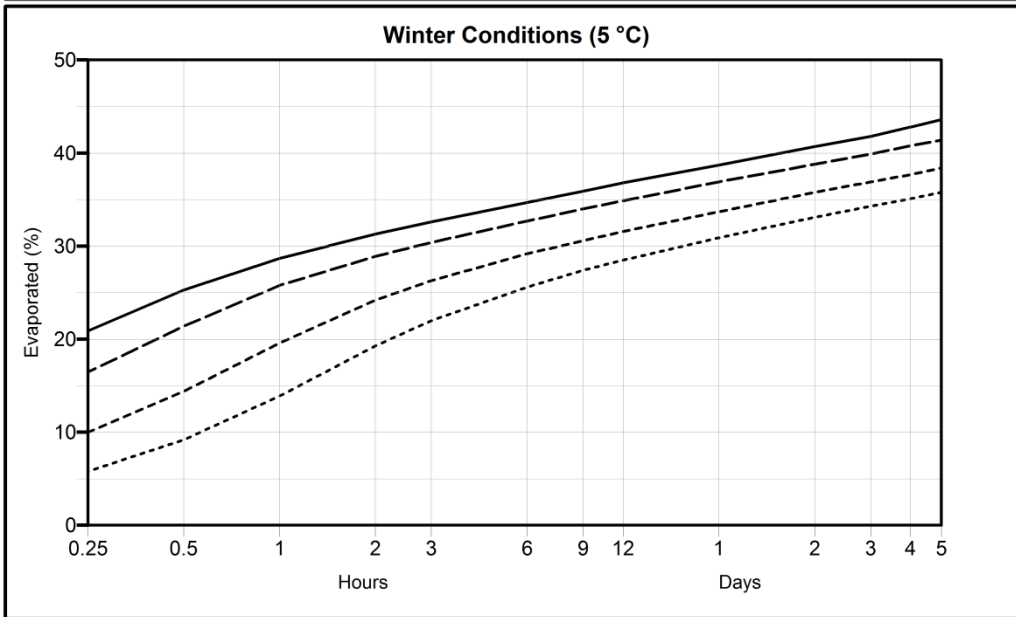


Figure 4-2: Evaporative loss of Luno II predicted at sea temperatures of 5 °C and 15 °C

Property: WATER CONTENT
Oil Type: LUNO II 2014 13°C (CRUDE)
Description: Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

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

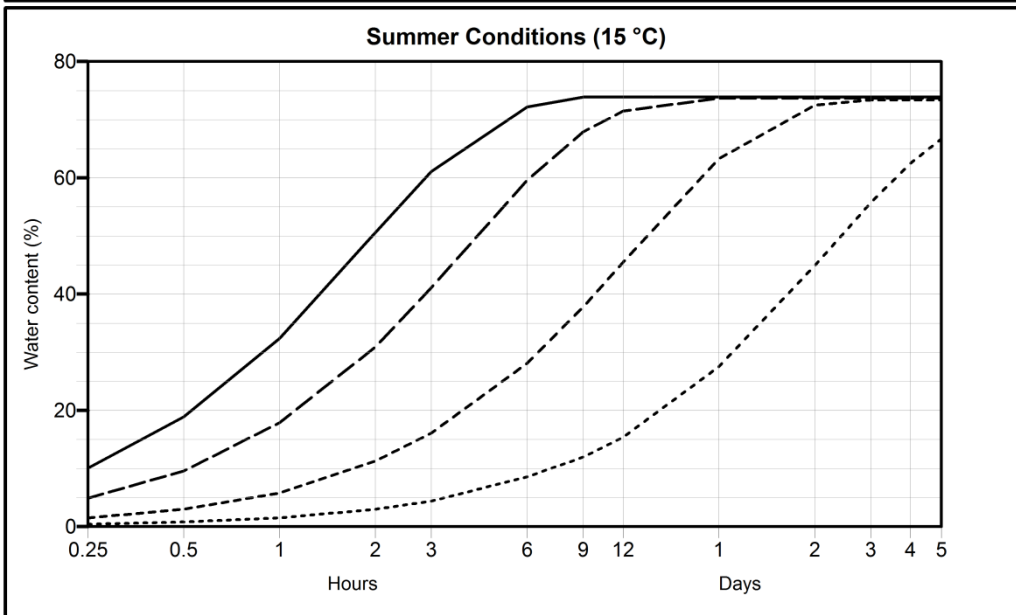
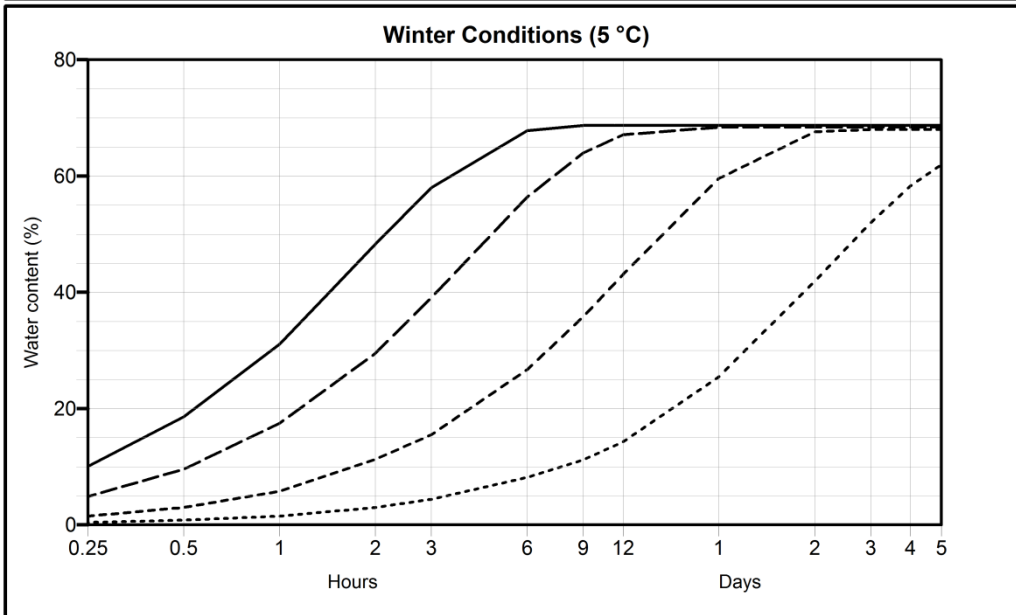


Figure 4-3: Water content for the Luno II emulsions at 5 °C and 15 °C

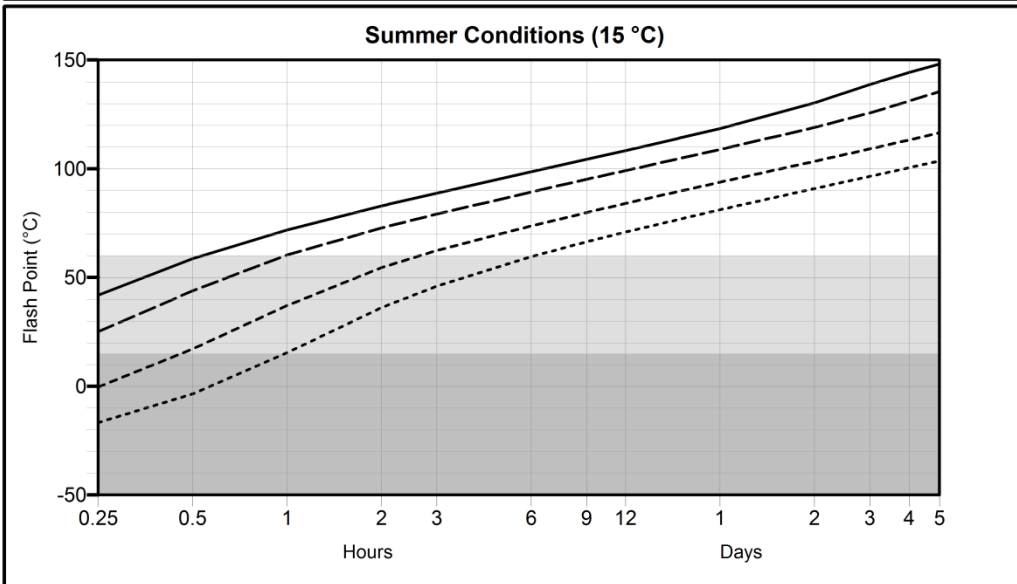
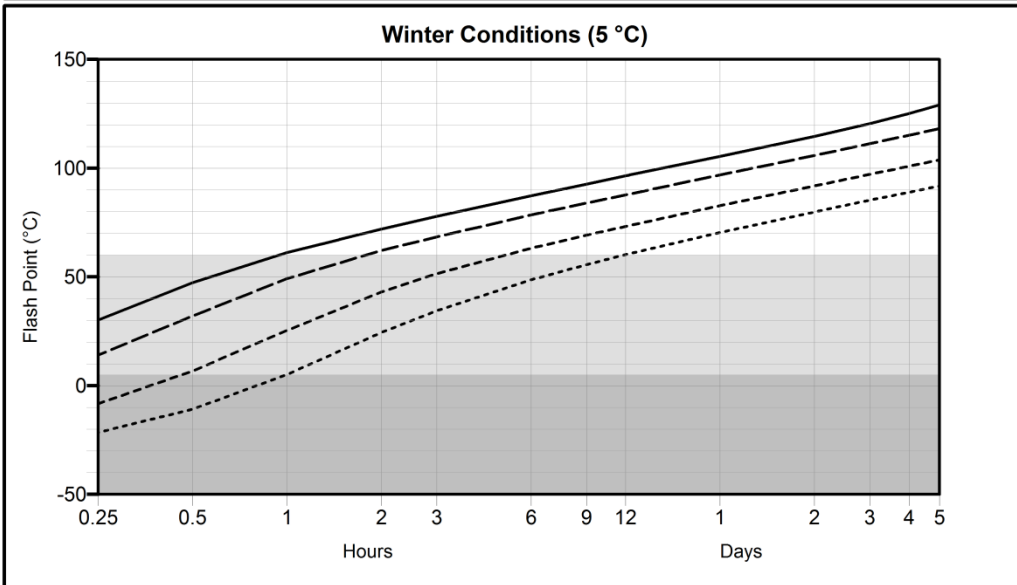
Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

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



Based on flash point measurements of weathered, water-free oil residues.

Figure 4-4: Flash point of Luno II predicted at sea temperatures of 5 °C and 15 °C

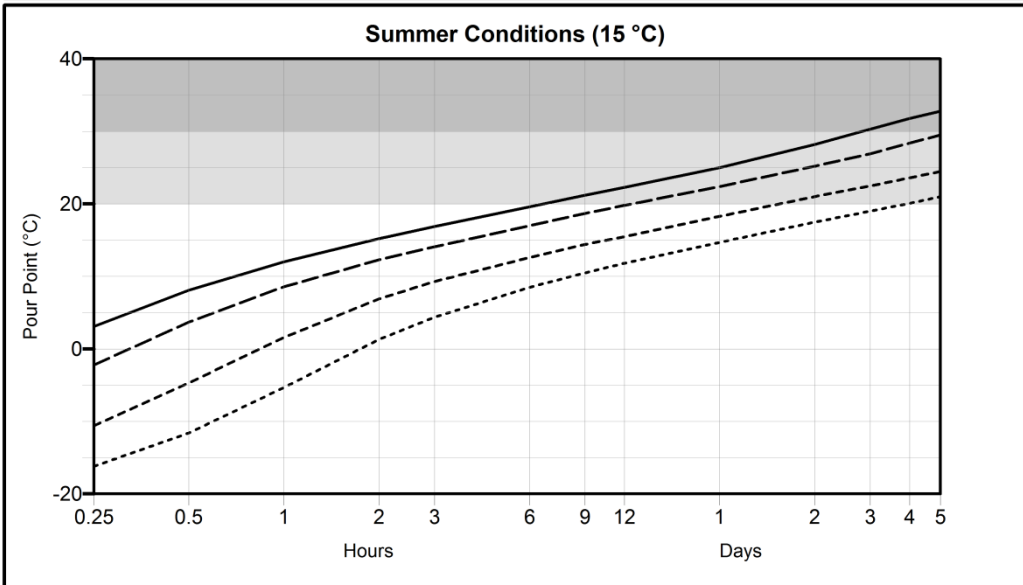
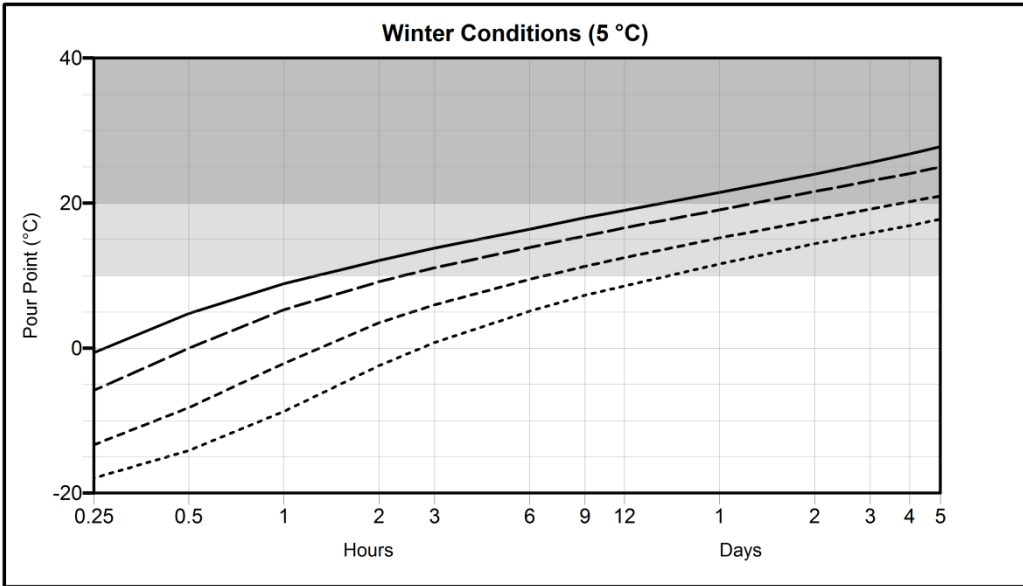
Property: POUR POINT FOR WATER-FREE OIL
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

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



Based on pour point measurements of weathered, water-free oil residues.

Figure 4-5: Pour point of Luno II predicted at sea temperatures of 5 °C and 15 °C

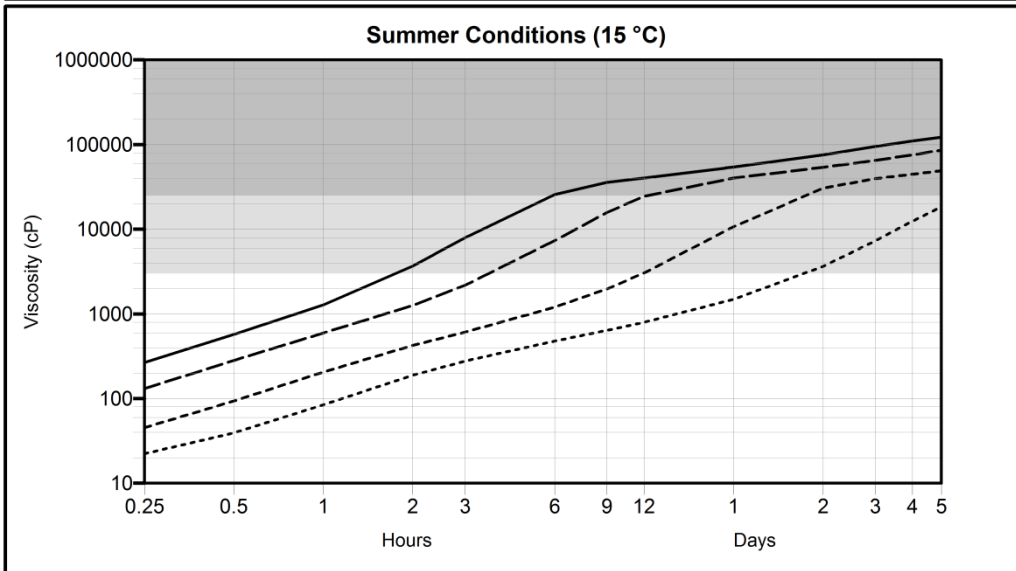
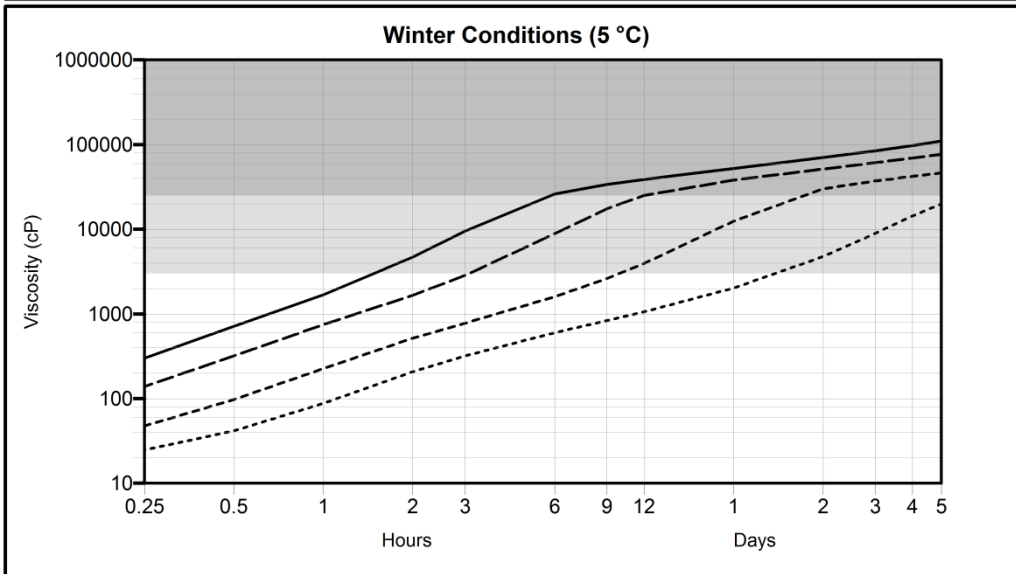
Property: VISCOSITY OF EMULSION
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
- - - - - Wind Speed (m/s): 2
- Chemically dispersible (<3000 cP)
- ▒ Reduced chemical dispersibility
- Poorly / slowly chemically dispersible (>25000 cP)



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 4-6: Viscosity of Luno II emulsion at sea temperatures of 5 °C and 15 °C.

Property: MASS BALANCE
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

- Evaporated
- Surface
- Naturally dispersed

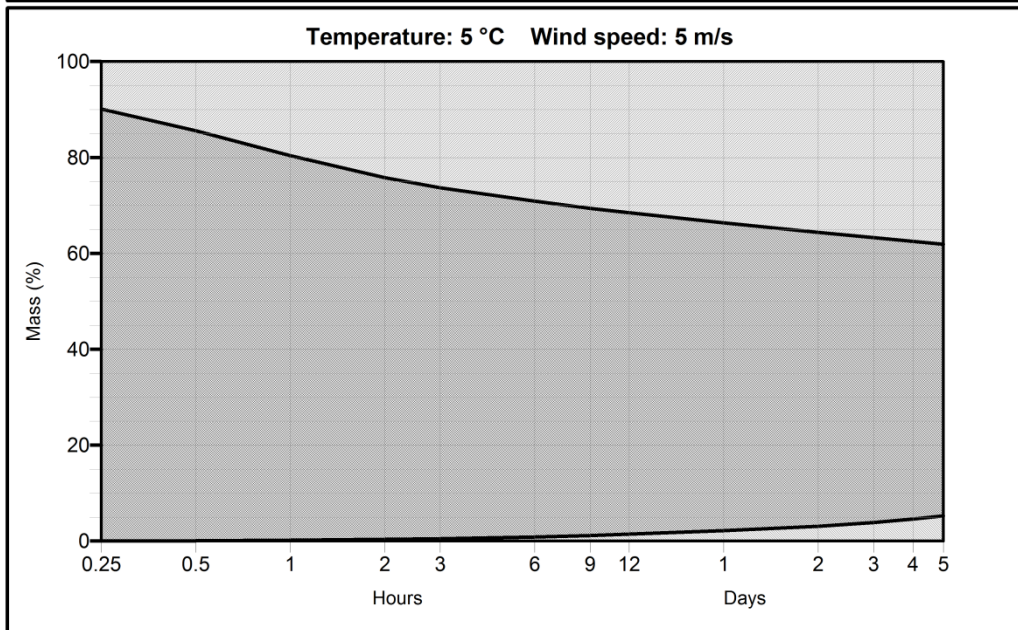
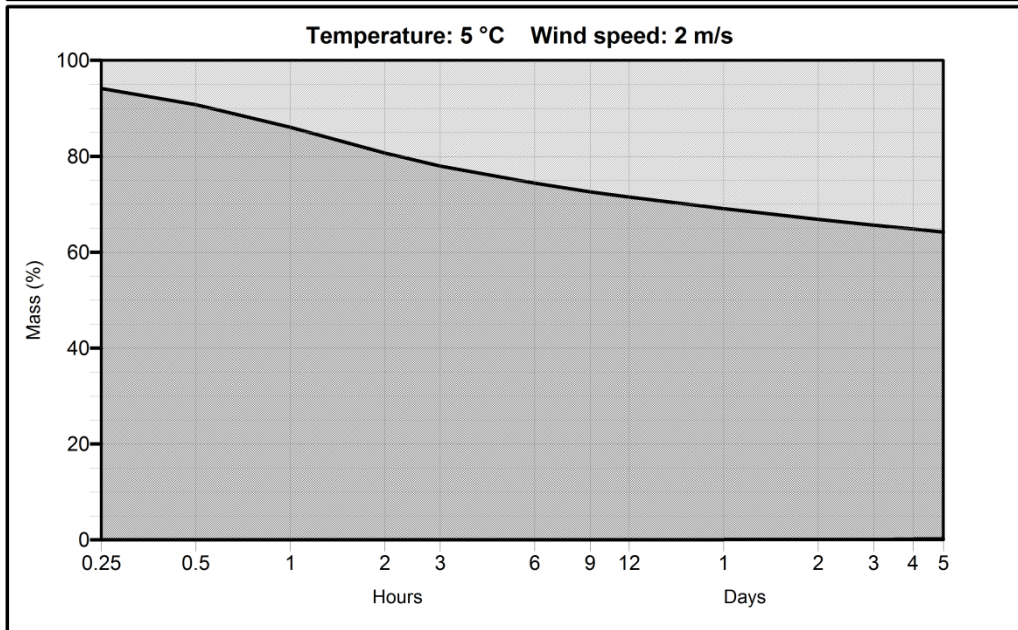


Figure 4-7: Predicted mass balance for Luno II at 5 °C and wind speeds of 2 and 5 m/s

Property: MASS BALANCE
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

- Evaporated
- Surface
- Naturally dispersed

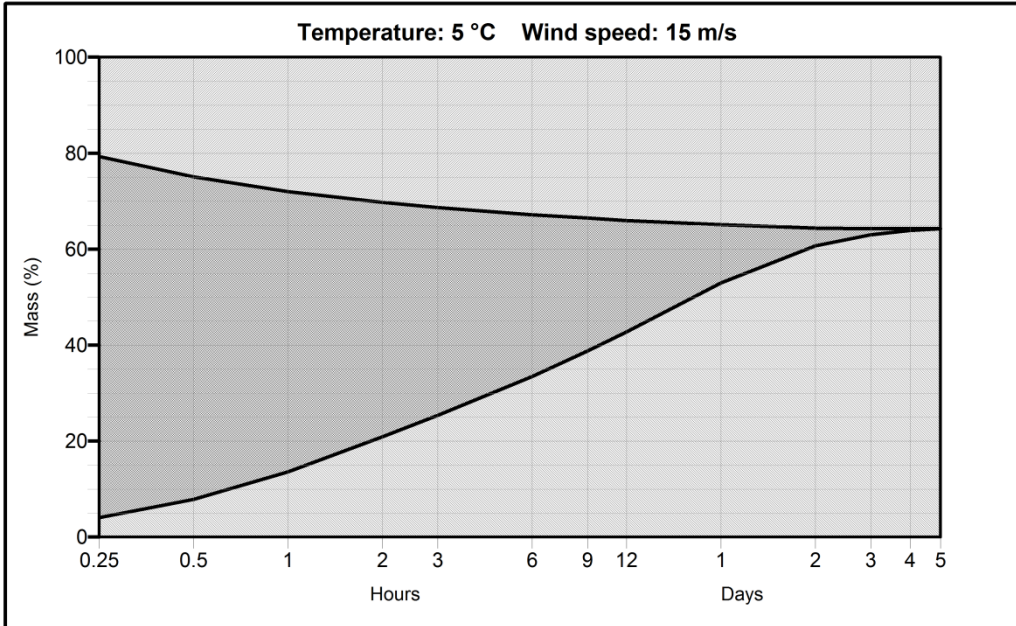
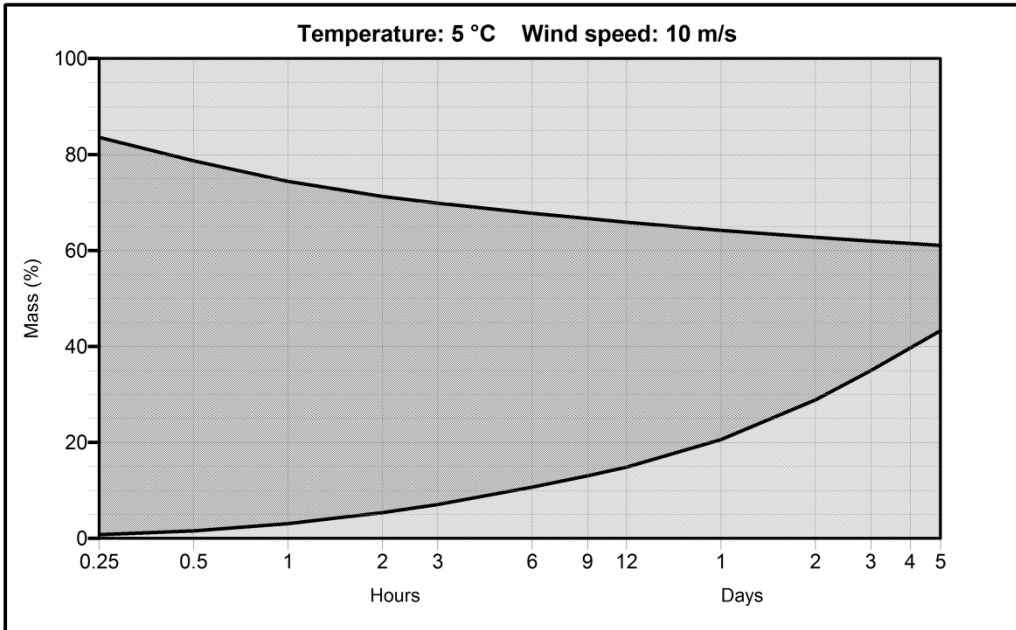


Figure 4-8: Predicted mass balance for Luno II at 5 °C and wind speeds of 10 and 15 m/s

Property: MASS BALANCE
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

- Evaporated
- Surface
- Naturally dispersed

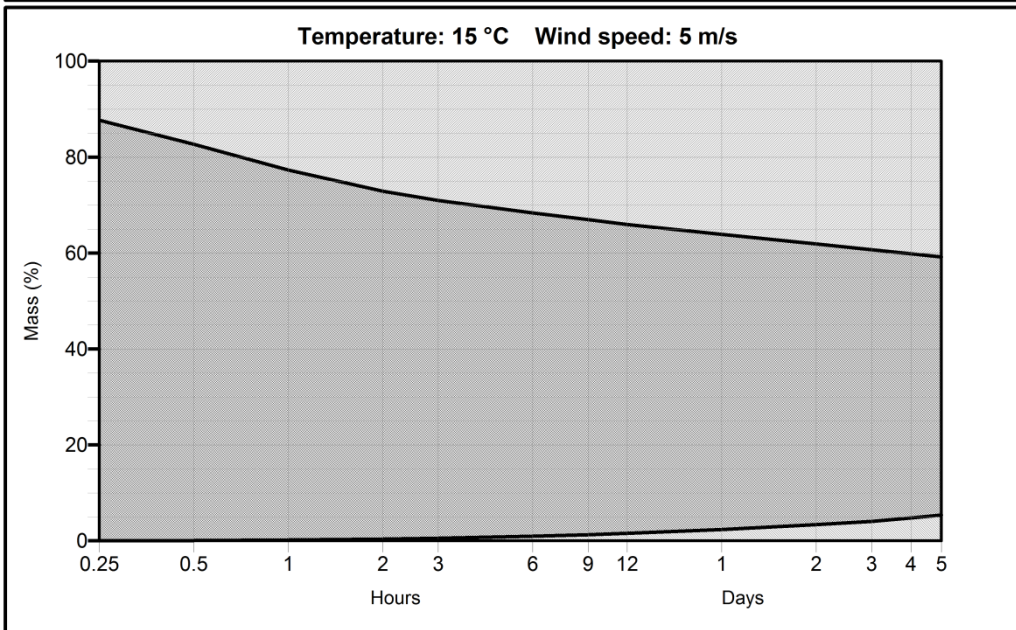
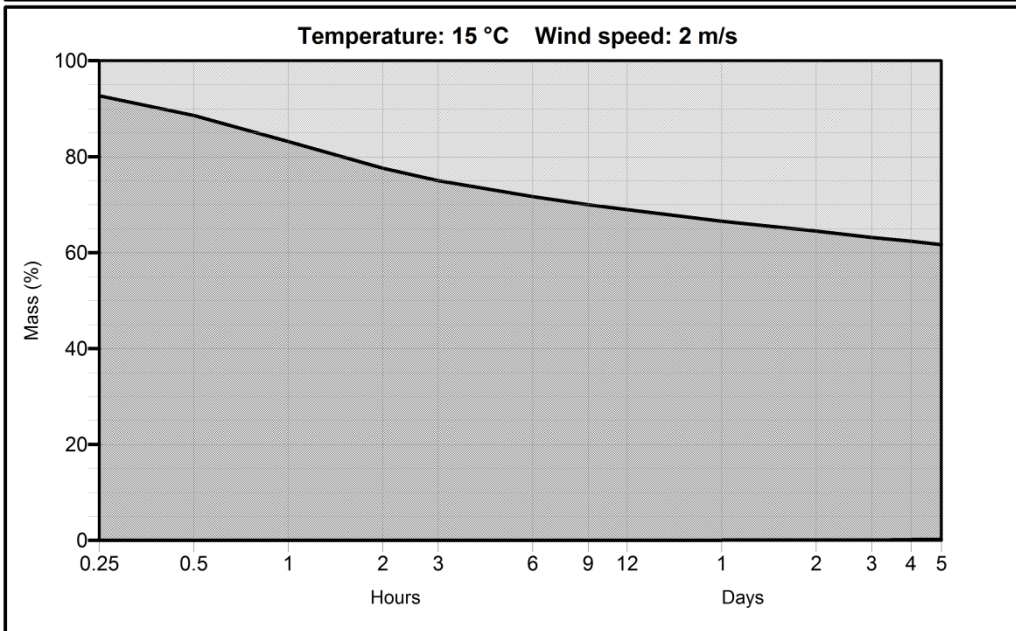


Figure 4-9: Predicted mass balance for Luno II at 15 °C and wind speeds of 2 and 5 m/s

Property: MASS BALANCE
Oil Type: LUNO II 2014 13°C (CRUDE)
Sintef ID: 2013-0580

OWModel

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

Pred. date: Mar. 07, 2014

- Evaporated
- Surface
- Naturally dispersed

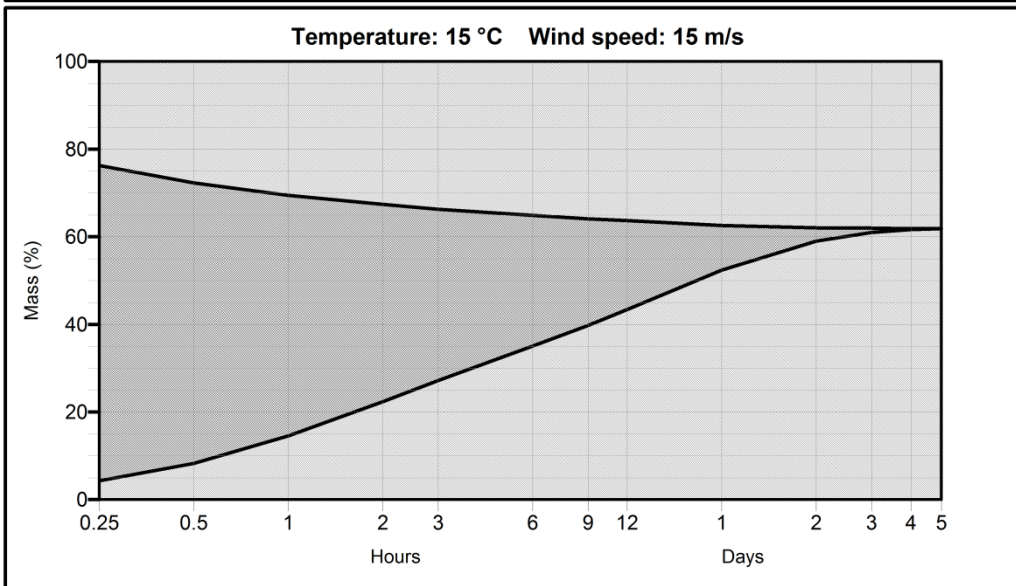
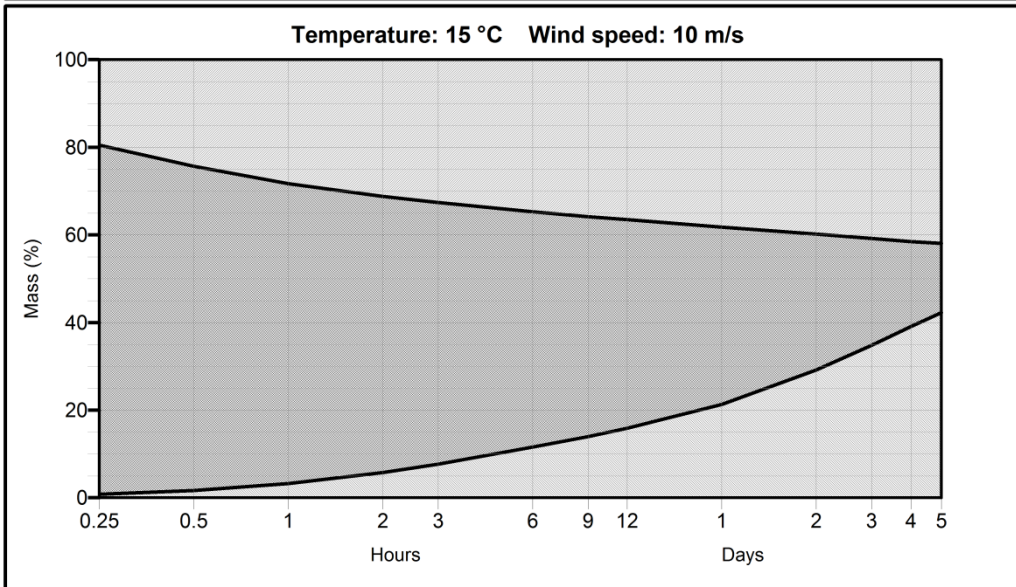


Figure 4-10: Predicted mass balance for Luno II at 15 °C and wind speeds of 10 and 15 m/s

4.3 Comparison with other oils

The weathering predictions of Luno II are compared with other Norwegian crude oils with varying properties. The oils chosen for comparison are Edvard Grieg, Ivar Aasen, Johan Sverdrup, Statfjord A and Grane, as listed in Table 3-1.

Evaporative loss

Luno II has an evaporative loss in similar range as the paraffinic crudes Statfjord A, Edvard Grieg and Ivar Aasen due to higher content of lighter components compared to the asphaltenic Grane and Johan Sverdrup.

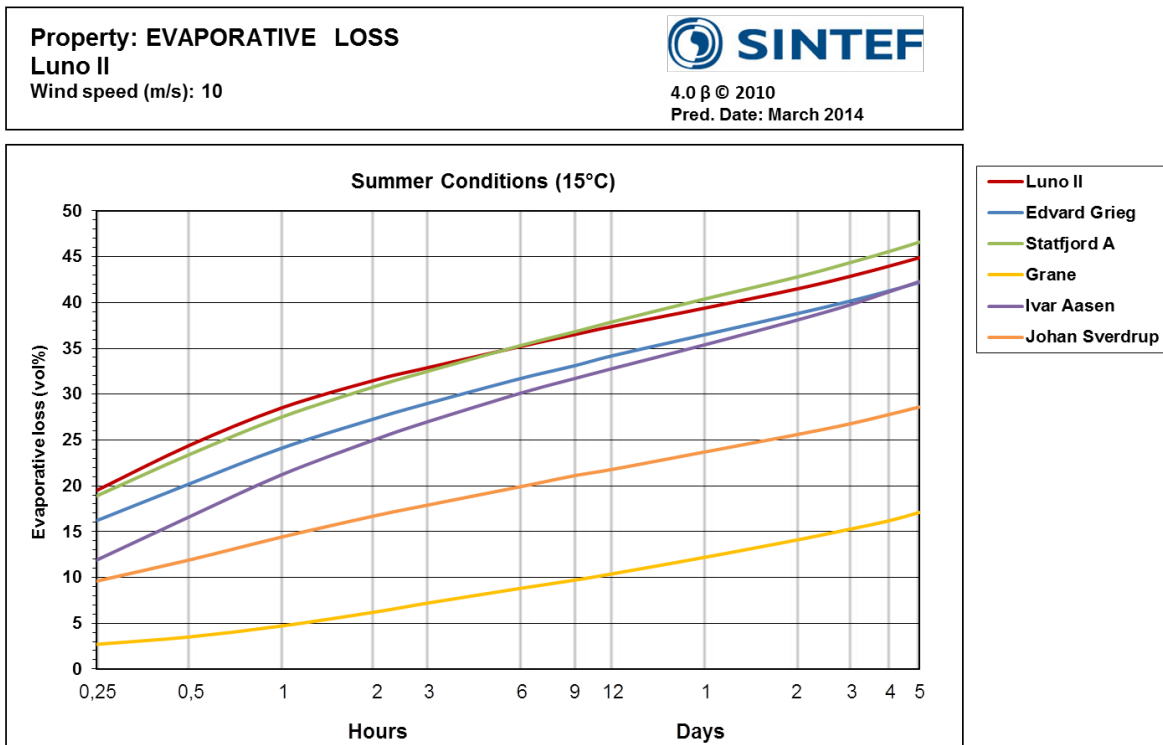


Figure 4-11: Predicted evaporative loss at 15°C and 10 m/s for Luno II compared to other oils

Flash point

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be high as long as the flash point of the oil is below the sea temperature. The fire hazard, dependent on the proportions of volatile components in oil, is usually over within a few minutes of weathering at sea due to the rapid evaporation of these components.

Neither Luno II nor any of the oils shown in Figure 4-12, exhibit risks of fire hazard after the first few minutes at sea. The flash point of Luno II is predicted to be similar to the other paraffinic crude oils, Ivar Aasen, Edvard Grieg and Johan Sverdrup, whilst the heavier Grane has a much higher flash point.

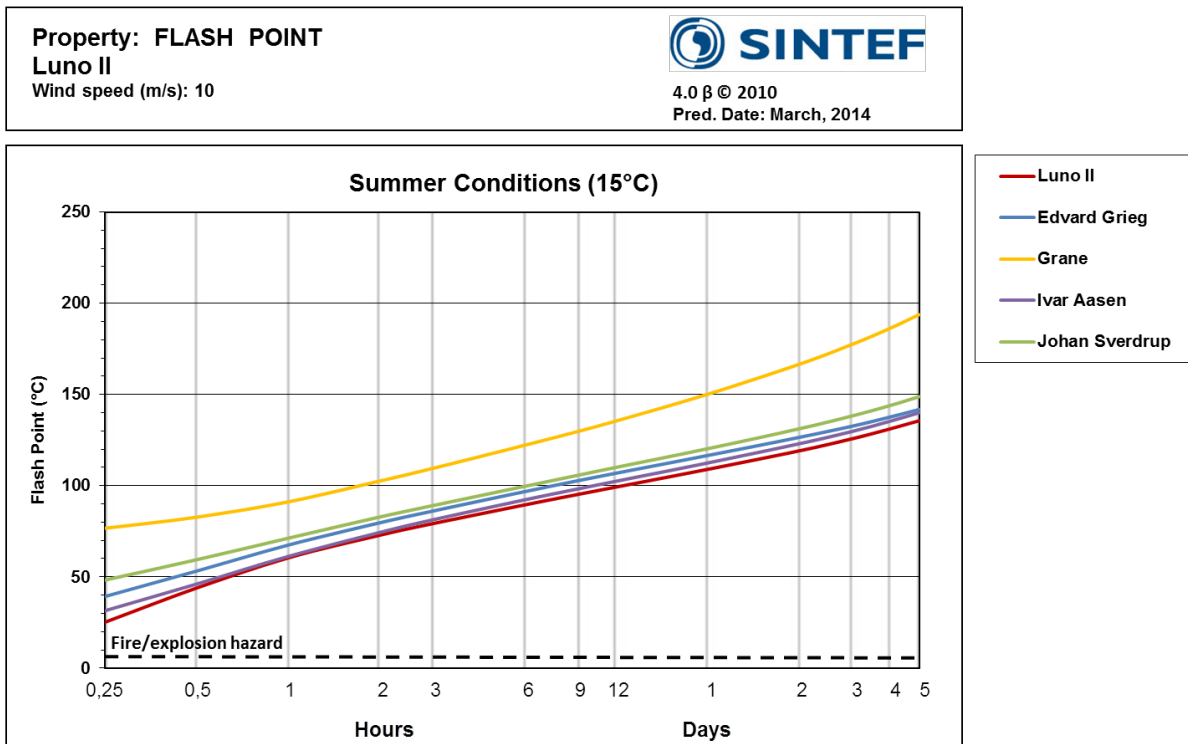


Figure 4-12: Predicted flash point at 15 °C and 10 m/s for Luno II compared to other oils

Pour point

Pour point depends on the oil’s wax content and the amount of light components that are able to keep the waxes dissolved in the oil. In addition, high asphaltene content prevents precipitation and lattice formation and lowers the pour point. The pour point of oil may influence the dispersant effectiveness.

Luno II has a low content of wax components and expresses a similar pour point as Ivar Aasen. In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification (elastic properties) when oil is spilled on the sea surface. Solidification typically arises at 10-15 °C above the sea temperature (se dotted line in Figure 4-13). This may imply solidification of Luno II after some days of weathering at sea at 10 m/s speed, as the range in Figure 4-13 expresses. A high pour point may prevent the dispersant to soak into the oil slick, thus reducing dispersant effectiveness.

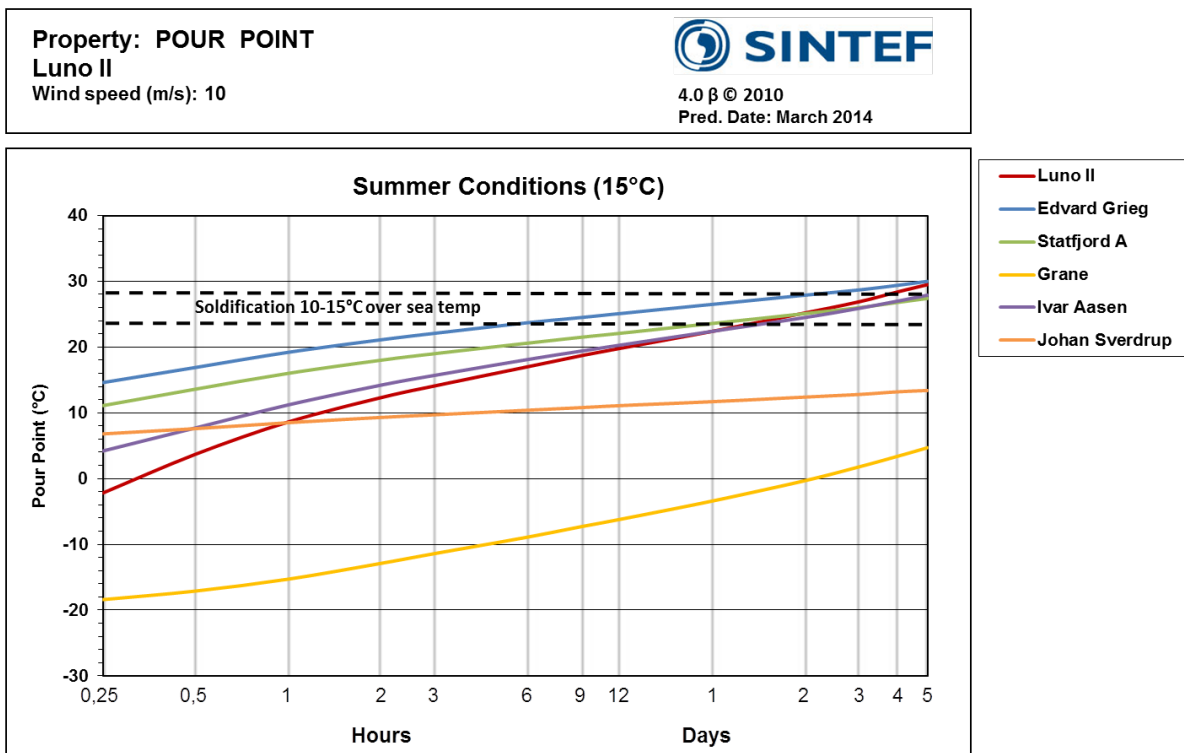


Figure 4-13: Predicted pour point at 15 °C and 10 m/s for Luno II compared to the other oils. Dotted line at predicted solidification point (10-15 °C above sea temperature).

Water content

Luno II has an intermediate predicted water uptake compared to the chosen oils. Luno II reaches a maximum water content of approximately 74 vol. % after one day of weathering at sea (wind speed of 10 m/s at 15 °C).

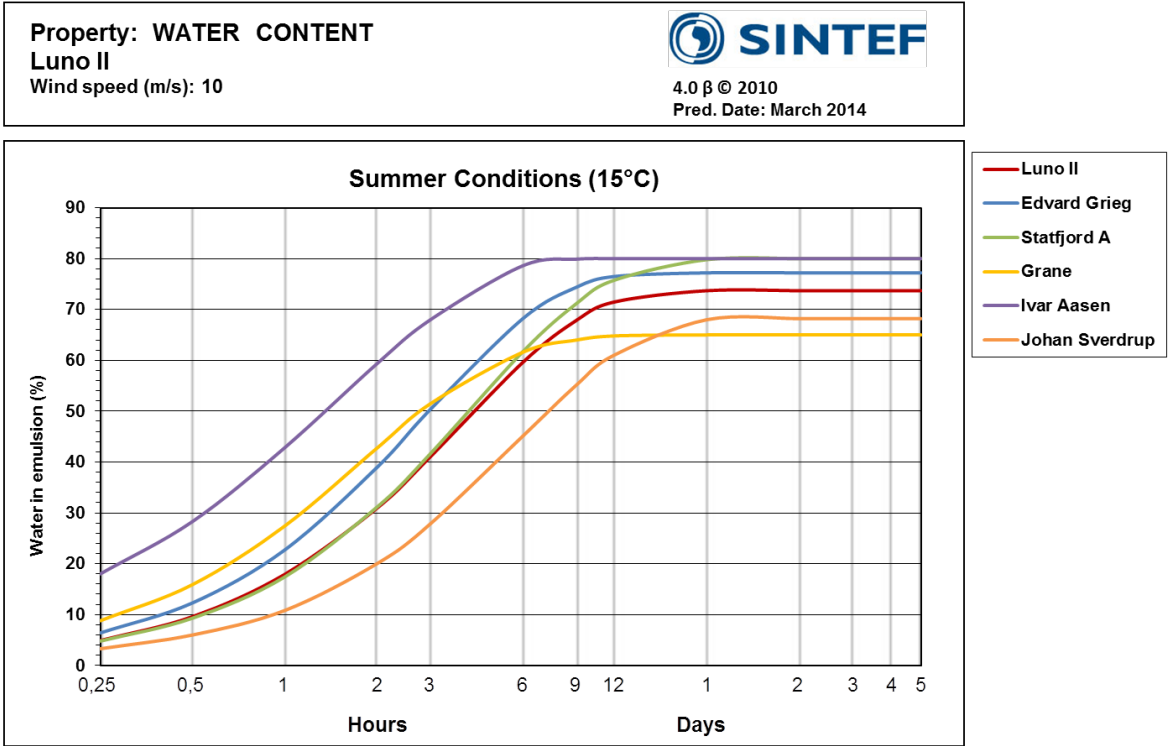


Figure 4-14: Predicted water uptake at 15 °C and 10 m/s for Luno II, compared to the other oils

Emulsion viscosity

Luno II forms stable water-in-oil emulsions with high viscosities. As Figure 4-15 expresses, the viscosities of the initial Luno II emulsions are fairly low but increases significantly with higher water content. The same trend and similar curve can be seen for Edvard Grieg.

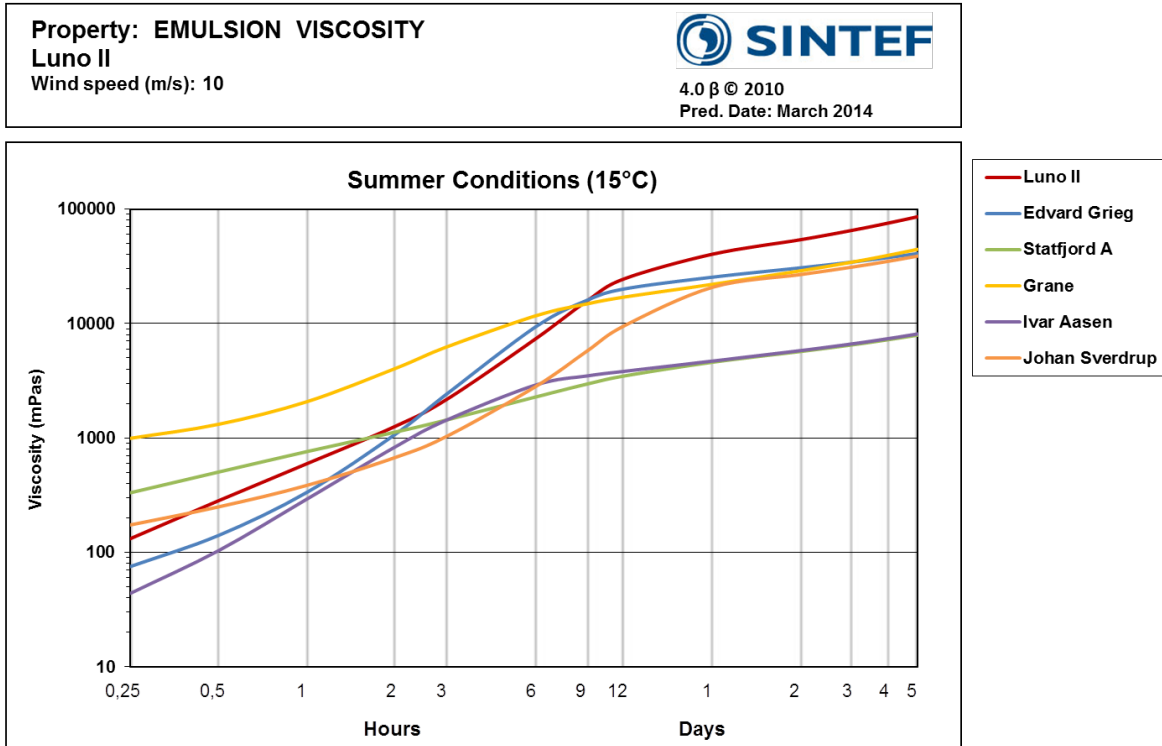


Figure 4-15: Predicted viscosity of the emulsions for Luno II compared with the other oils at 15 °C and 10 m/s.

Mass balance of surface slick

Due to evaporative loss and natural dispersion the oil on the sea surface will gradually be reduced. Figure 4-16 illustrates the predicted mass balance of the Luno II surface slick compared to other oils. Luno II and Edvard Grieg express similar lifetimes at sea, also comparable to the lifetimes of Statfjord A and Ivar Aasen. Johan Sverdrup is predicted to have a slightly longer lifetime at sea, while Grane, as a heavy and asphaltenic crude oil, is predicted to be most persistent on the sea surface of the selected oils.

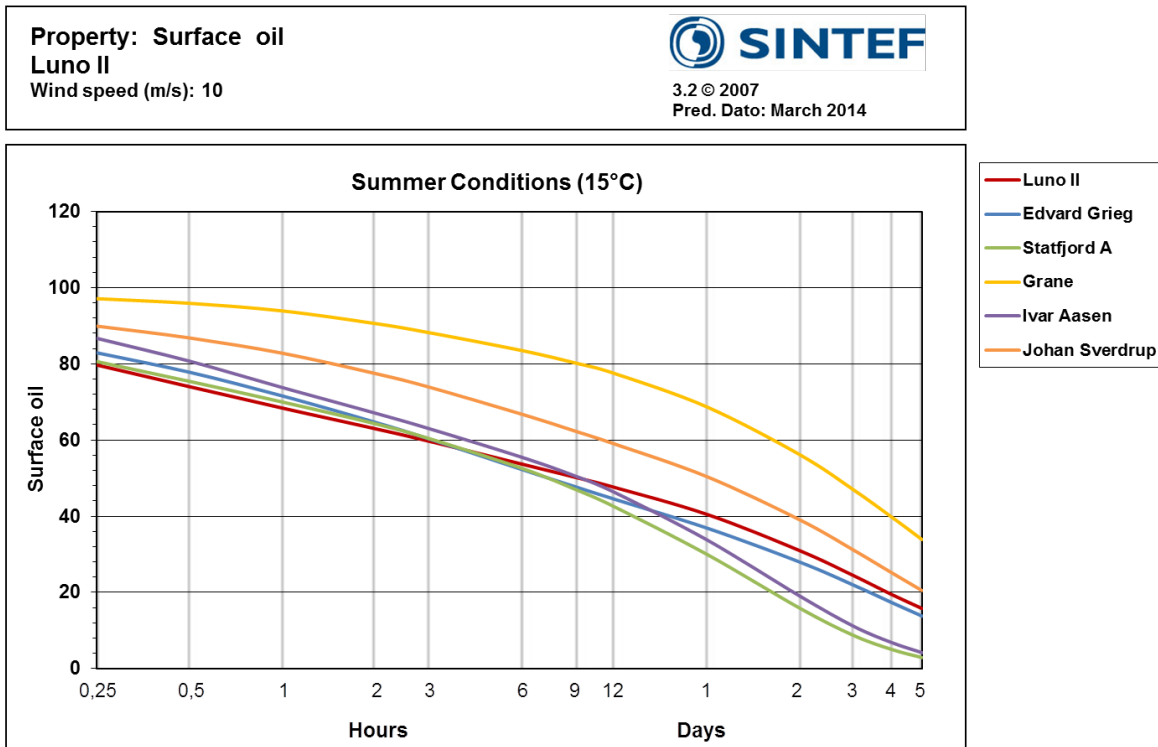


Figure 4-16: Predicted surface slick at 15 °C and 10 m/s for Luno II compared to the other oils

The surface oil is reduced due to evaporation and natural dispersion during weathering. However, the sea that is mixed into the oil will increase the total volume, as illustrated in Figure 5-2 on page 58.

5 Weathering properties of Luno II crude oil related to oil spill properties

5.1 Oil properties

Luno II has a density of 0.851 and is a medium heavy crude oil. It has a medium asphaltene content of 0.5 wt. % and a low wax content of 2.7 wt. % compared to other Norwegian crude oils. The GC chromatograms in Figure 3-1 and Figure 3-2 characterize Luno II as a paraffinic crude oil. Luno II has a high initial evaporative loss common to medium heavy paraffinic oils, and cause a rapid increase of the relative wax and asphaltene concentrations in the early stages of weathering. These changes will result in altered physical properties of the oil. Knowledge of the changes in physical properties during weathering of oil is important for oil spill response.

5.2 Flash point - fire/explosion hazard

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. For Luno II crude the flash point will be above the sea temperature within one hour low wind and winter conditions, and faster in summer temperature.

Some vessels engaged in oil recovery operations may not be classified to carry liquids with flash point lower than 60 °C (e.g. towing vessels, smaller cargo or vessels available in the emergency situation). Luno II will reach this limit in low wind conditions (2 m/s) after 12 hours at winter temperatures and after six hours in summer temperatures.

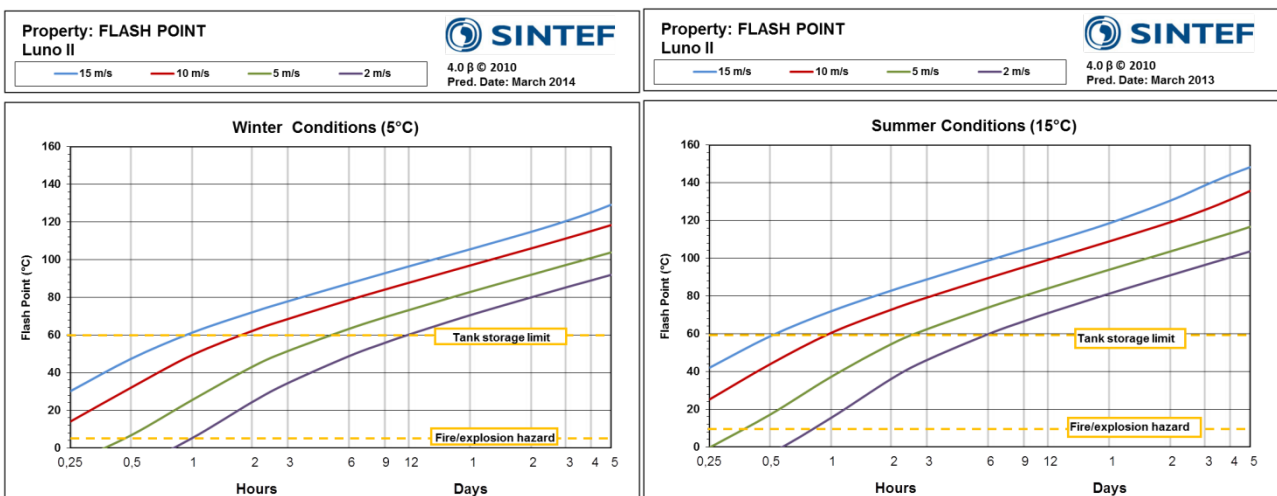


Figure 5-1: Flash point at different sea states of Luno II crude oil in winter and summer conditions

5.3 Emulsion formation

Luno II forms stable w/o-emulsions. The total amount of oil on the sea surface is reduced due to evaporation and natural dispersion in the initial stages of weathering after release. However, as the oil takes up water and form emulsions the volume increases considerably, as Figure 5-2 illustrates.

Luno II will emulsify rapidly on the sea surface and forms stable water-in-oil emulsions with relatively high water content.

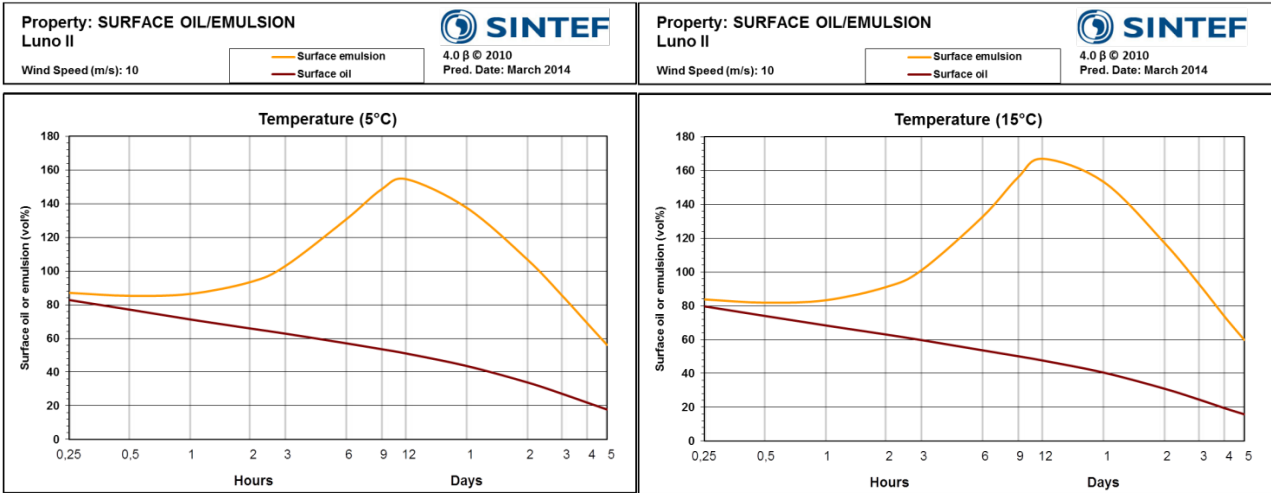


Figure 5-2: Difference in the total slick volume due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion predicted at 10 m/s wind speed at temperatures of 5 °C and 15 °C

5.4 Breaking of emulsion with addition of emulsion breaker

Emulsion breaker can be used during an oil spill operation to increase water release from an emulsion, normally after recovery prior to transfer to storage tank. The emulsion breaker is normally not added directly on the oil spill at sea surface.

Figure 5-3 illustrates the relative volumetric composition of water-in-oil emulsion and free water, approximately one week after a spill of Luno II oil both with and without the addition of emulsion breaker (Alcopol O 60 %). At this stage of weathering, the addition of emulsion breaker at a concentration of 2000 ppm will have limited effect; approximately 10 vol. % of water was released from the emulsion at both test temperatures (5 °C and 13 °C). Addition of emulsion breaker at a concentration of 500 ppm had only limited effect in summer conditions, and no effect in winter conditions.

As Table 3-7 on page 17 express, addition of emulsion breaker will be more effective on emulsions from earlier stages of weathering.

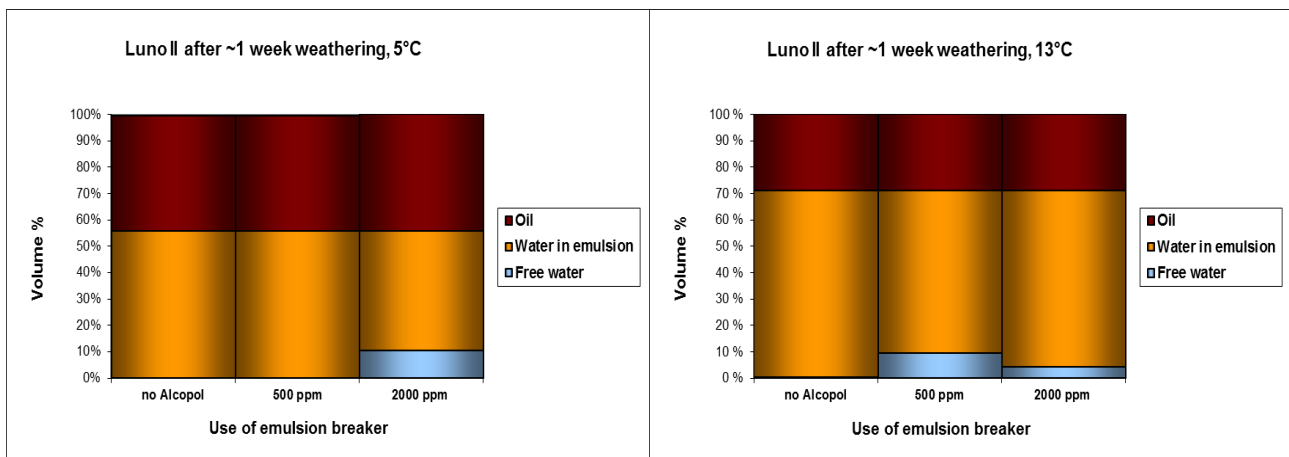


Figure 5-3: Relative volumetric composition of water-in-oil emulsion and free water

5.5 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 5-4 shows the remaining surface oil over time for different sea states and temperature conditions. Considerably larger spills are expected to produce longer lifetimes, and individual modelling may be necessary.

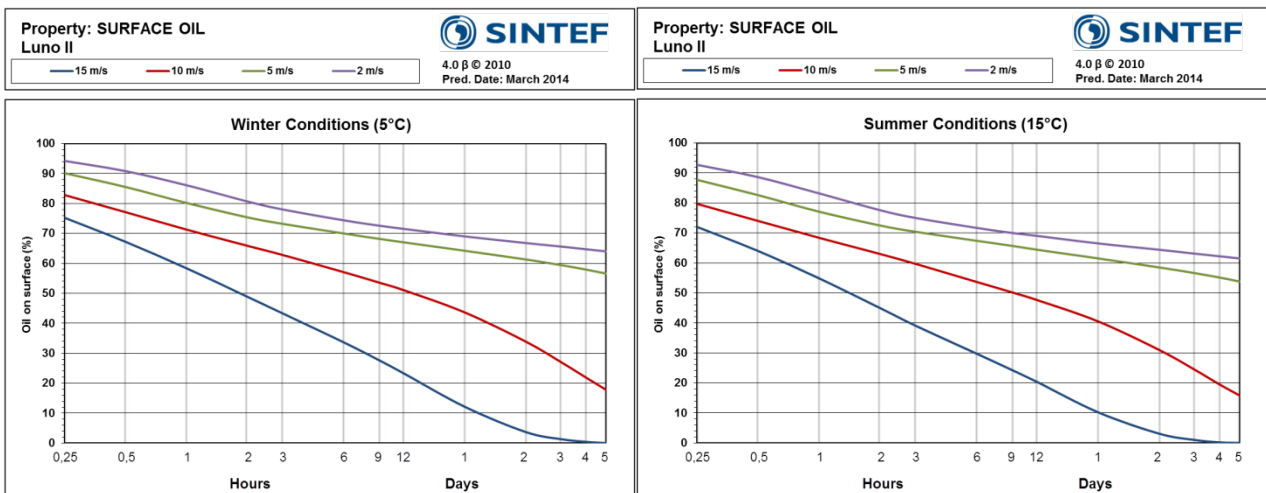


Figure 5-4: Remaining surface oil under different sea states for Luno II at 5 °C and 15 °C (predictions for an instant surface release of 20 tonnes)

5.6 Oil spill response

5.6.1 Mechanical recovery

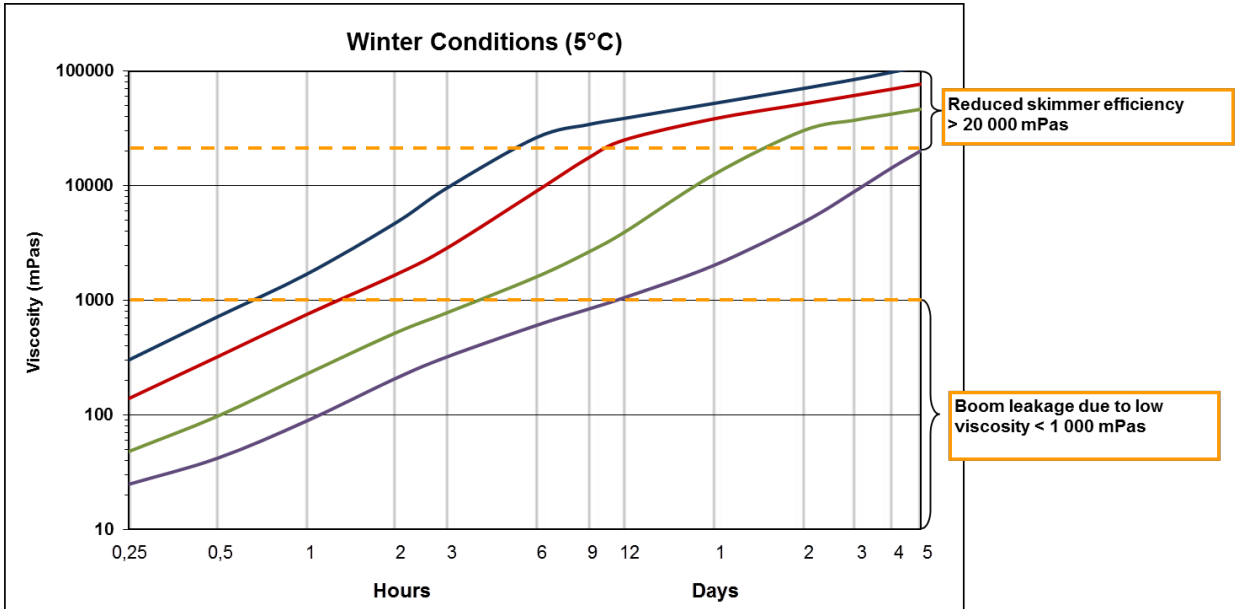
Experiences from Norwegian field trials have demonstrated that the effectiveness of various mechanical clean-up operations is reduced due to the high degree of leakage of the confined oil or w/o emulsion from the oil spill boom. This leakage is particularly pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPas (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been set at 1000 mPas. It should be emphasized that boom leakage is also influenced by other factors as e.g. the operational speed of recovery vessel and weather conditions. As Figure 5-5 illustrate Luno II will remain below this limit for 4 hours in wind conditions of 5m/s at winter temperatures and approximately 5 hours at summer temperatures.

Studies at SINTEF have shown that weir skimmers may have reduced recovery rate (m^3/t) at viscosities of 15,000-20,000 mPas (Leirvik *et al.*, 2001). Emulsions of the Luno II crude oil is expected to reach this viscosity limit after 1-2 days of weathering in 5m/s wind speeds, at both winter and summer temperatures. In higher sea states this limit will be reached even faster. The use of "high visc." skimmer could therefore be recommended. However, the efficiency of different types of skimmers is also influenced on other oil properties, such as the wax content. It has been observed that the recovery rate of rope skimmer also varies among different categorizations of crude oils (Singsaas *et al.*, 2000). Solidification could likely be a possible scenario for Luno II due to its relatively high viscosities and pour point.

Property: EMULSION VISCOSITY
Luno II

— 15 m/s — 10 m/s — 5 m/s — 2 m/s

SINTEF
 4.0 β © 2010
 Pred. Date: March 2014



Property: EMULSION VISCOSITY
Luno II

— 15 m/s — 10 m/s — 5 m/s — 2 m/s

SINTEF
 4.0 β © 2010
 Pred. Date: March 2014

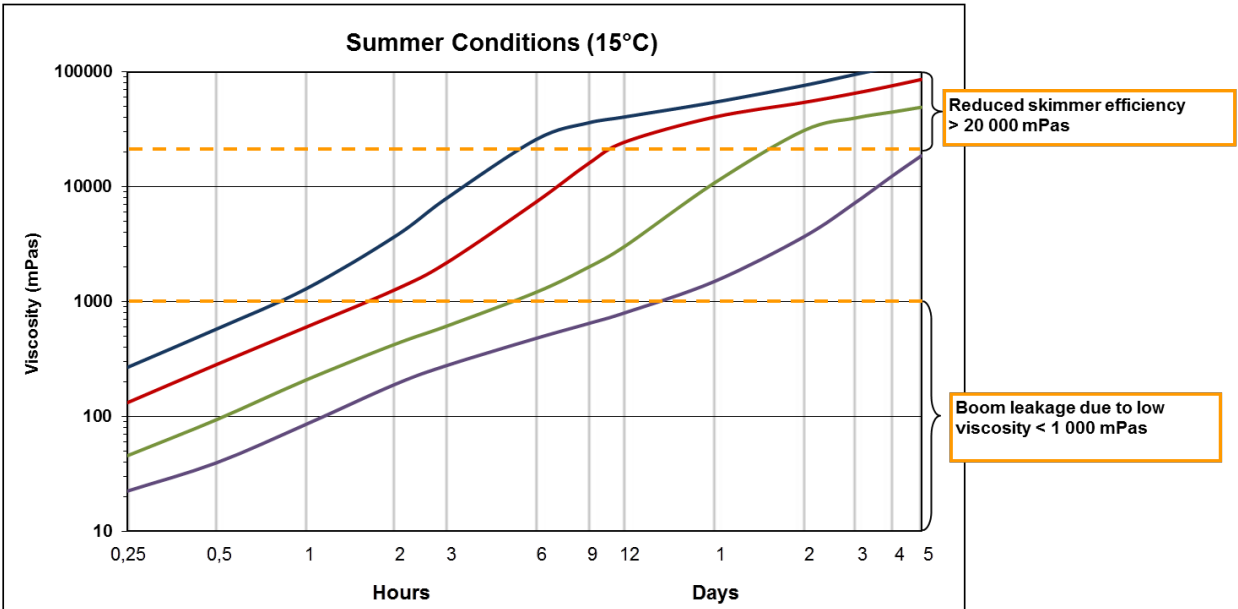


Figure 5-5: Predicted emulsion viscosity for Luno II at 5 °C and 15 °C compared with expected viscosity limits for extensive boom leakage and poor flow to weir skimmers

5.6.2 Use of chemical dispersants

In general, Luno II has a potential for use of chemical dispersants. The window of opportunity for use of chemical dispersant (Dasic NS) is given in Figure 5-6 for both winter and summer temperatures.

The viscosity limit for when the oil is dispersible was estimated to 3000 mPas based on the IFP low energy test (reflecting non-breaking waves), while the limit for when the oil is not dispersible was measured by MNS high energy test (reflecting breaking waves) to 25,000 mPas.

For optimal results the dispersants should be applied as quickly as possible; in strong wind (15 m/s) the emulsion will reach the viscosity limit for dispersibility within six hours. Once the oil is expected to have reduced chemical dispersibility, additional energy or a higher dispersant dosage (DOR= dosage to oil ratio) should be applied. Repeated application of dispersant may also increase the effectiveness, especially in calmer sea states. Additional energy can be provided using firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application in order to enhance dispersant rate more efficiently.

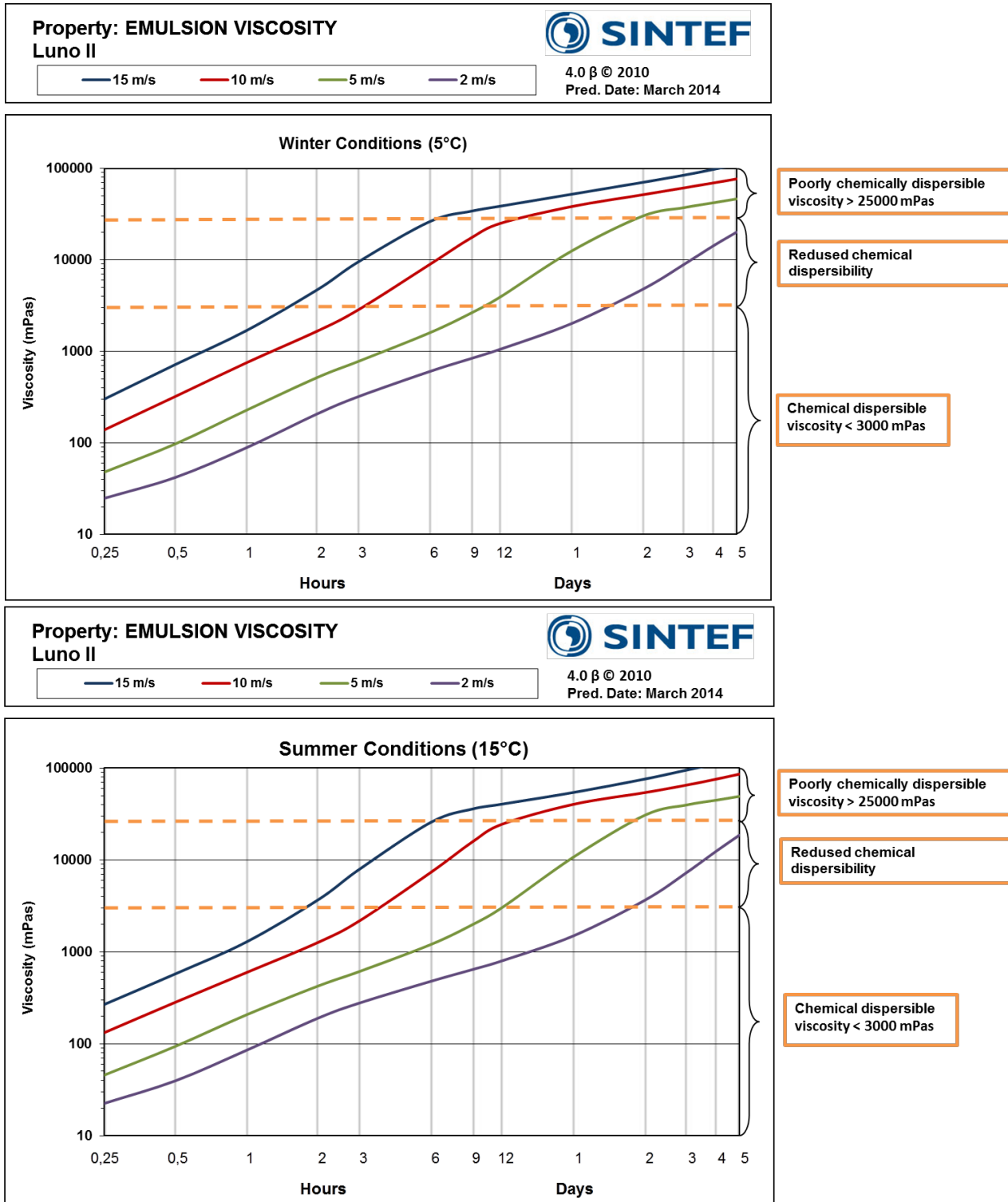


Figure 5-6: Time window for use of chemical dispersants as a function of viscosity for Luno II at 5 °C and 15 °C

6 Categorization of Luno II versus other Norwegian crudes

SINTEF has developed a concept for tentative categorization of oils into main groups; paraffinic, waxy, naphthenic, and asphaltenic oils, as described below:

- **Naphthenic oils**, characterized by a disrupted n-alkanes pattern in the gas chromatogram due to biodegradation of the oil in the reservoir. The content of paraffin's is therefore normally low.
- **Paraffinic oils**, often characterized by a low density which reflects a high content of light components (paraffines).
- **Asphaltenic oils**, with a high content of heavier components. The content of lighter components is correspondingly low, reflected by high density and low evaporation.
- **Waxy oils**, often exhibit high pour points due to a large content of wax components. At low temperatures these oils can have a tendency to solidify at the sea surface, especially if the sea water temperature is 10-15°C below the pour point.

The categorization of a selection of Norwegian crude oils is presented below. Luno II, as well as the crude oil used for comparison above, can be found in Figure 6-1.

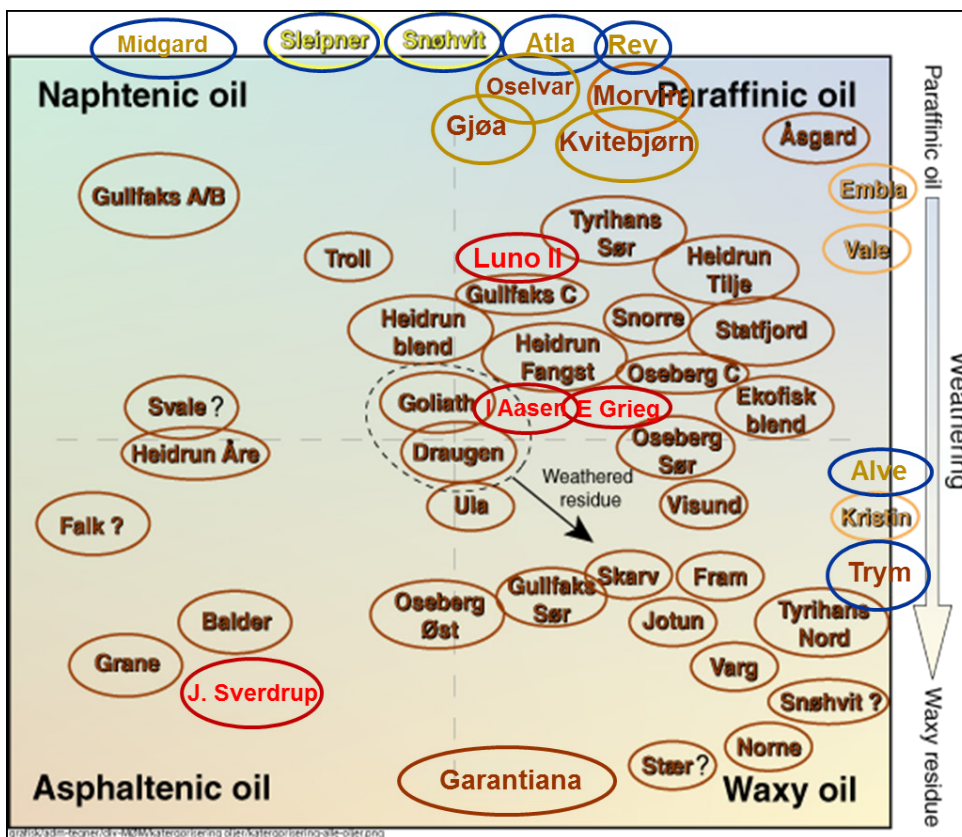


Figure 6-1: Categorization of a selection of Norwegian crude oils

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A - The behaviour of crude oil on the sea surface

A.1 The chemical composition of crude oils

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 heteroatomic organics see Figure A 1.

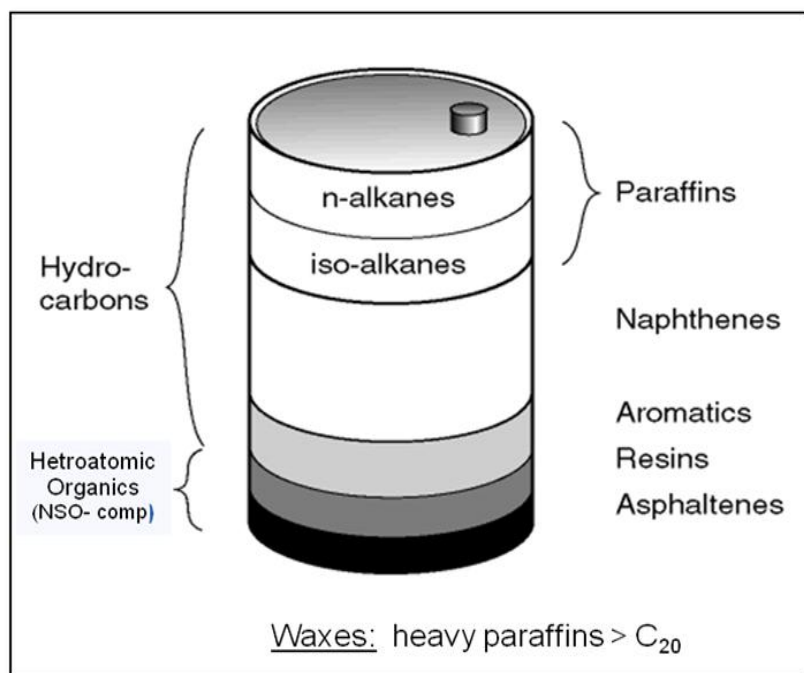


Figure A 1: The chemical composition of crude oils

A.1.1 Hydrocarbons

The majority of 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 isoalkane 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 Heteroatomic organics

In addition to pure hydrocarbons, 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. The two most important groups of heteroatomic organic compounds are resins and asphaltenes.

Resins

Resins are relatively polar compared to the hydrocarbons, 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

This 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 1000-10000). Asphaltenes may be classified as "hard" or "soft" on the basis of 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

The relative composition of oils will differ extremely, resulting in great variations in physical properties and following, behaviour after a spill at sea.

Related to weathering oils can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

Crude oils contain relatively more heavy components than the other two categories (light oils and condensates), and the 250°C+ residue (corresponds to 0.5 to 1 week after a spill at sea) evaporates typically less than 50 vol. %. The heavier components make possible formation of stable water-in-oil (w/o) emulsions, which reduces the 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 differentiated in the reservoir terminology. However, related to weathering studies, it is suitable to deal with the light oils as a separate category. Light oils have a high content of light components, and the 250°C+ residue evaporates less than 50 - 70 vol. %. In contrast to condensates light oils also contain heavier components. The content of these heavier, emulsion-stabilizing components cause that light crudes may emulsify water. These w/o emulsions are, however, very unstable. Light oils spread less than a condensate, and a final film thickness of 0.5 mm is estimated for these oil types.

Condensates evaporates typically more than 70 vol. % for the 250°C+ residue. Condensates will not contain any significant amounts of components as asphaltenes and heavier waxes, and will not emulsify significantly amounts of water. The spreading is vast, with a final film thickness in the range order of 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 the hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing large amounts of high molecular weight aromatics, naphthenes and asphaltenes.

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

$$^{\circ}\text{API} = \frac{141,5}{\text{Secific gravity}} - 131,5$$

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 is: *force distance/area speed* and has the unit: $\text{dyn}\cdot\text{sec}/\text{cm}^2 = 1 \text{ Poise}$. The industry is often using the unit $\text{mPas} = \text{centipoise (cP)}$. The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPas (cP) at ambient sea temperature. In comparison water has an “absolute” viscosity of 1 cP and syrup 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 in the area of typically 0.9 – 1 g/ml, the units cSt and cP may often have similar values.

The 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 quite 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 mPas for fresh crude oils and several hundred/thousand mPas 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.

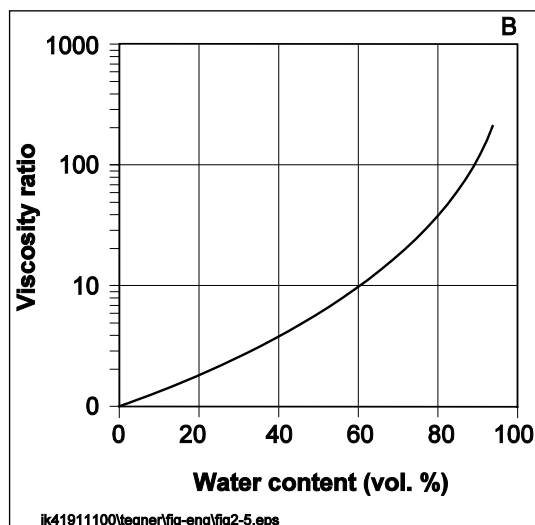


Figure A 2: Example of viscosity ratio as a function of water content

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. The method accurately determines the temperature at which the oil becomes 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°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 important information 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 particular 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.

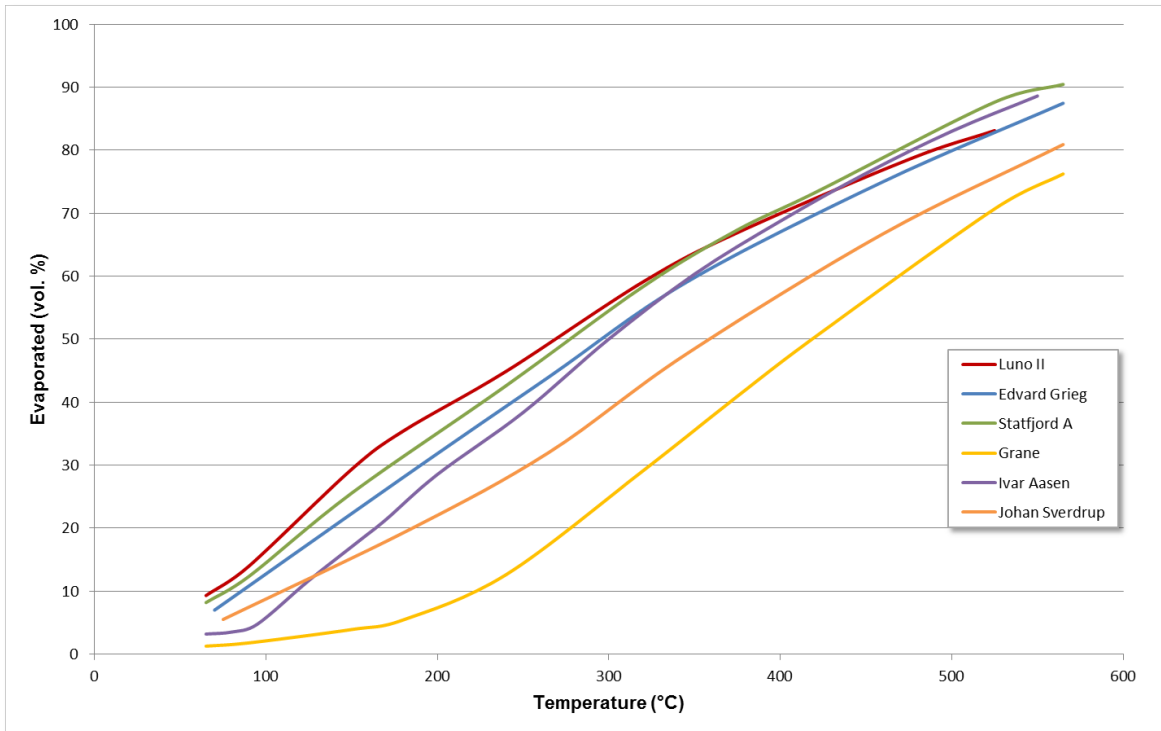


Figure A 3: Distillation curves for Luno II crude oil with other Norwegian crude oils

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:

Moving in an oil slick where the oil's flash point is close to or lower than the sea temperature implies a fire and/or explosion hazard.

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

When crude oil is spilled at sea, a number of 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 and the release of oil components into the water column, 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.

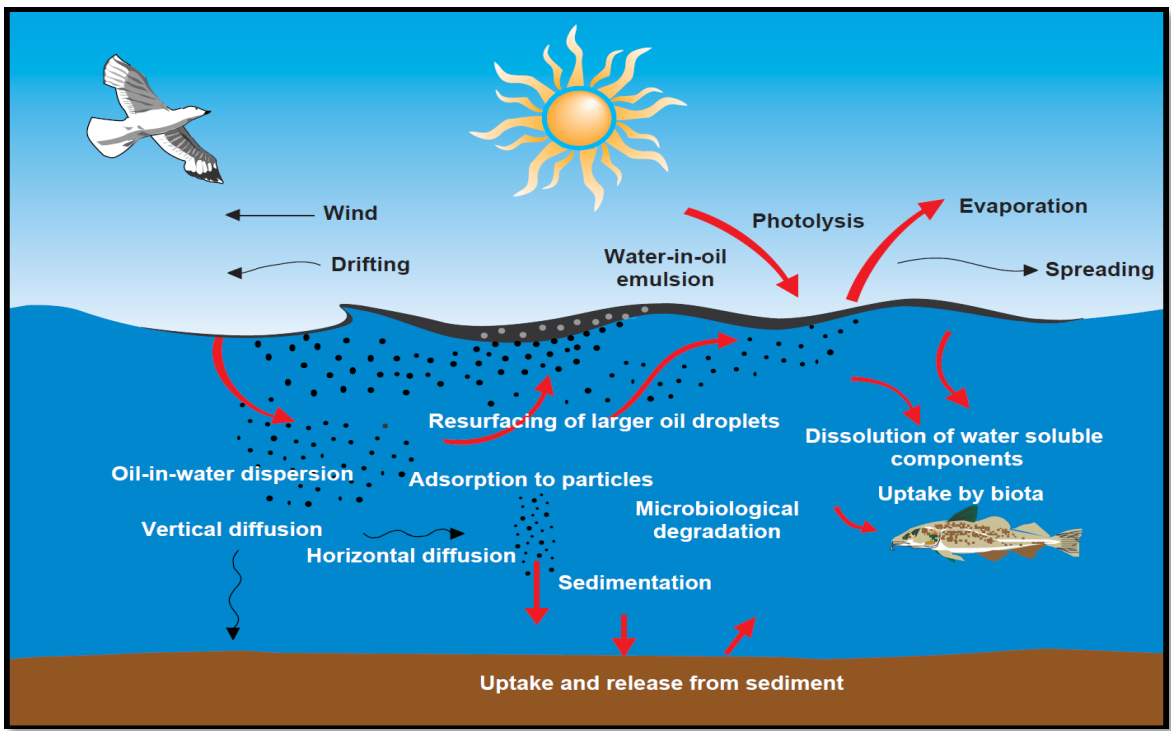


Figure A 4: Illustrating the weathering processes that take place when oil is spilled on the sea surface

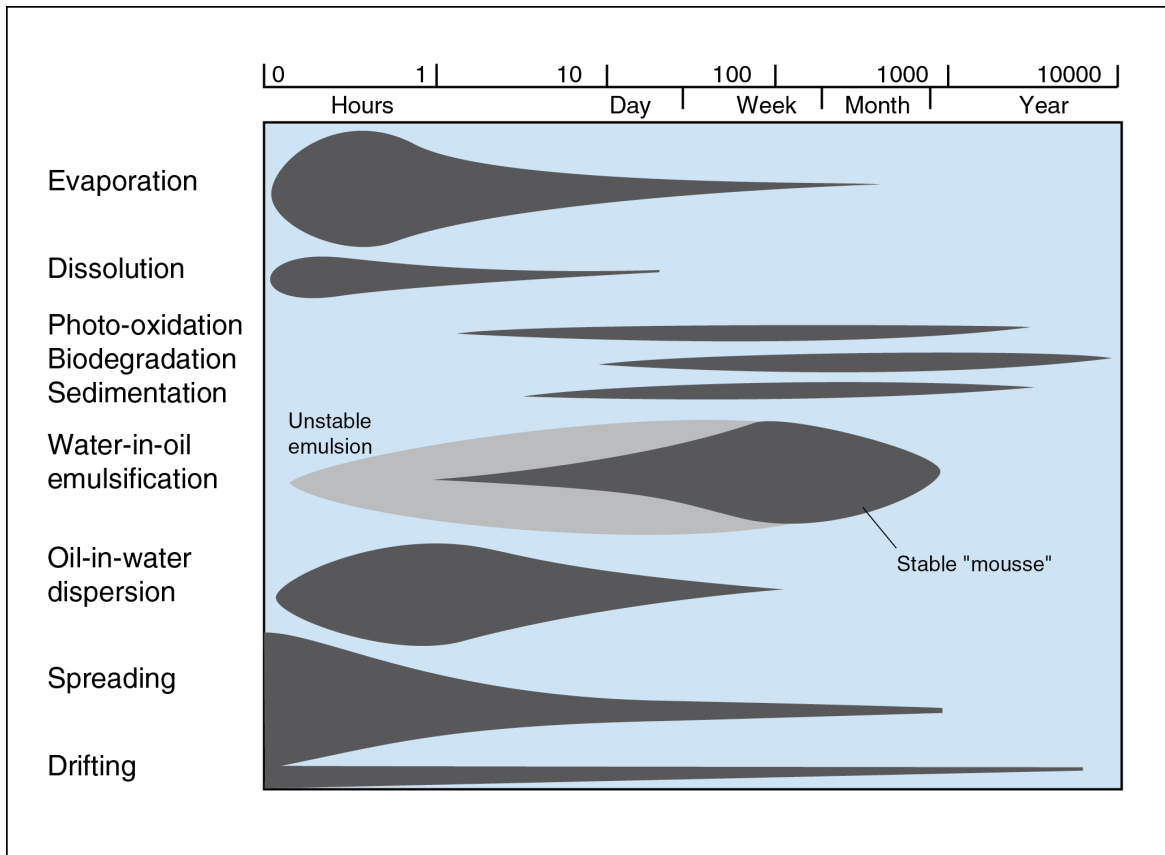


Figure A 5: Weathering processes' relative importance over time. Note: logarithmic scale.

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 retarded if the oil's pour point is 10-15°C below the sea temperature.

Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into windrows 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 e.g. 90 vol. % of the oil spilled may consist of patches of w/o emulsion with a film thickness of 1 to 5 mm, which often constitutes less than 10 % of the total oil slick area. The remaining 5-10 vol. % usually covers 90 % of the spill area in the form of a sheen (<1 μm oil thickness).

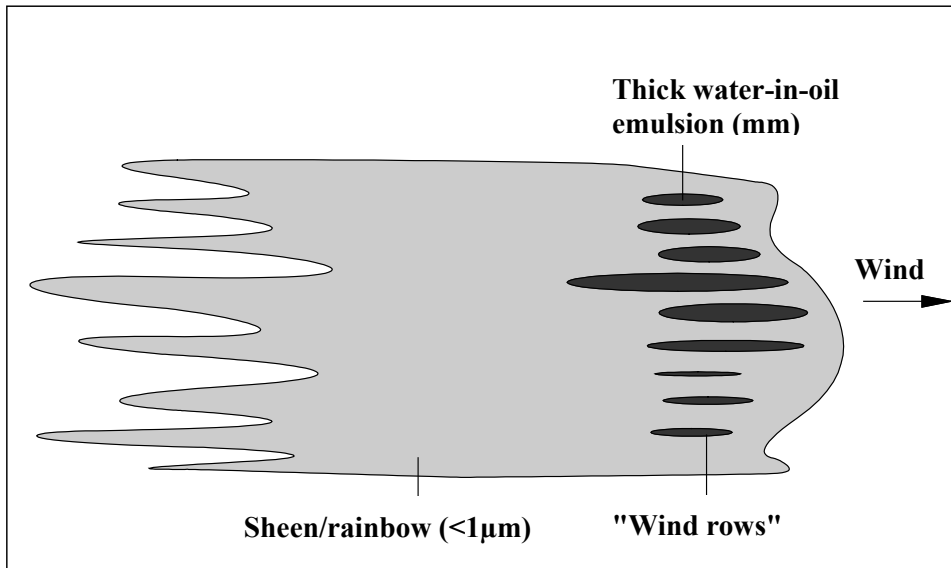


Figure A 6: The spreading of oil spilled on the sea surface and the distribution within the oil slick

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 (Reed *et al.*, 1994). In the absence of wind, the oil drift is governed by the prevailing (background) current.

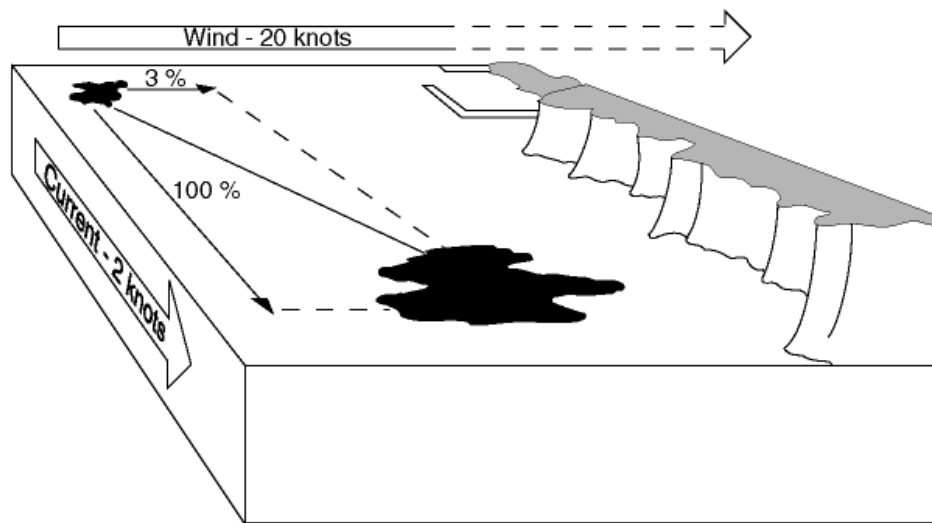


Figure A 7: An illustration showing how wind and current can influence the drifting of an oil slick

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. As a result 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.

A minimum criterion for the formation of w/o emulsions is often 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 fairly independent of the prevailing weather conditions as long as 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.

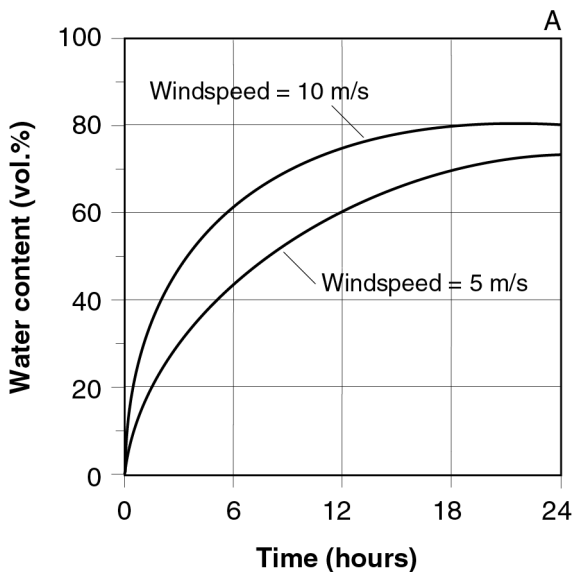


Figure A 8: Example of how weather conditions influence the w/o emulsion formation for typical oils

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 of time, the emulsion may only contain small water droplets with diameters of 1 to 10 μm , yielding a more stable emulsion.

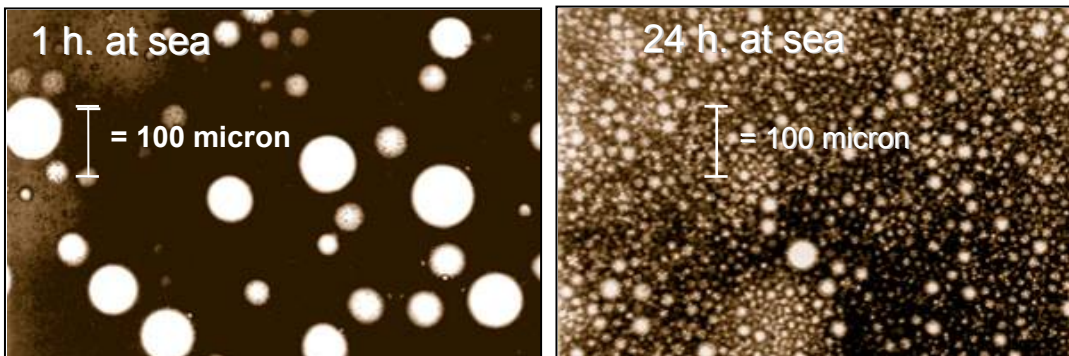


Figure A 9: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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.

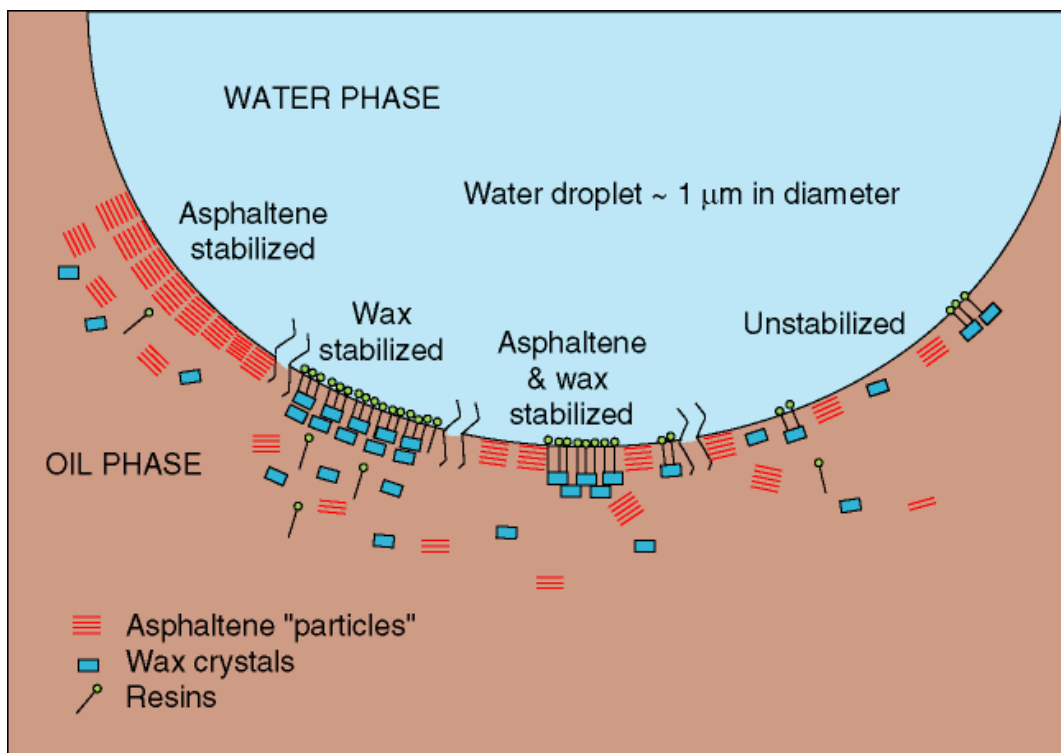


Figure A 10: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

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 SINTEF's 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 droplets of diameters, typically 1 μm - 1 mm, which are then mixed into the water mass. The largest oil droplets will resurface and form a thin oil

film (typically <math><50\ \mu\text{m}</math>) behind the oil slick. 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 the 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 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. The dispersant reduces the interfacial tension between water and oil and thus promotes dispersion. When effective chemical dispersion is achieved, small oil droplets are formed with diameters typical 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.

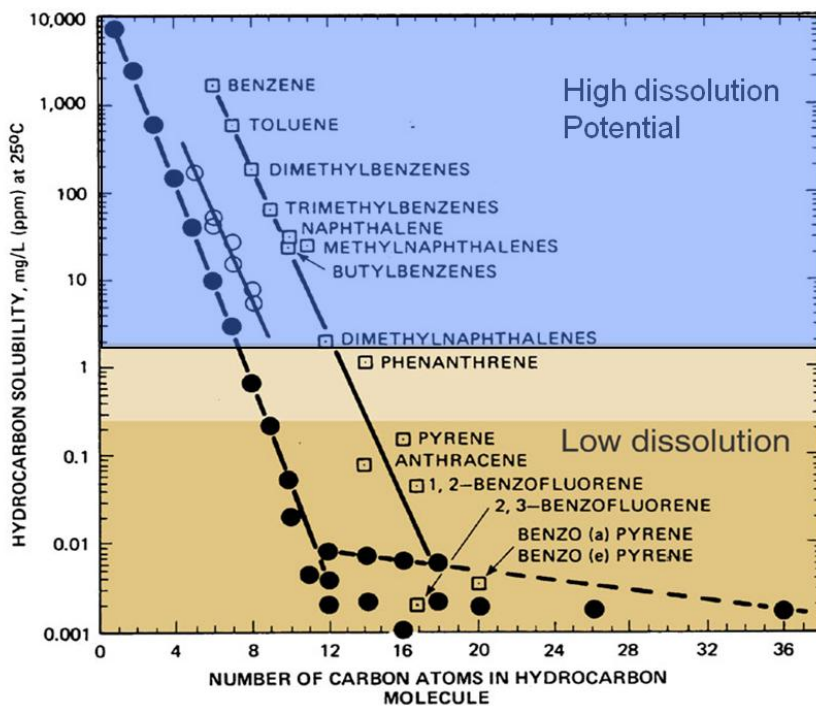


Figure A 11: Solubility potential per carbon number for hydrocarbon molecules (modified from McAuliffe, 1987)

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 (<math><1\ \text{mg/L}</math>), 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. This contributes to the stability of w/o emulsions (chapter A.4.4), therefore exerting a large influence on the oil's persistence on the sea surface. The photo-oxidized components will stabilize the w/o emulsions. After a long period of weathering at sea, tar balls, mainly consisting of asphaltenes, may be formed and can break down very slowly, both at sea and on beaches.

A.4.8 Biodegradation

Seawater contains an abundance of micro-organisms that can break down all types of oil components. The various micro-organisms prefer specific oil components as their energy source. Bacteria can only degrade oil in contact with water and depend 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 in the water mass.

Important factors influencing the biodegradation rate are temperature, the nutritive supply that contain nitrogen and phosphorus, the oxygen supply, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched isoalkanes > cyclic alkanes > cyclic naphthenes > aromatics > resins > asphaltenes (Perry, 1984). PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000). Degradation of oil in contact with seawater depends highly on the water/oil interface area. The interfacial area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil into the water column.

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, and it has been shown that *n*-alkanes are biodegraded within 2-4 weeks at North Sea conditions (Brakstad and Lødeng, 2005). Other higher molecular-weight oil compounds are biodegraded 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 a particular material 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 particular 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 come in contact with the sea-bed sediment. This can cause some sedimentation of oil droplets to the sea-bed in the vicinity of 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.

B Experimental setup

B.1 Oil samples and test temperature

Three barrels of 25 litres of Luno II crude oil, was received at SINTEF's laboratory on 2013-07-01, Figure B 1.

Luno II was given the unique SINTEF ID: **2013-0580**.

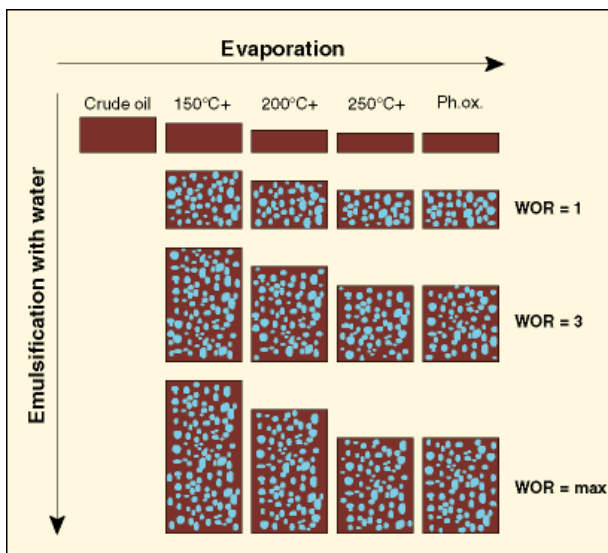


Figure B 7-1: Barrels with Luno II crude oil

The testing of the weathering properties was performed at 5°C and 13°C, which are regarded as typical winter and summer North Sea temperatures.

B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The weathering process 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 evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh condensate was carried out as a simple one-step distillation to vapour temperatures of 150°C, 200°C and 250°C, which resulted in condensate 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 flash point 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	Drop shape analysis system DSA100, KRUSS GmbH

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 (nC₅-nC₄₀) 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 (C₀-C₄) 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 nC₅-nC₁₀ 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.

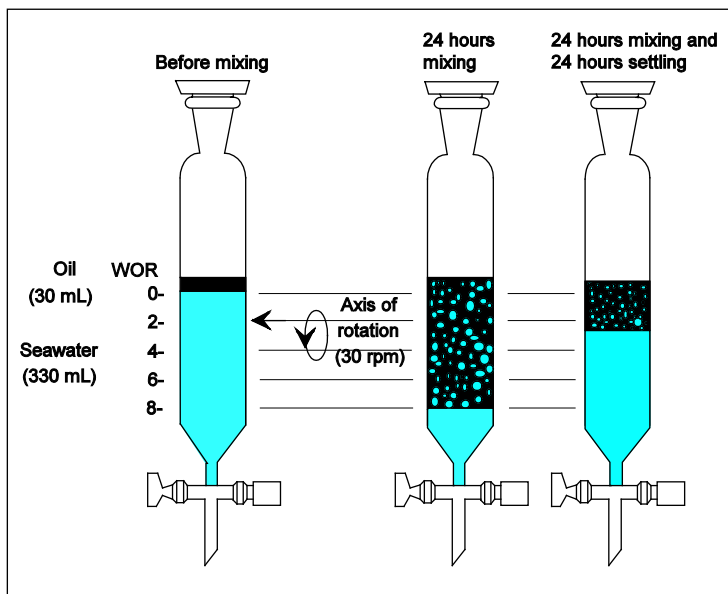


Figure B 3: Principle of the rotating cylinder method

B.2.3.1 Calculation of Emulsion Stability

The stabilities of the created emulsions and the effect of demulsifier were calculated using the following formulas.

Formation and properties of water-in-oil emulsions

- $t_{1/2}$ Express relative rate of water-in-oil emulsification ability of an oil, i.e. the time needed for picking up half the maximum water content (in vol. %)
- WOR Volumetric water to oil ratio in the emulsion
- WOR_{max} Maximum volumetric relation of water to oil in the emulsion after a rotating time of 24 hours.

Stability of water-in-oil emulsions:

An emulsion is defined to be totally stable if no water is separated during a 24 hours settling period (no dehydration). The stability is thus expressed through the volumetric dehydration (D_{24h} , definition below) of the emulsion.

Breaking of water-in-oil emulsions by the use of demulsifiers:

WOR	Volumetric water to oil ratio in the emulsion
WOR _{ref}	Volumetric water to oil ratio in the emulsion after 24 hours rotation
WOR _{im}	Water to oil ratio in the emulsion "immediately" (i.e. 5 min. soaking + 5 min. mixing + 2 min settling) after treatment with emulsion breaker
WOR ₂₄	Water to oil ratio in the emulsion after 24 hours of rotation + 24 hours of settling + 10 revolutions

D: fractional dehydration of emulsion:
$$D = \frac{WOR_{ref} - WOR_x}{WOR_{ref}}$$

where x means either im or $24h$

$D = 1$ means a totally unstable, or broken, emulsion

$D = 0$ means a totally stable emulsion

D_{im}	Dehydration obtained immediately (after 5 min. soaking + 5 min. mixing + 2 min. settling) after treatment with emulsion breaker
D_{24h}	Dehydration obtained after treatment with emulsion breaker and a 24 hour settling period.

B.2.4 Chemical dispersibility testing

As a screening test, the oils dispersibility properties were tested using different dispersants at a dosage of 1:25 (4 wt. %). For the dispersant showing greatest dispersibility, the optimal dosage and the time window for use of dispersants were surveyed. The screening and dosage tests were performed using the IFP method. In the systematic testing of all residues and emulsions, to establish the "time window" for effective dispersant use, both the IFP and the MNS tests were used. The viscosity of all the weathered samples was determined.

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

IFP (Institute Francais du Petrole test, Bocard *et al.*, 1984) is a low energy test estimated to represent low wave energies (2-5 m/s wind speed). A ring beating up and down in the test vessel at a given frequency, gives energy input to the seawater column. The water column is continuously diluted, which gives a more realistic approach to field conditions, compared to other tests. The test apparatus is shown in Figure B 4.

MNS (Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea-state condition. The energy input in this system, applied by streaming air across the oil/water surface, produces a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min. The test apparatus is shown in Figure B 4.

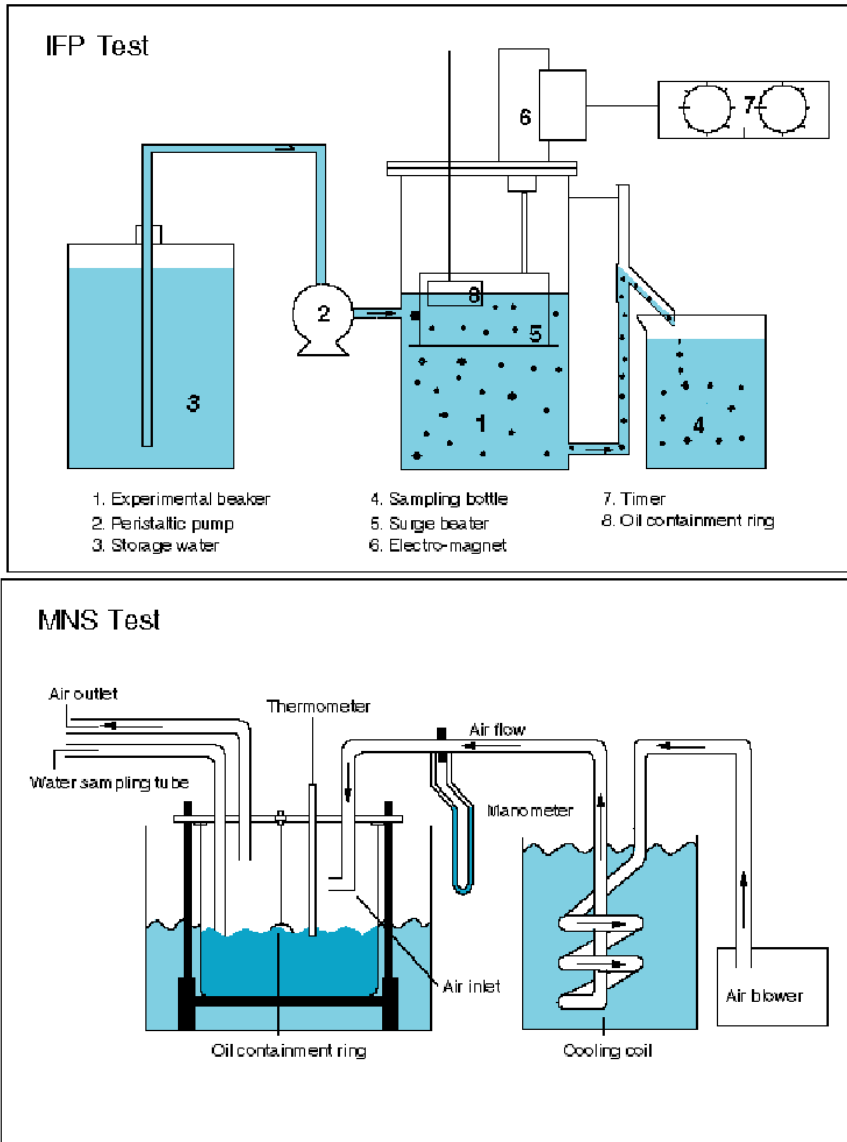


Figure B 4: IFP and MNS test apparatus

B.3 Meso-scale laboratory testing

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. It is therefore very important to weather the oils under realistic conditions when studying their behaviour when spilled on the sea surface.

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. A flume with an updated instrumentation was built in 2006, with a schematic drawing of the flume given in Figure B 5.

Approximately 5 m³ seawater circulates in the 10-metre-long flume. The flume basin is located in a temperature controlled room (0°C-20°C), and two fans placed in a covered wind tunnel control 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.

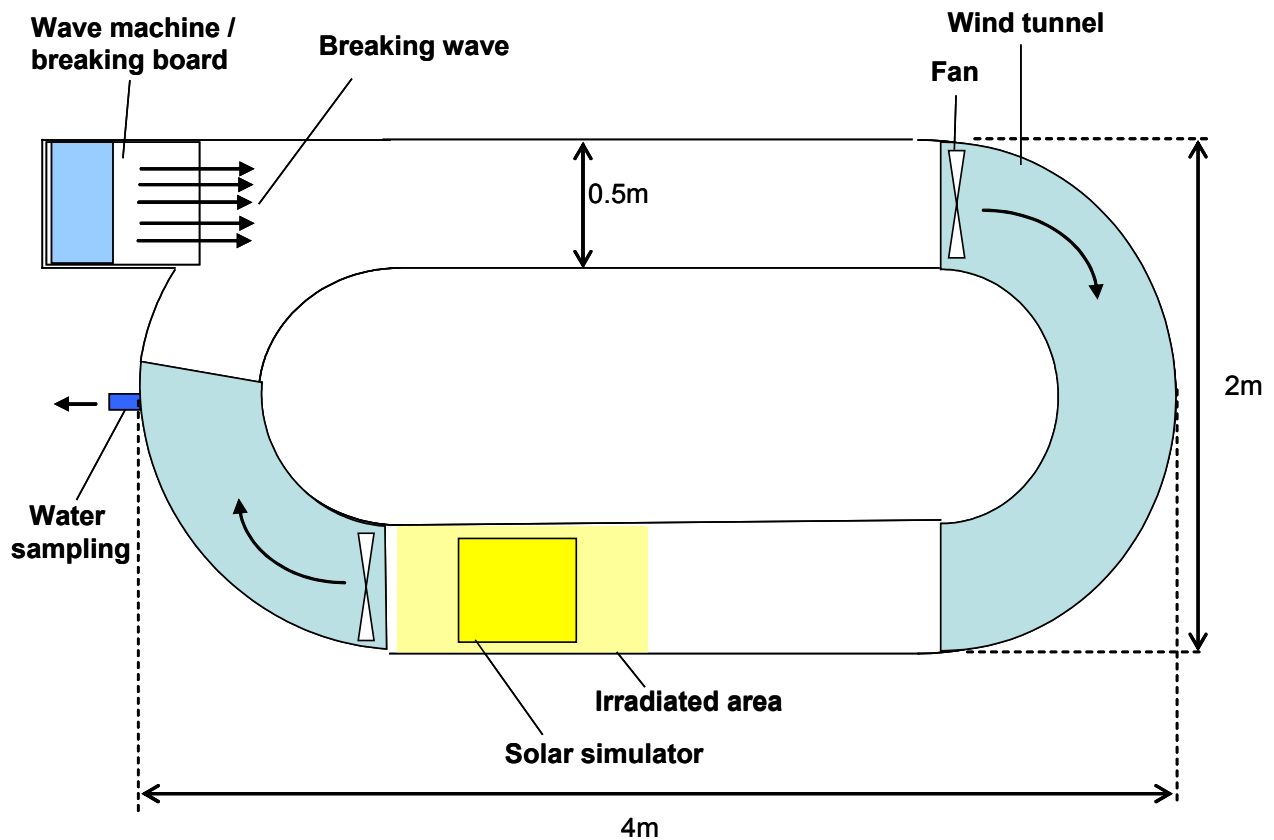


Figure B 5: Schematic drawing of the meso-scale flume

B.3.2 Oil weathering in the flume basin

The oil sample (9 L) is carefully released on the seawater surface. The oil was weathered for 3 days in the flume. Samples of the surface oil were taken frequently in the first hours of the experiment and then only once a day. Dispersant was applied to the weathered oil *in-situ* on Day 3 of the experiment. Water samples were taken a few times during the weathering part of the experiment, and at a higher frequency after the dispersant application

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

- Evaporative loss
- Density
- Water content
- Viscosity

Analysis was performed on a limited amount of samples for:

- Emulsion stability
- Oil concentration in the water column (droplets and dissolved components)

Samples of surface oil/emulsion

Samples of the surface oil/emulsion were taken using an aluminum tray and transferred to a 0.5 L separating funnel. The free water was removed after settling for 10 minutes in the climate room. The oil phase was further handled for an analysis of viscosity, water content of emulsion and density.

Analytical methods for surface oil/emulsion

The methods used to determine the physical properties of the surface oil/emulsion are listed in **Table B 3**.

Table B 3: Methods used to determine the physical properties of the surface oil/emulsion

Physical property	Analytical method	Instrument	Comments
Viscosity	McDonagh and Hokstad, 1995	Physica MCR 300	-
Water content	Adding approximately 2000 ppm emulsion breaker (Alcopol 2000) to the sample and heating the vial. As the emulsion broke, the water height and the total height were measured.	Sample vials	The relative amount of water compared to the total sample volume was calculated.
Density	ASTM method D4052-81	Anton Paar, DMA 4500	Measured on water-free samples (after removal of the water with emulsion breaker and heat).
Evaporative loss	The density of the oil depends linearly on the vol. % of evaporative loss.	-	The evaporative loss was calculated based on the density.

Collection of water samples

Water samples were taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water was acidified with some droplets of 10 % HCl (pH < 2), and the sampling position is shown in Figure B 5. Samples were extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultra Violet (UV) spectrophotometer.

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 when there are no clouds in the sky. Figure B 6 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).

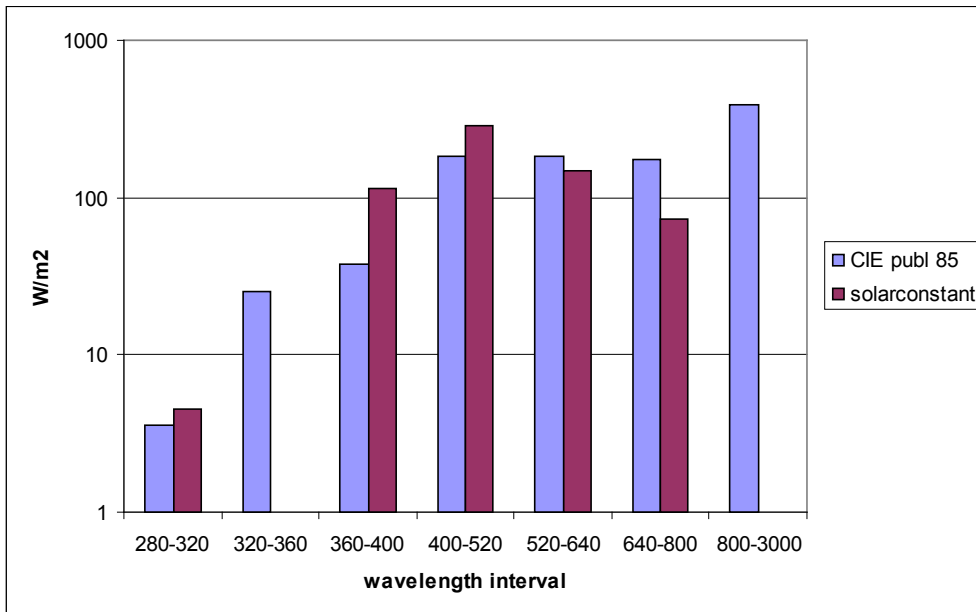


Figure B 6: Measured wavelength compared to standard spectrum suggested in CIE publication 85

The exact exposure of 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 surface. An estimated irradiation pr. day is compared with the average irradiation pr. day for some Norwegian cities in Figure B 7.

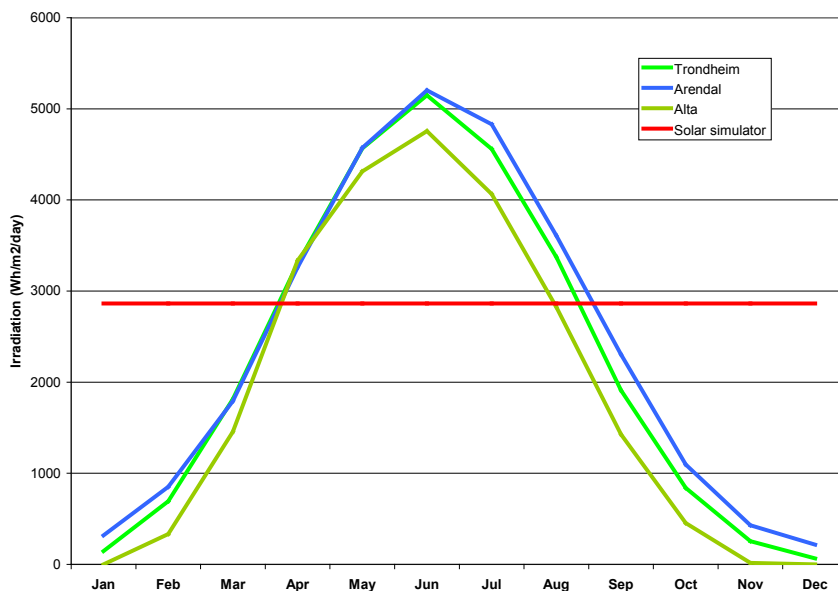


Figure B 7: Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume ([irradiation calculator](#))

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 taking clouds into consideration. The real irradiation will be lower than that predicted in Figure B 7.

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input in to the SINTEF OWM for Luno II crude oil are given in Table C1. The predictions were based on 13 °C study as predictions performed with 5 °C laboratory data harmonized well with the predictions performed with 13 °C laboratory data.

Table C 1: Physical and chemical properties for Luno II at 13 °C, used as input in the oil weathering model

Properties of fresh oil	Value
Specific Gravity (60 F/15.5 °C)	0.851
Pour point (°C)	-27
Reference temperature (°C)	13
Viscosity at ref. temp. (mPas = cP) *	11
Asphaltenes (wt. %)	0.49
Flash Point (°C)	-
Wax Content (wt. %)	2.67
Dispersable for visc. <	3000
Not dispersable for visc. >	25000

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

- No data available

Table C 2: True boiling point (TBP) curve for Luno II based on received distillation data adjusted to distillation data obtained in the present study. The True Boiling Point (TBP) is based on Crude Assay; Saybalt report nr 12002/00016046/13.

Temperature (°C)	Volume (%)
65	7.3
90	12.0
150	27.3
180	33.4
240	42.9
320	57.1
375	64.9
475	76.5
525	81.1

Table C 3: Lab weathering data for Luno II Crude oil, 13 °C

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	193	243	301
Vol. topped (%)	0	25	26	45
Weight Residue (wt. %)	100	79	69	61
Specific Gravity (g/ml)	0.851	0.898	0.915	0.931
Pour point (°C)	-27	6	12	18
Flash Point (°C)	-	31.5	69	108
*Viscosity of water-free residue (mPas =cP),	11	99	569	3165
*Viscosity of 50 % emulsion (mPas = cP)	-	529	1904	9615
*Viscosity of 75 % emulsion (mPas = cP)	-	2105	6227	-
*Viscosity of max water (mPas = cP)	-	20155	23888	24632

Max. water cont. (vol. %)	-	83	80	71
(T _{1/2}) Halftime for water uptake (hrs)	-	0.14	0.29	0.93
Stability ratio	-	0.98	1	1

* Measured at shear rate 10 s⁻¹

- No data

D Chemical characterisation of the fresh oil on GC/MS

Table D 1: The chemical composition based on GC/MS analysis of the fresh Luno II crude oil

Group no.	Chemical Composition	Luno II wt. %
1	C1-C4 gasses (dissolved in oil)	3.000
2	C5-saturates (n-/iso-/cyclo)	3.000
3	C6-saturates (n-/iso-/cyclo)	2.727
4	Benzene	0.273
5	C7-saturates (n-/iso-/cyclo)	4.000
6	C1-Benzene (Toluene) et. B	1.013
7	C8-saturates (n-/iso-/cyclo)	7.987
8	C2-Benzene (xylenes; using O-xylene)	2.081
9	C9-saturates (n-/iso-/cyclo)	2.543
10	C3-Benzene	1.376
11	C10-saturates (n-/iso-/cyclo)	4.000
12	C4 and C5 Benzenes	0.135
13	C11-C12 (total sat + aro)	3.865
14	Phenols (C0-C4 alkylated)	0.000
15	Naphthalenes 1 (C0-C1-alkylated)	0.221
16	C13-C14 (total sat + aro)	6.779
17	Unresolved Chromatographic Materials (UCM: C10 to C36)	0.000
37	metabolite 1	0.000
38	metabolite 2	0.000
18	Naphthalenes 2 (C2-C3-alkylated)	0.399
19	C15-C16 (total sat + aro)	4.601
20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkylated; <4 rings)	0.233
21	C17-C18 (total sat + aro)	4.767
22	C19-C20 (total sat + aro)	5.000
23	C21-C25 (total sat + aro)	6.780
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.220
25	C25+ (total)	35.00

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 25 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.



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