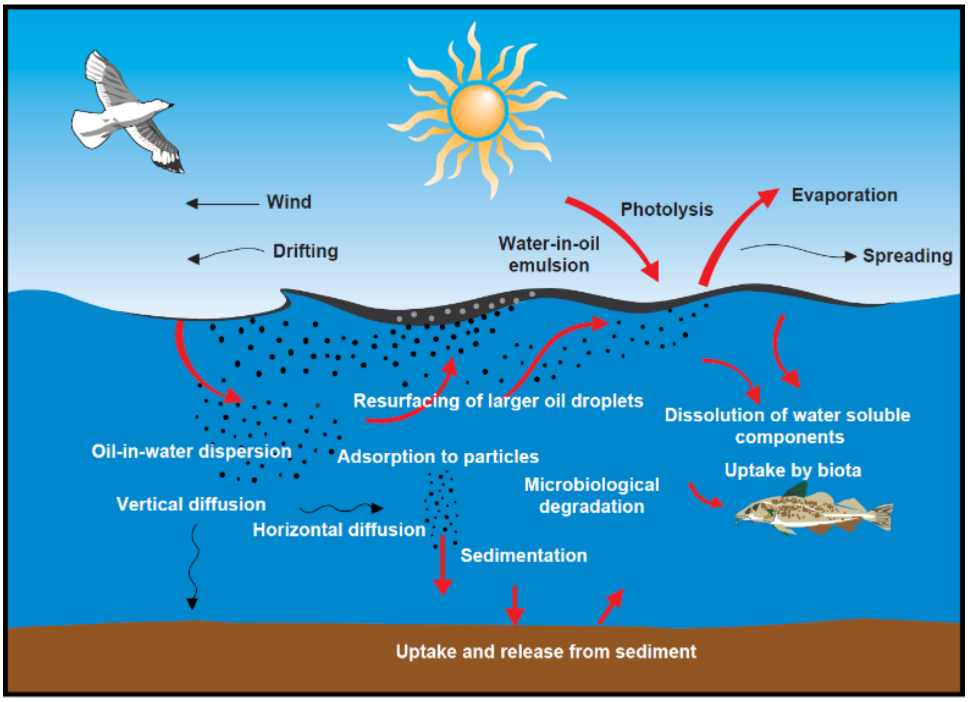
Report

Dugong – Weathering properties and behaviour at sea

In relation to oil spill response

Author(s)
Kristin Rist Sørheim
Oddveig M. Bakken, Thor-Arne Pettersen



SINTEF Ocean AS

2022-08-23

SINTEF Ocean AS
Address:
Postboks 4762 Torgarden
NO-7465 Trondheim
NORWAY
Switchboard: +47 46415000

Enterprise /VAT No:
NO 937 357 370 MVA

Report

Dugong – Weathering properties and behaviour at sea

In relation to oil spill response

REPORT NO.
OC2022 A-083

PROJECT NO.
302006649

VERSION
1.0

DATE
2022-08-23

KEYWORDS:
Dugong crude oil
Weathering properties
Oil spill response

AUTHOR(S)
Kristin Rist Sørheim
Oddveig M. Bakken, Thor-Arne Pettersen

CLIENT(S)
Neptune Energy

CLIENT'S REF.
Kari Large

NUMBER OF PAGES/APPENDICES:
81 incl. 4 Appendices

CLASSIFICATION
Open

CLASSIFICATION THIS PAGE
Open

ISBN
978-82-7174-443-4

ABSTRACT

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

PREPARED BY
Kristin Rist Sørheim
Kristin R. sørheim
Kristin R. sørheim (Aug 23, 2022 15:34 GMT+2)

CHECKED BY
Per S. Daling
Per S. Daling
Per S. Daling (Aug 23, 2022 14:31 GMT+2)

APPROVED BY
Tore Aunaas
Tore Aunaas (Aug 23, 2022 14:41 GMT+2)

Document History

VERSION	DATE	VERSION DESCRIPTION
0.1	2022-08-11	Draft version for review
1.0	2022-08-23	Final version

Table of Contents

1 Executive summary ... 6

2 Introduction ... 8

3 Small-scale laboratory testing of Dugong ... 9
3.1 Gas chromatographic (GC-FID) characterization ... 9
3.2 Asphaltenes and wax content ... 12
3.3 Physical properties of the fresh and weathered residues ... 13
3.4 Emulsifying properties ... 15
3.4.1 Emulsification ... 15
3.4.2 Kinetics of water uptake ... 16
3.4.3 Efficiency of emulsion breaker and stability of emulsions ... 16
3.5 Emulsion viscosities and yield stress ... 17
3.6 Chemical dispersibility ... 18
3.6.1 Screening testing of dispersants ... 18
3.6.2 Dosage testing ... 19
3.6.3 Systematic dispersant testing and dispersibility limits ... 20

4 Meso-scale laboratory testing of Dugong ... 22
4.1 Flume weathering data vs. predictions ... 22
4.2 Mass balances ... 24
4.3 *In-situ* chemical dispersion ... 25
4.4 Observations from flume the experiment ... 26
4.5 Remarks from the meso-scale flume testing of Dugong ... 29

5 Predictions with SINTEF Oil Weathering Model (OWM) ... 30
5.1 Description of SINTEF OWM ... 30
5.2 Predictions of weathering properties of Dugong ... 31

6 Comparison of OWM predictions ... 42
6.1 Evaporative loss ... 42
6.2 Pour point ... 43
6.3 Water uptake ... 44
6.4 Emulsion viscosity ... 45
6.5 Surface oil and emulsion ... 46

7 Weathering properties and response of Dugong (surface release) ... 47
7.1 Oil properties ... 47
7.2 Flash point – Fire/explosion hazard ... 47
7.3 Solidification ... 48

7.4 Emulsion formation ... 49
7.5 Entrained oil and evaporation ... 50
7.6 Film thickness from surface release ... 50
7.6 Mechanical recovery by boom and skimmer ... 51
7.7 Mechanical dispersion by high-capacity water flushing ... 53
7.8 Chemical dispersion ... 53

8 Summary of response options of Dugong ... 55

9 Comparison of Dugong to other Norwegian crude oils and condensates ... 56

10 References ... 58

A The behaviour of oil on the sea surface ... 60
A.1 The chemical composition of crude oils and condensates ... 60
A.2 Main oil categories related to weathering ... 61
A.3 Physical properties of crude oils ... 61
A.3.1 Rheological properties ... 62
A.3.2 Pour point ... 63
A.3.3 Distillation curve ... 63
A.3.4 Flash point ... 63
A.4 The behaviour of crude oil spilled at sea ... 64
A.4.1 Evaporation ... 65
A.4.2 Spreading ... 65
A.4.3 Drift of an oil slick ... 66
A.4.4 Water-in-oil (w/o) emulsion ... 67
A.4.5 Oil-in-water (o/w) dispersion ... 69
A.4.6 Water solubility ... 69
A.4.7 Photo-oxidation ... 69
A.4.8 Biodegradation ... 69
A.4.9 Sedimentation ... 70
A.4.10 Deep water releases ... 70
A.4.11 Shallow releases ... 72

B Experimental setup and HSE ... 74
B.1 Oil sample and test temperature ... 74
B.2 HSE - Water content and Mercury analysis ... 74
B.3 Small-scale laboratory testing ... 75
B.4 Evaporation ... 75
B.5 Physical and chemical analysis ... 75
B.6 Emulsification properties ... 76
B.7 Chemical dispersibility testing ... 76
B.8 Meso-scale laboratory testing ... 77

C Input data to SINTEF Oil Weathering Model (OWM) 80

D Chemical characterization – OSCAR composition file 81

1 Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill preparedness. Oil weathering varies over time and with different environmental conditions. The lifetime of an oil spill at sea depends on the oil's properties, emulsification, release scenario, and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that reduced oil volumes of oil spills from the sea surface. Based on input from the experimental weathering data of the Dugong oil, the SINTEF Oil Weathering Model (OWM) has been used to predict the properties of oil as it weathered over time. This summary gives a brief overview of the main changes predicted for Dugong crude oil when weathered on the sea surface.

Compared to many other Norwegian crude oils, this weathering study of Dugong shows the following properties relevant for the behaviour if spilled at sea with film thickness that is sufficient high to emulsify, i.e., typically higher than 0.1 mm.

- Dugong is a medium paraffinic crude oil with a density of 0.833 g/mL with a volatile loss of 43 vol.% for the 250°C+ residue that cause a moderate degree of evaporation. For example, after 12 hours, the evaporative loss is in the range of 34-37% at 10 m/s wind speed.
- The combination of wax content (5.1wt.%), asphaltenes (0.33 wt.%) and density, Dugong forms stable water-in-oil emulsions with high water uptake of ~80 vol. % in winter and summer conditions.
- The emulsion formed are expected to have a high persistency on the sea surface, e.g., the predictions indicate a lifetime of 2-3 days at 15 m/s wind speed. In calmer weather conditions the lifetime is predicted to be >5 days.
- As much as 70-75 % of the oil can still remain on the sea surface in very calm weather conditions (2 m/s wind speed) after 5 days.
- The overall volume of the spilled oil can increase 2-2.5 times relative to the volume due to emulsification.
- The residue at sea may form semi-solid lumps/materials particularly in calm sea conditions (< 2-5 m/s wind speeds) due to the high pour points of +18 and +27 °C for the 150 and 250°C+ residues, expecting to be less pronounced in summer conditions than in colder seawater temperatures.

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

The flash points for Dugong are expected to surpass the sea temperature within a few minutes at 5 and 15 °C, at wind speeds of 5-15 m/s, and within 0.5-1 hours at 2 m/s, predicted with the standardized surface release (80 m^3/ h). However, for larger surface release rates, e.g., spill from a blowout, pipeline rupture, or incident due to tanker loading, the time for the flash point to exceed the sea temperature can be extended. Moreover, some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Dugong reaches this limit (60 °C) in 6 hours after a spill at calm wind speed (2 m/s) at summer and 12 hours in winter conditions respective, and more rapidly at higher wind speeds. However, this limit is not considered as relevant for oil recovery vessels with A class certification for transport of liquids (Class I/II, flash point <60 °C).

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

Effect of adding emulsion breaker:
The emulsions of Dugong were stable but released about 95-100% incorporated water for the 150°C+ residue when adding concentrations (500 and 2000 ppm by weight) of the emulsion breaker (Aerosol OT-SE

surfactant). The highest concentration (2000 ppm) was shown to be more effective than 500 ppm, particularity for the higher residues of 200 and 250°C+. Use of emulsion breaker may therefore effectively be used during an oil spill operation to remove or reduce water from the recovered oil/emulsion which minimizes the storage volume. Emulsion breakers are normally injected at the skimmer head prior to transferring the collected oil/water to storage tanks.

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

Mechanical recovery :
The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous emulsions (lower than 1000 mPa.s) compared to emulsions that are more viscous. Boom leakage is also influenced by other factors such as operational speed and weather conditions. This study shows that the emulsion viscosities of Dugong surpassed 1000 mPa.s about 1.5-2 hours at 10 m/s wind speed at 5 and 15 °C, but the time may be stretched up to about 1-day for very low wind speed (2 m/s). Moreover, viscosities larger than 20 000 mPa.s are known to reduce the flowability of the oil/emulsion when using traditional weir skimmers. Dugong has predicted emulsion viscosities lower than this limit within 3-5 days weathering at summer and winter conditions. Overall, Dugong is expected to have a wide window of opportunity for use of traditional weir-skimmer head.

Chemical dispersion (viscosity limits):
Dugong is expected to have a good potential for chemical dispersion with use of Dasic Slickgone NS (DOR; dispersant-to-oil ratio 1:25) for viscosities <3000 mPa.s based on the low-energy test (IFP), and poorly dispersible for viscosities >18 000 mPa.s based on the high-energy test (MNS). In the field, if the oil is reduced dispersible, additional energy e.g., thrusters, Fire Fighting (Fi-Fi) systems, higher DOR by repeated dispersant application may increase the efficacy of the dispersant treatment.

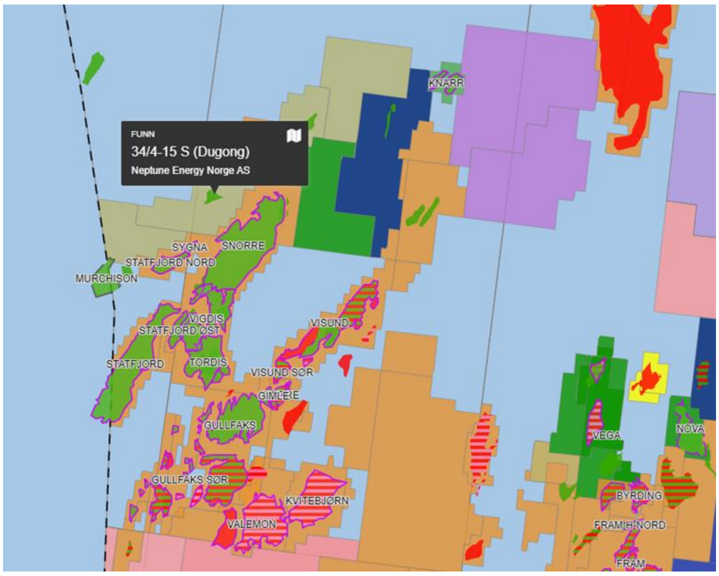
High-capacity water flushing (mechanical dispersion):
The oil emulsion viscosity and oil film thickness are the limiting factors for this strategy. The predicted film thicknesses are >0.2-0.3 mm which is the estimated upper limit for effective use of water flushing. Water flushing should therefore not be a main response option for Dugong but could be a supplementary method if there are areas on the sea surface with thin oil films e.g., metallic /rainbow appearance in very calm weather conditions.

Monitoring and remote sensing: Monitoring and remote sensing should always be used a support in a response operations for Dugong.

2 Introduction

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

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



34/4-15 S (Dugong) is a discovery in the northern North Sea, 10 kilometres northwest of the Snorre field. Licence PL882.

The water depth is 332 metres.

The discovery was proven in 2020 and delineated by well 34/4-16 S in 2021.

The reservoir contains oil in Middle Jurassic sandstone in the Rannoch Formation at a depth of 3,280 metres.

Development solutions are under evaluation. The plan for development and operation (PDO) is expected early 2024.

Figure 2-1 https://www.norskpetroleum.no/en/facts/discoveries/34-4-15-s/

3 Small-scale laboratory testing of Dugong

Description of the oil sample of Dugong for testing and the experimental setup for the small-scale and meso-scale weathering, and dispersibility methods are described in Appendix B. Physico-chemical parameters and weathering properties of Dugong are also compared with previous weathering studies of Duva, Nova (former Skarfjell), and Gjøa, in addition to Sygna Brent (Statfjord) and Snorre TLP from the neighbouring fields at the Tampen area. The crude oils for comparison were selected in agreement with Neptune Energy (Table 3-1).

Table 3-1 Crude oils compared with Dugong (SINTEF Id 2022-185) in this report.

Oil name	SINTEF Id	SINTEF report no	Reference
Duva	2022-4882	OC2021 A-108	Sørheim et al. 2021
Nova (aka Skarfjell)	2013-0595	A26006	Ramstad el al. 2014*
Gjøa	2010-0504	A20859	Sørheim et al. 2011
Sygna Brent (Statfjord)	2020-8434	OC2021 A-090	Sørheim and Hellstrøm, 2021
Snorre TLP**	2002-0067	STF66 F04041	Resby, 2004

**Refers to the Skarfjell weathering report. Skarfjell is denoted as Nova in this report. ** Snorre TLP is similar as Snorre A.*

3.1 Gas chromatographic (GC-FID) characterization

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

The gas chromatograms show the *n*-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, are shown as a broad and poorly defined bump below the sharp peaks and are often described as the "Unresolved Complex Mixture" (UCM). Heavier compounds such as asphaltenes (> $n\text{C}_{40}$) are not possible to analyze with this technique.

Dugong is a paraffinic crude oil with a main range of n-alkanes from nC_5 to nC_{30} (Figure 3-1). Figure 3-2 shows the GC/FID profile of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP. Based on hydrocarbon profiles, all the oils for comparison are typically paraffinic crudes. However, Gjøa has a characteristic feature where the pristane peak is higher than the $n\text{C}_{17}$ peak (Table 3-2), which is typically for naphtenic oils that have undergone a biodegradation process in the reservoir. However, the biodegradation is not very distinct compared with highly biodegraded oils that lack or have minor content of straight chained n-alkanes.

Moreover, GC/FID is an important tool for oil characterization 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 $n\text{C}_{17}$/Pristane and $n\text{C}_{18}$/Phytane ratios. Table 3-2 shows the ratios of Dugong in comparison the other oils.

*Table 3-2 $n\text{C}_{17}$/Pristane and $n\text{C}_{18}$/Phytane ratios**

Oil name	$n\text{C}_{17}$/Pristane	$n\text{C}_{18}$/Phytane
Dugong	1.6	2.3
Duva	2.2	4.0
Nova	1.6	3.2
Gjøa	0.9	1.4
Sygna Brent	1.4	1.9
Snorre TLP	1.5	1.9

**Ratios >1 typical for paraffinic oils, ratios <1 typical for biodegraded oils.*

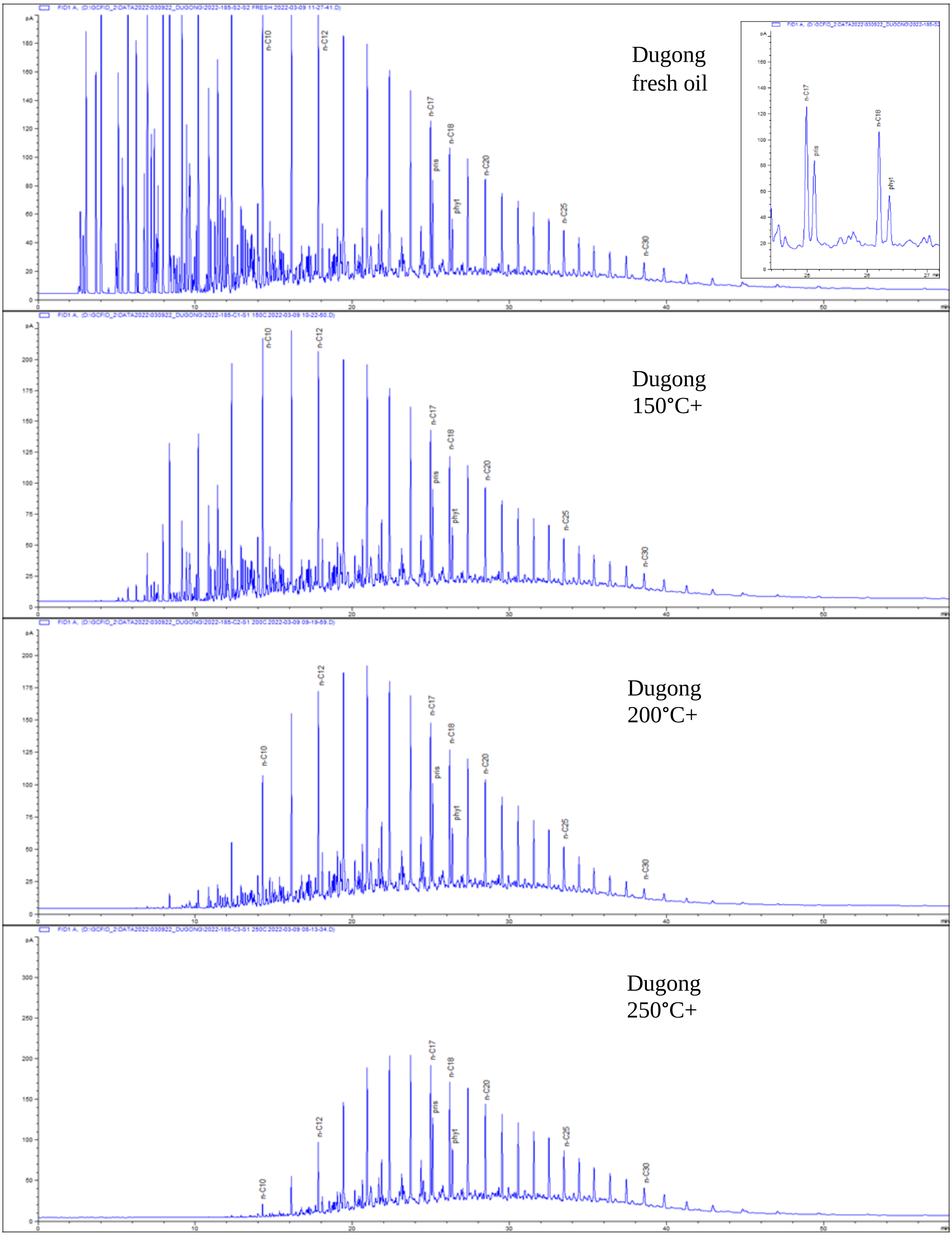
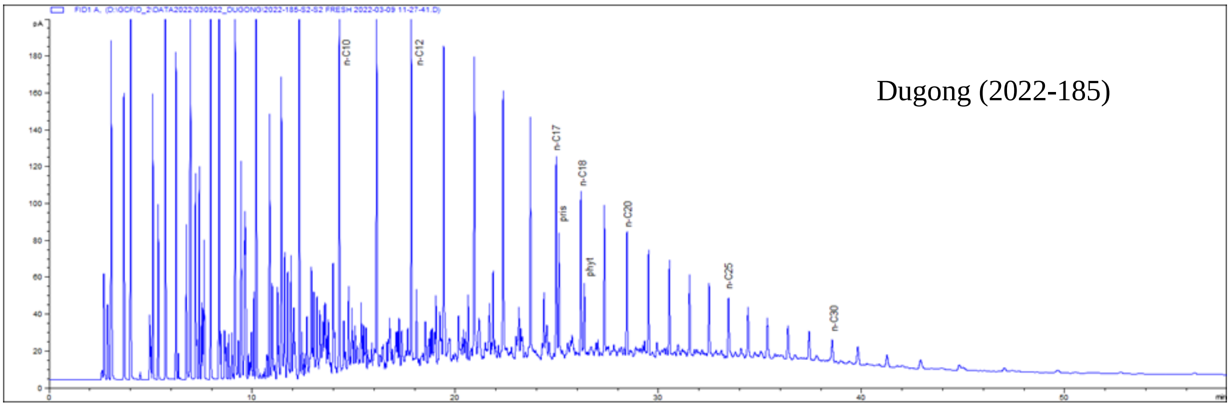
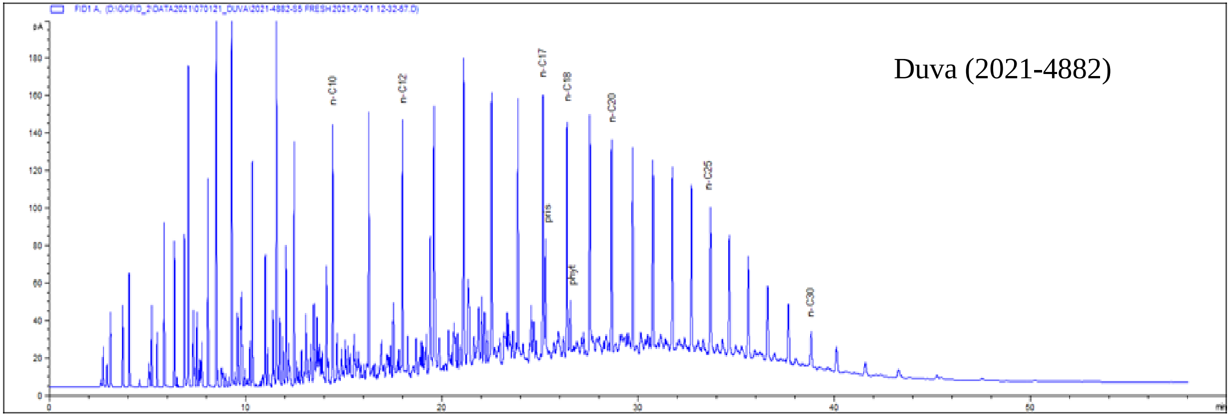
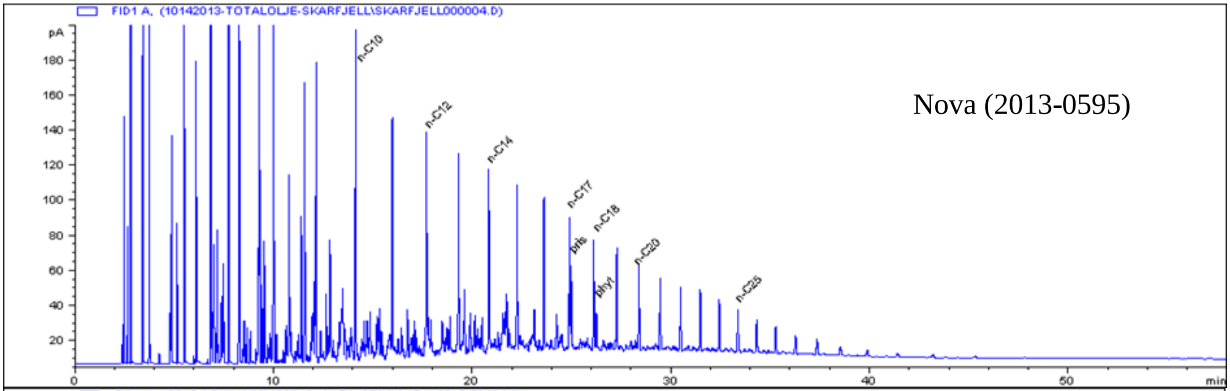
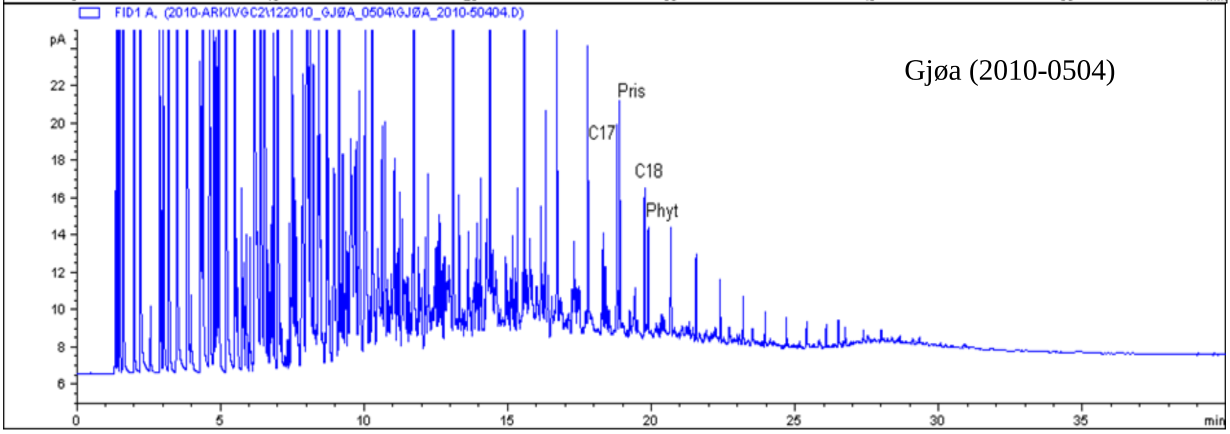


Figure 3-1 GC-FID chromatograms of fresh oil and evaporated residues of Dugong.


FID1 A, (D:\GCFID_2\DATA2022\030922_DUGONG\2022-185-S2-S2 FRESH 2022-03-09 11-27-41.D)
Dugong (2022-185)
pA
0
20
40
60
80
100
120
140
160
180
n-C10
n-C12
n-C17
pris
n-C18
phyt
n-C20
n-C25
n-C30
0
10
20
30
40
50
min


FID1 A, (D:\GCFID_2\DATA2021\070121_DUVA\2021-4882-S5 FRESH 2021-07-01 12-32-57.D)
Duva (2021-4882)
pA
0
20
40
60
80
100
120
140
160
180
n-C10
n-C12
n-C17
pris
n-C18
phyt
n-C20
n-C25
n-C30
0
10
20
30
40
50
min


FID1 A, (10142013-TOTALOLJE-SKARFJELL\SKARFJELL000004.D)
Nova (2013-0595)
pA
20
40
60
80
100
120
140
160
180
n-C10
n-C12
n-C14
n-C17
pris
n-C18
phyt
n-C20
n-C25
0
10
20
30
40
50
min


FID1 A, (2010-ARKIV\GC2\122010_GJØA_0504\GJØA_2010-50404.D)
Gjøa (2010-0504)
pA
6
8
10
12
14
16
18
20
22
Pris
C17
C18
Phyt
0
5
10
15
20
25
30
35
min

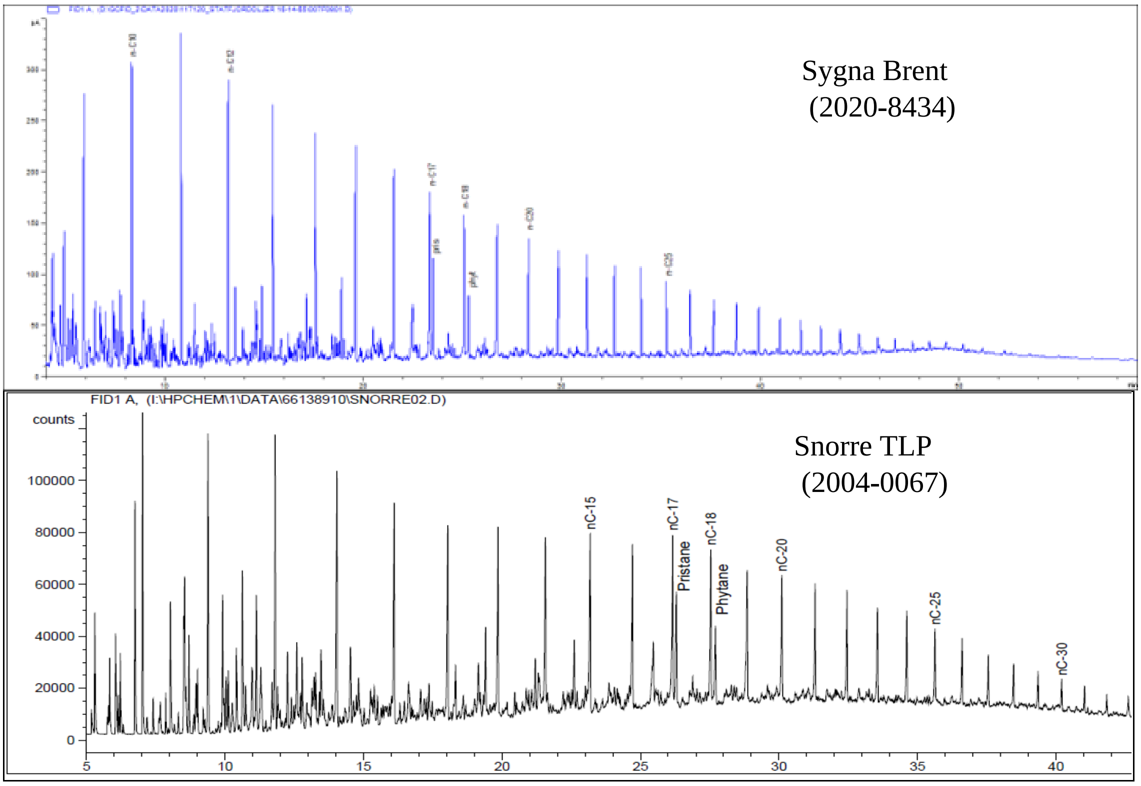


Figure 3-2 *GC-FID chromatograms for fresh oils of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP. The retention times may differ between the chromatograms due to different temperature programs (relative comparison).*

3.2 Asphaltenes and wax content

The content of asphaltenes and wax of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP are given in Table 3-3. Dugong (fresh oil) has a medium wax content of 5.1 w% and medium content of asphaltenes (0.33 wt.%) compared with many other Norwegian crude oils, and the values are most comparable with Sygna Brent and Snorre TLP from the Tampen area. Sygna Brent has a wax content of 5.3 wt.% and asphaltenes of 0.48 wt.%, whilst Snorre TLP has a wax content of 5.2 wt.% and asphaltenes of 0.28 wt.%. Nova has also a medium content of wax (4.6 wt.%) but exhibits very low content of asphaltenes (0.03 wt.%), whilst Gjøa has both low content of wax (1.5 wt.%) and asphaltenes (0.03 wt.%). Duva is as high waxy crude oil but expresses a relatively low content of asphaltenes (0.11 wt.%).

Note that the analytical method of wax precipitation has been performed with the similar method at SINTEF (Appendix B) for all oils listed in Table 3-3, and the results are therefore comparable with each other. The wax content can vary between analytical methods used and can also be dependent on the paraffinic /wax fraction of the oil, as shown for Duva.

Table 3-3 Asphaltene ("hard") and wax content of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TPL.

Oil type	Residue	Asph* (wt. %)	Wax (wt. %)
Dugong	Fresh	0.33	5.1
	150°C+	0.40	6.3
	200°C+	0.46	7.2
	250°C+	0.53	8.2
Duva	Fresh	0.11	6.8 (13.9)**
	150°C+	0.11	7.3
	200°C+	0.12	7.9
	250°C+	0.13	8.3 (18.1)**
Nova	Fresh	0.03	4.6
	150°C+	0.04	6.0
	200°C+	0.04	6.8
	250°C+	0.04	8.2
Gjøa	Fresh	0.03	1.5
	150°C+	0.03	1.9
	200°C+	0.03	2.2
	250°C+	0.03	2.6
Sygna Brent	Fresh	0.48	5.3
	150°C+	0.58	6.4
	200°C+	0.65	7.2
	250°C+	0.78	8.6
Snorre TLP	Fresh	0.28	5.2
	150°C+	0.34	6.2
	200°C+	0.39	7.2
	250°C+	0.45	8.3

**n-heptane (nC_7) precipitation*

***: The wax values in brackets are based on method UOP 46-64 Intertek Westlab*

3.3 Physical properties of the fresh and weathered residues

The physical properties of Dugong are shown in Table 3-4 in comparison with Duva, Nova, Gjøa, Sygna Brent, and Snorre TLP. The physical property of Dugong expresses overall most similarities with Snorre TLP and Sygna Brent.

The fresh Dugong has a medium density of 0.833 g/mL and is in the same range (0.824-0.843 g/mL) as the other oils in comparison, except for Duva that has a higher density of 0.868 g/mL. The evaporative loss of Dugong is 43 vol% (250°C+ residue) and is most like Sygna Brent (43 vol.%) and Snorre TLP (41 vol.%). Similar, Nova and Gjøa have the highest evaporative losses of 48 vol.% , whilst Duva exhibits the lowest of 20 vol.%.

Dugong has similar pour point (3 °C) of the fresh oil as Sygna Brent and Snorre TLP. Nova and Gjøa (fresh oils) have very low pour points of -12 °C and <-36 °C, respectively, whilst Duva expresses a very high pour point of 30 °C. The pour point increases upon evaporative loss. For 250°C+ residue the pour point of Dugong has increased to 27 °C and is in the same range as for the other oils herein, except for Gjøa that has the lowest pour point of 12 °C for the residue.

The viscosities of Dugong are most like Snorre TLP, followed by Sygna Brent. The 250°C+ residue of Dugong and Snorre TLP have viscosities of 2017 mPa.s and 1300 mPa.s (13°C), respective, whilst the same residue of Sygna Brent has a higher viscosity of 7115 mPa.s. Duva exhibits very high viscosities of the fresh oil of 6412 mPa.s and 250 °C+ residue (19968 mPa.s). Nova and Gjøa on the other hand have both low viscosities of the fresh oils at 13°C ($10s^{-1}$) of 39 and 5 mPa.s, respectively. However, Nova has an increased high viscosity of the 250°C+ residue of 15000 mPa.s, whilst Gjøa has a very low viscosity the 250°C+ residue of 98 mPa.s.

Table 3-4 Physical properties of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP.

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 13°C (10 s^{-1})	IFT (mN/m), init.5 min)
Dugong	Fresh	0	100	0.833	-	3	17	32
	150°C+	22	81	0.867	38	18	192	28
	200°C+	33	71	0.881	77	21	407	31
	250°C+	43	62	0.894	113	27	2017	30
Duva	Fresh	0	100	0.868	-	30	6412	21
	150°C+	7	94	0.876	43	30	12303	20
	200°C+	16	86	0.883	91	33	12437	17
	250°C+	20	82	0.886	110	33	19968	19
Nova	Fresh	0	100	0.824	-	-12	39	23[1)]
	150°C+	27	77	0.862	37	15	780	21
	200°C+	36	68	0.874	68	21	2300	21
	250°C+	48	56	0.883	110	27	15000	23
Gjøa	Fresh	0	100	0.836	-	<-36	5	-
	150°C+	25	78	0.866	40	-24	14	-
	200°C+	36	68	0.879	75	3	34	-
	250°C+	48	56	0.892	112	12	98	-
Sygna Brent	Fresh	0	100	0.843	0	3	45	-
	150°C+	20	83	0.873	43	21	518	-
	200°C+	30	74	0.887	79	24	1409	-
	250°C+	43	62	0.903	123	27	7115	-
Snorre TLP	Fresh	0	100	0.834	-	3	8	19[2)]
	150°C+	19	83	0.865	30	15	26	20
	200°C+	32	72	0.882	74	24	110	22
	250°C+	41	62	0.894	110	30	1300	23

-:No data

[1)] *Measured by spinning drop method at 30 °C*

[2)] *Measured with ASTM-method 971-82 (Du Noüy ring method)*

The True Boiling Point curves (TBP) of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP are shown in Figure 3-3. Dugong, Sygna Brent and Snorre TLP have very similar boiling point curves. The TBPs reflect the evaporative loss of the 150, 200 and 250°C+ residues (Table 3-4), indicating evaporative loss at sea.

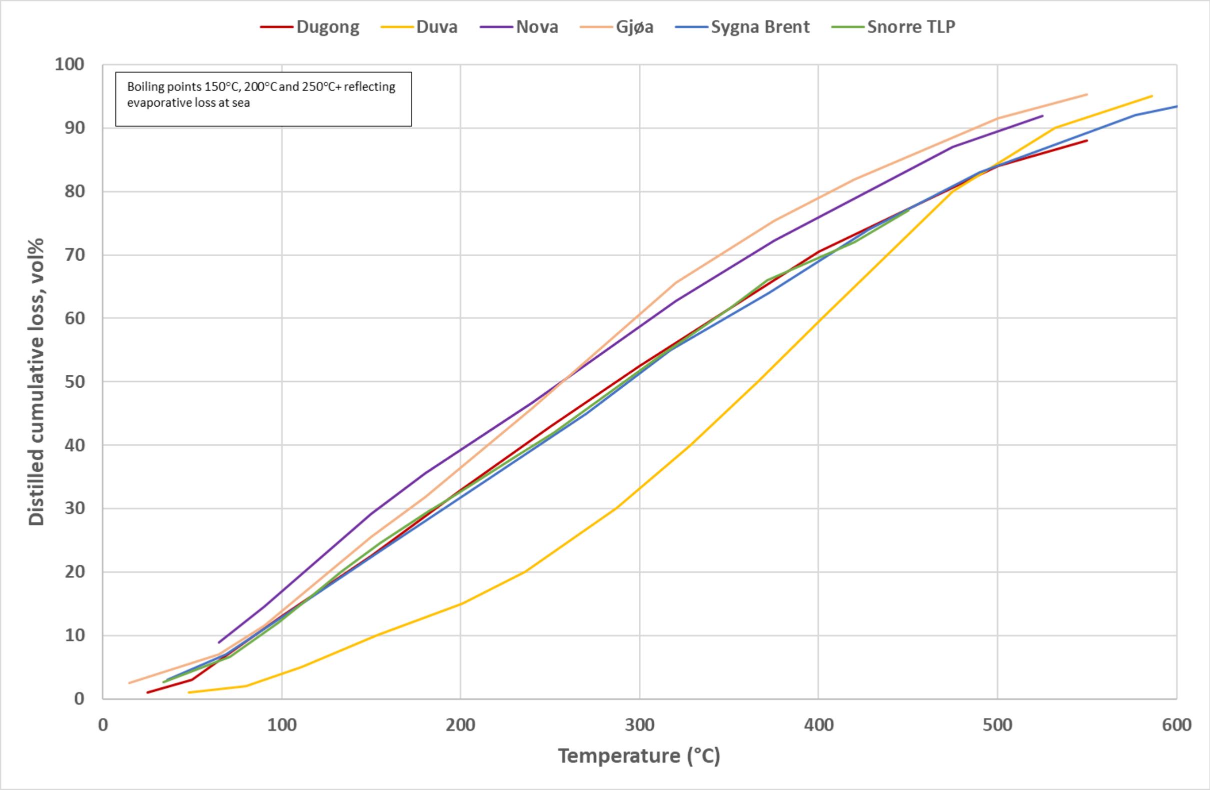


Figure 3-3 TBP of Dugong in comparison with Duva, Nova, Gjøa, Sygna Brent and Snorre TLP.

3.4 Emulsifying properties

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

3.4.1 Emulsification

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

Figure 3-4 Rotating cylinders of water-in-oil (w/o) emulsions of Dugong after 24 hours at 13 °C.

3.4.2 Kinetics of water uptake

The rate (kinetics) of water content in the water-in-oil (w/o) emulsions as a function of time is tabulated in Table 3-5. The $t_{1/2}$ values are defined as the time (hours) it takes to incorporate half of the maximum water uptake (vol. %) in 24 hours (rotating time).

Table 3-5 Kinetics ($t_{1/2}$) for the emulsified residues of Dugong at 13 °C.

Mixing time	**150°C+ * (vol. % water)**	**200°C+ * (vol. % water)**	**250°C+ * (vol. % water)**
Start	0	0	0
5 min	41	21	11
10 min	55	38	15
15 min	62	46	24
30 min	71	59	52
1 hour	91**	85	80
2 hours	91**	85	80
4 hours	91**	85	80
6 hours	91**	85	80
24 hours	91**	85	78
$t_{½}$	**0.14**	**0.23**	**0.34**

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

*** 91 vol. % is due to supersaturation of emulsion and will likely not occur at sea.*

3.4.3 Efficiency of emulsion breaker and stability of emulsions

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

The results show that the emulsified oil volume decreased after treatment with the emulsion breaker, as water was released from the emulsion as shown in Table 3-6 at 13 °C. Overall, adding 2000 ppm (0.2 wt.%) of the emulsion breaker relative to the oil was shown to be more efficient (86-100%) to break the emulsion compared with a lower concentration of 500 ppm, particularly for the 200 and 250°C+ emulsions (< 50% effectiveness).

The emulsion stability was studied by quantifying the amount of volume fraction of water released from the emulsion after 24 hours settling time. Overall, Dugong formed stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first main row of and Table 3-6. The emulsions released only a small amount of water after settling time, with stability ratios in the range of 0.98-1.00.

Table 3-6 Stability of emulsion and the effectiveness of emulsion breaker at 13 °C of Dugong.

Residue Dugong	Emulsion breaker	Water-in-oil emulsion (vol. %) at 13 °C		Stability ratio**	% Effect. (released water)
		Reference	24 hours settling *		
150ºC+	None	91	91	0.98	2
200ºC+	None	85	83	0.99	1
250ºC+	None	78	78	1.00	0
150ºC+	Aerosol OT-SE 500 ppm	91	33	0.05	95
200ºC+	Aerosol OT-SE 500 ppm	85	74	0.50	50
250ºC+	Aerosol OT-SE 500 ppm	78	75	0.84	16
150ºC+	Aerosol OT-SE 2000 ppm	91	0	0.00	100
200ºC+	Aerosol OT-SE 2000 ppm	85	19	0.04	96
250ºC+	Aerosol OT-SE 2000 ppm	78	33	0.14	86

ppm: parts per million
** Reference: w/o emulsion after 24 hours rotation*
**: w/o-emulsion after 24 hours rotation and 24 hours settling.*
*** Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling; all the water is settled out for 24 hours settling. Stability ratio of 1 implies a totally stable emulsion.*

3.5 Emulsion viscosities and yield stress

The viscosities of emulsified residues of Dugong at 13 °C are given in Table 3-7 (including fresh oil and waterfree residues). The emulsions behave as *non-Newtonian* fluids due to the increasing degree of weathering (evaporation and water uptake), with higher viscosities at a lower shear rate (10 s^{-1}) compared to the viscosities measured at higher shear rate (100 s^{-1}). This decrease in viscosity with increasing shear rate is due to the shear thinning property of emulsion with increased mechanical force.

Yield stress is defined as the force that must be overcome so that an oil can spread / flow like a liquid on the sea (also known as the flow limit). This force is called the fluids "yield stress" or flow limit and is given the unit Pascal (Pa). Yield stress is measured with Physica MRC 300 rheometer. Many crude oils (particularly weathered residues and emulsions) are so-called *Bingham-plastic* fluids at sea temperature. This means that applied force must be exerted to the fluid to make it flow and spread and is mainly pronounced for *non-Newtonian* oils where the viscosities vary with the shear rate. Results are given in Table 3-7. Dugong has relatively high yield stress of the 200 and 250°C+ emulsions (75 % and maximum water), and the oil may have both reduced flowability and spreading properties after some days at sea.

Table 3-7 Viscosities waterfree residues and emulsions of Dugong at 13 °C.

Dugong	**Water content (vol. %)**	**Viscosity 13 °C (mPa.s) 10 s^{-1}**	**Viscosity 13 °C (mPa.s) 100 s^{-1}**	**Yield stress Pa**
Fresh	0	17	15	n.d.
150°C+	0	192	83	n.d.
200°C+	0	407	171	0.42
250°C+	0	2017	348	2.88
150°C+	50	396	229	n.d.
200°C+	50	838	417	0.45
250°C+	50	4114	1004	1.10
150°C+	75	1455	521	12.9
200°C+	75	4054	1088	11.5
250°C+	75	8645	2375	64.4
150°C+	91	2375	490	6.96
200°C+	85	9340	1570	123
250°C+	78	18611	1585	55.9

n.d: not detected.

3.6 Chemical dispersibility

The dispersibility testing of Dugong included:

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

3.6.1 Screening testing of dispersants

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

The IFP test showed dispersant effectiveness in the range 45-74%, where Dasic Slickgone NS was most efficient (74 %) followed by Corexit 9500A (57 %). Dispersant efficiency >50 % for the low-energy test is considered as good dispersion. Dispersant efficiency >75 % for the high-energy MNS test is considered as good dispersion, and all the dispersants tested showed good dispersibility of 100 %. However, Dasic NS and Corexit 9500A visually seemed to promote smaller oil droplets. No effect of breaking up the emulsion when no dispersant added. DOR=Dispersant to oil ratio /DER=Dispersant to emulsion ratio.

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

Dispersant (DOR/DER =1:25)	**Efficiency dispersant (200°C+ /50 vol. % emulsion)* IFP**	**Efficiency dispersant (200°C+ /50 vol. % emulsion)* MNS**
Dasic NS	74	100
Corexit 9500A	57	100
Finasol OSR 52	45	100
Gamlen OD 4000	53	100
No dispersant	-	<5

** Emulsion viscosity: 838 mPa.s (10s^{-1})*

-: Not analysed

3.6.2 Dosage testing

The dosage test helps to identify optimal design conditions for dispersant use and was performed with DOR/DER of 1:25, 1:50, 1:100 and 1:200, and with no dispersant added. Dosage testing at 13 °C was performed using Dasic Slickgone NS on Dugong emulsion (150 and 200°C+ / 50 vol. %). Dasic Slickgone NS is the main dispersant agent in NOFO’s stockpile today. Results from the dosage testing are presented in Table 3-9. Examples (images) from the dosage testing (MNS test) on Dugong are given in Figure 3-7.

The tests show a clear dosage dependant effect for the low-energy test (IFP), where DOR/DER 1:25 and 1:50 showed the highest effects (53-74%). The MNS test gave high dispersion effectiveness for alle the dosage tested, but dosage of 1:25 and 1:50 clearly produced smaller oil droplets compared to the lower dosages of 1:100 and 1:200. No effect was observed with no dispersant added to the emulsion of Dugong. Images from the MNS testing are shown in Figure 3-5.

Table 3-9 Dosage testing on 200°C+/50% emulsion of Dugong at 13 °C.

Dispersant (dispersant-to-emulsion ratio)	**% Effectiveness 200 °C+/ 50%* IFP**	**% Effectiveness 200 °C+/ 50%* MNS**
Dasic NS (1:25)	74	100
Dasic NS (1:50)	53	100
Dasic NS (1:100)	22	100
Dasic NS (1:200)	7	100
No dispersant	-	< 5

** Emulsion viscosity 200°C+(1:25): 838 mPa.s (10s^{-1})*

** Emulsion viscosity 200°C+ (1:50, 1:100, 1:200): 1157 mPa.s (10s^{-1})*

-: Not analyzed

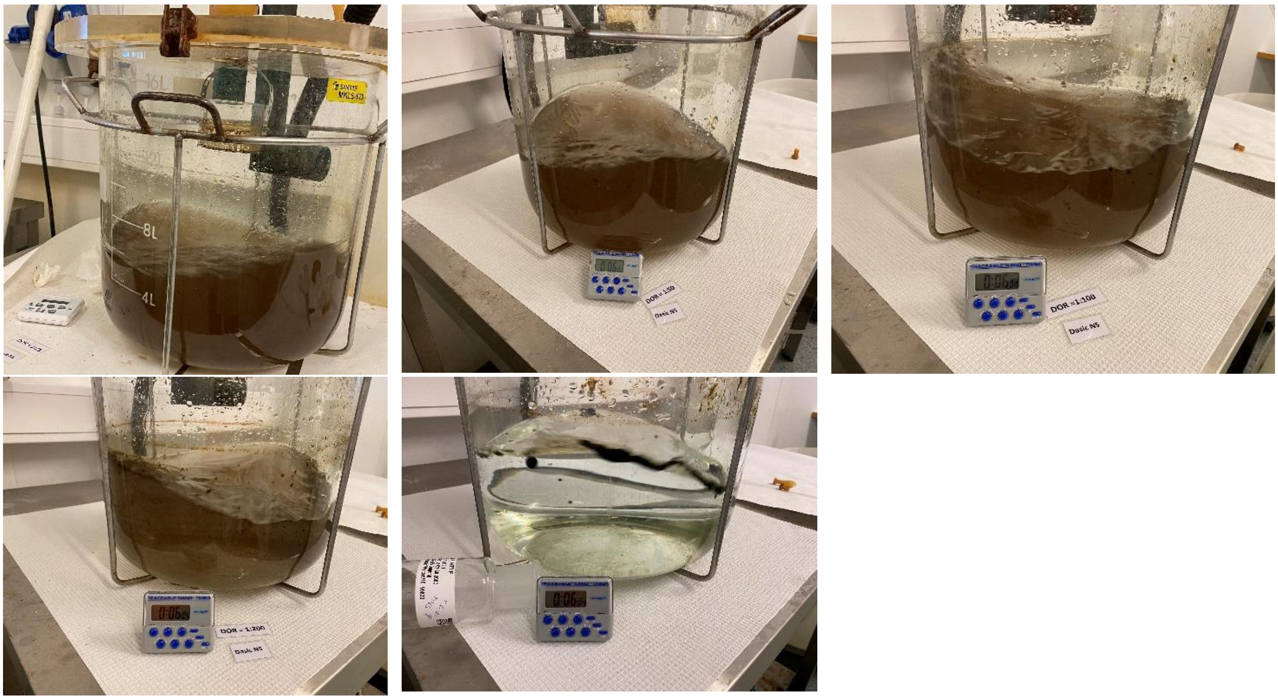


Figure 3-5 *Example MNS high energy test on 200°C+ 50% emulsion (Dugong). Upper Left to right: After adding DOR/DER 1:25, 1:50 and 1:100 of Dasic Slickgone NS. Below: After adding DOR/DER 1:200 of Dasic Slickgone and no dispersant added on the emulsion (no effect).*

3.6.3 Systematic dispersant testing and dispersibility limits

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

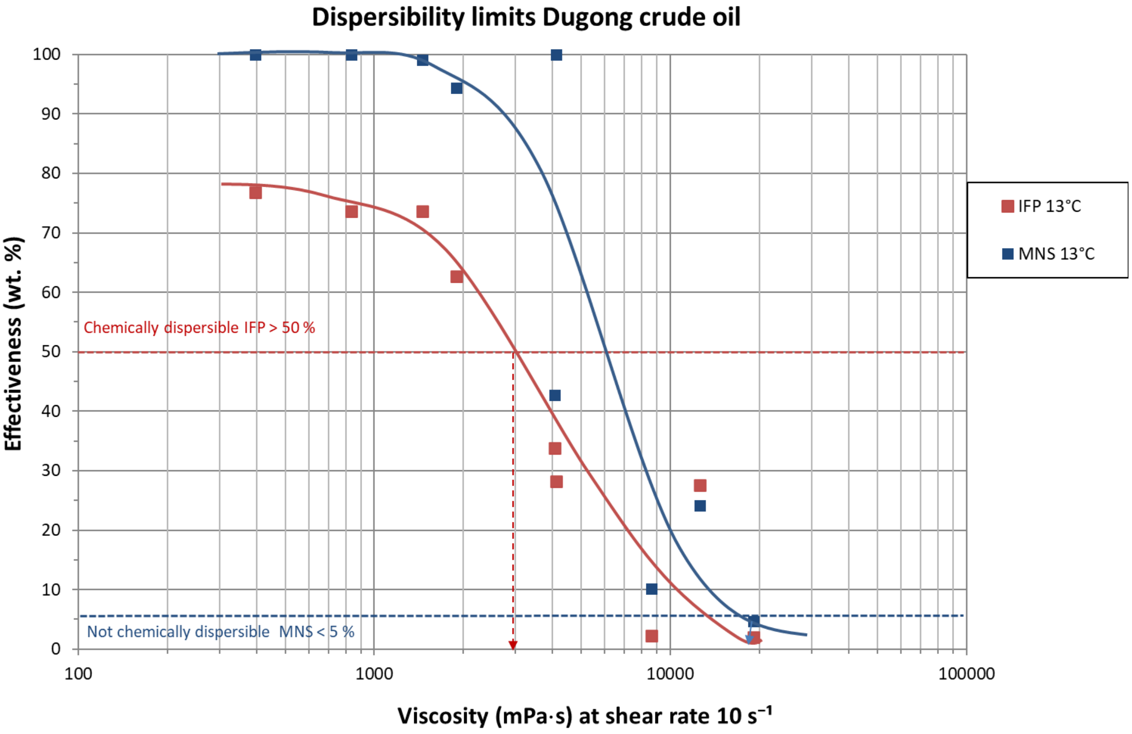


Figure 3-6 *Dispersant effectiveness limits of Dugong at 13 °C.*

Table 3-10 Systematic testing and effectiveness of Dasic Slickgone NS on Dugong at 13 °C.

Dugong	**Water content (vol. %)**	**Viscosity 13 °C (mPa.s) 10 s^{-1}**	**Effectiveness (%) IFP**	**Effectiveness (%) MNS**
150°C+	0	192	70	100
200°C+	0	407	55	100
250°C+	0	2017	1	11
150°C+	50	396	77	100
200°C+	50	838	74	100
250°C+	50	4114	28	100
150°C+	75	1455	74	99
200°C+	75	4054	34	43
250°C+	75	8645	2	10
150°C+	91	1896	63	94
200°C+	85	12598	28	24
250°C+	78	19059	2	5

Dugong was found to be good chemically dispersible for viscosities lower than 3000 mPa.s (IFP test) and found not or poor chemically dispersible >18000 mPa.s based on the high energy MNS-test, reflecting breaking waves conditions (> 5 m/s wind speeds). Dugong is expected to be reduced dispersible with viscosities between 3000 and 18000 mPa.s, this means that the oil is still dispersible but may require additional energy and/or higher dispersant dosage or multiple applications to enhance effective dispersion. The dispersibility limits are also summarised in Table 3-11.

Table 3-11 Estimated viscosity limits for Dugong for use of dispersant and definition of time window.

Dispersibility	**Criteria for effectiveness (wt. %)**	**Dispersibility limits based on emulsion viscosity (mPa.s)**
Good chemically dispersible	IPF >50%	3000
Not/poor chemically dispersible	MNS < 5 %	18000

4 Meso-scale laboratory testing of Dugong

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

A total of 9.4 litres of the fresh crude oil was applied carefully and evenly onto the surface seawater using a watering can. The seawater and air-temperature for this experiment was 13 °C (±2 °C) due to sequence of the climate system. Setpoint wave: 34 (18 cm). After application of the crude oil onto the seawater, the wind and wave energy were switched on. Artificial sunlight using a solar simulator was turned on after 30 minutes simulating photo-oxidation. Samples of the water phase at 0.5m depth and surface oil/emulsion were taken during the experiments. The oil was weathered for 72 hours (3 days) in the flume before *in-situ* application of dispersant (Dasic Slickgone NS) on the surface oil.

The experimental results obtained for Dugong are presented below. Table 4-1 shows the water content, evaporative loss, viscosity, and concentration of dispersed oil in the water column (naturally and chemically dispersed) at 13 °C at different time steps throughout the testing period.

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

Sample nr.	**Time (Hours)**	**Water Content (vol%)**	**Evaporation (wt%)**	**Viscosity (mPa·s) 10 s^{-1}**	**Oil-in-water ppm**	**Oil-in-water, % of original amount**
1	0.5	37	19	110	87	5
2	1	69	22	540	-	-
3	2	73	25	710	57	3
4	4	77	27	1450	43	2
5	6	76	30	2380	30	2
6	24	79	34	4680	11	1
7	48	80	36	6670	-	-
8	72	80	37	7480	8	0
1. Application of dispersant: 107 g Dasic NS (DOR 2.4 wt.%)						
10 min. disp 1	-	-	-	-	93	5
30 min. disp 1	-	64	-	21769	91	5
2. Application of dispersant: 111 g Dasic NS (DOR 2.5 wt. %)						
10 min. disp 2	-	-			470	26
30 min. disp 2	-	40		16076	409	24
3. Application of dispersant: 104 g Dasic NS (DOR 2.3 wt.%)						
10 min. disp 3	-	-	-	-	582	33
30 min. disp 3	-	-	-	-	570	33
80 min. disp 3	-	33	-	2340	546	31

Total dispersant: 322 g (DOR= 7.1 wt.%)
-: samples were not analysed
ppm: parts per million

4.1 Flume weathering data vs. predictions

The oil weathering from the meso-scale flume basin (maximum water uptake, evaporative loss, and emulsion viscosity) were compared with weathering predictions using the SINTEF Oil Weathering Model (OWM) with input data from the small-scale study at 13 °C. More information about the OWM is described in chapter 5. Figure 4-1 shows the evaporative loss from the meso-scale testing compared to the predictions. The evaporative loss harmonizes well with the weathering predictions. Figure 4-2 below shows the water uptake of the emulsion in the meso-scale testing compared to predicted values. Dugong reaches a maximum water uptake of ~80 vol. % within 1 day in the meso-scale flume and corresponds well with the predicted values. The higher water uptake within the first hours in the meso-scale flume can be explained by formation of unstable emulsions in with large water droplets during the first hours of weathering, and this phenomenon has also been observed for other paraffinic crude oils from flume experiments, as well. The results from the meso-scale testing also support the emulsion predictions as shown in Figure 4-3.

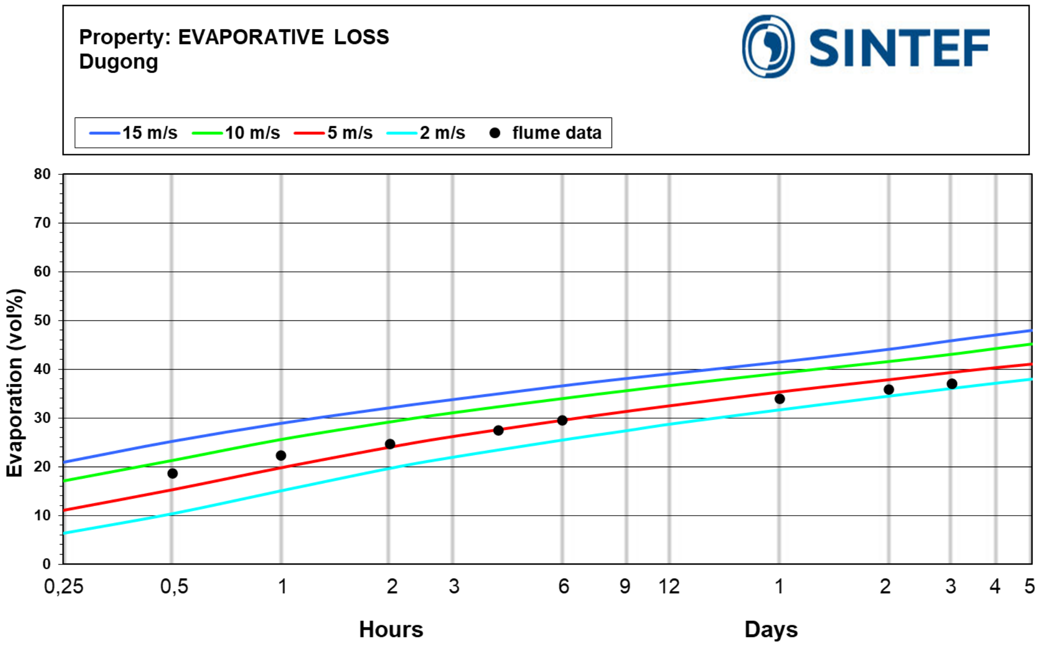


Figure 4-1 *Predicted evaporative loss for Dugong. The dots represent the experimental data from the meso-scale flume testing at 13 °C.*

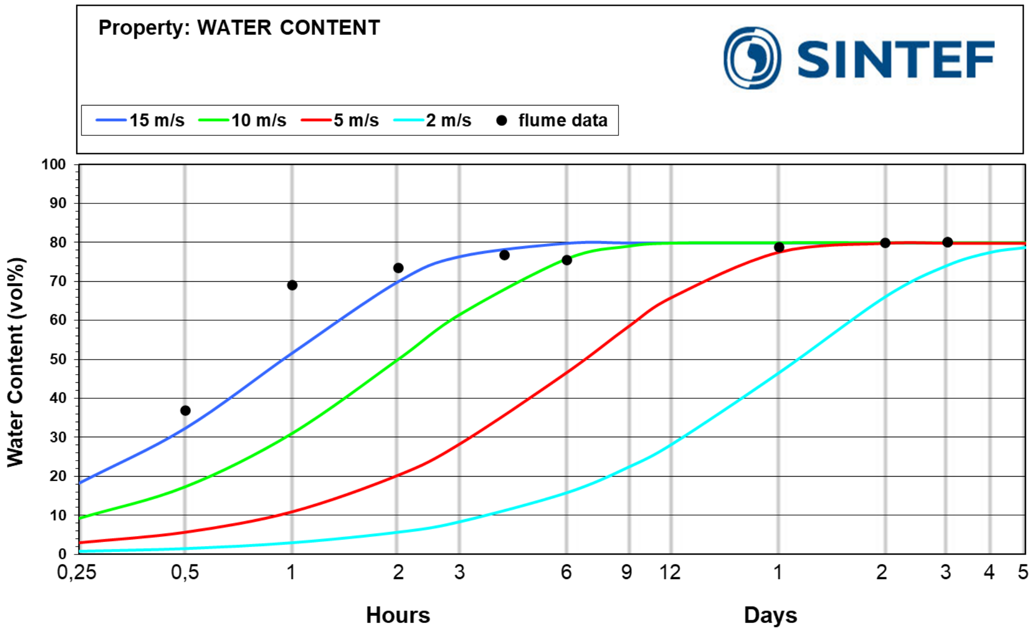


Figure 4-2 *Predicted water uptake for Dugong. The dots represent the experimental data from the meso-scale flume testing at 13 °C.*

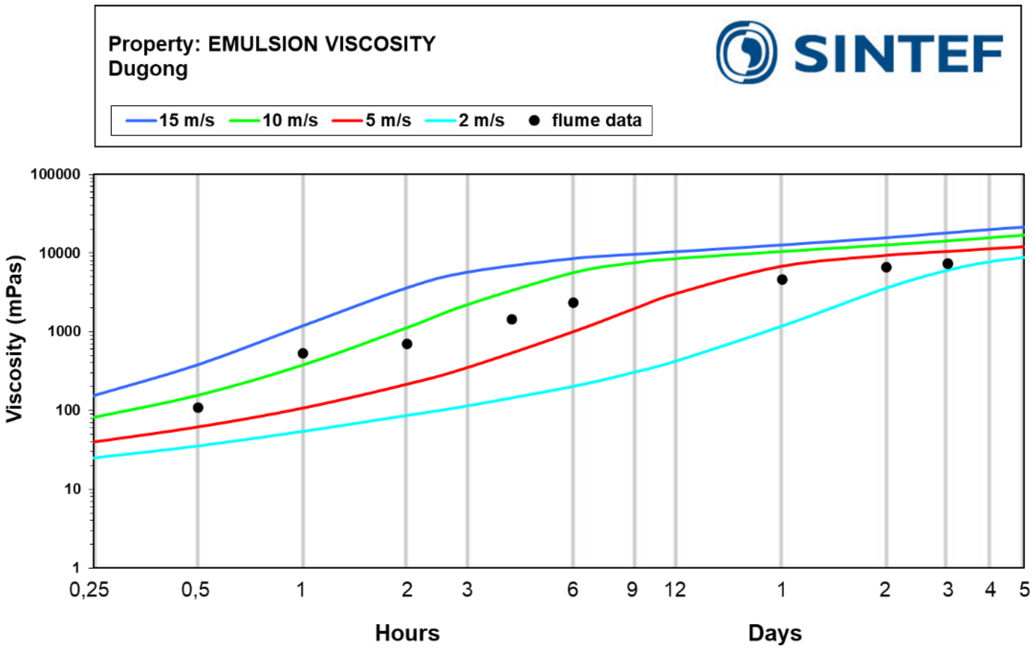


Figure 4-3 *Predicted emulsion viscosities for Dugong. The dots represent the experimental data from the meso-scale flume testing at 13 °C.*

4.2 Mass balances

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

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

Table 4-2 *Tabulated values of the estimated mass balance of Dugong by weight. Example after 24 hours weathering time at 5 and 13 °C.*

Properties	**Mass balance (% of initial oil) 13 °C**
Evaporated	34
Oil on water surface	54
Dispersed oil	0.6
Sampled amount of oil	6.6
Oil adsorbed to the flume walls*	5

**Estimated and after the oil adsorbed to the wall interior had been scraped off.*

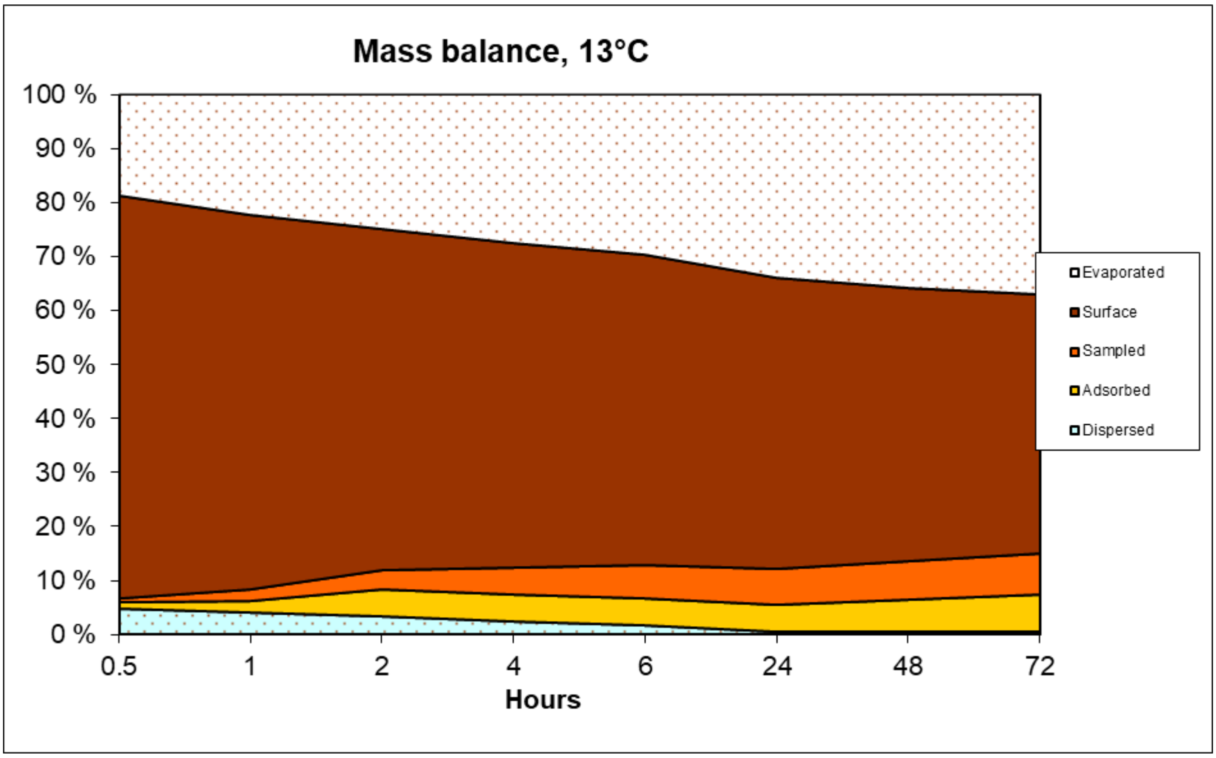


Figure 4-4 Mass balance for Dugong in the meso-scale flume basin at 13 °C, before dispersant application.

4.3 *In-situ* chemical dispersion

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

Table 4-3 Dispersant dosage on Dugong in the meso-scale flume basin (in-situ application) at 13 °C.

Dispersant application (#)	**Dasic NS application (g)**	**Dispersant -to -Oil Ratio (DOR /DER)**	**Dispersant (wt. %)**
1	107	1:42	**2.4**
2	111	1:41	**2.5**
3	104	1:43	2.3
1+2+3 cumulative	**322**	**1:14***	**7.1**

**Dispersant-to-emulsion Ratio (DER) 1:71*

The efficiencies of dispersion (Figure 4-5) are given as percentage (%) of the available oil after 72 hours of weathering (oil sample taken before application of dispersant), at 13 °C. Note, this differs from the mass balances that show efficiency in percentage of originally applied amount of oil. Here we show that the percentage of available oil dispersed or entrained oil in the water phase increase from about 10% from the first round to 66-69% after the third round of dispersant application.

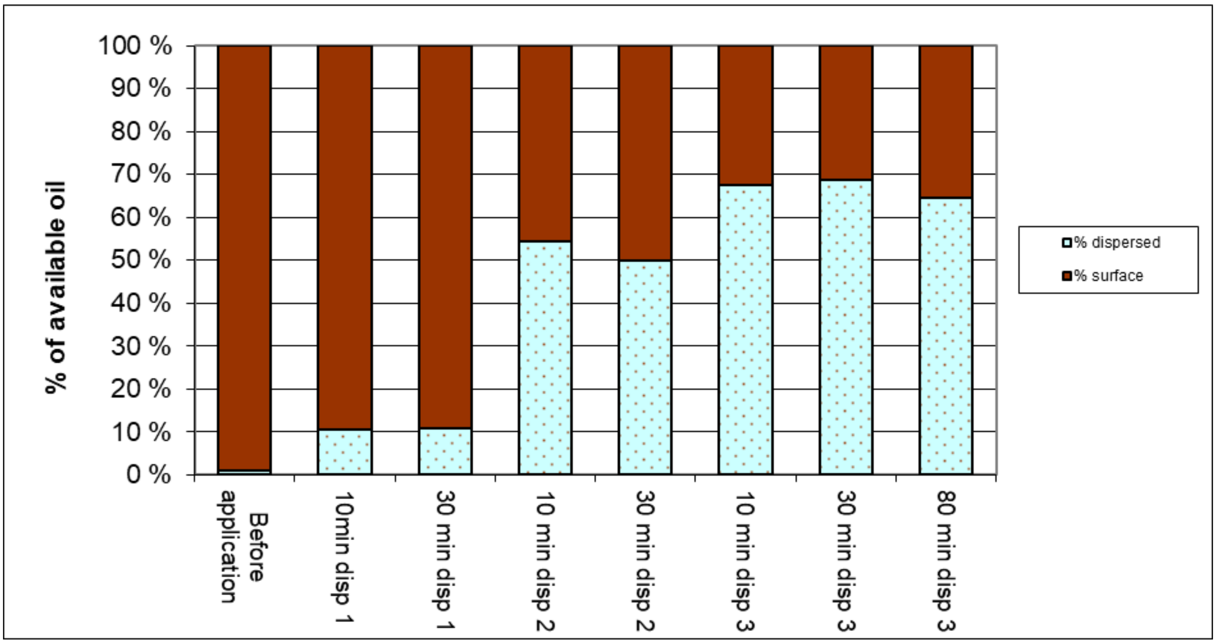


Figure 4-5 *Mass balance of Dugong after application of Dasic Slickgone NS as percentage of available surface oil at 13 °C.*

4.4 Observations from flume the experiment

A selection of images taken during the flume experiments of Dugong are presented below at 13 °C. The apparent difference in colour among the pictures is due to the changing colour of the oil as evaporation and emulsification takes place.

The applied fresh oil quickly spread out across the water surface of the flume. Some boiling and bubbling were observed in the initial oil slick. Short time after application, large oil droplets was quickly entrained into the water phase by waves, however, such large droplets in mm-size will easily resurface and may contribute to an "over-estimation" of the amount of naturally dispersed oil. The emulsion of Dugong was highly unstable during the first hours, but during the experiment the oil emulsified to a thick, homogeneous, and light brownish emulsion. The emulsion appears to be stable by time.

After 30 minutes, the fresh oil reached a water uptake of 37 vol. % and 19 % of the lighter compounds had evaporated. The emulsion viscosity was measured to 110 mPa.s (shear 10s^{-1}, 13 °C).

After 6 hours, the oil had become a thicker emulsion. Larger pockets of seawater were seen in the emulsion. The amount of oil droplets in in the water phase was reduced. Water uptake: 76 vol.%, evaporation: 30% and the viscosity: 2380 mPa·s.

After 24 hours. Even further thickening of the emulsion was observed together with some pockets of seawater incapsulated in the emulsion. The emulsion appears more homogeneous, but still has a slightly grainy texture with particles of lighter brown colour scattered throughout the emulsion. Minor amount of dispersed oil was observed in the water phase. The water uptake had reached 79 vol. %, evaporation 34% and the viscosity had further increased to 4680 mPa.s.

After 72 hours the water content has increased to 80 vol.%, with an evaporation of 37%. The viscosity of the emulsion at 72 hours was 7480 mPa.s.

Figure 4-6 shows an overview of pictures (time laps) from the weathering of Dugong after 30 min, 4 hours, 6 hours, 48 hours and 72 hours, respectively.

Figure 4-6 *Weathering of Dugong from top left to bottom right: t= 0min, 30min, 1 hour, 2 hours, 4 hours, 6 hours, 24 hours, 48 hours and 72 hours. For the first 3 photos (0 to 1 hour) the sun lamp is not turned on and slightly effects the colour of the oil in the pictures.*

Dasic Slickgone NS was applied as an aerosol by using a Wagner, sprayer on the remaining emulsion (in-situ application) in three rounds (replicates). About 4.5 litres of the total volume of oil (9.4 litres) was available for chemical dispersion and corresponds to 23 litres of emulsion. The dispersant was applied three times on the surface oil/emulsion giving a cumulative dispersant-to-oil ratio (DOR) of 1:14, reflecting a dosage-to-emulsion ratio (DER) of 1:71.

In the first round, the dispersant slightly reduced the water-content from 80 to 64vol. %, and the emulsion viscosity was reduced from 7480 to 3290 mPa.s. The second application of dispersant further reduced the water-content to 40 vol. % and the emulsion viscosity to 2870 mPa.s. In addition, the water phase turned into a light brown colour that indicated formation of small oil droplets in µm-size. The third application of dispersant further reduced the water-content to 33vol.% and emulsion viscosity to 2340 mPa.s. Figure 4-7 to Figure 4-9 show images of the surface emulsion after treatment of dispersants.

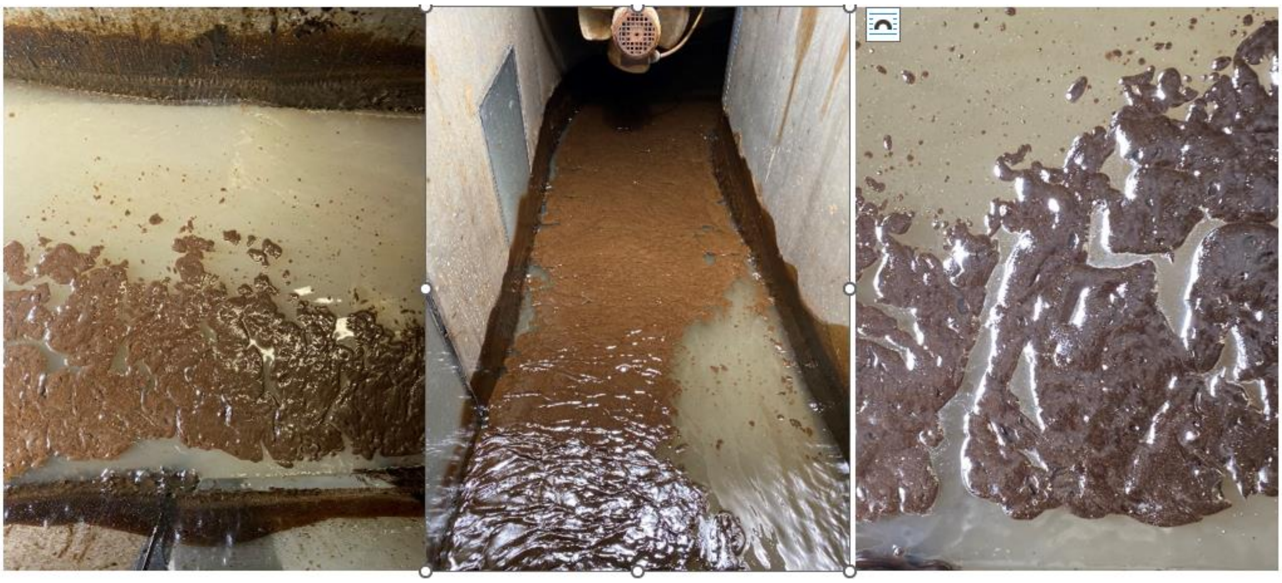


Figure 4-7 Dugong: 30 minutes after first application of Dasic Slickgone.

Figure 4-8 Dugong: 30 minutes after second application of Dasic Slickgone.

Figure 4-9 Dugong: 30 minutes after third application of Dasic Slickgone.

4.5 Remarks from the meso-scale flume testing of Dugong

Overall, the meso-scale flume experiment of Dugong showed consistent weathering data with the small-scale study and the OWM predictions.

In the flume the dispersed or entrained oil droplets in mm-sizes shown to be easily re-resurfaced. The flume testing also indicated that the emulsified oil would require repetitive application rounds of dispersant (cumulative DOR 1:14) to break up the "slick" into patches and disperse or entrain the oil droplets into the water phase (i.e., 66-69% of available oil). The third round of dispersant application also showed that the dispersant needed time, in combination of waves, to give an effect on the stable emulsions of Dugong. Moreover, the emulsion of Dugong showed to be reduced dispersible after 72 hours with a viscosity of 7480 mPa.s. However, it is expected that Dugong could be good dispersible <24 hours of weathering for viscosities lower than 3000 mPa.s, as the estimated viscosity limit from the small-scale study.

5 Predictions with SINTEF Oil Weathering Model (OWM)

5.1 Description of SINTEF OWM

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

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

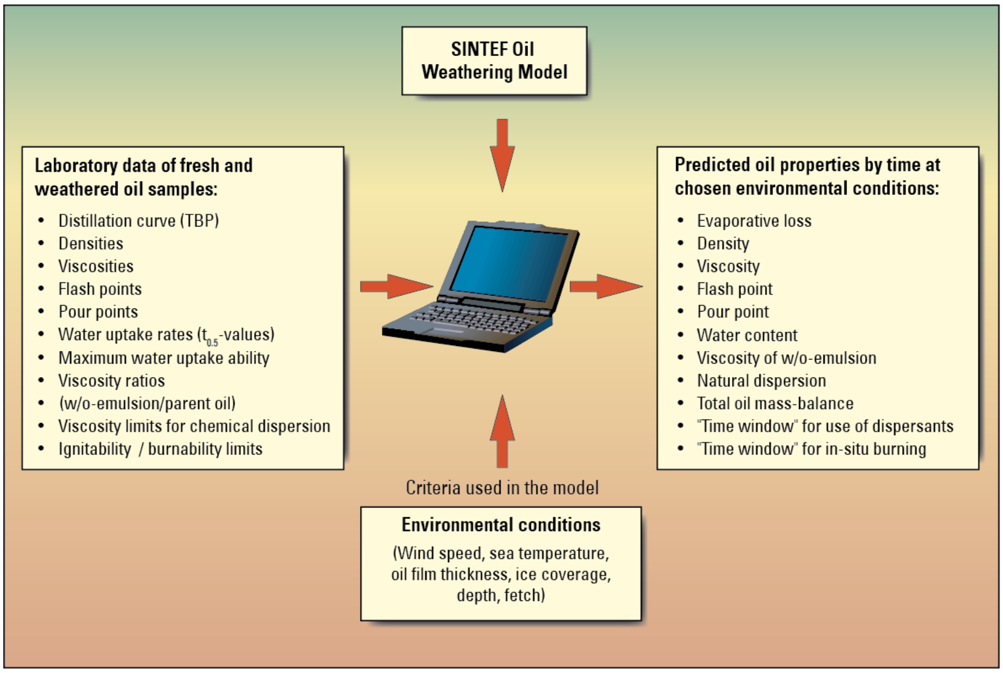


Figure 5-1 Schematic input data to the SINTEF OWM and the predicted output oil properties.

Oil film thickness

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

Seawater temperature

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

Wind speed

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

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

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

5.2 Predictions of weathering properties of Dugong

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

Input to SINTEF OWM

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

Predicted properties

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

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

How to use the prediction charts: an example

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

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

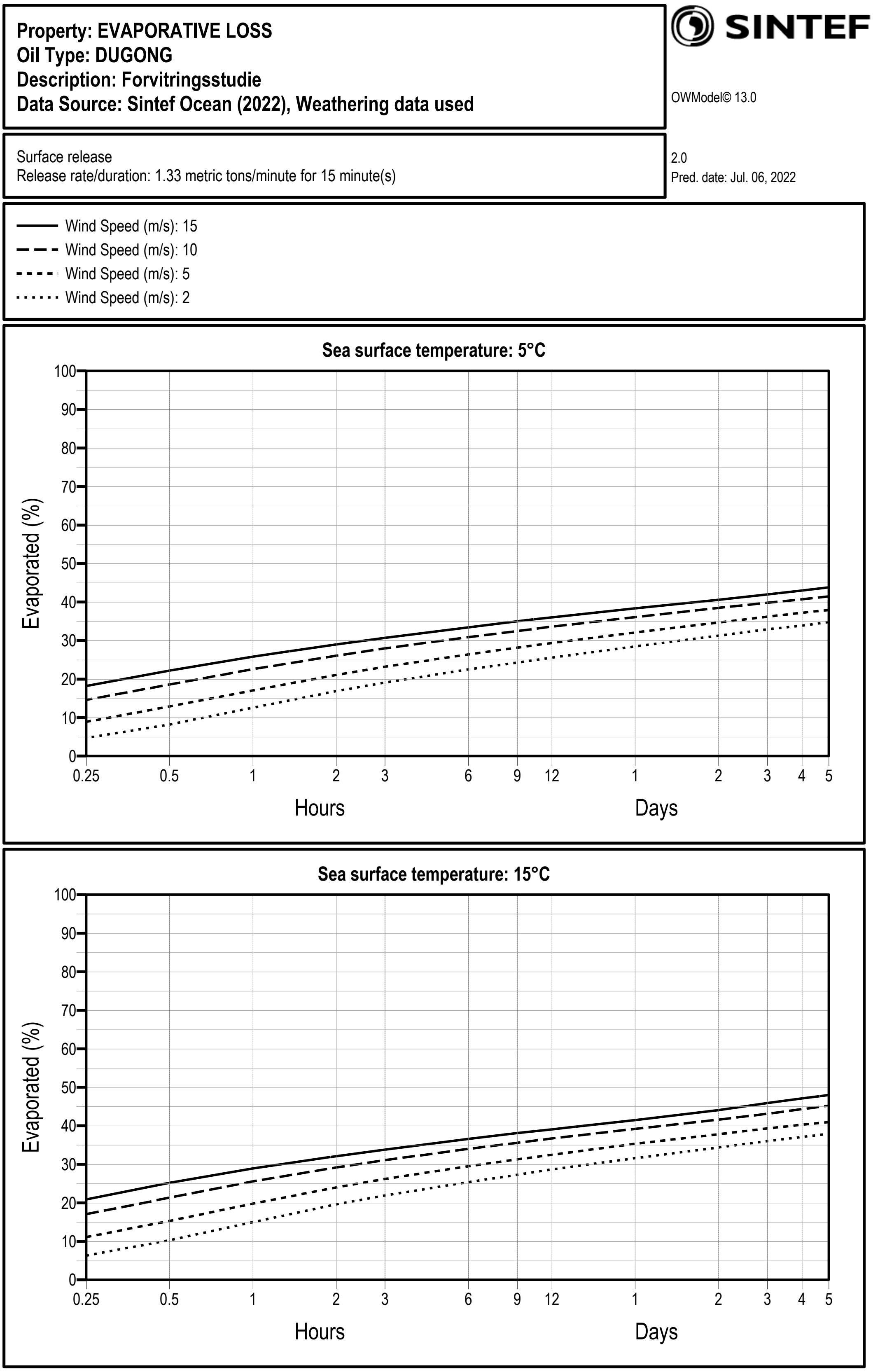
Weathering properties	**12 hours 5 ˚C 2 m/s**	**12 hours 5 ˚C 5 m/s**	**12 hours 5 ˚C 10 m/s**	**12 hours 5 ˚C 15 m/s**
Evaporation, wt. %	26	29	34	36
Flash point, °C	61	76	93	103
Pour Point, °C	20	22	25	26
Water content, vol.%	28	66	78	79
Viscosity, mPa.s *	570	4160	11150	14000
Mass balance / Oil on surface wt.%	74	69	51	19

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

Table 5-3 Example of weathering properties of Dugong obtained from the OWM predictions after 12 hours of weathering at 2, 5 and 10 m/s at 15 °C.

Weathering properties	**12 hours 15 ˚C 2 m/s**	**12 hours 15 ˚C 5 m/s**	**12 hours 15 ˚C 10 m/s**	**12 hours 15 ˚C 15 m/s**
Evaporation, wt. %	29	33	37	39
Flash point, °C	73	89	109	116
Pour Point, °C	22	24	27	28
Water content, vol.%	28	66	80	80
Viscosity, mPa.s *	430	3100	8510	10400
Mass balance / Oil on surface wt.%	71	66	46	14

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



Property: EVAPORATIVE LOSS
Oil Type: DUGONG
Description: Forvitringsstudie
Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

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

2.0
Pred. date: Jul. 06, 2022

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

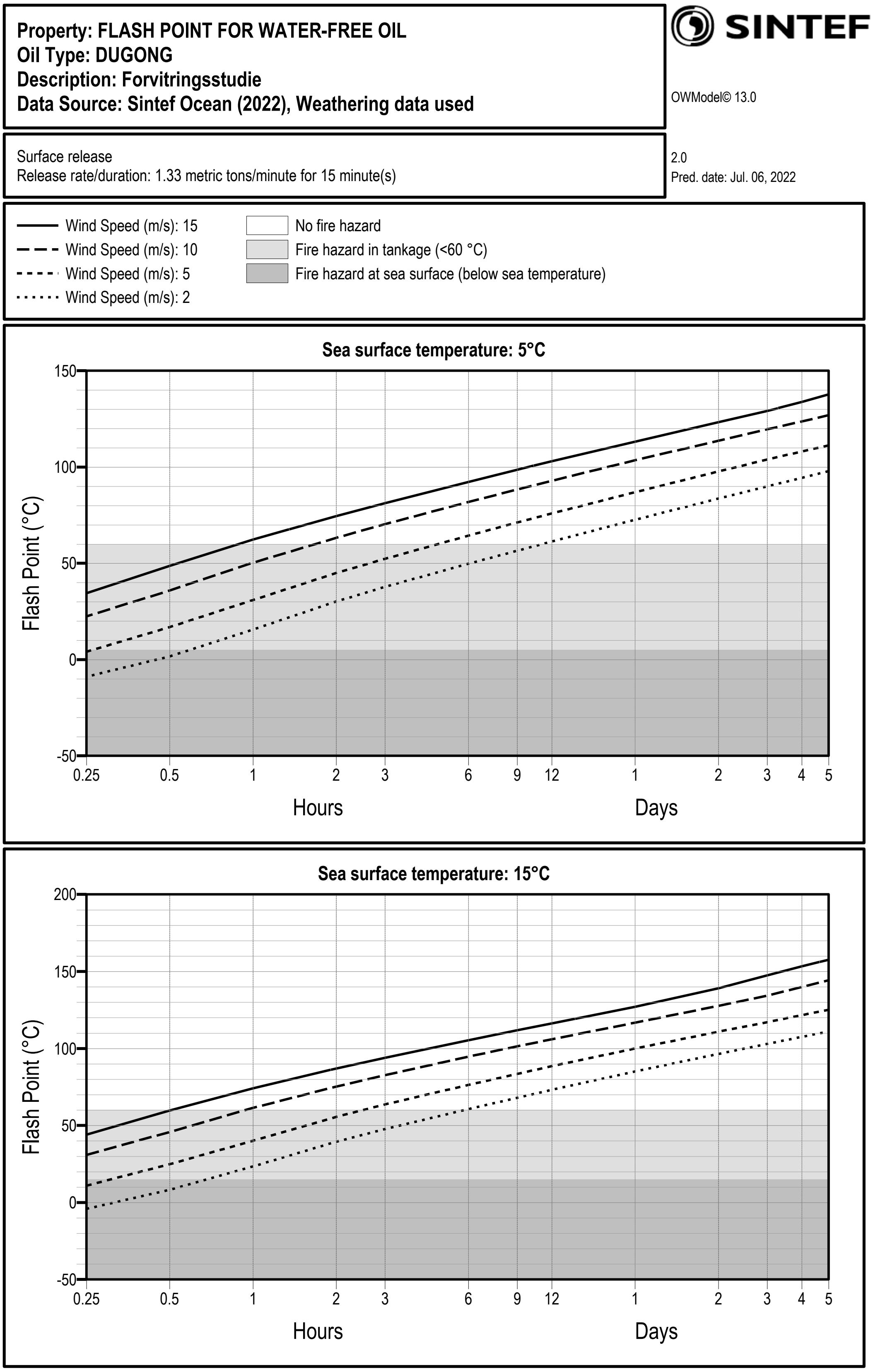
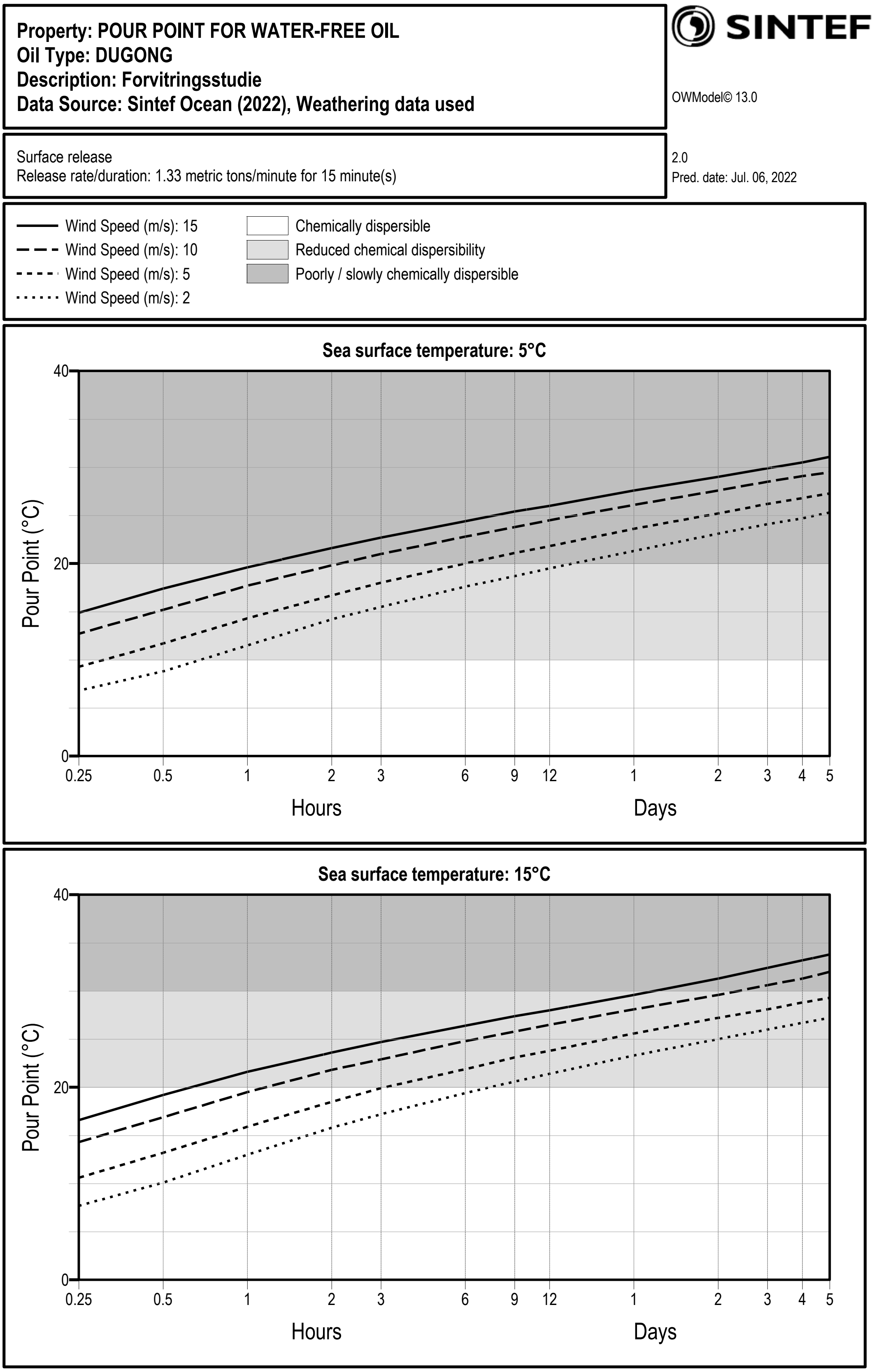


Figure 5-3 Flash point of water-free Dugong predicted at sea temperatures of 5 and 15 °C.



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: DUGONG
Description: Forvitringsstudie
Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

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

2.0
Pred. date: Jul. 06, 2022

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

Property: WATER CONTENT
Oil Type: DUGONG
Description: Forvitringsstudie
Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

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

2.0
Pred. date: Jul. 06, 2022

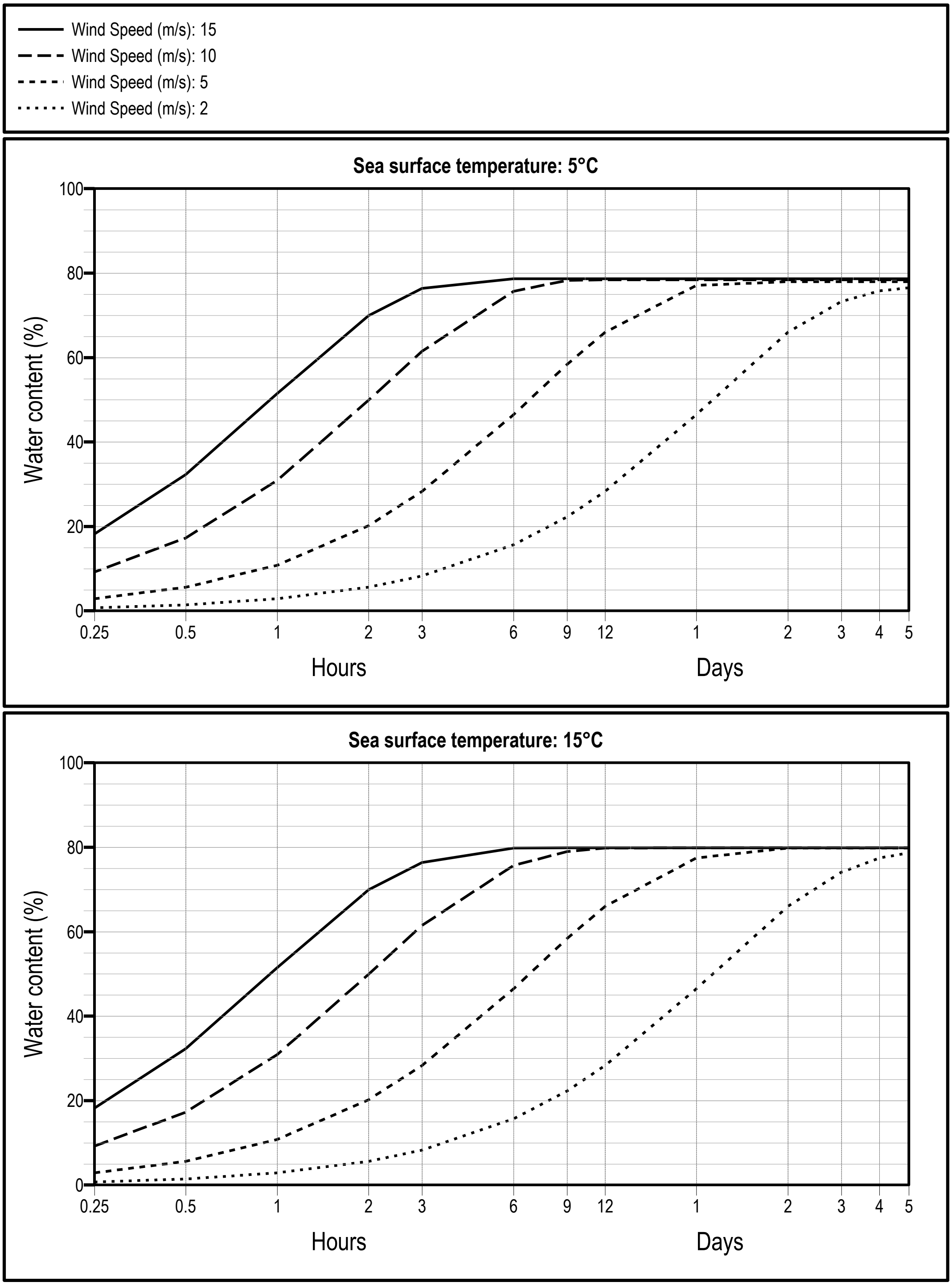


Figure 5-5 *Water content of Dugong predicted at sea temperatures of 5 and 15 °C.*

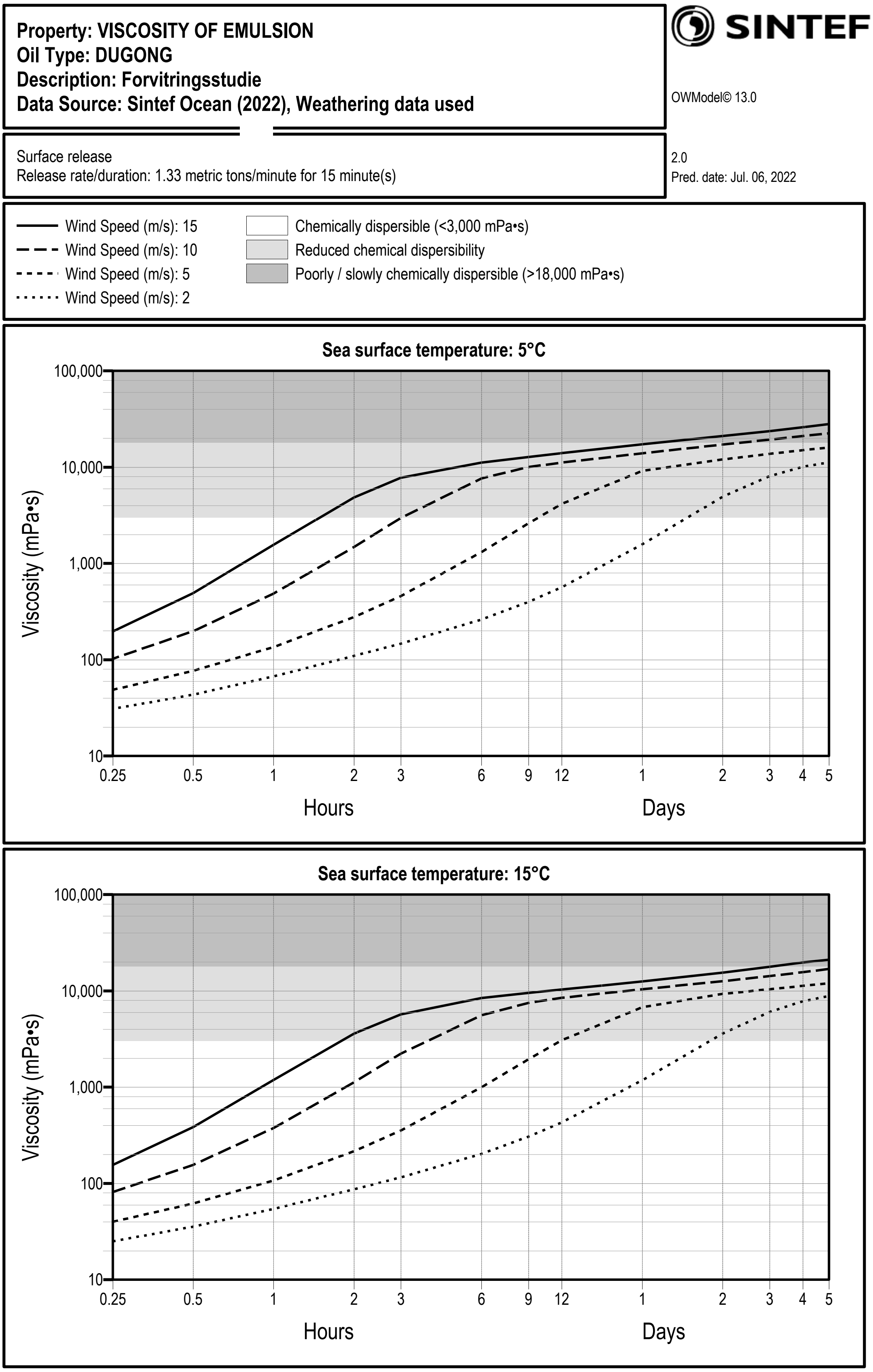


Figure 5-6 *Viscosity of Dugong predicted at sea temperatures of 5 and 15 °C.*

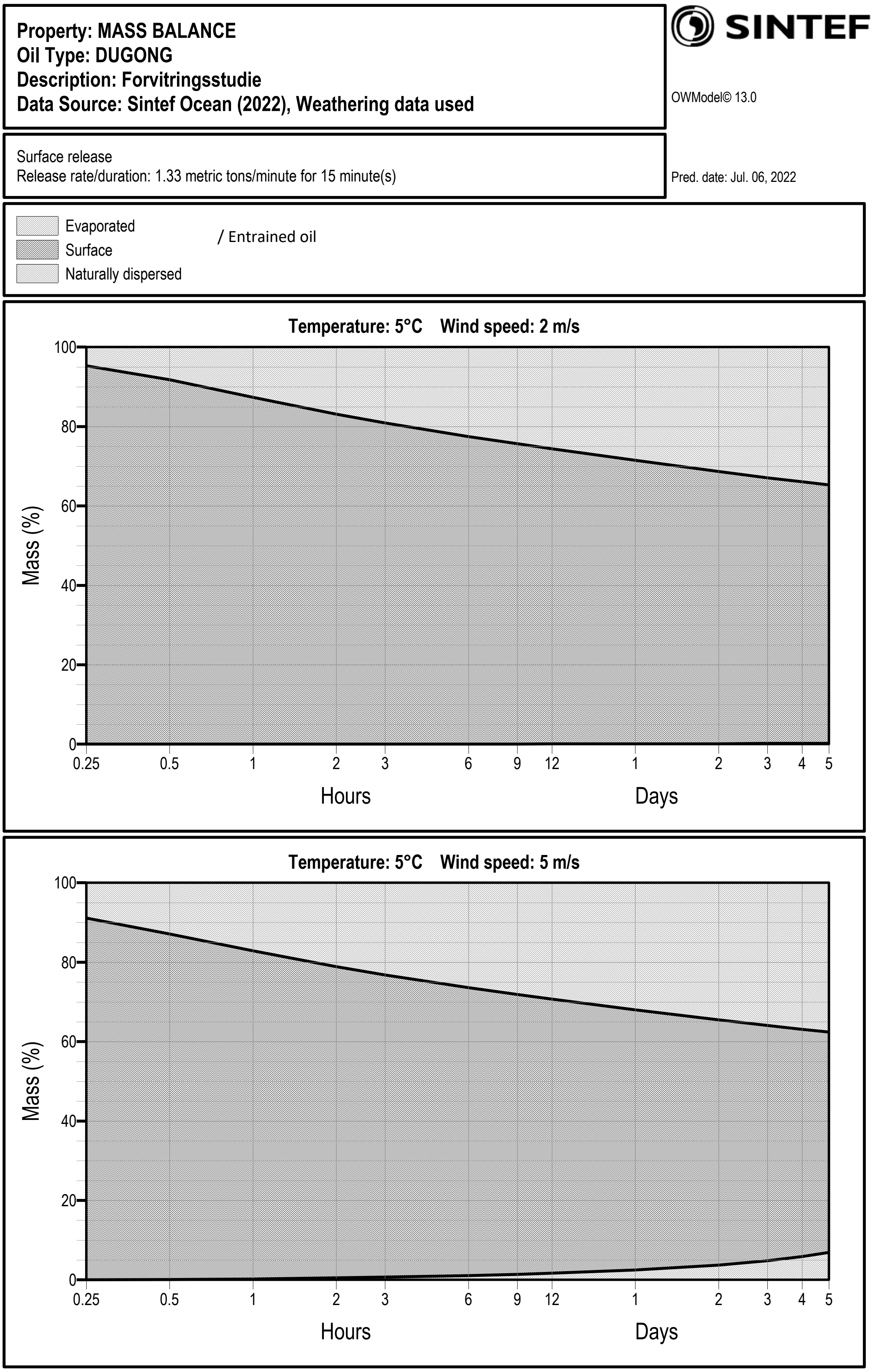


Figure 5-7 Predicted mass balance of Dugong predicted 5 °C, wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: DUGONG
Description: Forvitringsstudie
Data Source: Sintef Ocean (2022), Weathering data used

SINTEF
OWModel© 13.0

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

Pred. date: Jul. 06, 2022

▨ Evaporated
▨ Surface
▨ Naturally dispersed
/ Entrained oil

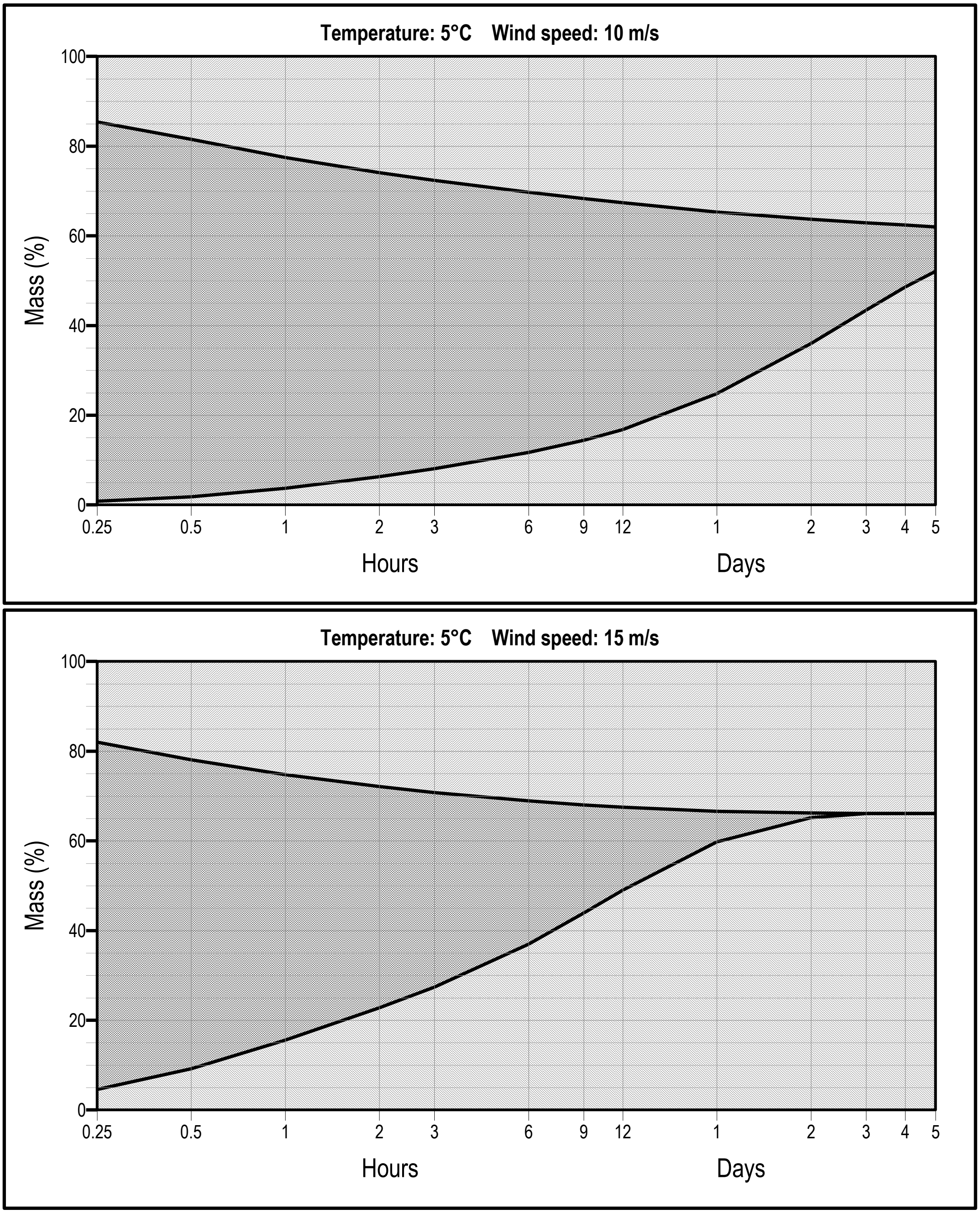


Figure 5-8 *Predicted mass balance of Dugong predicted 5 °C, wind speeds of 10 and 15 m/s.*

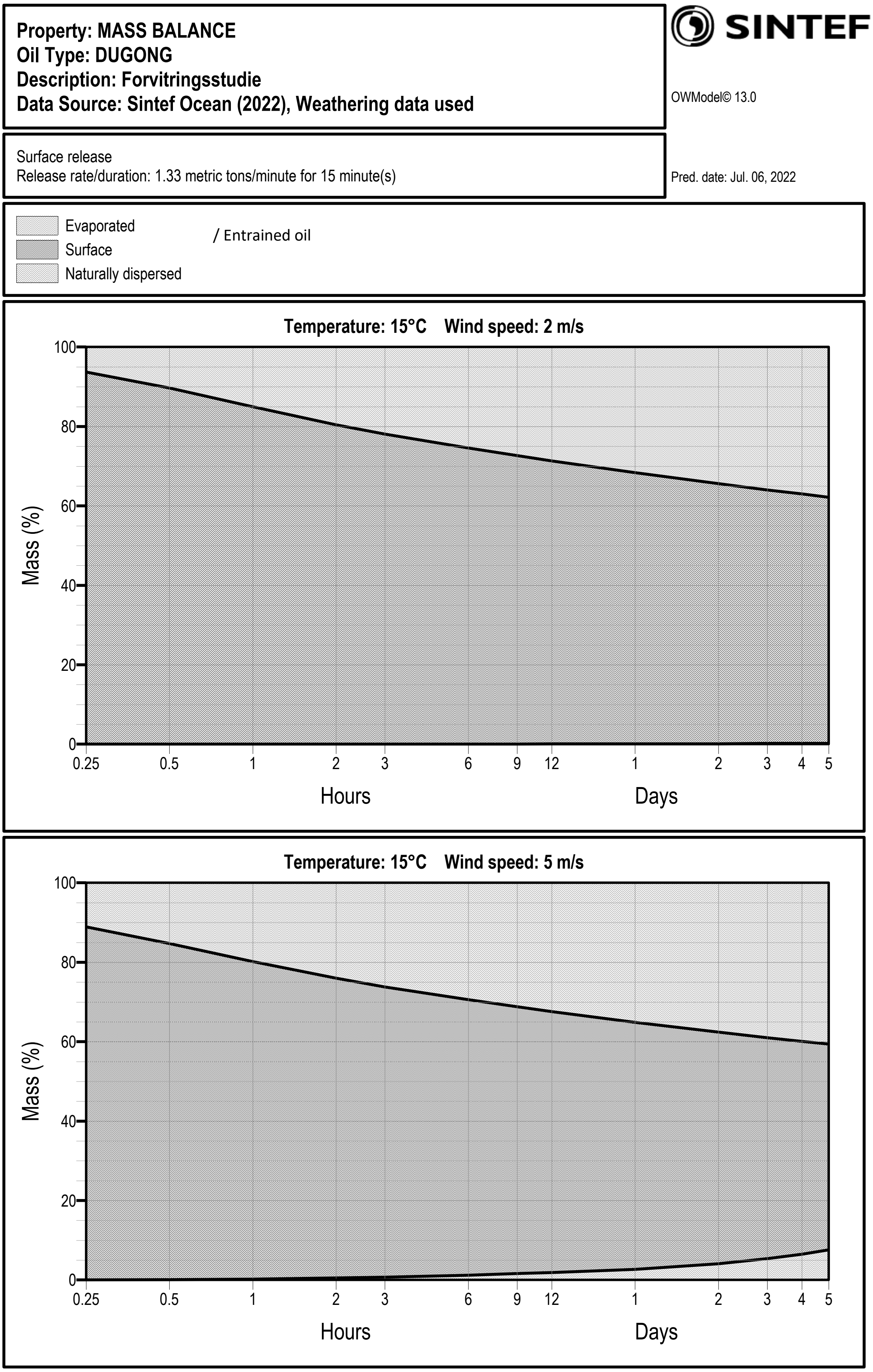
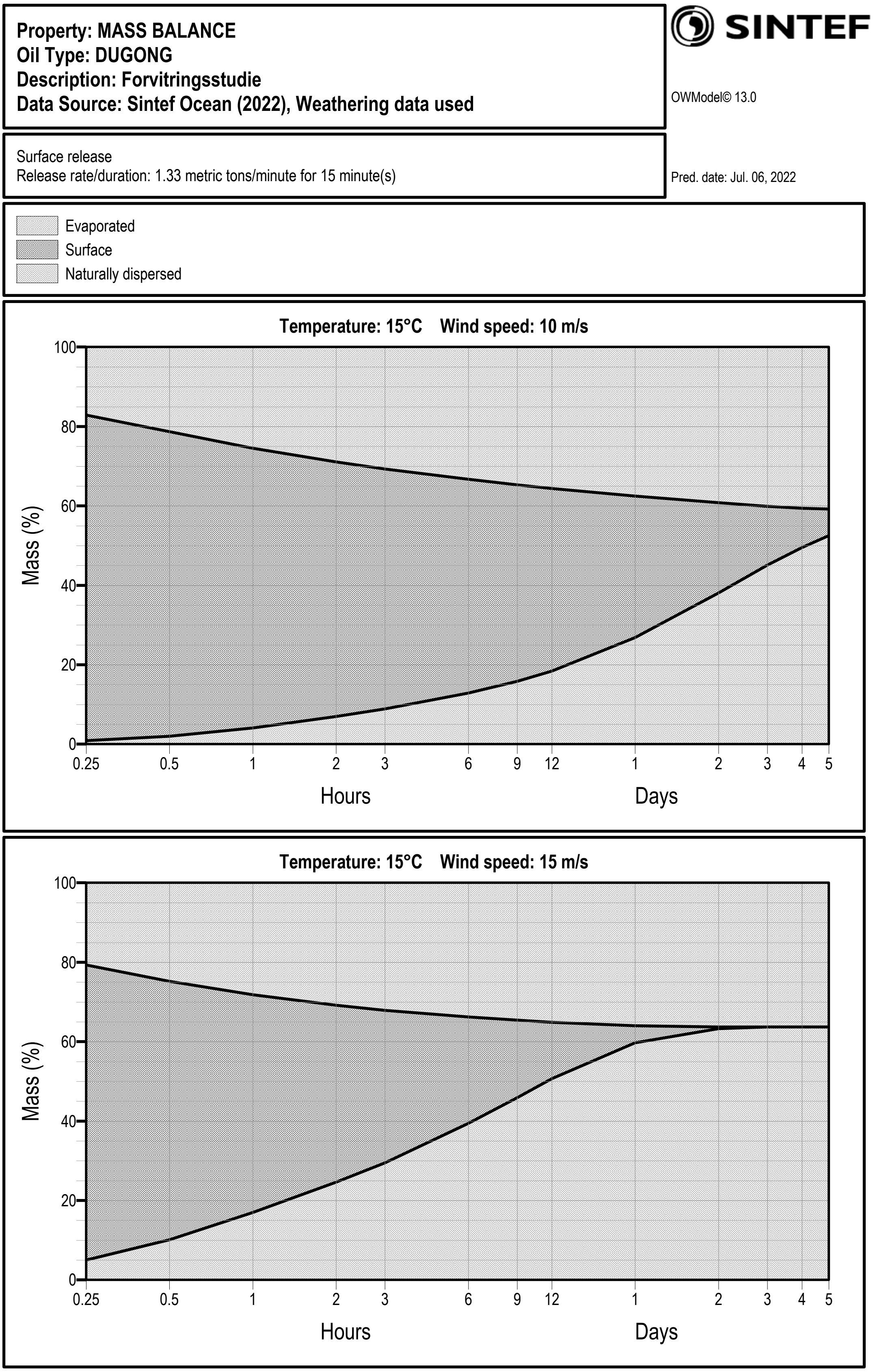


Figure 5-9 *Predicted mass balance of Dugong predicted 15 °C, wind speeds of 2 and 5 m/s.*



Property: MASS BALANCE
Oil Type: DUGONG
Description: Forvitringsstudie
Data Source: Sintef Ocean (2022), Weathering data used

OWModel© 13.0

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

Pred. date: Jul. 06, 2022

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

6 Comparison of OWM predictions

Weathering predictions from surface release of Dugong were compared with predictions of Duva, Nova (former called Skarfjell), Gjøa, in addition to Sygna Brent and Snorre TLP crude oils from the Tampen area. The prediction scenario for comparison is based on sea temperature of 15 °C and wind speed of 10 m/s.

6.1 Evaporative loss

Evaporation is one of the natural processes that helps reducing the surface oil volume if the oil is spilled at sea. The evaporative loss of Dugong is most like Sygna Brent and Snorre TLP (Figure 6-1). The high wax / high pour point oil Duva have the lower evaporative loss, whilst Nova and Gjøa exhibit the highest evaporative loss among these oil for comparison.

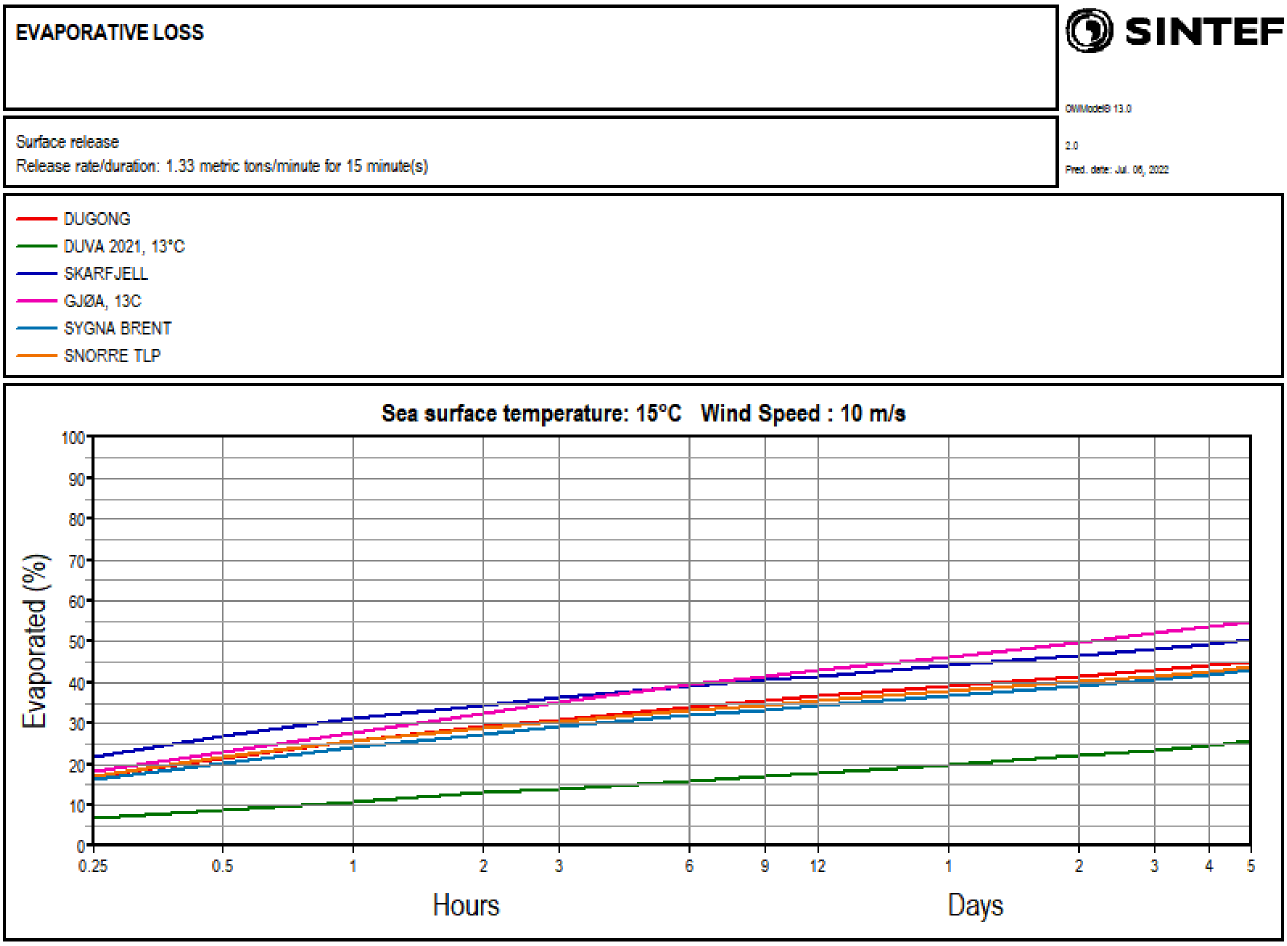


Figure 6-1 Predicted evaporative loss at 15 °C and 10 m/s for Dugong in comparison with Duva, Nova (aka Skarfjell, Gjøa, Sygna Brent and Snorre TLP.

6.2 Pour point

The pour points of the paraffinic Dugong, Sygna Brent and Snorre TLP are very similar, whilst the very waxy/high pour point Duva exhibits much higher pour point from the start, and the curve is not increasing by weathering time (Figure 6-2). Gjøa has the lowest pour points after 5 days of weathering compared with the other oils.

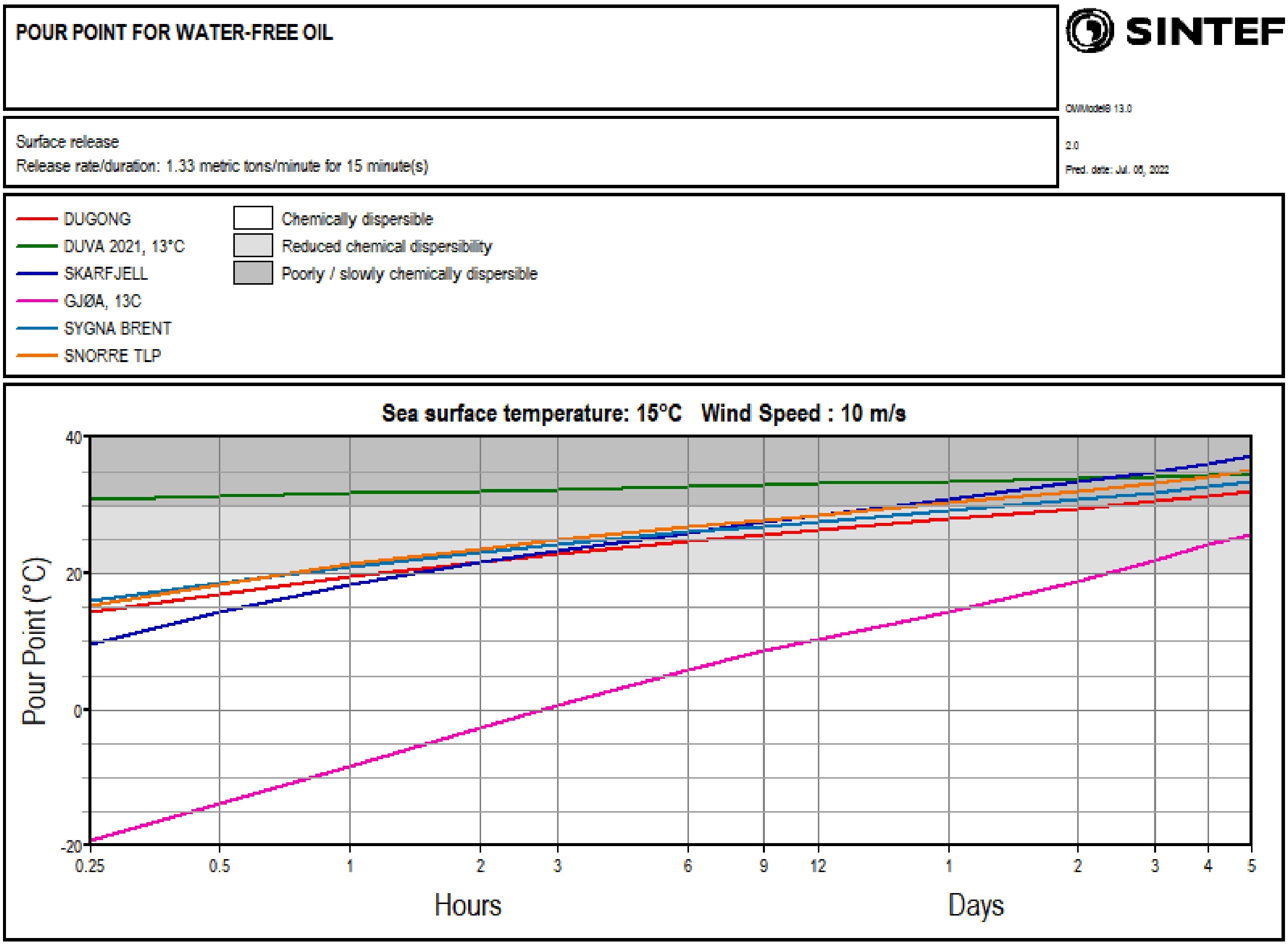


Figure 6-2 Predicted pour point at 15 °C and 10 m/s for Dugong in comparison with Duva, Nova (aka Skarfjell, Gjøa, Sygna Brent and Snorre TLP.

6.3 Water uptake

The water uptake of Dugong compared with the other oils are shown in Figure 6-3. Dugong, Nova, Snorre TLP and Sygna Brent reach a maximum water uptake of ~78-80% vol% but follow different kinetics (rate of the water uptake). Nova and Snorre TLP express very similar kinetics and reach the maximum water content after 6 hours of weathering, whilst Duong reach the maximum water uptake after 12 hours, followed by Sygna Brent that reaches the maximum water after 1 day. Duva and Gjøa differ from the other oils in comparison with the lowest kinetics and water uptakes of 65 and 55 % vol., respectively.

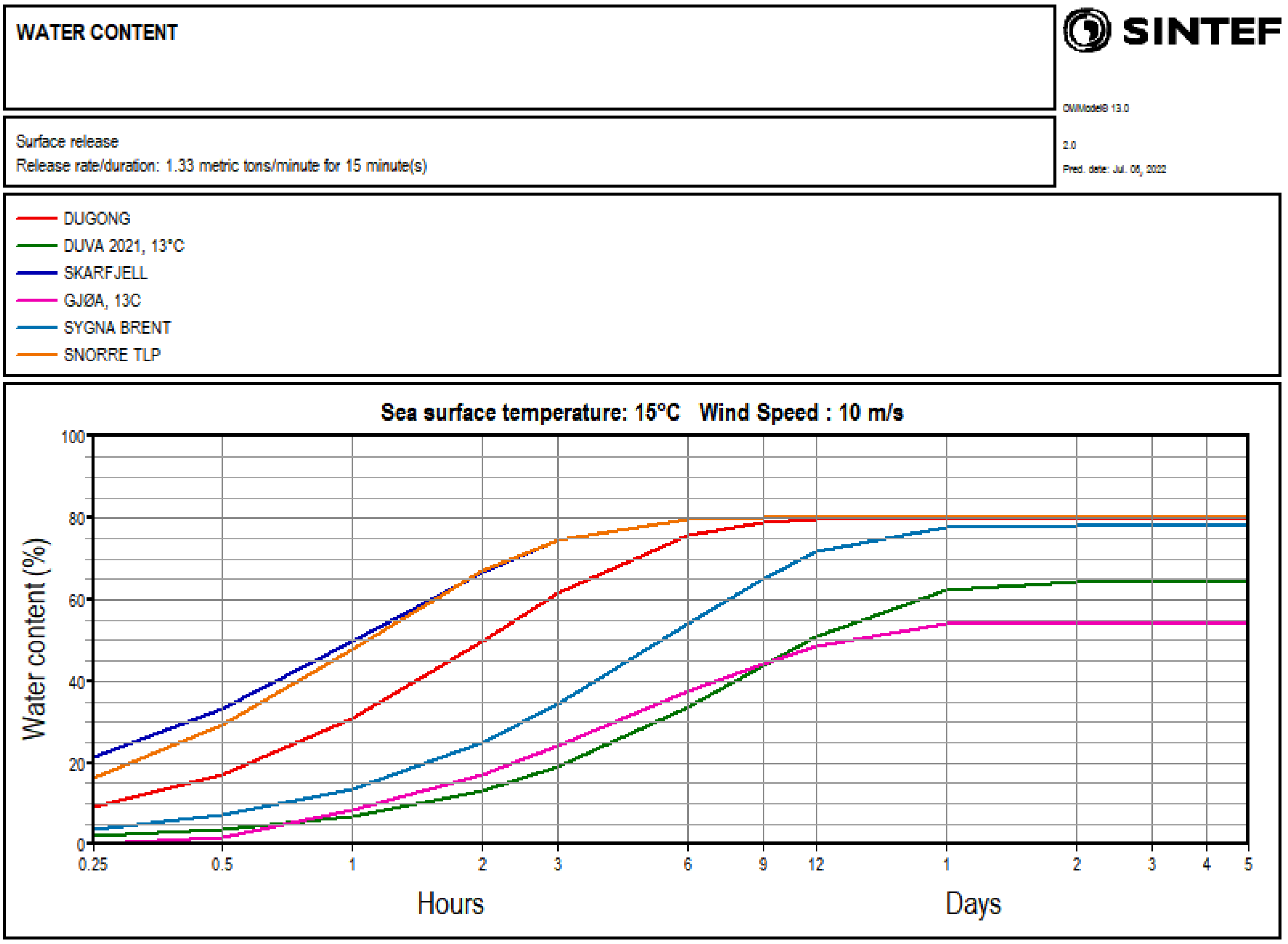


Figure 6-3 *Predicted water uptake at 15 °C and 10 m/s for Dugong in comparison with Duva, Nova (aka Skarfjell, Gjøa, Sygna Brent and Snorre TLP.*

6.4 Emulsion viscosity

Figure 6-4 shows the predicted (emulsion) viscosities of Dugong compared with the other oils. The viscosity of Dugong is most similar with Sygna Brent and Snorre TLP, followed by Nova. Duva has initial very high viscosity due the high pour point and solidifies at sea, and exhibits a low water content, and the viscosity is shown to decrease by time due to emulsification. Gjøa exhibits the lowest emulsion viscosity among these oils.

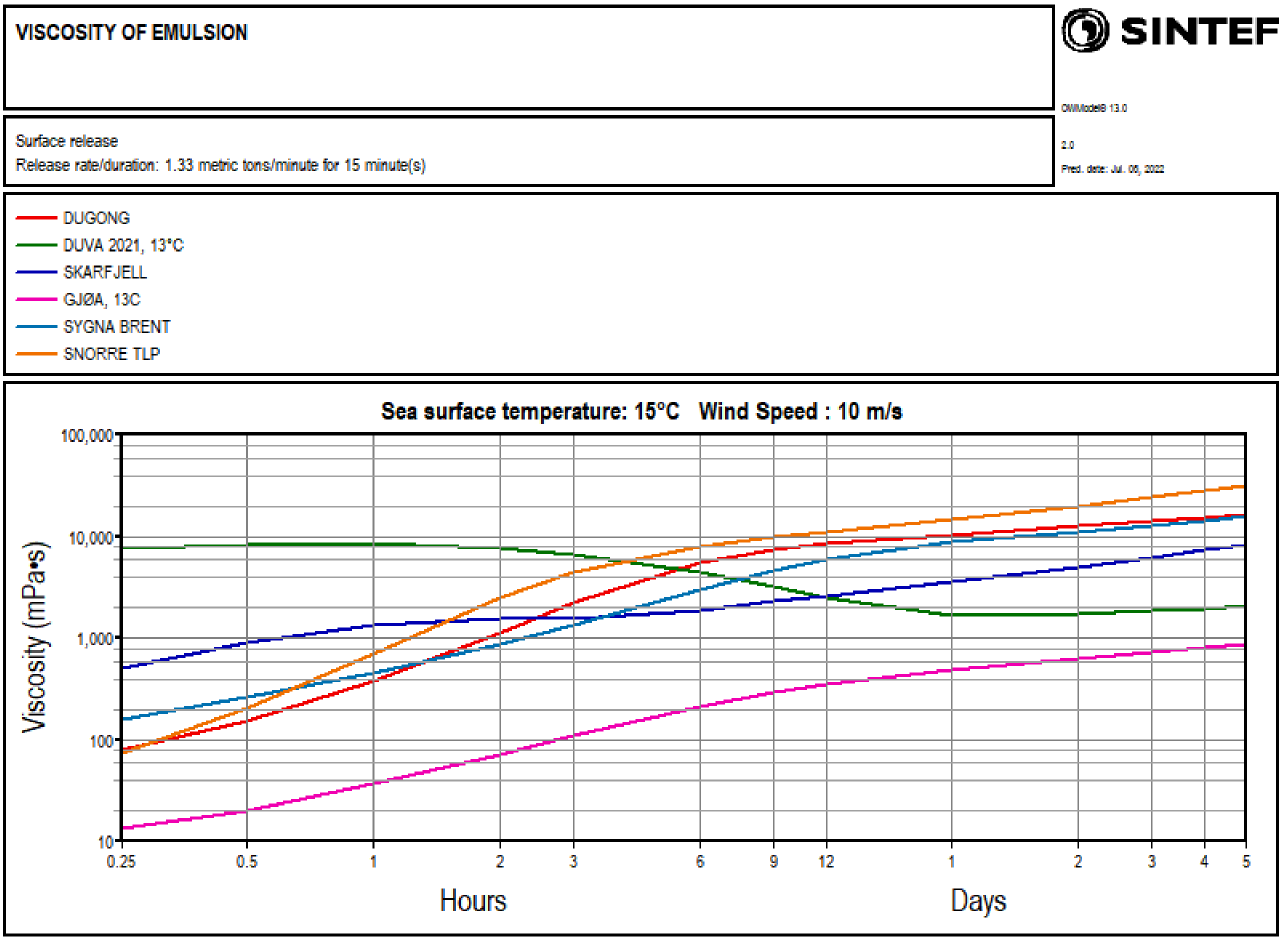


Figure 6-4 *Predicted (emulsion) viscosity at 15 °C and 10 m/s for Dugong in comparison with Duva, Nova (aka Skarfjell, Gjøa, Sygna Brent and Snorre TLP.*

6.5 Surface oil and emulsion

The predicted surface oil volume is based on the evaporative loss, natural dispersion/entrainment, whilst surface emulsion also includes emulsification that may increase the oil volume subsequently (see example of Dugong in Figure 7-2). Figure 6-5 shows the predicted mass balance of remaining surface oil as a function of weathering of the oils in comparison. The mass balance (surface oil) of Dugong is most like Sygna Brent followed by Snorre TLP and Nova. Moreover, the oils in comparison are all persistent on the sea surface with a predicted lifetime >5 days, except from Gjøa that is predicted to have a lifetime of 2 days for this scenario.

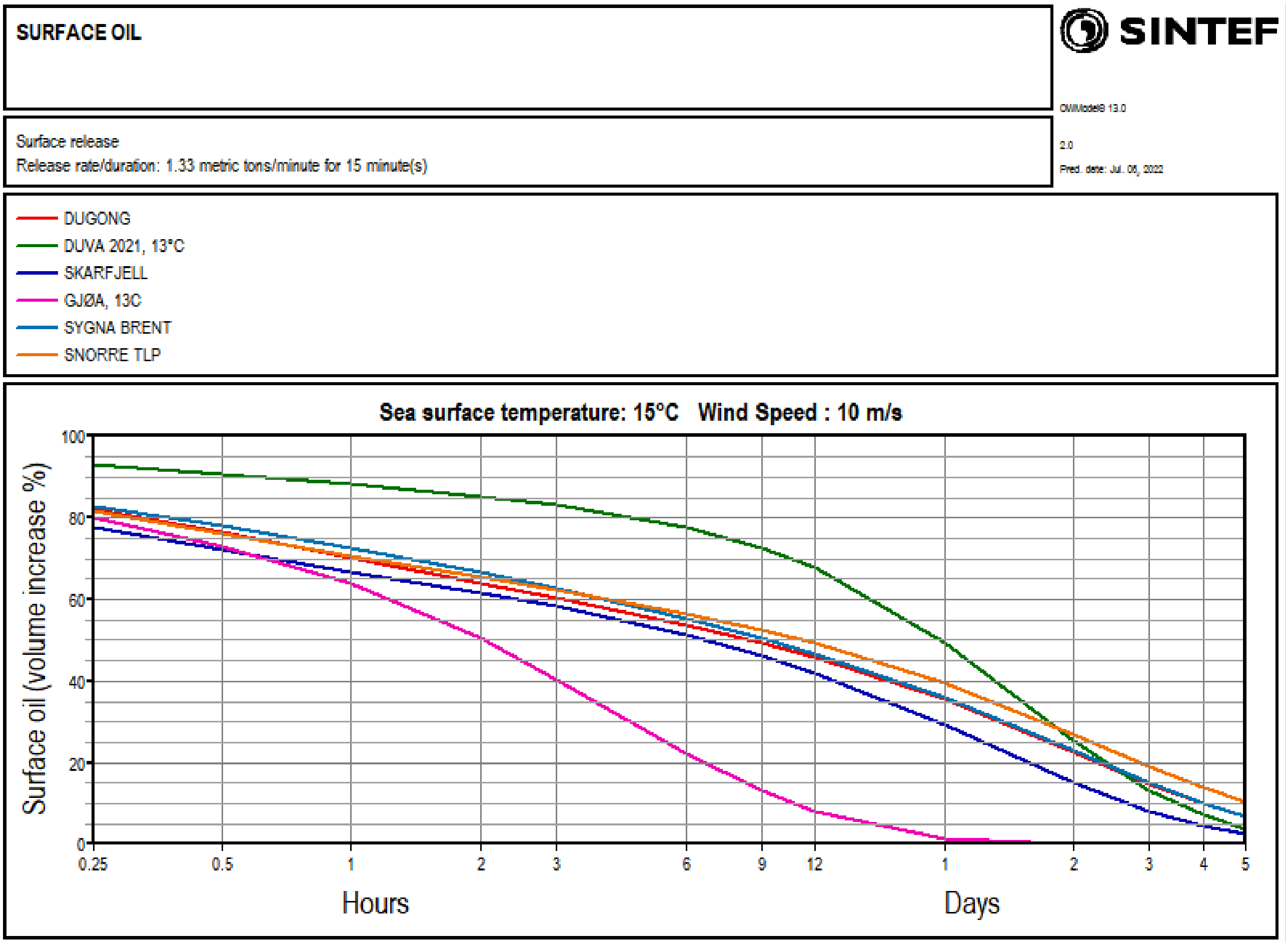


Figure 6-5 Predicted remaining surface oil at 15 °C and 10 m/s for Dugong in comparison with Duva, Nova (aka Skarfjell, Gjøa, Sygna Brent and Snorre TLP.

7 Weathering properties and response of Dugong (surface release)

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

7.1 Oil properties

The specific physico-chemical parameters of Dugong are input to SINTEF OWM for oil weathering predictions. The physico-chemical analysis of the fresh and topped residues show that Dugong is medium paraffinic crude oil with a density of 0.832 g/mL, with a medium content of wax (5.1 wt.%) and asphaltenes (0.11 wt. %). Dugong has a moderate evaporative loss of 43 vol.% for the 250°C+ residue. The fresh oil has a low viscosity of 17 mPa.s at 13°C ($10s^{-1}$) that increases by evaporation to 2017 mPa.s for the 250°C + residue. The fresh oil has a pour point of 3 °C that increase significantly to 27 °C upon evaporation (250°C+). Moreover, Dugong forms stable water-in-oil emulsions with moderate to high viscosities that partly or totally breaks with application of emulsion breaker (Aerosol OT-SE surfactant).

7.2 Flash point – Fire/explosion hazard

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

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

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C, e.g., towing vessels, smaller cargo, or other vessels available in the emergency. This means that oils with the flash point less than 60 °C, are for those type of vessels not permitted as cargo. However, this limit is not considered as relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flashpoints <60 °C), according to NFPA classification of Flammable and Combustible Liquids (http://www.thetankshop.ca). Refers to the flash point predictions in Figure 5-3 and Figure 7-1.

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

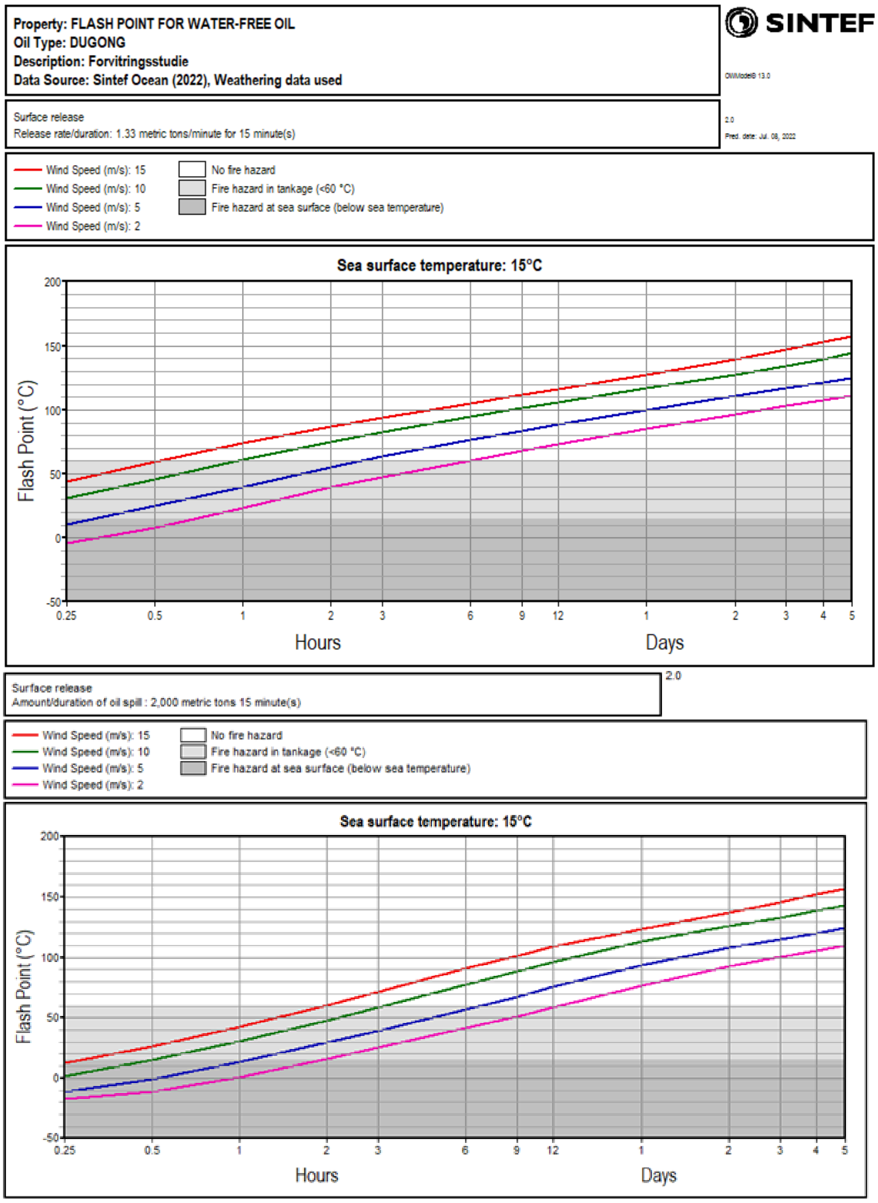


Figure 7-1 Predicted flash points for Dugong at 15°C (upper) with a release rate of 80m3/h, and below) with release rate 8000 m^3/ h.

7.3 Solidification

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

Dugong has high pour points of its residues (18-27 °C), and a possible remaining water-free residue may therefore have a potential to solidify at sea, particularly in winter condition as shown for the pour point prediction in Figure 5-4.

7.4 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion in the early stages of weathering. However, as water is mixed into the oil and emulsions are formed, the total volume will increase. Figure 7-2 shows example of the predicted mass balance of remaining surface emulsion and surface oil as a function of weathering of Dugong at 10 m/s windspeed at 5 and 15 °C. The figure shows an increase in the volume of emulsion relative to the volume og released oil with a factor of 2-2.5.

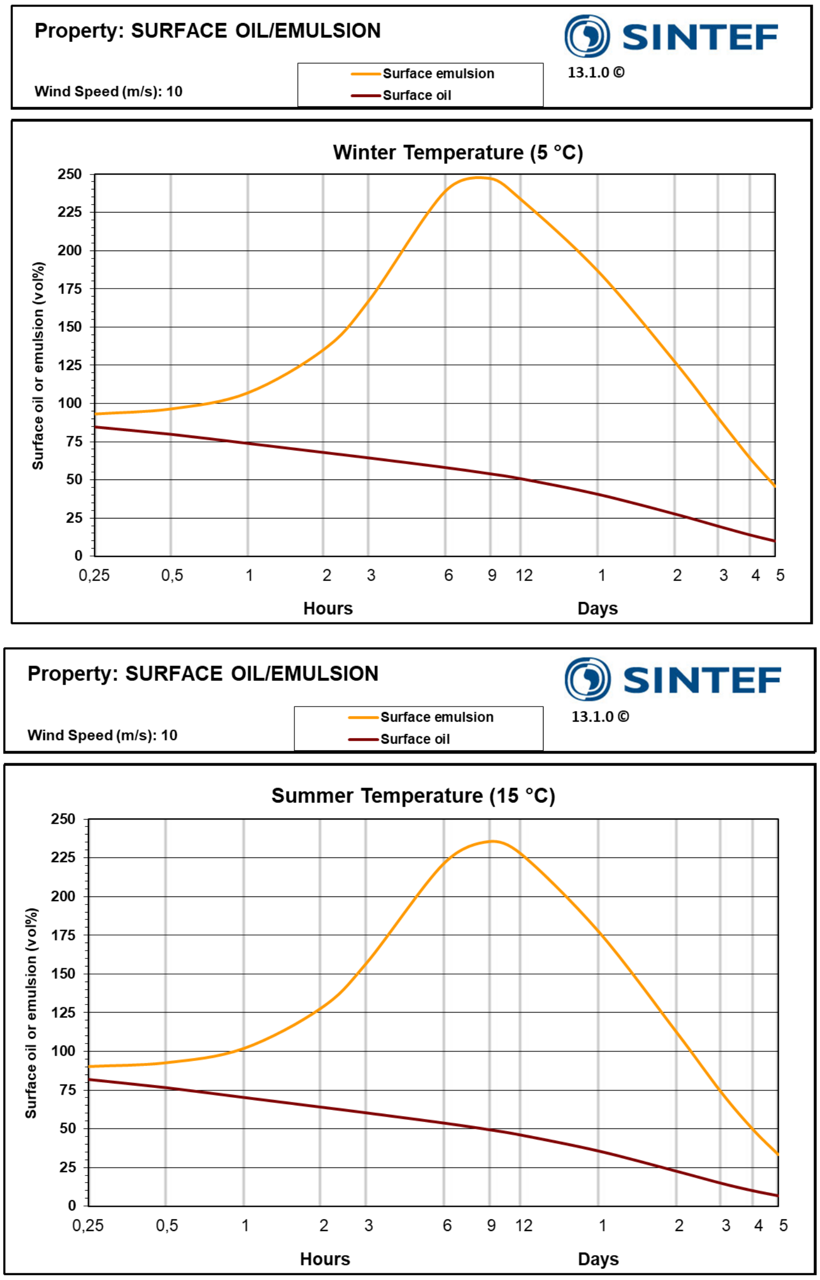


Figure 7-2 Difference in the total slick volume due to emulsification compared to non-emulsified oil of Dugong. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 °C and 15 °C.

7.5 Entrained oil and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g., on the surface, underwater) and environmental conditions (temperature, wind, waves). Entrained oil and evaporation are the main weathering processes that reduce the surface oil volume from a spill. The remaining surface oil after a release depends on the wind speeds and typically oils are more persistent on the sea surface with lower wind.

Figure 7-3 shows the predicted remaining surface oil over time for different wind speeds at 5 and 15 °C for Dugong. There is only some minor difference in lifetime between 5 and 15 °C for Dugong. At high wind speeds of 15 m/s, no oil is predicted to remain on the sea surface after 2-3 days of weathering at 15 °C. Lower wind speeds will not provide sufficient energy to remove Dugong entirely from the surface within the first 5 days. For the lowest wind speed (2 m/s), the prediction indicates about 65-72 % of the spilled oil remains on the sea surface after 5 days. Considerably larger spills are expected to produce longer lifetimes, and spesific modelling may be necessary.

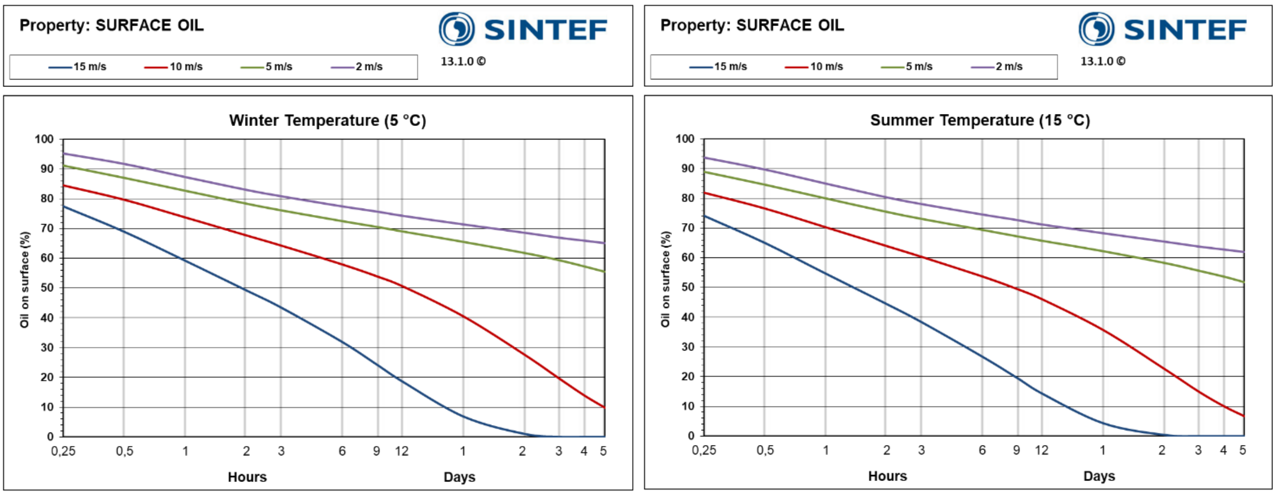


Figure 7-3 Remaining surface oil under different sea states for Dugong at 5 °C and 15 °C. Release rate 80m^3/h.

7.6 Film thickness from surface release

In general, mechanical recovery requires normal minimum film thickness >0.1-0.2 mm. Film thickness >0.05-0.1 mm is considered for application of oil spill dispersants. Lower film thicknesses are likely to disperse naturally under breaking waves conditions and may be enhanced in non-breaking waves by mechanical dispersion (chapter 7.7). Figure 7-4 shows the predicted film thickness of Dugong for a surface release at 5 and 15 °C with an initial surface release of 80 m^3/h, if the initial film thickens is sufficient high to emulsify, typically>0.1 mm. The increase in film thickness after few hours is due to emulsification that is most pronounced at 15 °C (summer conditions) than at 5 °C (winter conditions). Other factors than film thickness should also be considered when evaluate response options, as described in the next chapters.

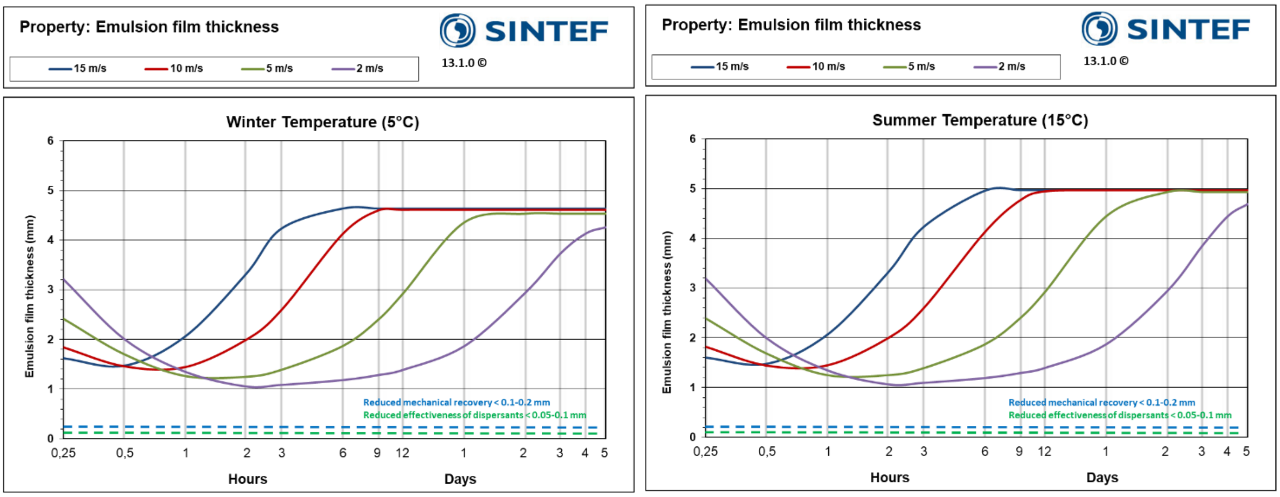


Figure 7-4 Predicted film thickness of Dugong emulsion from a surface (batch) release at 5 and 15 °C with terminal film thickness of 1 mm (80 m^3/h).

7.6 Mechanical recovery by boom and skimmer

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

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

The emulsion viscosities of Dugong are shown in Figure 7-5 and Figure 7-6 at 5 and 15 °C, respectively. For boom leakage of confined oil, the emulsion viscosity exceeds 1000 mPa.s after 1.5-2 hours at 10 m/s wind speed, but the time may be stretched up to about 1-day for very low wind speed (2 m/s). Overall, Dugong has a wide window of opportunity for use of traditional weir-skimmer head for viscosities <20 000 mPa.s.

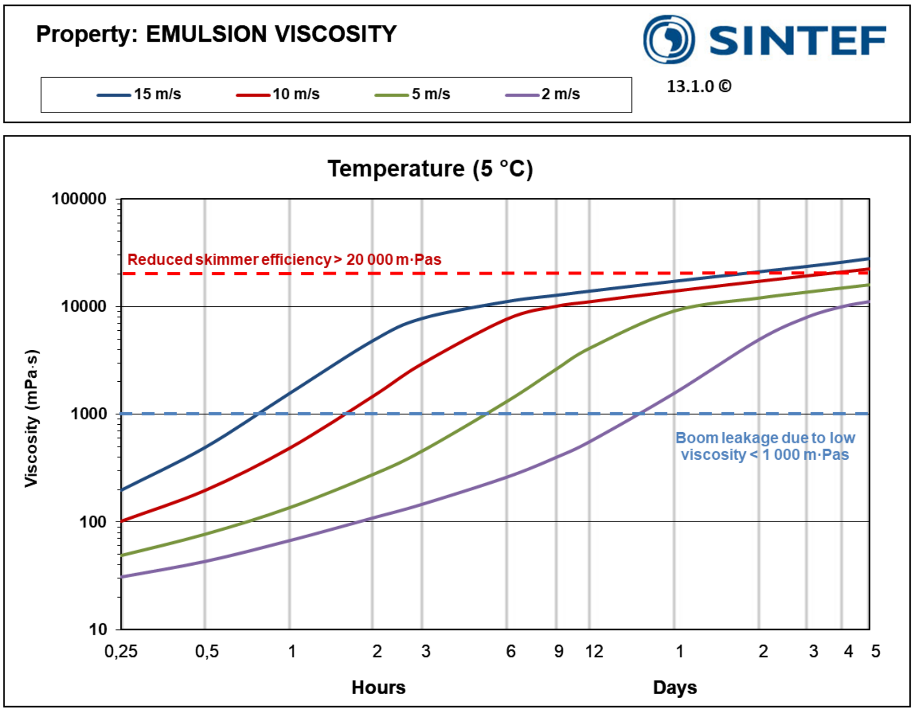


Figure 7-5 *Predicted emulsion viscosity for Dugong at 5 ° C compared with expected viscosity limits for boom leakage and poor flow to weir skimmers.*

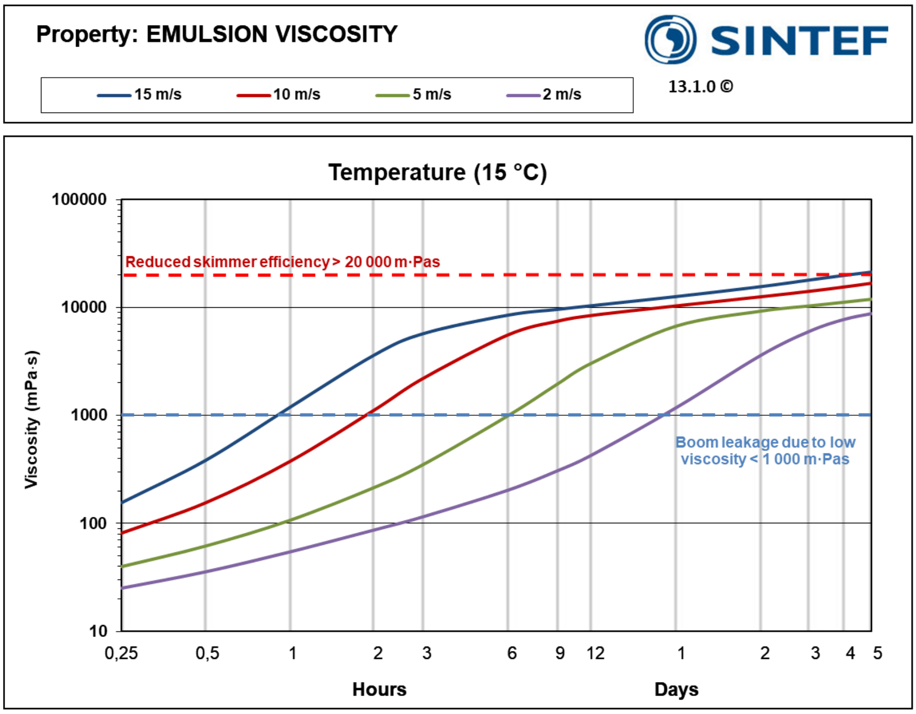


Figure 7-6 *Predicted emulsion viscosity for Dugong at 15 °C compared with expected viscosity limits for boom leakage and poor flow to weir skimmers.*

7.7 Mechanical dispersion by high-capacity water flushing

In general, mechanical dispersion by high-capacity water flushing without using dispersants could have a potential for oil spill with thin (initial) film thickness up to 0.2-0.3 mm and viscosities <150-300 mPa.s. In such cases, water flushing from high-capacity water flush boom and/or firefighting (FiFi) systems could possibly break up the oil/residue into smaller droplets and enhance the dispersion into the water column. Moreover, water flushing could also be used in combination with application of dispersant in calm weather condition to enhance dispersant efficiency with use of artificial energy some minutes after the dispersant treatment. This technology was tested in a full-scale trial (NOFO Oil-on-Water trial) in 2016 and described by Daling et al., 2017 and Sørheim et al., 2017.

However, for Dugong mechanical dispersion by water flushing only is not considered as a main strategy in oil spill response due to the formation of high emulsion film thicknesses (Figure 7-4) by emulsification, even the oil has low emulsion viscosities in the very early stage after an oil spill, as shown in Figure 7-5 and Figure 7-6. The rapidly emulsification of Dugong is the limiting factor for this strategy. However, use of water-flushing can be a supplementary method in "peripheral" areas with thin oil films, e.g., metallic /rainbow appearance.

7.8 Chemical dispersion

The viscosity limit for effective dispersant use was estimated to 3000 mPa.s and the viscosity limit for when the emulsified oil is not or poorly dispersible was estimated to 18000 mPa.s. The viscosity limits were based the high energy MNS-test on Dugong reflecting breaking waves >5 m/s wind. This means that Dugong requires breaking waves to break up a chemically treated slick. In cases were the oil (emulsion) is expected to be reduced dispersible, additional energy or use of a higher dispersant dosage by repeated dispersant application is recommended to possible enhance the dispersant efficiency. Providing additional energy through use of FiFi systems or thrusters after dispersant application may increase the dispersion effectiveness in calm weather condition.

The window of opportunity for use of dispersant Dasic Slickgone NS is presented in Figure 7-7 at 5 and 15 °C. The oil-emulsion is e.g., predicted to be (reduced) dispersible up to about 5 days at summer conditions, and 1.5-2 days in winter conditions with wind speeds 10-15 m/s, and longer time-window in calmer wind speeds (2-5 m/s wind speeds).

Solidification reduces the dispersant effectiveness, as the dispersant droplets will have a reduced ability to migrate into the oil layer and will easily be washed off by wave activity. In certain weather conditions, low emulsification rate may enhance formation of solidified lumps, particularly at winter temperature (5 °C). In a spill situation, the use of a simplified dispersibility testing kit is recommended to assess the potential for chemical dispersion.

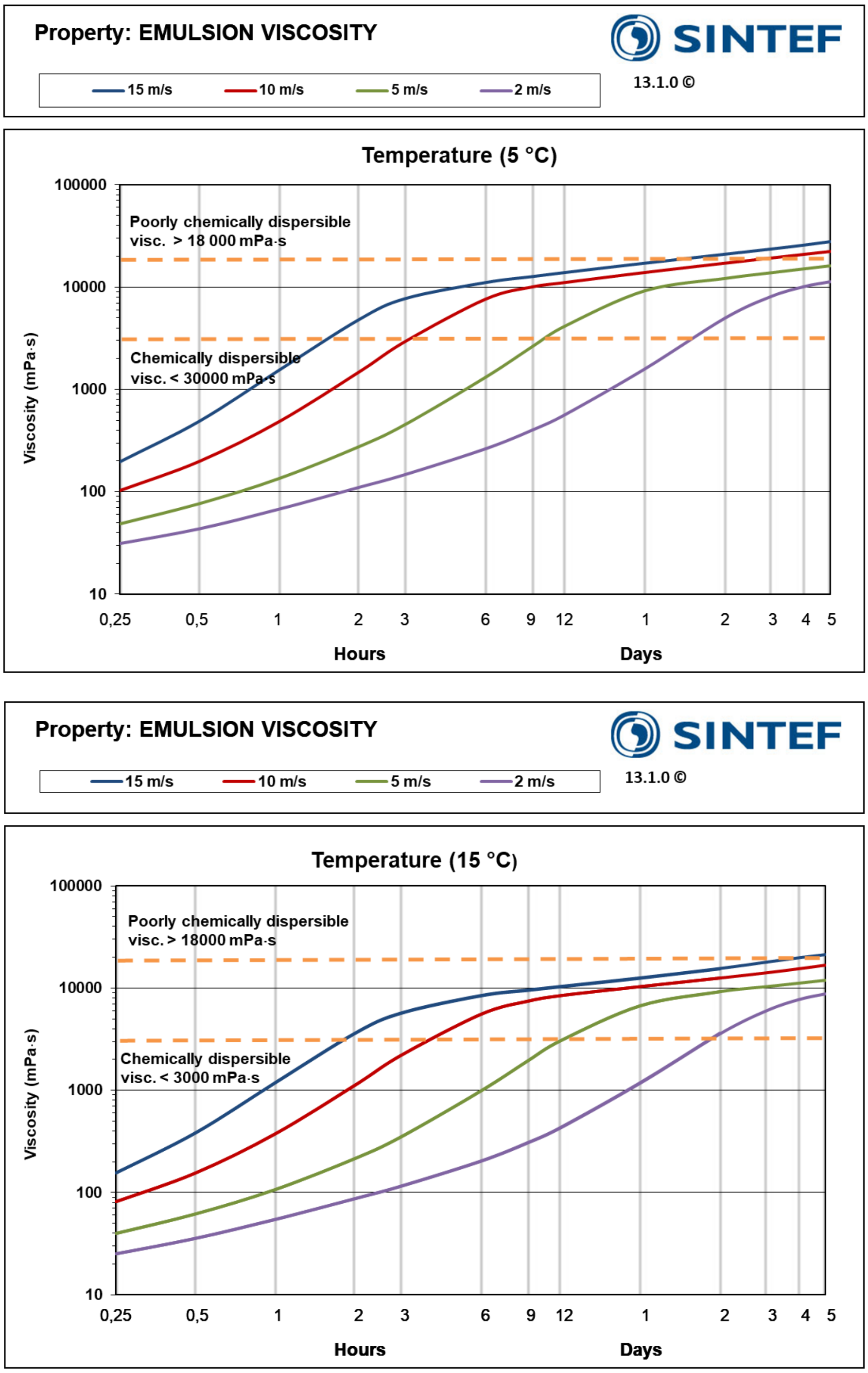


Figure 7-7 *Predicted emulsion viscosity for Dugong at 5 °C and 15 °C compared with dispersibility limits stated in chapter 3.*

8 Summary of response options of Dugong

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

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

Mechanical recovery:

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

Use of chemical dispersants*:*

- Emulsions of Dugong is found to be good dispersible with use of Dasic Slickgone NS for viscosities <3000 mPa.s (DOR 1:25) in non-breaking waves (<5m/s wind speeds), and not/poorly dispersible for viscosities >18 000 mPa.s assuming breaking waves conditions (>5m/s wind speeds).
- In the field, additional energy or higher DOR by repeated dispersant application may increase the dispersant effectiveness when the oil is reduced dispersible for viscosities in the range of 3000 -18000 mPa.s.

High-capacity water flushing (mechanical dispersion):

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

Monitoring and remote sensing:

- Monitoring and remote sensing should be used a support in a response operations for Dugong.

9 Comparison of Dugong to other Norwegian crude oils and condensates

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

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

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

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

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

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

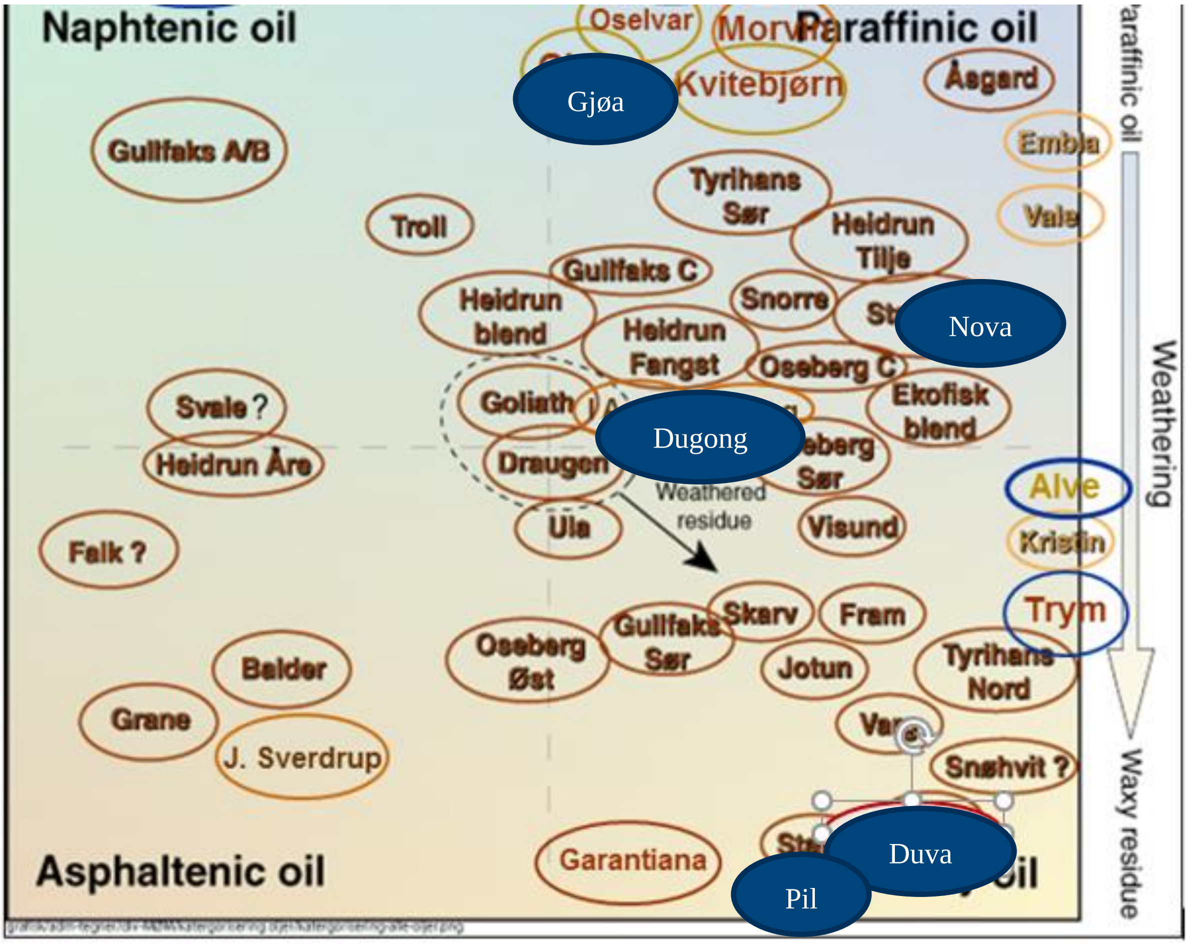


Figure 9-1 *Categorization of a selection of Norwegian crude oils from previous studies including Dugong, Duva, Nova (aka Skarfjell), Gjøa, and Pil (Fenja field).*

10 References

Bocard, C., Castaing, C. G. and Gatellier, C. 1984. "Chemical oil dispersion in trials at sea and in laboratory tests: The key role of the dilution process." Oil spill chemical dispersants: Research Experience and recommendations, ASTM STP 840. (T. E. Allen, ed.), Philadelphia, USA, pp. 125-142.

Brakstad, O.G., and Faksness, L.-G., (2000). Biodegradation of water-accommodated fractions and dispersed oil in the seawater column. Proceedings for the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Stavanger, 26-28 June 2000

Brakstad, O-G and A.G.G Lødeng 2005. Microbial diversity during micro biodegradation of crude oil in seawater from the North Sea. Microbial Ecology 49:94-104

Bridié, A.L., Wanders, T. H., Zegweld, W. V. and den Heijde, H. B., 1980. Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. Marine Poll. Bull., vol. 11, pp. 343-348.

Commission Internationale De L'Eclairage (CIE), No. 85, ISBN No. 3 900 734 22 4, 1989.

Daling, P. S., Brandvik, P. J., Mackay, D. and Johansen, Ø. (1990): Characterisation of crude oils for environmental purposes. Oil & Chemical Pollution 7, 1990, pp. 199-224.

Daling, P.S., Lewis, A., Sørheim, K.R., Gjesteland, I. 2017. Full-scale field testing of thin oil films from releases of light crude oil at sea. NOFO Oil-on-Water field trial in 2016. SINTEF report 2017:00030 Unrestricted. ISBN:978-82-21-40670-8.

Hokstad, J. N., Daling, P. S., Lewis, A. and Strøm-Kristiansen, T. 1993: Methodology for testing water-in-oil emulsions and demulsifiers. Description of laboratory procedures. Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC, Alberta June 14-15, 24 p.

Johansen, Ø. 1991. "Numerical modelling of physical properties of weathered North Sea crude oils." DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open.

Leirvik, F., Moldestad, M. and Johansen, Ø., 2001. Kartlegging av voksrike råoljers tilflytsevne til skimmere.

McAuliffe, C.D. (1987). Organism exposure to volatile/soluble hydrocarbons from crude oil spills - a field and laboratory comparison. In: Proc. 1987 Oil Spill Conference. Washington, D.C., American Petroleum Institute. pp. 555-566.

Mackay, D. and Zagorski, W. 1982. "Studies of W/o Emulsions". Report EE-34: Environment Canada, Ottawa, Ontario.

Mackay, D. and Szeto, F. 1980. "Effectiveness of oil spill dispersants - development of a laboratory method and results for selected commercial products." Institute of Environmental Studies, University of Toronto, Publ. no. EE-16.

McDonagh, M., Hokstad, J. N. and Nordvik, A. B. 1995. Standard procedure for viscosity measurement of water-in-oil emulsions. Marine Spill Response Corporation, Washington, D.C. MRSC Technical Report Series 95-030, 36 p.

Nordvik, A. B., Daling, P. and Engelhardt, F. R. 1992. Problems in the interpretation of spill response technology studies. In: Proceedings of the 15th AMOP Technical Seminar, June 10-12, Edmonton, Alberta, Canada, pp. 211-217.

Perry JJ (1984). Microbial metabolism of cyclic alkanes: Atlas RM (Ed) Petroleum Microbiology Macmillan Publ Co New York pp 61-98

Ramstad, S., Pettersen, T-A., Krause, D.F.2014. Weathering of Skarfjell crude oil. Oil behaviour and properties related to oil spill response. SINTEF report A26006. ISBN 9788214057331. Unrestricted.

Reed M., and C. Turner, 1991: Field Tests of Satellite tracked buoys to simulate oil drift. In Proceeding of the IOSC, SanDiego, CA. US., pp. 619 – 628

Reed, M., Turner, C. and Odulo, A. 1994. The role of wind and emulsification in modelling oil spill and surface drifter trajectories. Spill Science and Technology, Pergamon Press (2): .143-157.

Resby, J.L.M. 2004. Snorre TLP, Snorre B og Vigdis oljene- Forvitringsegenskaper relatert til beredskapstiltak. SINTEF rapport: STF66 F0401.

Singsaas, I., Daling, P.S., Moldestad M. Ø and Jensen, H. 2000.Samle rapport: Effektivitet av Foxtail skimmer på IF-30 bunkersolje og forvitret Ula, Balder, Jotun og Troll råoljer. SINTEF report. STF66 A00082

Singsaas, I., Daling, P. S. and Jensen, H., 1993. Meso-scale laboratory weathering of oils. IKU report 22.2042.00/04/93, IKU, Trondheim, Norway, 81 p.

Stiver, W. and Mackay. D. 1984. Evaporation rate of spills of hydrocarbons and petroleum mixtures. Environ, Sci. Technol., vol. 18 (11), pp. 834-840.

Singsaas, I., Sørheim, K. R. and Daling, P.S., 2017. Project recommendations for response to oil spills from condensates and light crude oils. SINTEF report no.: OC2017A-205. ISBN: 9788271743208.

Sørheim, K.R., Altin, D., and F., Leirvik., 2010. Gjøa crude oil-Weathering properties related to oil spill response, chemical and toxicological characterization of WAF". SINTEF report A20859. ISBN:9788214051490. Unrestricted.

Sørheim, K.R., Daling, P.S., and F., Leirvik., 2017: Mekanisk dispergering av tynne oljefilmer. Oljevern 2015. WP048. SINTEF rapport: OC2017 A-125, ISBN: 978-82-7174-300-0.

Sørheim, K.R., Pettersen, T-A., Johnsen, M., Hellstrøm, K.C. 2021: Duva - Weathering Properties and behaviour at sea. SINTEF report: OC2021 A-108, ISBN: 978-82-7174-428-1.

Sørheim, K.R., and K.C., Hellstrøm. 2021. Characterization of oil properties and weathering studies on Statfjord crude oils. SINTEF report: OC2021 A-090, ISBN: 978-82-7174-424-3

A The behaviour of oil on the sea surface

A.1 The chemical composition of crude oils and condensates

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

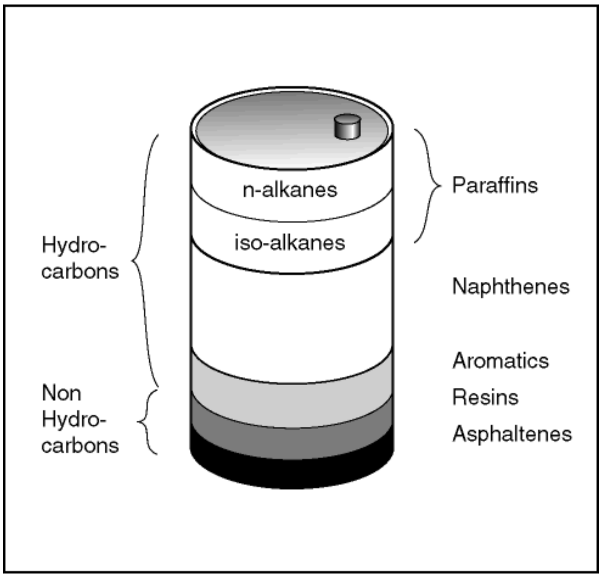


Figure A-1 The chemical composition of crude oils.

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

Paraffins

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

Naphthenes

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

Aromatics

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

Non-hydrocarbons

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

Resins

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

Asphaltenes

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

A.2Main oil categories related to weathering

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

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

- Crude oils
- Light oils
- Condensates

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

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

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

A.3Physical properties of crude oils

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

Density

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

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

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

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

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

A.3.1 Rheological properties

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

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

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

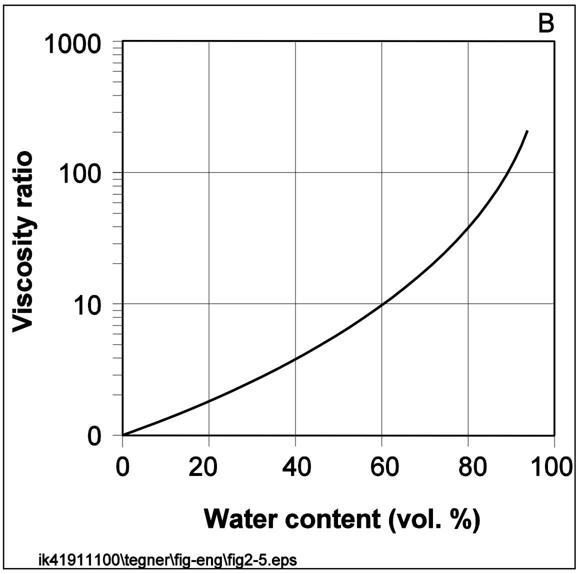


Figure A-2 Example of viscosity ratio as a function of water content.

A.3.2 Pour point

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

A.3.3 Distillation curve

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

A.3.4 Flash point

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

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

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

A.4The behaviour of crude oil spilled at sea

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

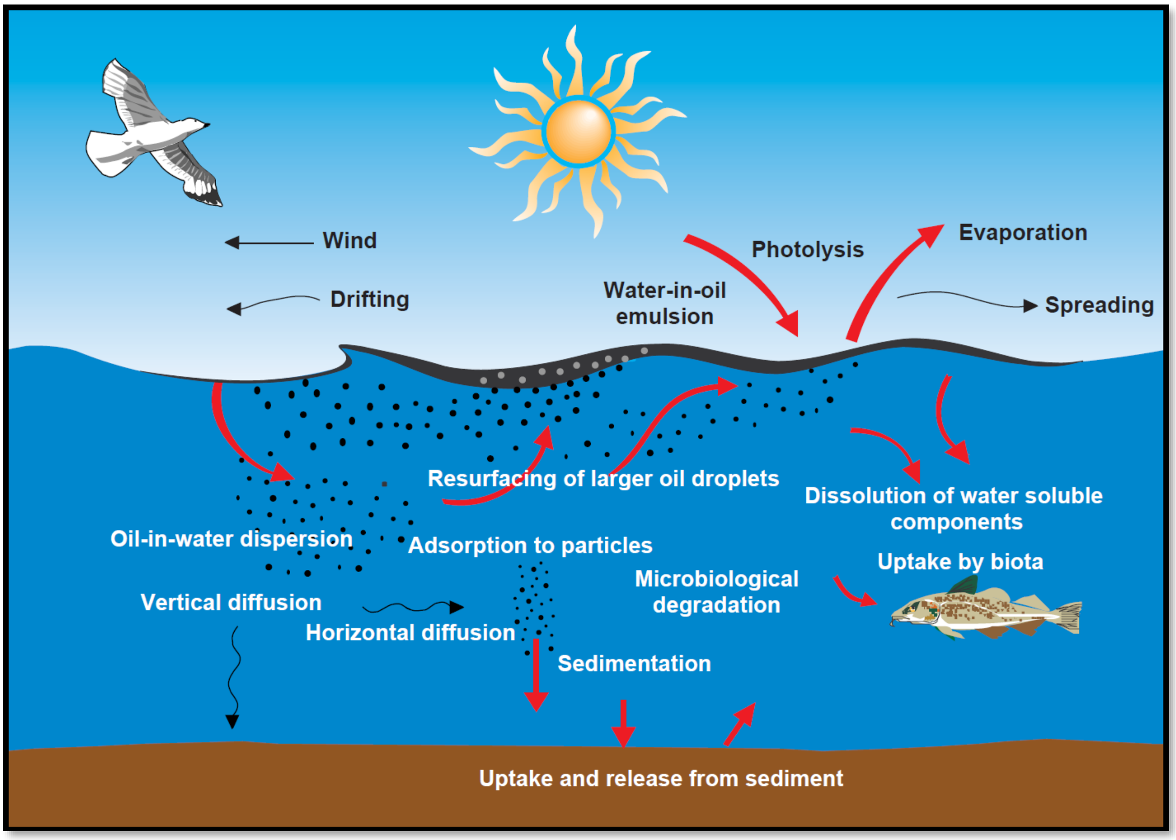


Figure A-3 Illustrating the weathering processes that take place when oil is spilled on the sea surface.

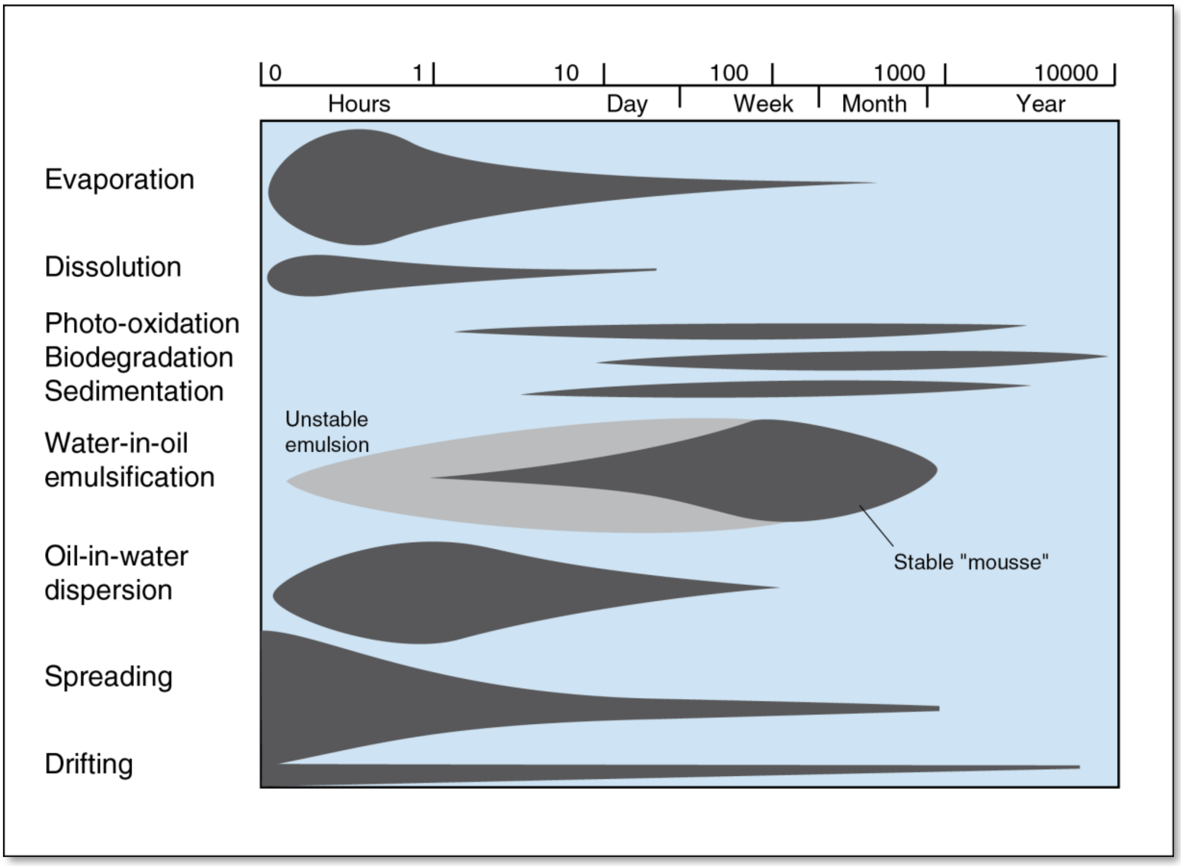


Figure A-4 Weathering processes' relative importance over time. Note: logarithmic scale.

A.4.1 Evaporation

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

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

A.4.2 Spreading

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

Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into "wind rows" aligned in the direction of the wind, see Figure A-5. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that most of the total oil slick area consists of a thin film (<1 µm oil thickness) that only contains 10% of the oil volume. Most of the oil volume (~90%) is in small patches of w/o emulsions with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area.

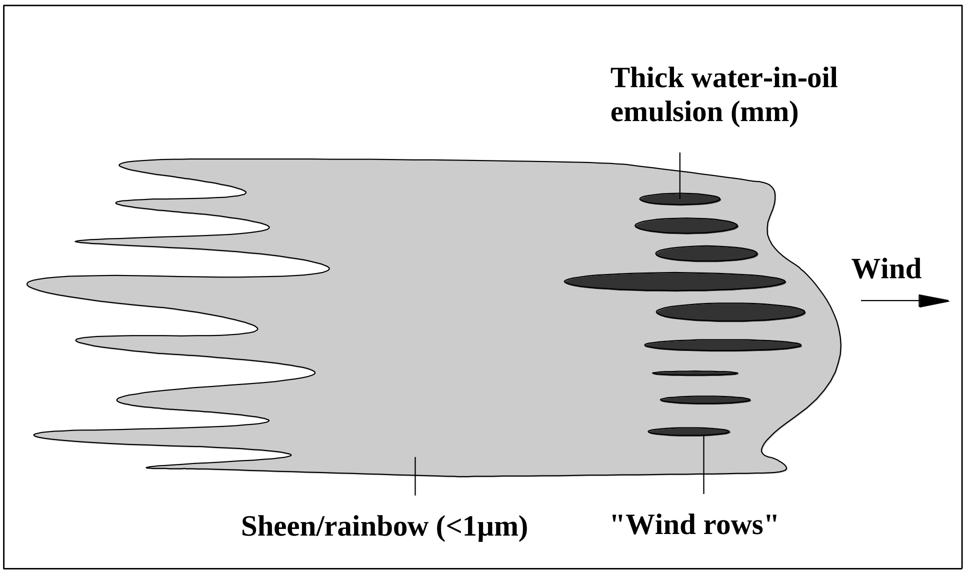


Figure A-5 *The spreading of oil spilled on the sea surface and the distribution within the oil slick.*

A.4.3 Drift of an oil slick

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

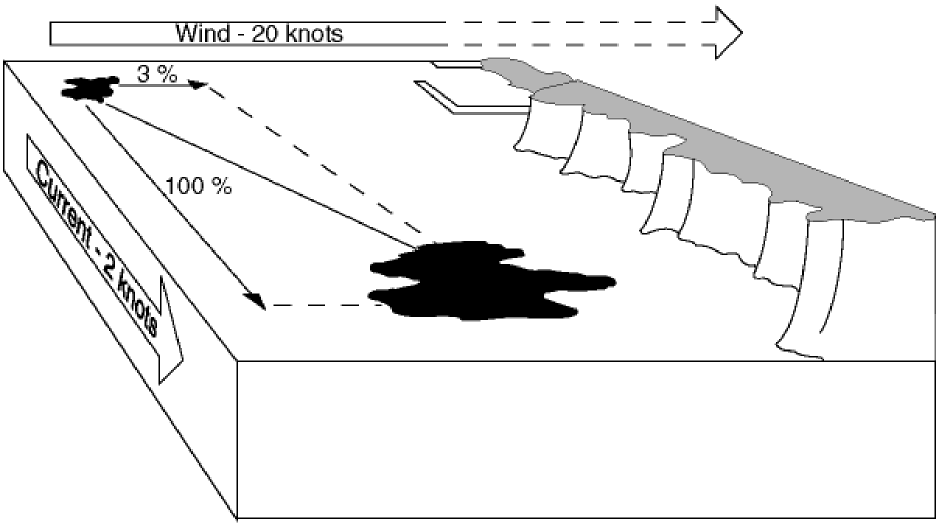


Figure A-6 *An illustration showing how wind and current can influence the drifting of an oil slick.*

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

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

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

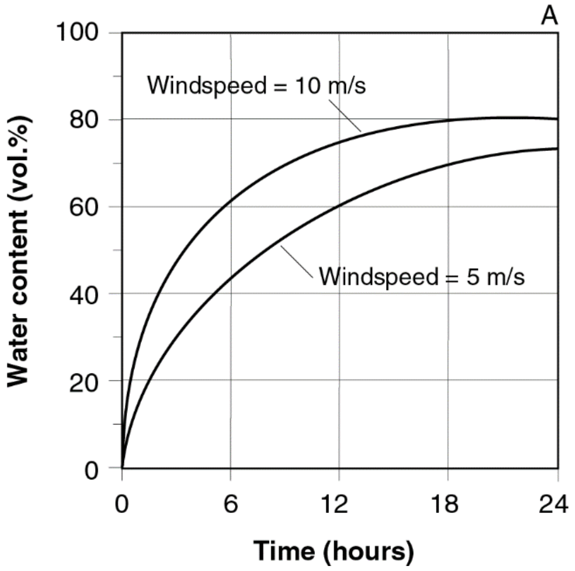


Figure A-7 *Example of how weather conditions influence the w/o emulsion formation for typical oils.*

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

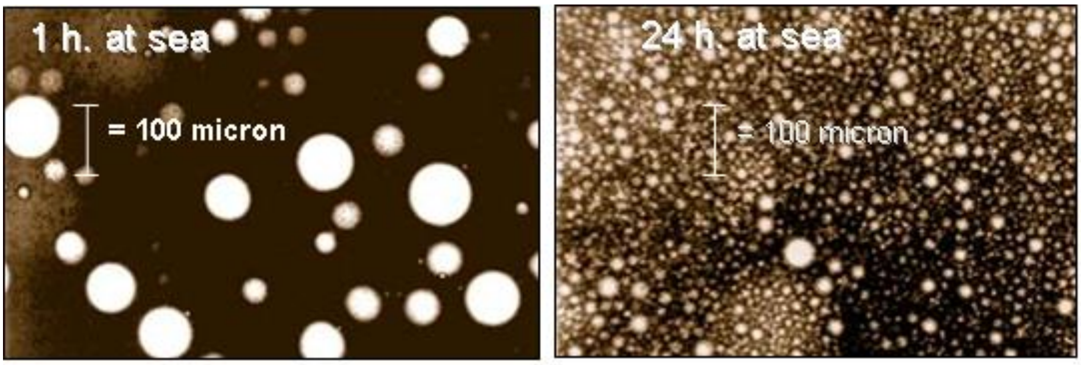


Figure A-8 Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder.

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

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

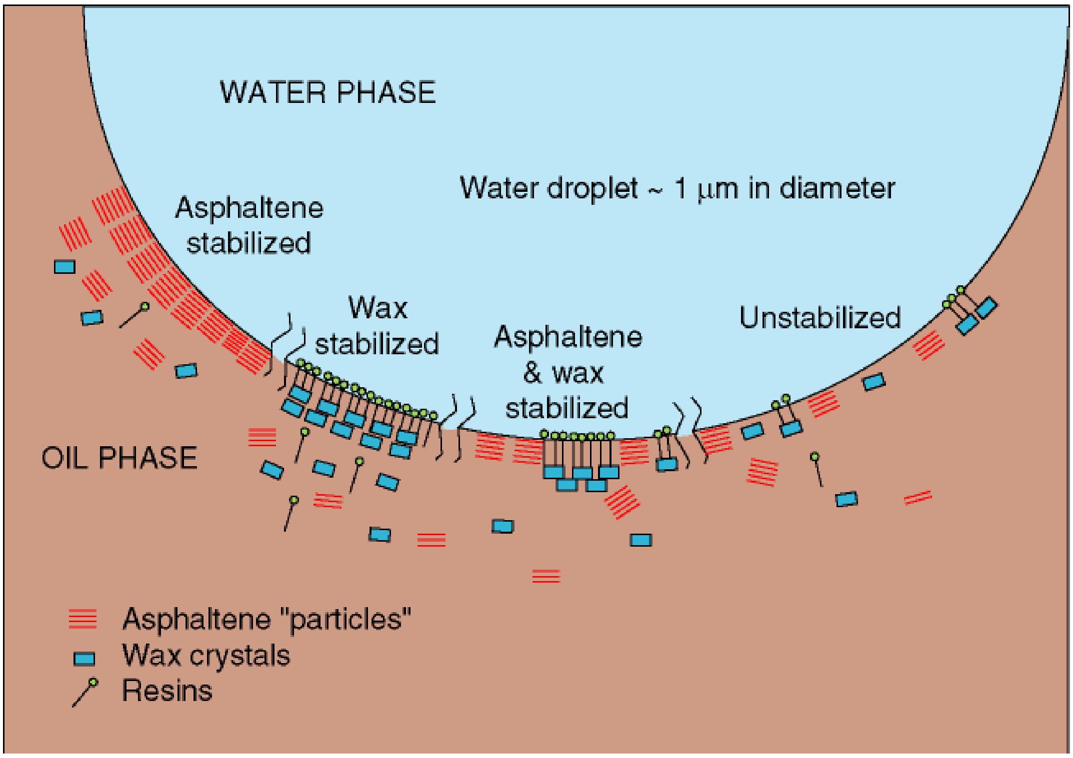


Figure A-9 Interfacial layer stabilized by wax and asphaltenes in w/o emulsion.

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

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

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

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

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

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

A.4.6 Water solubility

The water solubility of saturated hydrocarbons is generally very low, while lower molecular weight aromatic compounds are water-soluble to some extent; particularly aromatics, such as BTEX, 2-ring PAH and paraffin's up to C_7) have a potential to be dissolved in the water column (McAuliffe, 1987). Within the various types of hydrocarbons, the water solubility decreases from aromatics to naphthenes and from *iso*-alkanes to *n*-alkanes. In each series, the water solubility decreases with *increasing* molecular weight.

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

A.4.7 Photo-oxidation

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

A.4.8 Biodegradation

Seawater contains an abundance of microorganisms that can break down all types of oil components. Various microorganisms prefer specific oil components as their energy source. Bacteria prefer to degrade oil in contact with water and the rate of biodegradation depends on the water/oil interface area. The interface area increases as the oil is spread over the sea surface in a thin layer or by chemical or natural dispersion of oil into the water column. Important factors influencing the biodegradation rate are temperature, the concentration of available nutrients (i.e. nitrogen and phosphorus), oxygen, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the high molecular weight/heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched *iso*-alkanes > cyclic alkanes > cyclic naphthenes > aromatics> resins > asphaltenes (Perry, 1984).

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

A.4.9 Sedimentation

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

A.4.10 Deep water releases

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

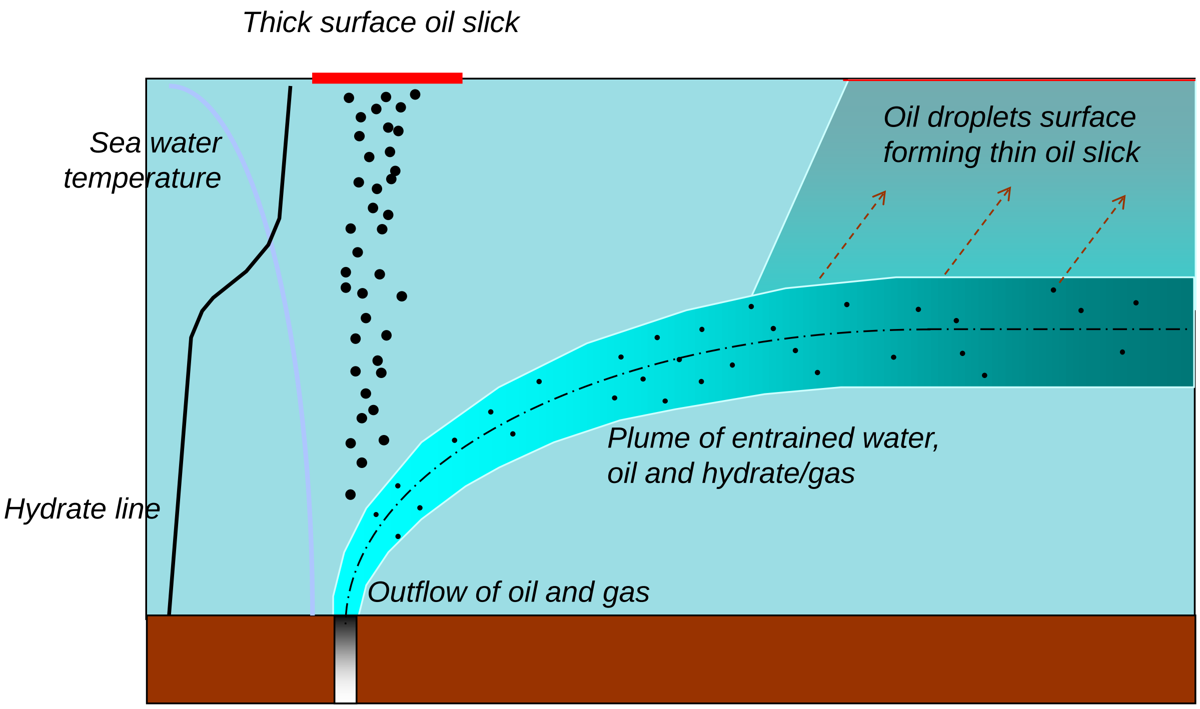


Figure A-10 Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil.

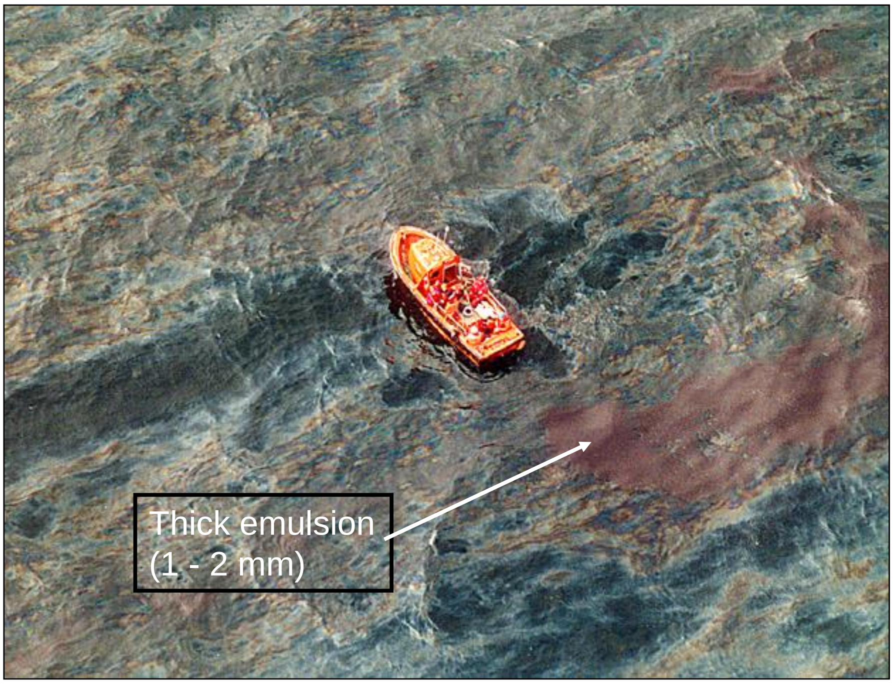


Figure A-11 Surface oil slick (initial thickness > 200 µm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying like an oil slick from a surface batch release (from Leirvik et al., 2011).

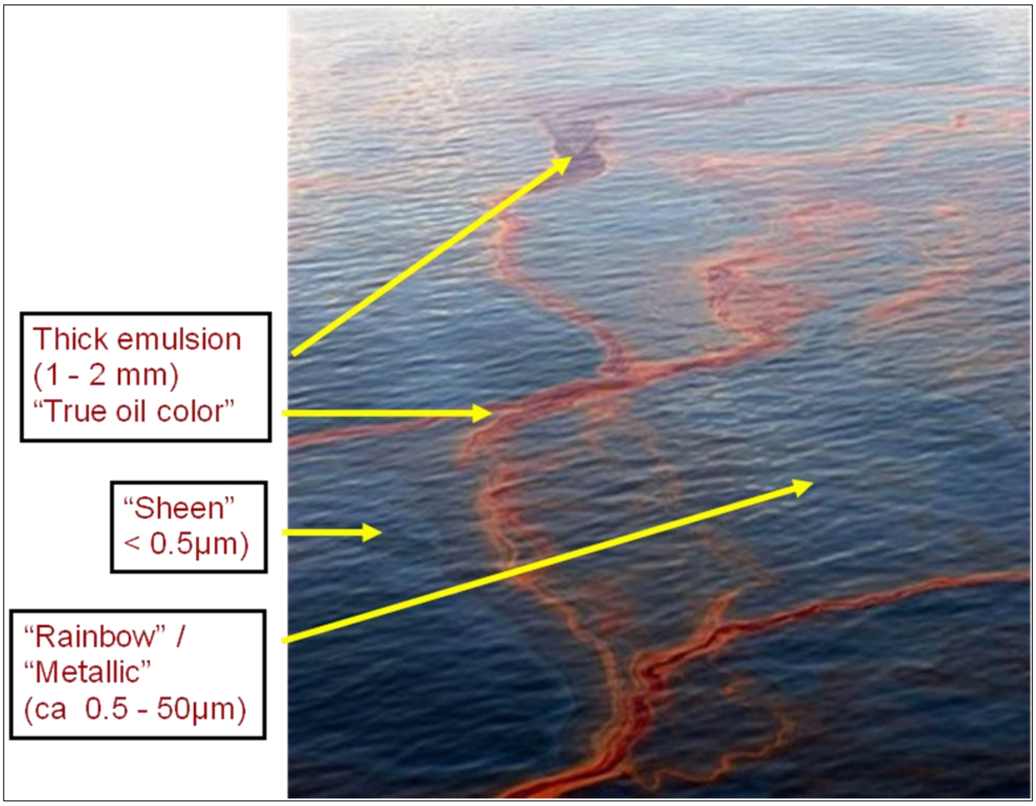


Figure A-12 Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release.

A.4.11 Shallow releases

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

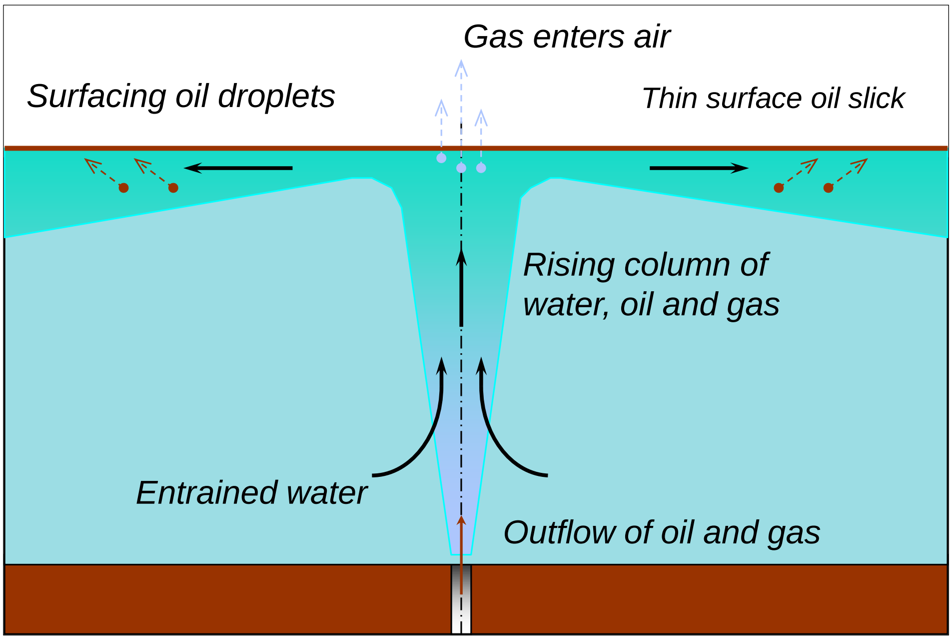


Figure A-13 *Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m).*

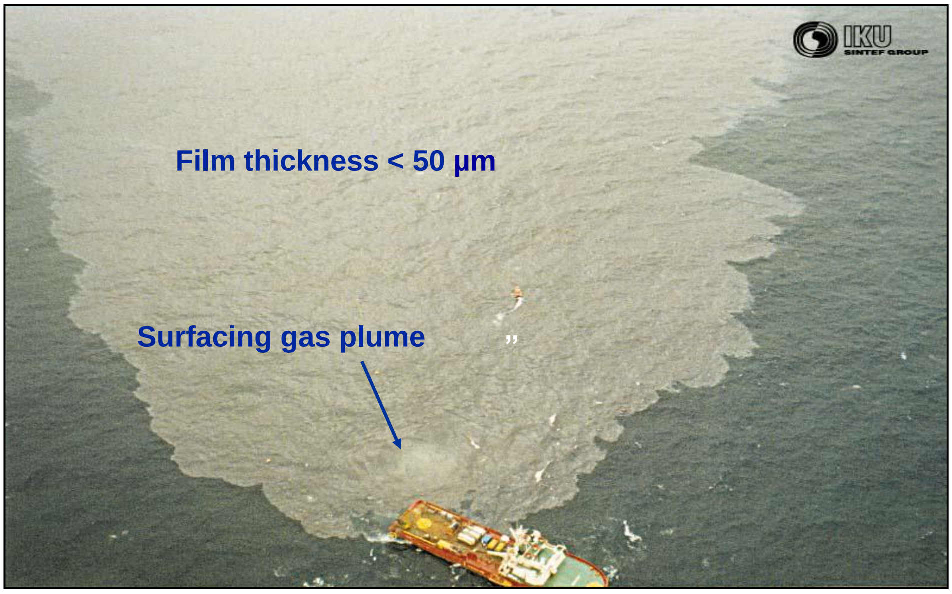


Figure A-14 *Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil did not emulsify and had a very limited lifetime (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind).*

B Experimental setup and HSE

B.1Oil sample and test temperature

SINTEF Ocean received 2x25 (50 litres) litres steel drums of Dugong crude oil on 13.01.2022. The oil sample were registered in LIMS and given SINTEF ID: 2022-185. The weathering study (small-scale and meso-scale) were performed at 13 °C. The oil sample was pre-handled, heated to about 50 °C and homogenised before distillation and further analysis (see HSE, below)

Figure B-1 Dugong crude oil 2x25L. RS-107994 Neptune Dugong 34/4-16S

B.2 HSE - Water content and Mercury analysis

Water content in the oil phase was quantified by use Karl Fisher titration for HSE and risk assessment prior to the topping/distillation step to simulate evaporative loss at sea by topping/distillation. The water content was well below the HSE limit < 2 vol. %, and no extra precautions were needed for Dugong prior to topping.

Mercury (Hg)-analysis was measured on the Dugong batch, received at SINTEF Ocean. In addition, the content of mercury was also analyzed on a selection of other Neptune crude oils for comparison (as in agreement with Neptune Energy). The results were as followed:

- Dugong fresh crude oil: Hg < 5ng/g
- Dugong weathered 250°C+ residue: Hg <5 ng/g
- Duva fresh crude oil: Hg <9 ng/g
- Pil (Fenja) fresh crude oil: Hg <5 ng/g
- Gjøa fresh crude oil: Hg <5 ng/g

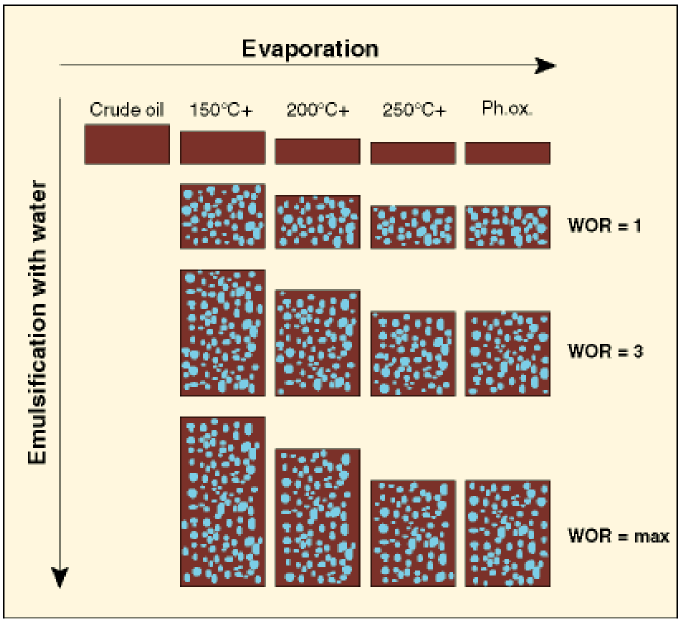
The mercury analysis was conducted by Intertek UK, ASTM method D7622. The results indicate very low content of mercury for all the crude oils tested, including the weathered residue of Dugong. This harmonizes well with the result from the Intertek Dugong Crude Oil Assay Report No: 21-010335-1-ABDN, showing Hg content lower than the detection limit of <5 ng/g (ppb).

Hg-vapor and particles in the air atmosphere were also measured in the bench-scale laboratory when pre-handling the crude oil (e.g., heating the oil to 50 °C, homogenization etc.) and topping, and in addition to weathering the meso-scale laboratory during the first day. The measurements are based on random samples. Occupation hygienist at Anonova Helse (Trondheim) was responsible for experiment set-up equipment's, and analysis. The Hg content was conducted by Eurofins Environment Testing. A standard setup for mercury was chosen, with a quartz filter (37 mm, for aerosol/particle fraction) connected in series with adsorption tubes (carulite, for vapor fraction) and connected a working environment pump (SKC AirChek) with flow restrictor to achieve low flow pump speed on 0.2 l/min. The sampling method is in accordance with standard NS ISO 17733:2015.

The samplers (opening on the filter) were mounted in the workers' breathing zone, and the sampling time was adapted to the lab experiments on the relevant days in the period 21.02-05.04.22. The sampling times were between 5 and 7.5 hours, depending on what was practical work tasks and time spent in the lab on the relevant days. The results for mercury vapor (and possibly aerosols/particles) sampled gave no findings above the quantification limit for the analysis method. In all samples < 1.0-1.1 (max) µg/m^3 Hg was recorded. According to the occupational hygienist, the air atmosphere measurements showed low and completely unproblematic levels of mercury.

B.3 Small-scale laboratory testing

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



WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

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

B.4 Evaporation

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

B.5 Physical and chemical analysis

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

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

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

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

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

Chemical characterization by GC-FID and GC-MS

- The distribution of hydrocarbons (nC_5-nC_{40}) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC-FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols, and alkylated phenols (C_0-C_4) were completed using an Agilent 6890 Gas Chromatograph coupled with 5973 MSD detector (GC-MS) operating in SIM mode (Selected Ion Monitoring)

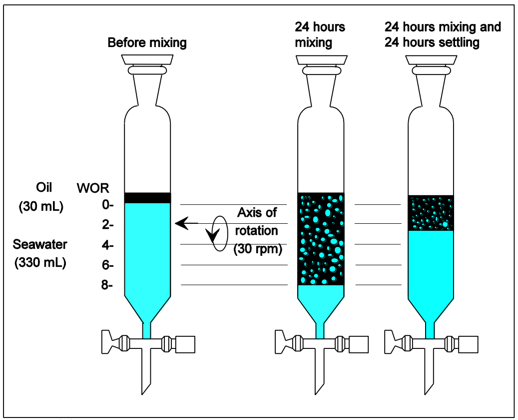
The volatile components were in the range of nC_5-nC_{10} and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode and using a modified version of the EPA 8260 analysis method).

B.6 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.



6621/handbøker/grafisk/fig-eng/3skilletrakter.eps

Figure B-3 Principle of the rotating cylinder method

B.7 Chemical dispersibility testing

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

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

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

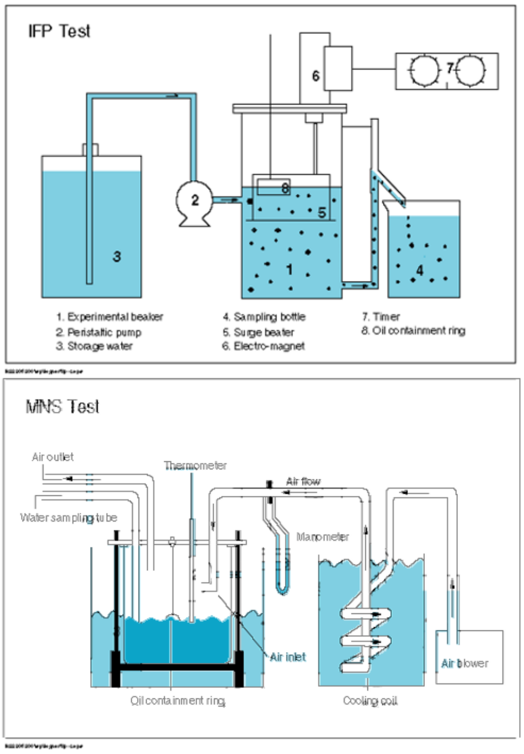


Figure B-4 *Laboratory apparatus for effectiveness testing of dispersants.*

B.8 Meso-scale laboratory testing

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

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

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

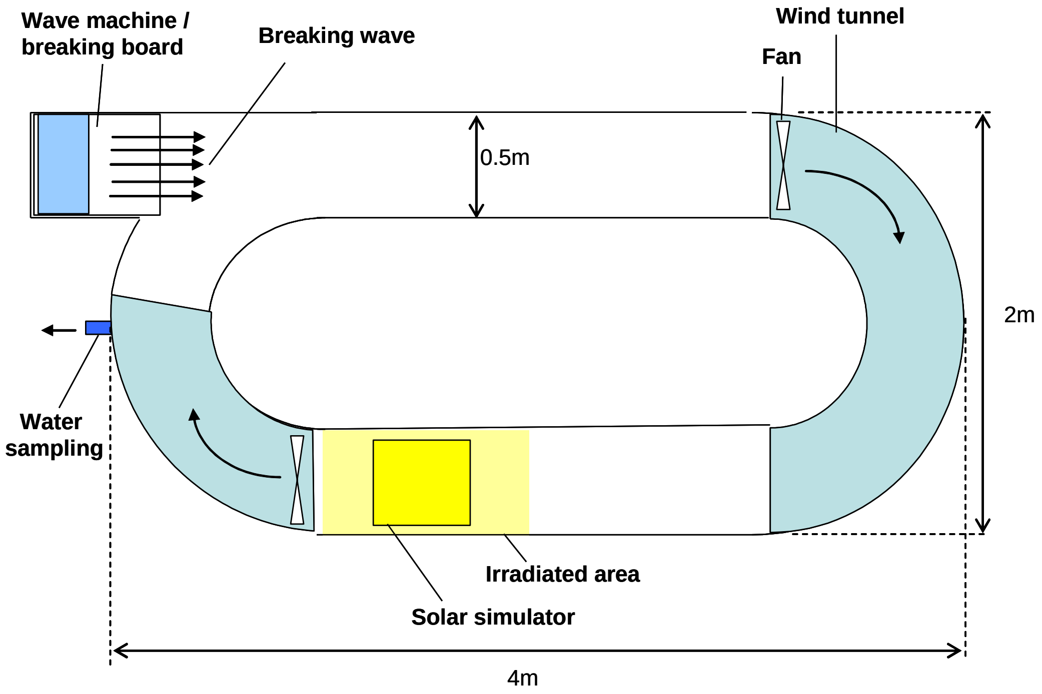


Figure B-4 Schematic drawing of the meso-scale flume.

In a meso-scale flume study, a standard volume sample (9 L) of the relevant oil is carefully released on the seawater surface under calm conditions. The wave machine and fans are then started, and the experiment begins. A reference water sample is collected before the beginning of the experiment. Both surface oil/emulsion and water column are sampled frequently the first 6 hours, then after 12 hours and subsequently every day. After three days (72 hour) dispersant is applied to the surface emulsion. Water samples are then collected more frequently. The addition of dispersant may be repeated once or twice, in which case water samples are also collected.

Analysis of surface oil/emulsion

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

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

Analysis of water samples

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

Solar simulation in the meso-scale flume

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

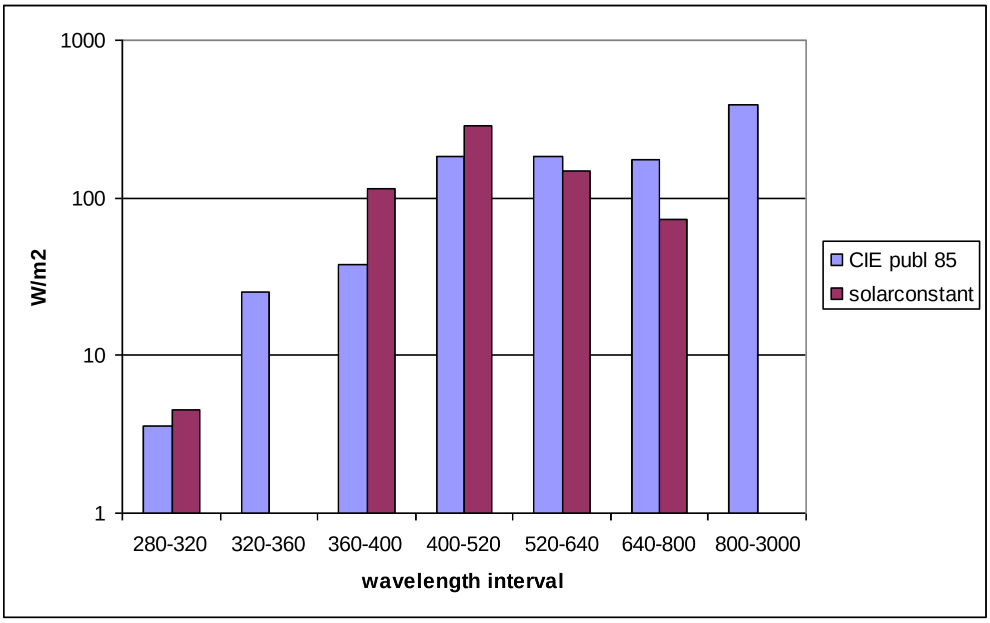


Figure B-5 Measured wavelength compared to standard spectrum suggested in CIE publication 85.

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

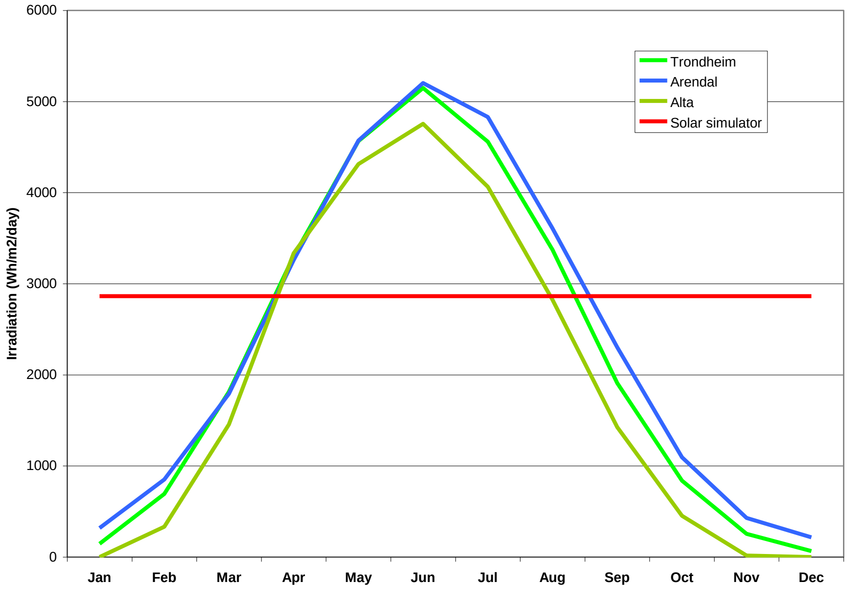


Figure B-6 Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume.

C Input data to SINTEF Oil Weathering Model (OWM)

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

Table C-1 Physical and chemical properties Dugong

Properties of fresh oil	**Dugong**
Density (g/mL)	0.8325
Pour point (°C)	3
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	15
Flash point (°C)	-
Asphaltenes (wt. %)	0.33
Wax Content (wt. %)	5.06
Dispersible for visc. <	3000
Not dispersible for visc. >	18000

** Measured at shear rate 100 s^{-1}-: Not analyzed /no data*

Table C-2 True boiling point (TBP) curve of Dugong

TBP based on results from Intertek, ref: 21-010335-1-ABDN. Adjusted slightly by SINTEF to fit the topping results.

Temp. °C	**Dugong Vol. %**
25	1.0
50	3.0
100	13.0
150	22.5
200	33.0
250	43.0
300	52.5
400	70.5
500	84.0
550	88.0

Table C-3 Lab weathering data for Dugong, 13 °C

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Boiling Point Temp. (°C)	-	196	253	303
Vol. Topped (%)	0	22.4	33.3	42.7
Weight Residue (wt. %)	100	80.8	70.7	61.5
Density (g/mL)	0.8325	0.8666	0.8809	0.8935
Pour point (°C)	3	18	21	27
Flash Point (°C)	-	37.5	77.0	113
*Viscosity of water-free residue (mPa.s =cP)	15	83	171	348
Viscosity of 50% emulsion (mPa.s = cP)**	-	396	838	4114
Viscosity of 75% emulsion (mPa.s = cP)**	-	1455	4054	8645
Viscosity of max water (mPa.s = cP)**	-	2375	9340	18611
Max. water cont. (vol. %)	-	90.9	85	77.9
(T1/2) Halftime for water uptake (hrs)	-	0.14	0.23	0.34
Stability ratio	-	0.98	0.99	1

** Measured at shear rate 100 s^{-1} ** Measured at shear rate 10 s^{-1} - No data – not measured*

D Chemical characterization – OSCAR composition file

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

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

Wt.%	Comp. group no.	Dugong SINTEF ID 2021-4882
2.400	1	C1-C4 gasses (dissolved in oil)
3.300	2	C5-saturates (n-/iso-/cyclo)
2.930	3	C6-saturates (n-/iso-/cyclo)
0.370	4	Benzene
3.600	5	C7-saturates (n-/iso-/cyclo)
1.040	6	C1-Benzene (Toluene) et. B
6.060	7	C8-saturates (n-/iso-/cyclo)
1.250	8	C2-Benzene (xylenes; using O-xylene)
3.240	9	C9-saturates (n-/iso-/cyclo)
0.810	10	C3-Benzene
3.800	11	C10-saturates (n-/iso-/cyclo)
0.070	12	C4 and C4 Benzenes
5.307	13	C11-C12 (total sat + aro)
0.023	14	Phenols (C0-C4 alkylated)
0.382	15	Naphthalenes 1 (C0-C1-alkylated)
7.418	16	C13-C14 (total sat + aro)
0.000	17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0
0.000	18	Naphthalenes 2 (C2-C3-alkylated)
0.000	19	C15-C16 (total sat + aro)
0.478	20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)
5.022	21	C17-C18 (total sat + aro)
0.326	22	C19-C20 (total sat + aro)
5.174	23	C21-C25 (total sat + aro)
5.500	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
8.698	25	C25+ (total)

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