

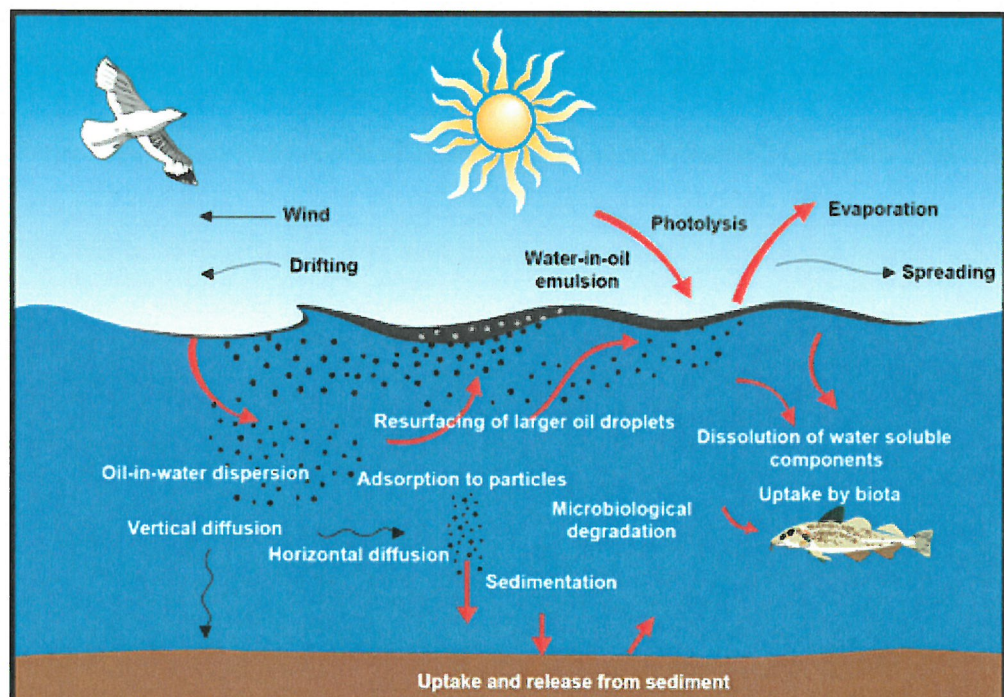
# Report

## Limited laboratory study of Luno II Blend in comparison with existing weathering properties of Luno II A

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**ABSTRACT**

The aim of this project was to assist Lundin Norway AS to select a model oil as input data for environmental risk and oil spill contingency analysis for a blend from segment B and C from the Luno II field.

A pre-evaluation of data from an earlier weathering study on segment A (Luno II A) and crude assay / PVT data for segment B and C indicated that the existing weathering data for segment A could possibly be used as a model oil.

A limited laboratory study of the blend was suggested to verify the conclusions. The properties of the new blend were compared with the existing weathering data of Luno II A. The obtained data were used in SINTEF's Oil Weathering Model (OWM) in combination with the existing data to generate new predictions for comparison with the previous predictions for Luno II A.

Based on a total evaluation from the laboratory study and OWM predictions, the previous Luno II A could be recommended as a model oil for the new Luno II blend. Due to the lower density and viscosity of Luno II blend, the existing weathering data of Luno II A can be considered as a conservative alternative for Luno II blend.

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# Table of contents

<b>1</b>	<b>Background and scope .....</b>	<b>4</b>
<b>2</b>	<b>Laboratory analysis and results .....</b>	<b>4</b>
<b>3</b>	<b>OWM predictions .....</b>	<b>8</b>
<b>4</b>	<b>Summary &amp; conclusion .....</b>	<b>8</b>
<b>5</b>	<b>References .....</b>	<b>9</b>

## APPENDICES

A – Pre-evaluation of Luno II

B – GC-FID chromatograms

C – OWM predictions

## 1 Background and scope

The aim of this project was to assist Lundin Norway AS to select a model oil as input data for environmental risk and oil spill contingency analysis with use of OSCAR modelling for a blend from segment B and C from the Luno II field. An pre-evaluation of data from an earlier weathering study on segment A (hereinafter called Luno II A) (Hellstrøm and Johnsen, 2014) and crude assay / PVT data for segment B and C indicated that the existing weathering data for segment A could possibly be used as model oil, see analytical data and true boiling point curve (TBP) in Appendix A. Therefore, a limited laboratory study (re-check parameters) of the blend (50:50) was suggested to verify the conclusions. The properties of the blend were compared with existing weathering data of Luno II A.

## 2 Laboratory analysis and results

SINTEF received (13.02.2017) approximately 10 litres of the blend (50:50) from segment B and C, hereinafter called Luno II blend. The oil sample was registered in SINTEF's laboratory information management system (LIMS) and given SINTEF Id: 2017-626.

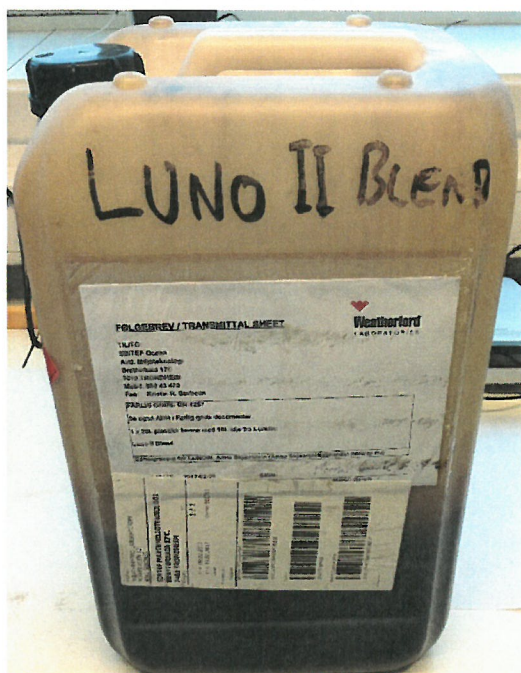


Figure 2-1: Luno II blend received by SINTEF

The laboratory study of the Luno II blend included the following analysis parameters:

- Topping / distillation of the fresh oil into residues (200 and 250 °C+)
- Gas chromatographic (GC-FID) analysis of hydrocarbon distribution from  $nC_5$ - $nC_{40}$
- Density and viscosity of fresh oil and residues
- Pour point of fresh oil and residues
- Content by weight % of wax and asphaltenes
- Emulsification kinetics and maximum water uptake
- Emulsion viscosity
- Emulsion stability

The laboratory study was conducted at 13°C. The results from the laboratory study are given in figures and tables below.

### Topping /distillation

The topping procedure 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 200°C and 250°C, with an evaporation loss corresponding to approximately 0.5-1 day and 0.5-1 week of weathering on the sea surface. The residues are referred to as 200°C+ and 250°C+, respectively.

### Hydrocarbon distribution

The hydrocarbon distribution of Luno II blend compared with Luno II A by use of gas chromatography flame ionization detector (GC-FID) is shown in Figure 2-2. The gas chromatograms show the n-alkanes as systematic narrow peaks, where the first peaks in the chromatogram represent components with the lowest boiling points.

The hydrocarbon distribution ( $nC_5$ - $nC_{40}$ ) of Luno II blend and Luno II A are very similar. Both oils are typically medium to light paraffinic crude oils, with a relatively high amount of the lightest compounds. The chromatograms also indicate a medium amount of wax/paraffinic compounds in the range of  $nC_{20}$ - $nC_{30}$  for both oils.

The fresh oil and the residues (200 and 250°C+) of Luno II blend were also analyzed by use of GC-FID to verify the artificial evaporation (topping of the blend). (Appendix B)

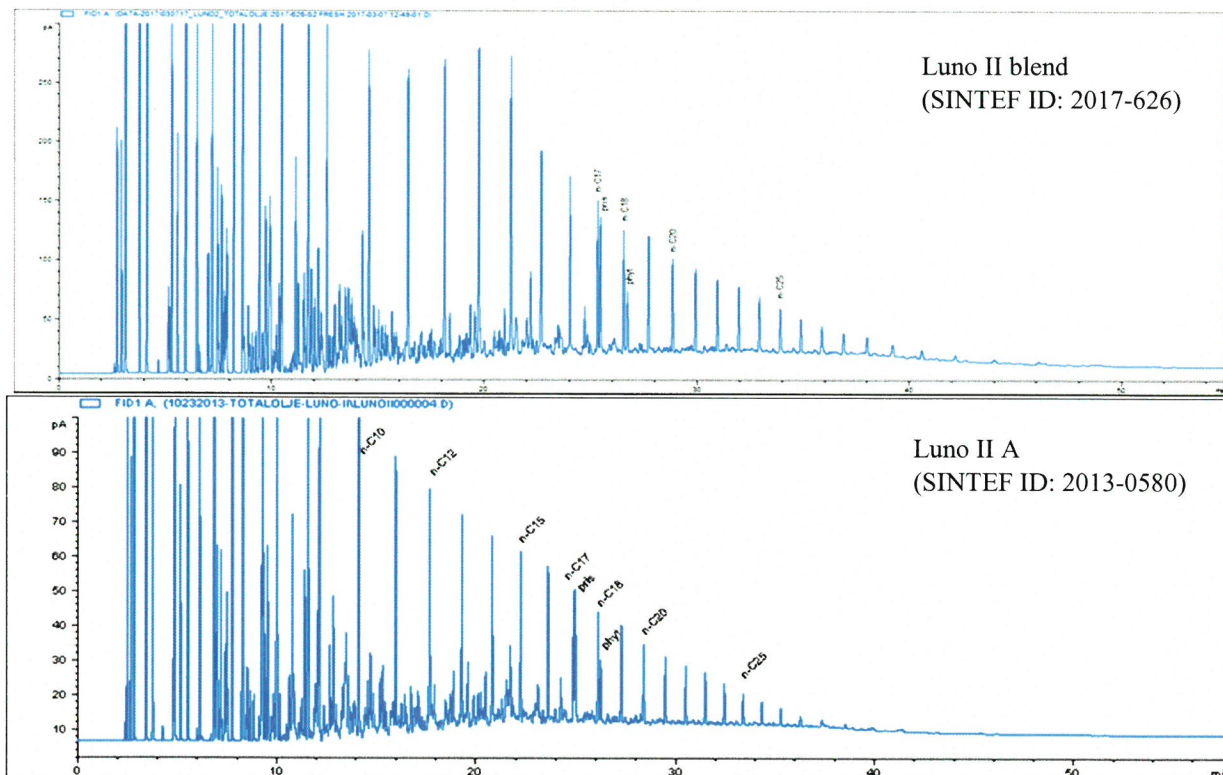


Figure 2-2: GC/FID chromatograms for the fresh oil of Luno II blend and Luno II A

Common screening parameters for oil spill identification, as well as for the degree of biodegradation, are the  $nC_{17}$ /Pristane and  $nC_{18}$ /Phytane ratios derived from the GC-FID analyses. The ratios of Luno II blend and Luno II A are given in Table 2-1. The ratios of Luno II blend and Luno II A are comparable.

Table 2-1: Ratios of  $nC_{17}$ /Pristane and  $nC_{18}$ /Phytane of Luno II blend and Luno II A

Oil name	$nC_{17}$ /Pristane	$nC_{18}$ /Phytane
Luno II blend	1.1	2.0
Luno II A	1.0	1.8

### Chemical and physical properties

The content of asphaltene and wax for Luno II blend and Luno II A are given in Table 2-2. The asphaltene and wax content are quite similar for both the Luno II A and Luno II blend oils. Physical parameters of the fresh oils and residues are given in Table 2-3.

Table 2-2: Asphaltene and wax content of Luno II blend and Luno II A

Oil name	Residue	Asph (wt. %)	Wax (wt. %)
Luno II blend	Fresh	0.4	2.9
	150°C+	-	-
	200°C+	0.6	4.4
	250°C+	0.7	5.3
Luno II A	Fresh	0.5	2.7
	150°C+	0.6	3.4
	200°C+	0.7	3.9
	250°C+	0.8	4.4

- Not analysed

Table 2-3: Physical parameters of Luno II blend and Luno II A

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Pour point (°C)	Visc. (mPas) 13°C (10 s <sup>-1</sup> )
Luno II blend	Fresh	0	100	0.838	-24	5
	150°C+	-	-	-	-	-
	200°C+	37	67	0.900	15	239
	250°C+	50	55	0.920	21	659
Luno II A	Fresh	0	100	0.851	-27	11
	150°C+	25	79	0.898	6	99
	200°C+	36	69	0.915	12	569
	250°C+	45	61	0.931	18	3165

- Not analysed

Luno II blend is a slightly lighter crude oil (0.838 g/mL) compared with Luno II A (0.851 g/mL), reflected by a slightly higher evaporative loss for the 250°C+ residue. Both oils show a similar trend of increasing pour points as evaporative loss increases. The viscosities of fresh Luno II blend and its residues are lower than those for Luno II A, particularly for the 250°C+ residue.

### Emulsification and emulsion viscosities

The emulsification was performed by use of rotating cylinders (e.g. Hokstad et al., 1993). The maximum water uptake (kinetics) for the water-in-oil (w/o) emulsion as a function of time is shown in Table 2-4. The  $T_{1/2}$  value, which is derived from the tabulated data, is defined as the time needed to incorporate half the

maximum water uptake. This is an important input to the SINTEF Oil Weathering Model (OWM) to predict the water uptake.

Table 2-4: Water uptake of the evaporated residues of Luno II blend and Luno II A

	Luno II A	Luno II blend	Luno II A	Luno II blend
Mixing time	200°C + (vol. % water)	200°C + (vol. % water)	250°C + (vol. % water)	250°C + (vol. % water)
Start	0	0	0	0
5 min	25	37	10	5
10 min	33	50	10	9
15 min	40	55	10	14
30 min	50	68*	24	35*
1 hour	59	71	40	47
2 hours	68	84	54	71
4 hours	76	86	63	74
6 hours	81	84	66	74
24 hours	80	82	71	75
T <sub>1/2</sub>	0.29	0.13	0.93	0.71

\*Measurement done at 45 minutes for Luno II blend

Stability testing of the emulsion and the efficiency of the emulsion breaker (Alcopol O 60%), are shown in Table 2-5. Both oils formed stable w/o-emulsions, and are partly broken adding emulsion breaker. The main difference observed here was that the emulsions of Luno II blend are less stable, compared to Luno II A, in the presence of high concentration of emulsion breaker.

Table 2-5: Stability of Luno II blend and Luno II A for emulsions with no emulsion breaker, and efficiency of emulsion breaker

Residue	Emulsion breaker	Stability ratio* Luno II A	Stability ratio* Luno II blend
200°C+	none	1.00	0.96
250°C+	none	0.98	1.00
200°C+	Alc. O 60 % 500 ppm	0.61	0.83
250°C+	Alc. O 60 % 500 ppm	0.65	0.70
200°C+	Alc. O 60 % 2000 ppm	0.19	0.08
250°C+	Alc. O 60 % 2000 ppm	0.82	0.15

ppm: parts per million

\*: Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling.

Stability ratio of 1 implies a totally stable emulsion.



The emulsion viscosities are shown in Table 2-6. The viscosities of the Luno II blend emulsions are lower for the 200°C+ residue and similar to Luno II A for the 250°C+ residue.

Table 2-6: Emulsion viscosities of Luno II blend and Luno II A

Oil	Residue	Water content (vol. %)	Viscosity (mPa.s)	
			10 s <sup>-1</sup>	100 s <sup>-1</sup>
Luno II blend	200°C+	82	15609	2879
Luno II A	200°C+	80	23888	4094
Luno II blend	250°C+	75	21820	4252
Luno II A	250°C+	71	24632	4208

### 3 OWM predictions

Analytical data generated from the limited laboratory study of Luno II blend was combined with existing weathering data of Luno II A. The updated dataset was used as input to the SINTEF Oil Weathering Model (OWM) in order to compare some relevant weathering properties from the existing predictions with updated predictions. The predictions of water uptake, emulsion viscosity, pour point and mass balances of Luno II blend and Luno II A are given in Appendix C.

### 4 Summary & conclusion

Luno II blend and Luno II A are medium to light paraffinic crude oils. Luno II blend (0.838 mg/mL) is a slightly lighter crude oil than Luno II A (0.851 g/mL) and the evaporative loss was 5 vol.% higher for the 250°C+ residue of the Luno II blend. The viscosity of the 250°C + residue was 10 fold lower for the blend compared with Luno II A. However, parameters as the pour points, wax and asphaltene contents, viscosities of the fresh oil and 200°C+ residue, and the GC-FID chromatograms showed consistent data compared to Luno II A.

The emulsion testing showed a more rapid water uptake and lower viscosities for Luno II blend than Luno II A, however, a combination of rapid water uptake and the lower emulsion viscosities resulted in a high maximum water uptake. Both oils reached a relatively high comparable water uptake. The oils also formed stable w/o-emulsions, and the emulsions were partly broken when adding emulsion breaker (Alcopol 60% O).

The data obtained from the Luno II blend study was used in combination with the existing data of Luno II A in OWM predictions. The weathering predictions of water uptake, emulsion viscosities, pour points and mass balances were comparable. The predominant deviation was that the predicted emulsion viscosity when using data from Luno II blend was somewhat lower at higher wind speeds (15 m/s).

Based on a total evaluation, using the limited laboratory study and new OWM predictions, the existing weathering data of the previous Luno II A can be used as a model oil for the new Luno II blend in environmental risk and oil spill contingency analysis (OSCAR modelling). Due to the somewhat lower density and viscosity of the Luno II blend, the existing weathering data of Luno II A can be considered as a conservative alternative for Luno II blend.

## 5 References

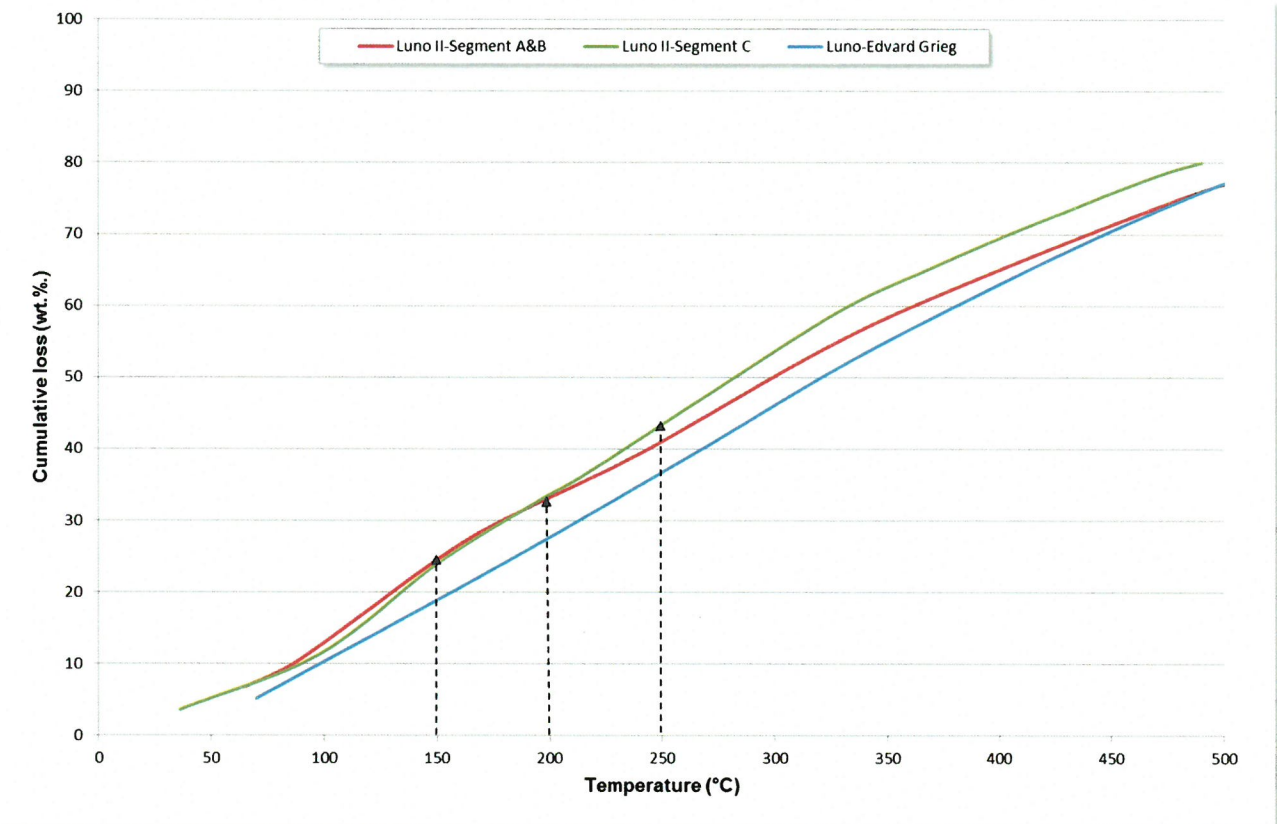
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Hellstrøm K.C and M. Johnsen 2014. Luno II crude oil – properties and weathering at sea. SINTEF report A26115. ISBN 978-82-14-05738-6

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

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

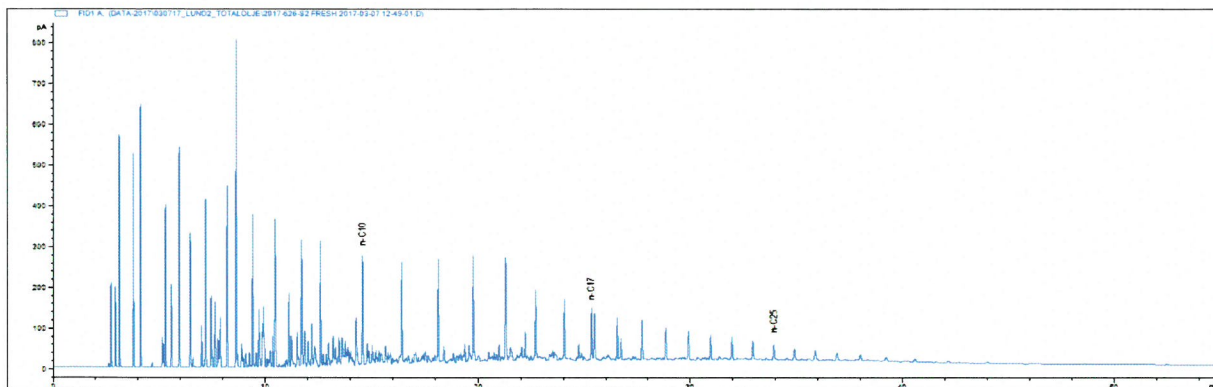
## A Pre-evaluation of Luno II



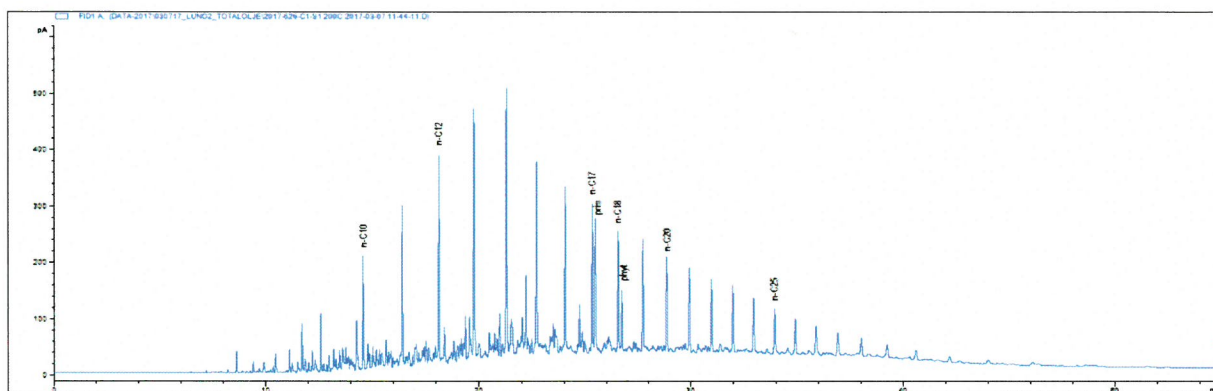
	Density (g/mL)	Pour Point (°C)	Visc 13°C, mPas	Asph. (wt.%)	Wax (wt.%)	Evap, wt% 150°C	Evap, wt% 200°C	Evap, wt% 250°C
Luno II								
Segment A	0.851	-27	11	0.5	2.7	24	34	41
Segment B	0.850	-12	9	0.5*	3.9	24	34	41
Segment C	0.842	<- 20*	9*	0.8	3.9	24	34	43
Luno								
Edvard Grieg	0.850	6	30	0.2	3.9	19	28	36

\* No data: Estimated parameters

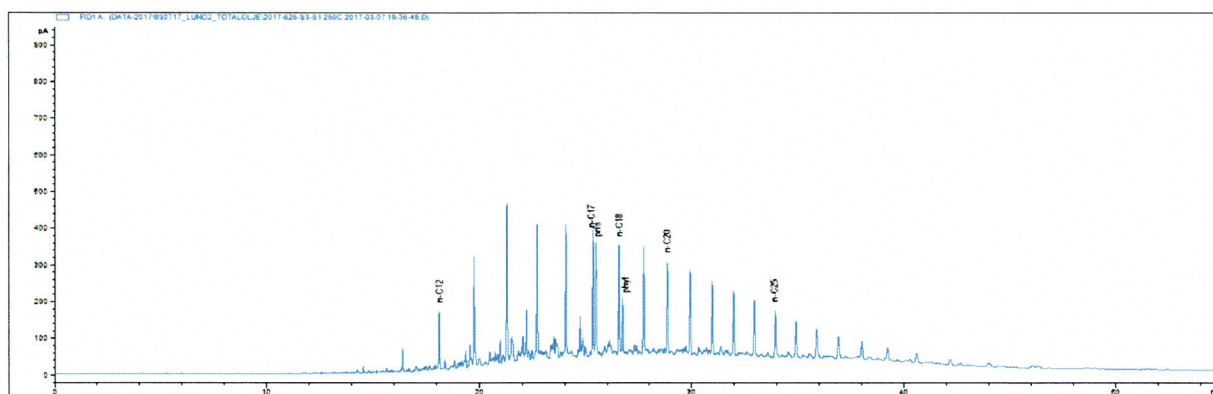
**B GC-FID chromatograms**



*B 1 – GC-FID chromatogram of Luno II blend, fresh*




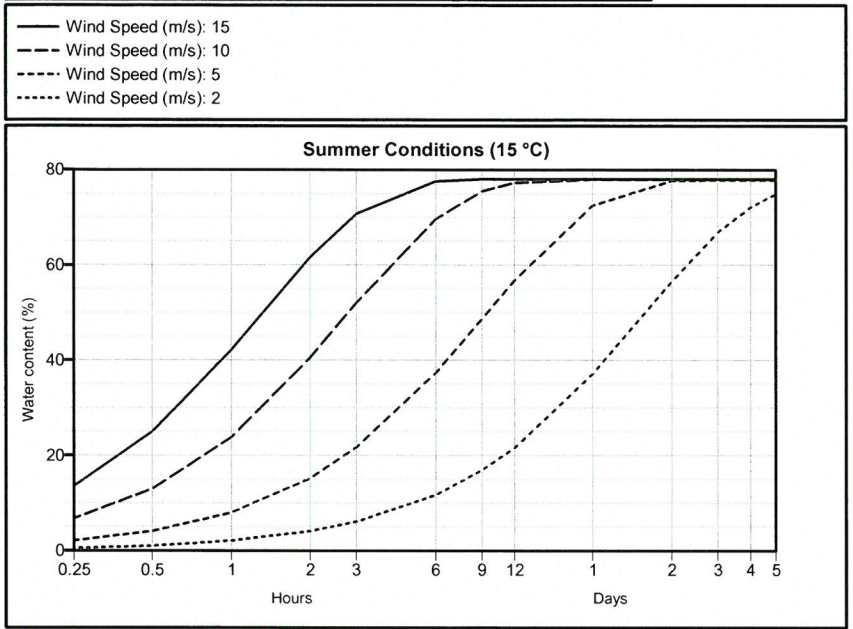
*B 2 – GC-FID chromatogram of Luno II blend, 200°C+*




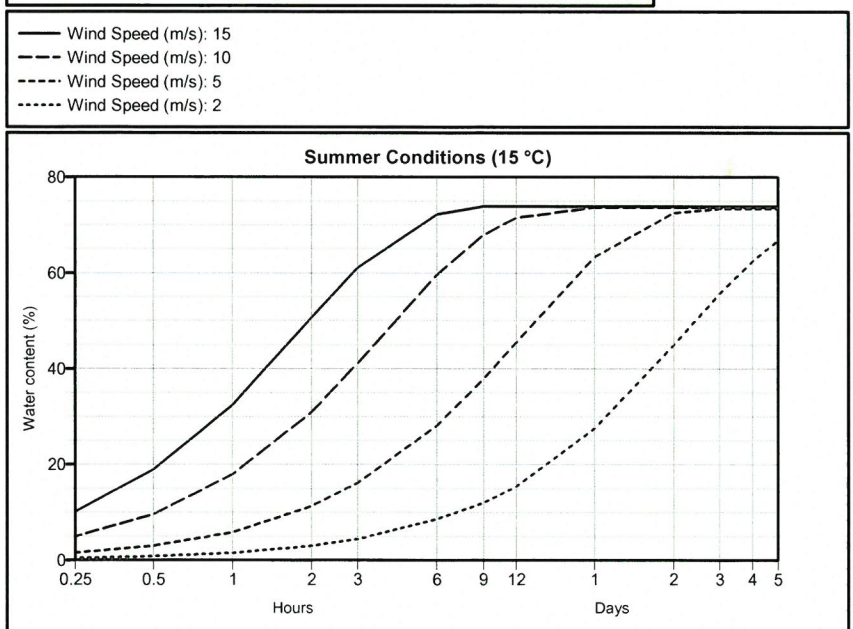
*B 3 – GC-FID chromatogram of Luno II blend, 250°C+*

**C OWM predictions**

<b>Property: WATER CONTENT</b> <b>Oil Type: LUNO II BLEND 2017 13C</b> <b>Description: Sintef ID: 2017-626</b> <b>Data Source: SINTEF Materials and Chemistry (2017), Weatherir</b>	 OWMModel Pred. date: Mar. 23, 2017
Surface release - Terminal Oil film thickness: 1 mm Release rate/duration: 1.33 metric tons/minute for 15 minute(s)	



<b>Property: WATER CONTENT</b> <b>Oil Type: LUNO II 2014 13°C (CRUDE)</b> <b>Description: Sintef ID: 2013-0580</b> <b>Data Source: SINTEF Materials and Chemistry (2014), Weatherir</b>	 OWMModel Pred. date: Mar. 23, 2017
Surface release - Terminal Oil film thickness: 1 mm Release rate/duration: 1.33 metric tons/minute for 15 minute(s)	



A 1: Water uptake of Luno II blend (above) and Luno II A (below)

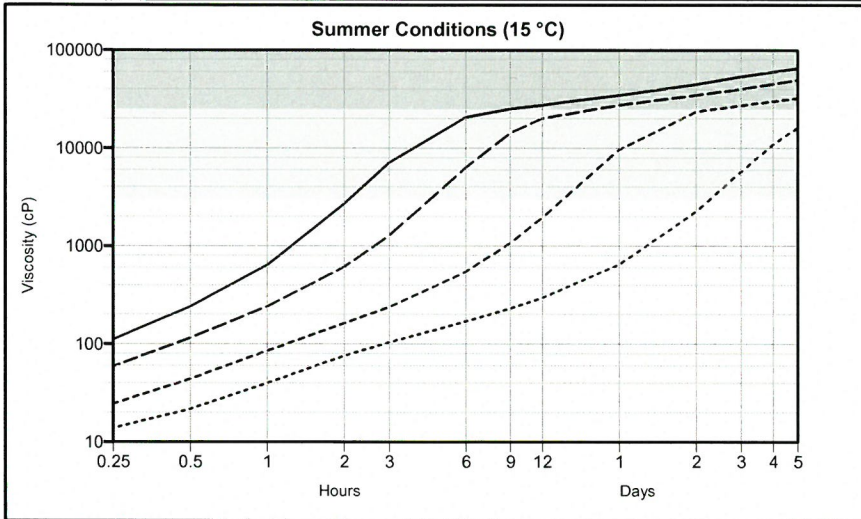
**Property: VISCOSITY OF EMULSION**  
**Oil Type: LUNO II BLEND 2017 13C**  
**Description: Sintef ID: 2017-626**  
**Data Source: SINTEF Materials and Chemistry (2017), Weatherir**

OWModel

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

Pred. date: Mar. 23, 2017

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



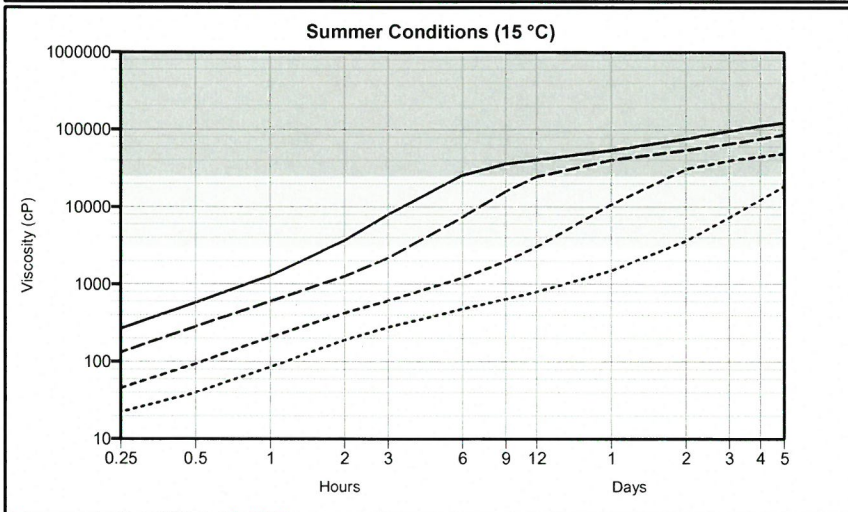
**Property: VISCOSITY OF EMULSION**  
**Oil Type: LUNO II 2014 13°C (CRUDE)**  
**Description: Sintef ID: 2013-0580**  
**Data Source: SINTEF Materials and Chemistry (2014), Weatherir**

OWModel

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

Pred. date: Mar. 23, 2017

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



A 2: Emulsion viscosity of Luno II blend (above) and Luno II A (below)

**Property: POUR POINT FOR WATER-FREE OIL**  
**Oil Type: LUNO II BLEND 2017 13C**  
**Description: Sintef ID: 2017-626**  
**Data Source: SINTEF Materials and Chemistry (2017), Weatherir**

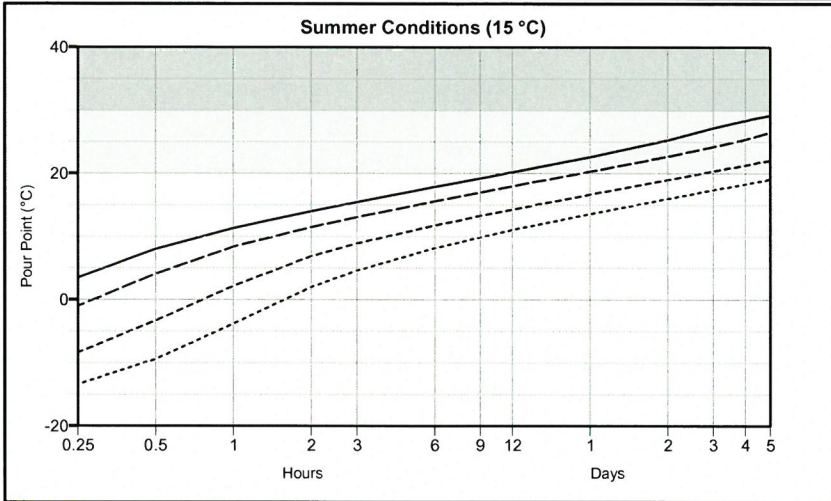


OWModel

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

Pred. date: Mar. 23, 2017

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



**Property: POUR POINT FOR WATER-FREE OIL**  
**Oil Type: LUNO II 2014 13°C (CRUDE)**  
**Description: Sintef ID: 2013-0580**  
**Data Source: SINTEF Materials and Chemistry (2014), Weatherir**

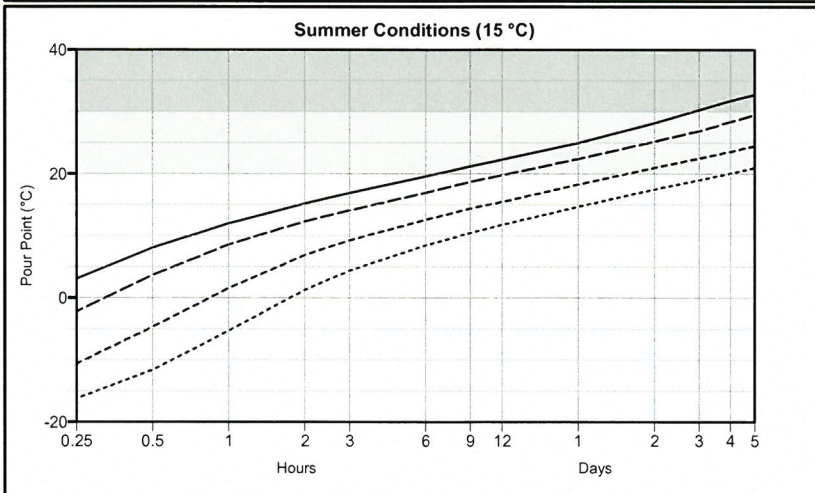


OWModel

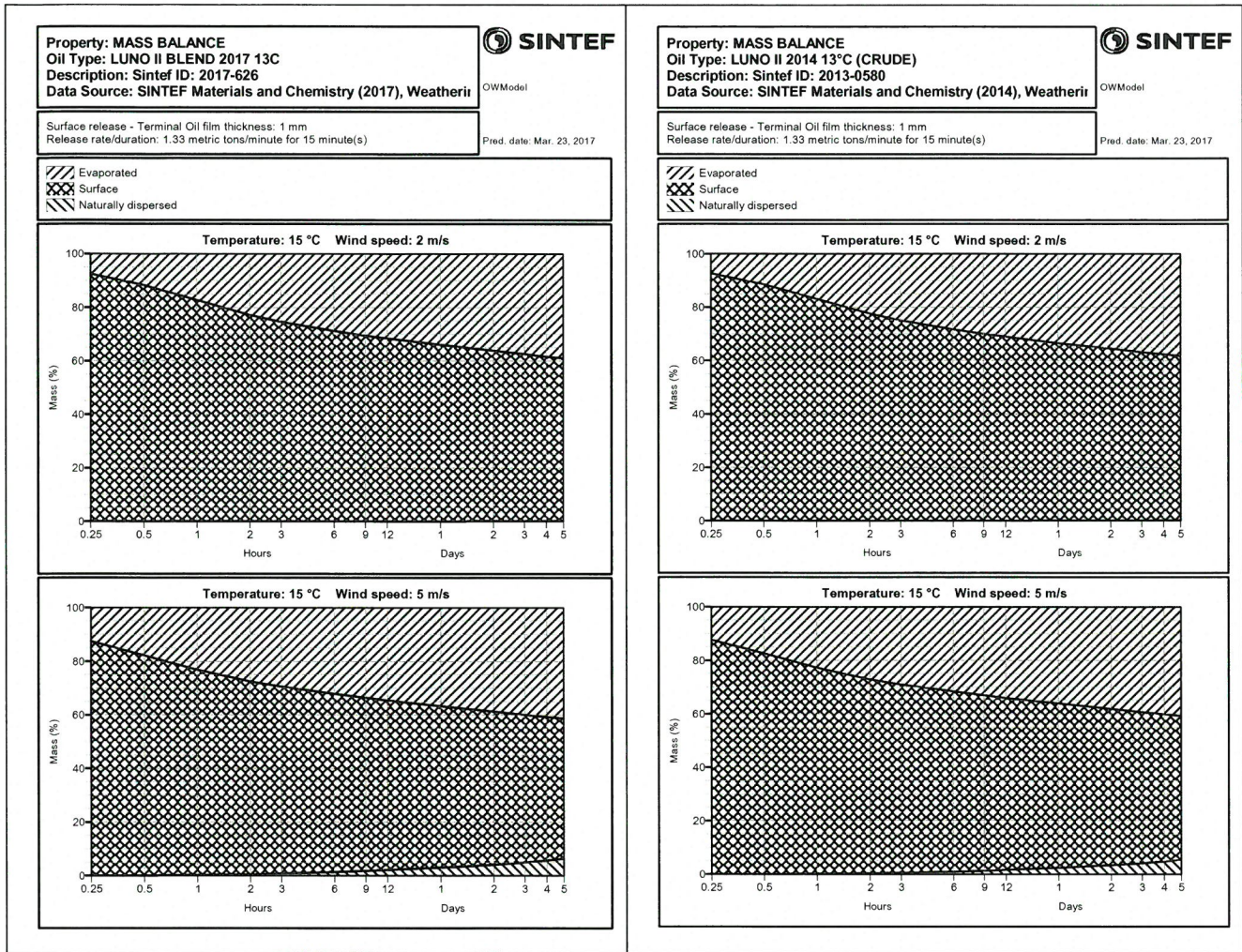
Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Mar. 23, 2017

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
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- · · · · Wind Speed (m/s): 2
- Chemically dispersible
- Reduced chemical dispersibility
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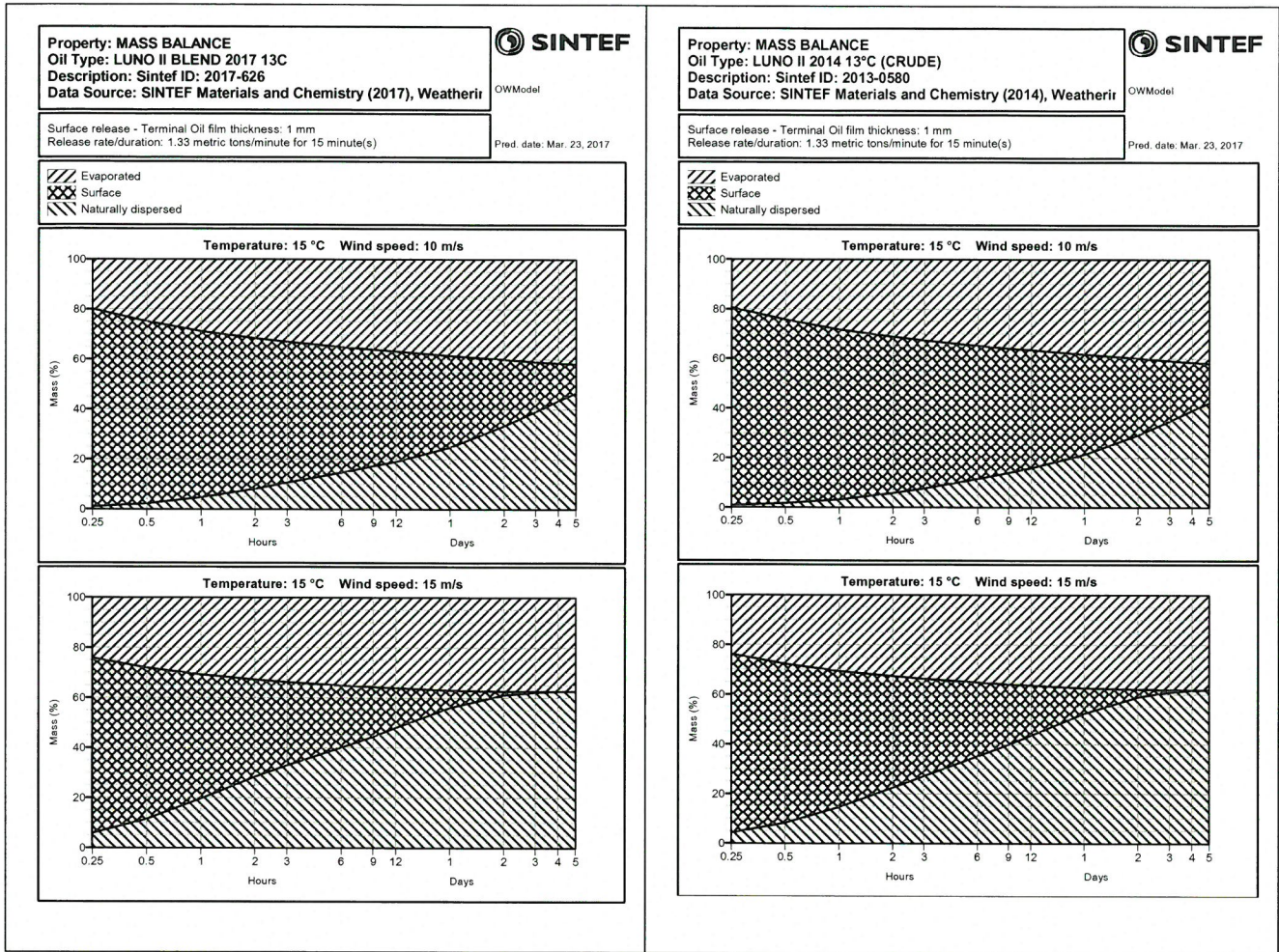


A 3: Pour point of Luno II blend (above) and Luno II A (below)



A 4: Massbalances at 2 and 5 m/s. Luno II blend (left) and Luno II A (right)





A 5: Massbalances at 10 and 15 m/s. Luno II blend (left) and Luno II A (right)