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EVALUATION OF DISPERSANTS IN OPEN WATER CONDITIONS

ABSTRACT

In order to show if ice movement increases the surface turbulence and thereby increases dispersion, flume tests comparing non-breaking waves in open water with non-breaking waves in ice were done. The dispersant efficiency (DE) of the crude oils Alaska North Slope, Troll Blend, Oseberg Blend, and Grane were tested using Corexit 9500 as the dispersant.

The results indicated that the presence of ice had a positive effect on the DE for the naphthenic oil Troll Blend and the paraffinic oil Oseberg Blend. For the more viscous crudes, Grane and Alaska North Slope, no significant difference between open water and with ice was observed.

TABLE OF CONTENTS

ABSTRACT 2

1 INTRODUCTION 5

2 MATERIALS AND METHODS 6

2.1 Oils and dispersants 6

2.2 Test tank preparation 6

2.3 Test matrix overview 8

3 RESULTS AND DISCUSSION 9

4 SUMMARY AND CONCLUSIONS 11

5 REFERENCES 12

APPENDIX A GC CHROMATOGRAMS 13

APPENDIX B DATA ON PARTICLE DISTRIBUTION 16

LIST OF FIGURES

Figure 2.1 Sketch of the SINTEF and SL Ross flumes 7

Figure 3.1 Dispersant efficiency vs salinity (open water) and with 80% ice in 35 ppt water. DE calculated from water grab samples collected after medium energy input. No DE was calculated for ANS in 5 ppt water. 10

Figure A 1 GC chromatograms of Grane crude oil weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3. 13

Figure A 2 GC chromatograms of Troll Blend weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3 14

Figure A 3 GC chromatograms of Oseberg Blend weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3. 15

Figure B 1 TRL-C-0-35-M 17

Figure B 2 TRL-C-0-15-M 17

Figure B 3 TRL-C-0-5-M 17

Figure B 4 TRL-C-80-35-M 17

Figure B 5 GRN-C-0-35-M 18

Figure B 6 GRN-C-0-15-M 18

Figure B 7 GRN-C-0-5-M 18

Figure B 8 GRN-C-80-35-M (with ice) 18

Figure B 9 OSB-C-0-35-M 19

Figure B 10 OSB-C-0-15-M 19

Figure B 11 OSB-C-0-5-M 19

Figure B 12 OSB-C-80-35-M 19

Figure B 13 ANS-C-0-35-M 20

Figure B 13 ANS-C-0-15-M 20

Figure B 15 ANS-C-0-5-M 20

Figure B 16 ANS-C-80-35-M 20

LIST OF TABLES

Table 2.1 Oil properties for the crude oils. Viscosity was measured at 2 ºC at SINTEF and at 0 ºC at SL Ross. 6

Table 2.2 Key figures for the flume tests 7

Table 2.3 Description of the tests with Test ID and test parameters. (Abbreviations used in Test ID are as follows: TRL: Troll, OSB: Oseberg, GRN: Grane; ANS: Alaska North Slope; C: Corexit 9500; 0: No ice; 80: 80% ice; 35, 15 or 05: salinity in seawater; M: medium energy). 8

Table 3.1 Oil properties prior to dispersant application, oil concentration in the water and dispersant efficiency. (Abbreviations used in Test ID are as follows: TRL: Troll, OSB: Oseberg, GRN: Grane; ANS: Alaska North Slope; C: Corexit 9500; 0: No ice; 80: 80% ce; 35, 15 or 05: salinity in seawater; M: medium energy). Density of ANS is measured at 20 ºC. 9

Table B 1 Summary of LISST data and oil concentration in water grab samples. 16

1 INTRODUCTION

As a part of the Arctic Oil Spill Technology – Joint Industry Program project "Dispersant testing under realistic conditions", SINTEF and SL Ross have previously performed approximately 70 tests with ice in their two identical recirculation flumes, varying parameters such as oil type, dispersant type, mixing energy, ice coverage and water salinity. The results from these studies are summarized in Faksness et al. (2017).

In the current phase of the project (Task 5), the goal was to compare dispersant effectiveness in open water to that in ice under the same wave energy conditions. The dispersibility of the crude oils Alaska North Slope, Troll Blend, Oseberg Blend, and Grane were measured using Corexit 9500 as the dispersant. The same weathering protocol as was used in Tasks 2 and 4 were followed.

2 MATERIALS AND METHODS

2.1 Oils and dispersants

The properties of the tested oils are given in Table 2.1. The commercial dispersant Corexit 9500 was used in all tests at a dispersant-to-oil ratio of 1 to 20 by volume.

Table 2.1 Oil properties for the crude oils. Viscosity was measured at 2 ºC at SINTEF and at 0 ºC at SL Ross.

Oil ID	Oil type	Density (g/mL)	Viscosity (cP) $100s^{-1}$ ($10s^{-1}$)	Pour point (°C)
2014-0335	Troll Blend (SINTEF)	0.855 (15.5 °C)	22 (34)	-30 °C
2015-0060	Oseberg Blend (SINTEF)	0.823 (15.5 °C)	10 (17)	-15 °C
2015-0061	Grane (SINTEF)	0.932 (15.5 °C)	978 (1019)	-15 °C
2014-BSEE	Alaska North Slope (SL Ross)	0.874 (20 °C)	40	-18 °C

2.2 Test tank preparation

A sketch of the recirculating flumes is shown in Figure 2.1 and the flume settings are provided in Table 2.2. A more detailed description of the flumes and their settings is provided in Faksness et al. (2014).

The tests in Task 5 were conducted in non-breaking wave conditions with and without ice, and in water with varying salinity. The wave maker settings to produce the non-breaking waves were similar to a setting used in the first phase of the project, in which "medium" energy was tested (Faksness et al., 2014). Then the dispersant efficiency in the medium energy environment (non-breaking waves) was almost as good as achieved with a high energy setting (breaking waves) in tests without ice. In the present tests, the wave makers were set to a slightly higher frequency than the medium energy (Table 2.2) that was used in the first phase of the project, which avoided producing excessive turbulence around the wave paddle.

The results of the tests in open water were compared with tests with 80 % ice, after applying the same wave energy. The ice blocks were prepared using 0.5% salinity water. The containment area for oil weathering, located in the straight section of the flume on the opposite side of the wave maker, was reduced to 0.2 m^2 in the tests without ice to obtain the same oil film thickness as with ice.

The protocol and methods described in Faksness et al. (2016) were followed to weather the oil in the flume, prior to dispersant application.

The tests were conducted for 30 minutes with medium energy input, and water grab samples were collected to measure oil concentration in the water column. No propeller wash was applied during the tests in Task 5.

The oil concentration in water samples was determined by liquid-liquid extraction with dichloromethane followed by colorimetric analysis of concentration using a response curve for the weathered oil samples. In addition, the LISST particle size analyzer was used to detect and monitor the oil droplet size distribution and dispersed oil concentration during the tests.

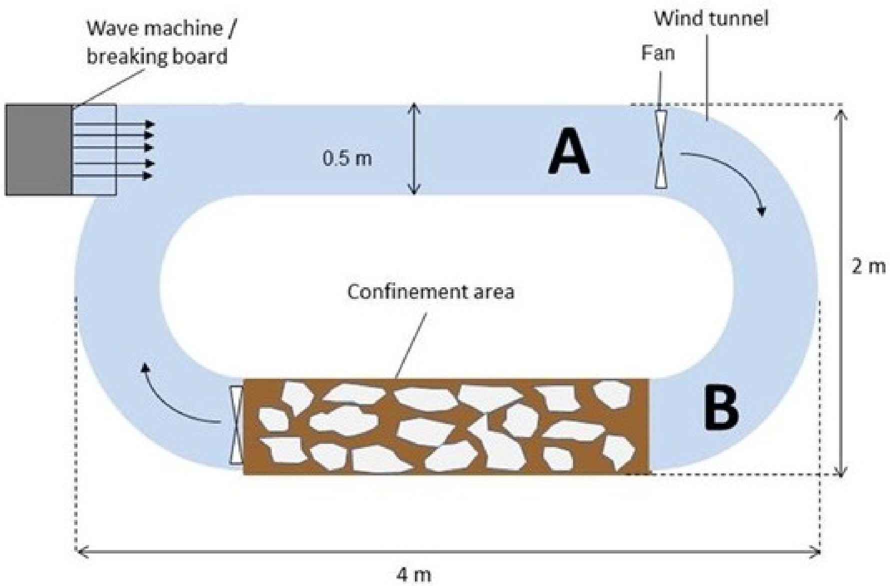

Figure 2.1 Sketch of the SINTEF and SL Ross flumes

Table 2.2 Key figures for the flume tests

	With ice	Open water
Temperature water	-2 to 0 °C	-2 to 0 °C
Ice concentration	80%	None
Containment area for oil and dispersant application	1 m^2	0.20 m^2
Oil volume	1 L	1 L
Initial oil film thickness in containment area	5 mm	5 mm
Dispersant to oil ratio (DOR)	1:20	1:20
Low energy settings (for oil weathering)		
Frequency wave maker	24 rpm	24 rpm
Amplitude wave maker	12 cm	12 cm
Medium energy settings		
Frequency wave maker	34 rpm	34 rpm
Amplitude wave maker	16 cm	16 cm

2.3 Test matrix overview

The experimental conditions for the tests performed in Task 5 are provided in Table 2.3. A weathering time of 18 hours and a dispersant to oil ratio of 1 to 20 was used in all tests.

Table 2.3 Description of the tests with Test ID and test parameters. (Abbreviations used in Test ID are as follows: TRL: Troll, OSB: Oseberg, GRN: Grane; ANS: Alaska North Slope; C: Corexit 9500; 0: No ice; 80: 80% ice; 35, 15 or 05: salinity in seawater; M: medium energy).

Test ID	Oil	Dispersant	Salinity	Ice cons	Energy
GRN-C-0-35-M	Grane	Corexit 9500	35	None	Medium
GRN-C-0-15 M	Grane	Corexit 9500	15	None	Medium
GRN-C-0-5 M	Grane	Corexit 9500	5	None	Medium
TRL-C-0-35-M	Troll	Corexit 9500	35	None	Medium
TRL-C-0-15-M	Troll	Corexit 9500	15	None	Medium
TRL-C-0-5-M	Troll	Corexit 9500	5	None	Medium
OSB-C-0-35-M	Oseberg	Corexit 9500	35	None	Medium
OSB-C-0-15-M	Oseberg	Corexit 9500	15	None	Medium
OSB-C-0-5-M	Oseberg	Corexit 9500	5	None	Medium
ANS-C-0-35-M	ANS	Corexit 9500	35	None	Medium
ANS-C-0-15-M	ANS	Corexit 9500	15	None	Medium
ANS-C-0-5-M	ANS	Corexit 9500	5	None	Medium
GRN-C-80-35-M	Grane	Corexit 9500	35	80	Medium
TRL-C-80-35-M	Troll	Corexit 9500	35	80	Medium
OSB-C-80-35-M	Oseberg	Corexit 9500	35	80	Medium
ANS-C-80-35-M	ANS	Corexit 9500	35	80	Medium

3 RESULTS AND DISCUSSION

A summary of the results is given in this chapter. More details, such as GC chromatograms of the oils prior to dispersant application and LISST monitoring performed during the tests are provided in Appendix A and Appendix B, respectively.

SL Ross performed all tests with Alaska North Slope, while the tests with the Norwegian crudes Troll, Oseberg and Grane were done by SINTEF.

The physical properties of the oil samples collected after the weathering period, immediately prior to dispersant application, are given in Table 3.1, which also includes the measured oil concentrations in the water grab samples and the calculated dispersant efficiencies (DE).

For the open-water tests, the estimated evaporative loss and measured oil viscosities and densities (prior to dispersant application) were relatively consistent for the different oil types, indicating that the weathering process was repeatable. For the oils weathered in 80 % ice, slightly higher values for density, viscosity and evaporative loss were observed. Looking at the GC chromatograms in Appendix A, these observations are confirmed, with quite similar evaporative loss for the oils weathered on open water, and higher loss of the most volatile components in the oils weathered in ice.

Table 3.1 Oil properties prior to dispersant application, oil concentration in the water and dispersant efficiency. (Abbreviations used in Test ID are as follows: TRL: Troll, OSB: Oseberg, GRN: Grane; ANS: Alaska North Slope; C: Corexit 9500; 0: No ice; 80: 80% ce; 35, 15 or 05: salinity in seawater; M: medium energy). Density of ANS is measured at 20 ºC.

Test ID	Applied oil (g)	Density (15.5 °C) g/mL	Viscosity 2 °C, 100 s^{-1} (10 s^{-1}) cP	Water content %	Estimated evap loss (%)	Oil in water from UV (ppm)	Disp eff medium energy (%)	Comments
GRN-C-0-35-M	895	0.938	1985 (2145)	10	3	117	64	No ice
GRN-C-0-15 M	899	0.937	1586 (1716)	12	3	44	24	No ice
GRN-C-0-5-M	827	0.938	1533 (1533)	9	4	24	15	No ice
GRN-C-80-35-M	872	0.942	2571 (2757)	11	6	103	60	80 % ice
TRL-C-0-35-M	782	0.886	146 (245)	2	24	85	69	No ice
TRL-C-0-15-M	782	0.887	152 (227)	4	25	59	48	No ice
TRL-C-0-5-M	786	0.889	151 (211)	0	26	23	19	No ice
TRL-C-80-35-M	772	0.895	198 (336)	4	31	110	99	80 % ice
OSB-C-35-M	750	0.868	140 (501)	7	30	36	32	No ice
OSB-C-15-M	738	0.870	156 (586)	3	32	17	16	No ice
OSB-C-0-5-M	762	0.873	188 (587)	3	33	7.7	7.3	No ice
OSB-C-80-35-M	766	0.875	221 (589)	11	34	67	63	80% ice
ANS-C-0-35-M	881	0.911	468	0	19	26	19	No ice
ANS-C-0-15 M	884	0.912	504	0	19	14	10	No ice
ANS-C-0-5-M	875	0.910	433	0	18	0.6	None	No ice
ANS-C-80-35-M	886	0.919	1135	0	23	21	16	80% ice

DE was calculated from direct oil-in-water concentration measurements. The data presented in Table 3.1 are based on water samples taken at the end of the mixing cycle. The oil concentration was determined by extraction of the samples followed by spectrophotometric quantification as described in Faksness and Belore (2014). The DE values were corrected for oil sampling (approximately 5%) and evaporative loss during oil weathering.

The DE calculated from the oil concentration in the water grab samples show that the effectiveness was significantly reduced with decreased salinity for all oils in open water (Figure 3.1), as was also observed previously in ice (e.g. Faksness et al., 2017).

In the tests with Grane in 35 ppt water, the DE in open water was approximately the same as in 80% ice. Simularly, the DE for Alaska North Slope crude oil was approximately the same for the test in ice (16%) compared to the test in open water (19%). For the less viscous weathered crudes Troll Blend and Oseberg Blend (< 200 cP at shear rate $100s^{-1}$), the DE in the tests with 80% ice concentration are clearly higher than in open water, indicating that for these oils, the presence of ice has a positive effect on the DE with an increase from 69 to 99% for Troll and from 32 to 63% for Oseberg (Figure 3.1).

The LISST results are given in Appendix B. The oil droplet size was increasing with decreasing salinity for all oils, and the concentrations in the water column measured with the LISST shows the same trend as in the water grab samples: Higher DE in 35 ppt seawater than at lower salinities.

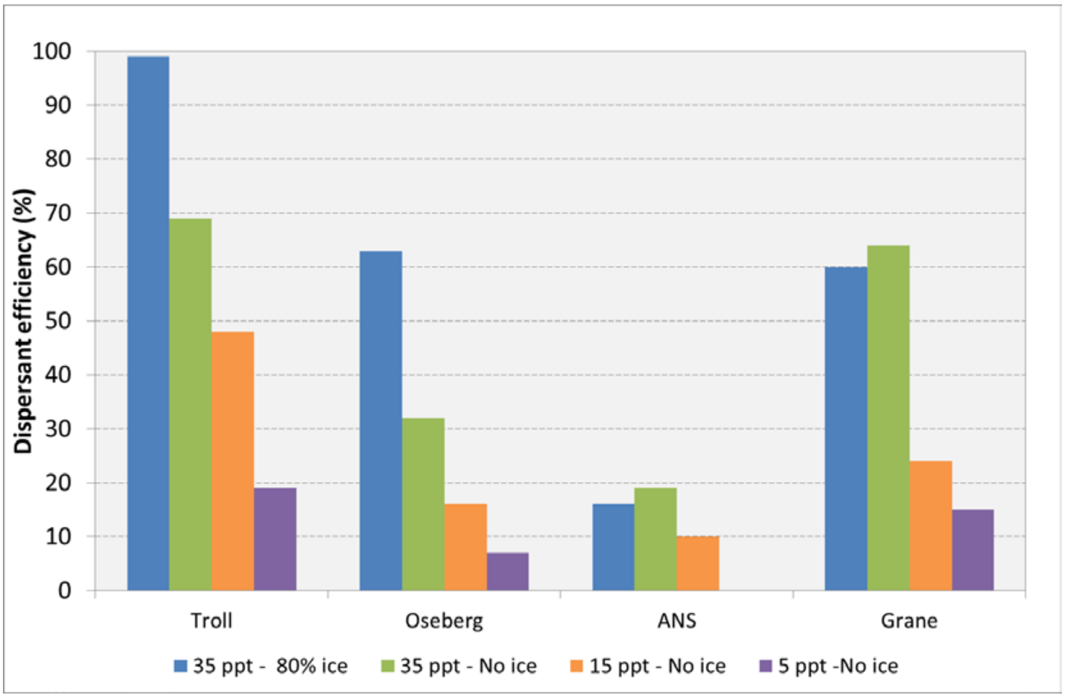

Figure 3.1 Dispersant efficiency vs salinity (open water) and with 80% ice in 35 ppt water. DE calculated from water grab samples collected after medium energy input. No DE was calculated for ANS in 5 ppt water.

4 SUMMARY AND CONCLUSIONS

We note that the conclusions below are based on the findings from the tests performed under the conditions in the SINTEF and SL Ross flumes, and may not be directly transferable to realistic conditions in the Arctic. However, flume testing gives repeatable controlled comparisons of relative DE with different oils, dispersants, weathering times, and other "fixed" conditions, which cannot easily be performed in the field.

In order to show if ice movement increases the surface turbulence and thereby increases dispersion, tests in non-breaking waves in open water were compared tests in ice. The results indicated that the presence of ice had a positive effect on the DE for the naphthenic oil Troll Blend and the paraffinic oil Oseberg Blend, the DE increased from 69 to 99% for Troll and from 32 to 63% for Oseberg when ice was present. For the more viscous oils Grane and Alaska North Slope, no significant difference in DE between open-water and 80% ice conditions was observed. The results indicate that the presence of ice is not an impediment to dispersant effectiveness, and may even enhance it for some oils.

The results in open water confirmed that reduced salinity decreased the DE, as previously shown in tests with ice in earlier phases of the project.

5 REFERENCES

Faksness, L.G., R. Belore, and F. Merlin. 2014. Test tank inter-calibration for dispersant efficiency. Arctic Response Technology – Joint Industry Program. Project 2: Dispersant testing under realistic conditions. SINTEF report F26018. http://www.arcticresponsetechnology.org/research-projects/dispersant-testing-under-realistic-conditions/research-report

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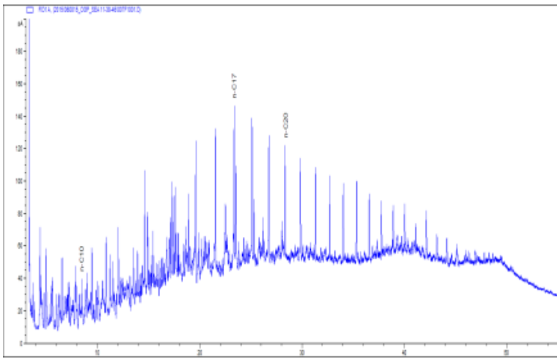
Faksness, L.G., R. Belore, J. McCourt, and D. Dunnebier. 2017. Evaluation of dispersant efficiency. Arctic Response Technology – Joint Industry Program. Project 2: Dispersant testing under realistic conditions. SINTEF report OC2017 F-036.

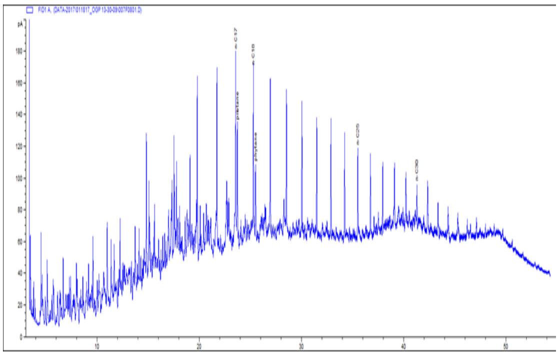
Faksness, L.G., R. Belore, J. McCourt, M. Johnsen, T.A. Pettersen, and P.S. Daling. 2017. Effectiveness of chemical dispersants used in broken ice conditions. In: Proceedings of the 2017 International Oil Spill Conference, Long Beach, CA, May 15 to May 18, 2017.

APPENDIX A GC CHROMATOGRAMS

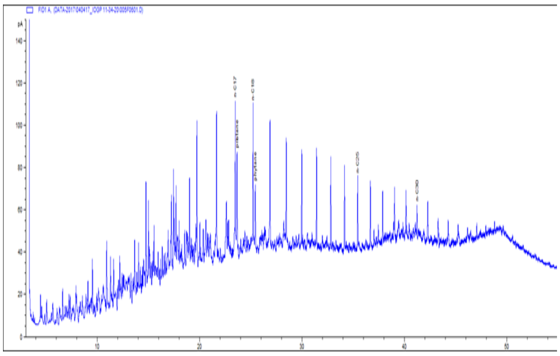
No GC chromatograms of the Alaska North Slope are provided.



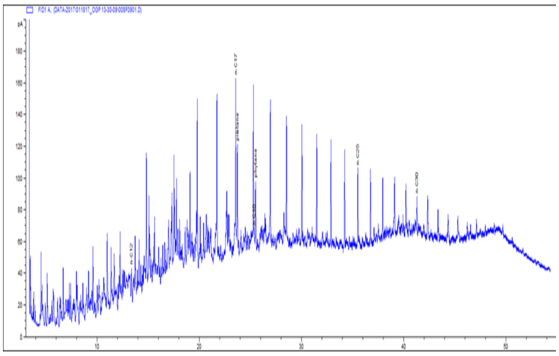
Grane fresh oil (2015-0061)



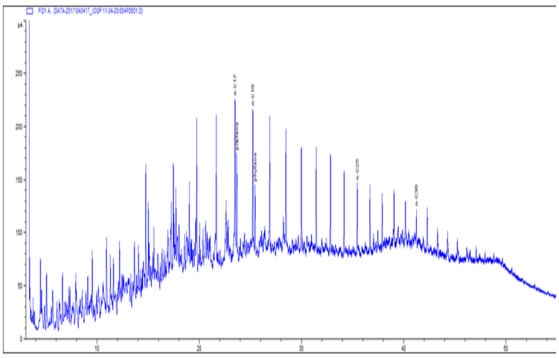
GRN-C-0-35-M



GRN-C-80-35-M

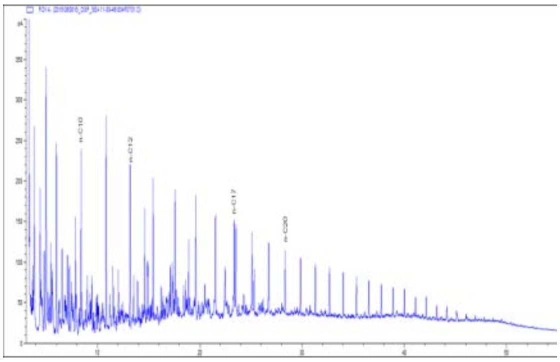


GRN-C-0-15-M

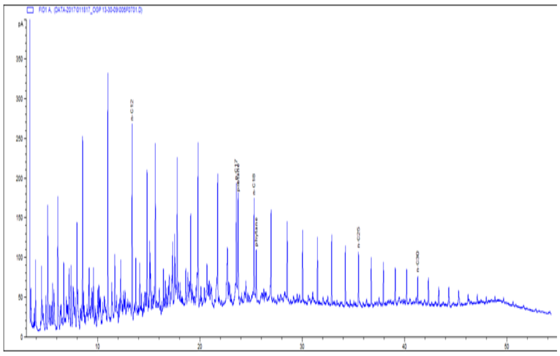


GRN-C-0-5-M

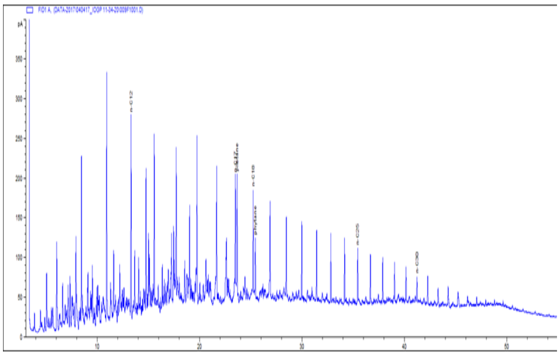
Figure A 1 GC chromatograms of Grane crude oil weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3.



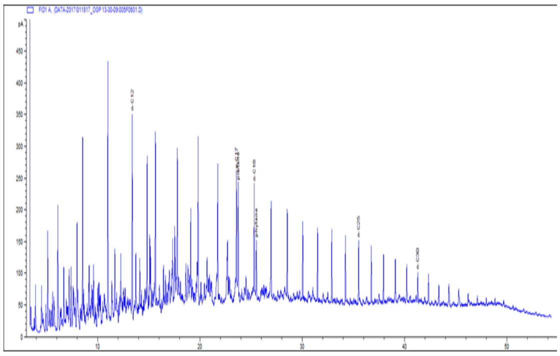
Troll Blend fresh oil (SINTEF ID 2014-0335)



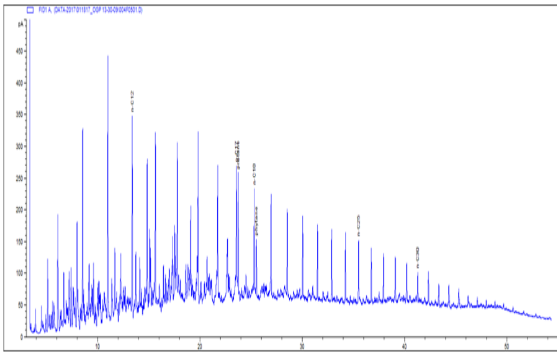
TRL-C-0-35-M



TRL-C-80-35-M

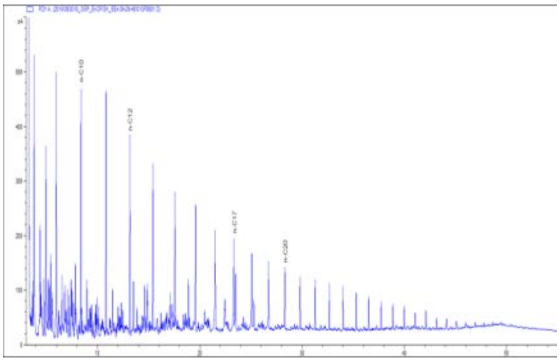


TRL-C-0-15-M

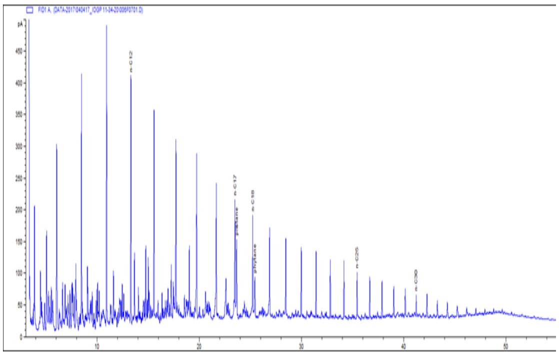


TRL-C-0-5-M

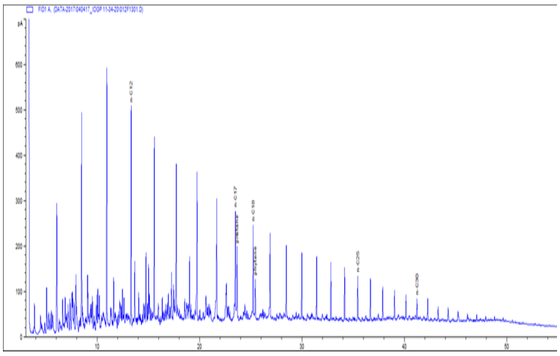
Figure A 2 GC chromatograms of Troll Blend weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3



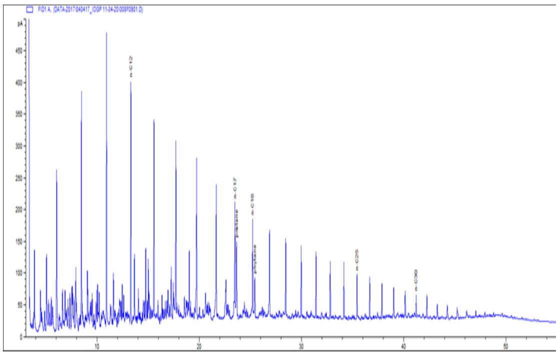
Oseberg Blend fresh oil (SINTEF ID 2015-0060)



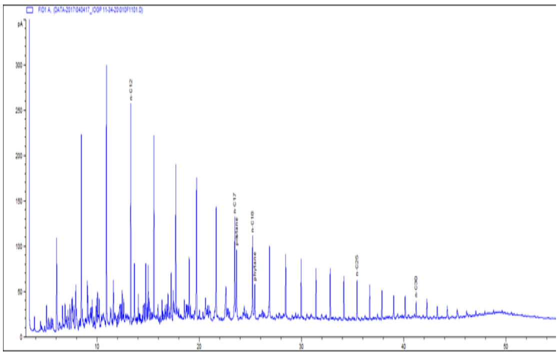
OSB-C-0-35-M



OSB-C-80-35-M



OSB-C-0-15-M



OSB-C-0-5-M

Figure A 3 GC chromatograms of Oseberg Blend weathered for 18 hrs prior to dispersant testing. Explanation of test identification is provided in Table 2.3.

APPENDIX B DATA ON PARTICLE DISTRIBUTION

The LISST is a system based on laser diffraction. The LISST used in the experiments was a LISST-100x type C, which can detect droplets in the range of 5-500 µm.

Data shown in Table B 1 (and Figure B 1 to Figure B 12) is obtained from an average of one minute of readings immediately prior to the time of water sampling. The largest size class (bin 32) has been discarded for all figures data shown and in calculations of concentration and d50. This is due to concerns regarding possible contamination from particles exceeding 500 µm.

The data were collected in conditions in which Schlieren may be present (i.e., possible temperature gradients over the sample volume). Caution should therefore be applied to the interpretation of high concentrations of apparently large particles reported by the LISST-100.

The d50 is calculated from the 50th percentile of the cumulative sum of the volume distribution for the first 31 size classes. The concentration is calculated from the sum of volume concentration over the first 31 size classes.

Table B 1 Summary of LISST data and oil concentration in water grab samples.

		Medium Energy		
	LISST d50	LISST conc.	Water sample	Comments
Test ID	µm	ppm	ppm	
TRL-C-0-35-M	81	47	85	No ice
TRL-C-0-15-M	86	34	59	No ice
TRL-C-0-5-M	118	15	23	No ice
TRL-C-80-35-M	68	66	110	80 % ice
GRN-C-0-35-M	45	69	117	No ice
GRN-C-0-15-M	133	31	44	No ice
GRN-C-0-5-M	208	15	24	No ice
GRN-C-80-35-M	52	56	103	80 % ice
OSB-C-0-35-M	62	35	36	No ice
OSB-C-0-15-M	111	13	17	No ice
OSB-C-0-5-M	137	8	7,7	No ice
OSB-C-80-35-M	62	46	67	80% ice
ANS-C-0-35-M	11	32	26	No ice
ANS-C-0-15-M	55	15	14	No ice
ANS-C-0-5-M	111	14	0,6	No ice
ANS-C-80-35-M	31	25	21	80% ice

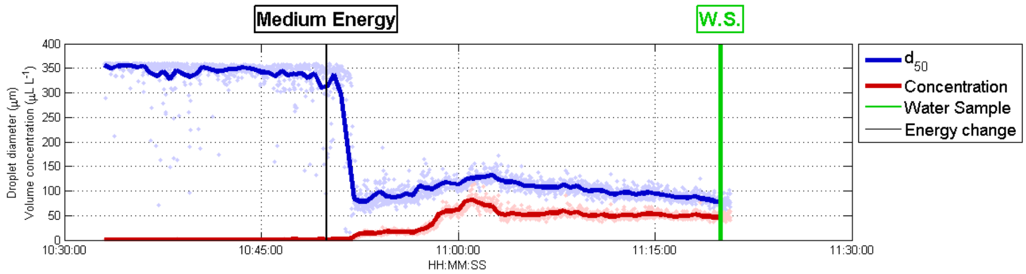


Figure B 1 TRL-C-0-35-M

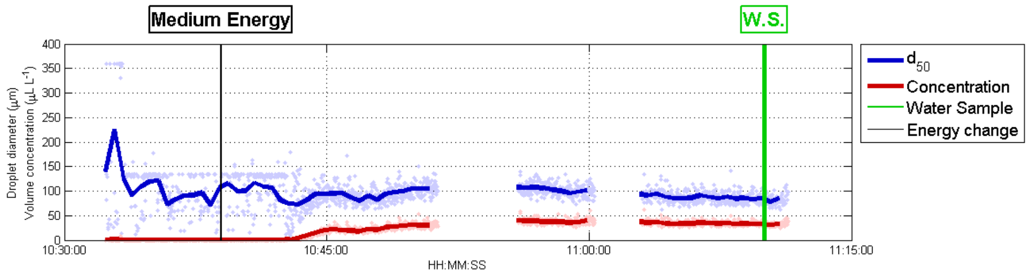


Figure B 2 TRL-C-0-15-M

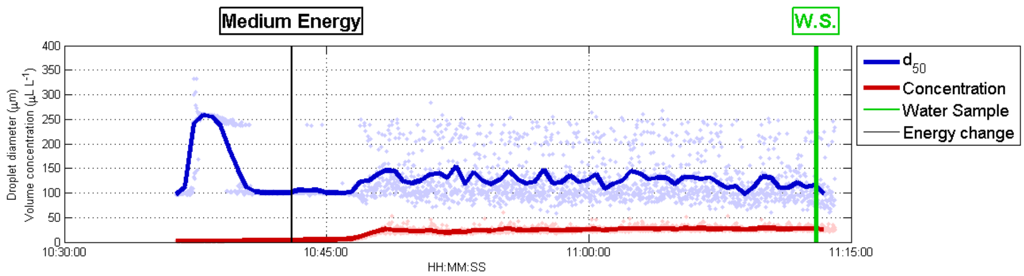


Figure B 3 TRL-C-0-5-M

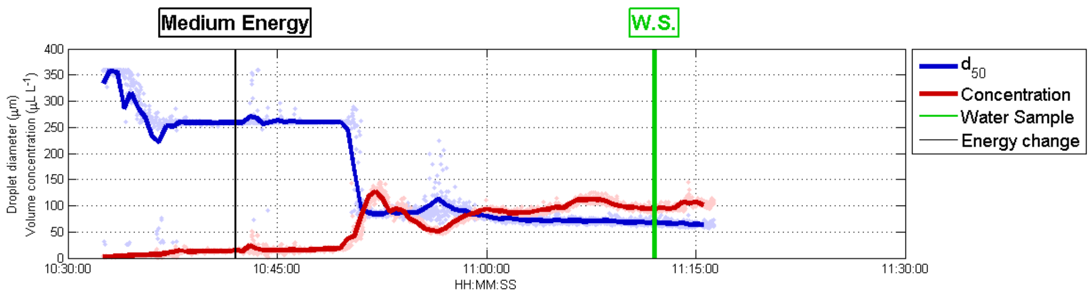


Figure B 4 TRL-C-80-35-M

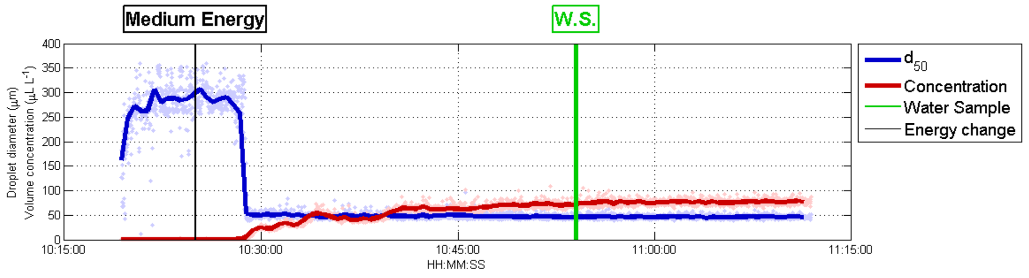


Figure B 5 GRN-C-0-35-M

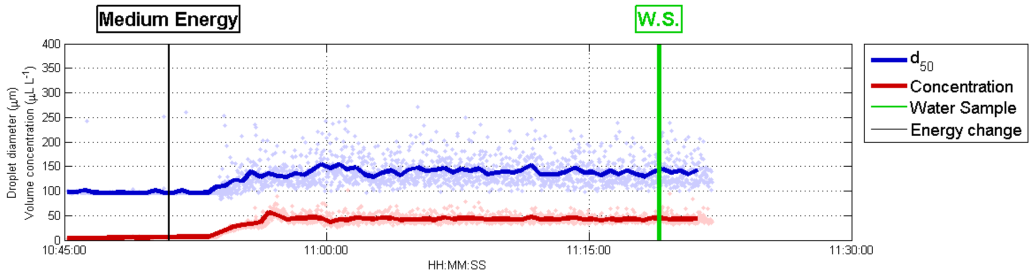


Figure B 6 GRN-C-0-15-M

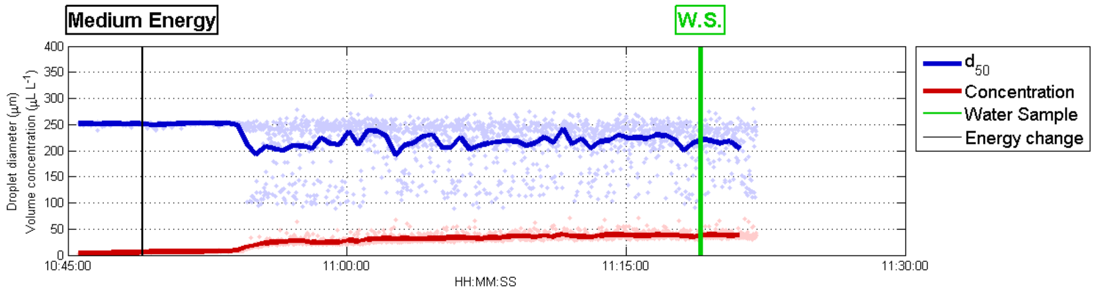


Figure B 7 GRN-C-0-5-M

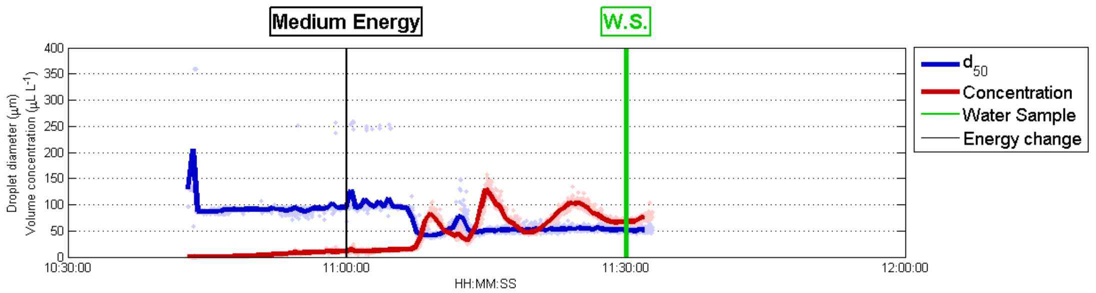


Figure B 8 GRN-C-80-35-M (with ice)

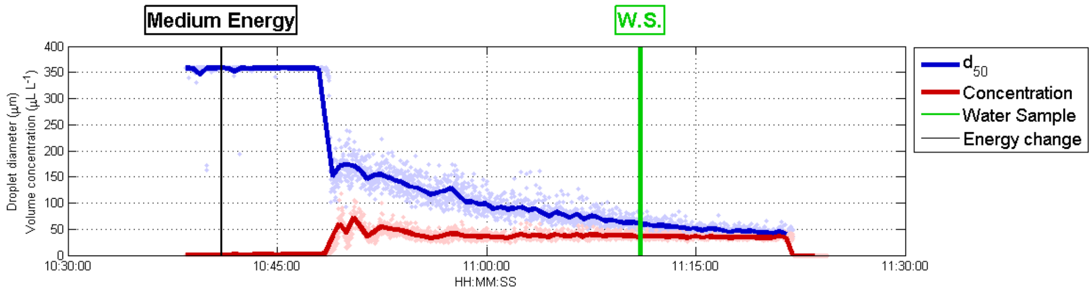


Figure B 9   OSB-C-0-35-M

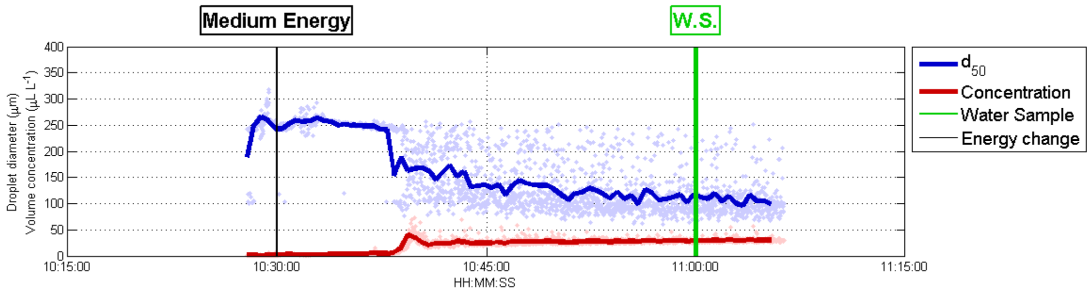


Figure B 10   OSB-C-0-15-M

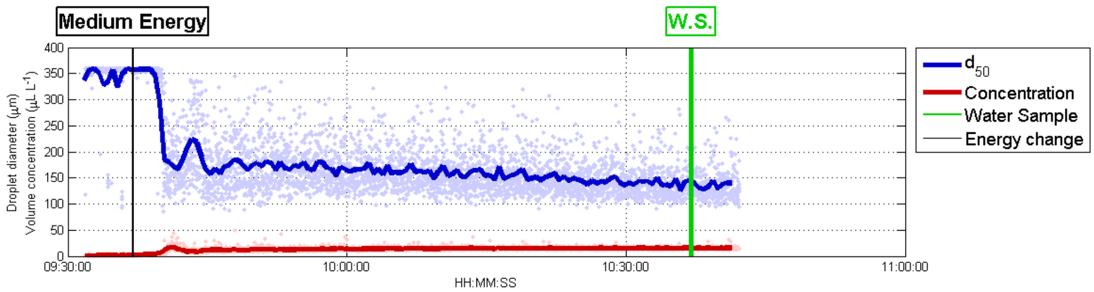


Figure B 11   OSB-C-0-5-M

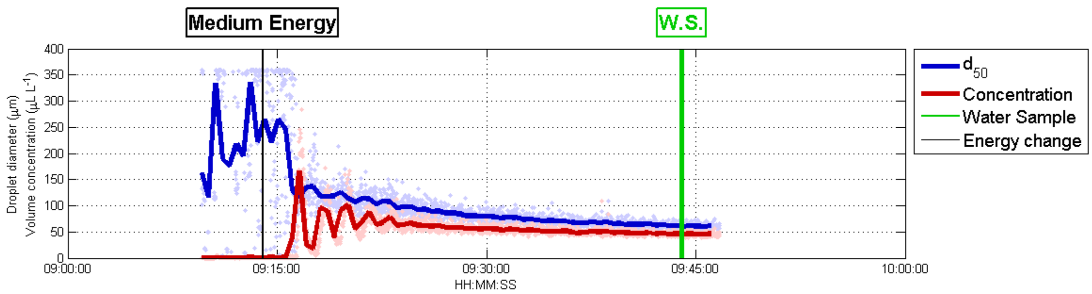


Figure B 12   OSB-C-80-35-M

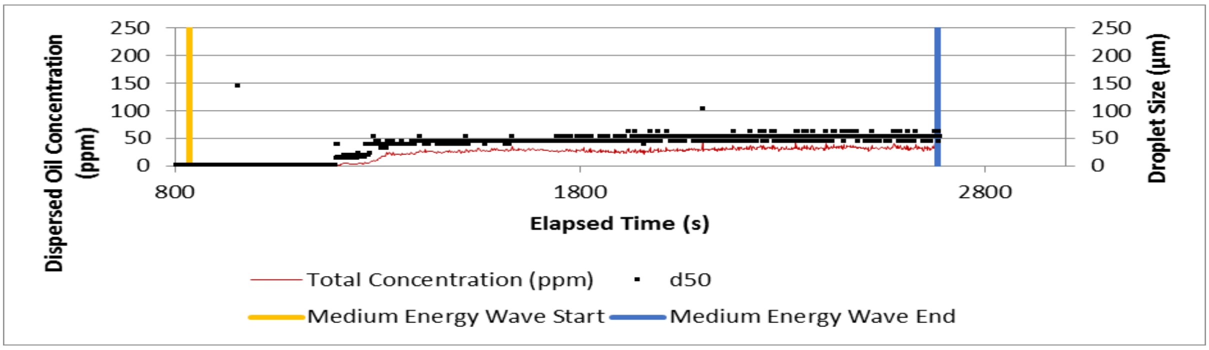


Figure B 13 ANS-C-0-35-M

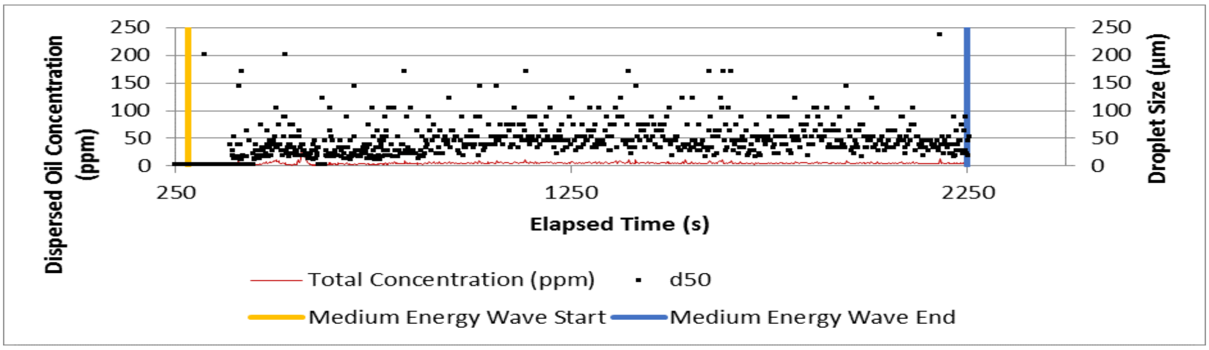


Figure B 13 ANS-C-0-15-M

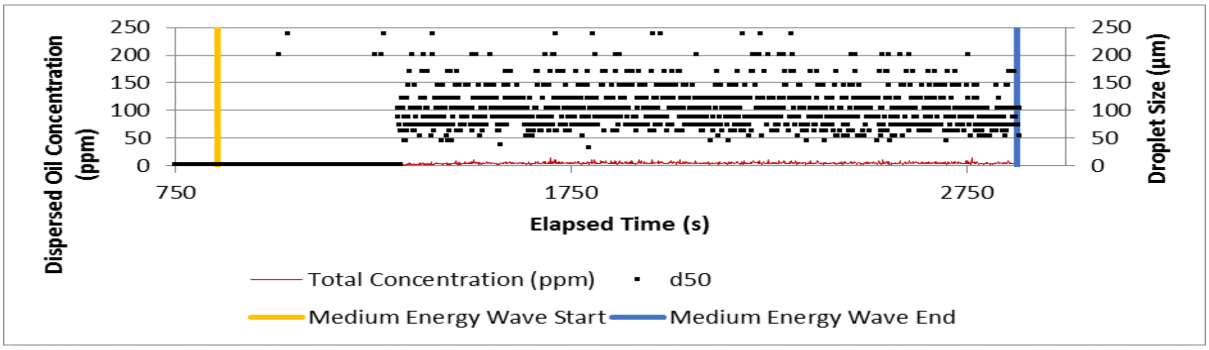


Figure B 15 ANS-C-0-5-M

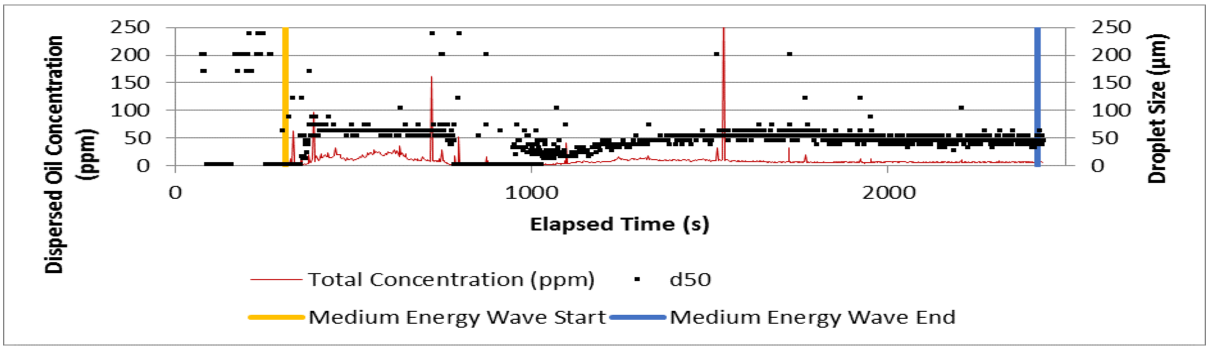


Figure B 16 ANS-C-80-35-M