Validation of Dispersant Window of Opportunity Model for U.S. OCS Crude Oils

for:

Bureau of Safety and Environmental Enforcement
U.S. Department of the Interior
381 Elden Street
Herndon, VA 20170

by:

S.L. Ross Environmental Research Ltd.
200-1140 Morrison Drive
Ottawa, ON
K2H 8S9
tel: 613-232-1564
fax: 613-232-6660
e-mail: Randy@slross.com

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Executive Summary

SL Ross conducted a study for Minerals Management Service (MMS) (fore-runner of BSEE) to evaluate the potential time window for dispersant use on Gulf of Mexico crude oils (SL Ross 2007). The study recommended that data be collected from large tank tests or field spills to validate both the spill modeling results and the oil dispersibility criteria used to develop the dispersant time window models. The objective of this project was to use the Ohmsett test facility to collect the data required to conduct this model validation.

Several oils were subjected to long-term weathering and wave activity in the Ohmsett test tank. The breaking wave density measured at Ohmsett was similar to those that have been recorded in the offshore during 4 to 5 m/s winds suggesting that the rate of weathering at Ohmsett should also be similar to such offshore conditions. The long-term, on-tank, weathering was successful in generating realistic oils and emulsions.

Oil property changes and chemical dispersibility were monitored throughout the exposures and the resulting data have been used to validate the fresh oil property - dispersant time window of opportunity models previously developed.

The fresh oil property dispersant time window correlations were compared to the results from the Ohmsett tank test dispersant time window determinations. The fresh oil property correlations generally matched the short (less than 2 hours), moderate (2 to 24 hrs) and long-term (greater than 24hours) time windows that were identified in the Ohmsett tank testing. However, the correlations did not accurately predict the actual individual time windows for the different oils.

In conclusion, the fresh oil property correlation appears to be a useful tool to categorize the likely time that dispersants will be effective into coarse time window categories that would be useful to assist in operational dispersant use decisions. Ohmsett tank testing of more oils would improve the confidence in the dispersant time window modeling and validation process.

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1. Background

In a previous study conducted for MMS of the US Department of the Interior (SL Ross 2007) analyses were completed to determine if commonly available, fresh oil properties could be used to predict the time window for chemical dispersibility of oils. An oil spill model was used to predict the change in viscosity of oil over time after spillage. It was assumed that oil would be amenable to chemical dispersion up to viscosities of 7500 cP. The time that the model predicted the oil would reach 7500 cP was then used as the likely maximum time window for chemical dispersibility. Detailed correlations were then completed between commonly available fresh oil properties and the modeled time window to develop empirical models for the prediction of the dispersant time window.

The correlation of fresh oil sulfur, saturate and wax contents with the time window generated the best model for prediction of dispersant time window for both 1,000 and 10,000 barrel spill scenarios.

The best model identified for the 1,000 barrel spill was:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.997657*\text{Sulfur}+0.107833*\text{Saturate}-0.326005*\text{Wax}-1.35108)}$$

$$(R^2 = 0.979)$$

The best model identified for the 10,000 barrel spill was:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.30926*\text{Sulfur} +0.05534*\text{Saturate} -0.28146*\text{Wax}+2.7153)}$$

$$(R^2 = 0.971)$$

2. Objective

The objective of this research was to validate the previously derived best-fit correlations between readily available fresh oil properties and the window of opportunity for successful chemical dispersant use on Gulf of Mexico (GOM) crude oils through the collection of data from large tank tests conducted at Ohmsett (The National Oil Spill Response Research & Renewable Energy Test Facility).

3. Study Approach

The approach taken to complete the study was to first identify suitable oils and then conduct testing at Ohmsett as described in the following sections 3.1 and 3.2.

3.1 Identification of Suitable Oils

A current list of oils stockpiled at the Ohmsett facility and the volumes of each was acquired from MAR, the Ohmsett facility operators. Crude oils with sufficient quantities for testing at Ohmsett (50 gallons or more) were identified. A search was then made for fresh and weathered oil property data sets for each of the available oils sufficient for use in both the dispersant window of opportunity correlation model and in oil spill fate modeling. Adequate data was found for the oils shown in Table 1, primarily using Environment Canada's Emergencies Science and Technology Divisions (ESTD) online oil property database (Env. Can. 2012). The data was processed for use in the SL Ross oil spill model and the fates of 1000 m^3 spills of each oil was modeled to identify the approximate time for the oil to reach 7500 cP. This was the viscosity upper limit selected for chemical dispersibility in the original development of the 'window of opportunity' model under evaluation. Columns 10 in Table 1 shows the time limits for dispersibility based on the fresh oil property correlation model for small spills. Columns 11 and 12 show the time window correlations using 5% and 10% wax contents to show the sensitivity of the correlation to wax content for those oils where wax content was not available. The two oils where the wax content has the most significance with respect to the time window prediction based on the fresh oil properties are the Platform Gail and Anadarko oils. Column 13 shows the time window for dispersibility based on the oil spill model. These predicted times were used to help select the test oils and determine the order of testing during the work at Ohmsett.

It should be noted that oil property data for the Oseberg and Endicott oils were developed using different oil samples from those available at Ohmsett. Wax contents were not measured by Environment Canada for the five oils in Table 1 that were analyzed for BOEMRE in 2011. Wax contents of 0% were used for these oils in determining the 'Fresh Oil Property Correlation Time Window' data in column number 10 of Table 1. The fresh oil property correlation equation for small spills is negatively correlated to the wax content data (time window decreases with increased wax content) so the predicted time windows in column 10 are maximum values based on the data available. The 2011 Environment Canada analyses also only included physical properties of the oil when fresh and for one weathered state. The lack of data for at least two weathered states limits the accuracy of the oil spill modeling predictions for these oils. The only impact that this had on the study was in the column 11 spill model predictions of the time for the oils/emulsions to reach 7500 cP viscosity. This was used to estimate the likely time that the oil would have to be weathered on the Ohmsett tank prior to loss of dispersant effectiveness.

The oils in Table 1 were identified as potential candidates for testing during the Ohmsett test program. The only oil not tested was the Lompoc PXP 01 oil as its viscosity fresh was above the 7500cP cutoff value used in the development of the correlation model.

Table 1. Oils in Ohmsett Inventory Suitable for the Project

Oil Name (oil property data source)	Correlation Variables					Fresh Oil Viscosity mPa.S 15° C	Emulsion Formation (fresh oil)	Emulsion Formation (weathered oil)	Fresh Oil Property Correlation Time Window (hr) 0% wax	Fresh Oil Property Correlation Time Window (hr) 5% wax	Fresh Oil Property Correlation Time Window (hr) 10% wax	Time to 7500 cP by Spill Model (hr)
	Sulphur Content	Saturate Content	Wax Content	Resin Content	Asphaltene Content							
Column #->	1	2	3	4	5	6	7	8	10	11	12	13
Neptune: BHP Billiton (ESTD[1] 2011)	2.88	57.9	na[2] used 0	18.6	10.1	402	Stable	Stable	0.42	0.08	0.02	2
Endicott (ESTD 94)	1.24	na used 70	8	0	4	84	meso stable	meso stable	3			57
Venoco E-19 Platform Gail (ESTD 2011)	1.9	77.3	na used 0	11.4	5.8	53	no	stable	24	4.8	0.9	13.5
Oseberg (ESTD 96)	0.31	65	5	2	2	10	no	stable	30			24
Sockeye (ESTD 2000)	4.51	49.2	1.6	15.1	18.5	761	meso	entrained	0.00			4
Anadarko (ESTD 2011)	0.65	72.6	na used 0	4.6	0	14	no	no	178	35	6.8	>480
PER Platform Ellen Well 038: (ESTD 2011)	3.28	39.2	na used 0	24.1	14.3	3098	entrained	no	0.03	0.005	0.001	2
Lompoc: PXP01 (ESTD 2011)	5.21	37.7	na used 0	32.7	19	8514	entrained	no	0.00	0.000	0.000	0.25

[1]Emergencies Science and Technology Division, Environment Canada [2] Data not available

3.2 Ohmsett Testing

Tests were conducted at the Ohmsett facility from May 29 through June 6 (including weekends) on a 24/7 basis. The MAR staff operated in 3 shifts to enable the weathering process to continue non-stop throughout the testing. Oil quantities between 30 to 100 gallons were used in each test. Larger quantities were used for the lighter oils to ensure that adequate quantities remained on the tank throughout the long-term weathering process. A total of seven oils were subjected to realistic weathering conditions on the Ohmsett tank. The oils were subjected to breaking wave conditions with a wave density similar to those present in offshore conditions and the prevailing wind speeds, temperatures and solar radiation at the time of the testing. Samples of the oil were taken periodically to track the weathering process. The samples were analysed for water content, viscosity, density of the parent oil (after removing water from the emulsions formed) and tested for dispersant effectiveness using the Exdet test in the laboratory. See Appendix A for a description of the Exdet test procedure. The Exdet test was selected because this method does not require the preparation of colorimetric standards for each unique oil tested. Each weathered state of oil sampled would have required a new set of standards be developed for the swirling flask, baffled flask or Labofina test methods at considerable effort and use of large quantities of solvents. On-tank dispersant effectiveness was not conducted for two reasons. First of all it was important to maintain surfactant free water in the tank for proper emulsion formation as a small amount of surfactant in the water can impede emulsion formation. Secondly, on-tank dispersant effectiveness testing is a one-shot proposition that does not allow for successive estimates of dispersibility over the period of weathering. Micro-photographs of the water-in-oil emulsions were also taken. These are provided in Appendix B. Weather data was collected throughout the test period and is summarized in Appendix C.

Light oils were initially subjected to non-breaking waves to minimize natural dispersion losses. The wave paddle was set to a 30 cpm frequency and 15.25 cm (6 inch) stroke when generating these non-breaking waves. Wave energies were increased to breaking conditions once the light oils had weathered and thickened. Heavier oils were subjected to breaking waves at the start of their test. A paddle frequency of 33 to 34 cpm and stroke of 15.25 cm (6 inches) inches were used to create the breaking waves. Oil was contained at the north end of the tank using five submerged 'ice-eater' pumps (see Figure 1) placed across the tank to create a surface current barrier. A containment boom with ice-eaters placed inside the boom side-wall attachments points was used to contain the oil at the south end of the tank. When the oil threatened to breach the down-wave north containment it was moved to the south using the water jet spray system shown in Figure 2. These arrangements minimized the loss of oil compared to physical containment booms normally deployed for these purposes and minimized the number of times that the oil had to be re-positioned on the tank. The oil weathering process was operated 24/7 until the oil dispersibility had dropped to below 40% in the Exdet test or the oil viscosity had increased to above 10,000 cP.

Figure 1. Ice-Eater Water Current Device Used to Generate Water Flow Barrier at Ends of Tank

Figure 2. Oil Movement Spray Jet System

4. Results

A summary of the test data collected is provided in Table 2. The data are organized by the test oils and the oil samples taken over the weathering period. Most of the column headings in the table are self explanatory, descriptions of the headings that may require some clarification follow. The oil name provided in column 1 is also a link to graphs of the wind speed and direction and air and water temperature data that were recorded during the oil weathering period for that oil. These graphs are provided in Appendix C. The water content data (in columns 7, 8) are the oil and water depths measured in a vial where an emulsion sample had been broken through addition of an emulsion breaker and heat. These depths were then used to determine the percent of water in the emulsion (column 9). The parent oil density is the density of the oil in the sample after the emulsion was broken and the water removed. The Exdet effectiveness test results are shown for each test repeat (separatory funnels, S.F. 1 through 4) and the average of the test duplicates.

The wave density in a 30 m (100 ft) section of the test tank nearest the north containment barrier was determined using video footage recorded with the wave paddle set to the test setting of 33 rpm and 15.25 cm stroke. The waves breaking in this section of the test area were counted over a nine minute time frame. The breaking wave density from this determination was 0.496 x 10^{-3} events/m^2/s. This compares favorably to the data presented by Ding and Farmer (1994) that show wave densities in the offshore at approximately 1.0 x 10^{-3} events/m^2/s at wind speeds of 4 to 5 m/s. The breaking wave density imparted during the testing appears to be similar to that which oil would encounter in a field situation under light to moderate wind speeds.

The wind speeds and directions and air and tank water temperatures measured during weathering periods for each crude oil can be viewed in Figures C1 through C7. The tank water temperature early in the test program was about 27 °C and this dropped slowly to about 21 °C by the end of the two week test program. The water temperature during individual oil weathering periods did not vary by more than a couple of degrees. The air temperatures during the testing covered a range between 13 °C to 32 °C and were more variable than the water temperature throughout each oil weathering period (especially those that lasted through the night). The primary effects of temperature on the weathering process are on the rate of evaporation and to some extent the viscosity of the oil which could affect emulsion formation rate.

Wind speeds ranged from calm to 8 m/s during the two week program. Because waves were generated using the wave paddle the wind speed data is not useful in estimating the energy imparted to the oil and the rate of formation of emulsions, as would be the case in the offshore. The wind speed may have had some effect on the evaporation rates of the oils but this is expected to be a secondary influence on the weathering and emulsion formation processes in these tests.

The dispersant time window correlations developed in the previous study were based on the assumption that oils or emulsions with viscosities greater than 7500 cP would no longer be dispersible. The dispersant effectiveness (DE) values measured using the Exdet test method in this project have been plotted against the emulsion sample viscosities and are presented in Figure 3. Fresh oil DE values were about 90% for all of the oils. Significant reduction in DE was recorded for 5 of the 7 test oils by the time the emulsion viscosities reached 7500 cP. The DE generally dropped to below 50% for these 5 oils by the time the viscosities reached 7500 cP. Only 2 data points were gathered for the PER 038 and Sockeye oils because of the rapid change in the emulsion viscosity but it is likely that the DE for these oils at 7500 cP would have been lower than that indicated by the linear plots for these oils in Figure 3. The Neptune and Oseberg oils achieved greater than 50% DE at viscosities approaching 15,000 cP. The 7500 cP value chosen as the cutoff for dispersibility was not shown to be universal for all oils and it appears to be a somewhat conservative upper limit for chemical dispersibility based on the Ohmsett field tests for the oils tested.

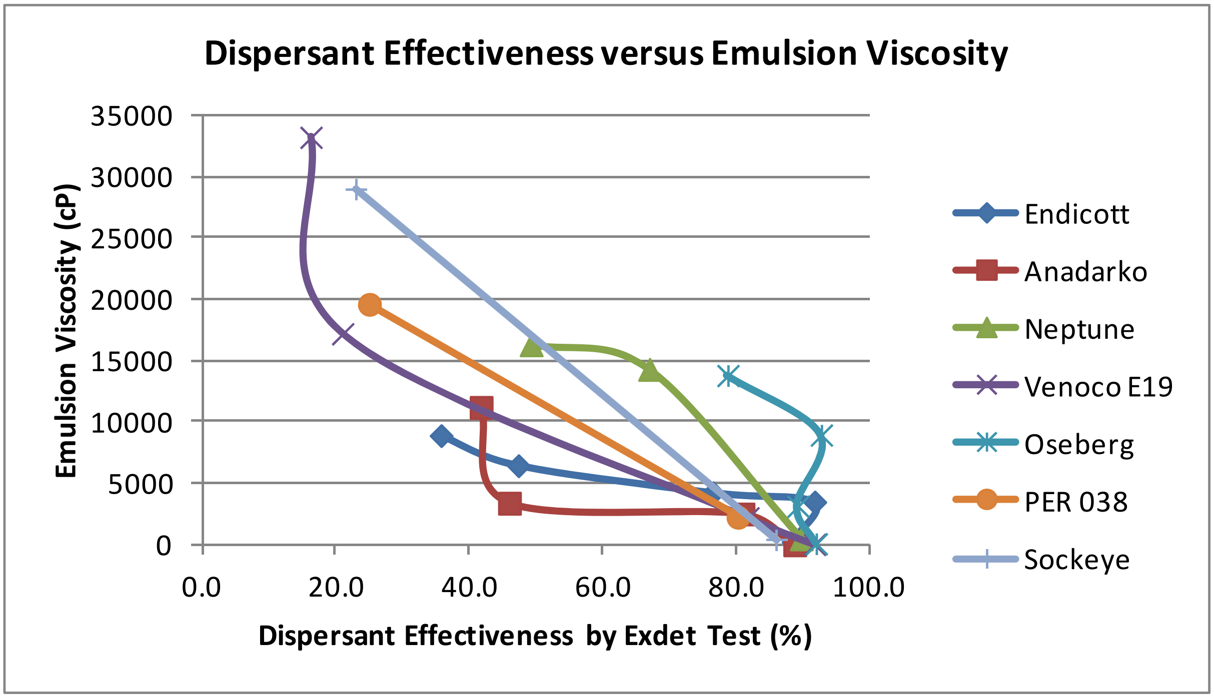


Figure 3. Dispersant Effectiveness versus Emulsion Viscosity

The relationships between chemical dispersant effectiveness as measured using the Exdet test versus weathering time on tank are shown in Figure 4. These curves have been interpolated or extrapolated (where necessary) to establish a time window where the DE has dropped to 30% and these time windows have been plotted in Figure 5.

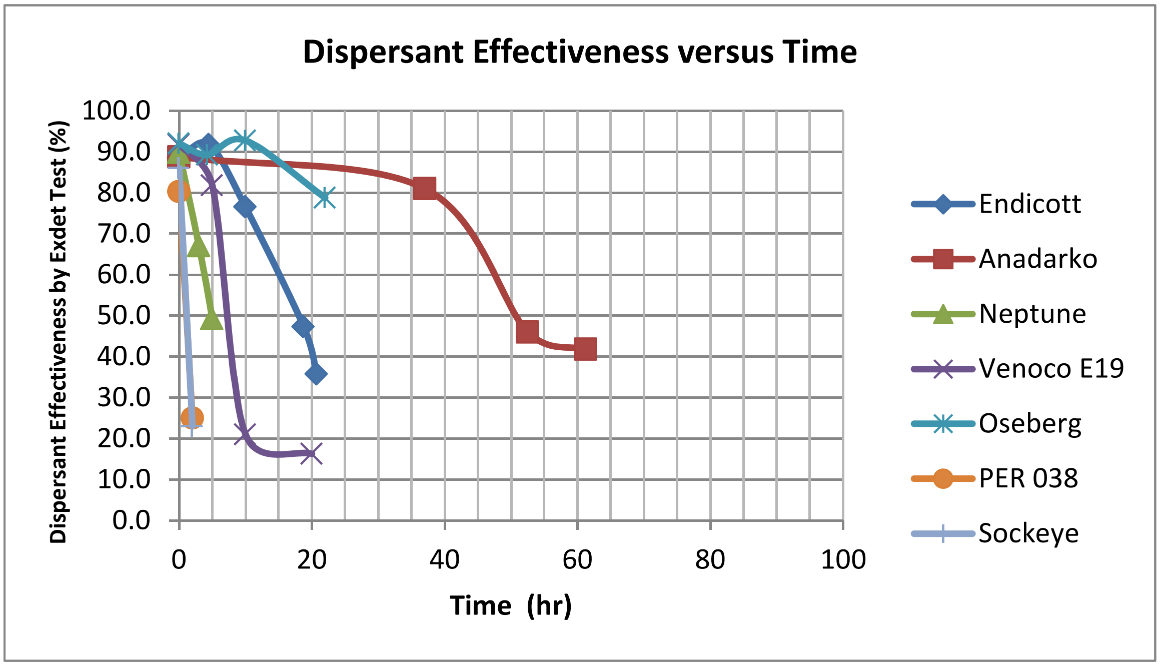


Figure 4. Dispersant Effectiveness versus On-Tank Weathering Time

Comparisons of the dispersant time windows as established in the Ohmsett test basin (time to 30% DE as per Exdet test) versus the correlation predictions from the earlier study are provided in Figure 5. The fresh oil property correlation over-estimates the time window for two of the oils (Anadarko and Venoco E19), is similar for the most persistent oils (PER 038, Neptune and Sockeye) and underestimates the time window for Endicott and Oseberg. From an operational perspective the fresh oil property correlation results provide a reasonable guide to the available time window for dispersants for the oils tested. The poorest correlation from an operational standpoint would be for the Endicott oil where the fresh oil property correlation indicates a considerably shorter window of opportunity than that identified in the Ohmsett testing.

The emulsion micro-photographs taken during the testing primarily serve to confirm the evolution of the emulsions formed during the testing. The photos can be accessed using the hypertext links provided in Table 2.

The parent oil densities were measured and reported primarily for use in future projects where this information would be useful in validating evaporative loss models

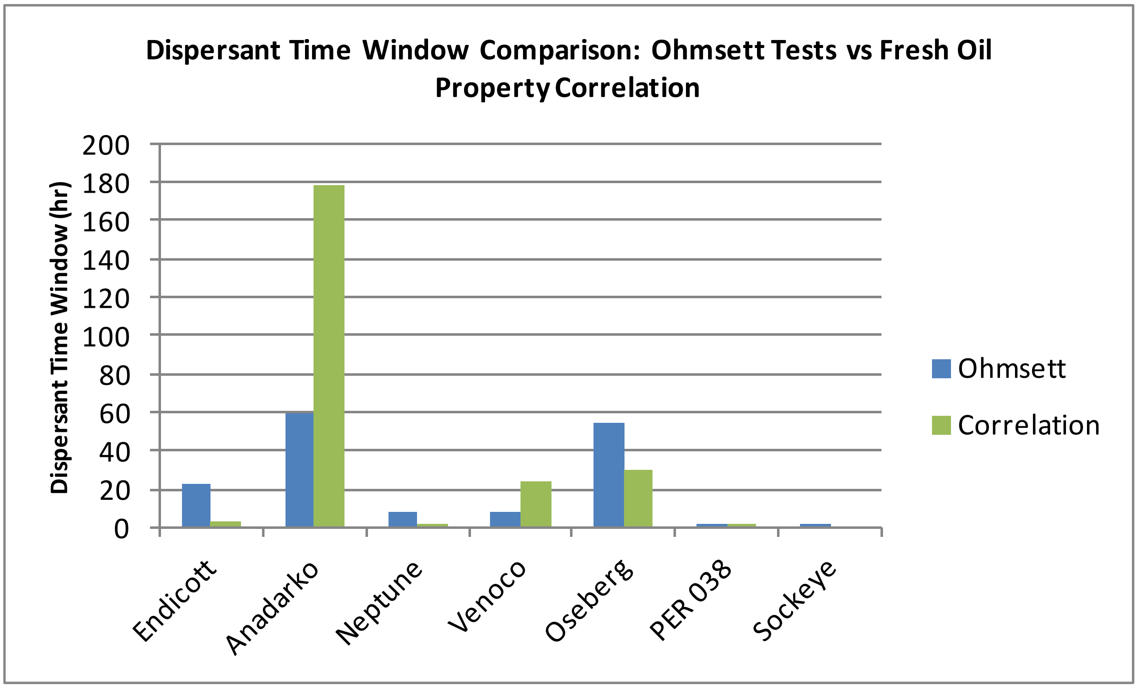


Figure 5. Dispersant Time Window Comparison: Ohmsett Tank Results versus Fresh Oil Property Correlation

Table 2. Test Result Summary

Test Oil & Link to Weather Data	Sample Number	Date (dd/mm/yy)	Time	Elapsed Time (hr)	Observed Weather Conditions	Water Content			Emulsion Micro-Photo Hypertext link	Parent Oil Density (g/cc 20 °C)	Emulsion Viscosity mPaS	Exdet Effectiveness (%)				
						Water (mm)	Oil (mm)	WC (%)				S.F. 1	S.F. 2	S.F. 3	S.F. 4	Ave.
Endicott	start	29/05/2012	6:45 PM	0	Sunny, hot				Appendix B							
	1	Fresh oil				-	-	0.0	EndTime0	0.896	120	88	91	86	89	88.5
	2	29/05/2012	11:15 PM	4.5		77	42	64.7	End 4.5	0.935	3500	92	92	92	91	91.8
	3	30/05/2012	4:45 AM	10.0		85	35	70.8	End 10	0.940	4250	52	80	92	82	76.5
	4	30/05/2012	10:45 AM	16.0	Cloudy	80	30	72.7	End 16	0.937	7400	dnt	dnt	dnt	dnt	
	5	30/05/2012	1:30 PM	18.75	Light rain	90	40	69.2	End 18.75	0.939	6460	61	47		34	47.3
	6	30/05/2012	3:30 PM	20.75	Cloudy	90	40	69.2	End 20.75	0.938	8910	44	36	30	33	35.8
Anadarko	start	30/05/2012	6:00 PM	0	Overcast, warm											
	1	fresh oil				0	115	0.0	Anadarko0	0.912	14	92	88	85	90	88.8
	2	31/05/2012	11:00 PM	5.0		0	110	0.0		0.924	10	dnt	dnt	dnt	dnt	
	3	31/05/2012	7:30 AM	13.5	Sunny	0	115	0.0		0.928	20	dnt	dnt	dnt	dnt	
	7	1/6/2012	7:00 AM	37	Sunny	89	20	81.7	Anadarko37	0.938	2520	dnt	dnt	dnt	dnt	
	7	1/6/2012	7:00 AM	37	Sunny	95	25	79.2	Anadarko37	0.939	2520	87	72	83	82	81.0
	8	1/6/2012	1:30 PM	43.5	Cloudy	89	34	72.4	Anadarko43.5	0.949	3170	dnt	dnt	dnt	dnt	
	9	1/6/2012	10:30 PM	52.5		102	25	80.3	Anadarko52.5	0.942	3400	63	46	51	24	46.0
	10	2/6/2012	7:15 AM	61.25	Cloudy	90	32	73.8	Anadarko61.25	0.948	11200	44	56	34	33	41.8
Neptune	start	2/6/2012	10:30 AM	0	Sunny											
	1	Fresh oil				0	125	0.0	Neptune0	0.925	390	88	91	92	88	89.8
	2	2/6/2012	12:00 PM	1.5	Sunny	48	72	40.0	Neptune1.5	0.949	2180	dnt	dnt	dnt	dnt	
	3	2/6/2012	1:30 PM	3.0	Sunny	55	77	41.7	Neptune3	0.954	14300	79	52	63	74	67.0
	4	2/6/2012	2:45 PM	4.25	Sunny	60	55	52.2	Neptune4.25	0.958	8680	dnt	dnt	dnt	dnt	
	5	2/6/2012	3:30 PM	5.0		72	60	54.5	Neptune5	0.969	16300	46	37	51	63	49.3
dnt – did not test																

Table 2 (cont.) Test Result Summary

Test Oil & Link to Weather Data	Sample Number	Date (dd/mm/yy)	Time	Elapsed Time (hr)	Observed Weather Conditions	Water Content			Emulsion Micro-Photo Hypertext link	Parent Oil Density (g/cc 20 °C)	Emulsion Viscosity mPaS	Exdet Effectiveness (%)				
						Water (mm)	Oil (mm)	WC (%)				S.F. 1	S.F. 2	S.F. 3	S.F. 4	Ave.
Venoco E19	start	3/6/2012	11:30 AM	0	Sunny											
	1	fresh oil				-	-	0.0		0.892	64	91	90	93	93	91.8
	2	3/6/2012	4:30 PM	5.0	Sunny	74	45	62.2	Venoco5	0.930	2215	75	82	87	83	81.8
	3	3/6/2012	9:30 PM	10.0		87	33	72.5	Venoco10	0.946	17200	20	32	20	12	21.0
	4	4/6/2012	2:30 AM	15.0		98	19	83.8	Venoco15	0.975	26700	dnt	dnt	dnt	dnt	
	5	4/6/2012	7:30 AM	20.0	Cloudy	95	27	77.9	Venoco20	0.978	33200	14	12	23	16	16.3
Oseberg	start	4/6/2012	9:30 AM	0	Overcast w											
	1	fresh oil			light rain	-	-	0.0	Oseberg0	0.881	-	91	94	92	91	92.0
	2	4/6/2012	1:45 PM	4.25	Overcast	92	31	74.8	Oseber4.25	0.898	3150	85	89	92	91	89.3
	3	4/6/2012	7:30 PM	10.0		93	21	81.6	Oseberg10	0.925	8950	93	92	92	94	92.8
	4	5/6/2012	1:30 AM	16.0		109	17	86.5	Oseberg16	-	6800	dnt	dnt	dnt	dnt	
	5	5/6/2012	7:30 AM	22.0	Partly cloudy	112	22	83.6	Oseberg22	0.941	13800	76	87	80	72	78.8
PER 038	start	5/6/2012	11:00 AM	0	Overcast											
	1	fresh oil				0	110	0.0	PER0	0.956	2255	86	73	86	76	80.3
	2	5/6/2012	1:00 PM	2.0	Overcast	12	112	9.7	PER2	0.962	19600	27			20	25.0
	3	5/6/2012	3:15 PM	4.25	Partly cloudy	6	117	4.9	PER4.25	0.979	31100	dnt	dnt 28	dnt	dnt	
Sockeye	start	6/6/2012	8:00 AM	0	Sunny											
	1	Fresh oil				-	-	0.0	Sockeye0	0.929	434	85	84	87	88	86.0
	2	6/6/2012	10:00 AM	2.0	Sunny			36	Sockeye2	0.960	29000	27	14	26	25	23.0
	3	6/6/2012	11:30 AM	3.5	Sunny			8.4	Sockeye3.5	0.979	68800	dnt	dnt	dnt	dnt	
dnt – did not test																

5. Discussion

The long-term weathering of oils at the Ohmsett facility was successful in generating realistic oils and emulsions that could be used to track the reduction in chemical dispersibility as the oil weathered. The oil weathering and emulsion formation rates experienced during the testing are specific to the energy conditions, air and water temperatures, and general weather conditions present during the actual weathering periods. It is likely that the wave energy level imparted had the most influence on the oil weathering and emulsification process and thus the time window estimates. The breaking wave density measured at Ohmsett was similar to those that have been recorded in the offshore suggesting that the rate of weathering at Ohmsett should also be similar to offshore wave conditions under light to moderate winds (4 to 5 m/s). Additional test series using different wave densities and under different temperatures/weather conditions would have to be completed to confirm the importance of each of these factors in the dispersant time window estimates.

The fresh oil property correlation developed in the earlier study appears to have merit in identifying the general trend of chemical dispersant time window of opportunity. The time window for dispersant use identified using large-scale testing at Ohmsett was compared to the results from the fresh oil property correlation. The fresh oil property correlations generally matched the short (less than 2 hours), moderate (2 to 24 hrs) and long-term (greater than 24hours) time windows that were identified in the Ohmsett tank testing (except for Endicott). However, the correlations did not accurately predict the actual individual time windows for the different oils. The fresh oil property correlation appears to be a useful tool to categorize the likely time that will be available for effective dispersant use into the coarse time window categories identified above.

Ohmsett tank testing with oils spanning a broader range of properties and compositions would improve the confidence in the dispersant time window model building and validation process.

The fresh oil property data required to complete the time window correlation were not complete for all of the oils. In particular, wax content data were not available for many of the oils. The fresh oil property correlation equation for small spills is negatively correlated to the wax content data (time window decreases with increased wax content) so the predicted time windows used in the report are maximum values. The two oils where the wax content has the most significance with respect to the time window prediction based on the fresh oil properties are the Platform Gail and Anadarko oils. If wax contents for the oils become available in the future the correlations should be re-calculated to determine the effect on the study conclusions. Oil properties derived from oil samples other than the actual oils tested at Ohmsett for both Endicott and Oseberg were used in the modeling. It is not known how significant an effect that this may have had on the correlations. The detailed oil analyses completed by Environment Canada in 2011 for a number of the oils used in this study only included physical properties for fresh and one weathered oil state. Properties for fresh and two or more weathered states are needed to generate accurate modeling parameters for use in oil spill fate modeling. Because of this we are not as confident with the modeled time windows for these oils. However, this did not affect the process used to validate the time window correlation model.

6. References

Ding, Li, D. Farmer. 1994. Observations of Breaking Surface Wave Statistics. Journal of Physical Oceanography. Volume 24, pp1368 to 1387.

Env. Can. 2012. Environment Canada's Online Spill Technology Database. Oil properties database. http://www.etc-cte.ec.gc.ca/databases/spills_e.html

SL Ross 2007. Identification of Window of Opportunity for Chemical Dispersants on Gulf of Mexico Crude Oils. Report to Minerals Management Service, U.S. Department of the Interior. November 2007.

7. Appendix A. Exdet Test Method Description

From: Becker (with modifications), K.W., M.A. Walsh, R.J. Fiocco, M.T. Curran. 1993. A New Laboratory Method for Evaluating Oil Spill Dispersants. Proceedings of the 1993 International Oil Spill Coference. Tampa, Florida, pp 507-510.

Equipment and supplies.

- Four 250 mL glass separatory funnels (such as Fisher 10-437 -1OC) for clamping onto the shaker. The 250 mL line should be approximately at the widepoint of the flask. (Funnels that are about 8 in from neck base to stopcock are recommended rather than shorter, pear-shaped separatory funnels.) Each funnel is stoppered to prevent splash-out.
- Four 16 oz glass jars (per test) for draining dispersed oil-in-water samples.
- Eight 4 oz glass jars (per test) for solvent extracts
- Four 500 mL separatory funnels with glass stoppers for extracting the dispersed oil-in-water samples
- 100µL and 1000 µL Drummond Digital Microdispensers (pipettes)
- Biochrom Novaspec III and adequate supply of appropriately matched sample tubes (cuvettes)
- Dichloromethane as a solvent, for extraction
- Ohmsett tank water Salinity of 32 ppt)
- Polypropylene sorbent pads (3M sorbent sheets cut into 1.5 in squares)
- Burrell Wrist-Action Shaker, Model 75 (Fisher 14-260), with arms holding two double clamps on each side (which can hold a total of eight separatory funnels)-For convenience, it is best to use only the four front clamps.

Initial Procedure

Shaker setup. The arms of the wrist-action shaker are level so that the 250 mL separatory funnels must be in an upright, non-slant position before starting each test. The funnels are clamped to the shaker just above the stopcock. Artificial sea water is added (approximately 250 mL) to reach the widest part of each test funnel.

Calibration. Use the adjustment handle to set the shaker deflection angle amplitude to between 1.5° and 1.6°. To measure the amplitude, a rod with pen attached to the end is clamped perpendicular to the shaker shaft, and the pen deflection is measured. A pen deflection of 6 mm at a 218 mm distance from the center of the shaft to the tip of the pen (tangent 1.57° = 6/218) is set using the adjustment handle. Before each test the deflection angle was measured to verify that the pen deflection was in the 5 to 7 mm range. The oscillation frequency of the current Burrell shaker is approximately 390 cycles per minute. This was verified by stopwatch.

Detailed test method

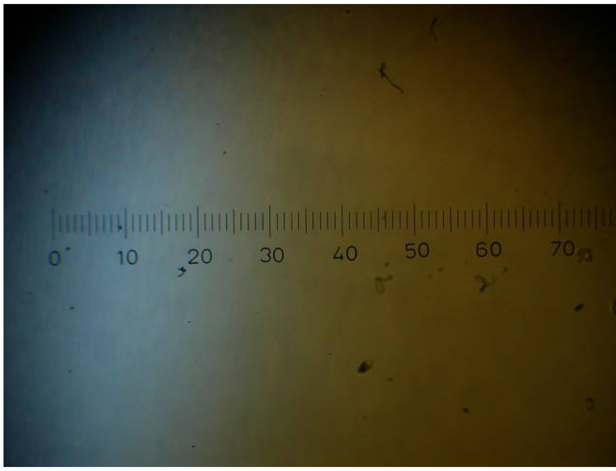
1. Fill each test funnel with artificial sea water to the widest part of the funnel (approximately 250 mL). Using the 1000 µL pipette, carefully add 1 ml of test oil to the top of the water in each test funnel. Then, sufficient dispersant was added to achieve a DOR of 1:25.. Stopper the funnels, start the shaker, and shake for 15 minutes. Then, without stopping the shaker, add one sorbent pad to each test funnel, replace the stopper, and continue shaking for 5 minutes more.
3. Do not stop the shaker, but remove the stoppers from each funnel, and drain the dispersed oil/water mixture from each funnel into 16 oz glass jars The sorbent pad remains in the funnel. Be sure to shut the stopcock immediately after the water drains to prevent any of the oil clinging to the sides of the test funnel from draining oil.
4. Stop the shaker, and add 50 mL of solvent to each funnel to extract the oil from the sorbent pads. Be sure to "wash" the sides of the funnel with solvent when adding the first 50 mL aliquot. Shake for 5 to 10 minutes, and then drain the oil/solvent mixture from each test funnel into separate 4 oz jars, squeezing the pad against the side of the glass jar to remove as much oil as possible. Repeat this procedure with a second 50 mL aliquot of solvent, adding the drainage to the first extract in the respective 4 oz jars. A total of 100 mL of solvent is used for each undispersed oil sample (see Note B). The shaking funnels are left in place at the end of the experiment, and, after rinsing with water, are ready for the next run.
5. While the pads are being extracted, the extraction of the dispersed oil/water fractions can begin. Transfer each of these fractions to a set of 500 mL separatory funnels. Rinse each of the 16 oz jars with 50 mL of solvent, and add this to the respective separatory funnels. Stopper, and shake the funnels vigorously by hand. After allowing the contents to separate completely, draw off the lower fraction into a set of 4 oz jars. Repeat the procedure with a second 50 mL aliquot of solvent for each sample, until the top fraction is clear of oil. A total of 100 mL of solvent is used for each dispersed oil sample.
These procedures result in two 4 oz jars (100 ml) of extracts for each test funnel, one of dispersed oil from the water, the other of undispersed oil from the sorbent pads.
6. The extracts are examined in the spectrophotometer at an appropriate wave-length setting, such as, 460 millimicrons. For some oils the extracts required dilution to fall in the linear range, 0.1 to 1.1, of the spectrophotometer. 7. Zero the spectrophotometer with a solvent blank. Read the absorbance of each pair of test samples, both water extract and sorbent pad extract.

The percent dispersed (%D) can be calculated without the use of a calibration curve as follows.

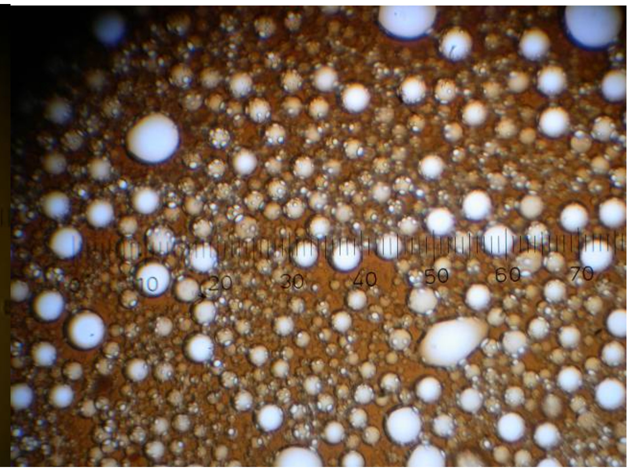
$$\%D = ((DD*DABS) / (DD*DABS + UD. UABS)) 100 \qquad (1)$$

Where: DD = dilution factor for the dispersed sample
UD = dilution factor for the undispersed sample
DABS = absorbance reading of the dispersed sample
UABS = absorbance reading of the undispersed sample

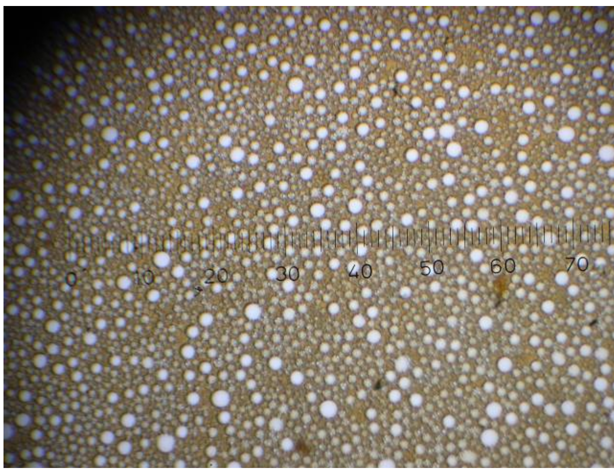
8. Appendix B. Emulsion Micro-Photographs



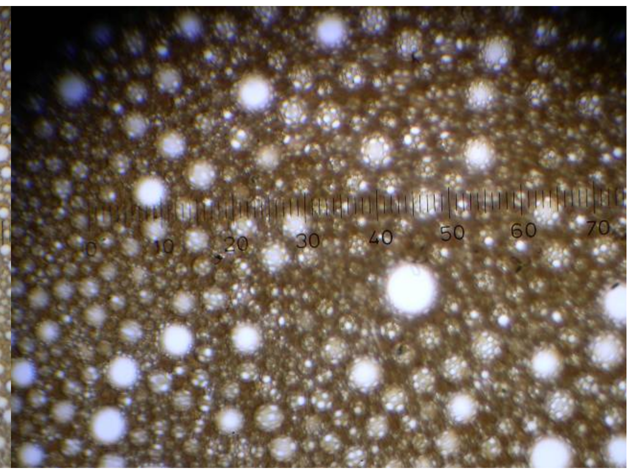
Fresh Endicott



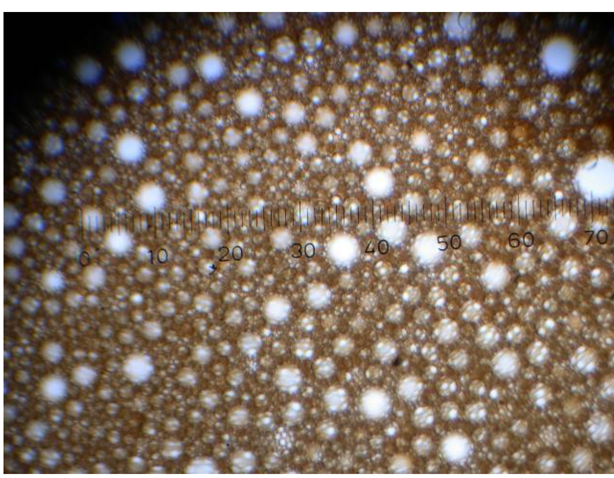
Endicott at 4.5 hours



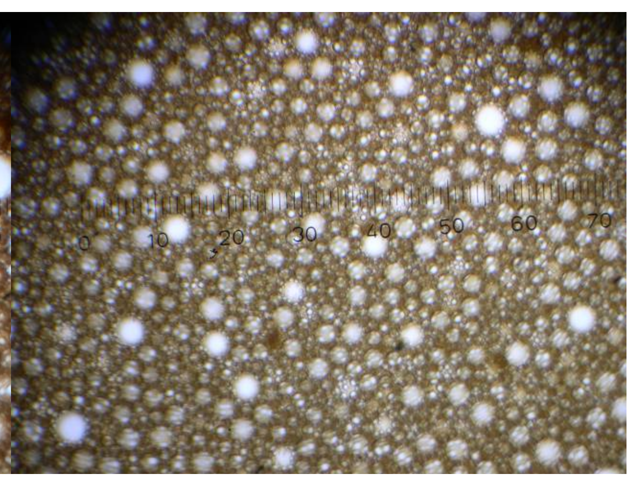
Endicott at 10 hours



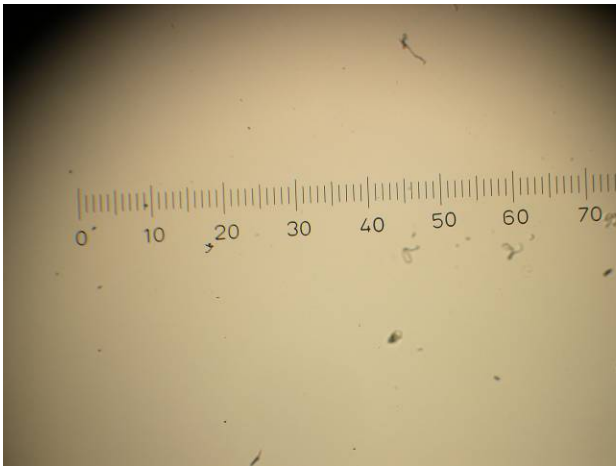
Endicott at 16 hours



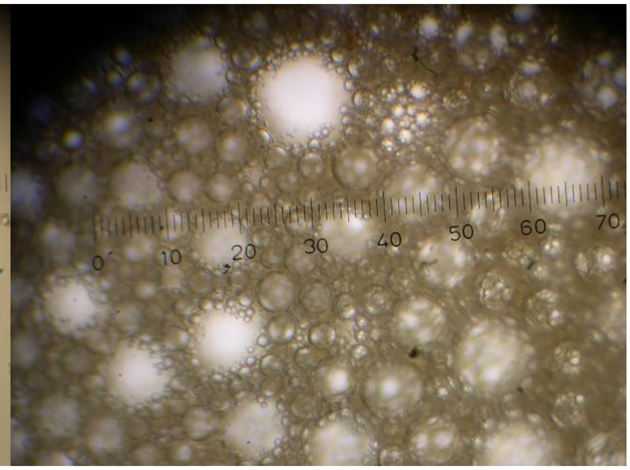
Endicott at 18.75 hr



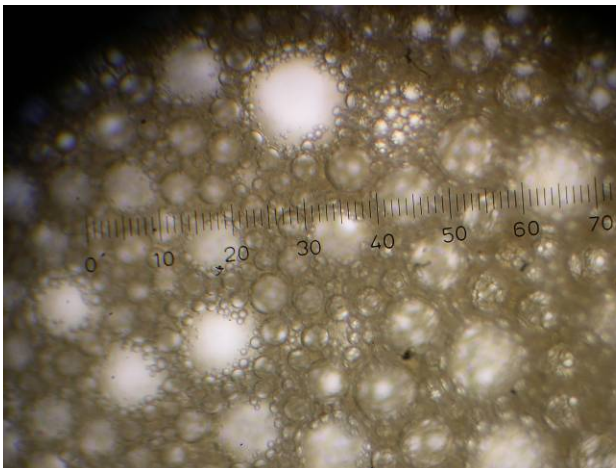
Endicott at 20.75 hr



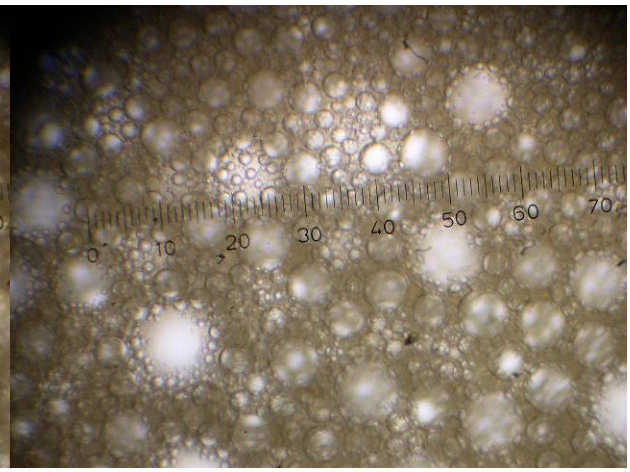
Anadarko Fresh Oil



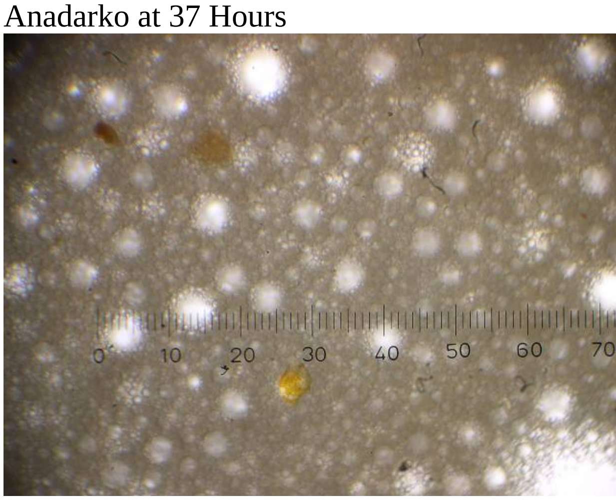
Anadarko at 37 Hours



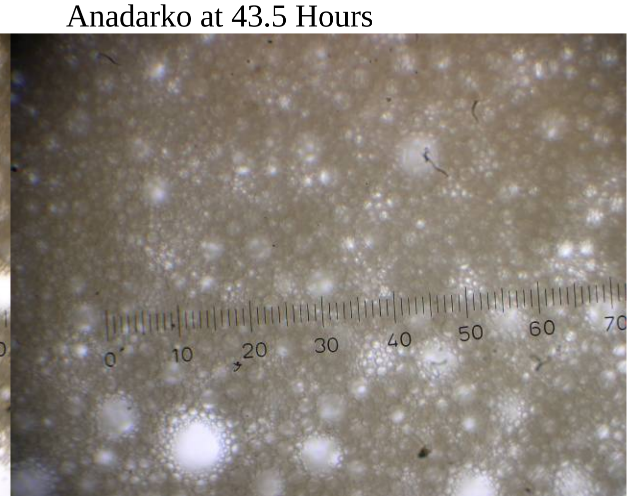
Anadarko at 37 Hours



Anadarko at 43.5 Hours

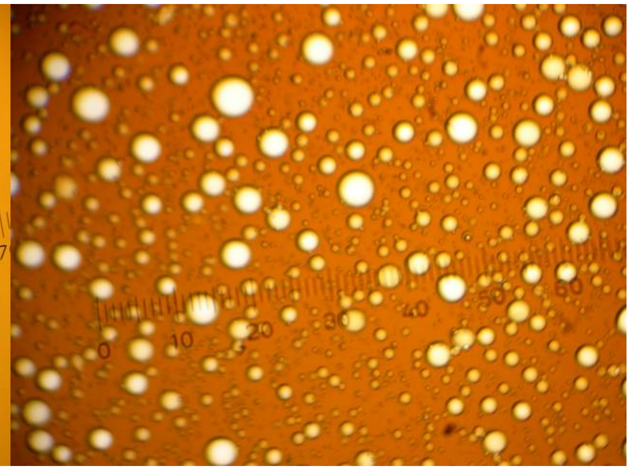


Anadarko at 52.5 Hours

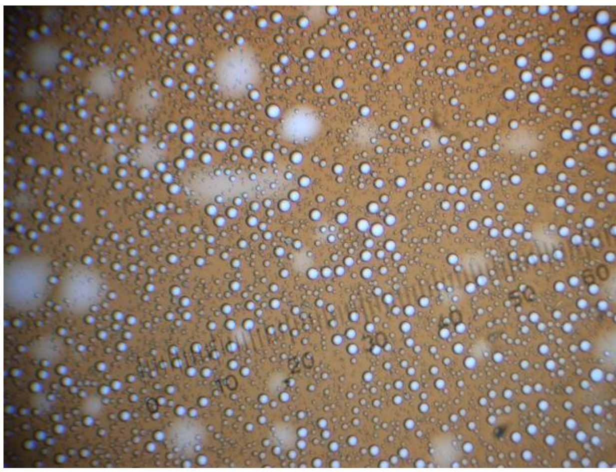


Anadarko at 61.25 Hours

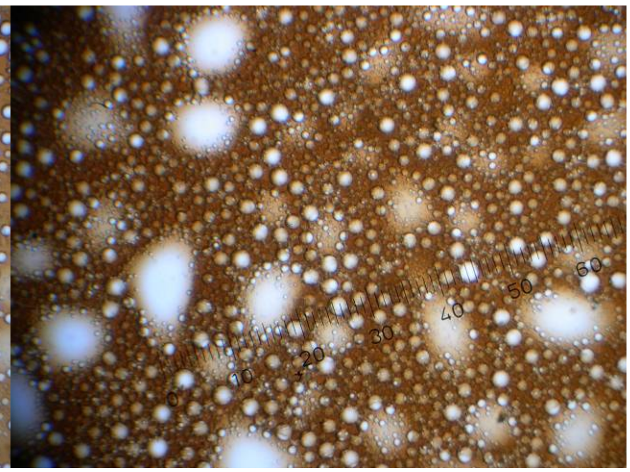
Neptune Fresh Oil



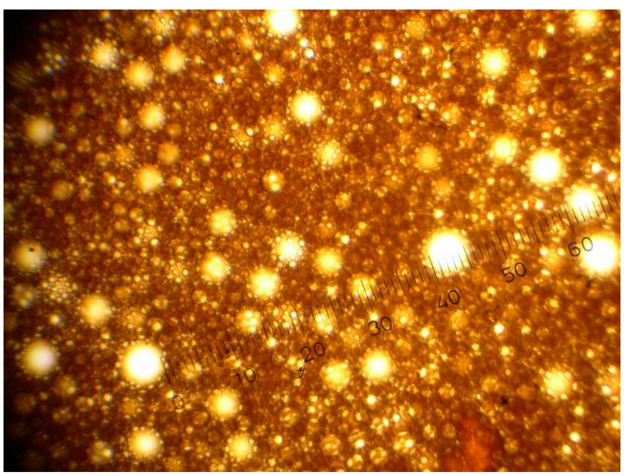
Neptune at 1.5 Hours



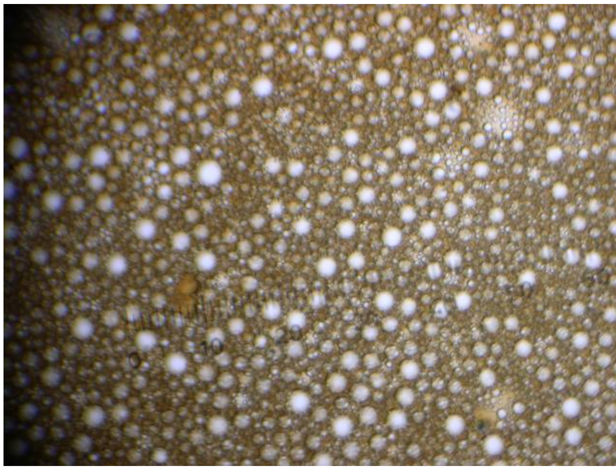
Neptune at 3.0 Hours



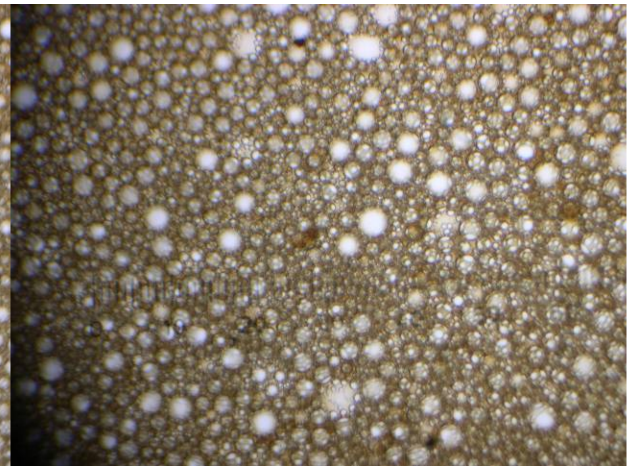
Neptune at 4.25 Hours



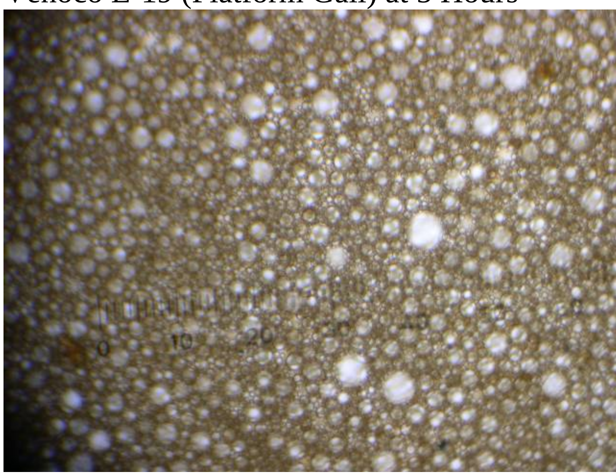
Neptune at 5 Hours



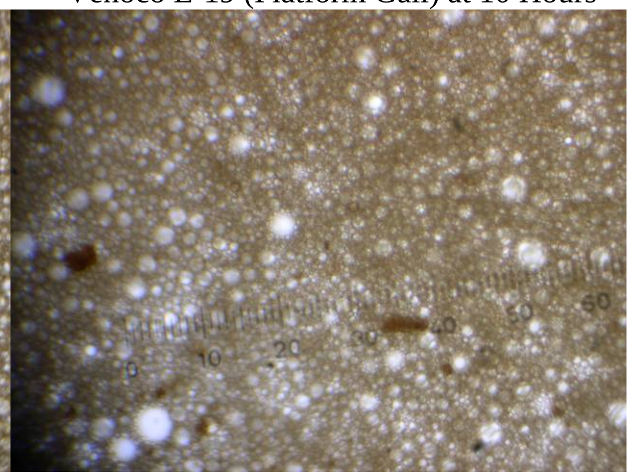
Venoco E-19 (Platform Gail) at 5 Hours



Venoco E-19 (Platform Gail) at 10 Hours

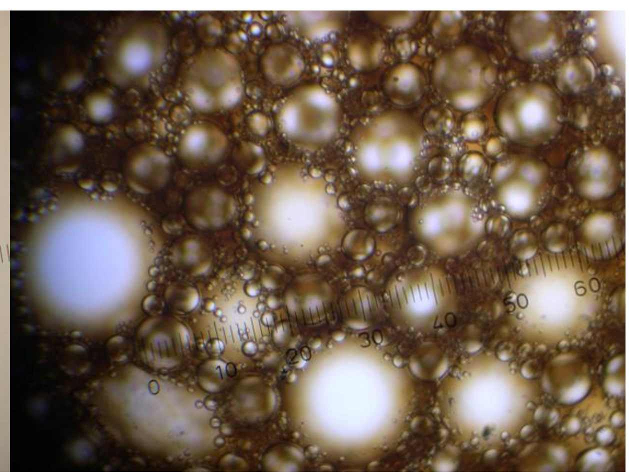


Venoco E-19 (Platform Gail) at 15 Hours

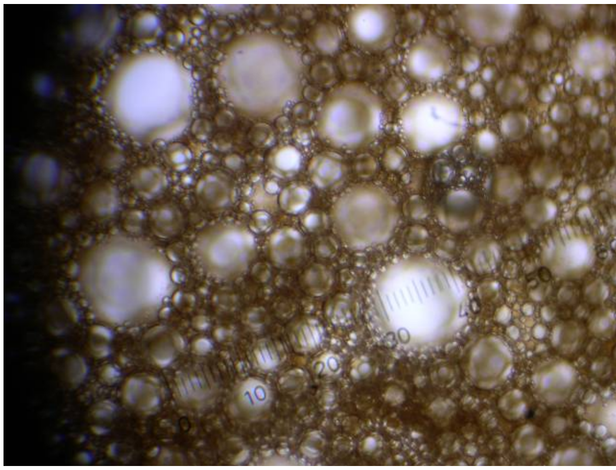


Venoco E-19 (Platform Gail) at 20 Hours

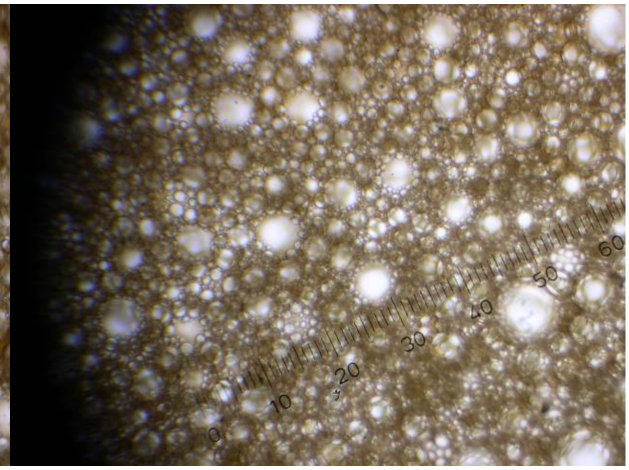
Oseberg Fresh Oil



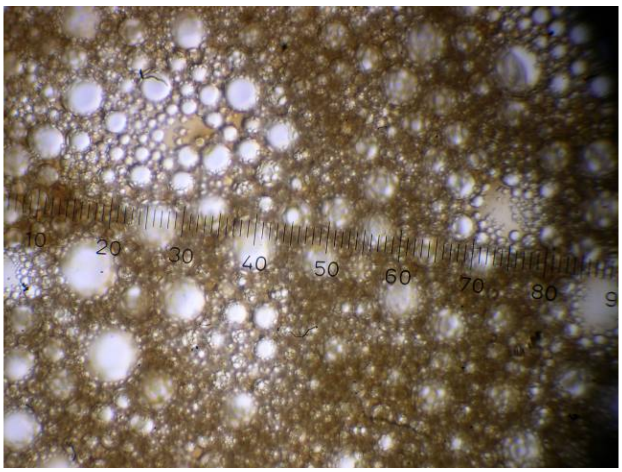
Oseberg at 4.25 Hours



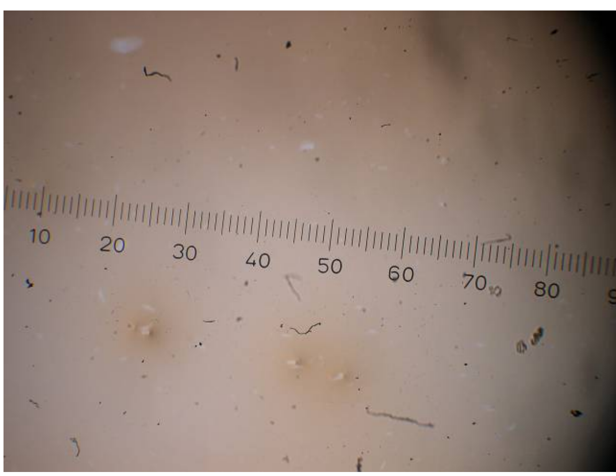
Oseberg at 10 Hours



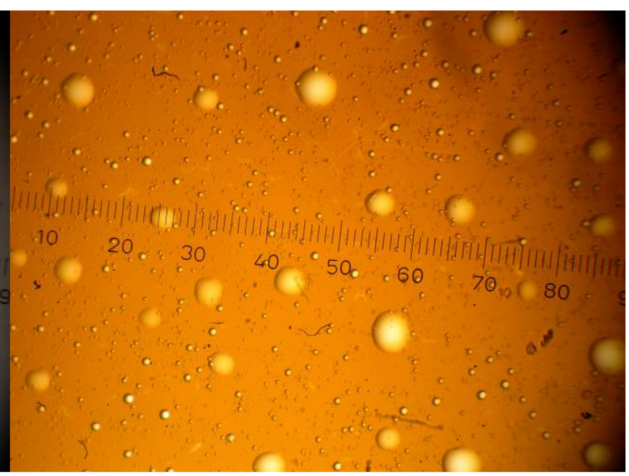
Oseberg at 16 Hours



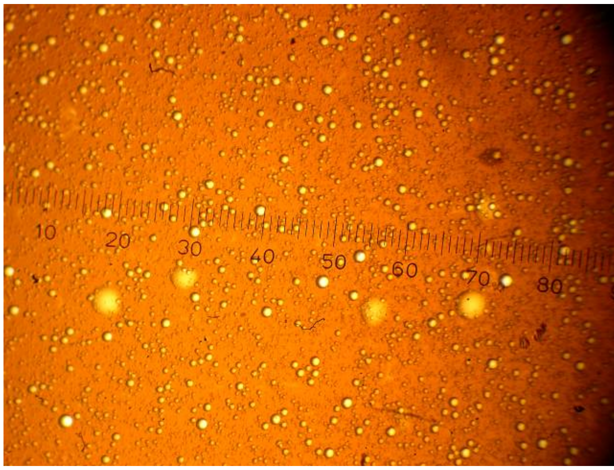
Oseberg at 22 Hours



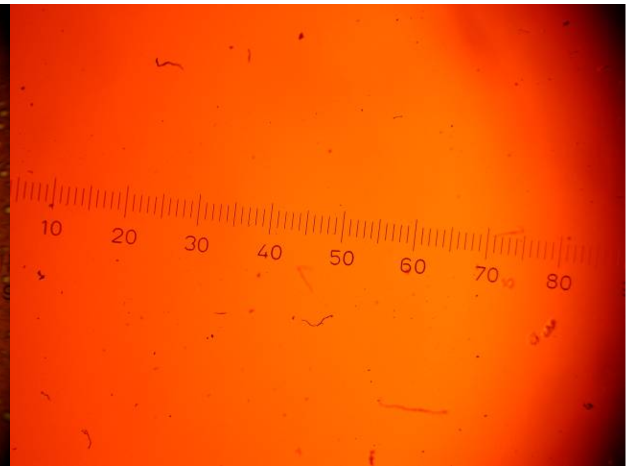
PER Platform Ellen 038 Fresh Oil



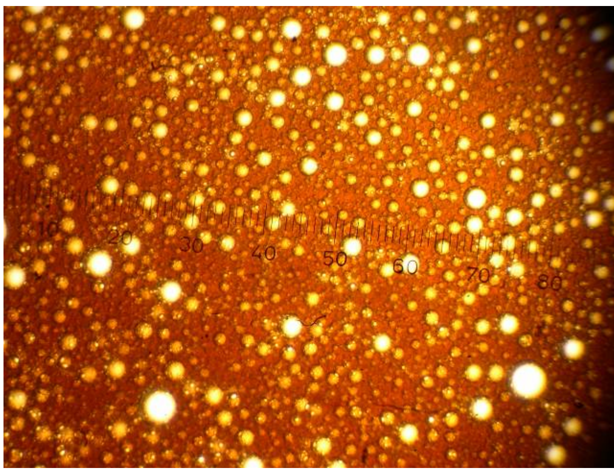
PER Platform Ellen 038 at 2 Hours



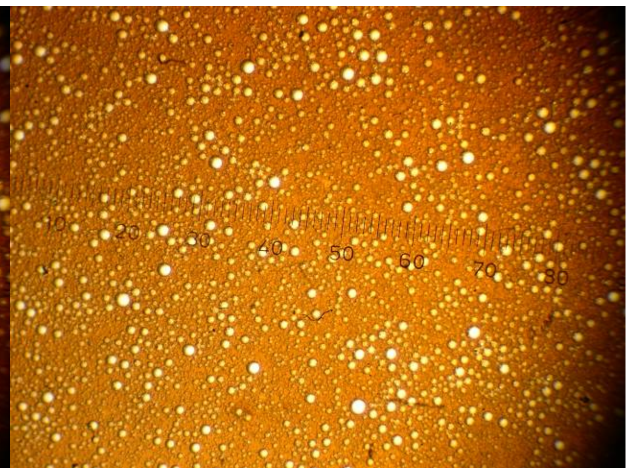
PER Platform Ellen 038 at 4.25 Hours



Sockeye Fresh

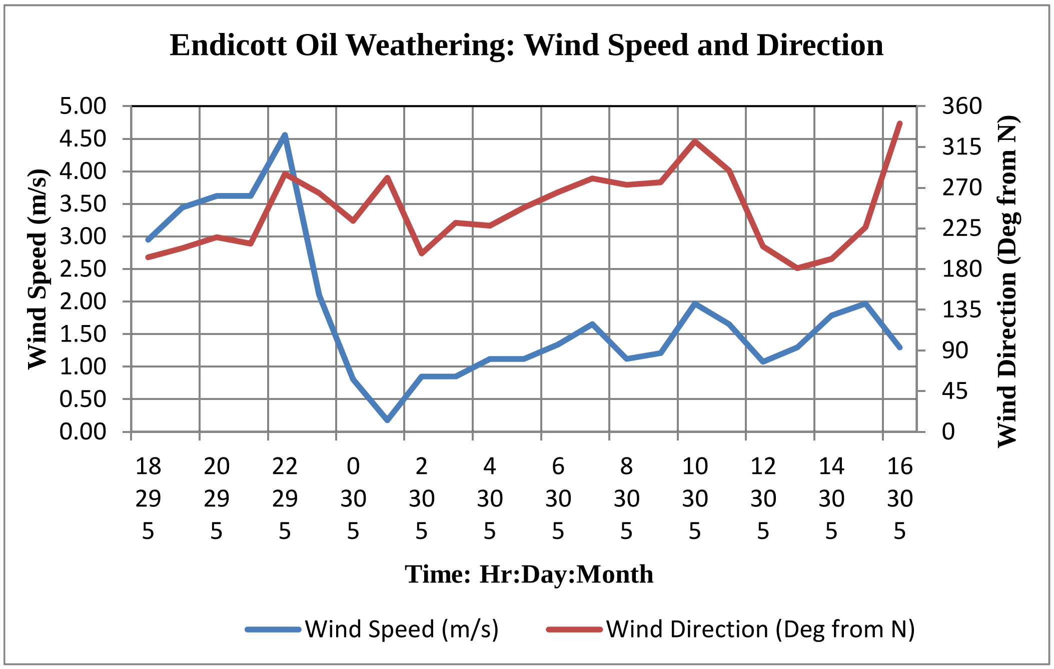


Sockeye at 2 Hours



Sockeye at 3.5 Hours

9. Appendix C. Weather Data During on Tank Weathering



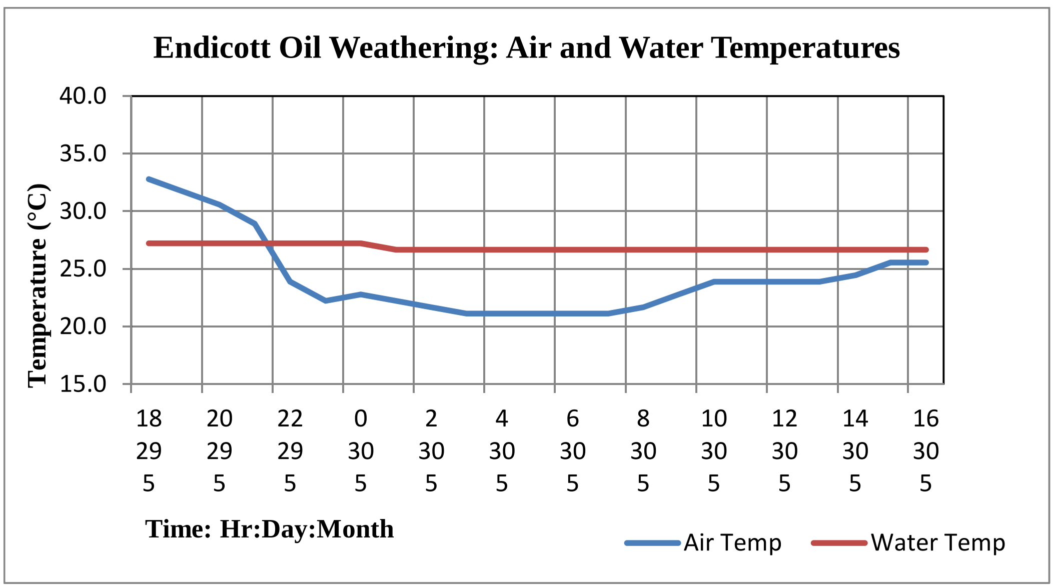
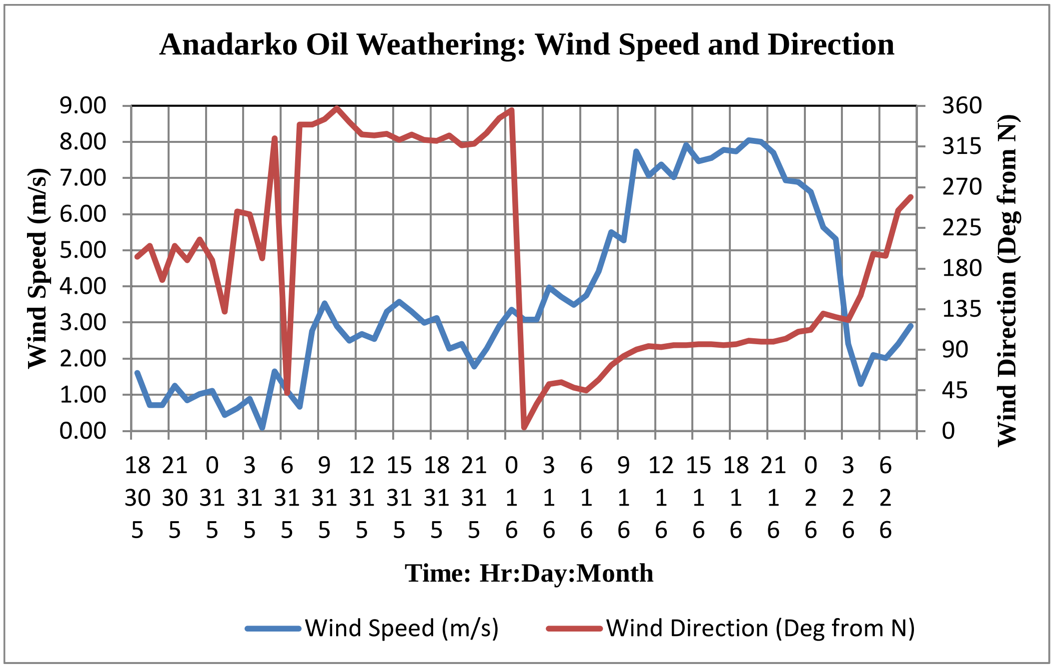


Figure C1. Weather conditions during the Endicott crude oil weathering period



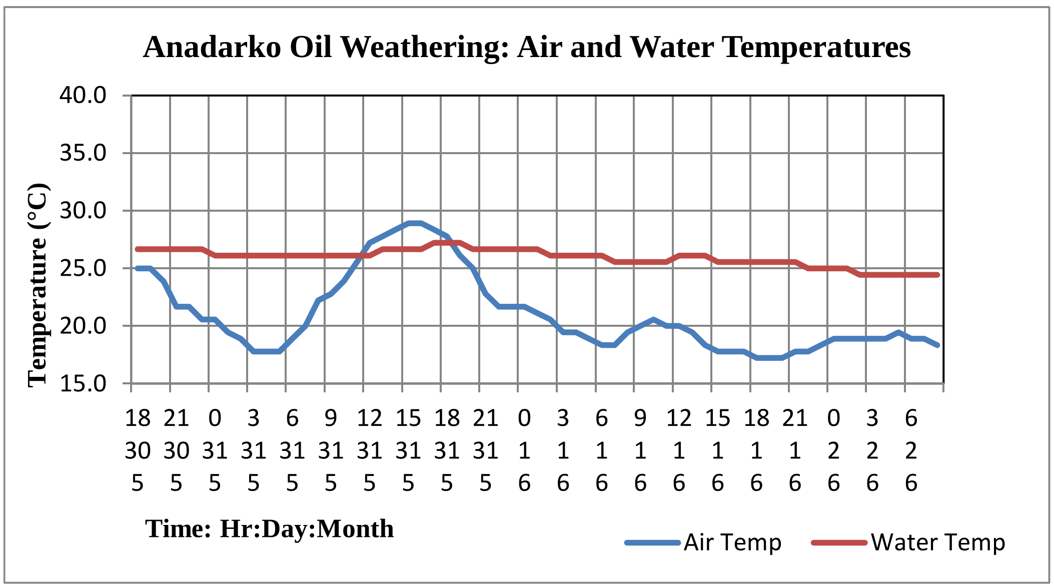
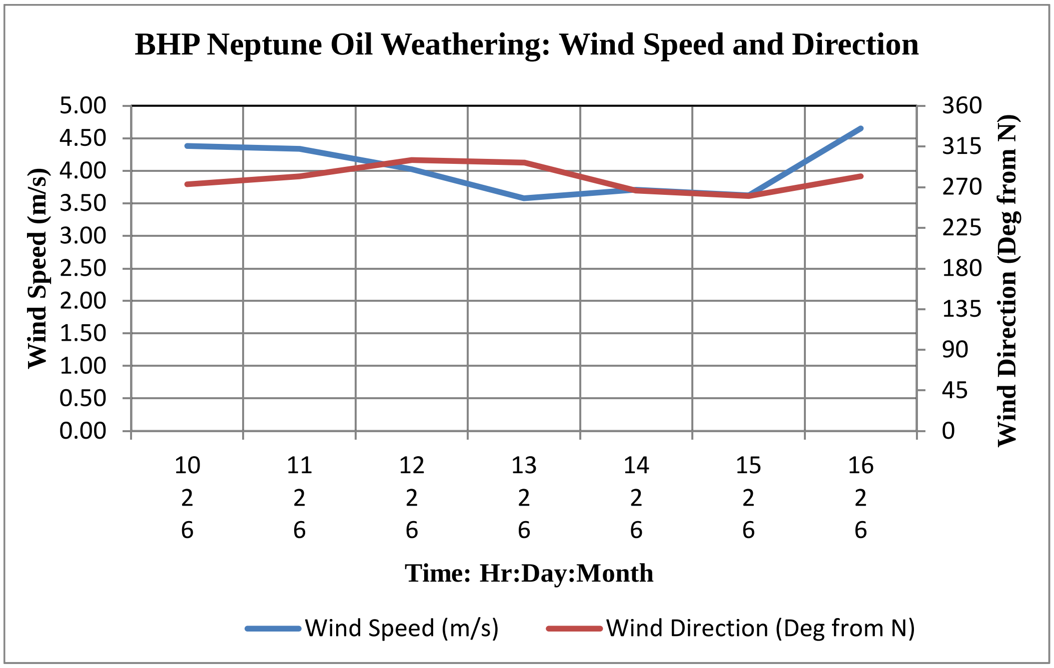


Figure C2. Weather conditions during the Anadarko crude oil weathering period



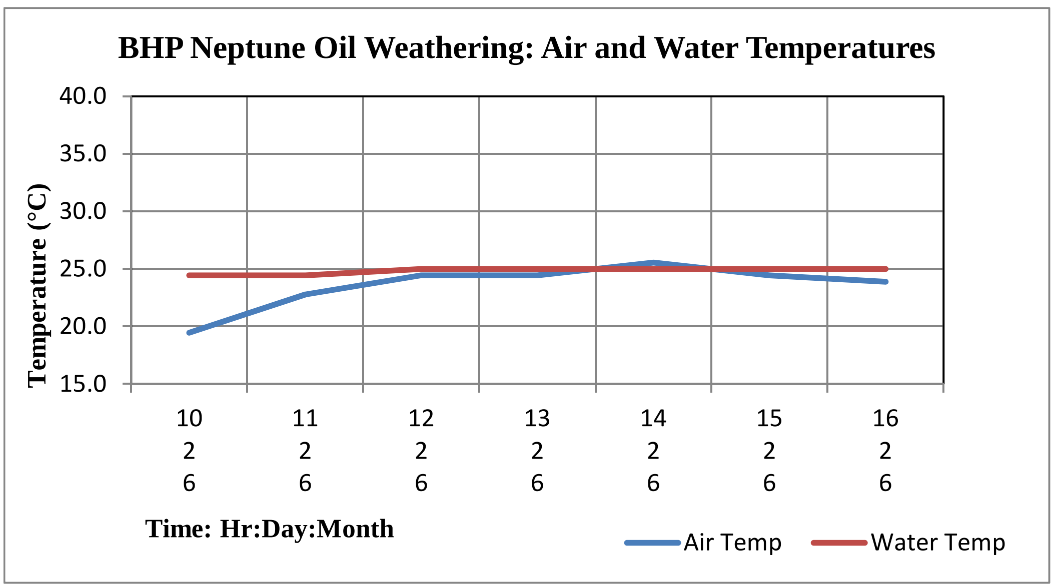
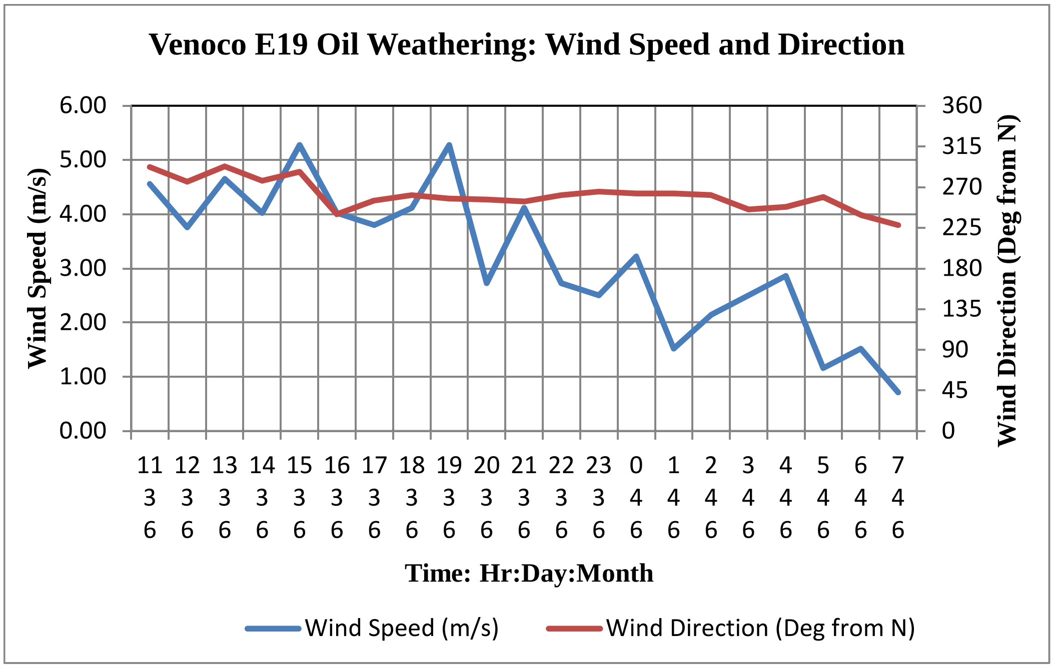


Figure C3. Weather conditions during the Neptune crude oil weathering period



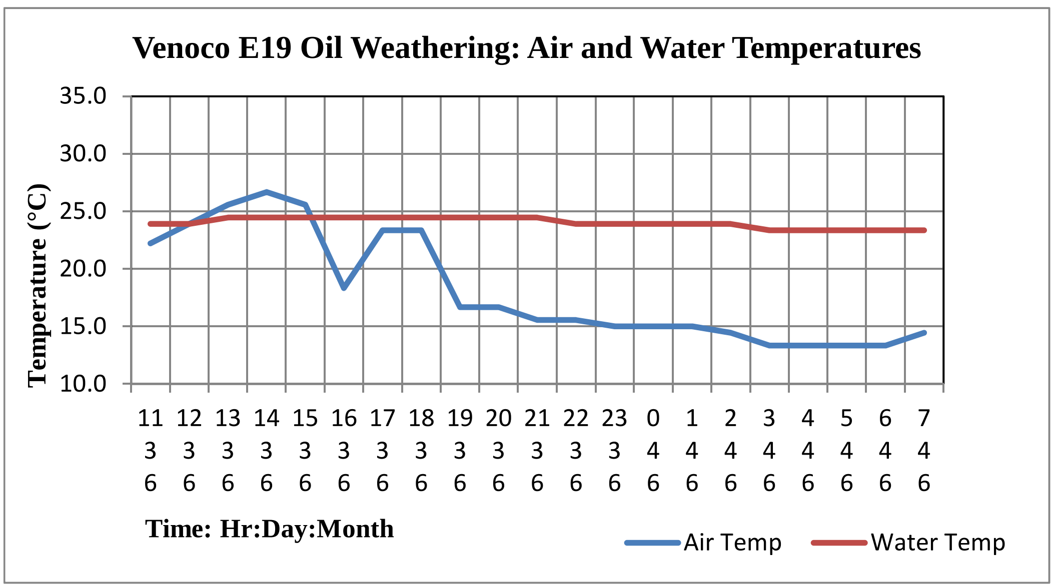
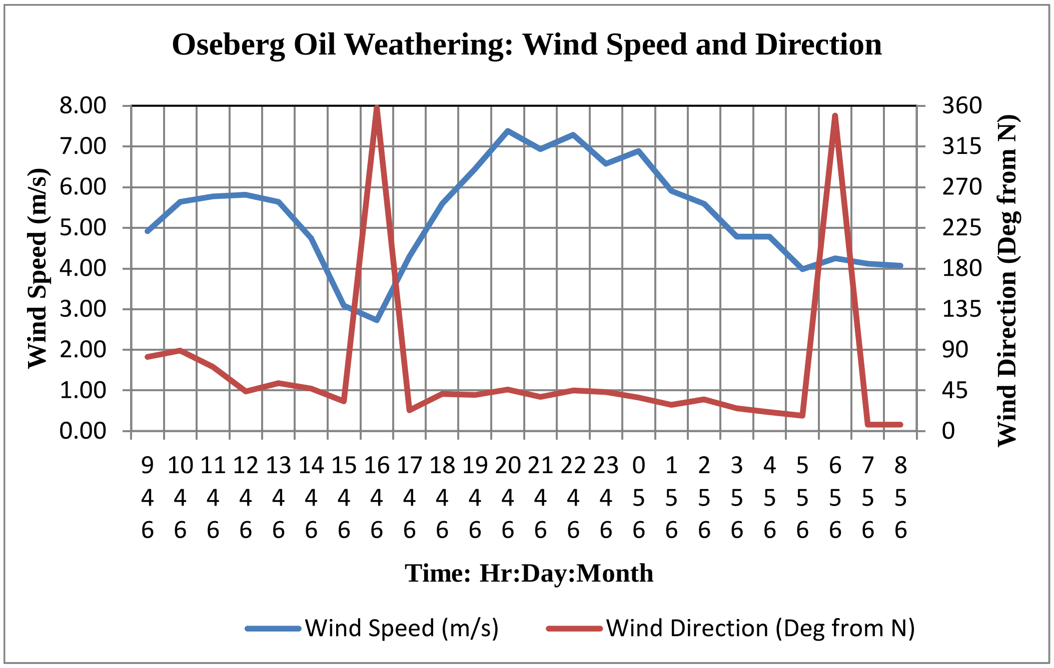


Figure C4. Weather conditions during the VenocoE19 crude oil weathering period



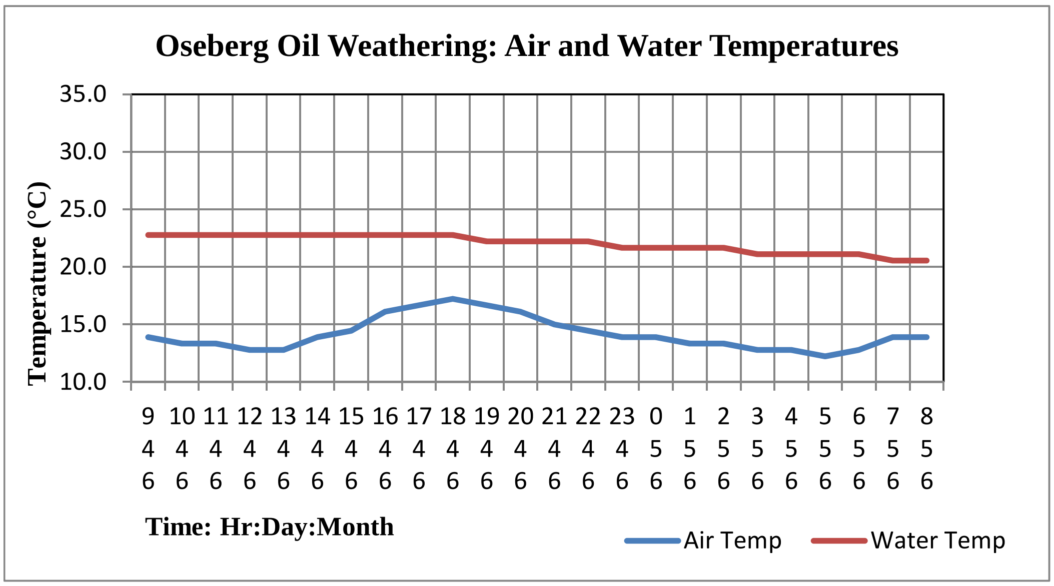
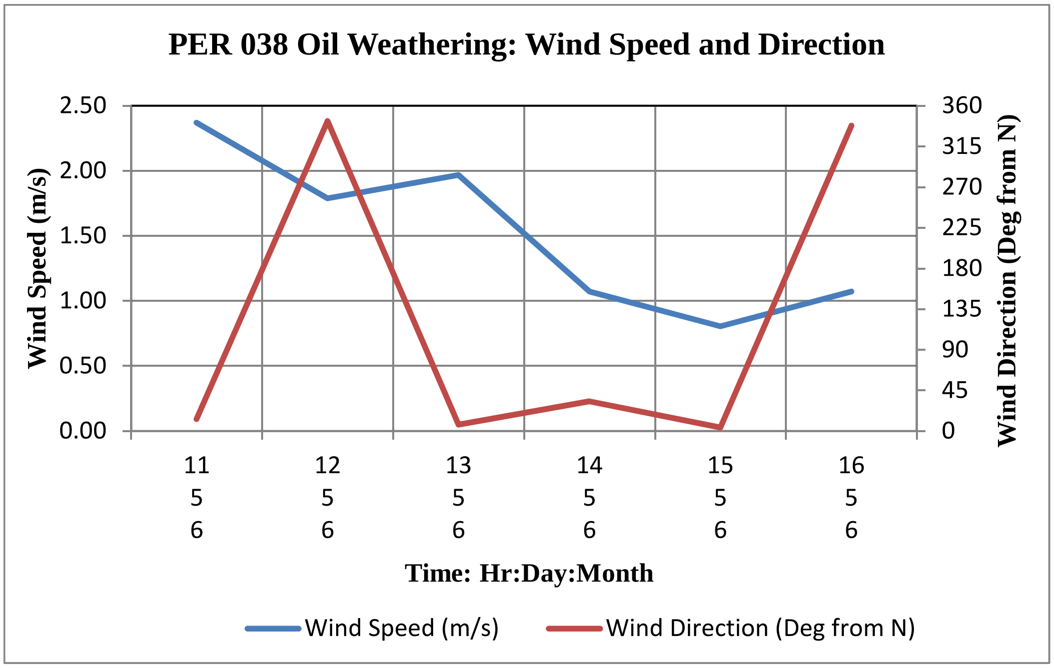


Figure C5. Weather conditions during the Oseberg crude oil weathering period



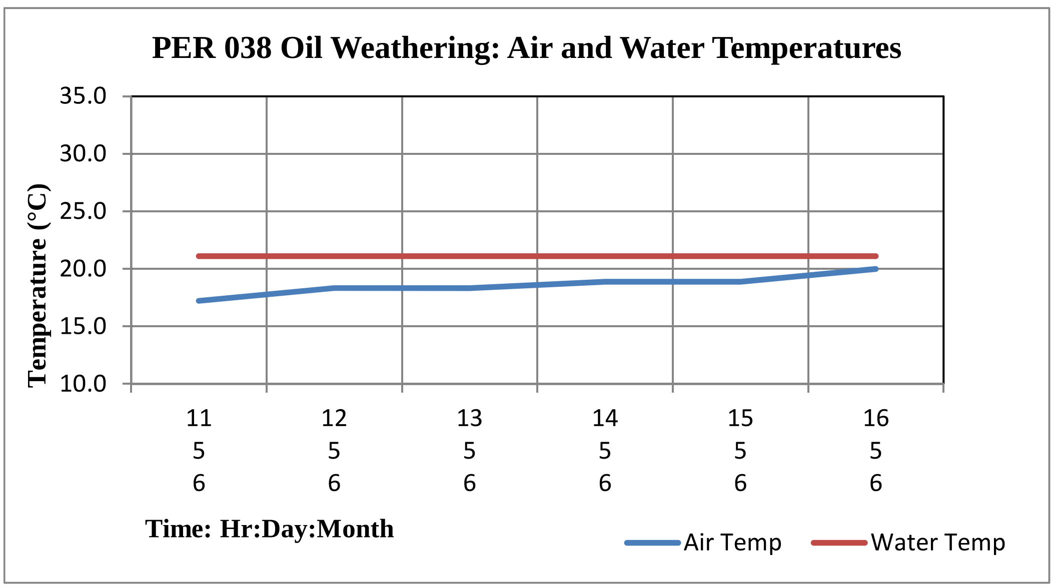
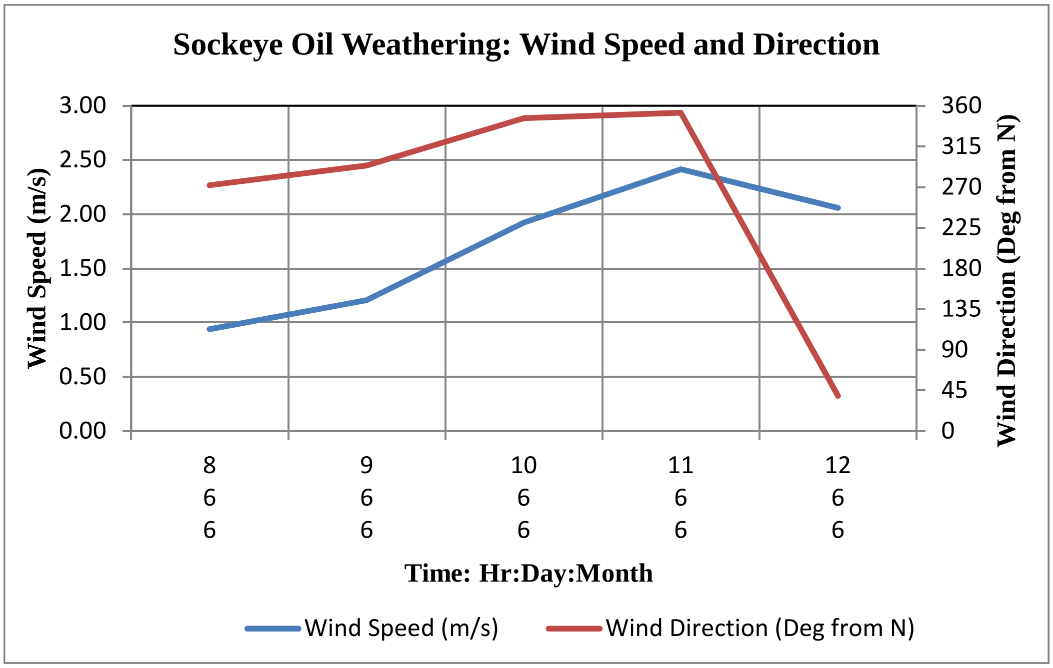


Figure C6. Weather conditions during the PER 038 crude oil weathering period



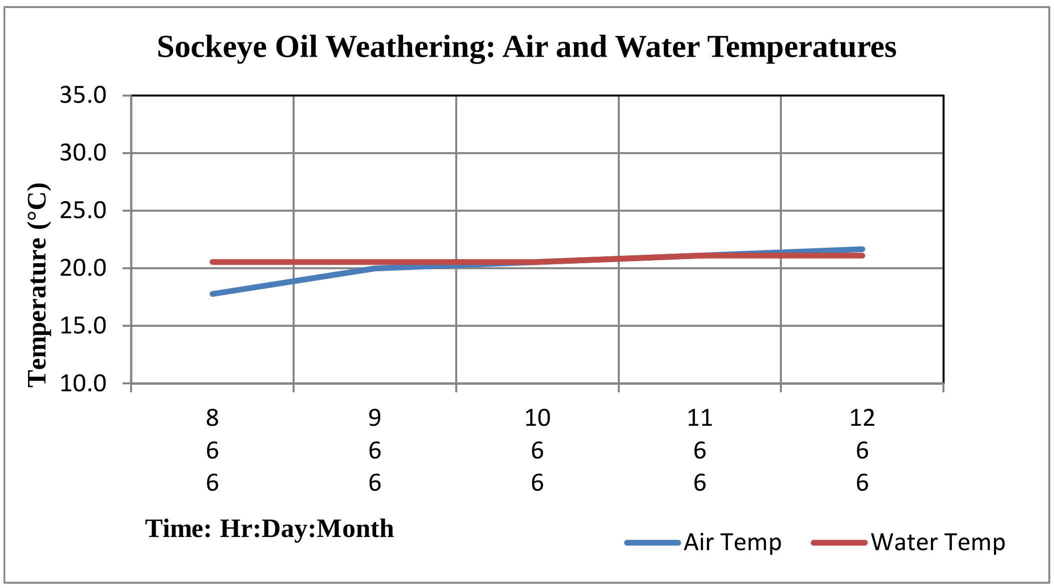


Figure C7. Weather conditions during the Sockeye crude oil weathering period