Final Report

Comparison of Large-Scale (Ohmsett) and Small-Scale Dispersant Effectiveness Test Results

For

U.S. Department of the Interior
Bureau of Ocean Energy Management, Regulation and Enforcement
Herndon, VA

By

SL Ross Environmental Research
Ottawa, ON

And

MAR Inc.

June 2011

Acknowledgements

This project was funded by the U.S. Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE). The authors wish to thank Joseph Mullin, of BOEMRE, for his guidance in the work. Jim Clark and Tom Coolbaugh of ExxonMobil provided the EXDET test results and the Corexit 9500a dispersant used in the Ohmsett testing. Pegasus Technical Services, Inc. completed the baffled flask tests under contract to EPA. The assistance of the following companies and their representatives in the sampling and shipping of oils used in the study is greatly appreciated: Susan Hathcock - Anadarko Petroleum Corporation, Paul Ardoin and Mike Kelly - BHP Billiton Petroleum (Americas) Inc., Scott Robertson - DCOR LLC, Brian Hansen – ExxonMobil, Steve Liles - Pacific Energy Resources Ltd., Derek Sullivan - Petro-Canada, East Coast Operations, David Rose and Byron Everist - Plains Exploration & Production Company, and Kieth Wenal -Venoco Inc

Disclaimer

This report has been reviewed by BOEMRE staff for technical adequacy according to contractual specifications. The opinions, conclusions, and recommendations contained in this report are those of the author and do not necessarily reflect the views and policies of BOEMRE. The mention of a trade name or any commercial product in this report does not constitute an endorsement or recommendation for use by BOEMRE. Finally, this report does not contain any commercially sensitive, classified or proprietary data release restrictions and may be freely copied and widely distributed.

Table of Contents

Executive Summary

The objective of the work was to compare the results of large-scale dispersant effectiveness tests conducted at the Ohmsett facility to those from a number of small-scale laboratory tests.

Large-scale DE testing was completed at the Ohmsett test tank in the week of October 26th through 30th, 2009 and on November 1st and 2nd, 2010 using the standard DE test protocol developed for dispersant testing at Ohmsett over the past several years.

A Sequoia Scientific LISST 100X particle size analyzer (LISST) was used to record data on oil drop sizes and in-water oil concentrations. A Turner Cyclops C3 *in-situ* fluorometer (C3) was also deployed to measure in-water oil concentrations.

The C3 device identified the same concentration peaks and valleys as the LISST system but the calibration-adjusted C3 peak concentration values were lower (by a factor of 1.5 to 5 times) than the peak LISST values in six of eleven tests where valid C3 values were recorded. For two of the tests the concentrations as determined by the C3 were similar to those as measured by the LISST. For three tests the C3 measured concentrations were higher than the LISST data by factors between 1.5 and 3.5. The C3 measurement may be sensitive to the oil drop size distribution as has been reported for similar *in-situ* fluorescence measurement systems.

Dispersant effectiveness (DE) results in the Ohmsett tank testing varied from 49 to 99%. With only two exceptions, oils with viscosities less than 3,500 cP resulted in dispersant effectiveness of 95% or greater in the Ohmsett tests. DE values between 49 and 78% were achieved on oils with viscosities between 9,500 and 31,195 cP.

A comparison of the Ohmsett test results with those from the three small-scale tests methods is summarized in the main body in Figure 5. Of the three small-scale test methods the EXDET test results most closely matched the Ohmsett efficiencies but under-estimated dispersant effectiveness (by between 6 and 33%) when compared to the large-scale Ohmsett results for the majority of the oils tested.

The baffled flask test results more closely matched the Ohmsett efficiencies than the WSL or swirling flask tests but under-estimated dispersant effectiveness by an even wider margin (between 11 and 67%) than the EXDET tests when compared to the large-scale Ohmsett results.

The small-scale WSL dispersant efficiency test results were lower than the swirling and baffled flask methods for the lightest oils but tended to be higher for the mid- to high- viscosity oils. We believe this is due to an oil density bias in the WSL test that generates low DE estimates for light, buoyant oils and inflated DE values for denser, less buoyant oils.

The swirling flask tests showed measurable dispersion (>10%) only for the lightest of the test oils (viscosity less than about 500 cP). None of the other tests generated as consistently low DE estimates on oils with viscosities between 500 and 20,000 cP. It appears that the swirling flask test underestimates DE when compared to the other test methods over a significant range of oil viscosities (between about 500 to 20,000 cP).

Oils with viscosities over 10,000 cP generally resulted in efficiencies below 10% in all of the small-scale test methods. The Ohmsett DE estimates for these higher viscosity oils ranged from 50% to as high as 88%.

Comparison of Large-Scale (Ohmsett) and Small-Scale Dispersant Effectiveness Test Results

1. Objective

The objective of the work was to compare the results of small-scale laboratory dispersant effectiveness tests on a range of oil types to results from large-scale tests conducted at Ohmsett, the National Oil Spill Response Research & Renewable Energy Test Facility.

2. Background

Bench scale dispersant effectiveness tests are routinely used around the world to rank the potential effectiveness of a dispersant product on standard oils or to study the effect of oil and dispersant type and environmental parameters on dispersant effectiveness. In the United States oils must achieve a measured effectiveness of 45% or greater in the swirling flask test to be placed on EPA's NCP Product Schedule as an approved dispersant. But, what do the effectiveness values recorded in these laboratory tests mean with respect to likely effectiveness in the field and do the bench scale tests fairly evaluate dispersant products? Attempts have been made to correlate the results of bench scale tests to one another with mixed success suggesting that few, if any, of the tests are representative of real-world situations. Very limited field data is available to allow the comparison of bench scale test results to field success and so this has also not been adequately done. In this project the Ohmsett test facility has been used as a surrogate to the field to provide "field" effectiveness estimates on a number of oils. Bench-scale tests have been completed using the same dispersant and oil combinations and the results compared to establish if the bench-scale test results provide a reasonable estimate of field performance. The EPA Baffled Flask Test (BFT), the WSL Laboratory test (WSL), ExxonMobil's EXDET test and the swirling flask test are the bench-scale test methods used in the study.

3. Large-Scale Ohmsett Testing

3.1 Methods

Large-scale DE testing was completed at the Ohmsett test tank in the week of October 26th through 30th, 2009 and on November 1st and 2nd, 2010. An overhead view of the Ohmsett facility is provided in Figure 1. The standard DE test protocol developed for dispersant testing at Ohmsett over the past several years was used in this project. Detailed descriptions of the test protocol, and its development, and equipment used in the testing can be found in previous publications (SL Ross et al 2000, 2003, 2004, 2006).

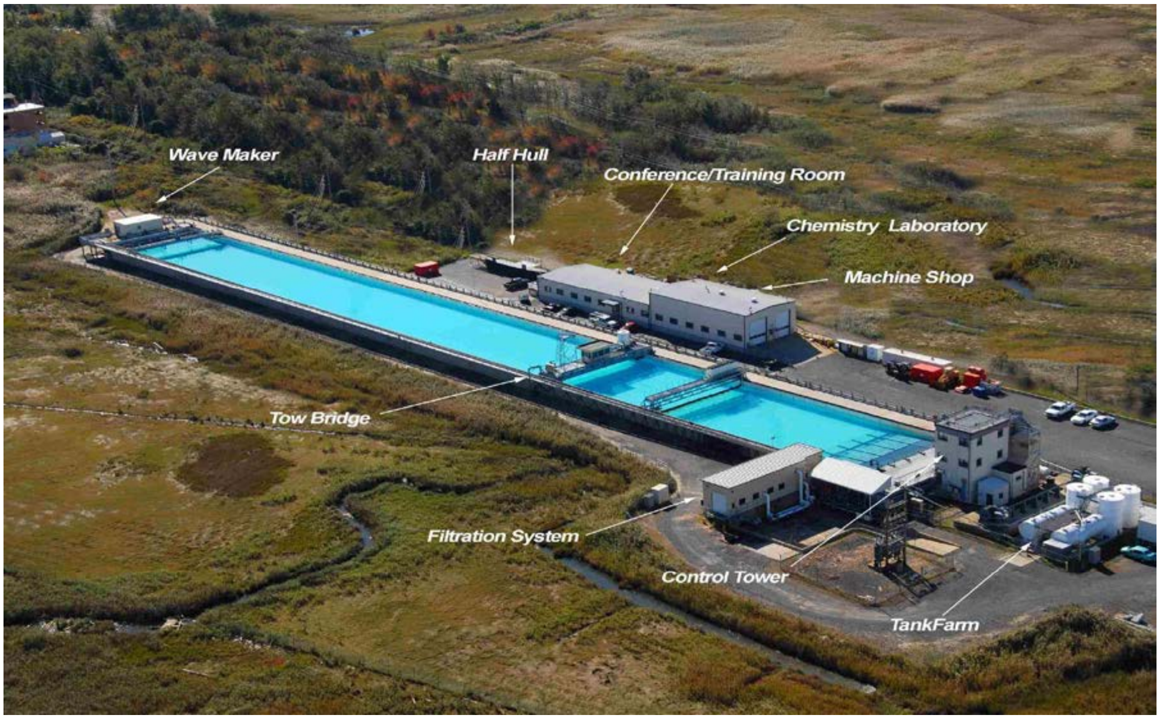


Figure 1. Ohmsett - The National Oil Spill Response Research & Renewable Energy Test Facility

The basic test procedure used for the dispersant effectiveness tests in this project was as follows.

1. The oil containment area was established by placing booms across the north and south ends of the Ohmsett tank.
2. The oil and dispersant were loaded into their respective supply tanks on the main bridge deck.

3. The main bridge was positioned at the southern quarter point within the boomed area. The wave paddle was started and the waves were allowed to develop to a stage just prior to the formation of breaking waves.
4. The wave paddle settings used in all of these tests were a 3.5-inch stroke and 34 to 35 strokes per minute.
5. The bridge was moved south at the required speed to achieve proper slick dimensions and dispersant application dosage (either 1 or ½ knot (0.5 or 0.25 m/s) for this test series).
6. The oil was pumped at the required rate onto the surface through the discharge manifold mounted on the south side of the bridge (nominally 20 gpm for one minute in this test program).
7. The dispersant was applied to the oil slick from the spray bar system mounted on the north side of the bridge in the same pass as the oil discharge.
8. The behavior of the treated oil was observed as the bridge was moved over the treated slick.
9. Slicks were agitated by the breaking wave-field for 30 minutes after which waves were stopped.
10. A LISST particle size analyzer and a Turner C3 fluorometer were towed from the main bridge through the test tank at 1.5 m depth for in-water dispersed oil characterization during the mixing period.
11. At the end of the test, surface water currents developed by the water spray from the bridge fire monitors were used to sweep any remaining surface oil to a common collection area at one corner of the containment boom.
12. The oil was then removed from the water surface using a double-diaphragm pump and suction wand or a hand ladle and placed in a 55 gallon (208L) collection drum or a 5 gallon (20L) pail.
13. The collected oil and water were allowed to stand at least overnight to allow the oil and water to separate before most of the free water was drained from the bottom of the collection container.
14. The remaining oil and water were well mixed and a sample was taken for water content and physical property determination.
15. The quantity of remaining liquid was measured and the amount of oil determined by subtracting the amount of water as determined using the water content analysis.

16. The effectiveness of the dispersant is reported as the volume of oil discharged minus the amount collected from the surface all divided by the amount discharged.
17. Each test was video taped for future visual reference.

The physical properties of the eleven oils tested in October 2009 and the two oils tested in November 2010 are provided in Table 2. Also included in this table are the properties of nine additional oils that had been tested at Ohmsett for DE under similar test conditions (water temperature, dispersant type and dosage) during previous test programs. All tests were conducted using Corexit 9500 dispersant. The tank water temperature was 14 ºC throughout the test program. Air temperatures ranged from 10 to 15 ºC. The tank water salinity was 32 ppt.

Table 2**.** Physical Properties of Oils Used in Large-Scale Tests

Generic Crude Oil Name (proper crude oil name)	Viscosity (cP) (at 15 °C)	Measured Density (g/cm^3 at ~15°C)
PXP 02 (Irene co-mingled)	31,195 @10s^{-1}	0.965
Venoco E-10 (Gail E010)	11,906 @10s^{-1}	0.961
PXP 01 (Irene Lompoc)	9,400 @10s^{-1}	0.951
PER 040 (Ellen 040)	18,500 @10s^{-1}	0.968
Rock	3,290 @100s^{-1}	0.957
PER 038 (Ellen (038)	2,977 @100s^{-1}	0.956
Doba	1,955 @100s^{-1}	0.918
Endicott -fresh	120 @100s^{-1}	0.896
BHP Billiton (Neptune)	388 @100s^{-1}	0.924
Terra Nova	380 @100s^{-1}	0.867
DCOR HE 5 – Nov 2010 test	109 @200s^{-1}	0.920
DCOR HE 26 – Nov 2010 test	64 @200s^{-1}	0.873
Venoco E-19 Gail E019)	64 @100s^{-1}	0.892
Anadarko (Independence Hub Atwater Valley Block 37)	10 @100s^{-1}	0.906
Previous Test Series Oils		
Endicott (18% evaporated)	516 @100s^{-1}	0.922
ANS (fresh)	35 @100s^{-1}	0.884
ANS (20% evaporated)	52 @100s^{-1}	0.890
Elly	9700 @20s^{-1}	0.958
Harmony	3588 @100s^{-1}	0.942
North Star	8 @100s^{-1}	0.848
IFO 120	1440 @100s^{-1}	0.948
IFO 380	10,490 @30s^{-1}	0.966

3.2 Results

3.2.1 Dispersant Effectiveness

The test conditions and estimated Dispersant Efficiencies (DE) for all of the large-scale tank tests completed in this study are summarized in Table 3. The DE values in the table were determined using the following formula: DE= (oil volume spilled – oil volume collected from the surface) / oil volume spilled * 100.

DE results in the Ohmsett testing varied from 49 to 99%. With only two exceptions (BHP Billiton and PER 038 crude oils) oils with viscosities less than 3,500 cP resulted in DE of 95% or greater in the Ohmsett test. DE values between 49 and 78% were achieved on oils with viscosities between 9,500 and 31,195 cP.

Hypertext links are provided in Table 3 to video clip segments of each of the tests. The video records can be viewed by double-clicking on a link when accessing this document digitally. The clips are in order from the start of the test progressing through to the end of each test and each dispersant application pass is labeled in the video record. The video clips provide a record of the behavior of the oil in each of the tests completed and it is recommended that they be viewed to get a full appreciation of the test program and the behavior of the oil after treatment.

Table 3. Ohmsett Tank Dispersant Effectiveness (DE) Test Results Summary

Oil			**Oil Viscosity (cP @ 15°C)**	**Oil Volume (liters)**	**Oil Thickness (mm)**	**DOR**	**DE (%)**	**Links to Video Segments**	**Test #**
PXP 02	14.4	13.0	31,195 @10s^{-1}	70	8.3	1:30	49	VideoT1	1
Venoco E-10	14.5	15.0	11,906 @10s^{-1}	74	8.8	1:32	88	VideoT2	2
PXP 01	14.3	13.0	9,400 @10s^{-1}	76	6.0	1:24	60	VideoT3	3
PER 040	14.0	13.2	18,500 @10s^{-1}	77	8.7	1:40	78	VideoT4	4
PER 038	14.0	13.1	2,977 @100s^{-1}	80	5.3	1:29	66	VideoT5	5
Endicott	14.2	13.7	120 @100s^{-1}	71	1.2	1:22	95	VideoT6	6
BHP Billiton	14.2	13.3	388 @100s^{-1}	76	1.8	1:40	89	VideoT7	7
Terra Nova	13.9	10.3	380 @100s^{-1}	83	1.3	1:38	95	VideoT8	8
Venoco E-19	13.9	11.0	64 @100s^{-1}	80	1.1	1:20	98	VideoT9	9
Anadarko	14.0	12.8	10 @100s^{-1}	92	1.4	1:31	95	VideoT10	10
Anadarko	14.0	12.5	10 @100s^{-1}	88	1.2	1:28	99	VideoT11	11
Rock	14.1	14.9	3,290 @100s^{-1}	98	6.7	1:35	97	VideoT12	12
Doba	14.1	14.3	1,955 @100s^{-1}	80	5.3	1:29	95	No video	13
DCOR HE-5	12.8	11.2	109 @200s^{-1}	86	1.3	1:22	98	VideoT2b[1]	2b
DCOR HE-26	11.7	9.4	64 @200s^{-1}	86	1.1	1:19	95	VideoT4b	4b
[1] tests with b designation were completed in November, 2010									

3.2.2 Dispersed Oil Concentrations and Drop Size Distributions

Several passes were made down the length of the test tank with the main bridge after the oil was discharged in each test to measure in-water oil concentrations and drop size distributions. A Sequoia Scientific LISST 100X particle size analyzer (LISST) recorded data on oil drop sizes and in-water oil concentrations. A Turner Cyclops C3 *insitu* fluorometer (C3) was also deployed to measure in-water oil concentrations. These measurements were made to confirm the presence of oil in the water column and to characterize the form of the oil (drop size distribution). Graphs of the oil drop size distributions and concentrations are provided in Appendix A. Hypertext links to these graphs are provided in Table 4.

The "continuous" traces on these plots are from the LISST and C3 instruments that were towed back and forth through the water. The high concentration zones correspond to the times that the sensors were in the dispersed oil cloud. Dispersed oil drops less than 70 to 100 microns in diameter are generally considered permanently dispersed in a typical offshore environment (Lunel 1993, Neff 1990).

The in-water oil characterizations qualitatively support the measurements of oil lost from the surface that are used to determine dispersant effectiveness.

In-water oil concentration was also measured using a Turner Cyclops-3 (C3) submersible sensor that measures the fluorescence of the oil in the water column. Rough calibrations of the C3 were completed for 11 of the 14 oils tested to permit the reporting of oil concentrations rather than raw fluorescence. The Terra Nova calibration data was applied to the Endicott C3 data and the raw fluorescence values recorded for DCOR HE-5 and HE-26 are reported as raw/10 due to the absence of calibration data. The available calibration data is provided in Appendix B. The calibration-adjusted fluorescence values acquired by the C3 are plotted along with the LISST data in Figures A1 through A13. The C3 device identified the same concentration peaks and valleys as the LISST system but the calibration-adjusted C3 peak concentration values were lower (by a factor of 1.5 to 5 times) than the peak LISST values in six of eleven tests where valid C3 values were recorded. For two of the tests (#2 -Venoco E10 and #11 -Anadarko) the concentrations as determined by the C3 were similar to those as measured by the LISST. For three tests the C3 measured concentrations were higher than the LISST data by factors between 1.5 and 3.5. The C3 measurement may be sensitive to the oil drop size distribution as has been reported for similar *in-situ* fluorescence measurement systems (SL Ross 2003, Lambert 2001). This makes it very difficult to complete valid calibrations of the system to specific oils. The oil drop size distribution used in the calibration would have to match the drop size distribution in the dispersed oil cloud to achieve a valid calibration. The C3 system was recently acquired by MMS to provide an additional in-water oil concentration measurement capability at Ohmsett that will be compatible with the new equipment being put into service by the U.S. Coast Guard Strike Teams. The Cyclops data provides confirmation of the presence of oil in the water since it detects oil through fluorescence at oil specific wavelengths. However, the use of the C3 to accurately determine oil-in-water concentration values may be problematic as discussed above.

Table 4. In-Water Oil Characterization and Graph Hypertext Links

Oil	DOR	Links to Oil Drop Size / Concentration Graphs	Test #	Oil Drop Size (Average D50) (microns)	Volume % < 70 microns	Ave. Elevated Oil Conc. by LISST (ppm)	LISST Peak Oil Conc. (ppm)	Oil Viscosity (cP @ 15°C)	DE (%)
PXP 02	1:30	FigureA1	1	49	68	60	425	31,195 @10s^{-1}	49
Venoco E-10	1:32	FigureA2	2	72	55	68	582	11,906 @10s^{-1}	88
PXP 01	1:24	FigureA3	3	161	40	50	742	9,400 @10s^{-1}	60
PER 040	1:40	FigureA4	4	87	50	88	525	18,500 @10s^{-1}	78
PER 038	1:29	FigureA5	5	126	48	78	647	2,977 @100s^{-1}	66
Endicott	1:22	FigureA6	6	29	82	59	168	120 @100s^{-1}	95
BHP Billiton	1:40	FigureA7	7	70	65	76	322	388 @100s^{-1}	89
Terra Nova	1:38	FigureA8	8	29	83	79	239	380 @100s^{-1}	95
Venoco E-19	1:20	FigureA9	9	10	90	100	225	64 @100s^{-1}	98
Anadarko	1:31	FigureA10	10	34	78	84	292	10 @100s^{-1}	95
Anadarko	1:28	FigureA11	11	34	78	120	445	10 @100s^{-1}	99
Rock	1:35	FigureA12	12	24	92	105	279	3,290 @100s^{-1}	97
Doba	1:29	FigureA13	13	22	90	118	330	1,955 @100s^{-1}	95
DCOR HE-5	1:22	Figure A2b	2b	57	69	29	208	109 @200s^{-1}	98
DCOR HE-26	1:19	FigureA4b	4b	36	74	39	233	64 @200s^{-1}	95

3.2.2.1 Oil Drop Size Analysis

The oil drop size data collected for each experiment have been analysed to determine 1) the average VMD drop size, 2) the volume percent of the oil present in the form of oil drops less then 70 microns in diameter, 3) the average elevated oil concentration, and 4) the peak oil concentration measured (see Table 4). The measured peak oil concentrations do not correlate well with the final DE. Some of the highest peak concentrations were recorded in tests with the lowest DE. The volume median drop diameters (d50) and the % of oil in drops smaller than 70 microns correlate very well with the measured DE. In seven out of eight tests where the d50 was less than 50 microns complete dispersion (>95%) was measured. The only exception to this was in test #1 with the very heavy PXP 02 oil. The "volume percent less than 70 micron" values were computed for each test to provide an indication of the likely permanence of the dispersions generated. In tests 6 and 8 through 13 greater than 80% of the oil volume was present in drops smaller than 70 microns suggesting that the dispersion in these tests would be permanent. These same tests had d50's below 35 microns and DE measurements of at least 95%. In the remaining tests, where measured DE ranged from 49 to 89%, the % volume of oil in drops less than 70 microns dropped to between 40 and 68%. The d50 and volume % <70 micron measurements correlate well with the DE measurements and provide additional validation of the DE results.

4. Small Scale Test Results

4.1 Warren Spring Laboratory (WSL) Rotating Flask Test

4.1.1 Test Method

A detailed description of the Warren Spring Laboratory (WSL) test method is provided in Appendix C. The following is a brief description of the test. Two hundred and fifty milliliters of 32 ppt salt water (prepared with instant ocean) is placed in a 250 ml separating funnel. Five ml of the test oil is placed on the water surface using a pipette. Dispersant is then applied drop-wise to the surface oil at a 1:20 dispersant-to-oil (DOR) ratio. The funnel is then rotated at 33 rpm's for 2 minutes. Fifty ml of water and dispersed oil is sampled from the bottom tap after the funnel and contents have remained stationary for 1 minute. The oil is then extracted from the sample using three successive 10 ml additions of dichloromethane. The extractions are filtered through a Whatman No 1 micron paper filter with 1.5g of anhydrous sodium sulphate to remove any water from the extraction. The filter is washed with an additional 10 ml of dichloromethane and the final extract made up to a total volume of 50 ml. The concentration of oil in the extraction is then determined using a spectrophotometer that is calibrated using a standard developed for the oil tested. The Labofina Test Apparatus is shown in Figure 2.

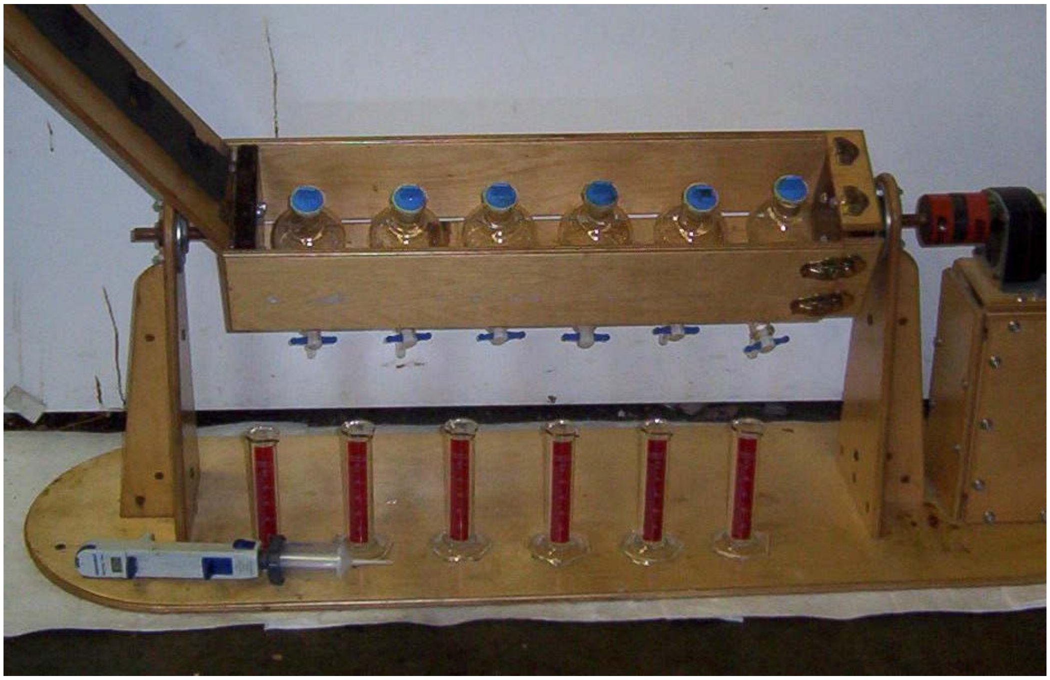


Figure 2. WSL Test Apparatus

4.1.2 Test Results

The WSL dispersant efficiency test results are summarized in Table 5 and plotted against oil viscosity in Figure 3. From Figure 3 it is evident that the WSL dispersant efficiency is not a strong function of oil viscosity. The measured efficiencies generally varied between 15 and 35% over nearly the full range of oil viscosities tested with some notable exceptions. There were three relatively viscous oils (3,500 to 10,000 cP) that achieved the highest efficiencies (45 to 60%). These are also relatively dense oils and it has been speculated based on past experimental experience with the WSL test that droplets of higher density oils rise out of suspension more slowly than those of lighter oils during the one-minute settling period prior to sampling and thus can result in higher efficiency measurements (A. Lewis pers. comm.). The very low effectiveness of the Terra Nova crude, a medium viscosity oil, (380 cP, 0.867 g/cc) may be due to its very light density and subsequent rapid rise of droplets in the settling period. With one exception, oils with viscosities over 10,000 cP resulted in efficiencies below 10%. These low efficiencies would be expected for these very viscous oils.

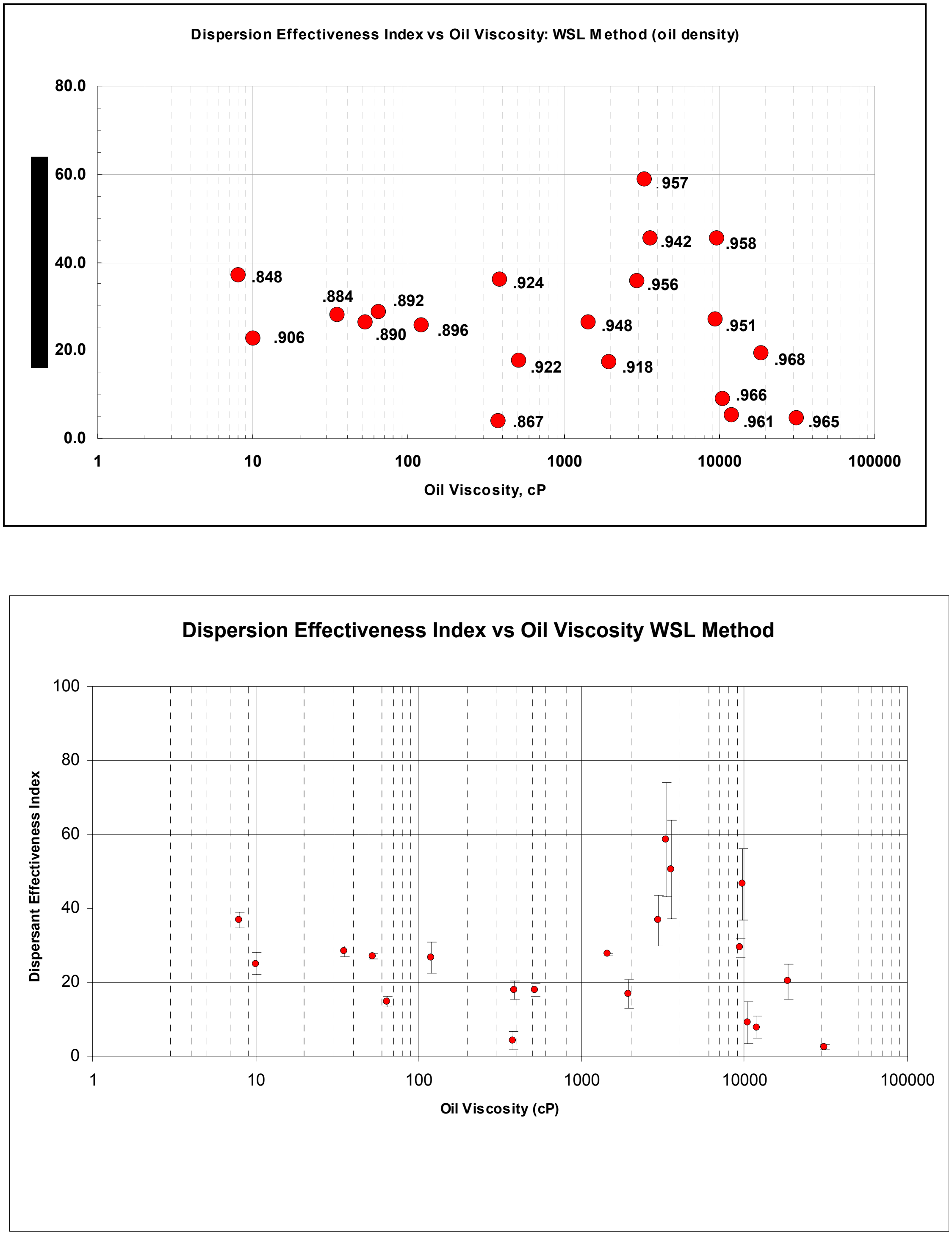


Figure 3. WSL Effectiveness Index vs Oil Viscosity (oil densities reported in top figure)

Table 5. WSL Small-Scale Laboratory Test Result Summary

Oil	Density		Viscosity @15 °C		Ohmsett Effectiveness	WSL Efficiency	
	(g/cc)	(ºC)	(cP)	(shear rate)	(%)	Efficency (%)	StdDev
North Star	0.848	15.7	8	100s^{-1}	99	36.9	2.0
Anadarko	0.906	16.2	10	10s^{-1}	97	25.0	2.9
ANS - Fresh	0.884	15.6	35	100s^{-1}	98	28.4	1.5
ANS - 20%	0.890	15.7	52	100s^{-1}	97	26.9	0.7
Venoco E19	0.892	14.7	64	100s^{-1}	98	14.7	1.5
Endicott Fresh	0.896	15.6	120	100s^{-1}	95	26.7	4.1
Terra Nova	0.867	15.6	380	100s^{-1}	95	4.2	2.4
BHP Billiton	0.924	15.6	388	100s^{-1}	89	17.8	2.4
Endicott 18.6%	0.922	15.6	516	100s^{-1}	94	17.9	1.9
IFO120	0.948	15.8	1,440	100s^{-1}	66	27.6	0.1
Doba	0.918	16.3	1,955	100s^{-1}	95	16.9	3.8
PER-038	0.956	15.9	2,977	100s^{-1}	66	36.7	6.9
Rock	0.957	16.6	3,290	100s^{-1}	97	58.7	15.5
Harmony	0.942	15.1	3,588	100s^{-1}	99	50.4	13.3
PXP-01	0.951	15.4	9,400	10s^{-1}	60	29.4	2.7
Platform Elly	0.958	16.4	9,700	20s^{-1}	65	46.6	9.6
IFO380	0.966	15.8	10,490	30s^{-1}	66	9.2	5.7
Venoco E10	0.961	15.1	11,906	10s^{-1}	88	7.8	3.0
PER-040	0.968	15.6	18,500	10s^{-1}	78	20.3	4.7
PXP-02	0.965	16.0	31,195	10s^{-1}	49	2.6	0.7

The WSL results are plotted against the corresponding large-scale Ohmsett test results in Figure 5. In all cases the WSL measured dispersant efficiencies are significantly lower than the Ohmsett dispersant effectiveness estimates. If the Ohmsett results are accepted as more indicative of likely field effectiveness results then it can be concluded that the efficiency ratings provided by the WSL results are not a good indicator of possible field performance of the dispersant.

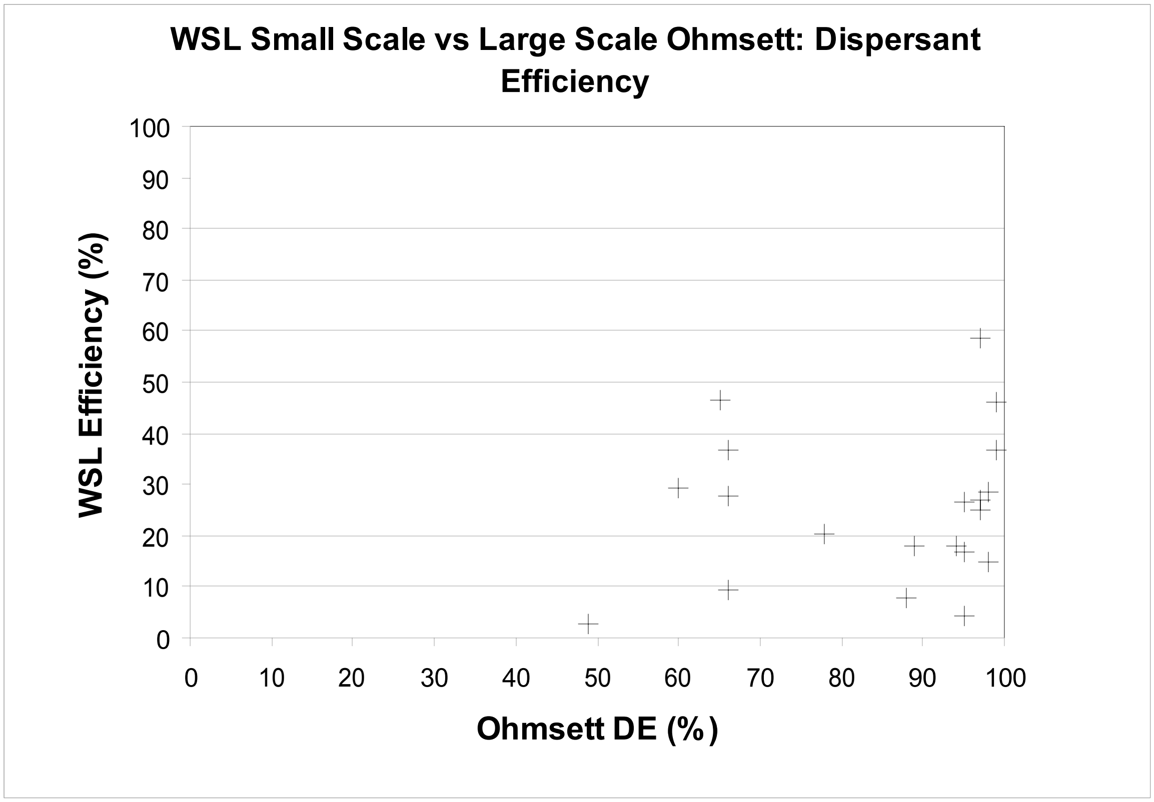


Figure 4. Comparison of Small-Scale WSL to Large-Scale Ohmsett Test Results

4.2 EPA Baffled Flask Test

The baffled flask tests were completed under an Inter-Agency agreement between MMS and EPA. Pegasus Technical Services, Inc. completed the tests under contract to EPA (Venosa and Holder, 2011).

4.2.1 Test Methods

A detailed description of the materials, methods and procedures used in EPA's Baffled Flask dispersant testing is provided in Appendix C. The following description of the general procedures used in the Baffled Flask test has been extracted from Venosa and Holder, 2011.

"A volume of 120 mL of synthetic seawater was added to the baffled flask, followed sequentially by addition of the oil and finally by the dispersant. A volume of 100 mL of oil was carefully dispensed directly onto the surface of the synthetic seawater using an Eppendorf repeater pipettor with a 5 mL syringe tip attachment. The dispersant was then dispensed onto the center of the oil slick by using a 100-mL syringe tip attachment set to dispense 4 mL, giving a volumetric ratio of dispersant-to-oil of 1:25 (DOR). This was similar to the average DOR reported in the BOEMRE Ohmsett report (~1:30) for 12 test oils. The DOR was not reported for the other 8 oils. Care was taken to make certain the dispersant contacted the oil without first touching the water. The flask was then placed on an orbital shaker (New Brunswick G24 shaker incubator) and mixed for 10 minutes at a rotation speed of 200 rpm. At the end of the mixing period, the flask was removed from the shaker and allowed to remain stationary on the bench top for 10 minutes. At the conclusion of the quiescent period, the first 2 mL of sample was drained from the stopcock and discarded, and then 30 mL of sample was collected in a 50 mL graduated cylinder. The 30 mL sample was transferred to a 125 mL separatory funnel and extracted 3 times with 5 mL fresh DCM. The extract was adjusted to a final volume of 20 or 25 mL and transferred to a 50 mL crimp style glass vial with an aluminum/Teflon seal. The vials were stored at 5 °C until the time of analysis. Dilutions were made in volumetric flasks for some of the oils to achieve the LDR of the spectrophotometer. Each of the four replicates was done separately so that shaking and settling times were exactly the same for all. In addition to the 4 replicate dispersant / oil / seawater mixtures, 4 replicate oil / seawater mixtures with no dispersant, and an overall total of 4 replicate method blanks (seawater alone) were also run for quality control purposes."

4.2.2 Test Results

A summary of the Baffled Flask test results is provided in Table 6. The average % oil dispersed values $\overline{DE_d}$ in column 3 of this table were derived in a similar manner to the dispersant effectiveness values reported for the Ohmsett and WSL test methods and so these values have been used when comparing test outcomes between test methods in this report. The Baffled flask results are compared to the other test method results in Section 6.

Table 6. Baffled Flask Results sorted in descending order by Dispersant Effectiveness LCL_{95DE} (from Venosa and Holden, 2011)

Test Oil	Kinematic Viscosity, cSt	Avg % oil dispersed, $\overline{DE_d}$	LCL_{95d}	Avg % oil dispersed in controls, $\overline{DE_c}$	LCL_{95c}	Nominal Dispersant Effectiveness, DE_{nom}	Final Dispersant Effectiveness, LCL_{95DE}
Anadarko	11	112.33	88.00	14.81	10.66	97.52	77.14
Terra Nova	438	81.00	75.91	3.57	2.20	77.43	73.08
Endicott Fresh	134	80.01	72.47	4.15	2.32	75.86	69.45
ANS Fresh	40	76.33	74.00	5.08	4.59	71.25	69.29
North Star	9	87.84	82.37	10.87	0.60	76.96	67.36
ANS, weathered	58	81.98	67.86	4.00	3.31	77.98	66.31
Endicott, weathered	560	71.97	68.24	5.32	1.51	66.64	62.24
IFO 120	1519	73.11	65.88	5.58	3.31	67.53	61.28
Venoco E-19	72	70.88	57.86	2.28	1.87	68.60	57.85
BHP Billiton	420	58.14	54.95	5.51	3.93	52.63	49.69
Rock	3438	56.84	50.40	2.50	1.72	54.35	48.98
Doba	2130	55.09	51.03	5.64	4.52	49.44	45.97
PER038	3114	53.89	37.97	2.97	1.63	50.92	37.73
Venoco E-10	12389	31.52	26.42	1.50	1.31	30.02	25.81
IFO 380	10859	40.44	26.93	4.34	2.02	36.10	24.78
Elly	10125	31.34	24.14	0.95	0.74	30.39	24.44
PER040	19112	31.56	21.34	0.61	0.24	30.96	22.51
Harmony	3809	32.28	19.78	1.69	0.83	30.59	20.24
PXP01	9884	11.12	4.67	0.72	0.56	10.40	5.07
PXP02	32326	7.04	3.88	0.99	0.46	6.05	3.41

4.3 Swirling Flask Test

Environment Canada conducted the swirling flask tests under separate contract with MMS.

4.3.1 Test Methods

The swirling flask test was developed by Environment Canada to provide a quick and simple testing procedure for evaluating dispersant effectiveness. It uses a modified Erlenmeyer flask with an added side spout for sampling water near the bottom of the flask without disturbing the surface oil layer. Seawater and a surface layer of oil are added to the flask. Mixing is provided by placing the flask on a shaker table at 150 rpm for 20 minutes to induce a swirling motion to the liquid contents. Following shaking, the flask is immediately removed from the shaker table and maintained in a stationary position for 10 minutes. A sample of water for chemical analysis is then removed from the bottom of the flask through the side spout, extracted with methylene chloride (dichloromethane-DCM), and analyzed for oil content by UV-visible absorption spectrophotometry at wavelengths of 340, 370, and 400 nm (2). Detailed test specifications are available as ASTM F2059.

4.3.2 Test Results

The swirling flask test results are summarized in Table 7. Only half of the oils tested registered a dispersant effectiveness above the lower reporting limit (10%) of the swirling flask test. When graphically comparing test results between test methods in Section 6, 5% DE has been used for the test results for the swirling flask reported as <10%.

Table 7. Swirling Flask Test Results

Oil	Density		Viscosity		Ohmsett Effectiveness	Swirling Flask Dispersant Efficiency
	(g/cc)	(ºC)	(cP)	(shear rate)	(%)	Efficency (%)
North Star	0.848	15.7	8	$100s^{-1}$	99	75.5
Anadarko	0.906	16.2	10	$10s^{-1}$	97	74
ANS - Fresh	0.884	15.6	35	$100s^{-1}$	98	67.0
ANS - 20%	0.890	15.7	52	$100s^{-1}$	97	49.2
Venoco E19	0.892	14.7	64	$100s^{-1}$	98	<10
DCOR HE-26	0.873	19.5	64	$200s^{-1}$	95	68.7
DCOR HE-05	0.920	20.0	109	$200s^{-1}$	98	67.1
Endicott Fresh	0.896	15.6	120	$100s^{-1}$	95	62.4
Terra Nova	0.867	15.6	380	$100s^{-1}$	95	43.4
BHP Billiton	0.924	15.6	388	$100s^{-1}$	89	<10
Endicott 18.6%	0.922	15.6	516	$100s^{-1}$	94	41.8
IFO120	0.948	15.8	1,440	$100s^{-1}$	66	12.4
Doba	0.918	16.3	1,955	$100s^{-1}$	95	10.1
PER-038	0.956	15.9	2,977	$100s^{-1}$	66	<10
Rock	0.957	16.6	3,290	$100s^{-1}$	97	<10
Harmony	0.942	15.1	3,588	$100s^{-1}$	99	<10
PXP-01	0.951	15.4	9,400	$10s^{-1}$	60	<10
Platform Elly	0.958	16.4	9,700	$20s^{-1}$	65	<10
IFO380	0.966	15.8	10,490	$30s^{-1}$	66	8.9
Venoco E10	0.961	15.1	11,906	$10s^{-1}$	88	<10
PER-040	0.968	15.6	18,500	$10s^{-1}$	78	<10
PXP-02	0.965	16.0	31,195	$10s^{-1}$	49	<10

4.4 EXDET Testing

ExxonMobil Research and Engineering Co. conducted the EXDET dispersant effectiveness tests.

4.4.1 Methods

The Exxon dispersant effectiveness test (EXDET) method is described in detail in Becker, 1993. The test uses three or four 250 ml separatory funnels clamped in a Burrell wrist-action shaker. One ml of oil is added to 250 ml of salt water in each funnel. The funnels are shaken for 15 minutes. Sorbent pads are then added to the water surface without stopping the shaking action. The mixing continues for another 5 minutes after the placement of the sorbent pads. The shaking is stopped, the water is immediately drained from the funnels and the oil in the water is extracted with solvent. The non-dispersed oil remaining in the funnel and on the sorbent pad is extracted separately. The oil content of the two extracts is determined using a spectro-photometer operated at an appropriate wavelength (e.g. 460 nm). The ratio of dispersed oil to dispersed plus undispersed oil is determined for each of the funnels and the average and standard deviations of the percent dispersed oil are determined.

4.4.2 Results

Two sets, of three tests, each were conducted on different days on each oil. The average and standard deviations from these six tests, for each oil, are summarized in Table 8.

Table 8. EXDET Test Results

Oil	Density		Viscosity		Ohmsett Effectiveness	EXDET Dispersant Efficiency	
	(g/cc)	(ºC)	(cP)	(shear rate)	(%)	Average Efficency (%)	Standard Deviation (from 6 tests)
North Star	0.848	15.7	8	$100s^{-1}$	99	85.1	1.9
Anadarko	0.906	16.2	10	$10s^{-1}$	97	87.5	9.6
ANS - Fresh	0.884	15.6	35	$100s^{-1}$	98	91.8	1.6
ANS - 20%	0.890	15.7	52	$100s^{-1}$	97	88.4	1.3
Venoco E19	0.892	14.7	64	$100s^{-1}$	98	87.5	4.3
DCOR HE-26	0.873	19.5	64	$200s^{-1}$	95	na	na
DCOR HE-05	0.920	20.0	109	$200s^{-1}$	98	na	na
Endicott Fresh	0.896	15.6	120	$100s^{-1}$	95	86.0	0.7
Terra Nova	0.867	15.6	380	$100s^{-1}$	95	83.1	5.9
BHP Billiton	0.924	15.6	388	$100s^{-1}$	89	90.3	2.3
Endicott 18.6%	0.922	15.6	516	$100s^{-1}$	94	89.9	3.2
IFO120	0.948	15.8	1,440	$100s^{-1}$	66	82.7	4.8
Doba	0.918	16.3	1,955	$100s^{-1}$	95	89.3	2.7
PER-038	0.956	15.9	2,977	$100s^{-1}$	66	90.6	1.0
Rock	0.957	16.6	3,290	$100s^{-1}$	97	89.9	4.4
Harmony	0.942	15.1	3,588	$100s^{-1}$	99	85.1	2.1
PXP-01	0.951	15.4	9,400	$10s^{-1}$	60	83.2	7.4
Platform Elly	0.958	16.4	9,700	$20s^{-1}$	65	57.0	10.4
IFO380	0.966	15.8	10,490	$30s^{-1}$	66	68.3	5.1
Venoco E10	0.961	15.1	11,906	$10s^{-1}$	88	67.9	17.4
PER-040	0.968	15.6	18,500	$10s^{-1}$	78	46.3	14.2
PXP-02	0.965	16.0	31,195	$10s^{-1}$	49	16.1	4.7

5. Comparison of Small Scale Test Results to Ohmsett DE

A summary of all of the DE test results collected for the 22 different oils is provided in Table 9. These results are plotted in Figure 5.

As discussed in section 5.1.2 the WSL test results correlated poorly with the Ohmsett test results. This is highlighted again in Figure 5. The WSL DE values also were lower than the swirling and baffled flask methods for the lightest oils but tended to be higher for the mid- to high viscosity oils. We believe this is due to the oil density bias in the WSL test that generates low DE estimates for light, buoyant oils and inflated DE values for denser, less buoyant oils.

The swirling flask tests showed measurable dispersion (>10%) primarily for the lightest of the test oils (less viscous than about 500 cP). None of the other tests generated as consistently low DE estimates on oils with viscosities higher than 500 cP. It appears that the swirling flask test underestimates DE when compared to the other test methods over a significant range of oil viscosities (between about 400 to 20,000 cP).

The baffled flask test results more closely matched the Ohmsett efficiencies than the WSL or swirling flask tests but generally under estimated dispersant effectiveness when compared to the large-scale Ohmsett results. The baffled flask DE was higher than the Ohmsett result for only 2 of the 20 oils and for one of these (Anadarko) the baffled flask estimate was higher only because it was >100% whereas the Ohmsett result was 99%. The other case was for IFO 120 where the baffled flask test DE was about 7% higher. For the remaining oils the baffled flask DE estimate were between 11 and 67% lower than the Ohmsett test results (on average they were about 38% lower).

The EXDET test results most closely matched the large-scale Ohmsett results. This may be due to the fact that in both of these tests a settling time is not used prior to making the effectiveness determination. The EXDET test DE was significantly higher (16 to 25%) than the Ohmsett results for IFO 12, PXP 01 and PER 038. For the remaining oils the EXDET DE results were between 6 and 33% lower than the Ohmsett results (on average they were about 13% lower).

Table 9. Dispersant Effectiveness Summary: All test Methods

Oil	Density @ 15°C	Viscosity @15 °C		Dispersant Efficiency (%)				
		cP	shear rate	Ohmsett	WSL	Baffled Flask	Swirling Flask	EXDET
North Star	0.848	8	100s^{-1}	99	36.9	87.8	75.5	85.1
Anadarko	0.906	10	10s^{-1}	97	25.0	112.3	74	87.5
ANS - Fresh	0.884	35	100s^{-1}	98	28.4	76.3	67.0	91.8
ANS - 20%	0.890	52	100s^{-1}	97	26.9	82.0	49.2	88.4
Venoco E19	0.892	64	100s^{-1}	98	14.7	70.9	<10	87.5
DCOR HE-26	0.873	64	200s^{-1}	95	-	-	68.7	-
DCOR HE-05	0.920	109	200s^{-1}	98	-	-	67.1	-
Endicott Fresh	0.896	120	100s^{-1}	95	26.7	80.0	62.4	86.0
Terra Nova	0.867	380	100s^{-1}	95	4.2	81.0	43.4	83.1
BHP Billiton	0.924	388	100s^{-1}	89	17.8	58.1	<10	90.3
Endicott 18.6%	0.922	516	100s^{-1}	94	17.9	72.0	41.8	89.9
IFO120	0.948	1,440	100s^{-1}	66	27.6	73.1	12.4	82.7
Doba	0.918	1,955	100s^{-1}	95	16.9	55.1	10.1	89.3
PER-038	0.956	2,977	100s^{-1}	66	36.7	53.9	<10	90.6
Rock	0.957	3,290	100s^{-1}	97	58.7	56.8	<10	89.9
Harmony	0.942	3,588	100s^{-1}	99	50.4	32.3	<10	85.1
PXP-01	0.951	9,400	10s^{-1}	60	29.4	11.1	<10	83.2
Platform Elly	0.958	9,700	20s^{-1}	65	46.6	32.3	<10	57.0
IFO380	0.966	10,490	30s^{-1}	66	9.2	40.4	8.9	68.3
Venoco E10	0.961	11,906	10s^{-1}	88	7.8	31.5	<10	67.9
PER-040	0.968	18,500	10s^{-1}	78	20.3	31.6	<10	46.3
PXP-02	0.965	31,195	10s^{-1}	49	2.6	7.0	<10	16.1

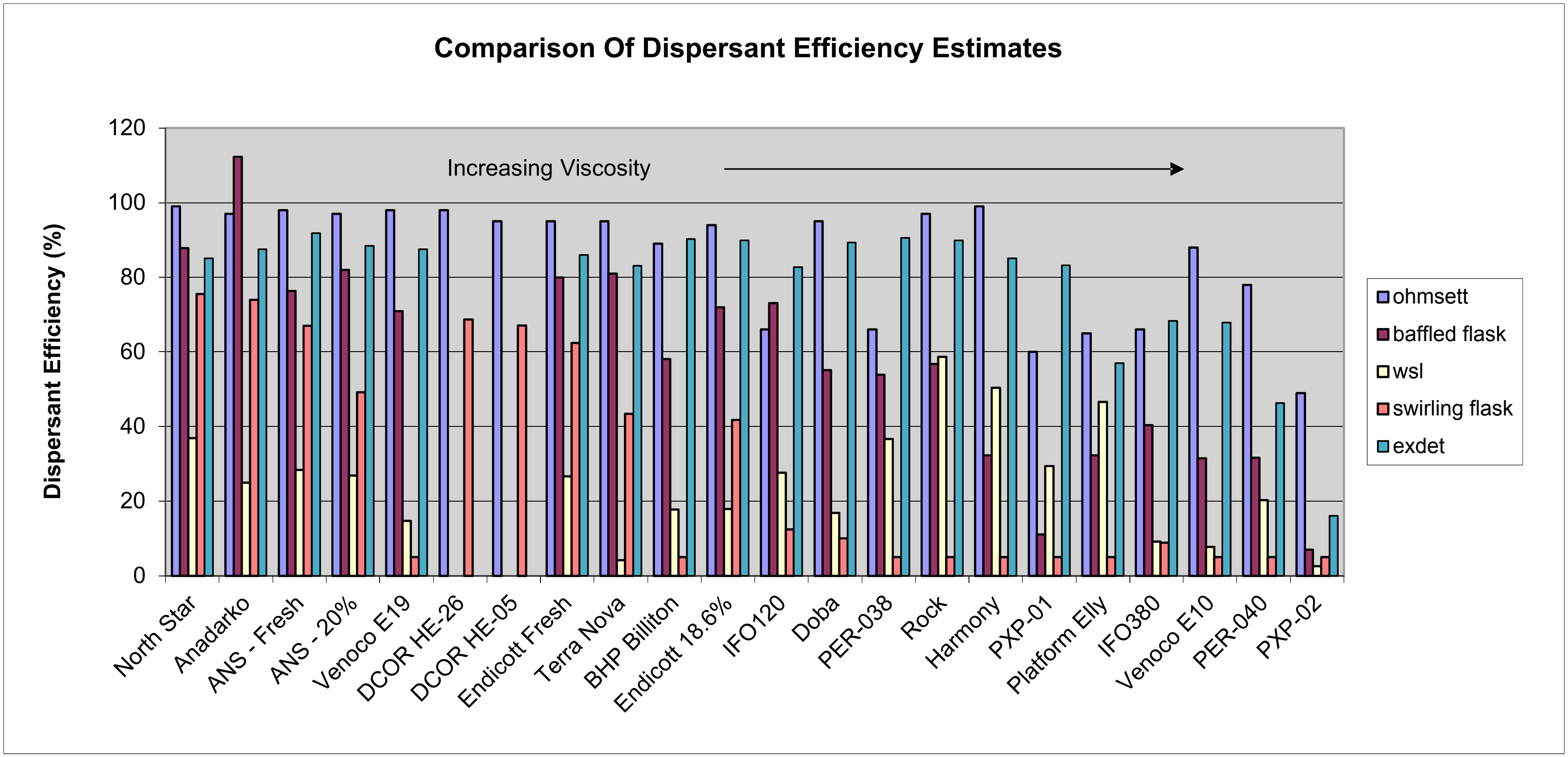


Figure 5. Comparison of Dispersant Efficiency Estimates

6. Summary of Key Results and Recommendations

The C3 device identified the same concentration peaks and valleys as the LISST system but the oil-specific calibration-adjusted C3 concentration peaks were generally lower or higher (by factors of 2 to 5x's) than the LISST values due to difficulty in preparing valid C3 calibration curves for the test oils. The C3 measurement may be sensitive to the oil drop size distribution. This problem has been reported for similar *in-situ* fluorescence measurement systems.

The use of the C3 system to accurately quantify the concentration of dispersed oil should be investigated more fully using a range of oils under differing dispersion conditions (drop size distributions) to improve the utility of this system in field monitoring programs.

Dispersant effectiveness (DE) results in the Ohmsett tank testing varied from 49 to 99%. With only two exceptions, oils with viscosities less than 3,500 cP resulted in dispersant effectiveness of 95% or greater in the Ohmsett tests. DE values between 49 and 78% were achieved in the Ohmsett test tank on oils with viscosities between 9,500 and 31,195 cP.

The EXDET test results most closely matched the Ohmsett efficiencies but for the majority of the oils under- estimated dispersant effectiveness (by an average of about 13% for 15 oils) when compared to the large-scale Ohmsett results.

The baffled flask test results under- estimated DE, when compared to the Ohmsett results, by a greater amount than the EXDET test (by an average of about 38% for 18 oils).

The WSL dispersant efficiency test results were lower than the swirling and baffled flask methods for the lightest oils but tended to be higher for the mid- to high- viscosity oils. We believe this is due to an oil density bias in the WSL test that generates low DE estimates for light, buoyant oils and inflated DE values for denser, less buoyant oils.

The swirling flask tests showed measurable dispersion (>10%) only for the lightest of the test oils (viscosity less than about 500 cP). None of the other tests generated as consistently low DE estimates on oils with viscosities between 500 and 20,000 cP. It appears that the swirling flask test underestimates DE when compared to the other test methods over a significant range of oil viscosities (between about 500 to 20,000 cP).

Oils with viscosities over 10,000 cP generally resulted in efficiencies below 10% in all of the small-scale test methods. The Ohmsett DE estimates for these higher viscosity oils ranged from 50% to as high as 88%.

7. References

Becker, 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.

Lambert, P. et al. 2001. Preliminary Results from the Laboratory Study of a Flow-Through Fluorometer for Measuring Oil-in-Water Levels. AMOP Technical Seminar.

Lunel, T. 1993. Oil droplet size measurement at sea. Proceedings of the Arctic and Marine Oilspill Program (AMOP) Technical Seminar , 1993.

Neff, J.M. 1990. Composition and fate of petroleum and spill treating agents in the marine environment. Sea Mammals and Oil: Confronting the Risks. J.R. Geraci and D.J. St Aubin (eds.). Academic Press: New York. Pp1-33.

SL Ross. 2000. Ohmsett Dispersant Test Protocol Development. Report to the U.S. MMS, September, 2000.

SL Ross. 2003. Dispersant Effectiveness Testing On Alaskan Oils In Cold Water. Report to Minerals Management Service, August 2003.

SL Ross. 2004. Correlating the Results of Dispersant Effectiveness Tests Performed at Ohmsett with Identical Tests Performed At Sea. Report to U.S. Minerals Management Service, 2004.

SL Ross. 2006. Dispersant Effectiveness Testing On Viscous, U.S. Outer Continental Shelf Crude Oils. Report to U.S. Minerals Management Service, 2006.

Venosa, D.A., E. Holder. 2011. Laboratory-Scale Testing of Dispersant Effectiveness of 20 Oils Using the Baffled Flask Test. Report prepared for the Bureau of Ocean Energy Management, Regulation, and Enforcement (BOEMRE).

Appendix A: Oil Drop Size and Concentration Graphs

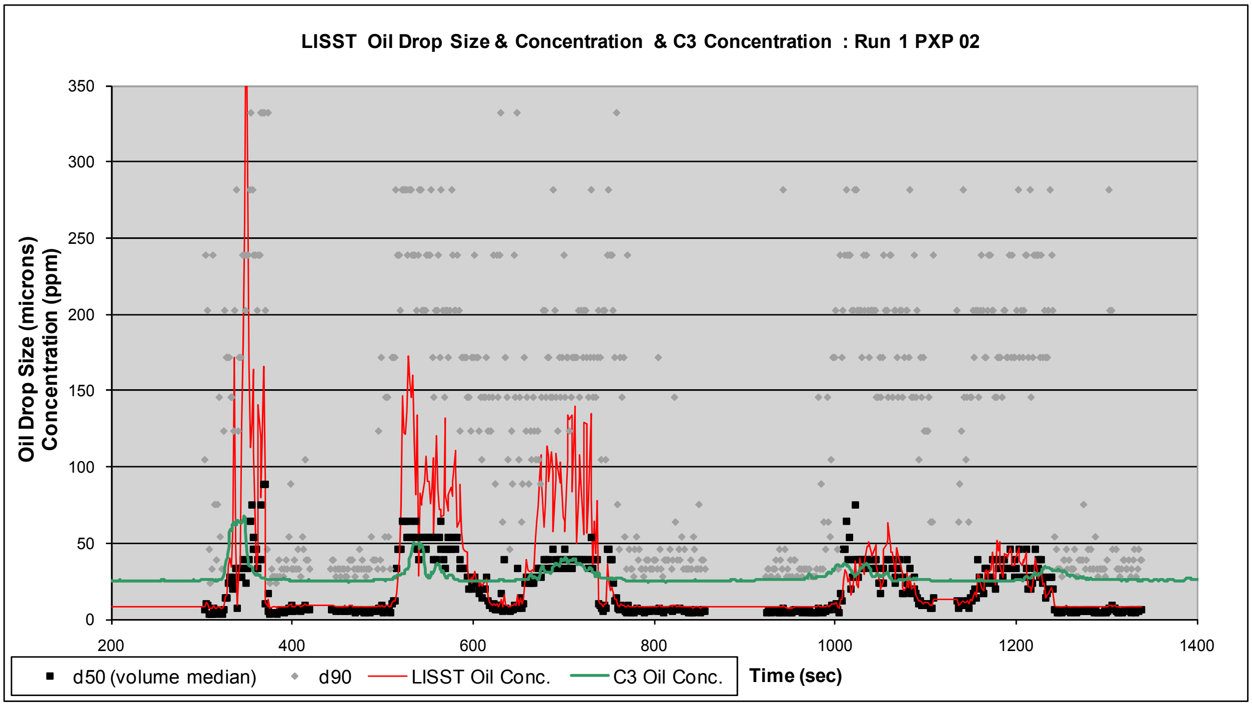


Figure A1: Oil Drop Size and Concentration Data: Test #1, PXP 02 Crude Oil

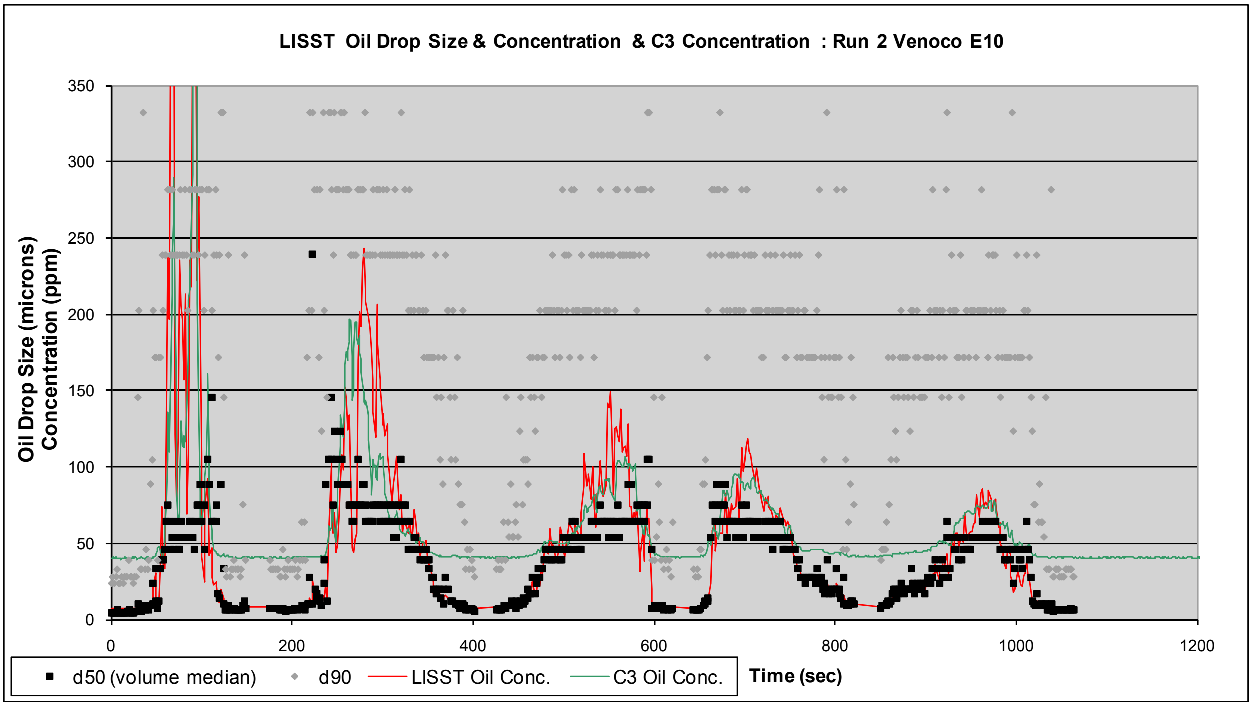


Figure A2: Oil Drop Size and Concentration Data: Test #2, Venoco E10 Crude Oil

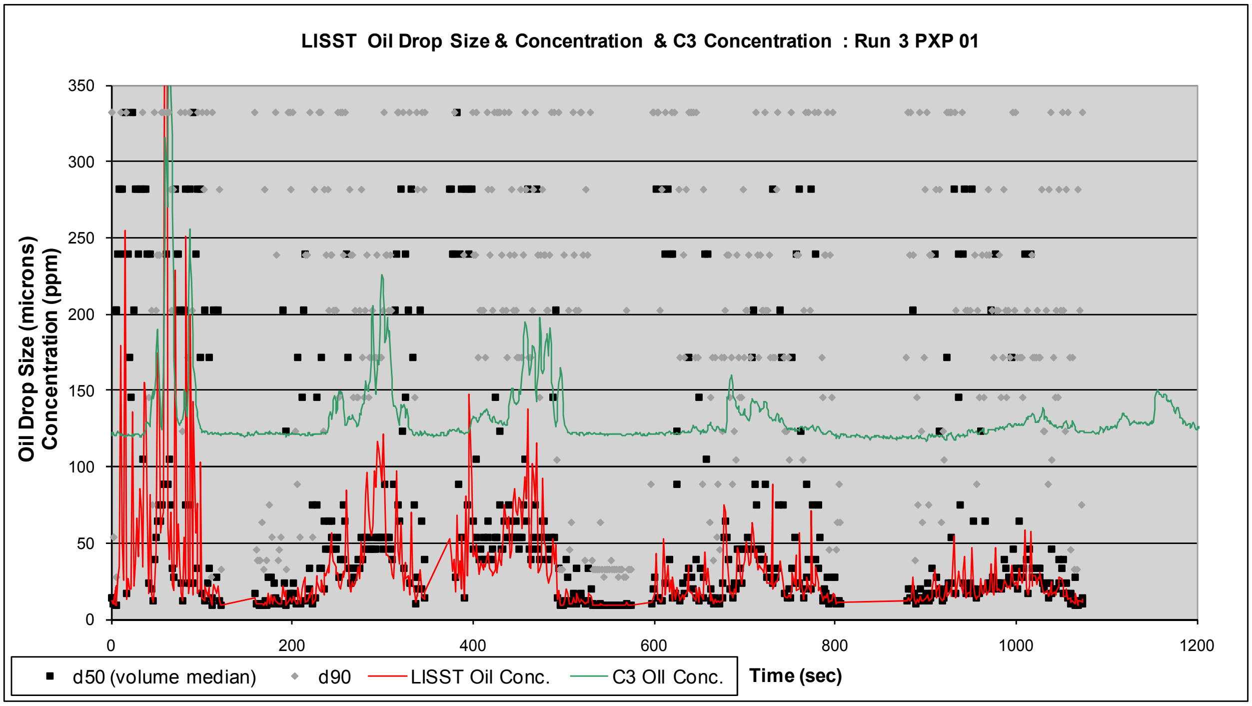


Figure A3: Oil Drop Size and Concentration Data: Test #3, PXP 01 Crude Oil

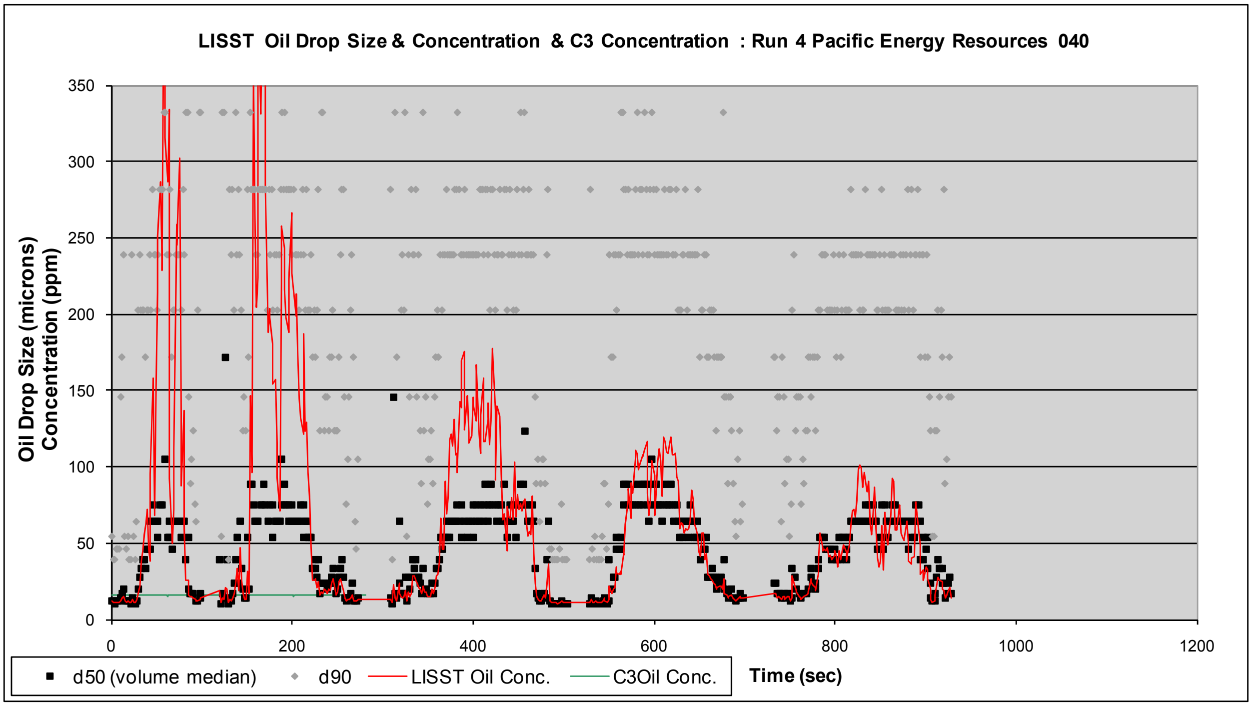


Figure A4: Oil Drop Size and Concentration Data: Test #4, PER 40 Crude Oil

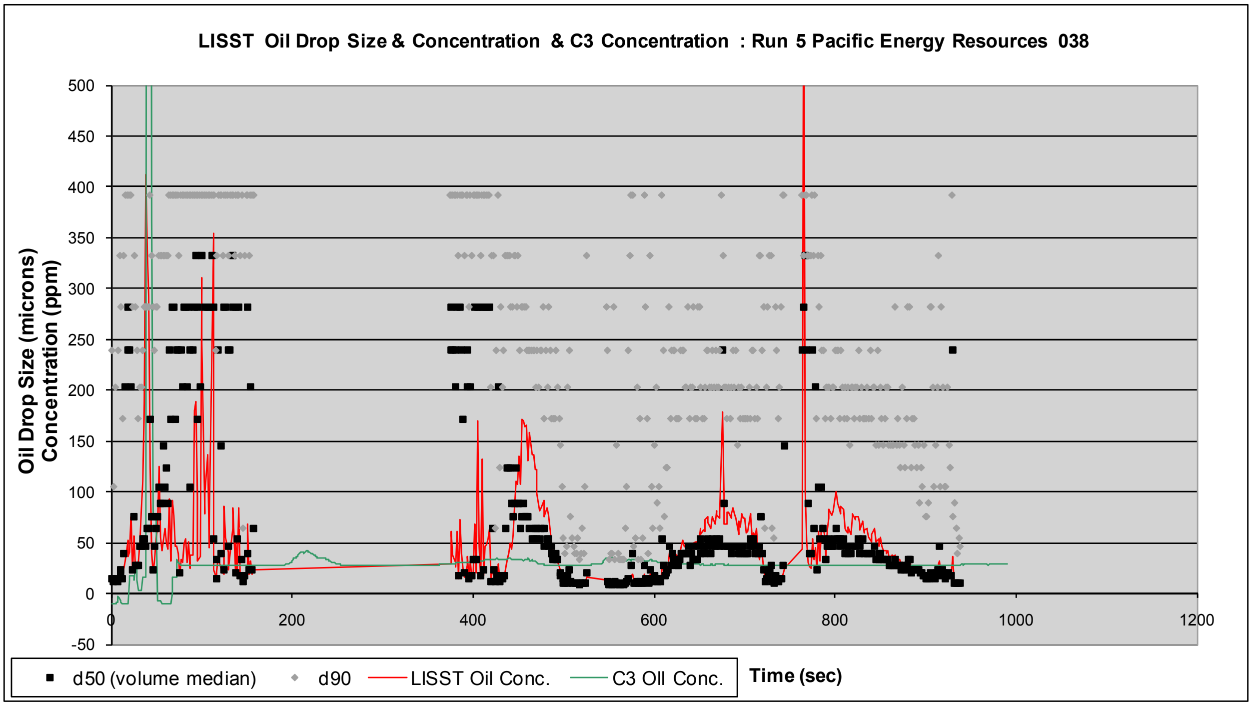


Figure A5: Oil Drop Size and Concentration Data: Test #5, Rock Crude Oil

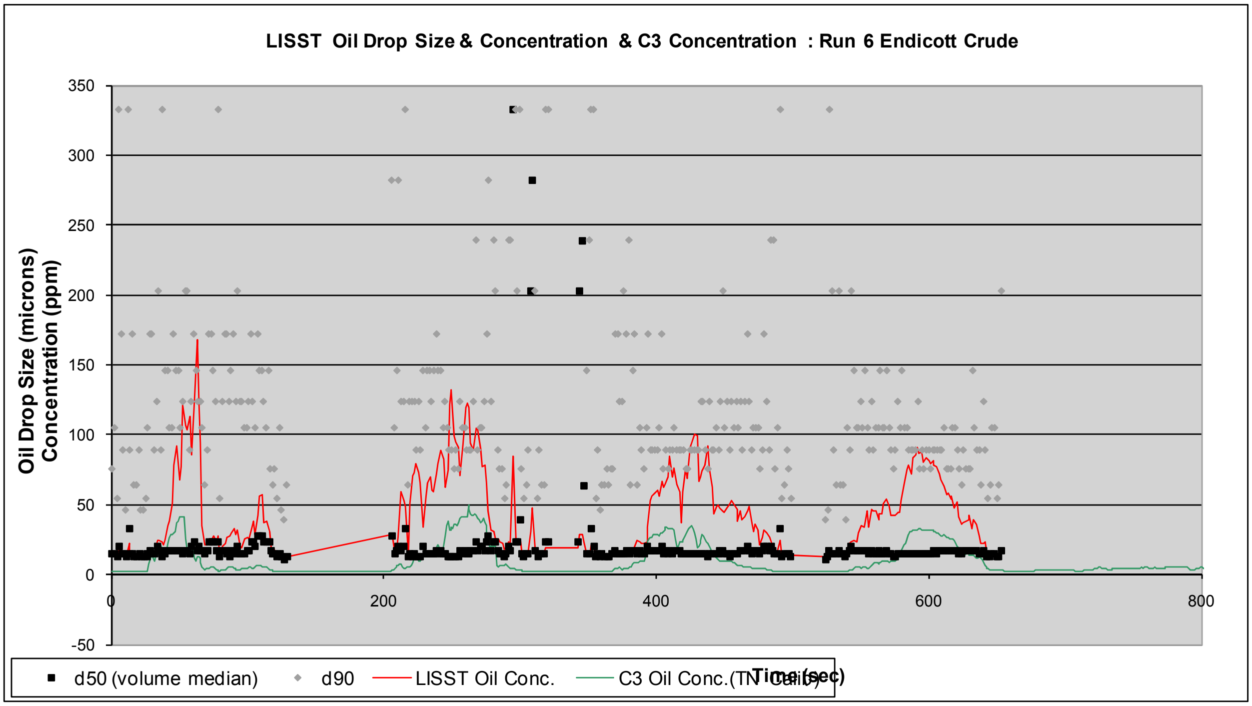


Figure A6: Oil Drop Size and Concentration Data: Test #6, Endicott Crude Oil

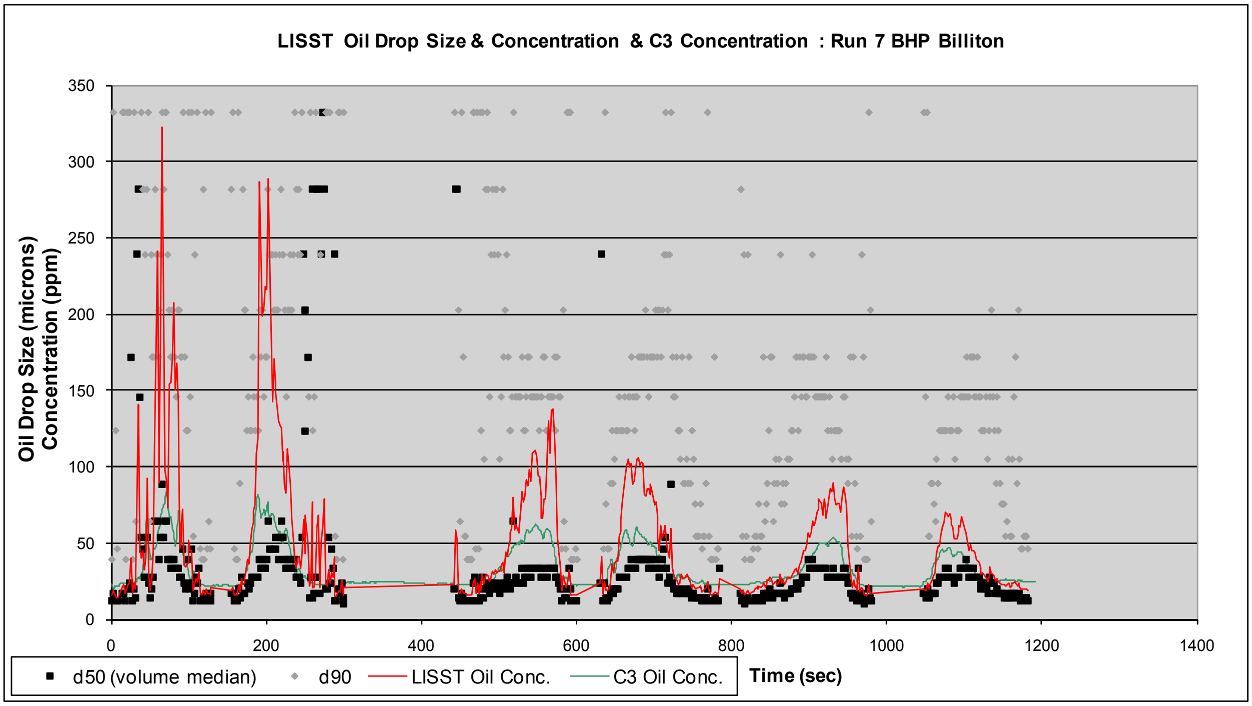


Figure A7: Oil Drop Size and Concentration Data: Test #7, BHP Billiton Crude Oil

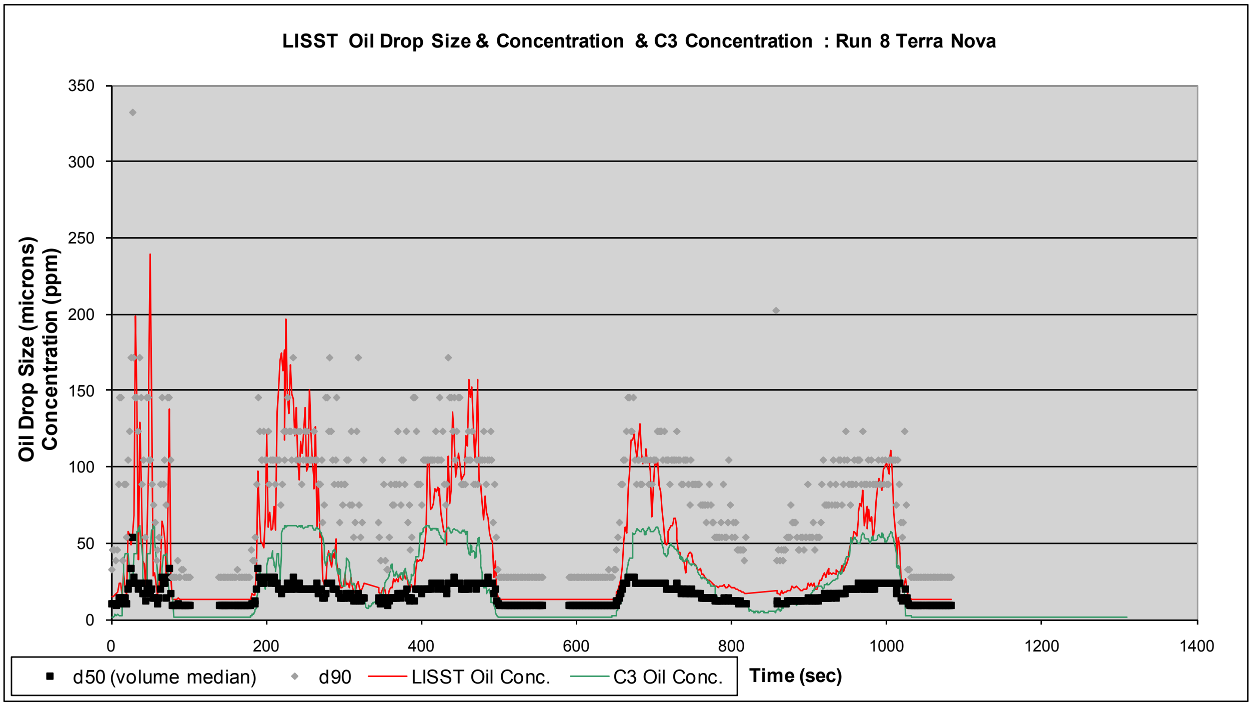


Figure A8: Oil Drop Size and Concentration Data: Test #8, Terra Nova Crude Oil

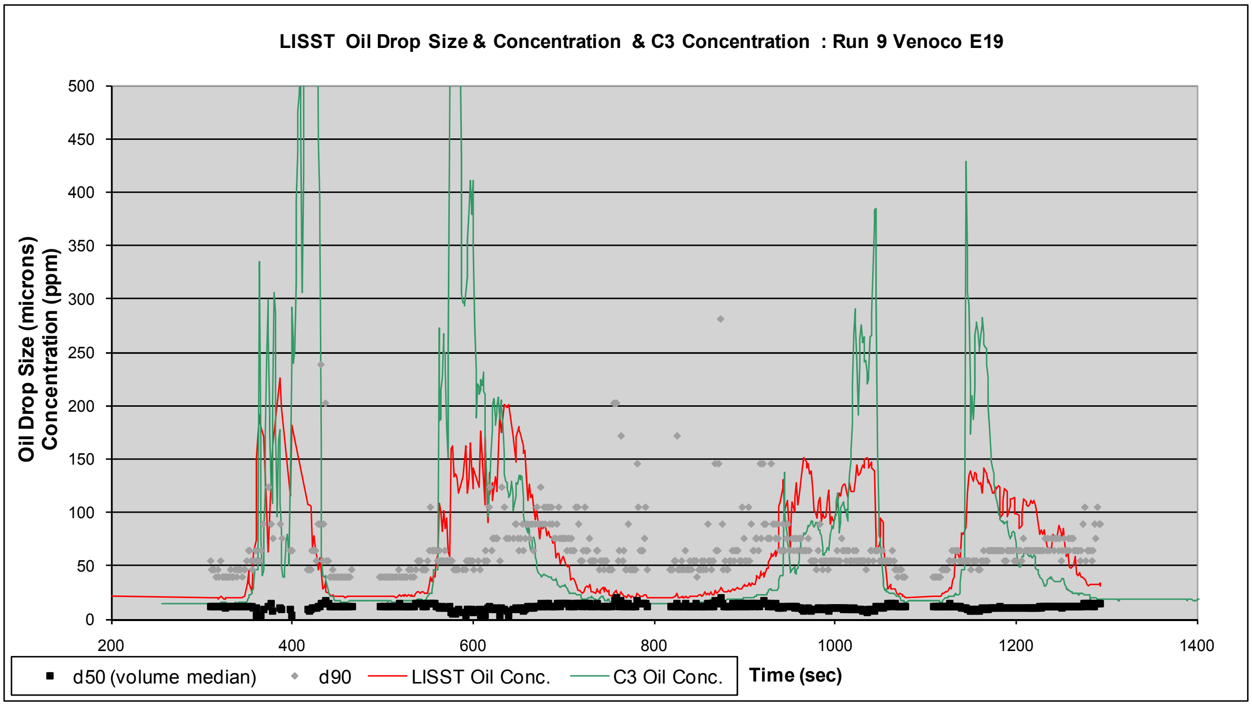


Figure A9: Oil Drop Size and Concentration Data: Test #9, Venoco E19 Crude Oil

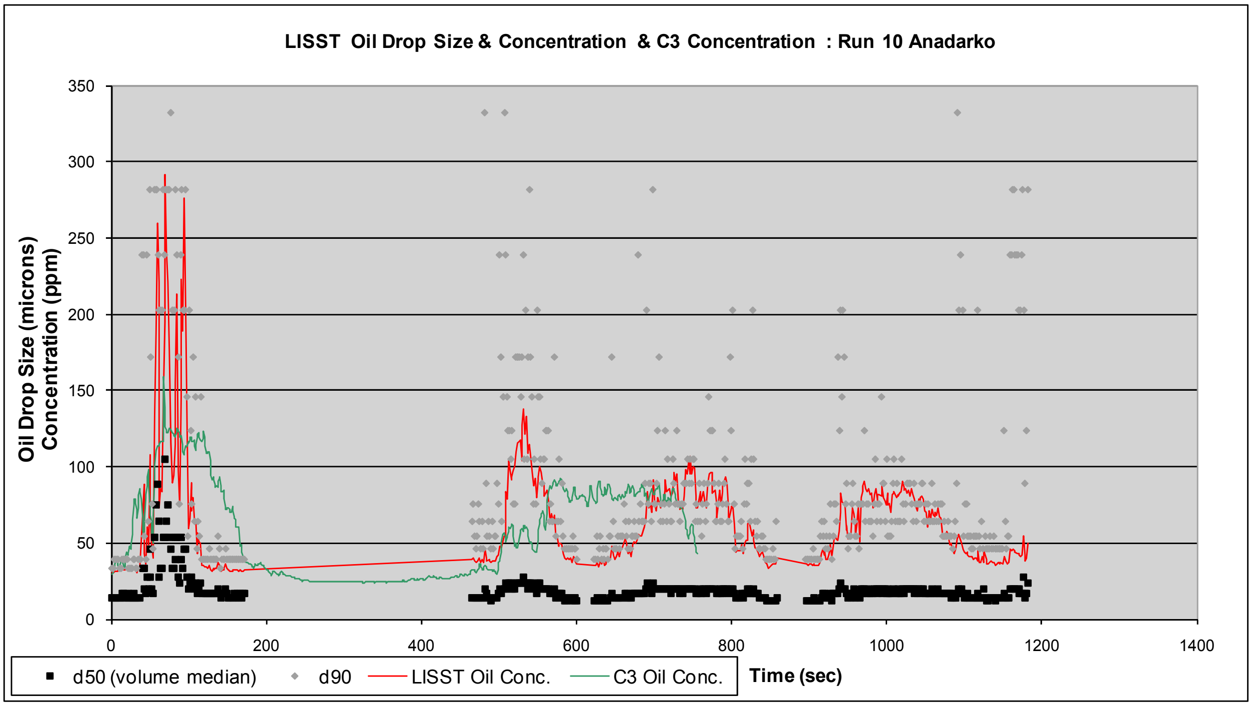


Figure A10: Oil Drop Size and Concentration Data: Test #10, Anadarko Crude Oil

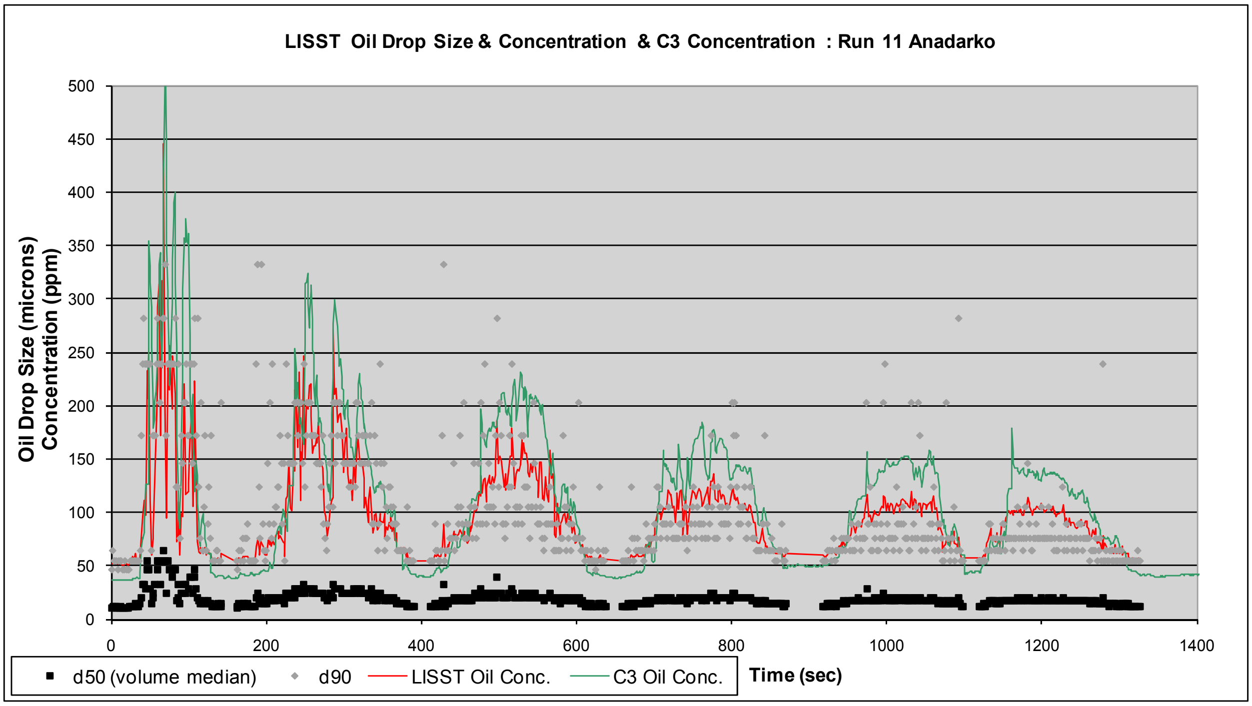


Figure A11: Oil Drop Size and Concentration Data: Test #11, Anadarko Crude Oil

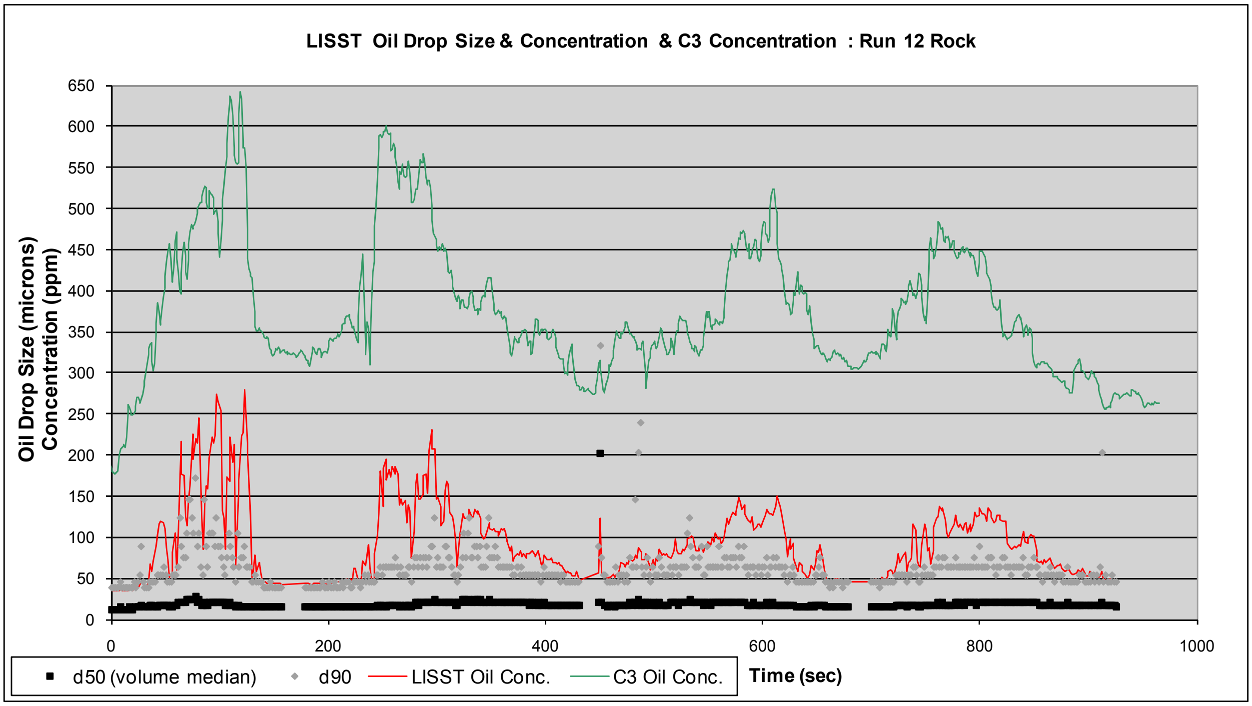


Figure A12: Oil Drop Size and Concentration Data: Test #12, Rock Crude Oil

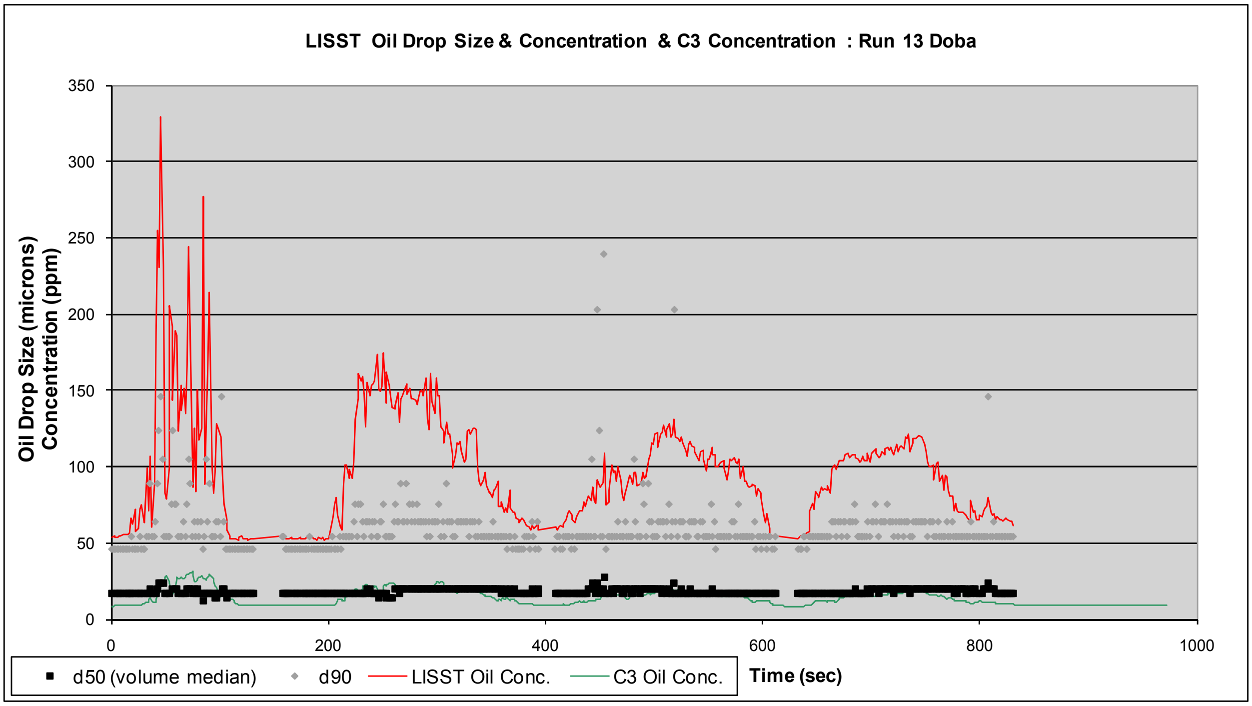


Figure A13: Oil Drop Size and Concentration Data: Test #13, Doba Crude Oil

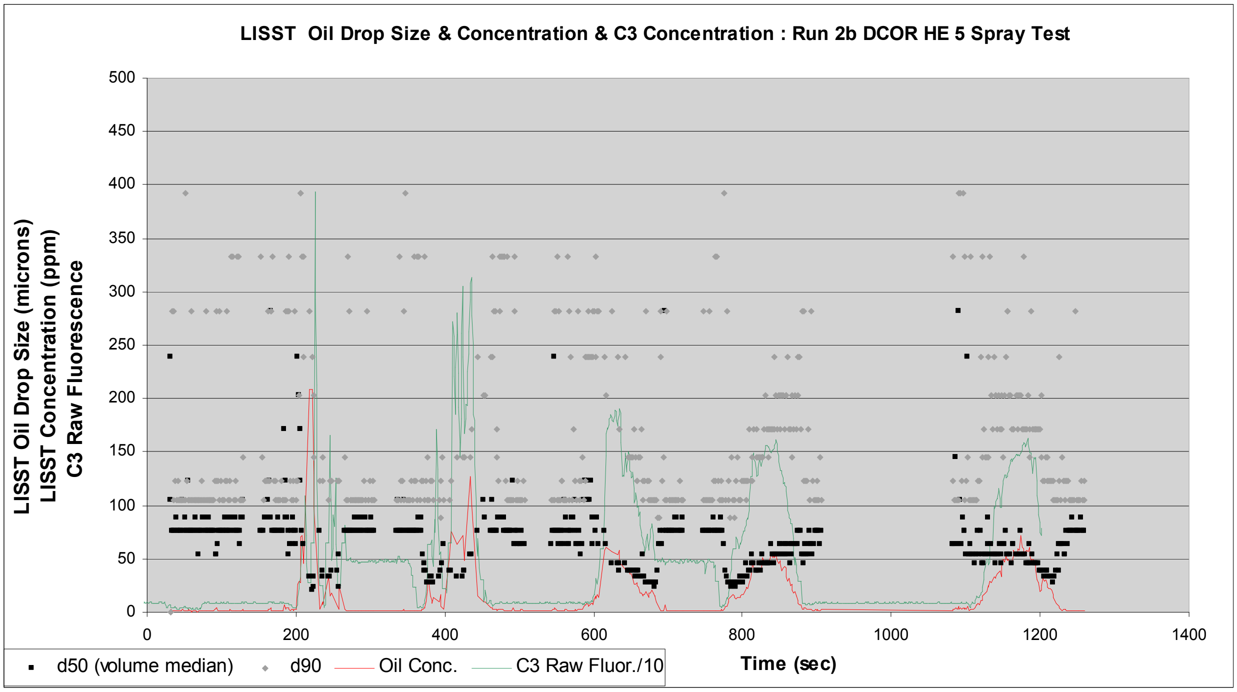


Figure A2b: Oil Drop Size and Concentration Data: Test #2b, DCOR HE 5 Crude Oil

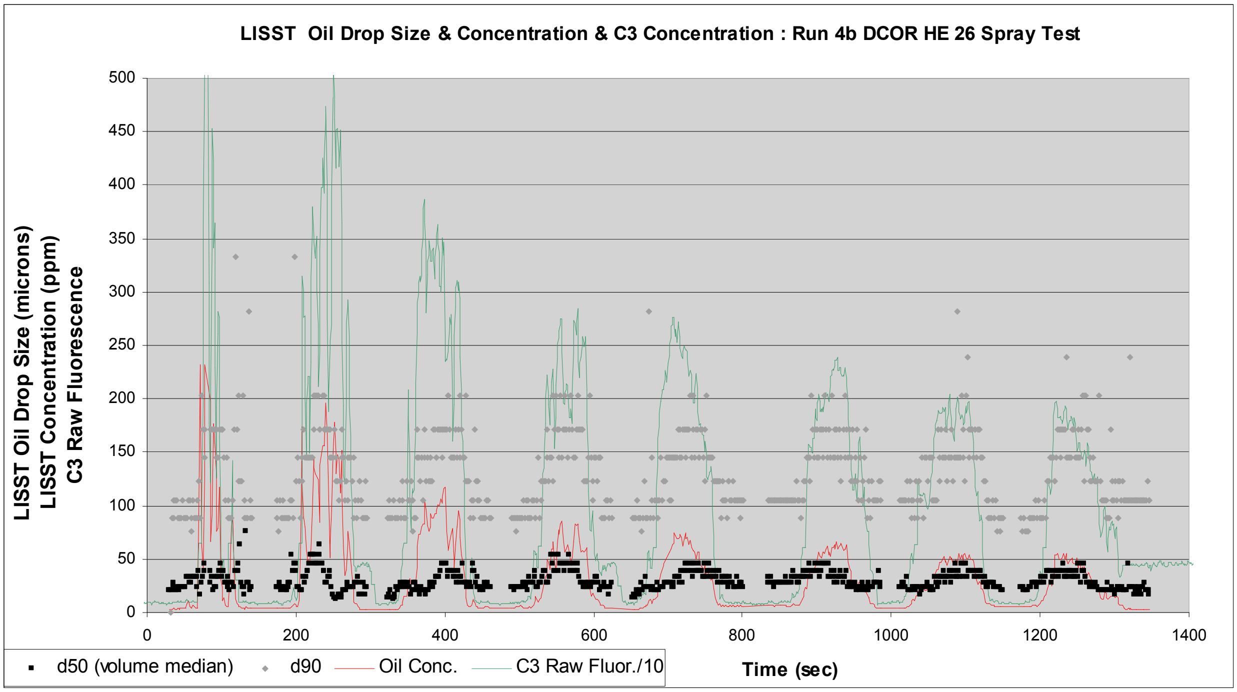


Figure A4b: Oil Drop Size and Concentration Data: Test #4b, DCOR HE 26 Crude Oil

Appendix B: Cyclops C3 Calibration Curves for Test Crude Oils

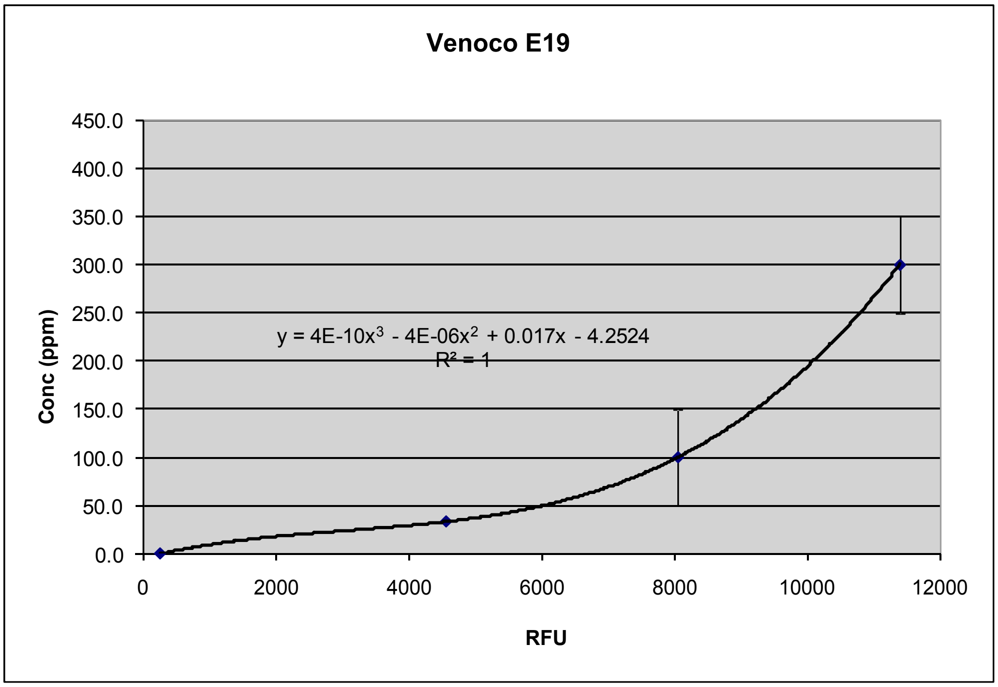


Figure B1. C3 Calibration for Venoco E19 Crude

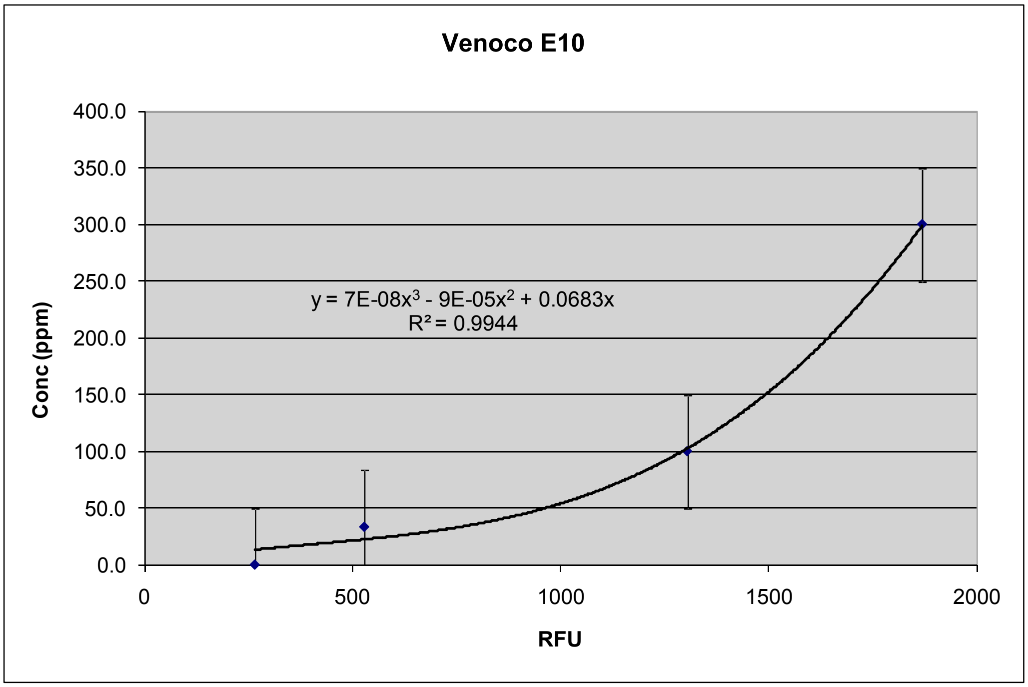


Figure B2. C3 Calibration for Venoco E10 Crude

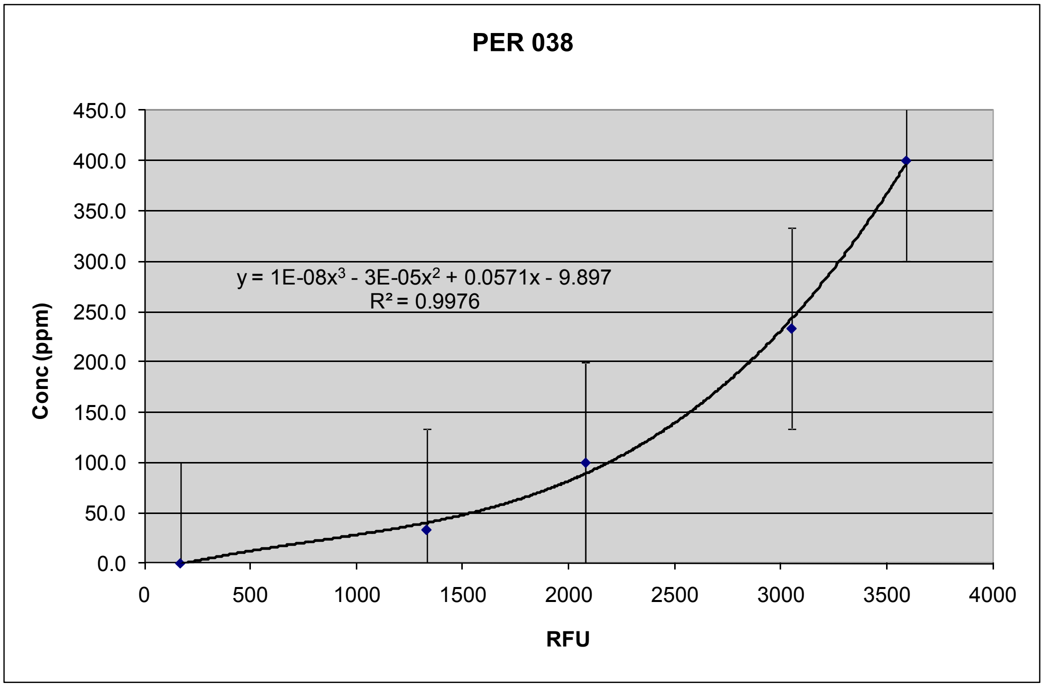


Figure B3. C3 Calibration for PER 038 Crude Oil

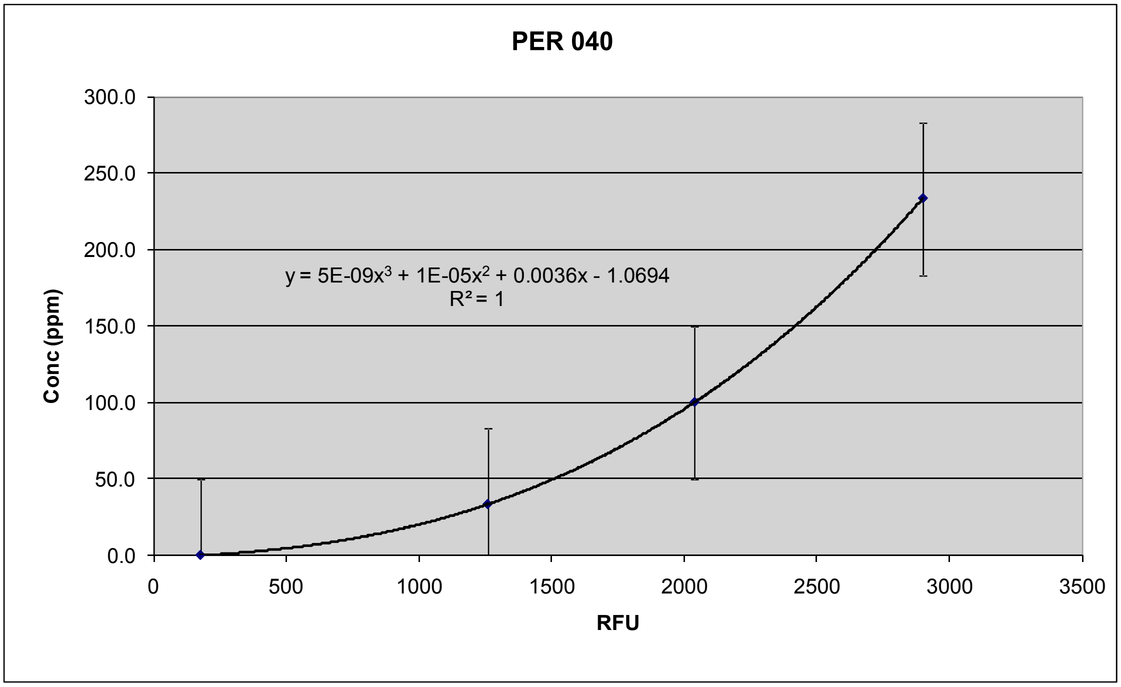


Figure B4. C3 Calibration for PER 040 Crude Oil

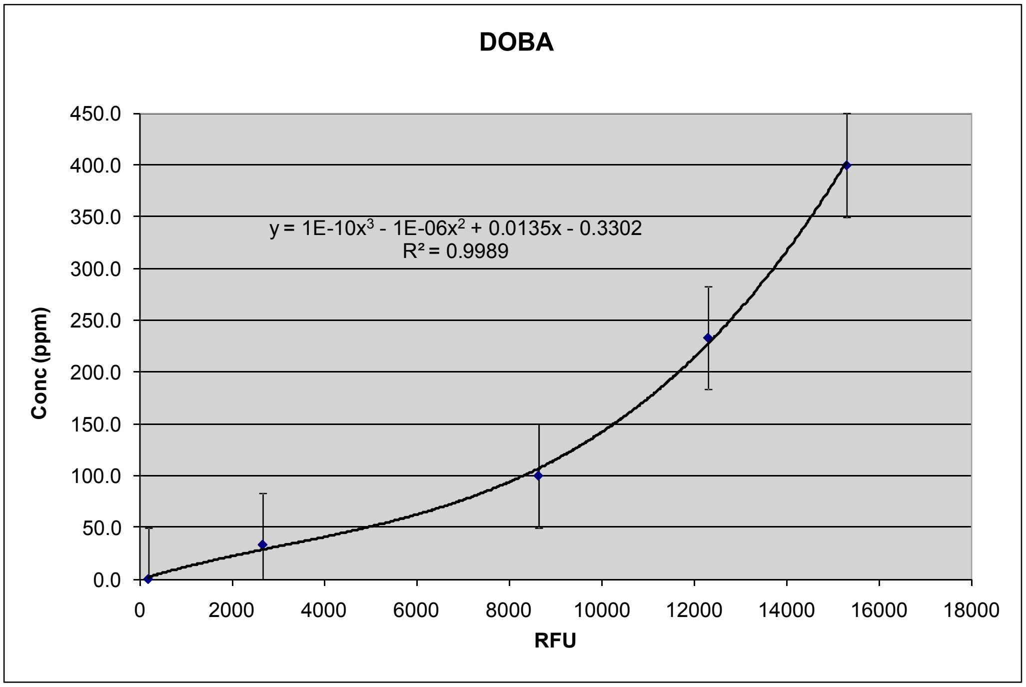


Figure B5. C3 Calibration for Doba Crude Oil

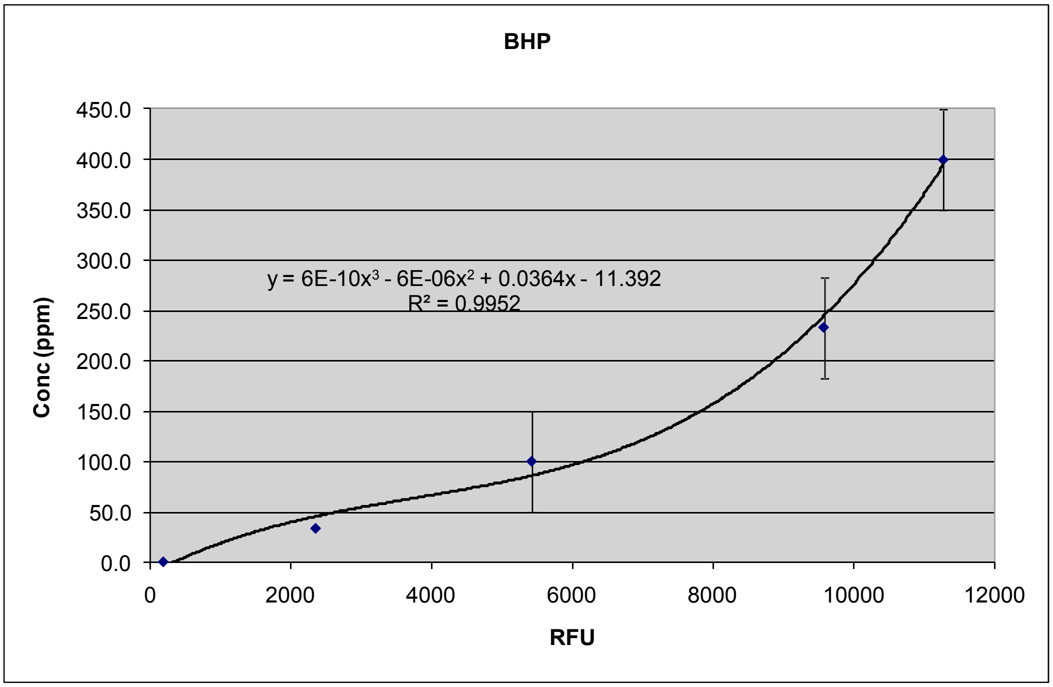


Figure B6. C3 Calibration for BHP Billiton Crude Oil

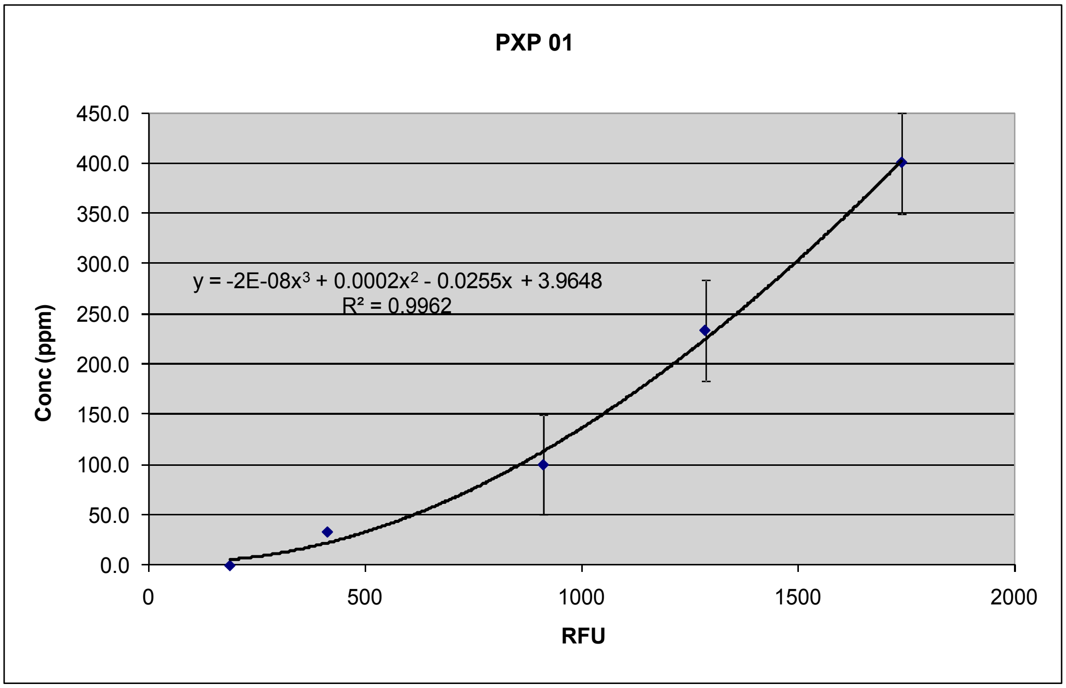


Figure B7. C3 Calibration for PXP 01 Crude Oil

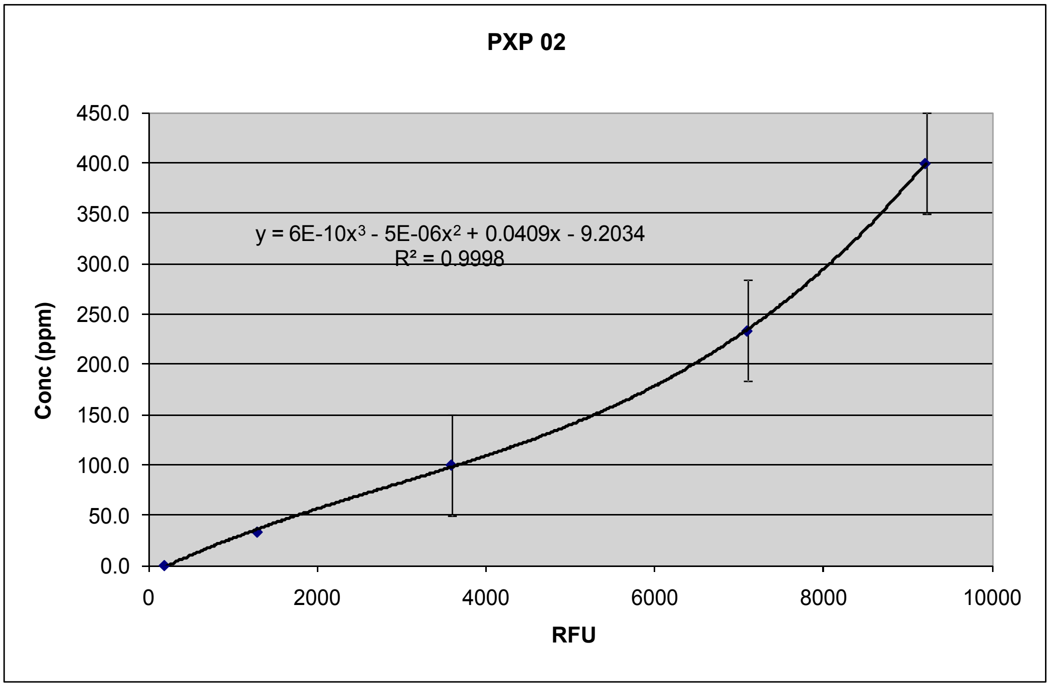


Figure B8. C3 Calibration for PXP 02 Crude Oil

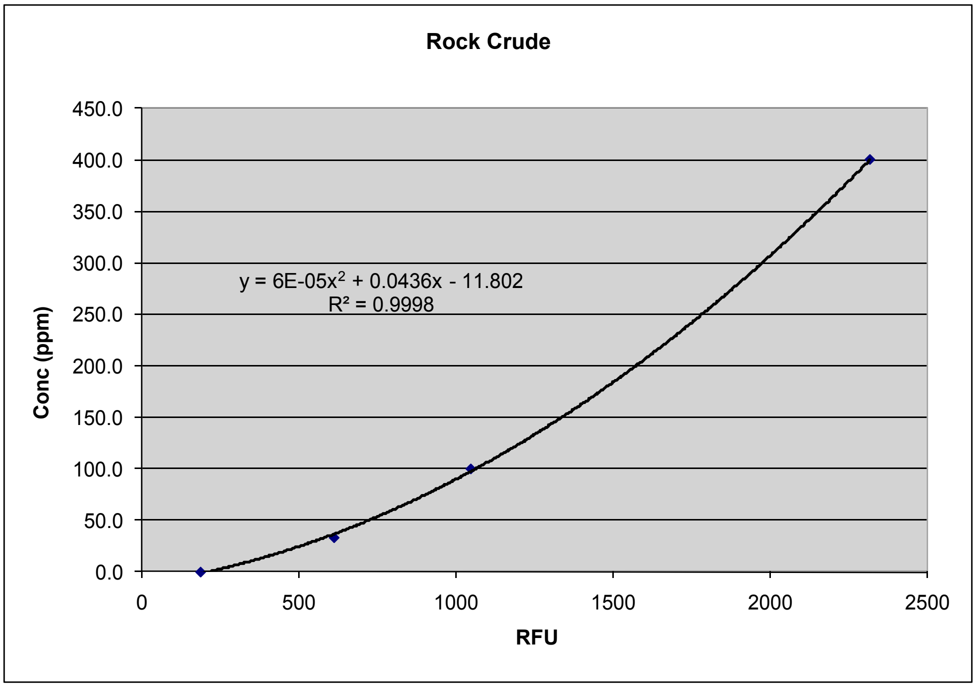


Figure B9. C3 Calibration for Rock Crude Oil

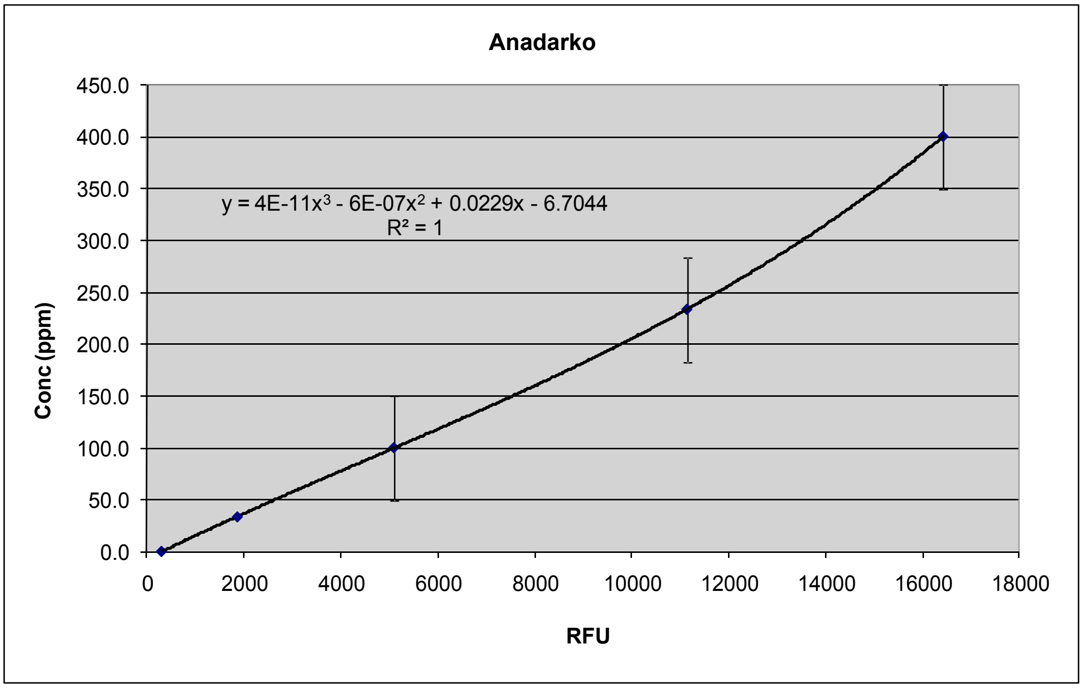


Figure B10. C3 Calibration for Anadarko Crude Oil

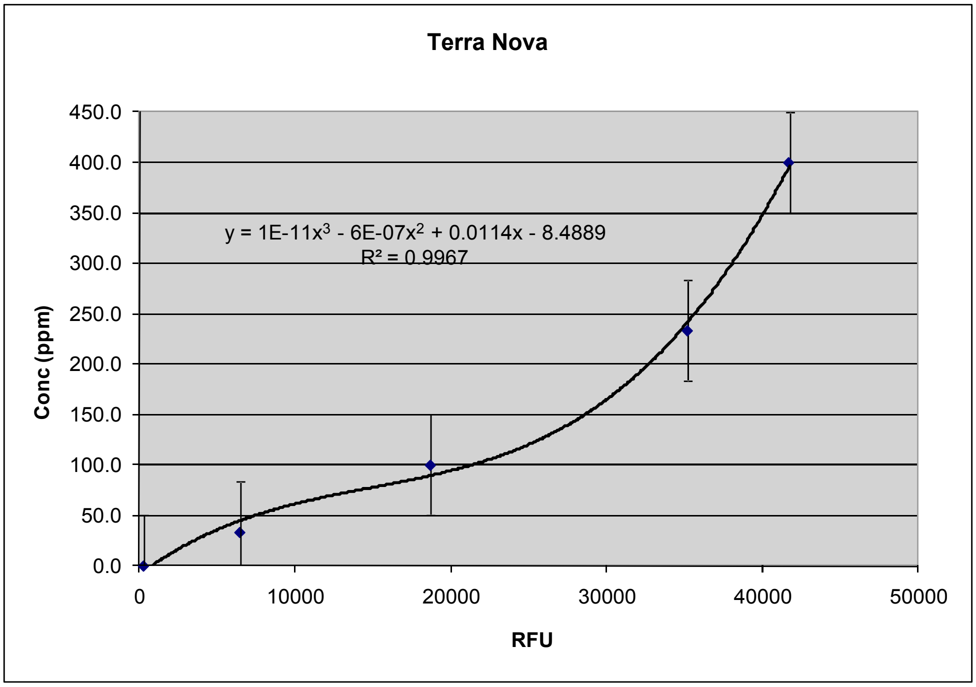


Figure B11. C3 Calibration for Terra Nova Crude Oil

Appendix C: Small Scale Test Procedures

Warren Spring Laboratory

ANNEX 1 TO
APPENDIX A
WSL REPORT
LR 448 (OP)
(revised 1990)

THE DETERMINATION OF THE EFFICIENCY INDEX OF OIL SPILL DISPERSANTS.

INTRODUCTION

The method for the determination of the Efficiency Index of oil spill dispersants is defined in the WSL report LR 448 (OP). This revision expands on that method and incorporates the analytical procedures currently in use.

DEFINITION

The Efficiency Index of an oil spill dispersant is defined as the percentage, by weight of the test oil which has been transferred, as small droplets into the water phase under the conditions of the test, assuming complete and even distribution at the time of sampling.

SUMMARY OF THE METHOD

The oil spill dispersant is added, dropwise, to a measured volume, (by weight) of the test oil on the surface of seawater at 10°C in a conical separating funnel.

The separating funnel is rotated about its horizontal axis, at right angles to its longitudinal axis, for a period of 2 minutes at 33 ±1 rpm. After rotation has ceased, the stopper is removed and after 1 minute standing time, 50ml of oily water are run off through the bottom tap. The quantity of oil present in the sample is then determined spectrophotometrically after extraction into chloroform.

The method may be used for determining the efficiency index of any of the three dispersant types, (types 1, 2 or 3).

APPARATUS

SEPARATING FUNNELS

(1) A conical separating funnel of nominal capacity 250ml, (Fig 1). After use the funnel should be rinsed thoroughly with chloroform to remove any oil remaining inside, then washed in a laboratory glasswasher. The washing programme should include a thorough rinse with distilled water to ensure that all traces of detergent are removed. The funnel should then be allowed to drain and cool before being placed in the temperature controlled cabinet ready for use.

(2) A separating funnel to BS 2021 with a nominal capacity of 100ml.

MOTOR DRIVEN RACK
A motor driven rack, into which can be fitted and clamped the 250ml separating funnel. The rack should rotate about a horizontal axis approximately 15 - 20 mm below the level of the seawater in the separating funnel.

SYRINGES
(1) A glass syringe, fitted with a needle, capable of accurately dispensing 0.2ml of dispersant in drops of 5 to 10 microlitres.

(2) A glass syringe capable of accurately dispensing 5.0ml of the test oil.

(3) A glass syringe, fitted with a needle, capable of accurately dispensing 2.0ml of Type 1 dispersant, and 2.0ml of Type 2 dispersant in drops of 5 to 10 microlitres

SPECTROPHOTOMETER
A spectrophotometer capable of measuring absorbance at 580nm, and equipped with glass cells of 10mm path length.

Stopclock

Measuring cylinders, 250ml and 50ml

REAGENTS

TEST OILS
(1) An oil of known density and having the following characteristics:

Dynamic viscosity at 10°C: 1800 to 2200 mPa s at $4s^{-1}$ shear
Asphaltenes (IP 143/78): 6.0% by weight, maximum.
Pour point (IP 15/67): <5°C

(2) An oil of known density having a dynamic viscosity at 10°C of 450 to 550 mPa s at a shear rate of $4s^{-1}$. This oil is prepared by diluting the higher viscosity oil, referred to above, with kerosine to reduce its viscosity to the required value.

KEROSINE
Odourless Kerosine to BS2869 Ams 1 and 2, Class C1

SEAWATER
Seawater taken from the sea and having a total solids content of 3.3 - 3.5%
Synthetic seawater is also permissible.

Sodium sulphate, anhydrous

Chloroform

METHOD

CALIBRATION

Transfer 0.1, 0.2, 0.3, 0.4 and 0.5g of the test oil, accurately weighed, into separate 100ml volumetric flasks. Dissolve the oil in chloroform and make each flask up to volume.

Measure the absorbance of each solution at 580nm in glass cells of 10mm path length, using the chloroform as a reference solution.

A graph may be plotted of absorbance against concentration of oil in the chloroform solution. Alternatively the line of best fit of the calibration points may be calculated to give linear regression coefficients.

PROCEDURE

The test procedure is carried out in a temperature controlled cabinet maintained at 10°C. All reagents, test materials and apparatus should be kept in the cabinet for 24 hours before conducting the test.

Place the unstoppered separating funnel in the motor driven rack. In a measuring cylinder, measure 250ml of seawater and transfer to the separating funnel.

Using the syringe, transfer 5ml, by weight, of the test oil to the surface of the seawater and start the stopclock. Weigh the syringe before and after use to calculate the weight (± 0.001g) of the 5ml of the oil.

Using the appropriate syringe, take the required volume of the dispersant to be tested, (0.2ml of type 3 dispersant, 2.0ml of undiluted type 1 dispersant and 2.0ml of freshly diluted type 2 dispersant). 1 minute after completing the addition of the test oil to the seawater, transfer the dispersant to the oil. The addition of the dispersant to the oil should be done dropwise, starting from the centre of the oil lens and working radially outwards so that the dispersant is distributed as evenly as possible. Place the stopper in the separating funnel and clip on the retaining cap of the motor driven rack. Close the door of the temperature controlled cabinet.

When the time of the stopclock shows 2.5 minutes from the addition of the oil to the seawater, start the rotation of the separating funnel, and continue for 2 minutes.

After 2 minutes switch off the motor driven rack and allow the separating funnel to stand, undisturbed for exactly 1 minute. Remove the stopper, and run off from the bottom tap, 50ml of oily water into a measuring cylinder. The taking of this sample should take no longer than 10 seconds.

The remainder of this determination may be done outside the temperature controlled cabinet.

Transfer the 50ml sample from the measuring cylinder to a 100ml separating funnel. Wash the measuring cylinder twice with 10ml of chloroform and add to the 100ml separating funnel. Stopper the funnel and shake for 1 minute. Allow the phases to separate completely and run off the chloroform layer into a 100ml volumetric flask through a 75mm glass filter funnel fitted with a 9.0cm Whatman No 1 filter paper and into which has been placed no more than 1.5g anhydrous sodium sulphate. Repeat the chloroform extraction twice more, using 20ml chloroform on each occasion. Thoroughly wash the filter paper and sodium sulphate, with chloroform and then dilute to the mark on the volumetric flask. Stopper the flask and shake well.

Measure the absorbance of the sample solution using glass cells of 10mm path length and a spectrophotometer set to a wavelength of 580nm. The calibration standards prepared from the test oil should be measured at the same time as the sample solution.

Using either the graph or the calculated regression coefficients convert the absorbance measurement from the sample solution into concentration figures expressed as 'grams of oil per 100ml of chloroform'. This is equivalent to the weight of oil contained in the 50ml sample of oily water taken from the 250ml separating funnel.

CALCULATION

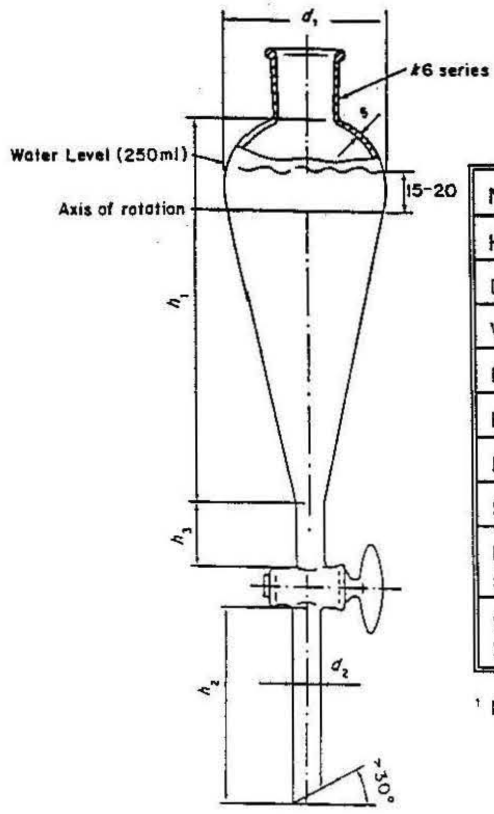
Calculate the efficiency index as follows:

$$\%\ \text{Efficiency} = \frac{\text{weight of oil in 50ml sample of oily water} \times 500}{\text{weight of test oil added to the 250ml separating funnel}}$$

REPORT

The Efficiency Index is the average of three separate determinations. The calculated average is reported to one decimal place for each of the two reference fuel oils.

ANNEX 1, FIGURE 1



Nominal capacity	250ml
Height of body, h1	185mm
Diameter of body, d1 max	83mm
Wall thickness of body, s min	1.2mm
Diameter of stem[1], d2 ± 0.5	12.5mm
Length of stem, h2 ± 10	70mm
Nominal bore of stopcock min	3mm
Size of stopper (see ISO 383)	k6 series
Length of tube between bulb and stopcock, h3 max	20mm
Wall thickness of tube between bulb and stopcock min	1.5mm

[1] Medium walled tubing (see ISO 4803)

STANDARD CONICAL SEPARATING FUNNEL 250ml CAPACITY

NB. The distance between the seawater level when filled with 250ml seawater at 10°C and the axis of rotation of the flask should be between 15mm and 20mm.

EPA Baffled Flask

MATERIALS AND METHODS (from Venosa and Holder, 2011)

Sampling Design and General Approach. The protocol uses a 150-mL screw-cap trypsinizing flask (essentially an Erlenmeyer flask with baffles) that has been modified by the placement of a glass stopcock near its bottom so that a subsurface water sample can be removed without disturbing the surface oil layer (Figure 1). After synthetic seawater and oil are added to the flask, a dispersant is added directly to the floating oil slick, and the flask is placed on an orbital shaker to receive moderate turbulent mixing at 200 rpm for 10 ± 0.5 min. The shaker table having a speed control unit with variable speed (40-400 rpm) and an orbital diameter of approximately 0.75 inches (2 cm) is used to impart turbulence to solutions in the test flasks. The mixing is equivalent to an energy dissipation rate of 0.163 W/kg water, which is approximately 2 orders of magnitude greater than that obtainable in the Swirling Flask Test. The rotational speed accuracy should be within ± 10%. The contents are allowed to settle for 10 ± 0.25 minutes to allow non-dispersed oil to return to the water surface before removing the subsurface water sample. Each replicate is run individually by the same analyst so that identical test conditions can be maintained for each replicate. The subsurface water sample is then processed by liquid-liquid extraction in dichloromethane (DCM). The oil concentration in the DCM is measured by UV-visible absorption spectrophotometry.

Figure 1. Photograph of the baffled trypsinizing flask.

Synthetic Seawater. "Instant Ocean," manufactured by Aquarium Systems of Mentor OH, was used as the exposure matrix for the study. The synthetic sea water was prepared by dissolving 34 g of the salt mixture in 1 L of Milli-Q water (final salinity of 34 ppt). Table 2 provides a list of the ion composition of the sea salt mixture. Following the preparation, the saltwater solution was allowed to equilibrate to the ambient temperature of the constant temperature room. The temperature in the constant temperature room was 15 ± 0.5 °C.

Table 2. Major Ion Composition of Instant Ocean^{TM} Synthetic Sea Salts

Major Ion	Salt Composition, % total weight	Salt Composition at 34 ppt Salinity, mg/L
Chloride (Cl^-)	47.470	18,740
Sodium (Na^+)	26.280	10,454
Sulfate (SO_4^{-2})	6.600	2,631
Magnesium (Mg^{+2})	3.230	1,256
Calcium (Ca^{+2})	1.013	400
Potassium (K^+)	1.015	401
Bicarbonate (HCO^{-3})	0.491	194
Boron (B^{3+})	0.015	6
Strontium (Sr^{2+})	0.001	7.5
Solids Total	86.11%	34,090
Water	13.88	--
Total	99.99%	--

Oil Extraction and Analysis. The solvent dichloromethane (DCM, pesticide quality) was used for extractions of oil-water samples from the baffled trypsinizing flasks and all experimental water samples. A Brinkmann Eppendorf repeater pipettor capable of dispensing 2 µL to 5 mL, depending on the tip selected, was used for dispensing the required amounts of the oil and the dispersant. Dispersed oil was measured with a Shimadzu Recording UV-VIS Spectrophotometer (Model UV-1800) capable of measuring absorbance at 340, 370, and 400 nm (these were the same wavelengths used in the original SFT protocol). Standard transmission-matched quartz 10-mm path length rectangular cells with PTFE cover were used having a transmittance of > 80% over the wavelength range of not > 190 nm at the low end of the spectrum to at least 1,100 nm at the high end of the spectrum.

Oil Standards Procedure. A stock solution of dispersant-oil mixture in DCM was prepared by adding 80 µL of the dispersant to 2 ml of the oil, and then 18 mL of DCM was added. Determinations of stock solution concentrations were based on the mass measurements after each addition. For generating a six-point calibration curve, a specific volume of the stock standard solution was added to 30 mL synthetic seawater in a 125 mL separatory funnel. The volumes of the stock solution used were adjusted to give absorbance readings that fell within the linear dynamic range (LDR) of the spectrophotometer. Liquid/liquid extractions of samples were then performed three times by using 5 mL of DCM for each extraction and adjusting the final extract to 20 or 25 mL (adjusted to maintain the LDR). The final extract was then transferred to 25 mL serum bottles with crimp-style aluminum/Teflon seals and stored at 5 °C until the time of analysis

.

Baffled Flask Test Procedure. A volume of 120 mL of synthetic seawater was added to the baffled flask, followed sequentially by addition of the oil and finally by the dispersant. A volume of 100 µL of oil was carefully dispensed directly onto the surface of the synthetic seawater using an Eppendorf repeater pipettor with a 5 mL syringe tip attachment. The dispersant was then dispensed onto the center of the oil slick by using a 100-µL syringe tip attachment set to dispense 4 µL, giving a volumetric ratio of dispersant-to-oil of 1:25 (DOR). This was similar to the average DOR reported in the BOEMRE Ohmsett report (~1:30) for 12 test oils. The DOR was not reported for the other 8 oils. Care was taken to make certain the dispersant contacted the oil without first touching the water. The flask was then placed on an orbital shaker (New Brunswick G24 shaker incubator) and mixed for 10 minutes at a rotation speed of 200 rpm. At the end of the mixing period, the flask was removed from the shaker and allowed to remain stationary on the bench top for 10 minutes. At the conclusion of the quiescent period, the first 2 mL of sample was drained from the stopcock and discarded, and then 30 mL of sample was collected in a 50 mL graduated cylinder. The 30 mL sample was transferred to a 125 mL separatory funnel and extracted 3 times with 5 mL fresh DCM. The extract was adjusted to a final volume of 20 or 25 mL and transferred to a 50 mL crimp style glass vial with an aluminum/Teflon seal. The vials were stored at 5 °C until the time of analysis. Dilutions were made in volumetric flasks for some of the oils to achieve the LDR of the spectrophotometer. Each of the four replicates was done separately so that shaking and settling times were exactly the same for all. In addition to the 4 replicate dispersant / oil / seawater mixtures, 4 replicate oil / seawater mixtures with no dispersant, and an overall total of 4 replicate method blanks (seawater alone) were also run for quality control purposes.

Analysis of Extracts. Although we used a recording spectrophotometer for all absorbance measurements, which is capable of measuring absorbance at multiple wavelengths, we recorded the absorbance at three discreet wavelengths of 340, 370, and 400 nm and calculated the area under the absorbance vs. wavelength curve by applying the trapezoidal rule according to the following equation:

$$Area = \frac{(\mathrm{Abs}_{340} + \mathrm{Abs}_{370}) \times 30}{2} + \frac{(\mathrm{Abs}_{370} + \mathrm{Abs}_{400}) \times 30}{2} \tag{1}$$

The dispersion effectiveness value that is reported is the lower 95% confidence level of the 4 independent replicates. Equation 2 summarizes the calculation of the LCL_{95}:

This area count is used to calculate the Total Oil Dispersed and then the percentage of oil dispersed (%OD) based on the ratio of oil dispersed in the test system to the total oil added to the system, as follows:

$$TotalOilDispersed(g) = \frac{Area}{CalibrationCurveSlope} \times V_{DCM} \times \frac{V_{tw}}{V_{ew}} \tag{2}$$

where:
V_{DCM} = volume of DCM extract,
V_{tw} = total volume of seawater in flask,
Vew = total volume of seawater extracted, and

$$\%OD = \frac{TotalOilDispersed}{\rho_{oil} \times V_{oil}} \tag{3}$$

where:
ρ_{oil} = density of the specific test oil, g/L, and
V_{oil} = volume (L) of oil added to test flask (100 μL = 10^{-4} L) (4)

The dispersion effectiveness value that is reported is the lower 95% confidence level of the 4 independent replicates. Equation 5 summarizes the calculation of the LCL_{95}:

$$LCL_{95} = \bar{x} - t_{n-1,1-\alpha}\left(\frac{s}{\sqrt{n}}\right) \tag{5}$$

where $\bar{x}$ = mean dispersion effectiveness of the n = 4 replicates,
s = standard deviation, and
$t_{n-1,1-\alpha}$ = 100 x $(1 - \alpha)^{th}$ percentile from the t-distribution with n-1 degrees of freedom.
For four replicates, $t_{n-1,1-\alpha}$ = 2.35, where $\alpha = 0.05$.

Since a certain amount of physical dispersion occurs when no dispersant is used, that fraction should be accounted for (i.e., subtracted) in the final reporting of chemical dispersion. The statistical equations governing the proper way to accomplish this are summarized below.

The average nominal percent oil dispersed due to dispersant alone is calculated using Equation 6 for coupled experiments with and without dispersant ($\overline{DE_d}$ and $\overline{DE_c}$, respectively):

$$DE_{nom} = \overline{DE_d} - \overline{DE_c} \tag{6}$$

where DE_{nom} = nominal percent oil dispersed due to dispersant alone,
$\overline{DE_d}$ = average percent oil dispersed in presence of dispersant (total dispersed oil), and
$\overline{DE_c}$ = average percent oil dispersed in absence of dispersant (natural dispersion).

The same comparison for reporting the LCL_{95} is made for the coupled experiments with and without dispersant (LCL_{95d} and LCL_{95c}, respectively). The LCL_{95DE} of a chemical dispersant is calculated after correcting for natural dispersion using the following equations:

$$LCL_{95_{DE}} = \overline{DE_d} - \overline{DE_c} - \left(t_{n_d+n_c-2,0.95} * SE_{\overline{DE_d}-\overline{DE_c}}\right) \tag{7}$$

where: LCL_{95DE} = lower confidence limit for dispersed oil due to dispersant only,
$t_{n_d+n_c-2,0.95}$ = 1.94, the 95% critical value for a t-distribution with ($n_d + n_c - 2$) degrees of freedom.
$SE_{\overline{DE_d}-\overline{DE_c}}$ = standard error, defined in Equation 8:

$$SE_{\bar{d}-\bar{c}} = \sqrt{\frac{s_d^{\ 2}}{n_d} + \frac{s_c^{\ 2}}{n_c}} \tag{8}$$

The data shown in this report (Figure 1) used Equation 7 for reporting the LCL_{95DE} after accounting for physical dispersion. Also reported are $\overline{DE_d}$ and $\overline{DE_c}$ (Figure 2) for comparison purposes.

EXDET Test

(from Becker 1993)

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 (Optional: see note A at the end of this appendix:)
- 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)
- Bausch and Lomb Spectrophotometer (Spectronic 21), and adequate supply of appropriately matched sample tubes (cuvettes)
- Chloroform or methylene chloride, as a solvent, for extraction (Fisher certified Optima, for HPLC, spectrophotometer, GC, Fisher C297-4)
- Sea water, as needed (Sea Salt ASTM D-1141-52, Lake Products Co., Maryland Heights, Missouri, recommended for artificial sea water)
- Polypropylene sorbent pads (3M sorbent sheets cut into 1.5 in squares)
- Bottletop dispenser, 50 mL (Fisher 13-688-70); optional, for dispensing aliquots of solvent when many tests are being run
- 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 must be level, that is, the 250 mL separatory funnels must be in an upright, non-slant position before starting each group of tests. The funnels are clamped to the shaker just above the stopcock. To assure a secure and stable clamping action, rubber or latex laboratory tubing can be fitted over the fingers of the clamp, and/or olypropylene padding wrapped around the lower part of the funnel where the clamp grips. Add artificial sea water (approximately 250 mL) to reach the widest part of each test funnel. Mark this level on each test funnel for future runs.

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. For example, 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. The oscillation frequency of the current Burrell shaker is approximately 390 cycles per minute. This can be checked by recording the pen deflections on a chart recorder. Older Burrell shakers run at a lower frequency (approximately 310 cycles per minute) and should be set for a slightly greater deflection amplitude, such as 2.1°.

Detailed test method

1. If testing a premixed sample, prepare the desired dispersant/oil (D/O) mixture, for example, 1 part of dispersant to 25 parts of oil.
2. 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 the test oil or D/O mixture (about 1 mL) to the top of the water in each test funnel. Then, if using the direct application method, carefully add the desired amount of dispersant to the oil. Stopper the funnels, start the shaker, and allow toshake 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. The sorbent will collect the undispersed oil.
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 or 500 mL separatory funnels (see Note A). 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. If 16 oz jars were used in Step 3, 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 (see Note B).
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. The extracts may have to be diluted to fall in the linear range, 0.1 to 1.1, of the spectrophotometer. If an undiluted sample is too low, select a wavelength to obtain a reading in this range if possible, and use this same setting for both extracts. The dilution can be carried out in the cuvettes used in the spectrophotometer, using pipettes to add known amounts of extract and pure solvent.
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

The dilution factor D, of the sample is calculated by:

$$D = TVOL / DVOL \qquad (2)$$

Where: $TVOL$ = volume of sample + volume of pure solvent
$DVOL$ = volume of sample

Equation 1 can be simplified to:

$$\%D = (1 /(1+AF)) *100$$

Where: $A = UABS / DABS$
$F= UD / DD$

A standard deviation can be calculated from the percent dispersed results of multiple replicates (at least four).

Notes.
A. A step in the water extraction procedure can be eliminated by placing the shaking apparatus on an elevated platform at a height at which the tips of the 4 shaking flasks (250 mL funnels) are sufficiently above the bench top (approximately 13 in) so that the 500 mL extracting funnels can be placed underneath. The samples can now be drained directly into the extracting funnels. Use of a rack to hold the extracting funnels enables the operator to simply slide all 4 of them at once under the shaking funnels to obtain the dispersed oil sample. Elimination of the sample transfer step via 16 oz jars saves time and material.

B. An alternative procedure is to use about 40 mL solvent aliquots in each of the extractions, and then bring the total extracts to 100 mL in 100 mL volumetric flasks, before putting the extracts into the 4 oz jars. The shaking funnels can be marked at the 40 mL level and solvent added from a squeeze bottle, for convenience. This also allows extra 5 to 10 mL extractions of the separatory funnels if desired, while still maintaining the 100 mL total solvent volume.