FINAL REPORT

DISPERSANT EFFECTIVENESS TESTING ON VISCOUS, U.S. OUTER CONTINENTAL SHELF CRUDE OILS: PHASE III

For

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And

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Executive Summary

The objective of the work was to study the mechanism by which oil viscosity limits the effectiveness of dispersants. Specifically, two viscosity issues were studied. One is the ability of the dispersant to penetrate into viscous oil upon initial application prior to being washed away by surface water (what we will call “mixing-one”). The other is the internal visco-elasticity of the oil-dispersant mix (in conjunction with the dispersant dosage that has successfully mixed into the oil) that may prevent the oil from being broken into droplets when wave energy is applied (what we will call “mixing-two”).

The first study goal was to investigate pre-mixed oil-dispersant viscosities and final dispersant dosages to determine limiting viscosities for successful “mixing-two” at different dispersant dosages. In the small-scale tests oils with viscosities greater than about 10,000 cP were not amenable to chemical dispersion at pre-mixed doses of 1:20 and less at the maximum mixing energy level that can be applied in the small wave tank. The dispersant was effective to varying degrees when pre-mixed with the oil at doses of 1:10 and 1:5. At these higher doses the oil-dispersant mix viscosities ranged from 3,720 to 13,740 cP. The success achieved at the high dose (DOR=1:5) for the most viscous oil indicates that the viscosity limit for dispersion is a function of both the amount of dispersant mixed into the oil (the final DOR) and the oil-dispersant mix viscosity. The viscosity of the oil-dispersant mix in this case was 13,780 cP and the measured effectiveness was 80%. All other oil-dispersant mixes with similar viscosities (11,010 to 11,500 cP) but lower DOR’s (1:50 or 1:20) resulted in minimal measured dispersion (0 to 9%) indicating that both the amount of dispersant mixed into the oil and the final product viscosity affect the final dispersion. A similar result was achieved in the large-scale pre-mixed tests. In the pre-mixed tests where final oil-dispersant mix viscosities were similar the higher dispersant dosage resulted in a higher DE. In the Ellen 040 crude oil, 1:10 DOR and the Gail E010 crude oil, 1:20 DOR tests at Ohmsett the final dispersant-oil mixes had viscosities of 10,400 and 10,470 cP, respectively. The higher dose test with the Ellen 040 crude oil had a DE of 67% while the lower dose test DE was only 38%. Based on the small- and large-scale test results of this study oil-dispersant mixes with final viscosities of about 10,000cP appear to need a DOR of 1:10 or better to achieve significant dispersion. Both the reduction in viscosity due to the addition of the more fluid dispersant and the presence of more surfactant improve the final DE.

The second study goal was to investigate if there is an initial oil viscosity that prevents successful "mixing one" or the penetration of the dispersant into the oil during spray applications prior to it being washed away by water.

Syringe application of dispersant in the small-scale tests, at the DOR level where success was achieved in the pre-mixed tests, resulted in some effectiveness though less than in the pre-mixed tests in all but one test case. The results show that about 30% to 60% of the dispersant applied to the oil-water interface by syringe was successfully mixing (mixing 1) with all of the oils tested (initial viscosities of between 11,310 and 47,920 cP). Multiple applications (4) of smaller doses to achieve the same final high dosage resulted in a poorer overall effectiveness in all oils than was achieved when one full dose was applied by syringe at the start of the test.

In large-scale Ohmsett tests, dispersant applied by spraying produced high levels of effectiveness in all three oils. Tests with pre-mixed oil and dispersant, at DORs similar to the spray tests, resulted in lower dispersant effectiveness (DE) than in corresponding spray tests. Twenty-five years of experience in dispersant effectiveness testing and the small-scale test results from this study would have predicted that the opposite result should have prevailed. Because the spray applications were at least somewhat effective in all cases and were more effective than pre-mixed tests with similar dispersant dosages the "mixing-one" limitation on dispersant effectiveness was not evident for the oils and conditions used in the large-scale Ohmsett tests.

This study demonstrated in both the small- and large-scale pre-mixed tests that the oil-dispersant mix viscosity and final DOR both are important in the mixing-two process and final DE outcome. Additional work could be completed to confirm this with additional oils and to refine the viscosity/DOR combinations that result in significant DE.

The large-scale test results did not confirm that effectiveness is controlled by oil viscosity preventing the penetration of the dispersant into the oil where it could do its work (mixing-one). This was an unexpected outcome. One possible explanation for this might be the difficulty in estimating the actual DOR in the large-scale spray tests and the possibility that higher doses than estimated were reaching the oil in the current work. The final oil-dispersant viscosity or the amount of dispersant that actually was in the oil immediately after application was not measured in the current test program due to the logistical and technical difficulty of doing so. This could be attempted in additional testing to provide more insight into the “spray versus pre-mixed results”. Researchers involved in the BP Horizon spill response have refined techniques for the measurement of dispersant quantities present in oil. It might be possible to apply these new techniques in future testing to quantify the amount of dispersant getting into the oil in the spray application. Additional insights might also be gained by working with one heavy oil that is adjusted to produce oil samples of varying viscosity by blending with marine gasoil, rather than working with a range of crude oils from different sources where the oil type itself might cause variation in effectiveness.

Dispersant Effectiveness Testing On Viscous, U.S. Outer Continental Shelf Crude Oils: Phase III

1. Objectives and Goals

The primary objective of the work was to study the mechanism by which oil viscosity limits the effectiveness of dispersants.

Specifically, two viscosity issues were studied. One is the ability of the dispersant to penetrate into viscous oil upon initial application prior to being washed away by surface water (what we will call "mixing-one"). The other is the internal visco-elasticity of the oil-dispersant mix (in conjunction with the dispersant dosage that has successfully mixed into the oil) that may prevent the oil from being broken into droplets when wave energy is applied (what we will call "mixing-two"). The primary goals were 1) to investigate pre-mixed oil-dispersant viscosities and final dispersant dosages to determine limiting viscosities for successful "mixing-two" at different dispersant dosages and 2) to investigate if there is an initial oil viscosity that prevents successful "mixing one" during spray applications.

2. Background

The chemical dispersion of heavy or viscous oils and the upper limit of viscosity for the successful dispersion of viscous oils have been studied by a number of researchers including past work at Ohmsett (Martinelli & Cormack 1979, Martinelli & Lynch 1980, Lee et al. 1981, ITOPF 1982, Cormack et al. 1986-1987, Fiocco et al. 1999, Canevari et al. 2001, Stevens & Roberts 2003, Colcomb et al. 2005, Lewis 2004, SL Ross 2006, 2008). This past work has focused on correlating oil viscosity with dispersant effectiveness to provide insight into the maximum useful range of chemical dispersants in an operational setting. These studies did not investigate processes that may be affecting the chemical dispersion of heavy oils to provide insight into how dispersants might be modified to improve their range of application. At least two dispersion processes may be affected by the oil's viscosity. One is the ability to get the applied dispersant to penetrate into the viscous oil in sufficient quantity to be effective before it is washed away in the dominant water phase ("mixing one"). The other is internal visco-elasticity of the oil that may prevent the oil from being broken into small droplets under the prevailing energy conditions even if a significant quantity of dispersant has penetrated into the oil ("mixing two"). This project studied the potential roles of both "mixing one" and "mixing two" in limiting dispersant effectiveness on heavy viscous oils. Small scale testing in the SL Ross wave tank, conducted in March 2010, was followed by full scale testing at Ohmsett, in April 2010. Ohmsett is the National Oil Spill Response and Alternative Energy Test Facility in Leonardo New Jersey and is the largest test tank world-wide that is made available for testing and training with crude oils.

Results from a recent study on low-dose repeat application of dispersants (SL Ross 2009) indicate that multiple low-dose applications of dispersant to viscous oil slicks may in fact result in a better dispersion outcome than one, single, high dose. In the present study, multiple low-dose dispersant applications were tested during the preliminary testing in the small-scale wave tank to determine if this approach might show promise in overcoming the "mixing-one" oil viscosity limits to chemical dispersion of oil.

3. Oils Used in Test Program

A total of 10 oils were acquired by MMS in late 2009 and early 2010 for use in R&D programs at the Ohmsett facility. SL Ross, MAR Inc. and MMS worked together with industry to identify oils of interest and to acquire and ship the oils to Ohmsett. Higher viscosity oils were of interest since research at Ohmsett often focuses on extending spill countermeasures capabilities to more difficult to treat and handle viscous oils. Since current viscosity data for many of the produced oils is not available potential oils had to be identified based primarily on API gravity, not an accurate predictor of oil viscosity. The API gravity values were also for oils sampled at other times and therefore were not necessarily representative of what was being produced when the samples were acquired for the OHMSETT test oils. Many of the heavy oils are produced with substantial quantities of water and production chemicals can be added to them at various stages of their handling. For these reasons the oils generally had to be collected offshore at the production platforms and decanted prior to shipping to ensure that the shipped product was primarily oil and free of production chemicals. Industry was very cooperative and helpful in the identification, acquisition, sampling and shipping of the oils. Six of the oils received had viscosities high enough to be of use in this test program. Unfortunately two of the most viscous oils (Heritage HE-05 and HE-26) were shipped with excessive amounts of water and not enough oil was available for full-scale testing. Table 1 identifies the oils recently acquired by MMS and highlights the subset of oils (Irene-Lompoc, Irene-Co-mingled, Ellen A040 and Gail E010) that were used in this study.

Table 1**.** Oils Used in Test Program

Oil Designation	Operator	Industry Contact	Well Completion Name	Density (g/ml @ 15 ºC)	Measured Viscosity (mPa.s at 15 ºC)
Irene - Lompoc	Plains Exploration & Production	David Rose	Irene Sampled from Lompoc O&G Facility	0.9591	9,400
Irene - Co-mingled	Plains Exploration & Production	David Rose	Co-mingled Irene	0.9787	31,195
Ellen A040	Pacific Energy Resources	Steve Liles	Ellen A040	0.9790	18,500
Gail E010	Venoco, Inc	Kieth Wenal	Gail E010	0.9709	11,906
Heritage HE-05	ExxonMobil U.S. Production	Brian Hansen	Heritage HE-05	0.9928	359,133
Heritage HE-26	ExxonMobil U.S. Production	Brian Hansen	Heritage HE-26	0.9856	185,567
Ind. Hub Atwater Valley Block 37	Anadarko Petroleum Company	Susan Hathcock	Independence Hub Atwater Valley Block 37	0.9148	13
Neptune	BHP Billiton	Mike Kelly	Neptune	0.9244	388
Gail E019	Venoco, Inc	Kieth Wenal	Gail E019	0.8996	64
Ellen A038	Pacific Energy Resources	Steve Liles	Ellen A038	0.9587	2,977
Oils used in this study are highlighted					

4. Small-scale Testing

Preliminary laboratory scale work in the SL Ross wave tank was completed in March of 2010.The tests were conducted by premixing dispersant into several viscous crude oils to determine: a) whether premixing might overcome the effect of oil viscosity in limiting dispersion and b) when the oil's viscosity might be preventing shearing of the oil dispersant mix into small droplets. The oils used in the testing were Irene-Lompoc, Irene-Co-mingled, Ellen A040 and Gail E010. The properties of these oils are provided in Table 1. Only four oils were available in sufficient quantities at Ohmsett and with high enough oil viscosities for this study. Corexit 9500 was used in all tests, as this is the most widely held and used dispersant in North America. The water temperature in these tests was 15°C. Dispersant doses ranging from 1:5 to 1:200 were pre-mixed with the test oils. Oil-dispersant mix viscosities were measured to help separate the surfactant penetration and viscosity influences on the dispersion process as the addition of dispersant, especially at the higher doses, can significantly alter the viscosity of the oil-dispersant mix. The viscous oils where dispersion occurred when pre-mixed with dispersant were then subjected to spray applications of dispersant at similar doses to determine if the "mixing one" process described above is a limiting factor in the chemical dispersion of the oil. Multiple low-dose applications of dispersant to the viscous oil were also tested to determine if this strategy improves the "mixing-one" process.

4.1 Small-scale Test Methods

The small-scale tests were completed in the SL Ross indoor wave tank. The methods used to assess dispersant effectiveness using the SL Ross wind-wave tank have been provided in detail elsewhere (SL Ross 2003). A brief synopsis of these methods is provided below.

The test tank is 11 meters long by 1.2 meters wide by 1.2 meters deep and is fitted with a wave-generating paddle at one end and a wave-dissipating beach at the other. The tank is filled with 32 ppt salt water to a depth of 85 cm for dispersant effectiveness testing. The tank is equipped with sand and activated carbon filtration. A photo of the test tank looking toward the wave-paddle end is shown in Figure 1. The photo shows the wave tank before the start of a test with the wave generator on, oil in the test area, and the wave paddle at the far end. An air curtain bubble barrier is used to contain the surface oil in the center of the tank.

Figure 1. SL Ross test tank with oil in test area and waves on.

Dispersant was either pre-mixed into the oil or applied to oil floating in the test area of the wave tank with waves on and by direct application to the oil surface using a syringe.

The wave paddle was set to operate at 39 strokes per minute during the test program. Maximum mixing energy in the tank was achieved at this setting with the oil still contained by the bubble barrier. At these settings a small breaking wave formed and broke just over the bubble zone at the paddle end of the containment area. The presence of this breaker indicated that the wave paddle frequency was properly set and the mixing energy in the tank was consistent with previous tests. The waves created at this paddle setting have periods of 1.54 seconds and a height of approximately 22 cm.

4.2 Small-scale Test Results

The first (of two) series of tests completed were with pre-mixed dispersant and oil. The results from these tests can be seen in the third and fourth columns of Table 2. Column three shows the viscosities measured for the dispersant and oil mixtures tested. Dispersant to Oil Ratios (DORs) of 1:100, 1:20 and 1:5 were used for the two most viscous oils (Irene-Co-mingled and Ellen A040). DORs of 1:200, 1:50 and 1:5 were used for the slightly less viscous Gail E010 and Irene-Lompoc oils. In all cases the viscosities of the oil-dispersant mixes dropped as the dispersant dose increased, as would be expected.

The low-dose pre-mixed tests (DOR's of 1:20 and less) resulted in insignificant DE (0 to 11%) in these small-scale tests. The oil viscosities ranged from a low of 11,010 cP to a high of 47,920 cP. It is apparent that oils with viscosities greater than about 10,000 cP are not amenable to chemical dispersion at doses of 1:20 and less at the mixing energy level applied in the small wave tank.

The dispersant produced some effectiveness when pre-mixed to doses of 1:10 and 1:5. The degree of effectiveness depended on the final dispersant-oil mix viscosity and the dispersant dosage. When comparing the effectiveness estimates for the 1:10 doses, the higher oil-dispersant mix viscosities resulted in lower effectiveness values for all but the Irene-Lompoc oil. The success achieved at the high dose (1:5) for Irene-Co-mingled, the most viscous oil, indicates that the viscosity limit for dispersion is a function of both the amount of dispersant mixed into the oil and the oil-dispersant mix viscosity. The viscosity of the oil-dispersant mix in this case was

13,780 cP and the measured effectiveness was 80%. All other oil-dispersant mixes with similar viscosities (11,010 to 11,500 cP) but lower DOR's (1:20 or 1:50) resulted in minimal measured dispersion (0 to 9%) indicating that both the amount of dispersant mixed into the oil and the final product viscosity affect the final dispersion.

Table 2. Small-Scale Test Results

Oil Type	Dispersant Dose	Oil + Dispersant Viscosity ($8s^{-1}$ & 15 ºC)	Dispersant Effectiveness: Pre-mixed Measured (Observed) %	Dispersant Effectiveness: Single Application by Syringe %	Dispersant Effectiveness: Multiple (4) Applications by Syringe (1 minute spacing) %	Dispersant Effectiveness: Multiple (4) Applications by Syringe (2 minute spacing) %	Previous Ohmsett Dispersant Effectiveness Test Results % (SL Ross 2010)
Irene-Co-mingled	1:100	47,920	0				1:6 to 1:30 DOR 49%
	1:20	27,680	0				
	1:10	21,680	13				
	1:5	13,740	80 (70+)	26	8	17	
Ellen A040	1:100	17,020	0				1:10 to 1:40 DOR 78%
	1:20	11,500	9 (25+)				
	1:10	7,990	62	43			
	1:5	4,860	(100)	70	37	23	
Gail E010	1:200	12,500	0				1:10 to 1:32 DOR 88%
	1:50	11,560	0 (20+)				
	1:20	8,680	11	17			
	1:10	6,300	(90)	47	13	5	
	1:5	3,980	99	39			
Irene-Lompoc	1:200	11,310	0				1:7 to 1:24 DOR 60%
	1:50	11,010	0				
	1:10	5,700	37, 39 (50)	40, 31	11	5	
	1:5	3,720	99	29			

In the second set of small-scale tests dispersant was applied by syringe to the surface of the oil placed in the oil containment zone with the waves on. Dispersant application by syringe at the DOR level where effectiveness was achieved in the pre-mixed tests resulted in reduced effectiveness for most tests. The only exception to this was the 'syringe applied' result for the 1:10 application to Irene-Lompoc where the syringe applied and pre-mixed results are very similar. A comparison of the 'highest dose syringe applied' effectiveness results in Table 2 to the pre-mixed effectiveness values at lower doses indicates that somewhere in the vicinity of 30% to 60% of the dispersant applied to the oil-water interface by syringe may be successfully mixing (Mixing 1) with the oils tested to achieve similar effectiveness to the lower-dose pre-mixed tests.

Multiple applications (4) of smaller doses to achieve the same final high dosage resulted in a poorer overall effectiveness in all oils than was achieved when one full dose was applied by syringe at the start of the test. One possible explanation for this is that the single high dose of dispersant is able to have a more pronounced effect on the surface layer of the viscous oil because of the higher quantity of dispersant available to the surface layer of oil at the time of application. The longer the dispersant was allowed to soak into the oil between applications, or "the soaking time" between doses, the poorer the end result, in three of the four oils tested. Only in the case of the most viscous oil did the effectiveness increase when the spacing between doses was increased from 1 to 2 minutes and the final effectiveness was still lower than when the full dose was applied in one application. The failure of multiple low doses of dispersant to produce a higher level of effectiveness than a single higher dose in theses viscous oils differs from the results observed in earlier small-scale tests with less viscous oils (SL Ross 2009). In the earlier tests similar amounts of dispersant produced similar, or in the case of the most viscous oil tested, higher levels of effectiveness when administered in multiple low doses rather than in a single large dose. In the earlier study the oil viscosities were much lower (5 to 4,300 cP) and the "mixing-one" process may not have been limiting the dispersant's effectiveness. Each application of dispersant in the earlier test, whether a full dose or a partial dose administered multiple times, appears to have had a complete effect on the treated oil with little loss to the surrounding water (with the possible exception of the most viscous oil tested). The following was the explanation given for the different behavior of the multiple applications on the viscous oil presented in the earlier study; “ The one exception of this would appear to be for the more viscous Rock crude oil where the multiple low-dose applications resulted in a better overall dispersion than an equivalent single dose. This may have been due to the poor initial mixing of the dispersant with this viscous oil and the wash-off of the larger quantity of dispersant applied in the single application, high-dose test. The low-dose applications may have succeeded in getting more dispersant into the oil through the multiple exposures or contacts.” It was this result in the earlier test program that prompted the multiple-dose application tests in this study.

5. Large-Scale Tank Testing at Ohmsett

5.1 Objectives and Goals

The primary Objectives and Goals of the large-scale testing were the same as those outlined in section 1 for the overall test program. The tests at Ohmsett were conducted to confirm that the small-scale results were valid under the more realistic dispersant application and wave energy conditions possible at this facility.

5.2 Background

Twelve large-scale dispersant effectiveness tests were completed at the Ohmsett facility in late April, 2010 using three of the viscous crude oils studied at small-scale (Gail E010, Irene-Co-mingled, and Ellen A040). For each of the three test oils four tests were completed, two in which dispersant was sprayed onto the oil and two in which dispersant was premixed into the oil. The least viscous of the oils tested in the small-sale testing (Irene-Lompoc) was not tested at the large-scale due to time constraints.

5.3 Test Methods and Equipment

The dispersant effectiveness testing protocol developed since 2000 at Ohmsett was used in the testing with the exception that in half of the tests dispersant was pre-mixed with the oil in the discharge hopper prior to discharge rather than being applied via the spray bar in these pre-mixed tests. Other than this modification the same test procedures were used as those implemented in the 2005 and 2008 heavy oil tests (SL Ross 2006, 2008). 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 2000a, 2000b, 2002a, 2002b, 2003a, 2003b, 2004, 2006).

The oil discharge and dispersant spray systems used in the testing were the same as that used in previous dispersant tests at Ohmsett. Corexit 9500 dispersant was used in all of the tests where dispersant was applied.

The basic test procedure used for all dispersant effectiveness tests is as follows.

1. The oil containment area is established by placing booms across the north and south ends of the Ohmsett tank.
2. The oil and dispersant are loaded into their respective supply tanks on the main bridge deck. (For the pre-mixed tests the dispersant was pre-mixed with the oil in the oil discharge hopper by re-circulating the oil and dispersant mixture using the oil discharge pump).
3. The main bridge is positioned at the southern quarter point within the boomed area. The wave paddle is started and the waves are 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 is moved south at the required speed to achieve proper slick dimensions and dispersant application dosage (1/2 knot or 0.25 m/s for this test series).
6. The oil is pumped at the required rate onto the surface through the discharge manifold mounted on the south side of the bridge (20 gpm (75.7 Lpm) for 1 minute).
7. The dispersant is applied onto the oil slick from the spray bar system mounted on the north side of the bridge in the same pass. (This step was omitted in the tests where the dispersant was pre-mixed with the oil in the oil discharge hopper prior to the oil discharge).
8. The waves are left on for 20 to 30 minutes and the wave paddle is stopped.
9. The water current developed by the water spray from the bridge fire monitors is used to sweep any surface oil remaining on the water surface at the end of the test to a common collection area at one corner of the containment boom.
10. The oil is then removed from the water surface using a double-diaphragm pump and suction wand or a hand ladle and placed in a collection drum or a 20 L pail.
11. The collected oil and water is allowed to stand at least overnight and most of the free water present is drained from the bottom of the collection container.
12. The remaining oil and water are well mixed and a sample is taken for water content and physical property determination.
13. The quantity of remaining liquid is measured and the amount of oil determined by subtracting the amount of water as determined using the water content analysis.
14. 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.
15. Each test was video taped for future visual reference.

5.4 Results

5.4.1 Dispersant Effectiveness Estimates

The test conditions and estimated Dispersant Efficiencies (DE) for all of the large-scale tank tests are summarized in Table 3. A patch of oil from a previous test program at Ohmsett remained within the boomed off area but went unnoticed until the first test in this program was underway. The waves in this first test also did not develop as planned. Because of these two issues a full data set for the first attempted test was not collected. The water temperatures during the test program remained relatively constant at between 59 to 61°F (15 to 16°C). The target dispersant-oil-ratios (DOR) for the tests were 1:10 or 1:20. Two different DOR's were calculated for the spray tests.

The maximum DOR was determined by dividing the average oil thickness (assuming the oil was evenly spread over the width of the slick) by the calculated thickness of the dispersant spray (assuming an even spray across the oil and a constant flow). This DOR assumes that all dispersant applied is contacting the oil and having an effect. All of the oils tested formed streamers of thick oil with significant areas of open water between the streamers such that the actual oil coverage over the full width of the slick ranged from 20 to 60% depending on the oil and the actual oil thickness was considerably higher than the calculated average oil thickness.

The minimum DOR was calculated by dividing the estimate of actual oil thickness (based on oil flow rate, bridge speed during discharge, oil coverage over the slick width and the slick width) by the same dispersant spray thickness. This second DOR estimate uses only the proportion of the dispersant actually landing on the oil. The actual effective DOR will be somewhere between these two extreme estimates.

The raw DE' values in the table were determined using the following formula:

DE'= (volume spilled – volume collected from the surface) / volume spilled * 100.

Due to time constraints control tests (no dispersant applied) were not conducted in this test program. All dispersant effectiveness values reported are thus not corrected for losses that would be experienced in a control test. Control corrected DE values are not needed in this test series because a comparison of results for test couplings, with the only difference being the method of dispersant application, was made in this study to determine if this variable had an effect on the test outcome. A raw DE estimate is as good as a control corrected value for this purpose.

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. The video clips provide a good record of the behavior of the oil in each of the tests completed and it is highly recommended that they be viewed to get a full appreciation of the test program.

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

Oil	Water Temp °C	Air Temp °C	Oil Viscosity (cP @ 15°C)	Oil – Dispersant Mix Viscosity (cP @ 15°C)	DOR (max)	DOR (min)	DE (%)	Links to Video Segments	Disp. Appl. Method	Test #
Irene-Co-mingled	15.5	17.5	46,000	32,570	1:20	1:20	nm	Test 1.mpg	P-mix	1
Irene-Co-mingled	15.2	16.4	46,000	32,240	1:20	1:20	46	Test 2.mpg	P-mix	2
Irene-Co-mingled	15.9	16.4	46,000	na	1:5	1:27	73	Test 3.mpg	Spray	3
Irene-Co-mingled	15.7	15.4	46,000	na	1:16	1:79	52	Test 4.mpg	Spray	4
Irene-Co-mingled	16.0	16.9	46,000	26,030	1:10	1:10	45	Test 5.mpg	P-mix	5
Ellen A040	16.4	19.4	18,495	10,400	1:10	1:10	67	Test 6.mpg	P-mix	6
Ellen A040	16.0	12.6	18,495	na	1:17	1:49	90	Test 7.mpg	Spray	7
Ellen A040	16.0	15.7	18,495	na	1:11	1:32	92	Test 8.mpg	Spray	8
Ellen A040	16.6	18.3	18,495	15,060	1:20	1:20	31	Test 9.mpg	P-Mix	9
Gail E010	17.0	21.1	11,000	na	1:15	1:30	84	Test 10.mpg	Spray	10
Gail E010	16.2	11.2	11,000	10,470	1:20	1:20	38	Test 11.mpg	P-mix	11
Gail E010	16.3	14.8	11,000	7090	1:10	1:10	73	Test 12.mpg	P-mix	12
Gail E010	14.5	15.0	11,000	na	1:10	1:32	88		Spray	A[1]

[1]Data from test 2 of 2009 test program (SL Ross, 2010)
na: not available – the instantaneous oil-dispersant mix viscosity was not measured during the spray tests.
Pre-mixed tests are highlighted in light blue.

The results in Table 3 show that dispersant applied by spraying produced relatively high levels of effectiveness in all three oils tested, including the 46,000-cP oil. A high level of effectiveness for this viscous oil is inconsistent with results of earlier tests in which dispersants produced minimal effectiveness in oils with a viscosity greater than 20,000 cP (Figure 2). However, this particular oil sample also showed a high level of effectiveness (49%) in other testing at Ohmsett that was completed to compare the large-scale Ohmsett results to DE results from small lab-scale DE tests (SL Ross 2010). This unexpectedly high level of effectiveness in this oil might be caused by presence of oil field chemicals containing surfactants. DE results measured in previous test programs at Ohmsett have been plotted in Figure 2 versus the viscosity of the oil during the test. The 2010 data shown in the Figure is the data from this test program.

In the pre-mixed tests where final oil-dispersant mix viscosities were similar the higher dispersant dosage resulted in a higher DE. This comparison can only be made between the Ellen

040 1:10 DOR and the Gail E010 1:20 DOR tests. In these tests the final dispersant-oil mixes had viscosities of 10,400 and 10,470cP, respectively. The higher dose test with the Ellen 040 crude oil had a DE of 67% while the lower dose test DE was only 38%.

Tests with pre-mixed oil and dispersant resulted in lower dispersant effectiveness (DE) than those where the dispersant was applied by spray. The experience gained in over 25 years of dispersant effectiveness testing would have dictated that the opposite result would have prevailed. In addition, these results are inconsistent with those of the preliminary-small scale tests in shown in Section 4.2. One of the primary goals of the study was to determine the oil viscosity where spray application becomes ineffective because the dispersant does not have the opportunity to mix with the oil before getting washed away by wave activity. The loss of effectiveness due to poor dispersant dosing by spray application to heavy oils or the "mixing-one" component to the viscosity effect theory discussed earlier, did not occur for these heavy oils since the spray applications were effective in all cases and actually were more effective than pre-mixed tests with similar dispersant dosages.

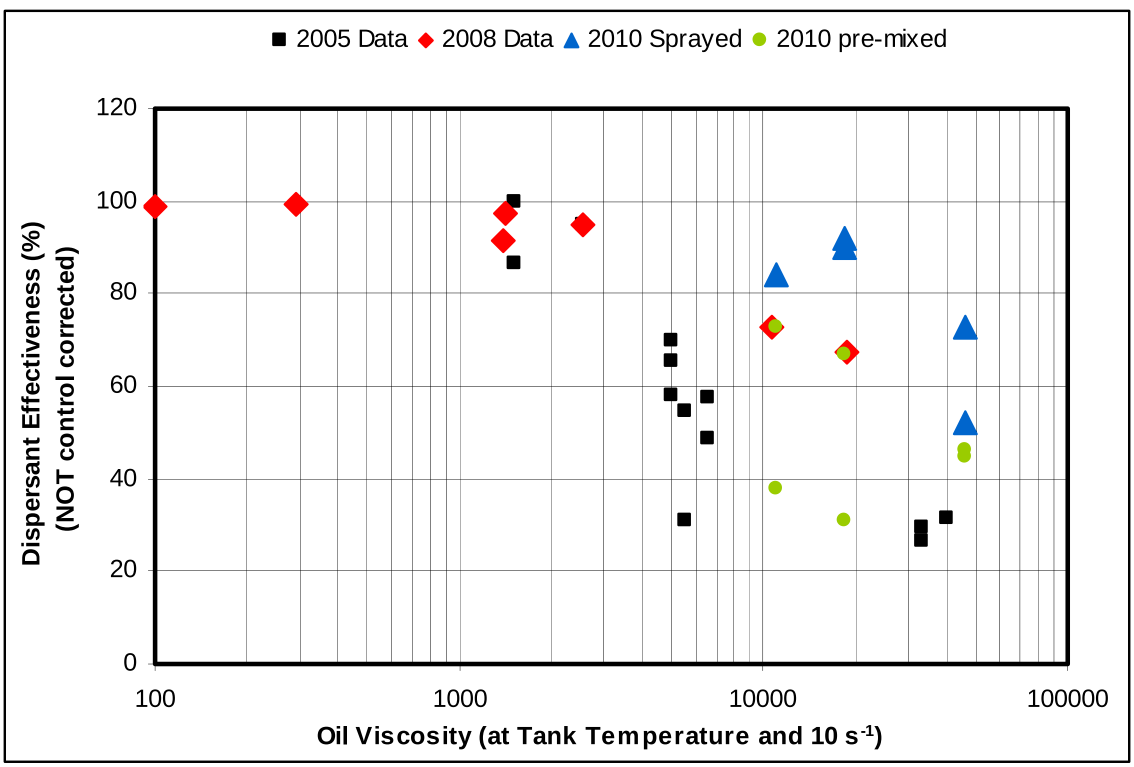

Figure 2. Ohmsett Test Tank Results: Dispersant Effectiveness versus Oil Viscosity

5.4.2 Dispersed Oil Concentrations and Drop Size Distributions

In all tests, up to six passes were made down the length of the test tank with the main bridge after the oil was discharged to measure in-water oil concentrations and drop size distributions as per the dispersant test protocol. A LISST 100 particle size analyzer recorded data on oil drop sizes and in-water oil concentrations and a Cyclops C3 in-situ fluorometer recorded raw fluorescence of the entrained oil. These measurements were made to characterize the form of the oil (drop size distribution) and to confirm the presence of oil in the water column. 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 100 device that sampled both oil concentration and oil drop size every few seconds as the bridge was moved back and forth dragging the device through the water. The high concentration zones in the graphs correspond to the times that the LISST sensor was in the dispersed oil cloud.

In-water oil concentration was also measured using a Turner Cyclops-3 in-situ fluorometer. The raw fluorescence and oil calibrated concentration values acquired by this device are plotted along with the LISST data. The Cyclops-3 identified the same concentration peaks and valleys as the LISST system in the raw trace, but the oil calibrated values were generally smaller than those measured by the LISST. The calibration of these fluorometers using heavy oils is problematic since raw fluorescence of an oil droplet suspension is a function the gross oil concentration, composition of the oil and the droplet size distribution. It is difficult to achieve a dispersed oil sample of known oil concentration and appropriate drop size distribution with which to gather the calibration data. The calibration data collected for each test oil and curves used to relate the raw fluoresense data to oil concentration are provided in Appendix B. The Cyclops system is of interest as it could easily and inexpensively be mounted alongside the LISST sensor and its output could be data logged through the LISST hardware. The Cyclops data would provide confirmation of the presence of oil in field use situations as it detects oil through fluorescence at oil specific wavelengths. The LISST device only measures particle size information and does not distinguish between oil and sediment or other particles. The two devices are thus complimentary.

The oil drop size data collected for each experiment (described above) has been analyzed to determine 1) the average VMD drop size, and 2) the volume percent of the oil present in the form of oil drops less than 70 microns in diameter (see Table 4). The VMD drop size for the pre-mixed oil and dispersant dispersions were consistently and significantly higher than for the dispersant applied by spray runs. The volume of oil present in the water column in the form of drops less than 70 microns in diameter was also much higher in the sprayed dispersant tests (54 to 70 %) when compared to the pre-mixed tests (only 8 to 33%). This result is not what would be expected since the pre-mixed dispersant and oil should have provided the best opportunity for the formation of small drops based on conventional wisdom. The measured drop size data support the final DE estimates for the pre-mixed versus spray-applied dispersant tests reported in Table 3 and 4.

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

Oil	**DOR (max)**	**DOR (min)**	Spray Or Pre-Mix	Links to Oil Drop Size / Concentration Graphs	Test #	Oil Drop Size (Average D50) (microns)	Volume % < 70 microns	Ave. Elevated Oil Conc. by LISST (ppm)	Peak Oil Conc. (ppm)	% Dispersed /Lost
Irene-Co-mingled	1:20	1:20	Pre-Mix	FigureA1	1	187	18	31	149	nm
Irene-Co-mingled	1:20	1:20	Pre-Mix	FigureA2	2	258	8	14	19	46
Irene-Co-mingled	1:5	1:27	Spray	FigureA3	3	57	63	40	477	73
Irene-Co-mingled	1:16	1:79	Spray	FigureA4	4	62	65	22	72	52
Irene-Co-mingled	1:10	1:10	Pre-Mix	FigureA5	5	182	24	17	102	45
Ellen A040	1:10	1:10	Pre-Mix	FigureA6	6	136	30	31	200	67
Ellen A040	1:17	1:49	Spray	FigureA7	7	81	54	53	570	90
Ellen A040	1:11	1:32	Spray	FigureA8	8	52	67	51	362	92
Ellen A040	1:20	1:20	Pre-Mix	FigureA9	9	194	33	28	166	31
Gail E010	1:15	1:30	Spray	FigureA10	10	41	70	73	357	84
Gail E010	1:20	1:20	Pre-Mix	FigureA11	11	191	21	16	99	38
Gail E010	1:10	1:10	Pre-Mix	FigureA12	12	146	23	33	208	73
Gail E010[1]	1:10	1:32	Spray	FigureA13	A[1]	72	55	68	582	88
[1]Data from test 2 of 2010 test program (SL Ross, 2010)										

6. Summary of Results and Recommendations

6.1 Results

The first study goal was to investigate pre-mixed oil-dispersant viscosities and final dispersant dosages to determine limiting viscosities for successful "mixing-two" at different dispersant dosages. In the small-scale tests oils with viscosities greater than about 10,000 cP were not amenable to chemical dispersion at pre-mixed doses of 1:20 and less at the maximum mixing energy level that can be applied in the small wave tank. The dispersant was effective to varying degrees when pre-mixed with the oil at doses of 1:10 and 1:5. At these higher doses the oil-dispersant mix viscosities ranged from 3,720 to 13,740 cP. The success achieved at the high dose for the most viscous oil indicates that the viscosity limit for dispersion is a function of both the amount of dispersant mixed into the oil (the final DOR) and the oil-dispersant mix viscosity. The viscosity of the oil-dispersant mix in this case was 13,780 cP and the measured effectiveness was 80%. All other oil-dispersant mixes with similar viscosities (11,010 to 11,500 cP) but lower DOR's (1:50 or 1:20) resulted in minimal measured dispersion (0 to 9%) indicating that both the amount of dispersant mixed into the oil and the final product viscosity affect the final dispersion. A similar result was achieved in the large-scale pre-mixed tests. In the pre-mixed tests where final oil-dispersant mix viscosities were similar the higher dispersant dosage resulted in a higher DE. In the Ellen 040 1:10 DOR and the Gail E010 1:20 DOR tests at Ohmsett the final dispersant-oil mixes had viscosities of 10,400 and 10,470 cP, respectively. The higher dose test with the Ellen 040 crude oil had a DE of 67% while the lower dose test DE was only 38%. Based on the small- and large-scale test results of this study oil-dispersant mixes with final viscosities of about 10,000cP appear to need a DOR of 1:10 or better to achieve significant dispersion. Both the reduction in viscosity due to the addition of the more fluid dispersant and the presence of more surfactant improve the final DE.

The second study goal was to investigate if there is an initial oil viscosity that prevents successful “mixing one” or the penetration of the dispersant into the oil during spray applications prior to it being washed away by water.

Syringe application of dispersant in the small-scale tests, at the DOR level where success was achieved in the pre-mixed tests, resulted in some effectiveness though less than in the pre-mixed tests in all but one test case. The results show that about 30% to 60% of the dispersant applied to the oil-water interface by syringe was successfully mixing (mixing 1) with all of the oils tested (initial viscosities of between 11,310 and 47,920 cP). Multiple applications (4) of smaller doses to achieve the same final high dosage resulted in a poorer overall effectiveness in all oils than was achieved when one full dose was applied by syringe at the start of the test.

In large-scale Ohmsett tests, dispersant applied by spraying produced high levels of effectiveness in all three oils and tests with pre-mixed oil and dispersant (at similar DORs) resulted in lower dispersant effectiveness (DE) than those where the dispersant was applied by spray. Twenty-five years of experience in dispersant effectiveness testing and the small-scale test results from this study would have predicted that the opposite result should have prevailed. Evidence that the data collected was valid includes 1) both pre-mixed and spray–applied tests were successfully replicated in the test program, 2) visual observations matched the measured test DE and 3) the in-water LISST and C3 fluorometry results were consistent with the DE measurements. Because the spray applications were at least somewhat effective in all cases and were more effective than pre-mixed tests with similar dispersant dosages the “mixing-one” limitation on dispersant effectiveness was not evident for the oils and conditions used in the large-scale Ohmsett tests.

6.2 Recommendations

In this study the pre-mixed tests showed that both the viscosity of the oil-dispersant mix and the DOR influence the “mixing-two” process and determine DE. Additional work is needed to isolate the contributions of the two variables in determining DE.

The results of large-scale test at Ohmsett did not confirm that effectiveness is controlled by the simple effect of oil viscosity preventing the penetration of the dispersant into the oil where it could do its work (mixing-one). This was an unexpected outcome based on 25 years of DE testing and the small-scale results in this project. One possible explanation for this might be the difficulty in estimating the actual DOR in the large-scale spray tests and the possibility that higher doses were reaching the oil than were estimated. The discharged oil spread quickly to forming a uniform slick covering all of the area sprayed with dispersant. Rather the discharged oil forms patchy streamers of oil that cover only 25 to 50% of the area sprayed. In the current test program the dispersant was sprayed using a fixed boom that sprayed dispersant evenly over a slightly wider area than that occupied by the oil. The range of DOR values for each test were estimated based on estimates of oil coverage and average dispersant spray coverage. There also was no attempt to measure the final oil-dispersant viscosity in the current test program or the amount of dispersant that actually was in the oil due to the logistical and technical difficulty of doing so. This could be attempted in additional testing to provide more insight into the “spray versus pre-mixed results”. Those involved in the BP Horizon spill response have refined techniques for the measurement of dispersant quantities present in oil. These new techniques could be applied in future testing to quantify the amount of dispersant getting into the oil in the spray application. Additional insights might also be gained by working with one oil (a heavy fuel oil) that is adjusted to produce oil samples of varying viscosity by blending with marine gasoil, rather than working with a range of crude oils from different sources where the oil type itself might cause variation in effectiveness.

7. References

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Appendix A. Oil Drop Size Distributions

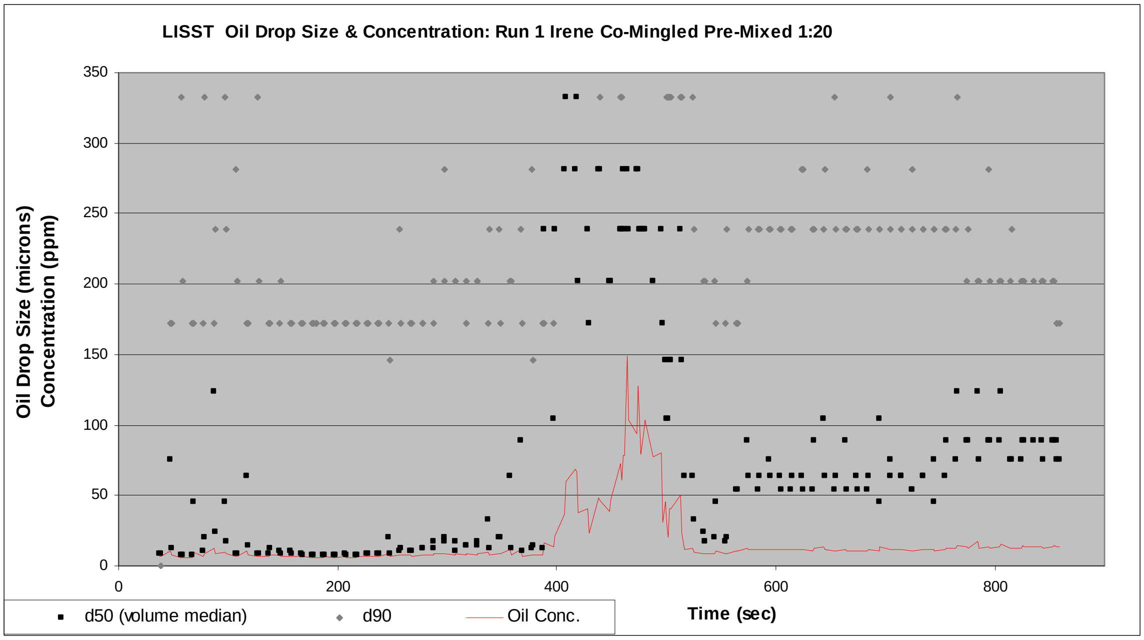

Figure A.1 - Run 1: Irene-Co-mingled Pre-Mixed 1:20

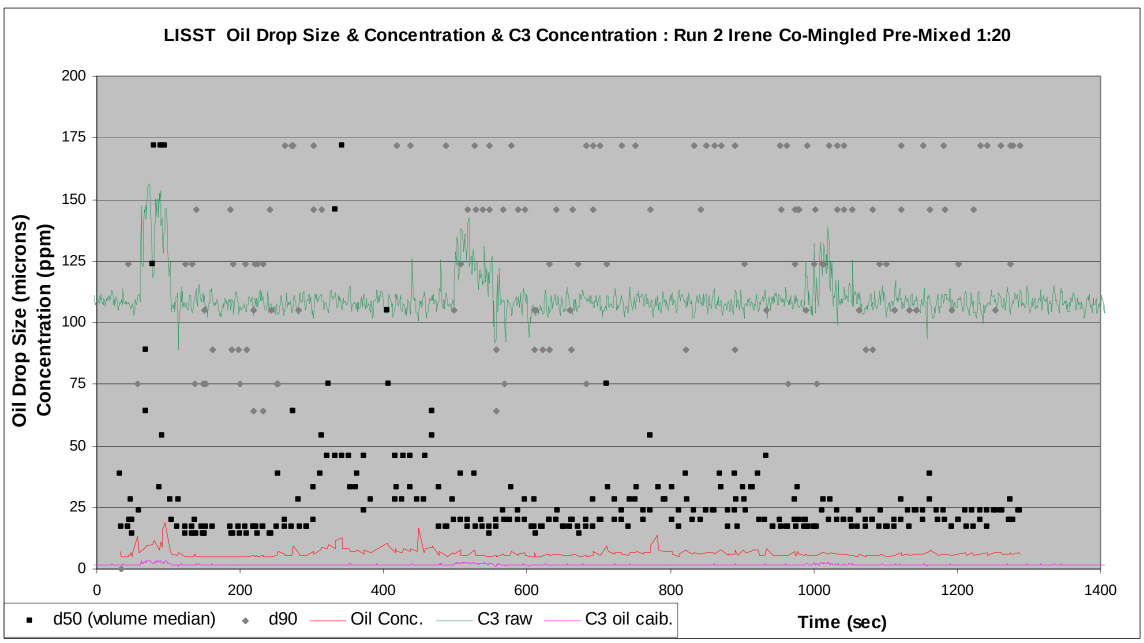

Figure A.2 - Run 2: Irene-Co-mingled Pre-Mixed 1:20 (re-do)

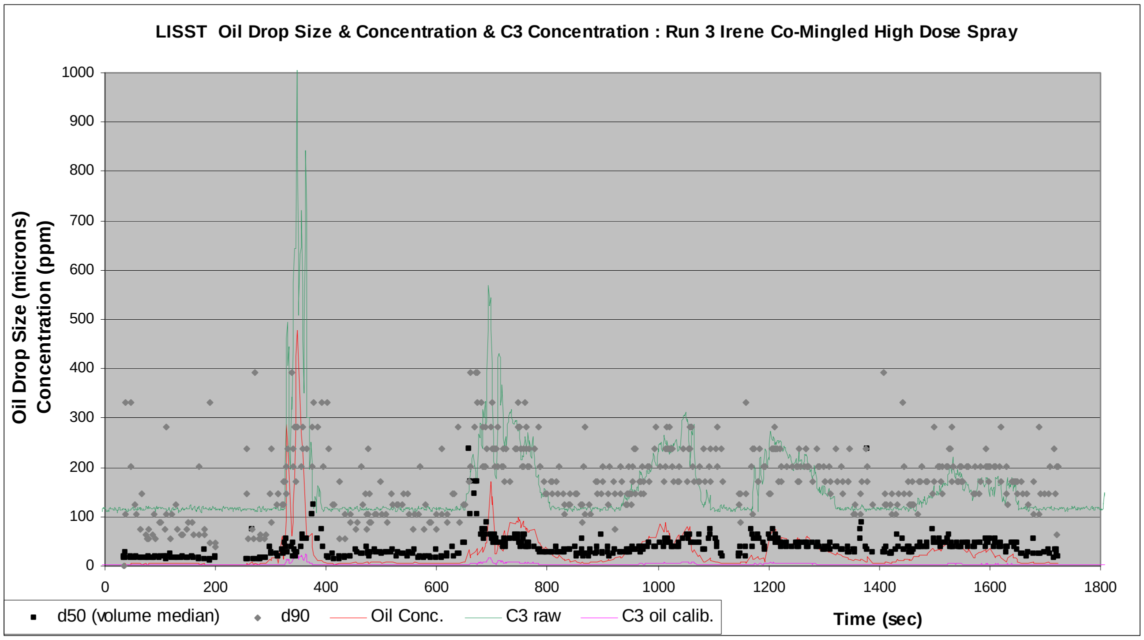

Figure A.3 - Run 3: Irene-Co-mingled High Dose Spray

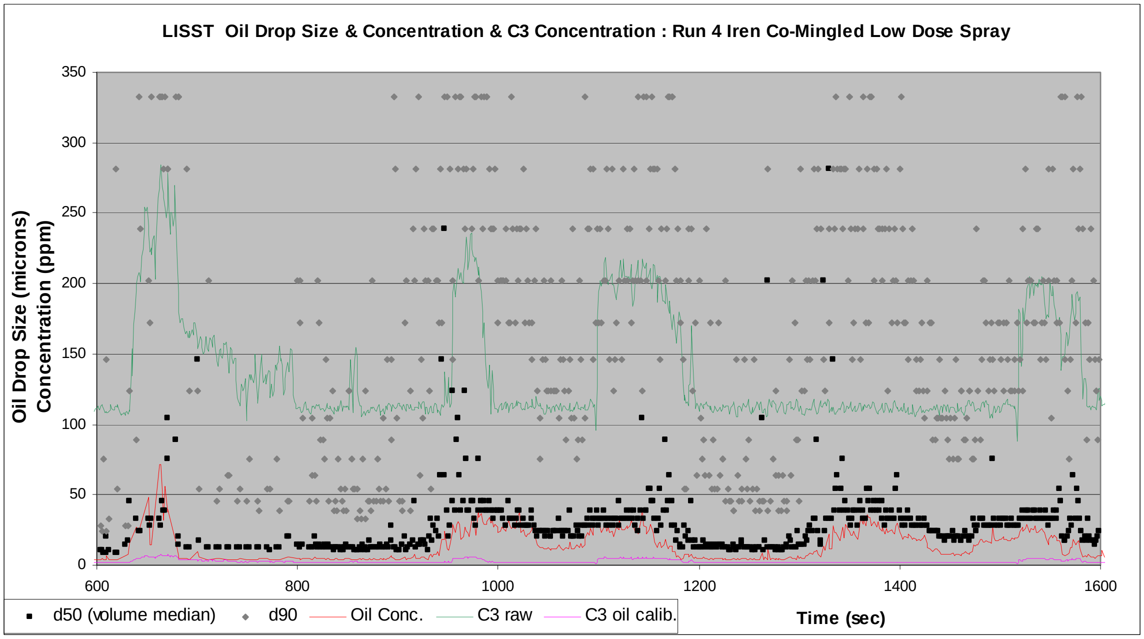

Figure A.4 - Run 4: Irene-Co-mingled Low Dose Spray

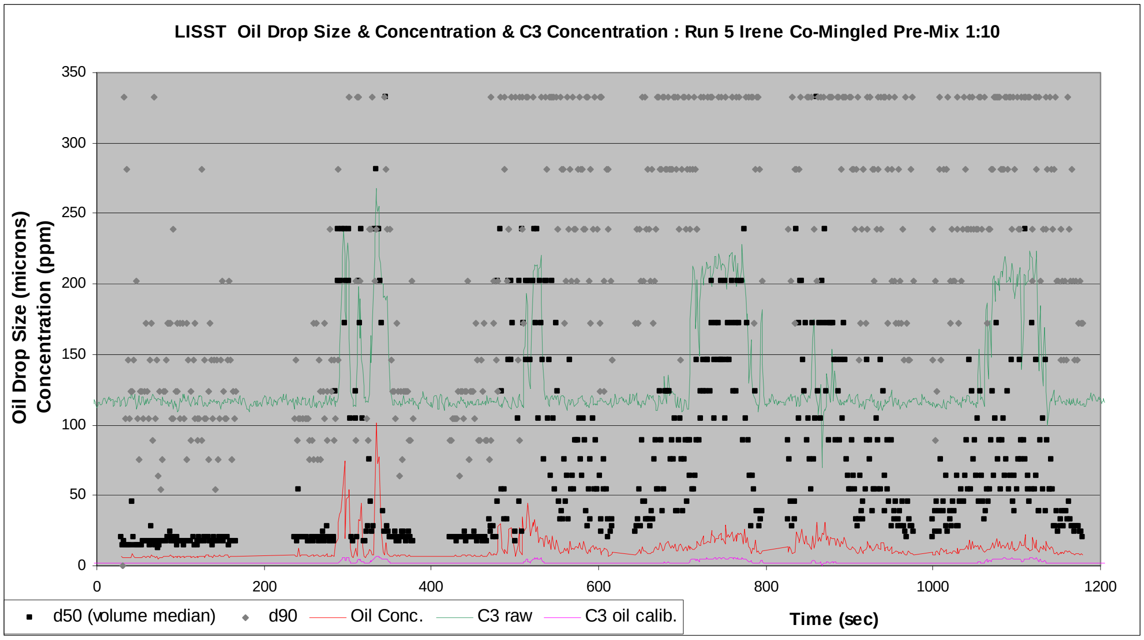

Figure A.5 - Run 5: Irene-Co-mingled Pre-Mix 1:10

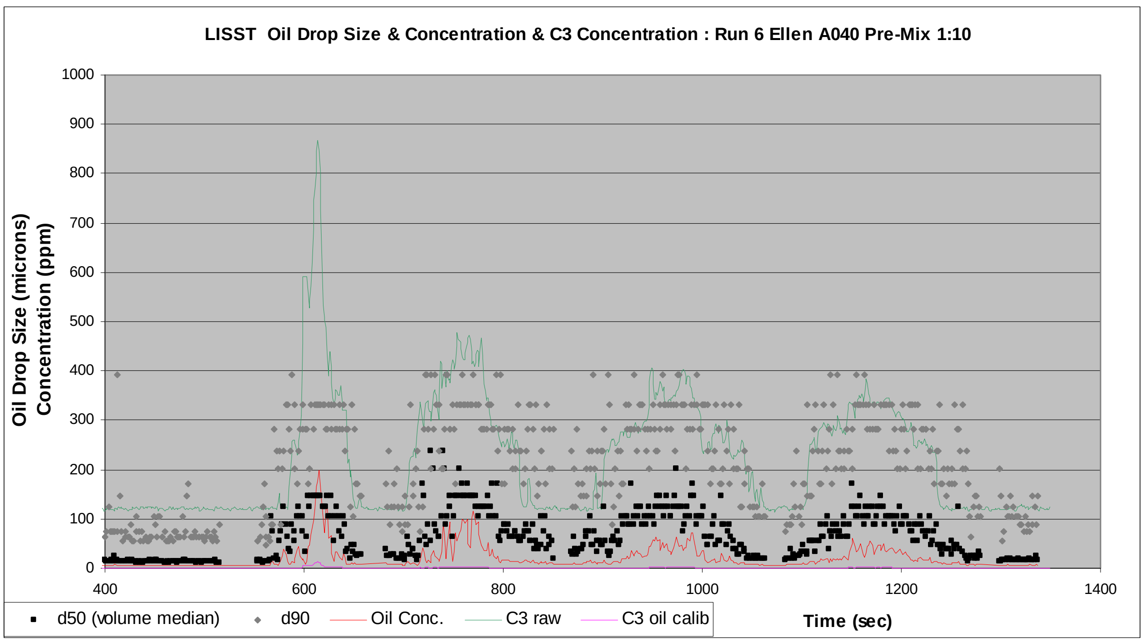

Figure A.6 - Run 6: Ellen A040 Pre-Mix 1:10

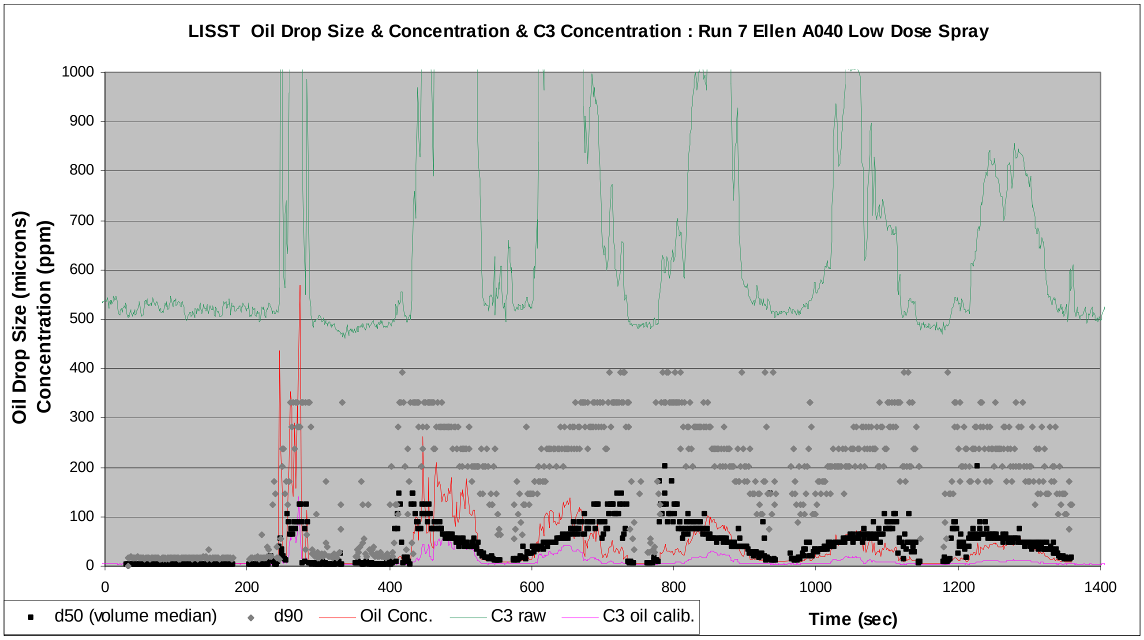

Figure A.7 - Run 7 Ellen A040 Low Dose Spray

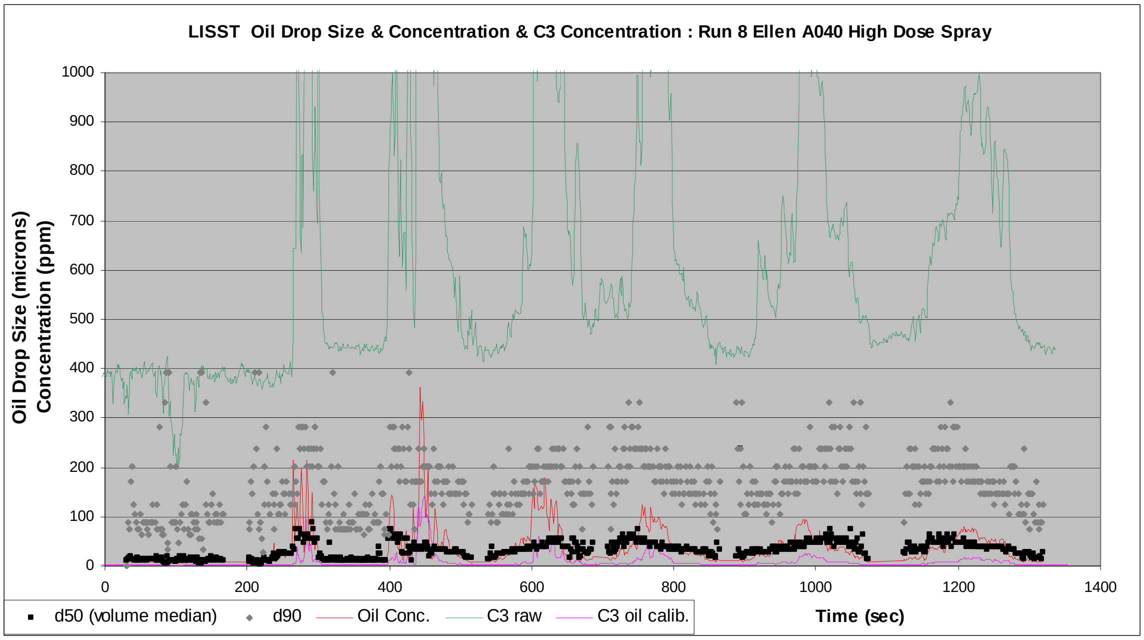

Figure A.8 - Run 8 Ellen A040 High Dose Spray

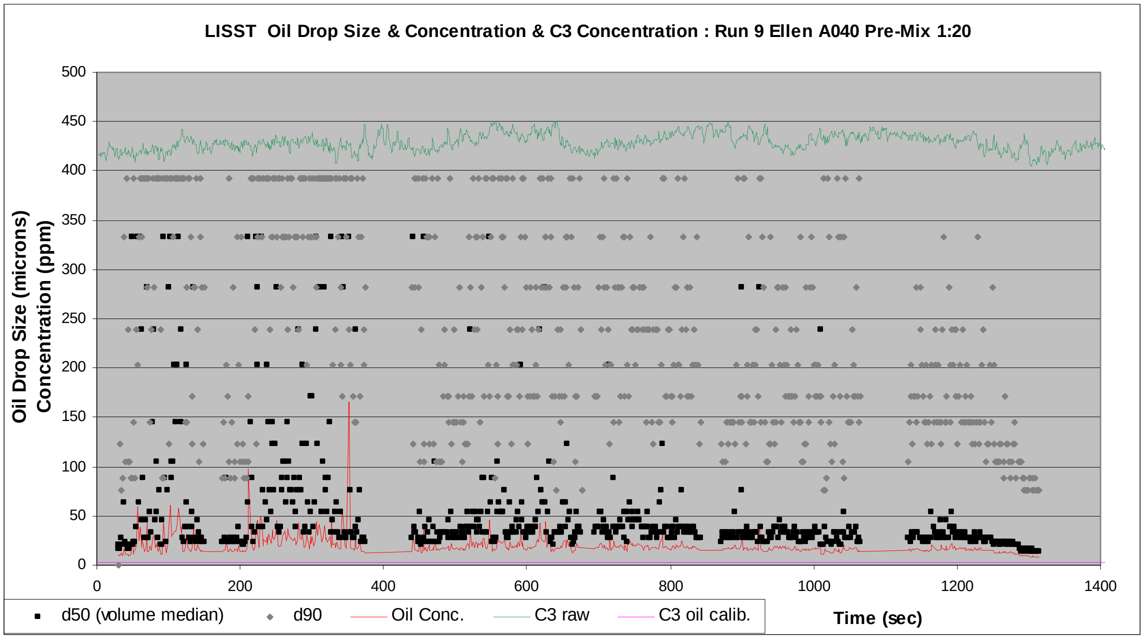

Figure A.9 - Run 9 Ellen A040 Pre-Mix 1:20

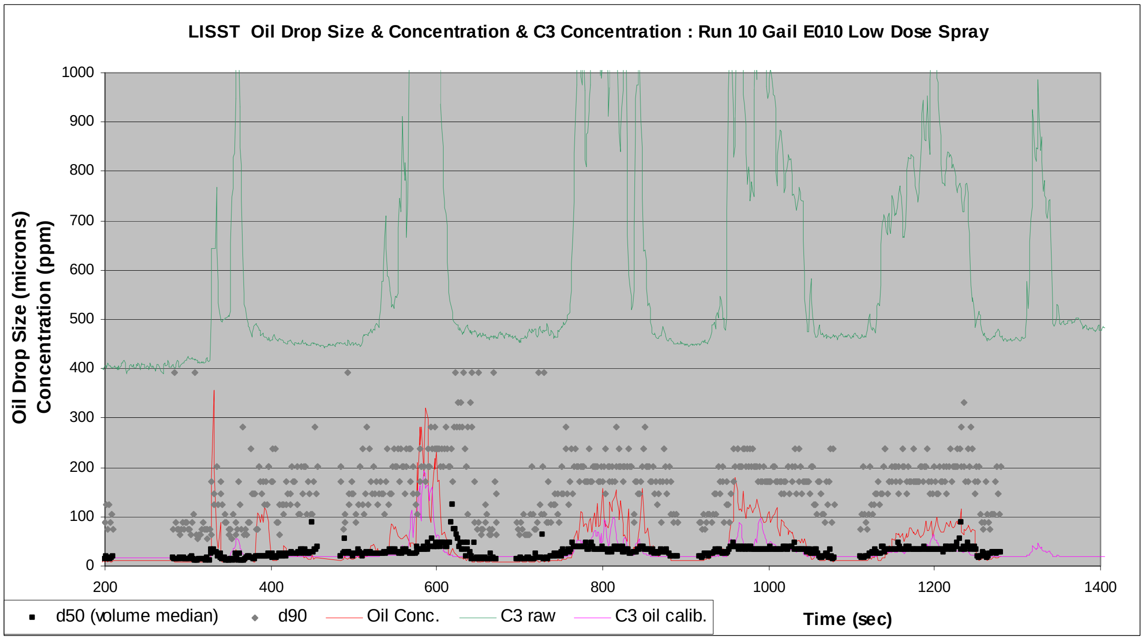

Figure A.10 - Run 10 Gail E010 Low Dose Spray

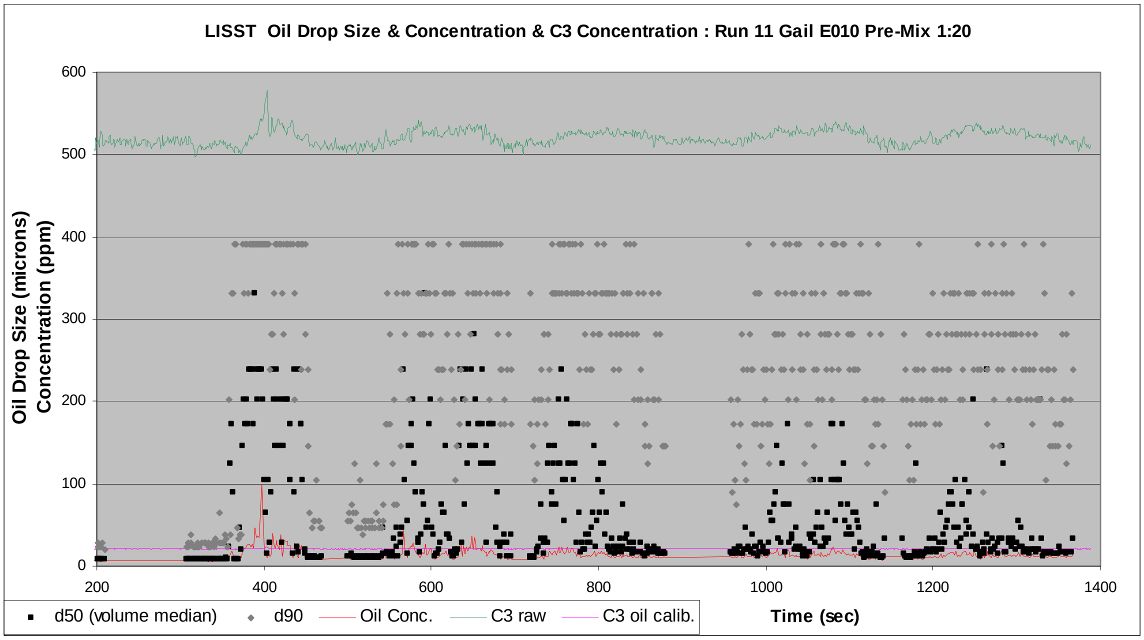

Figure A.11 - Run 11 Gail E010 Pre-Mix 1:20

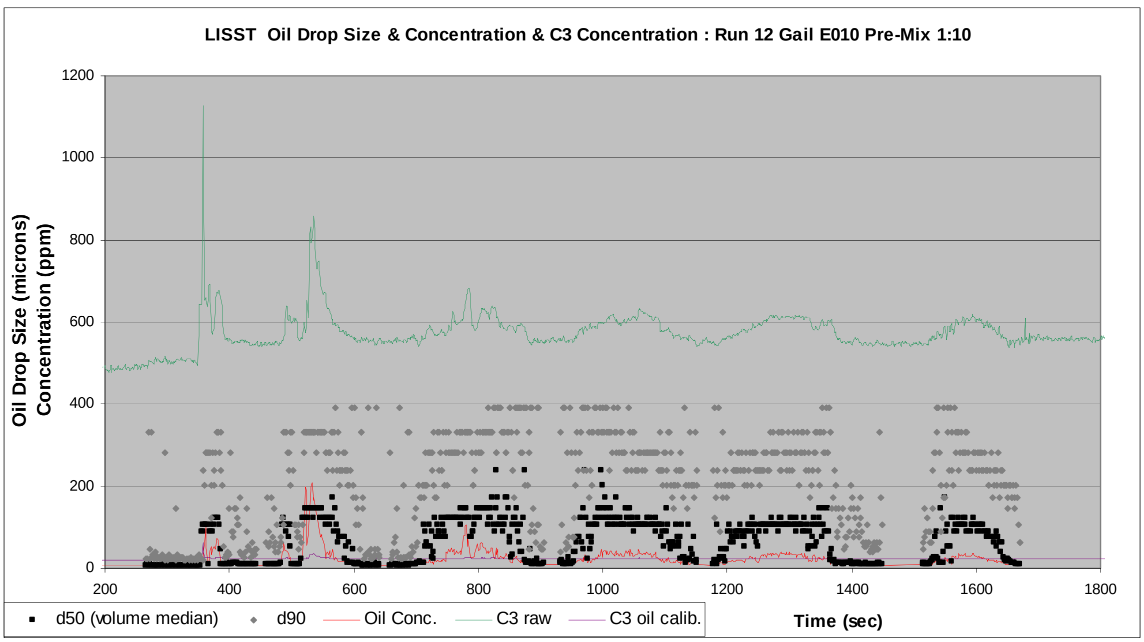

Figure A.12 - Run 12 Gail E010 Pre-Mix 1:10

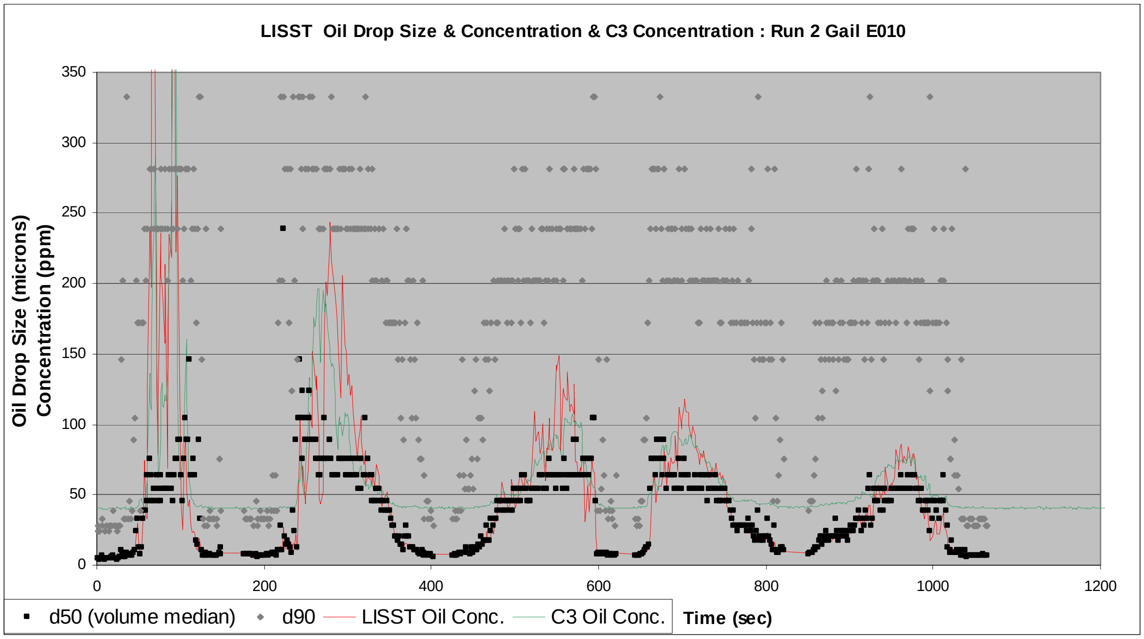

Figure A.13 - Run 2 from SL Ross 2010 Gail E010 Spray

Appendix B: Cyclops C3 Calibration Curves for Test Crude Oils

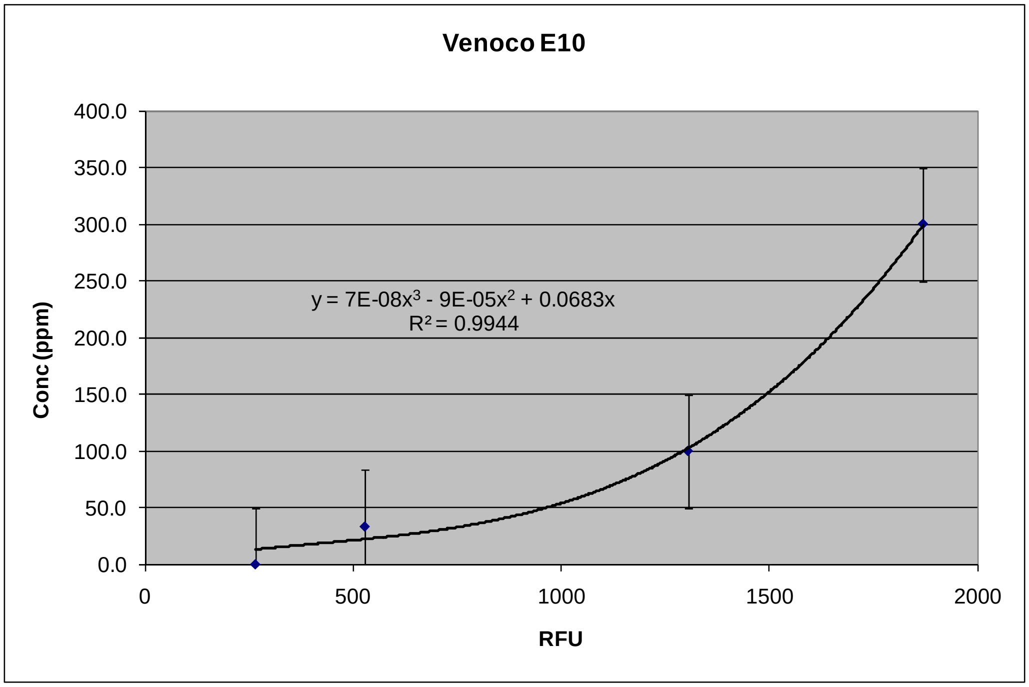

Figure B2. C3 Calibration for Gail E010 Crude

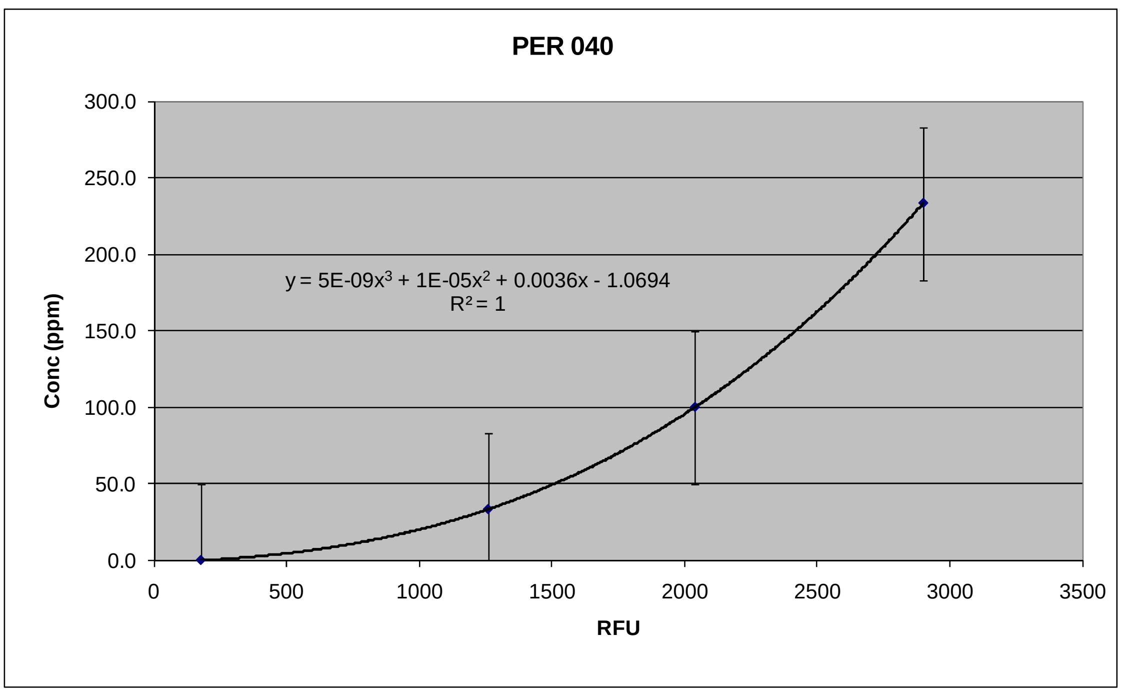

Figure B4. C3 Calibration for Ellen A040 Crude Oil

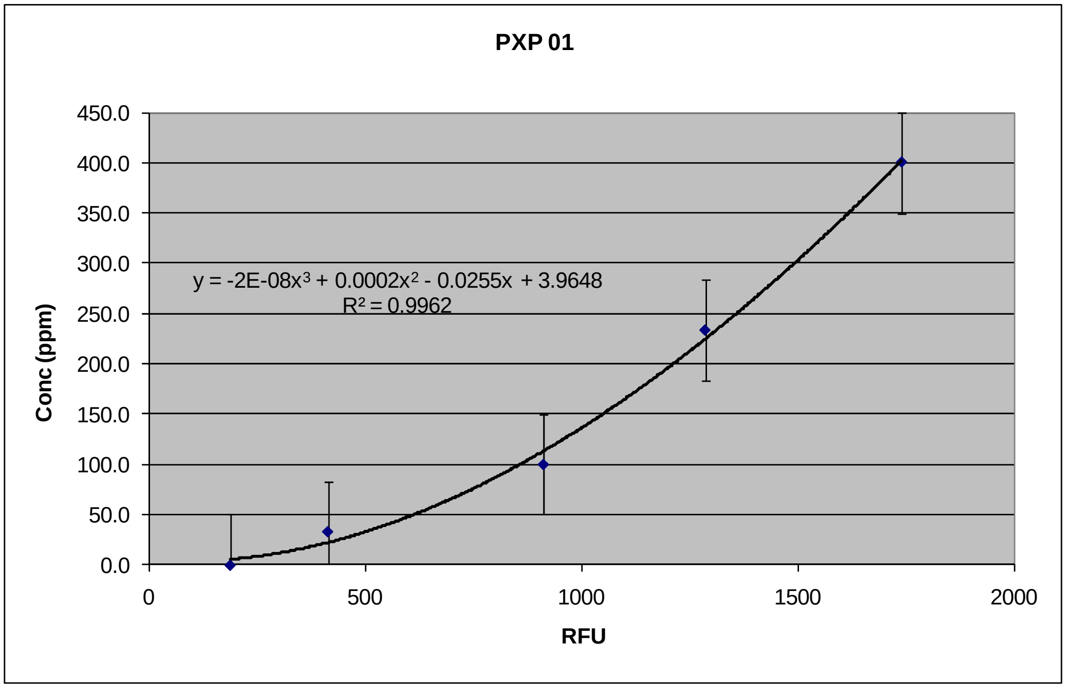

Figure B7. C3 Calibration for Irene-Lompoc Crude Oil

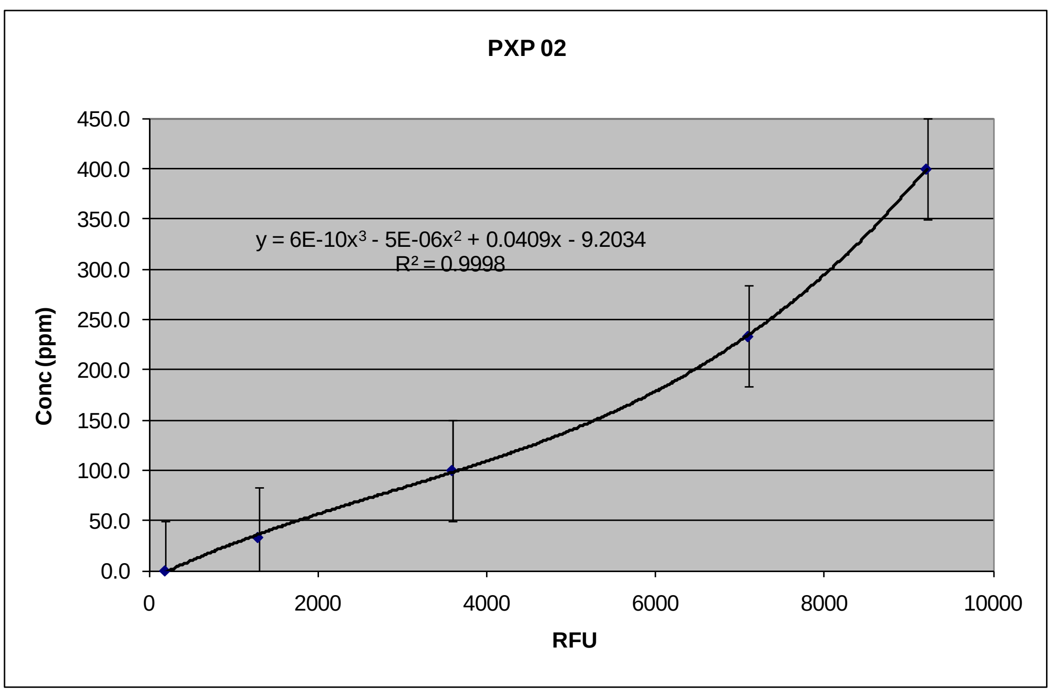

Figure B8. C3 Calibration for Irene-Co-mingled Crude Oil