

FINAL REPORT

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

For

**U.S. Department of the Interior
Minerals Management Service
Herndon, VA**

By

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And

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Disclaimer

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Executive Summary

The objective of the work was to continue to investigate the viscosity limit for the effectiveness of chemical dispersants applied to viscous US Outer Continental Shelf (US OCS) crude oils. Large-scale tests were completed in June 2008 at Ohmsett, the National Oil Spill Response Test Facility in Leonardo New Jersey to supplement results from similar tests conducted in April of 2005.

There is a need to improve our understanding of the dispersibility of heavy, viscous crude oils under at-sea conditions. It is generally thought that oils with viscosities less than 2000 cP are dispersible and that oils with viscosities higher than 20000 cP are not. There is considerable debate and uncertainty regarding the dispersibility of oils with viscosities between 2000 and 20000 cP.

Testing in April of 2005 at Ohmsett on viscous crude oils provided valuable insight into the dispersibility of heavy, viscous crude oils and possibly extended the range of oils that would be considered candidates for dispersant application. The 2005 tests did not include oils with viscosities between 6,500 and 30,000 cP and the primary focus in the current test program was to test dispersant effectiveness on oils in this viscosity range.

California oils with API gravities between 9 and 14 were identified as candidate oils for testing and 2 drums each of six different oils were shipped to Ohmsett for testing. The names of the oils used, in order of increasing viscosity, were: Henry, Edith, Gina H14, Heritage, Eureka, and Gina H7. Unfortunately only one of the six oils, Gina H7, had a viscosity in the range of interest.

Thirteen large-scale dispersant effectiveness tests were completed at the Ohmsett facility in June 2008 using the six OCS crude oils identified above and the Heritage crude oil acquired and tested in 2005. The physical oil properties for the oils tested are shown in [Table 2](#).

The effectiveness of the dispersant was influenced by oil viscosity as seen in [Figure 1](#). The oils with viscosities less than 3000 cp were almost completely dispersed when dispersant was applied

at about a 1:20 ratio (80 to 99% raw DE and 70 to 85% control adjusted DE). Both the 10,610 cP oil and the 18,690 cP oil were about 50% dispersed (after adjusting for control test losses).

Oils with similar viscosities yielded similar dispersant effectiveness results in both the 2005 and 2008 test programs suggesting that viscosity alone was a good measure of likely dispersant effectiveness, at least for the oils used and in the tests completed to date.

The oil drop sizes in the control tests were consistently larger than those generated in the dispersant applied tests demonstrating that the chemical dispersant had a dramatic effect on the oil drop formation process (see [Figure 3](#)). The volume median diameters (VMDs) of the oil drop distributions in the dispersant applied tests were consistently smaller than 100 microns, the value below which oil has been shown to be permanently dispersed in offshore situations.

Short video segments of each test have been provided through hypertext links provided in [Table 3](#).

The purchase of a Turner Cyclops submersible crude oil sensor is recommended for use in conjunction with the LISST particle size analyzer in future DE testing at Ohmsett.

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

1. Objective

The objective of the work was to continue to investigate the viscosity limit for the effectiveness of chemical dispersants applied to viscous US Outer Continental Shelf (US OCS) crude oils.

2. Background

Testing in April of 2005 at Ohmsett ([SL Ross 2006](#)) on viscous crude oils provided valuable insight into the dispersibility of heavy, viscous crude oils and possibly extended the range of oils that would be considered candidates for dispersant application. The 2005 tests did not include oils with viscosities between 6,500 and 30,000 cP and the primary focus in the current test program was to test dispersant effectiveness on oils in this viscosity range.

3. Oil Acquisition and Analysis

3.1 Identification of Appropriate Oils

Considerable effort was expended in the process of finding crude oils suitable for the test program, as was the case in for the 2005 test program. The primary criteria for oil selection for the 2008 test program included:

- 1) oils from US OCS waters;
- 2) oils with viscosities between 6,500 and 30,000 cP at test tank temperature;
- 3) oils free of production chemicals; and,
- 4) oils that could be acquired in sufficient quantities and in time for the large scale test program.

Only oils from the California OCS area were considered due to the difficulty in identifying heavy oils from other regions in the 2005 project. The relationship between API gravity and oil viscosity provided in [Appendix A](#) was used to identify potential oils because oil viscosities are

generally not reported for currently produced oils. [Table 1](#) identifies a number of oils considered for the project and the ones ultimately selected for testing.

Table 1. Oils Considered and Selected for Testing

Platform	Operator	Contact	Well #	Published API Gravity	Expected Viscosity ¹ (cP)	Measured Viscosity (at 26 °C)
						18,690
	Pacific Energy	S. Liles	na	12-14		2565
	ExxonMobil	B. Hansen	na	13.2		1407
						67
	DCOR	S. Robertson	B-20	14		290
	DCOR	S. Robertson	B-6ST	14		290
						290
						1393
Henry	DCOR	S. Robertson	17-B	16.2	remaining	
Henry	DCOR	S. Robertson	23-B	17.2	oils	
Henry	DCOR	S. Robertson	01-B	17.3	considered	
B	DCOR	S. Robertson	B-34	18.2	too light	
Gilda	DCOR	S. Robertson	S-62	18.3	for project	
Gilda	DCOR	S. Robertson	S-61	18.4		
Gilda	DCOR	S. Robertson	S-28	18.7		
C	DCOR	S. Robertson	C-16	18.9		
Henry	DCOR	S. Robertson	09-B	19.1		
B	DCOR	S. Robertson	B-35	19.3		
B	DCOR	S. Robertson	B-53	19.5		
note: highlighted oils were acquired and shipped to Ohmsett for testing						
¹ Based on graph presented in Appendix A						

Six oils were identified as good candidates for testing based on their reported API gravities and a correlation between API gravity and oil viscosity. The oils selected are highlighted in [Table 1](#). Two barrels each of these oils were acquired and shipped to Ohmsett for the project with the exception of the Edith oils where one barrel of each was provided and subsequently blended to provide a single test oil.

4. Large-Scale Tank Testing at Ohmsett

4.1 Background

Thirteen large-scale dispersant effectiveness tests were completed at the Ohmsett facility in June, 2008 using six viscous OCS crude oils. Sufficient time was not available to collect small samples

for property analysis prior to ordering the larger oil quantities required for the test program. From previous experience the properties of small oil samples does not always match those of large samples of the same oil. The viscosities of the received oils were measured to determine if they met the requirements of the test program (viscosity between 6,500 and 30,000 cP) and they are reported in [Table 2](#). Unfortunately only one of the shipped oils, Gina H7, had a viscosity (18,690 cP at 26.7° C) in the range of primary interest to this study. A small quantity of the Heritage oil used in the 2005 test program was still available for testing and its viscosity at the tank water temperature of 26.7° C was 10,610 cp, a value in the range of interest, so this oil was included in the test matrix.

Table 2. Physical Properties of Oils

					Water Content (% by Volume)
Henry	13.5	67	0.912	38.6	8
Edith	14	290	0.936	19.7	9
Gina H14	15.3	1393	0.964	15.7	2
Heritage (2008)	13.2	1408	0.951	17.3	5.5
Eureka	12-14	2565	0.963	15.4	15
Heritage (2005)	-	10,610	0.967	14.8	2.8
Gina H7	9	18,690	1.003	9.57	51

4.2 Test Methods and Equipment

The dispersant effectiveness testing protocol developed since 2000 at Ohmsett was used in the testing. The same test procedures were used as those implemented in the 2005 heavy oil tests ([SL Ross 2006](#)). 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 system includes:

1. a progressing cavity pump,
2. a pump speed control system,
3. a gravity fed oil hopper supply,
4. three-inch oil supply lines, and;
5. a stainless steel oil discharge manifold.

Oil is pumped into the hopper from drums or other supply tanks using the progressing cavity pump in reverse. The flow rate for this pump is precisely controlled by altering its rpm using the digital control module. The pump generates 0.19 gallons per minute per revolution of the pump. The quantity of oil discharged from the hopper is measured using a sonic probe mounted above the oil supply.

The dispersant spray system used in the testing was 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.
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.
8. The waves are left on for 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.

4.3 Results

The test conditions and estimated Dispersant Efficiencies (DE) for all of the large-scale tank tests are summarized in [Table 3](#). Problems were encountered in the oil discharge during test #3 and no data were collected or reported for this test. The water temperatures during the test program remained constant at 80°F (26.7°C). The target dispersant-oil-ratio (DOR) for all tests was 1:20. The target dosage was achieved within reason with the exception of tests #6 and #11 which were over-dosed and under-dosed, respectively. The DOR within the range tested (1:8 to 1:39) did not appear to have a significant affect on test outcomes. The raw DE' values in the table were determined using the following formula: $DE' = (\text{volume spilled} - \text{volume collected from the surface}) / \text{volume spilled} * 100$. The control test DE' values also were adjusted to account for the evaporative losses measured over the test duration.

The DE value in [Table 3](#) is the DE' value minus the amount of oil unaccounted for by collection or evaporation determination in the control run (no dispersant) for that oil. This value is only valid for the dispersant applied tests. The “control corrected” DE values have been used in [Figure 1](#) to show the variation in dispersant effectiveness with viscosity for the six oils tested. The results from this test series (2008) have been plotted along with the results from the 2005 testing.

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

									Test #
Henry	26.7	67	70.8	1.0	0	22.8		TO421T4	4
Henry	26.7	67	75.7	3.3	12	99.1	76.3	TO421T13	13
Edith	26.7	290	84.9	2.9	0	16.6		TO421T2	2
Edith	26.7	290	72.4	5.1	39	99.2	82.6	TO421T11	11
Gina H14	26.7	1393	75.1	2.3	0	22.7		TO421T1	1
Gina H14	26.7	1393	75.3	2.4	17	91.3	68.6	TO421T7	7
New Heritage	26.7	1408	72.4	4.1	18	97.4	67.4	TO421T12	12
Eureka	26.7	2565	66.5	1.8	0	23.9		TO421T5	5
Eureka	26.7	2565	60.1	2.1	8	95.0	71.1	TO421T6	6
Old Heritage	26.7	10610	73.3	10.4	18	72.9	46.9	TO421T10	10
Gina H7	26.7	18690	36.3	5.1	0	13.9		TO421T8	8
Gina H7	26.7	18690	39.7	6.3	10	67.6	53.7	TO421T9	9

Note: DE' is the dispersant effectiveness estimate prior to accounting for oil lost in the control run.

In general the oils with viscosities lower than 3000 cP were dispersible to a significant degree (90 to 99% raw DE' or 70 to 80% DE after control adjustment) whereas the DE dropped off to 47% and 54% for the two oils with viscosities of 10,610 and 18,690 cP, respectively. The general DE versus viscosity trend identified in the 2005 testing was supported by the 2008 data that provided two data points in the 6500 to 30,000 cP data gap from the 2005 testing.

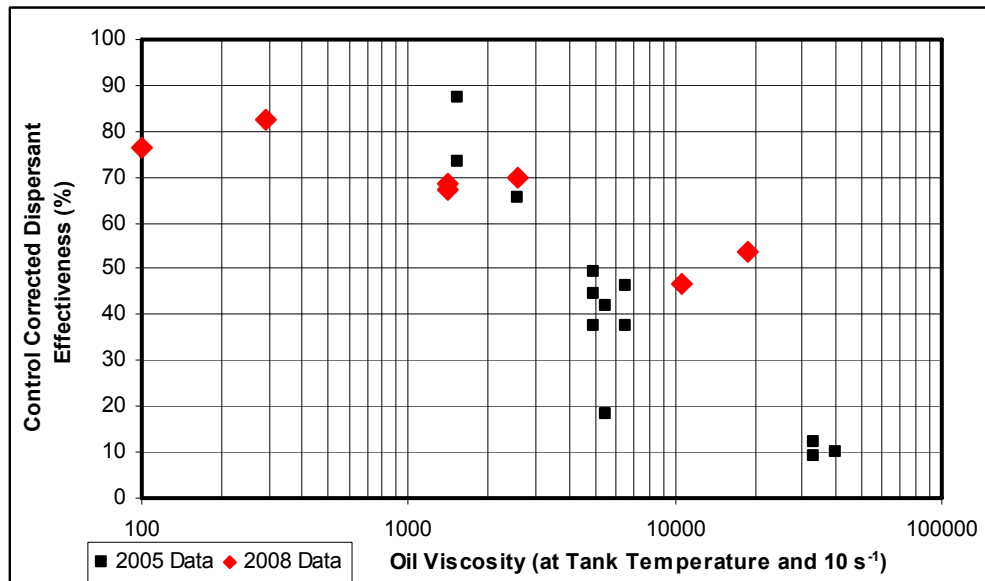


Figure 1. Ohmsett Test Tank Results: Dispersant Effectiveness versus Oil Viscosity

4.3.1 Change in Oil Properties

The oil remaining in the containment boom at the end of the tests was collected for volume, water content and density determination. [Table 4](#) summarizes the density and water content data. Most of the collected oils show an increase in density indicating that some oil was lost to evaporation. The largest evaporative loss was seen in Edith, one of the lightest oils tested. The amount of oil lost due to evaporation was determined by comparing the collected oil density (after de-watering) to the Density versus Volume evaporated relationships presented in Appendix A as [Figure A.2](#). The curves in [Figure A.2](#) were developed by evaporating samples of the crude oils in trays and weighing the trays after exposure to wind for a number of days in a protected outdoor area. The evaporative losses ranged from 21% for the lighter oil to 0% for the heavier oils tested. The evaporation estimates are valid for the control runs where a significant quantity of oil remained on the surface over the 30-minute test duration. The evaporation estimates are less valid for the dispersant applied cases where most of the oil dispersed in the early stages of the test and only the small amount of oil remaining at the end of the test actually experienced the evaporative process.

The water contents of the post-test oils in most tests were in the 20 to 25% range, a relatively small increase over the 2 to 15% water content of the spilled oil. The water uptake through emulsification was accounted for in estimating the final quantity of oil recovered at the end of each test.

Table 4. Oil Properties at End of Ohmsett Tank Tests

					ater Content (% by volume)	
						Oil After Test
Henry	4	0.912	0.915	1	8	30
Henry	13	0.912	0.912	0	8	20
Edith	2	0.936	0.964	13	9	24
Edith	11	0.936	0.982	21	9	22
Gina H14	1	0.964	0.969	4	2	8.5
Gina H14	7	0.964	0.975	11	2	22
New Heritage	12	0.951	0.952	0	5.5	20
Eureka	5	0.966	0.976	6	15	3
Eureka	6	0.966	0.980	8	15	12
Old Heritage	10	0.967	0.991	10	2.8	26
Gina H7	8	1.003	0.975	0	51	24
Gina H7	9	1.003	0.978	0	51	26

4.3.2 Dispersed Oil Concentrations and Drop Size Distributions

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. A LISST 100 particle size analyzer recorded data on oil drop sizes and 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 5](#).

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 correspond to the times that the LISST sensor was in the dispersed oil cloud. In the control experiments, elevated oil concentrations (9 to 37 ppm peak concentrations) were recorded under the slick, but the oil drop sizes in the zones of high oil concentrations were large (volume median diameters (VMDs) or d_{50} 's of 100 to 239 microns). In the dispersant applied cases, the oil drop size distributions were small (d_{50} 's 8 to 73 microns) in the high oil concentration zones (173 to 527 ppm peak concentrations). Elevated oil concentrations were measured in both the control and dispersant applied tests, but much smaller oil drop sizes were detected in the dispersant applied case. 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 drop-size results from the control runs suggest that much of the naturally dispersed oil will not likely be permanently dispersed. The small oil drops recorded in the dispersant applied tests suggest that the dispersant was effective in generating dispersed oil in small enough drops to be permanently dispersed. 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 was also measured using a Turner 10AU fluorometer (deployed by the US Coast Guard Sector Delaware Bay) and a Turner Cyclops-7 submersible sensor (deployed by Brian

Parscal of Clean Islands Council) for tests 6 and 7. The raw fluorescence values acquired by these two devices are plotted along with the LISST data in [Figures B.6](#) and [B.7](#). The two devices identified the same concentration peaks and valleys as the LISST system. Calibration of the devices would be necessary to allow them to identify actual oil concentrations. 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.

Table 5. In-Water Oil Characterization and Graph Hypertext Links

								% Dispersed /Lost
Gina H14	0	FigureB1	1	148	28	3	17	23
Edith	0	FigureB2	2	191	10	3	19	17
Henry	0	FigureB3	3	100	26	2	9	na
Henry	0	FigureB4	4	143	21	5	21	23
Eureka	0	FigureB5	5	120	50	4	37	24
Eureka	10	FigureB6	6	29	80	36	207	71
Gina H14	17	FigureB7	7	37	74	47	207	69
Gina H7	0	FigureB8	8	239	19	11	11	14
Gina H7	10	FigureB9	9	73	60	67	224	54
Old Heritage	18	FigureB10	10	60	64	56	527	47
Edith	43	FigureB11	11	22	86	61	212	83
New Heritage	19	FigureB12	12	21	83	68	215	67
Henry	14	FigureB13	13	8	95	69	173	76

4.3.2.1 Oil Drop Size Analysis and Adjusted DE Estimates

The oil drop size data collected for each experiment (described above) has been analysed 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 5](#)). The VMD drop size for the control test dispersions were consistently and significantly higher than for the dispersant applied 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 dispersant tests (60 to 95 %) when compared to the controls (10 to 50%). This would be expected since the role of surfactants in chemical dispersants is to reduce the oil/water interfacial tension and promote the formation of smaller

droplets of oil under a given mixing energy. As previously discussed, oil in drops 70 microns in diameter or less were permanently dispersed in offshore dispersant tests ([Lunel 1993](#), [Neff 1990](#)). These measurements indicate that a high percentage of the dispersed oil in the chemically treated tests in both of these programs would likely remain dispersed in an ocean setting.

The “volume percent less than 70 micron” values computed for each dispersant applied test and reported in [Table 5](#) have been multiplied by the DE’ (non control corrected) values shown in [Table 3](#) as a method to account for the possible resurfacing of large oil drops over time and to estimate a conservative DE value. It should be noted that this adjusted DE may be an underestimate of effectiveness because the oil present in the larger drops held in the water during wave activity may have re-surfaced shortly after the waves were stopped and prior to oil collection and were thus already accounted for in the DE estimates.

The primary physical oil property that affects dispersant performance is oil viscosity. The drop-size adjusted DE values were plotted against initial oil viscosity ([Figure 2](#)) to determine if there was any correlation between viscosity and DE. There was no significant variation identified in the control tests with all DE values below 15% but there was a distinct difference in the dispersant applied tests. Oils with initial viscosity below 2500 cP had DE’s of 70% to 95%, with a definite trend towards higher DE with the lighter oils, while the two oils with viscosity greater than 10,000 cp had DE of about 50%.

The oil drop VMD’s measured during peak oil concentration periods in each test have been averaged and plotted against the raw DE. The results in [Figure 3](#) clearly show that the dispersant applied tests that consistently had smaller oil drops resulted in increased DE as would be expected.

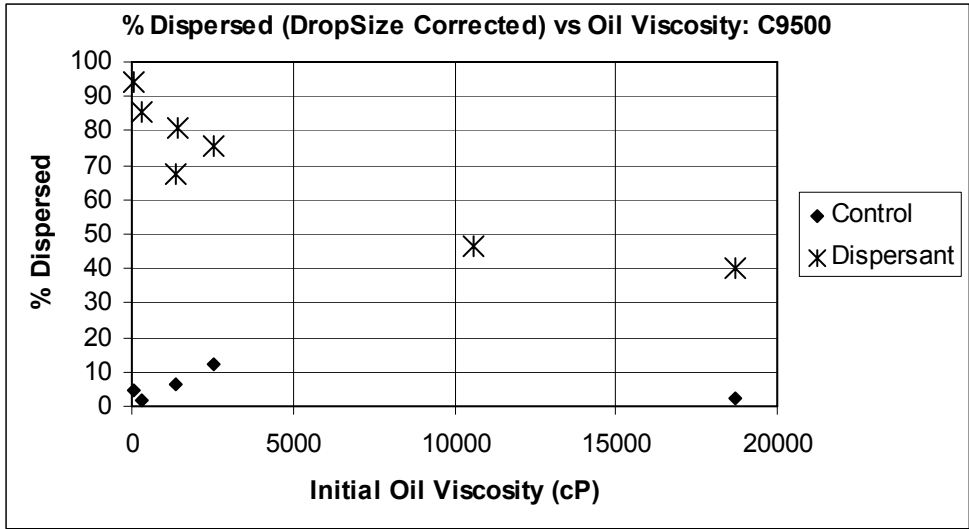


Figure 2. Drop Size Corrected Dispersant Effectiveness versus Initial Oil Viscosity

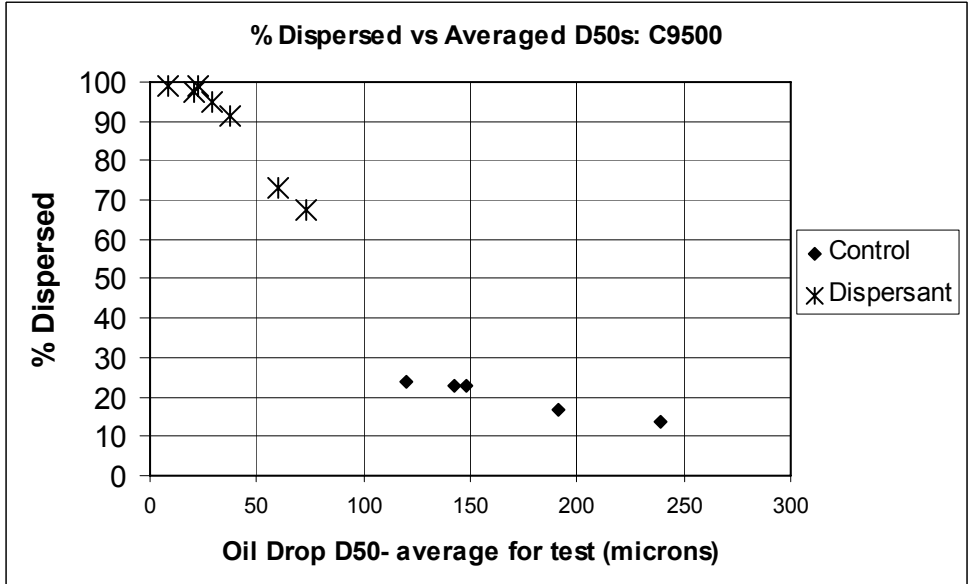


Figure 3. Raw Dispersant Effectiveness versus Test Averaged Oil Volume Median Diameter

5. Summary of Results and Recommendations

The oils with viscosities less than 3000 cp were almost completely dispersed when dispersant was applied at about a 1:20 ratio (80 to 99% raw DE and 70 to 85% control adjusted DE). The 10,610 cP oil and the 18,690 cP oil were both about 50% dispersed (after adjusting for control test losses as seen in Figure 1). If the DE values are corrected by the drop size measurement the heavier oil DE drops to 40% as seen in [Figure 2](#).

Oils with similar viscosities yielded similar dispersant effectiveness results in both the 2005 and 2008 test programs suggesting that viscosity alone was a good measure of likely dispersant effectiveness, at least for the oils used and in the tests completed to date.

In both test series the oil drop sizes in the control tests were consistently larger than those generated in the dispersant applied tests demonstrating that the chemical dispersant had a dramatic effect on the oil drop formation process.

The purchase of a Turner Cyclops submersible crude oil sensor is recommended for use in conjunction with the LISST particle size analyzer in future DE testing at Ohmsett.

6. References

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Appendix A: Supplemental Information

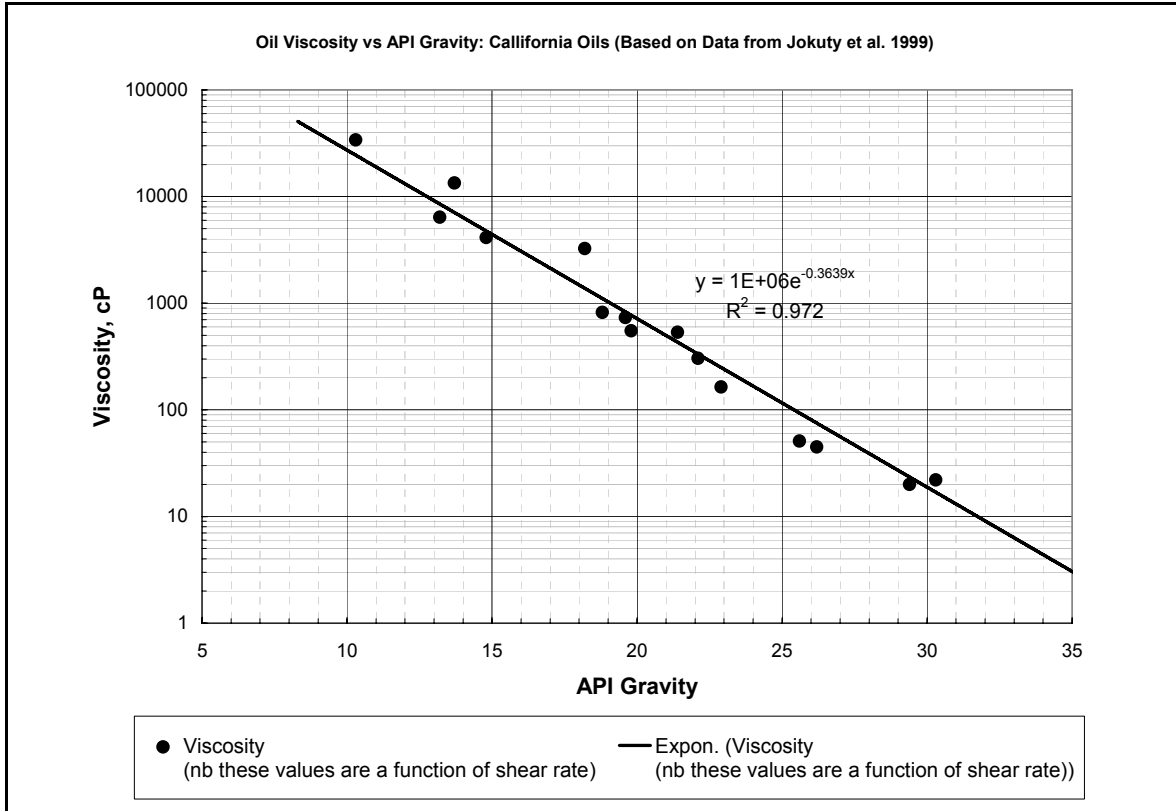


Figure A.1 Oil Viscosity versus API gravity

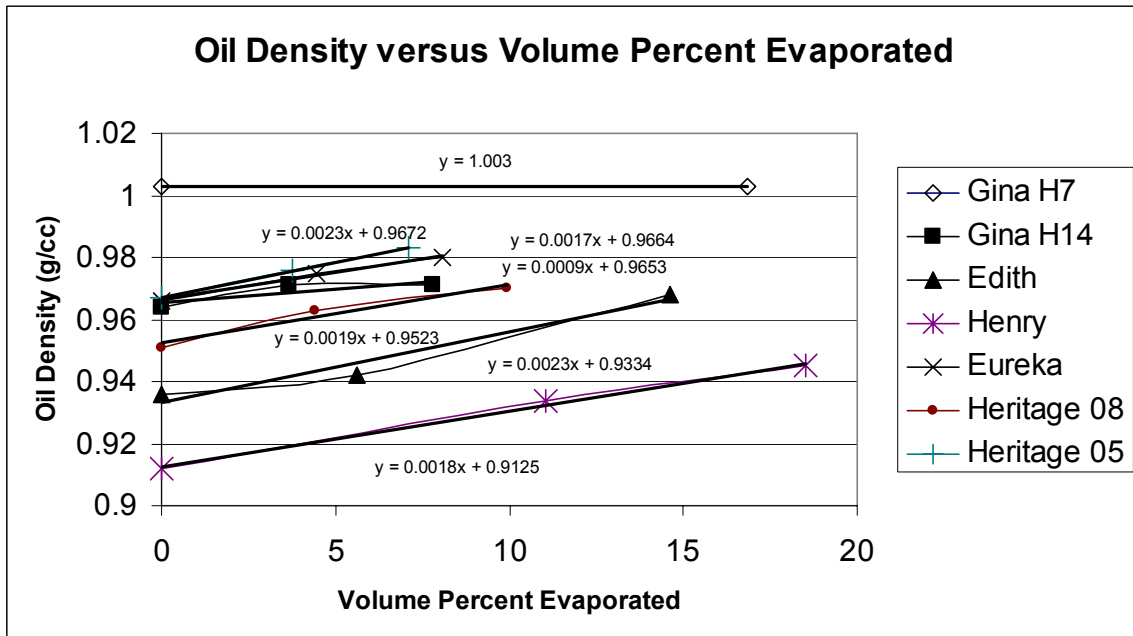


Figure A.2 Oil Density versus Volume Percent Evaporated (from tray evaporation)

Appendix B. Oil Drop Size Distributions

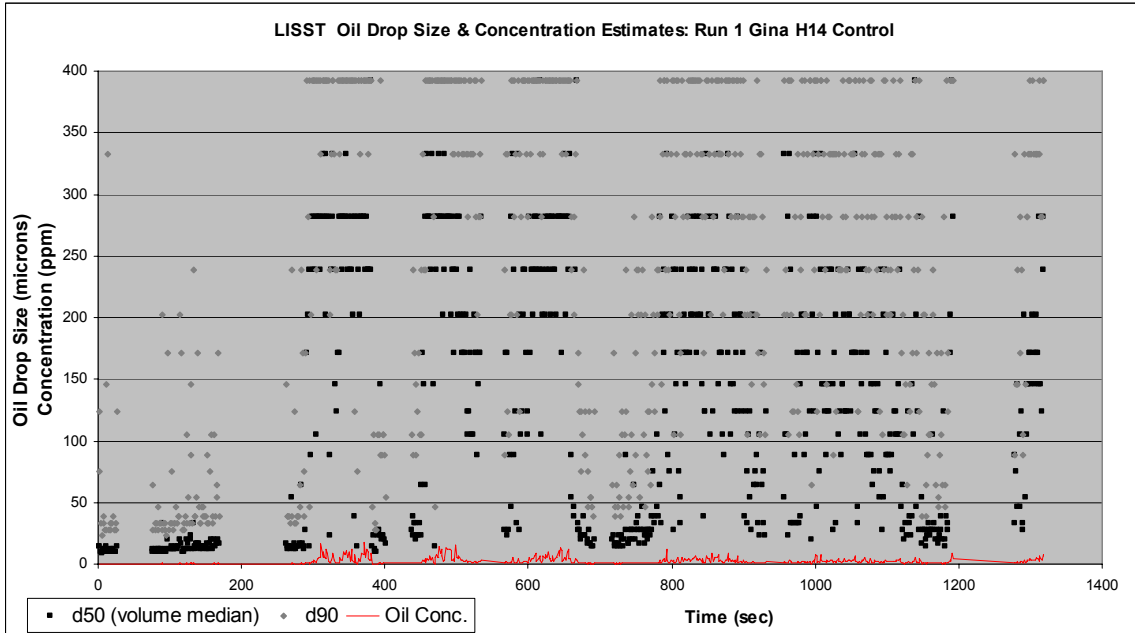


Figure B.1 - Run 1: Gina H14 Control

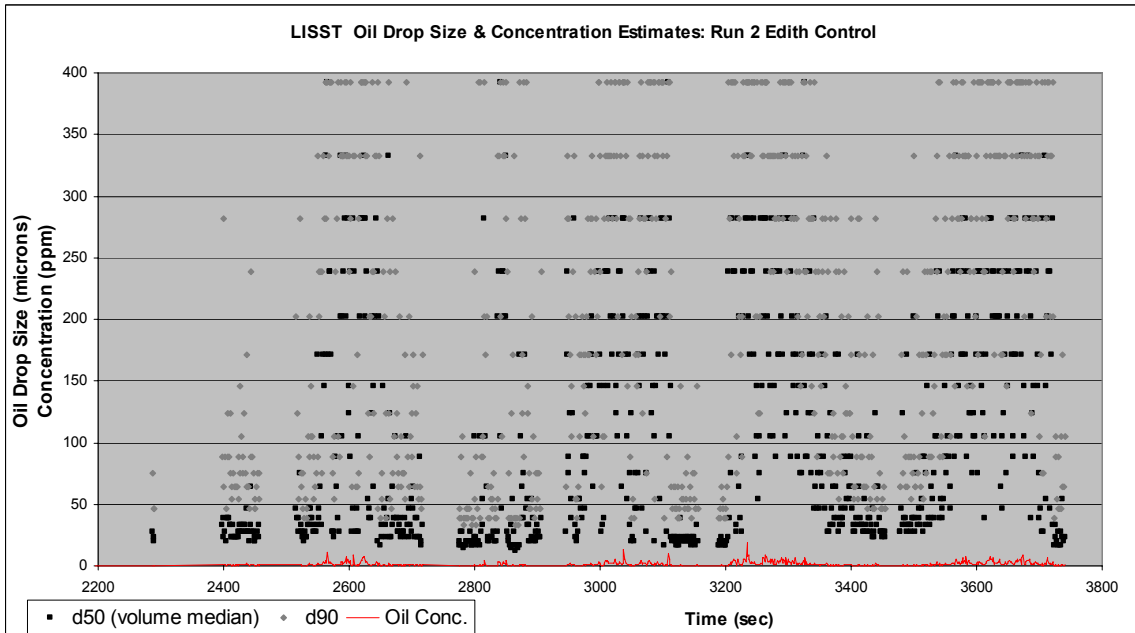


Figure B.2 - Run 2: Edith Control

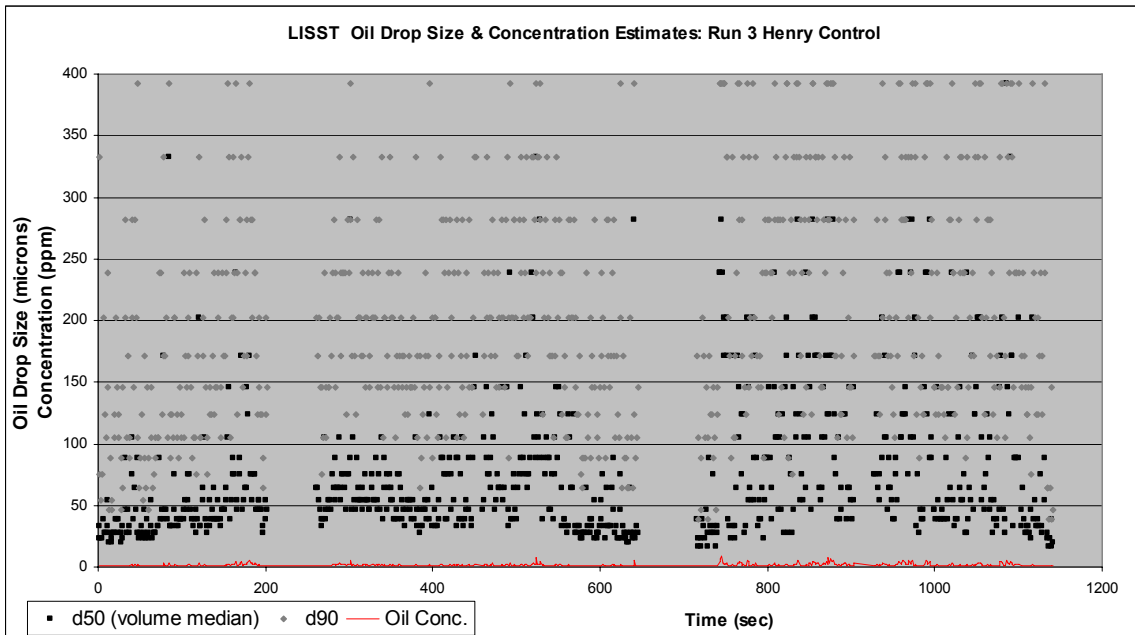


Figure B.3 - Run 3: Henry Control

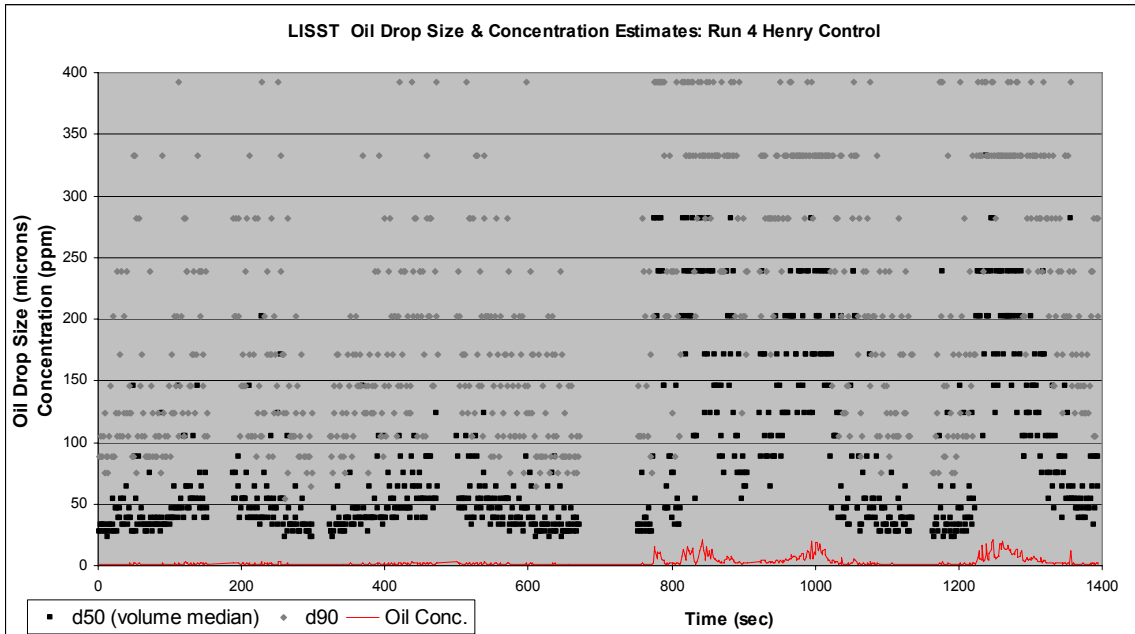


Figure B.4 - Run 4: Henry Control

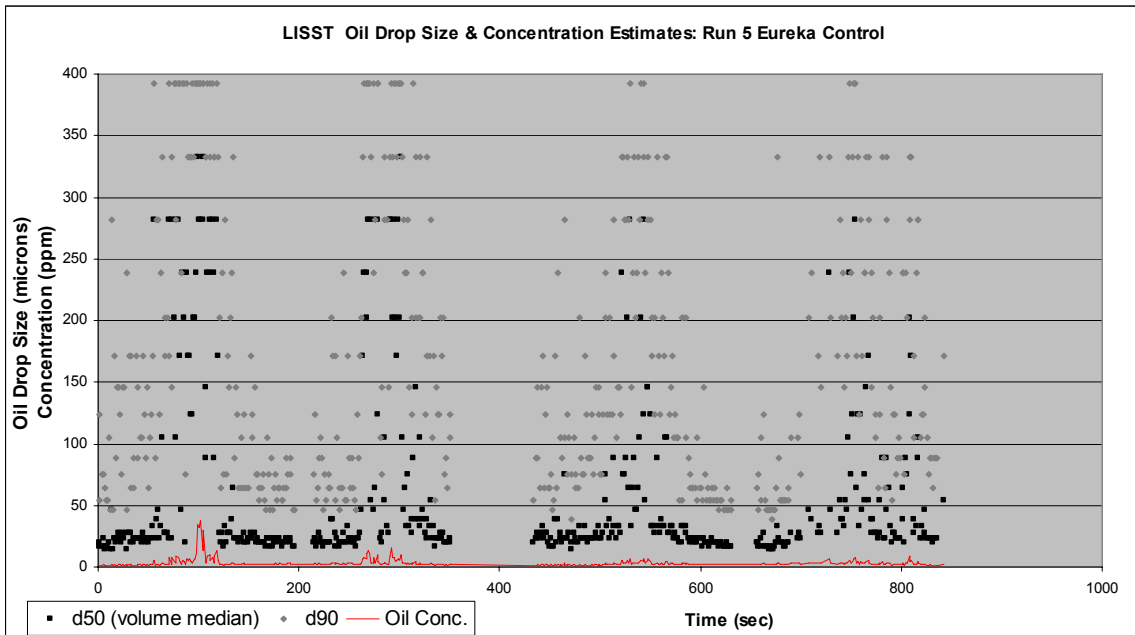


Figure B.5 - Run 5: Eureka Control

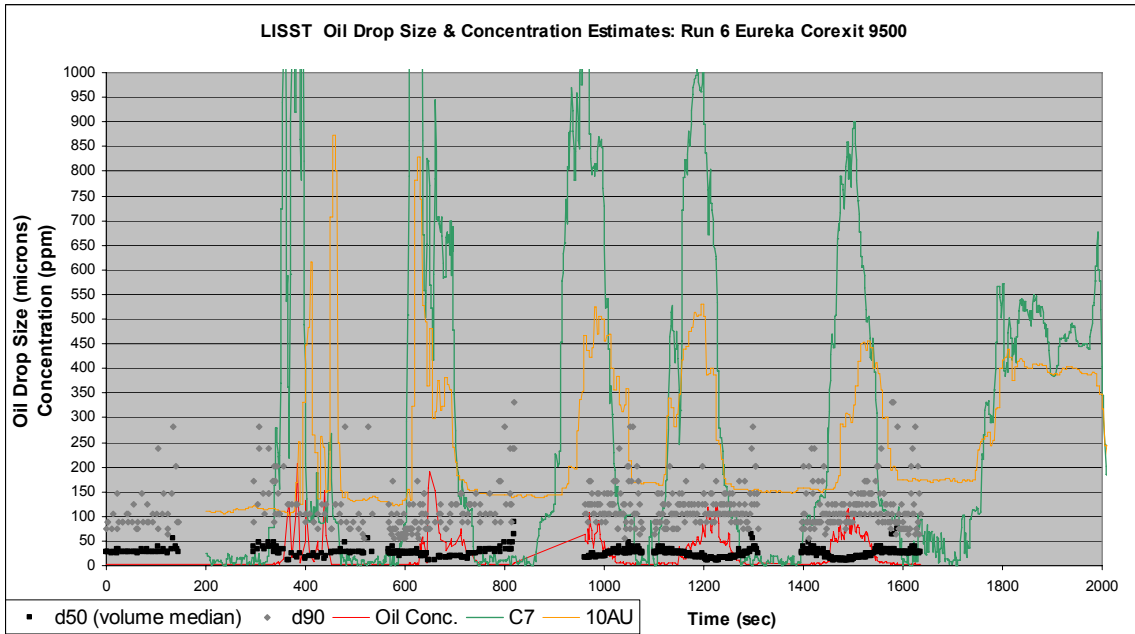


Figure B.6 - Run 6: Eureka Dispersant Applied

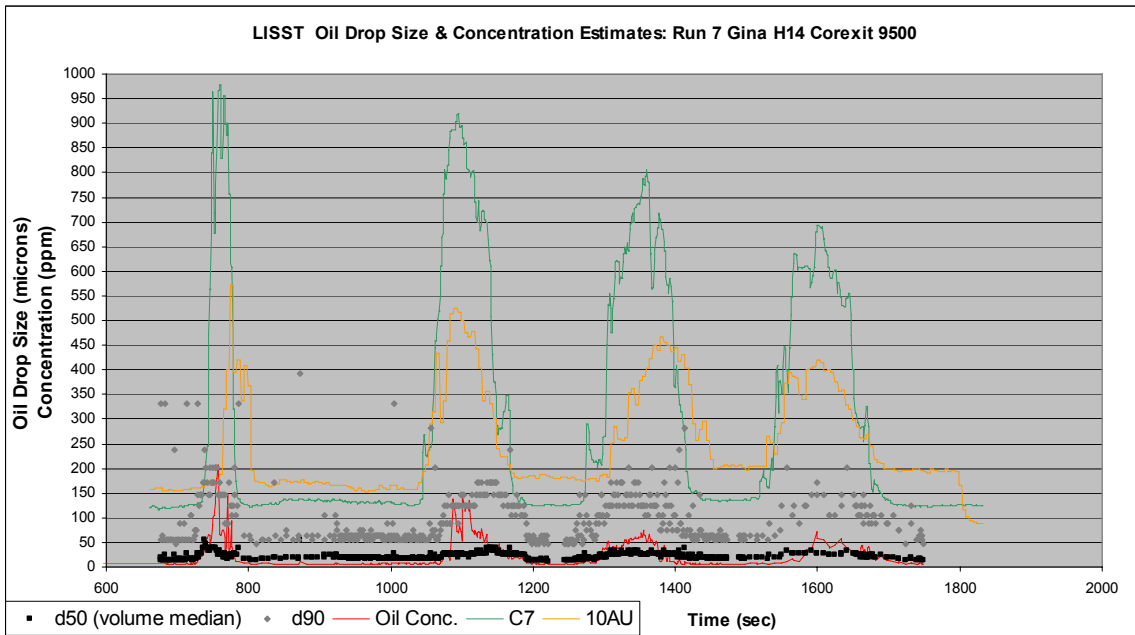


Figure B.7 - Run 7 Gina H14 Dispersant Applied

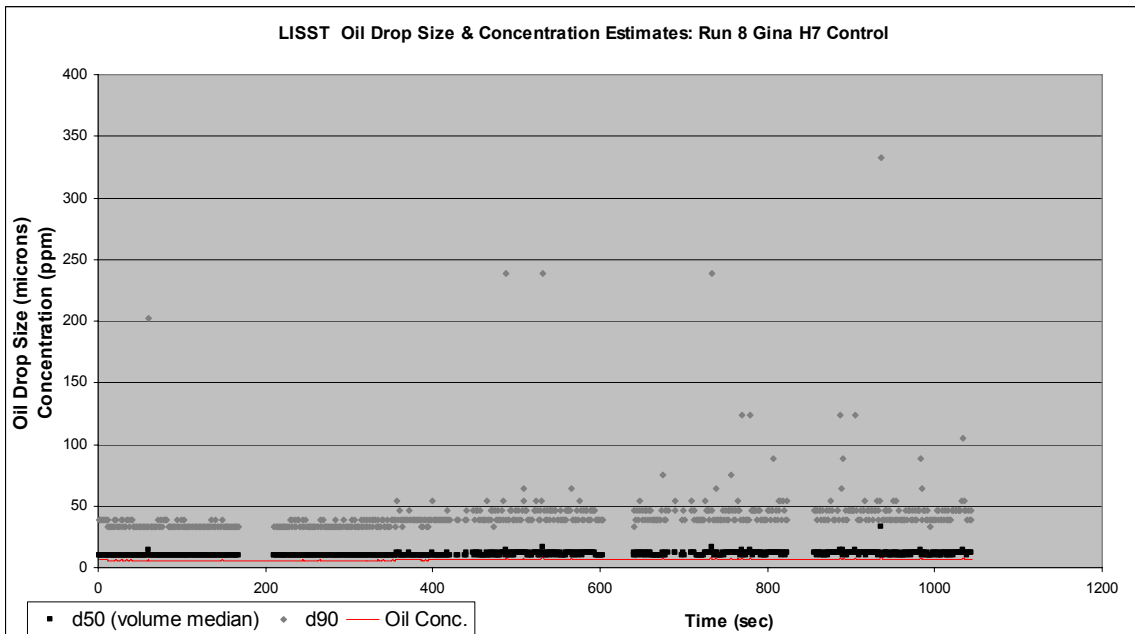


Figure B.8 - Run 8 Gina H7 Control

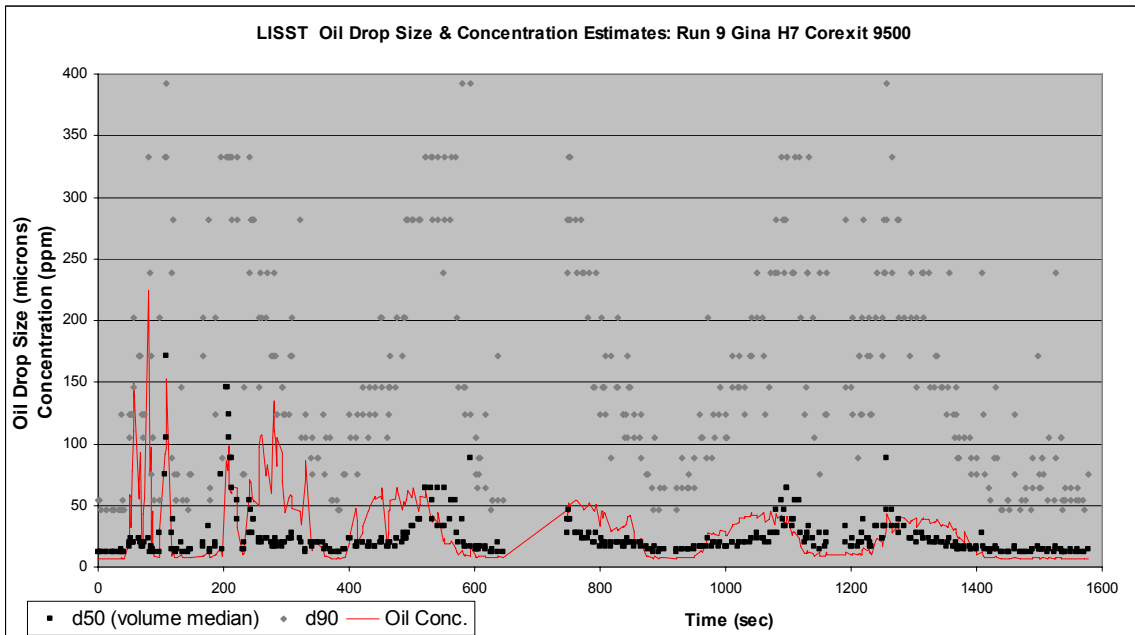


Figure B.9 - Run 9 Gina H7 Dispersant Applied

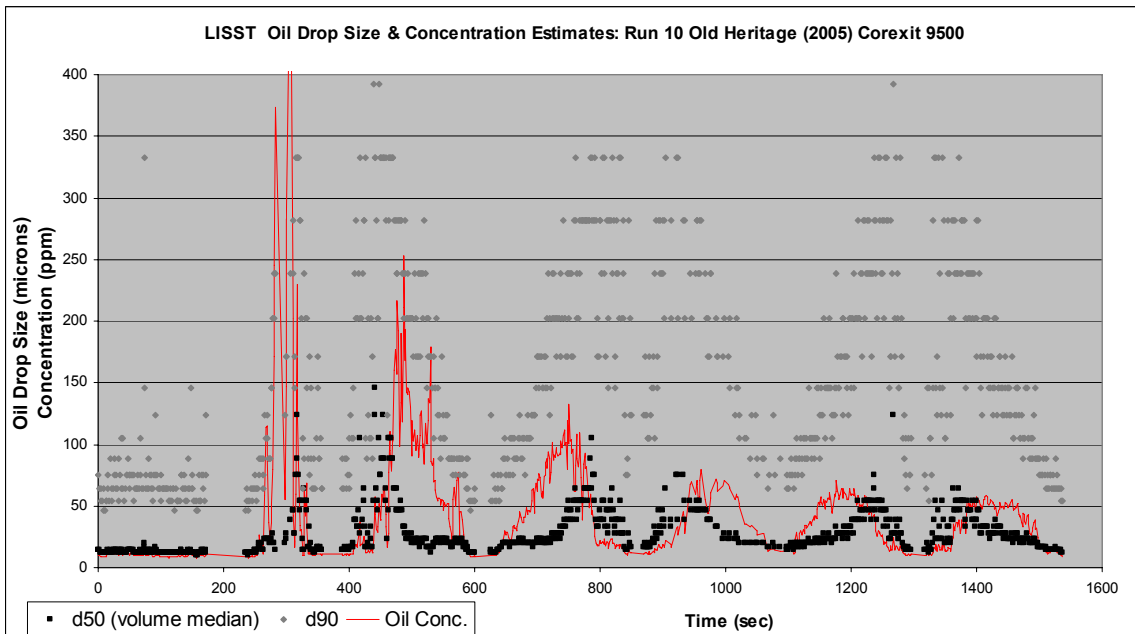


Figure B.10 - Run 10 Old Heritage (2005) Dispersant Applied

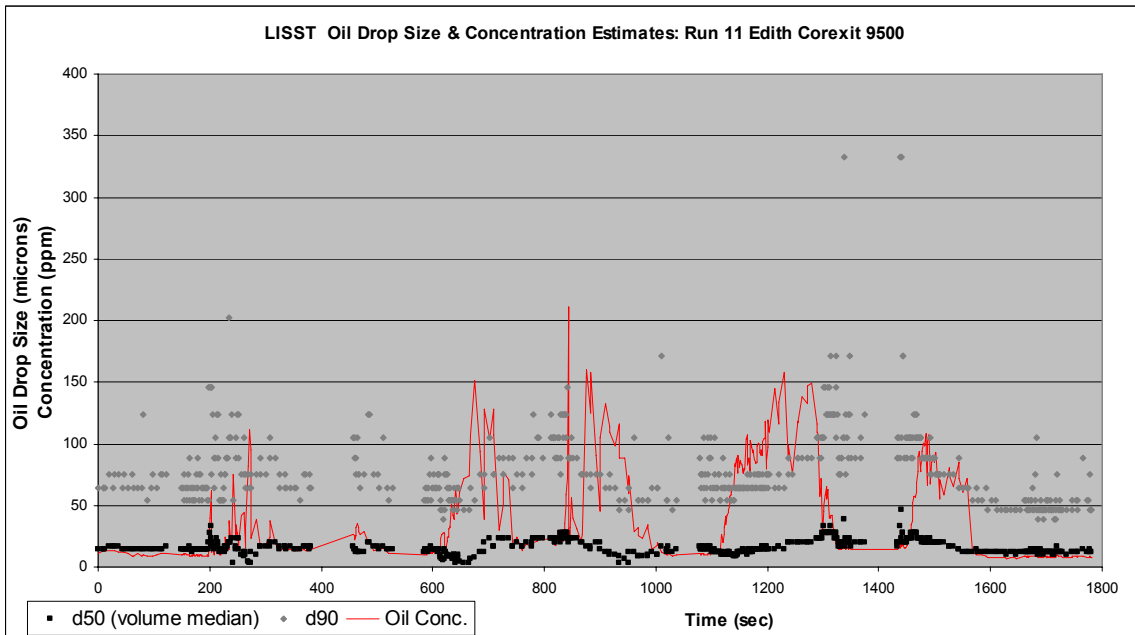


Figure B.11 - Run 11 Edith Dispersant Applied

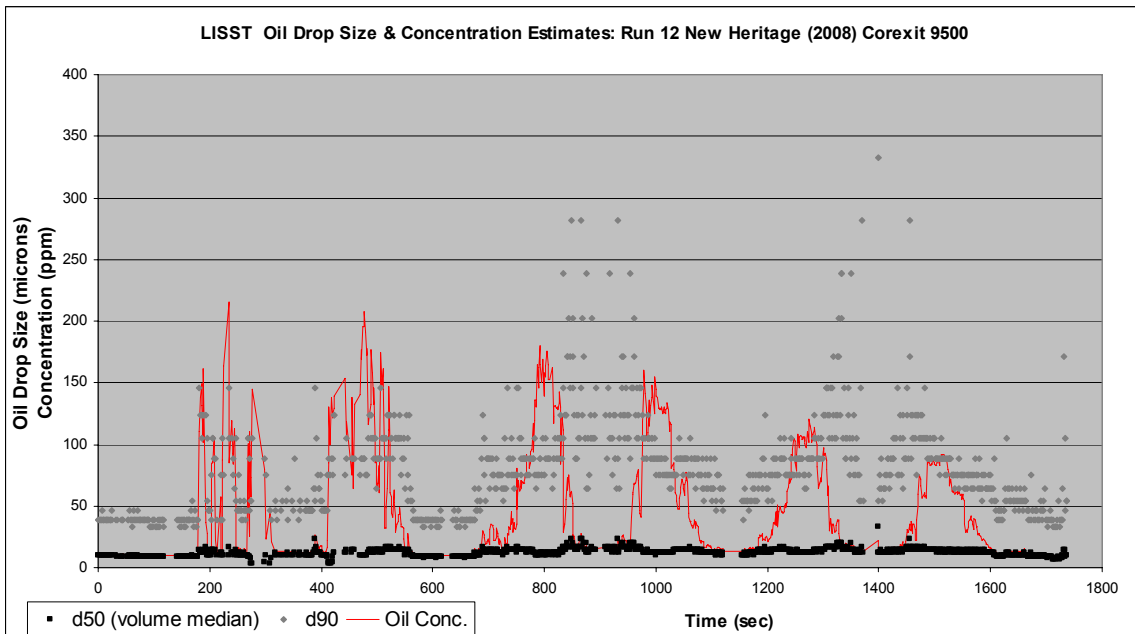


Figure B.12 - Run 12 New Heritage (2008) Dispersant Applied

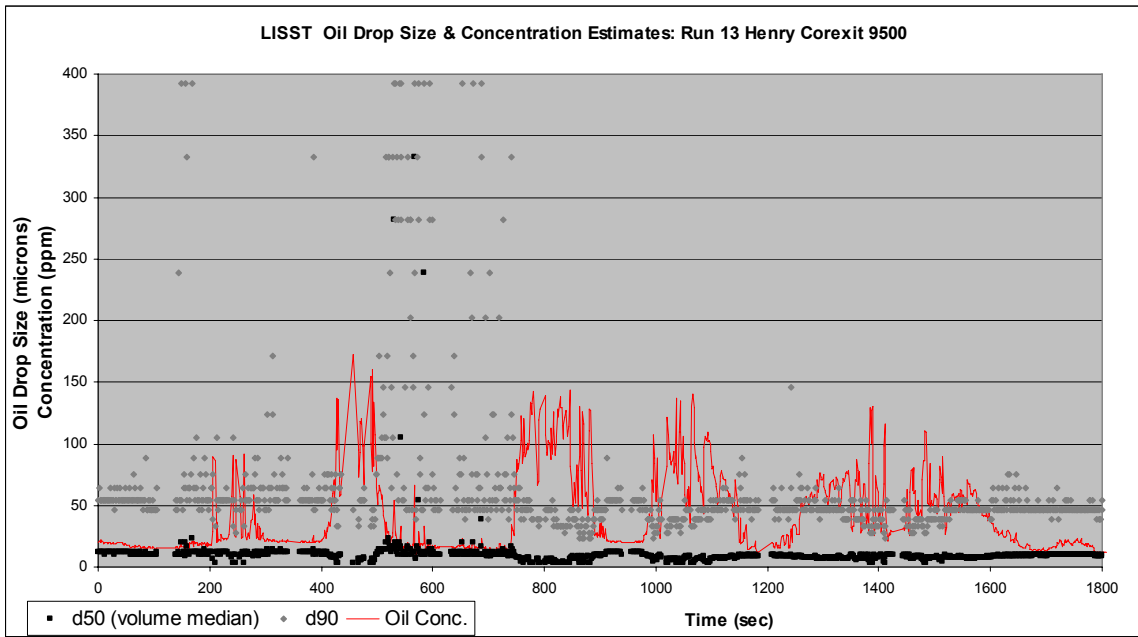


Figure B.13 - Run 13 Henry Dispersant Applied