Large Tank Effectiveness Testing of an Experimental Dispersant on Viscous Oils

For

U.S. Department of Energy
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By

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Disclaimer

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Executive Summary

ExxonMobil (EM) is developing a new chemical dispersant formulation designed to treat viscous oils thereby increasing the dispersant window of opportunity for conventional oils and effective dispersion of heavy oils. An important difference between the new formulation and traditional dispersants such as Corexit 9500 are the density and viscosity of the products. The new formulation is less dense than water so it floats on the water surface and has the opportunity to contact surface oil longer than traditional neutrally buoyant liquid dispersants. The new dispersant is also more viscous so it is not easily broken up or diffused into the water column prior to contacting surface oil. The new dispersant is more visible on the water and oil surface and so provides better feedback on slick coverage during a spray operation.

ExxonMobil funded a series of mid-scale indoor tank tests to refine this new dispersant product. A number of heavy crude and fuel oils dispersed more completely in the laboratory test tank when ED5, the most current version of this experimental product, was applied as compared to tests using the conventional Corexit 9500 dispersant. Testing of the ED5 product on these types of oils in a full-scale setting was deemed appropriate to further evaluate the potential of this new dispersant product.

A total of twenty-seven large-scale tank tests were completed at the Ohmsett facility in late October 2006. Three viscous crude oils, one heavy fuel oil (IFO 380) and three emulsified and/or weathered medium crude oils were used in the test program to compare the effectiveness of ED5 dispersant to that of Corexit 9500.

The oil viscosities tested ranged from a low of 600 cP for weathered Hibernia crude to 57,000 cP for the Irene crude oil.

The surface water temperatures during the test program ranged from 6 to 17 °C. The water temperature at 3 feet deep ranged from 9 to 17 °C and the air temperature ranged from 1 to 22 °C.

The water salinity in the Ohmsett tank was unrealistically high, about 40 ppt, during this test series. It was determined, through a series of small-scale tests undertaken shortly after the completion of the large-scale work at Ohmsett, that high water salinity improves the performance of the Corexit 9500 product relative to ED5. If the large-scale tests had been completed under more realistic water salinities (30 ppt) it is likely that the dispersant effectiveness (DE) values measured for the Corexit 9500 tests would have been lower than reported here. The following general observations, however, can be made when comparing the effectiveness of the ED5 and Corexit 9500 products under similar, albeit high salinity, test conditions.

For the tests on the lower-viscosity oils and emulsion, the two dispersants generated very similar effectiveness results. In the high-energy (breaking wave) tests on these lighter oils, the ED5 effectiveness values ranged between 91% and 94% dispersed and the Corexit 9500 results ranged between 86% and 89% dispersed. While the measured ED5 effectiveness results were consistently higher in these tests the differences were small and not likely significant given the precision of these large-scale tests. The effectiveness for both dispersants dropped when the lower-energy non-breaking harbor chop waves were used.

The ED5 dispersant outperformed Corexit 9500 (88% DE vs 40% DE) on Irene crude (32,500 cP at 15°C, $10s^{-1}$), the most viscous oil tested. This is consistent with earlier small-scale tests where the ED5 outperformed Corexit 9500 on the most viscous oils tested. The viscosity of the Irene crude oil was well above the 10,000 cP rule-of-thumb viscosity typically used as the limit for effective dispersion.

The tests completed on the IFO 380 and Doba emulsions were completed using a thinned ED5. Dispersant-to-oil-ratios (DORs) of 1:100, 1:50 and 1:20 were used on the Doba emulsions. The thinned ED5 and Corexit 9500 generated nearly identical DE at all DORs. Both dispersants achieved about 90% DE at 1:20, 75% at 1:50 DOR and 70% DE at 1:100 DOR. The thinned ED5 was about 15% more effective than Corexit 9500 on the IFO 380

emulsion and both dispersants were less effective (63% and 49%) on this emulsion than on the Doba emulsion which was slightly more viscous (22,000 vs 14,000 cP).

DORs of 1:100, 1:50 and 1:20 were used on IFO 380 fuel oil. The more viscous ED5 was used in these tests. Corexit 9500 outperformed ED5 by about 20% at the two lower DORs and ED5 was more effective by 7% at 1:20. For the 1:100 DOR test with ED5, the slick was not completely covered by dispersant. It would appear, based on these results and those for the IFO 380 and Doba emulsions, that the thinned ED5 shows more promise than the viscous ED5 at least for oils with viscosities in the 10,000 to 20,000 cP range and at lower doses. This may be because the thinner product can more quickly penetrate the viscous oil prior to being washed away by wave action.

The 17% weathered Hibernia crude oil was almost completely dispersed (93% DE) by Corexit 9500. No ED5 test was completed on the Hibernia crude due to time constraints.

In each of the tests, up to four passes were made down the length of the test tank after the oil was discharged to measure in-water oil characteristics. A LISST particle size analyzer recorded data on oil drop sizes and in-water oil concentrations. Water grab samples were taken from a continuously flowing sampling line that was pumped from the same depth as the LISST sensor position (1.5 m below the calm water surface) and these samples were analyzed for Total Petroleum Hydrocarbon concentration (TPH). Links to graphs of the oil drop size distributions and concentrations are provided in Table 4 in the main body of the report.

The water grab sample TPH measurements matched the total oil concentration output by the LISST very well suggesting that the LISST concentration estimates were accurate representations of the amount of oil being dispersed into the water column.

The oil concentration and drop size distributions measured by the LISST did not identify a clear difference between the two dispersants. A common observation that can be made regarding the results from all tests is that few of the dispersions generated were of extremely

fine oil drops as would be characterized by volume median drop sizes (VMDs) of 35 microns and lower. This is likely due to the relatively hard to disperse viscous oils that were used in the test program. The VMDs of the oil drop size distributions measured were more typically 75 to 150 microns.

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1.0 Background

ExxonMobil (EM) is developing a new chemical dispersant formulation designed to treat viscous oils thereby increasing the dispersant window of opportunity for conventional oils and effectively disperse of heavy oils. An important difference between the new formulation and traditional dispersants such as Corexit 9500 are the density and viscosity of the products. The new formulation is less dense than water so it floats on the water surface and has the opportunity to contact surface oil longer than traditional neutrally buoyant liquid dispersants. The new dispersant is also more viscous so it is not easily broken up or diffused into the water column prior to contacting surface oil. The new dispersant is more visible on the water and oil surface and so provides better feedback on slick coverage during a spray operation.

ExxonMobil funded a series of mid-scale indoor tank tests to refine this new dispersant product. A preliminary series of tests, Phase I (SL Ross, June 2005), was completed in the spring of 2005 where a new dispersant formulation (named ED4) was mixed with various amounts of microballoons (inert low density glass bubbles) to adjust the dispersant's buoyancy. A limited number of tests were also completed using an ED4 formulation with its carrier solvent removed to increase the viscosity of the dispersant in hopes that it would remain more cohesive and not break up and pass into the water column before moving into the oil phase. The addition of microballoons at 2% to 3% by weight to the more viscous, solvent-free, ED4 achieved the best results in the Phase I testing.

A second set of tests, Phase II (SL Ross, November 2005), was then completed to further investigate the potential of the solvent-free, 2 to 3% microballoons, formulation on a range of viscous crude oils and emulsions. In the Phase II testing the ED4 dispersant was at least as effective as Corexit 9500 in all tests and was more effective in a number of the test cases. The ED4 was significantly more effective on a bunker-diesel mix, a 23% weathered Hibernia crude and 23% weathered and 25% emulsified Hibernia crude. It was also found that the ED4 transferred into the viscous oils more effectively than Corexit 9500 and the dispersant would likely be available for improved dispersion in the long-term and under wave energies in excess of those possible in the SL Ross wave tank. The phase II work also found that the

ED4 formulation's initial viscosity is very dependant on the complete removal of its carrier solvent and that its viscosity increases with time after its initial formulation. Because of this an alternate solvent was selected for subsequent ED4 preparation. A Phase III test series was then initiated that used ED4 formulated with a new carrier (isopropyl alcohol) that resulted in a more stable product. The new product was called ED5.

The new ED5 formulation generated the best dispersant effectiveness improvement when compared to Corexit 9500 and the various ED4 formulations tested.

IFO 380 fuel oil and Gina, Gilda, Elly and Doba crude oils dispersed more completely in the laboratory test tank when ED5 was applied as compared to tests using the conventional Corexit 9500 dispersant. These lab-scale tests resulted in choosing the ED5 formula for tests at the full-scale Ohmsett facility to further evaluate the potential of this new dispersant product.

A large-scale dispersant effectiveness testing capability has been developed and refined at the Ohmsett facility over the past seven years and provides a full-scale testing opportunity without the problems associated with field testing.

2.0 Ohmsett Dispersant Effectiveness Test Methods

An overview of the dispersant effectiveness (DE) test method used at Ohmsett is provided by first describing the test tank and main apparatus used in the testing. This is accomplished primarily through photos of the equipment used in the dispersant experiments to give the reader an appreciation of the scale of the operation. Methods used to characterize the dispersed oil are then described. Finally, the step-by-step test procedure is itemized. The test procedure has been developed over a period of several years and has been refined from the experiences gained from several earlier dispersant effectiveness test projects (SL Ross 2000a & b, 2002a & b, 2003a & b, 2004, 2006).

2.1 Major Test Equipment Components

The main equipment components of the dispersant effectiveness (DE) test procedure include the Ohmsett tank, the wave making system, the main equipment bridge, the oil distribution system, the oil containment boom and the dispersant spray system. Photos of these components are provided in Figures 1 through 5. Additional details concerning this equipment can be found in SL Ross 2002b and 2006. Dispersed oil can be characterized using flow-through and in-situ fluorometry, dispersed oil particle size determination and water sampling (for Total Petroleum Hydrocarbon (TPH) determination).

The most recent dispersant effectiveness protocol calls for a single 24 inch boom to be placed across the tank close to the wave paddle at the south end of the tank and two 48 inch booms across the tank about 100 feet from the north end of the tank (see Figure 1). This provides a long and wide test area (approximately 500 feet long and 65 feet wide) with no side booms to minimize the influence of barriers on the dispersion process. Figure 1 provides a look at the extensive test area from both a south and north vantage point. The wave paddle is shown in Figure 2. Figure 3 shows the main bridge that is used to move equipment and observers along the length of the test basin.

Figure 1. Ohmsett Test Tank with Oil Containment Boom (looking north and then south)

Figure 2. Ohmsett Tank Wave Paddle System

Figure 3. Main Bridge

Photographs of the oil supply system and oil discharge header are provided in Figure 4.

The oil discharge system includes:

1. a progressing cavity pump (left photo Figure 4 bright green),
2. a pump speed control system,
3. a gravity fed oil hopper supply (white tank above pump),
4. three-inch oil supply lines, and;
5. a stainless steel oil discharge manifold (right photo Figure 4).

Oil is pumped into the hopper from drums or other supply tanks using the progressing cavity pump in reverse. The flow rate of this pump is precisely controlled by altering its rpm. 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.

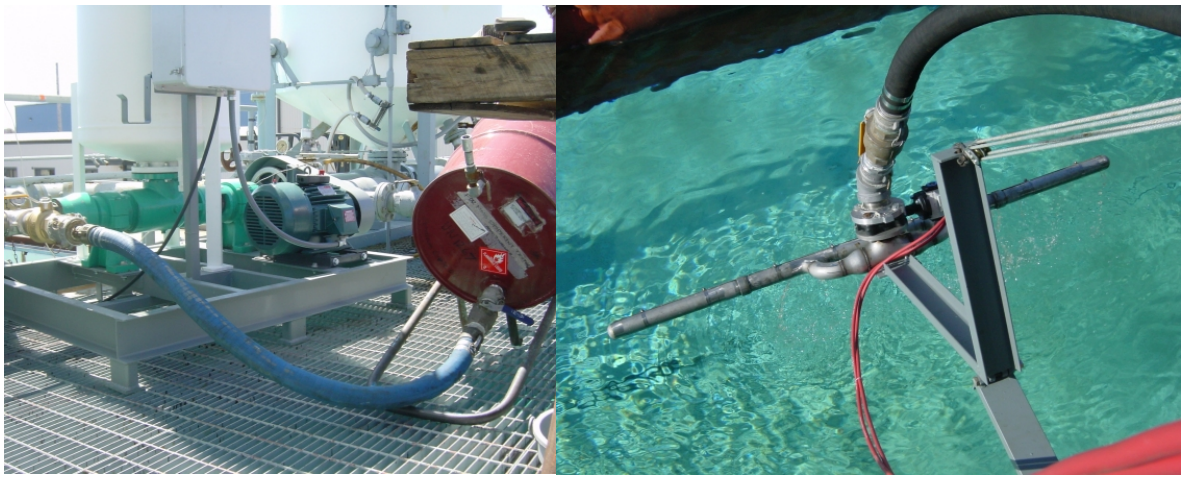


Figure 4. Oil Supply System and Discharge Header

The dispersant supply system and portable spray wand used to spray the liquid dispersant used in the study are shown in Figure 5. The viscous ED5 dispersant was applied using the RTX 1500 ceiling texture application system and spray gun seen in Figure 6.

Figure 5. Liquid Dispersant Supply Tank and Portable Spray Wand Applying Corexit 9500

Figure 6. RTX 1500 Spray System and Sprayer in Operation Applying ED5 Dispersant

2.2 Dispersed Oil Measurement

In this series of tests in-water oil concentrations were estimated using a LISST particle size analyzer and a Turner Designs TD500D oil-in-water analyzer. Dispersed oil drop size distributions were measured using the LISST particle size analyzer. The LISST device and the pump used for water sampling were positioned at 1.5 meters below the calm water level. Water samples were taken for subsequent extraction and analysis using the Turner Design, TD500D, hand held fluorometric hydrocarbon analyzer. Technical details for these two oil-in-water measuring systems can be found at the following web sites.

LISST : www.sequoiasci.com

Turner TD500D: www.oilinwatermonitors.com

2.3 Test Procedure

The basic test procedure used for the dispersant effectiveness testing was as follows.

1. The oil containment area was established in the Ohmsett tank by placing a single boom across the south end and a double boom barrier at the north end.
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.
4. The wave paddle was started and the waves were allowed to develop to a stage just prior to the formation of breaking waves. A three-inch stroke and 34 to 35 strokes per minute wave paddle settings were used in all of these tests. The beaches were lowered in tests 15 and 16 to generate a harbor chop wave rather than a regular wave.
5. The oil was pumped onto the surface through the discharge manifold mounted on the south side of the bridge with the bridge stationary and the bridge was then moved to the south so the oil could be sprayed with dispersant.
6. Dispersant was applied onto the oil slick from either the hand spray wand (Corexit 9500) or using the SprayTek spray system (ED5 application).
7. Each test was video taped for future visual reference.
8. The waves were left on for 30 minutes after which the wave paddle was stopped.
9. Two or three passes were made down the tank during the 30 minute mixing period with instrumentation towed through the water to measure oil concentration and oil drop sizes and to collect water samples for TPH determination.
10. After the wave paddle was stopped and the tank surface had quieted down, water spray from the bridge fire monitors was used to carefully 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.
11. The oil was then removed from the water surface using a double-diaphragm pump and suction wand and placed in a collection drum. If only very small quantities of oil remained at the end of a test, it was collected using a long-handled ladle and placed in a five-gallon bucket.

12. A small quantity of emulsion breaker was thoroughly mixed into the contents of the drum or bucket and they were allowed to stand overnight. The free water present was decanted from drums as shown in Figure 7. Water was decanted from the five-gallon buckets by drilling a small diameter hole in the bottom of the bucket and allowing any free water to drain away from the floating oil.
13. The remaining oil and water were well mixed and a sample was taken for water content and physical property determination.
14. The quantity of liquid in the drum or bucket was measured and then adjusted by subtracting the amount of water in the oil as determined by a water content analysis.
15. 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.

Figure 7. Drum Decanting Method. (Air inlet tube to bottom of drum is placed in drum bung. Water is decanted from drum vent when drum is inverted.)

3.0 Oils and Dispersant Used in Test Program

Corexit 9500 and the experimental product, ED5, were the dispersants used in the test program. Two versions of the ED5 product were tested; one with a viscosity of 4500 to 5000 cP at 20°C and one thinned (by adding additional isopropyl alcohol) to about 900 to 1000 cP at 15°C.

Three viscous crude oils, one heavy fuel oil (IFO 380) and three emulsified and/or weathered medium crude oils were used in the test program to compare the effectiveness of ED5 dispersant to that of Corexit 9500. The viscous crude oils used were Gilda, Elly and Irene crude oils, all produced in California. Doba, a medium crude oil from Nigeria, was tested after preparing a 50% water content emulsion using a gear pump and after weathering the oil 10% by weight. Sockeye crude oil was tested as a 50% water content emulsion. Hibernia crude oil was used after weathering to a 17% loss by weight. The physical properties of the various oils and dispersants used in the testing are provided in Table 1.

Table1. Physical Properties of Test Oils and Dispersants

Oil / Dispersant	Water Content (%)	Density (mg/l) @ 20ºC	Viscosity (cP) $10s^{-1}$, 10ºC	Viscosity (cP) $10s^{-1}$, 15ºC
Corexit 9500	0	nm	nm	70
ED5	0	nm	nm	4500 (20ºC)
thinned ED5	0	nm	nm	900
Gilda	0	0.961	6600	4500
Elly	0	0.961	8200	5400
Irene	0	0.964 @26ºC	57,000	32,500
IFO 380	0	0.961	18,000	11,000
IFO 380 (emulsified)	50	nm	nm	14,000
Doba (weathered 10% by wt)	0	0.923	3500	2000
Doba (weathered 10% by wt & emulsified)	50	nm	22,000	11000
Sockeye (emulsified)	50	0.973	15,000	6350
Hibernia (weathered 17% by wt)	0	0.878	600	nm

nm – not measured

Air sparging was used to weather the oils. This was completed by attaching an air hose to a perforated pipe that was submerged in the drum of oil to be weathered through the drum's bung. An exhaust line was fitted to the drum's vent hole and routed to the outdoors.

Compressed air was then pumped through the air hose into the oil and allowed to escape through the vent hose. A drum band heater was used to heat the oil to speed the evaporation process. The weight of the oil was recorded prior to the start of the weathering and checked periodically to establish the status of the weathering.

3.1 Test Matrix Completed

Twenty-seven dispersant effectiveness tests were completed in the test program. A summary of the tests completed is provided in Table 2. The standard test used a dispersant-to-oil ratio of 1:20, the original ED5 formulation with a viscosity of 4500 cP at $10s^{-1}$ and 20ºC and a regular wave pattern. Any deviations from the standard test conditions are identified in Table 2. The viscosity of the thinned ED5 was 800 cP at $10s^{-1}$ and 20ºC.

Table 2. Test Matrix

Oil	Unique Test Conditions	ED5 Test #	C 9500 Test #
Gilda		1	4
	harbor chop	16	15
Elly		2	3
Irene		5	6
IFO 380	1:100 DOR	8	7
	1:50 DOR	10	9
		12	11
IFO 380 emulsion	thin ED5	20	19
Sockeye emulsion		14	13
Doba emulsion	thin ED5	18	17
	1:50 DOR, thin ED5	24	23
	1:100 DOR, thin ED5	22	21
Doba weathered		26	25
Hibernia weathered			27

4.0 Test Results

4.1 Test Conditions and Dispersant Effectiveness Estimates

The test conditions and estimated Dispersant Effectiveness (DE) for all of the tests conducted at Ohmsett are summarized in Table 3. The oils and dispersants used in each test are provided in columns 1 and 2 of the table. The viscosities of the initial oils are provided in column 3. The oil viscosities tested ranged from a low of 600 cP for weathered Hibernia crude to 57,000 cP for the Irene crude oil. The viscosities of most of the test oils were recorded at both 10°C and 15°C (see Table 1). The viscosities shown in Table 3 are for the measurements made at the temperature closest to the surface water temperature at the time of the test.

Air, surface water, water at 3 ft depth, oil and dispersant temperatures just prior to each test are provided in columns 5 through 9. The surface water temperatures during the test program ranged from 6 to 17 °C. The water temperature at 3 feet deep ranged from 9 to 17 °C and the air temperature ranged from 1 to 22 °C.

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

Table 3. Dispersant Effectiveness (DE) Test Results Summary

Oil	Dispersant	Oil Viscosity (10 °C & $10s^{-1}$) (cP)	Water Content (%)	Air Temp °C	Surface Water Temp °C	Water Temp @3 ft °C	Oil Temp °C	Disp. Temp °C	DOR	DE	Links to Video Segments	Test #
Hibernia (17%)	C 9500	600	0	9	7	11	13	8	1:20	93	447Clip27.mpg	27
Doba (10%)	ED5	3500	0	1	7	11	-2	7	1:20	92	447Clip26.mpg	26
	C 9500	3500	0	9	8	12	11	7	1:20	89	447Clip25.mpg	25
Gilda	ED5	4500	0	15	14	10	12	17	1:20	94	447Clip1.mpg	1
	C 9500	4500	0	17	14	11	13	16	1:20	86	447Clip4.mpg	4
	ED5	4500	0	11	11	15	10	13	1:20	58[a]	447Clip16.mpg	16[a]
	C 9500	4500	0	12	8	14	6	4	1:20	65[a]	447Clip15.mpg	15[a]
Elly	ED5	5400	0	-	12	9	12	16	1:20	91	447Clip2.mpg	2
	C 9500	5400	0	-	14	9	14	14	1:20	-	447Clip3.mpg	3
Sockeye emul.	ED5	6,350	50	9	11	14	4	8	1:20	93	447Clip14.mpg	14
	C 9500	6,350	50	19	17	17	20	20	1:20	86	447Clip13.mpg	13
IFO 380	ED5	11,000	0		14	16	20	18	1:100	18	447Clip8.mpg	8
	C 9500	11,000	0	14	15	14	17	14	1:100	39	447Clip7.mpg	7
	ED5	11,000	0	22	17	17	20	19	1:50	37	447Clip10.mpg	10
	C 9500	11,000	0	22	17	17	23	24	1:50	56	447Clip9.mpg	9
	ED5	11,000	0	17	17	17	20	20	1:20	73	447Clip12.mpg	12
	C 9500	11,000	0	-	16	17	18	17	1:20	66	447Clip11.mpg	11
IFO 380 emul.	thin ED5	14,000	50	6	8	13	0	0	1:20	63	447Clip20.mpg	20
	C 9500	14,000	50	12	9	13	16	9	1:20	49	447Clip19.mpg	19
Doba emulsion	thin ED5	22,000	50	12	6	13	7	9	1:20	91	447Clip18.mpg	18
	C 9500	22,000	50	6	8	13	9	6	1:20	92	447Clip17.mpg	17
	thin ED5	22,000	50	7	7	12	12	7	1:50	74	447Clip24.mpg	24
	C 9500	22,000	50	7	9	12	21	10	1:50	78	447Clip23.mpg	23
	thin ED5	22,000	50	13	6	13	12	13	1:100	71	447Clip22.mpg	22
	C 9500	22,000	50	10	6	12	18	5	1:100	73	447Clip21.mpg	21
Irene	ED5	32,500	0	19	15	16	20	21	1:20	88	447Clip5.mpg	5
	C 9500	32,500	0	22	17	16	22	23	1:20	40	447Clip6.mpg	6

[a] – these two tests were completed with the beaches in the down position to generate harbor chop waves. There were no breaking waves in these tests.

The water salinity in the Ohmsett tank was unusually and unrealistically high, about 40 ppt, during this test series. The Ohmsett tank is filled with water from the nearby harbor that has a salinity of 15 to 18 ppt. Salt is then added to the tank to bring the salinity up to 32 to 35 ppt. The tank had been drained in the months prior to this test program and was refilled and salted just prior to testing. Excess salt was added to the tank in this re-filling operation and this resulted in the higher than usual water salinity. It was determined, through a series of small-

scale tests (SL Ross 2007) that were undertaken shortly after the completion of the large-scale work at Ohmsett, that high water salinity improves the performance of the Corexit 9500 product relative to ED5. This is also supported by dispersant effectiveness tests that were conducted at Ohmsett for the Minerals Management Service in 2005 (SL Ross 2006) on some of the same oils used in this study. The 2005 tests were conducted with similar mixing energies, DORs and water temperatures. The primary difference in the two test programs was the water salinity in the tank at the time of the tests. The dispersant effectiveness results from the 2005 testing are compared to the current results in Table 4. Corexit 9500 consistently was not as effective in the lower, more realistic, salinity water.

Table 4. Dispersant Effectiveness Comparison: 2005 Ohmsett Tests versus Present Results

Oil Type	Corexit 9500 DOR	DE @ 22 ppt (SL Ross 2006)	DE @ 40 ppt 1:20 DOR
Elly	1:13 & 1:17	58% & 70%	91%
Gilda	1:12 & 1:20	58% & 49%	86%
Irene	1:7 & 1:17	30% & 26%	40%

If the present tests at Ohmsett had been completed under more realistic water salinities (30 to 32 ppt) it is likely that the DE values measured for the Corexit 9500 tests would have been lower than reported here. This said, the following general observations can be made when comparing the effectiveness of the ED5 and Corexit 9500 products under similar, albeit high salinity, test conditions.

For the tests on the lower-viscosity oils and emulsion shown at the top of Table 3 (3500 to 6350 cP: Gilda, Elly, weathered Doba, Sockeye emulsion) the two dispersants generated very similar effectiveness results. In the high-energy tests on these lighter oils, the ED5 DE values ranged between 91% and 94 % and the Corexit 9500 results ranged between 86% and 89%. While the measured ED5 DE results were consistently higher in these tests the differences in DE were small and not likely significant given the precision of these large-scale tests. The DE for test #3 (Elly crude and Corexit 9500) was not measured as the oil collected at the end of this test was accidentally discarded prior to analysis. The DE for both dispersants dropped

when the harbor chop waves were used in tests 15 and 16. In these lower energy, non-breaking wave tests the Corexit 9500 DE was slightly higher than the ED5 DE (65% vs 58%) but again this difference is not likely significant given the large-scale test's precision.

The ED5 dispersant outperformed Corexit 9500 (88% DE vs 40% DE) on Irene crude (32,500 cP at 15°C, $10s^{-1}$), the most viscous oil tested. This is consistent with earlier small-scale tests where the ED5 outperformed Corexit 9500 on the most viscous oils tested. The viscosity of the Irene crude oil is well above the 10,000 cP rule-of-thumb viscosity typically used as the limit for effective dispersion.

The tests completed on the IFO 380 and Doba emulsions were completed using a thinned ED5 (see Table 1). Dispersant-to-oil-ratios (DORs) of 1:100, 1:50 and 1:20 were used on the Doba emulsions. The thinned ED5 and Corexit 9500 generated near identical DE at all DORs. Both dispersants achieved about 90% DE at 1:20, 75% at 1:50 DOR and 70% DE at 1:100 DOR. The thinned ED5 was about 15% more effective than Corexit 9500 on the IFO 380 emulsion and both dispersants were less effective (63% and 49%) on this emulsion than on the Doba emulsion which was slightly more viscous (22,000 vs 14,000 cP).

DORs of 1:100, 1:50 and 1:20 were used on IFO 380 fuel oil. The more viscous ED5 was used in these tests. Corexit 9500 outperformed ED5 by about 20% at the two lower DORs and ED5 was more effective by 7% at 1:20. For the 1:100 DOR test with ED5, the slick was not completely covered by dispersant. It would appear, based on these results and those for the IFO 380 and Doba emulsions, that the thinned ED5 shows more promise than the viscous ED5 at least for oils with viscosities in the 10,000 to 20,000 cP range and at lower doses. This may be because the thinner product can more quickly penetrate the viscous oil prior to being washed away by wave action.

The 17% weathered Hibernia crude oil was almost completely dispersed (93% DE) by Corexit 9500. No ED5 test was completed on the Hibernia crude due to time constraints.

4.2 Dispersed Oil Concentrations and Drop Size Distributions

For each dispersant effectiveness test conducted in the OHMSETT tank, up to four passes were made through the dispersed oil plume to measure in-water oil characteristics. A LISST particle size analyzer recorded data on oil drop sizes and in-water oil concentrations. For some of the tests, water grab samples were taken from a continuously flowing sampling line that was pumped from the same depth as the LISST sensor position (1.5 m below the calm water surface). These samples were analyzed for Total Petroleum Hydrocarbon concentration (TPH) using a Turner TD500D. Graphs of the oil drop size distributions and concentrations are provided in Appendix B. Hypertext links to these graphs are provided in Table 5. The tests where TPH was measured with the TD500 fluorometer are identified in Table 5 and the TD500 results are plotted with the LISST results for comparison.

The water grab sample total petroleum hydrocarbon measurements (TD500 analyses) matched the total oil concentration output by the LISST very well, especially for elevated concentrations. The LISST estimates of oil concentration seem to be artificially high at low concentrations as seen in Runs 7 and 8. Some of this discrepancy may be due to the LISST's inclusion of all particles, including silt and other fines in the tank, in the concentration estimate and thus overestimating the oil concentration somewhat.

The oil concentration and drop size distributions measured by the LISST did not identify a clear difference between the two dispersants. A common observation that can be made regarding the results from all tests is that few of the dispersions generated were of extremely fine oil drops as would be characterized by volume median drop sizes (VMDs) of 35 microns and lower within the regions of high oil concentration. This is likely due to the viscous oils that were used in the study.

The VMDs of the drop size distributions within the zones of high oil concentration are of primary interest as these VMDs describe the oil drop distributions generated during the time of peak dispersion in the test. The VMDs discussed below refer to those recorded when significant oil concentrations were present.

Table 5. In-Water Oil Characterization Graph Hypertext Links

Oil	Oil Viscosity (10°C & $10s^{-1}$) (cP)	Dispersant	DOR	DE	Oil Drop Size (Average D50)	Links to LISST Data Graphs	TD500 Data Collected	Test #
Hibernia (17%)	600	C 9500	1:20	93	54	LISSTR27		27
Doba (10%)	3500	ED5	1:20	92	98	LISSTR26	yes	26
	3500	C 9500	1:20	89	52	LISSTR25		25
Gilda	4500	ED5	1:20	94	81	LISSTR1		1
	4500	C 9500	1:20	86	194	LISSTR4		4
	4500	ED5	1:20	58[a]	15	LISSTR16		16
	4500	C 9500	1:20	65[a]	38	LISSTR15		15
Elly	5400	ED5	1:20	91	69	LISSTR2		2
	5400	C 9500	1:20	-	32	LISSTR3		3
Sockeye emul.	6,350	ED5	1:20	93	85	LISSTR14		14
	6,350	C 9500	1:20	86	140	LISSTR13		13
IFO 380	11,000	ED5	1:100	18	152	LISSTR8	yes	8
	11,000	C 9500	1:100	39	115	LISSTR7	yes	7
	11,000	ED5	1:50	37	95	LISSTR10	yes	10
	11,000	C 9500	1:50	56	103	LISSTR9	yes	9
	11,000	ED5	1:20	73	126	LISSTR12		12
	11,000	C 9500	1:20	66	101	LISSTR11		11
IFO 380 emul.	14,000	thin ED5	1:20	63	46	LISSTR20		20
	14,000	C 9500	1:20	49	146	LISSTR19		19
Doba emulsion	22,000	thin ED5	1:20	91	109	LISSTR18		18
	22,000	C 9500	1:20	92	90	LISSTR17		17
	22,000	thin ED5	1:50	74	131	LISSTR24		24
	22,000	C 9500	1:50	78	128	LISSTR23	yes	23
	22,000	thin ED5	1:100	71	124	LISSTR22	yes	22
	22,000	C 9500	1:100	73	149	LISSTR21	yes	21
Irene	32,500	ED5	1:20	88	182	LISSTR5		5
	32,500	C 9500	1:20	40	159	LISSTR6		6

The pair of tests that generated the most significant difference in drop size distributions between the Corexit 9500 and ED5 runs were for the weathered Doba crude tests 25 and 26. Consistently smaller VMDs (25 to 50 microns) were measured in the Corexit 9500 dispersion when compared to the ED5 test (50 to 100 microns). The two tests resulted in similar high DE values suggesting that the oil drops in the ED5 dispersion were still small enough to be entrained into the water column. The opposite trend is evident in the Gilda crude oil tests 1 and 4. In this case the oil dispersion generated using ED5 had VMDs generally smaller than those measured in the Corexit 9500 dispersion.

A comparison of the VMDs for the remainder of the tests shows no consistent, significant difference in the oil drop size distributions generated by the two dispersants. This is illustrated in Figure 8. In most of the tests the VMDs of the oil drop distributions fell between 50 and 150 microns. The D50 values reported in Table 5, and plotted in Figure 8, are the average of all of the volume median diameters measured in each test when the oil concentration was elevated at least 1.5 times above the tank background concentration. These average D50 values do not correlate well with the estimates of dispersant effectiveness as seen in Figure 8.

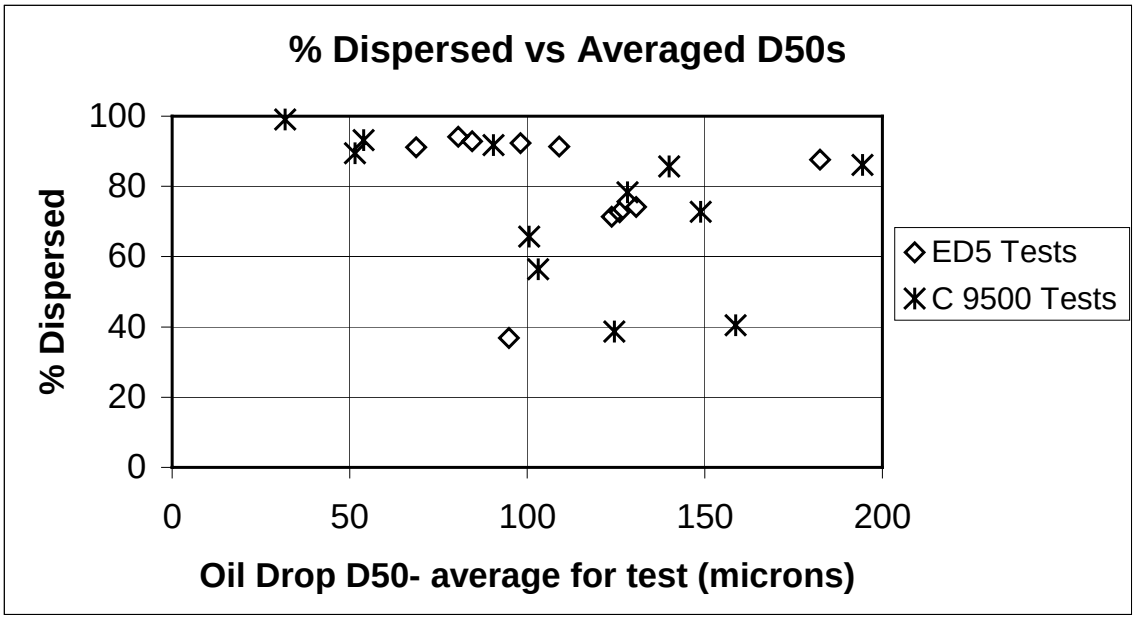


Figure 8. Dispersant Effectiveness versus Average Volume Median Diameter

5.0 Conclusions

It is likely that the high water salinity present during the testing improved the performance of the Corexit 9500 product relative to ED5. If the large-scale tests had been completed under more realistic water salinities (30 ppt) the dispersant effectiveness (DE) values measured for the Corexit 9500 tests likely would have been lower than reported here while the ED5 results would likely have remained the same. The following general observations, however, can be

made when comparing the effectiveness of the ED5 and Corexit 9500 products under similar, albeit high salinity, test conditions.

For the tests on the lower-viscosity oils and emulsion, the two dispersants generated very similar, and high (86 to 94%), effectiveness results.

The ED5 dispersant clearly outperformed Corexit 9500 on Irene crude, the most viscous oil tested. This is consistent with earlier small-scale tests where the ED5 outperformed Corexit 9500 on the most viscous oils tested.

The thinned ED5 and Corexit 9500 generated nearly identical DE at all DORs on the Doba emulsion. The thinned ED5 was about 15% more effective than Corexit 9500 on the IFO 380 emulsion.

On IFO 380 fuel oil Corexit 9500 outperformed the original ED5 formula at the two lower DORs and ED5 was more effective at the 1:20 application.

The thinned ED5 shows more promise than the viscous ED5 at least for oils with viscosities in the 10,000 to 20,000 cP range and at lower doses. This may be because the thinner product can more quickly penetrate the viscous oil prior to being washed away by wave action.

The 17% weathered Hibernia crude oil was almost completely dispersed by Corexit 9500.

Water grab sample TPH measurements matched the total oil concentration output by the LISST very well suggesting that the LISST concentration estimates were accurate representations of the amount of oil being dispersed into the water column.

The oil concentration and drop size distributions measured by the LISST did not identify a clear difference between the two dispersants. A common observation from all tests is that few of the dispersions generated were of extremely fine oil drops. This is likely due to the relatively hard to disperse viscous oils that were used in the test program.

6.0 References

NRC, 2005. Oil Spill Dispersants: Efficacy and Effects. National Research Council of the National Academies. The National Academies Press, Washington, D.C.

SL Ross. 2000a. Feasibility of Using Ohmsett for Dispersant Testing. Report to the MAR Inc., Atlantic Highlands, NJ. March, 2000.

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

SL Ross. 2002a. Dispersant Effectiveness Testing in Cold Water at Ohmsett. Report to U.S. Minerals Management Service, August 2002.

SL Ross. 2002b. Effectiveness Testing of Dispersants in Cold Water and Broken Ice at Ohmsett. Report to ExxonMobil Upstream Reseach Ltd., August 2002.

SL Ross. 2003a. Cold-Water Dispersant Effectiveness Testing on Five Alaskan Oils at Ohmsett. Report to U.S. Minerals Management Service, August 2003.

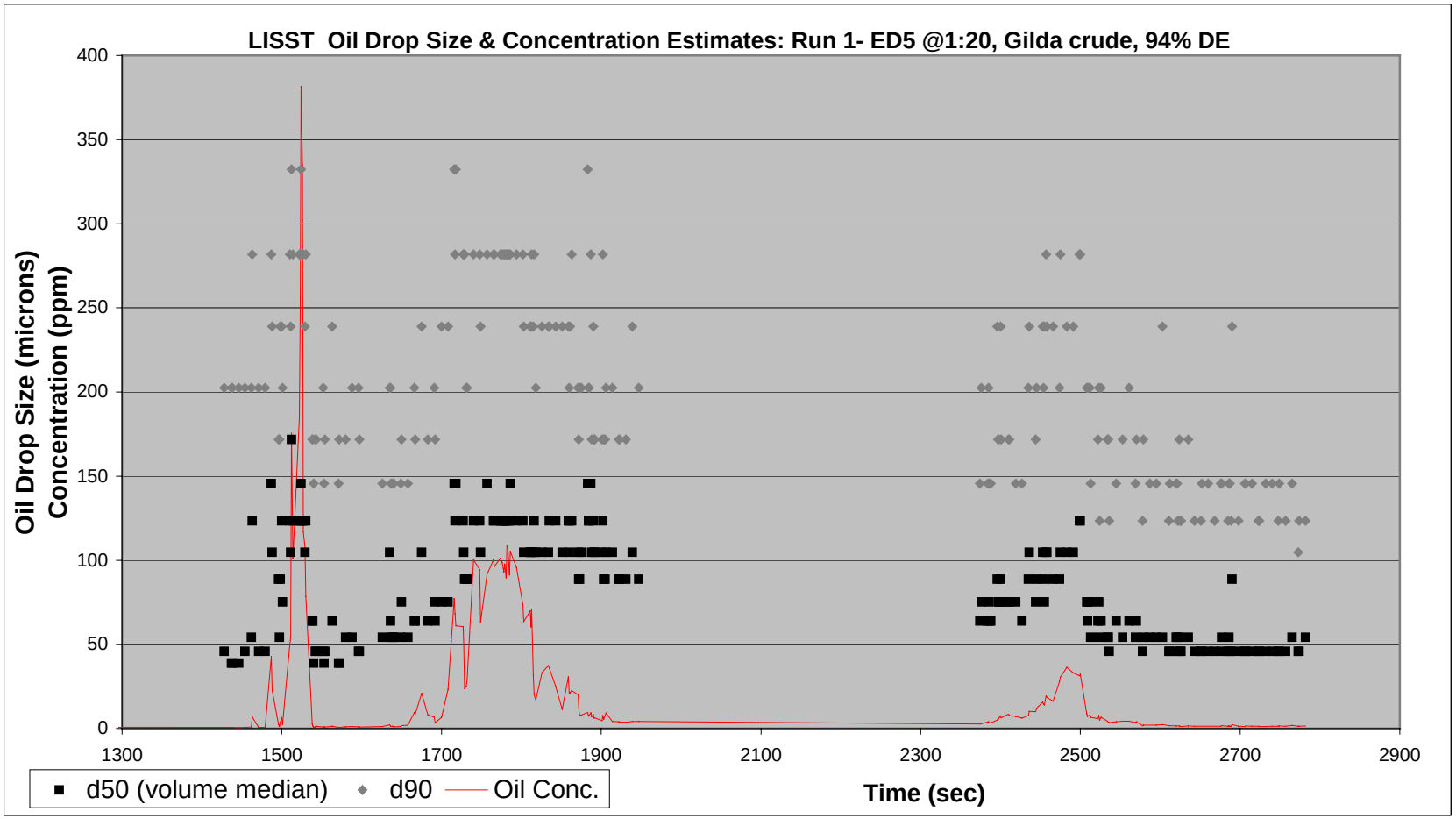
SL Ross 2003b. Research into Techniques to Remove Dissolved Dispersant from Ohmsett Basin Water. Report to U.S. Minerals Management Service, July 2003.

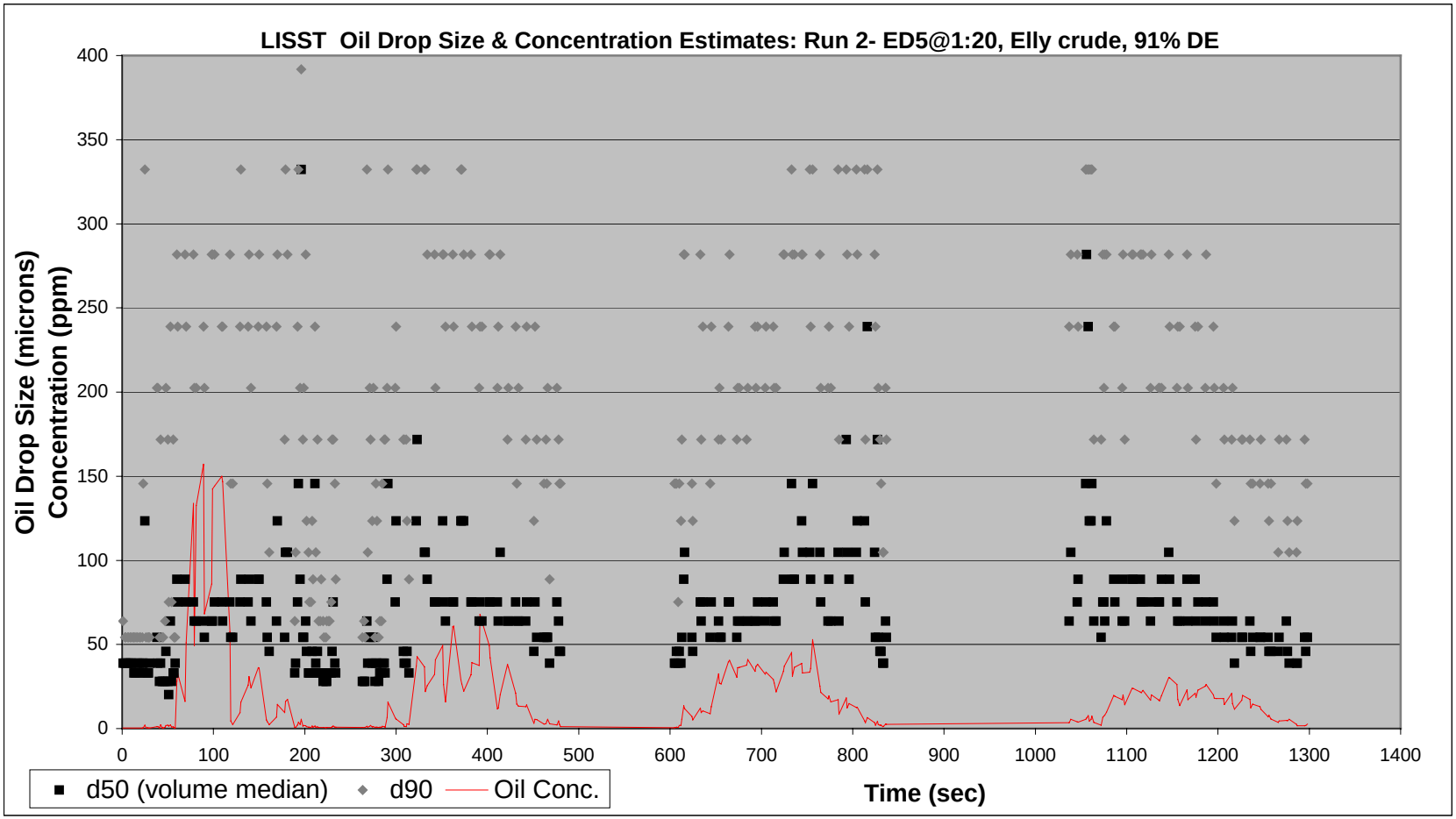
SL Ross. 2004. Correlating the Results of Dispersant Effectiveness Tests Performed at Ohmsett with Identical Tests Performed At Sea. Report to U.S. Minerals Management Service, 2004)

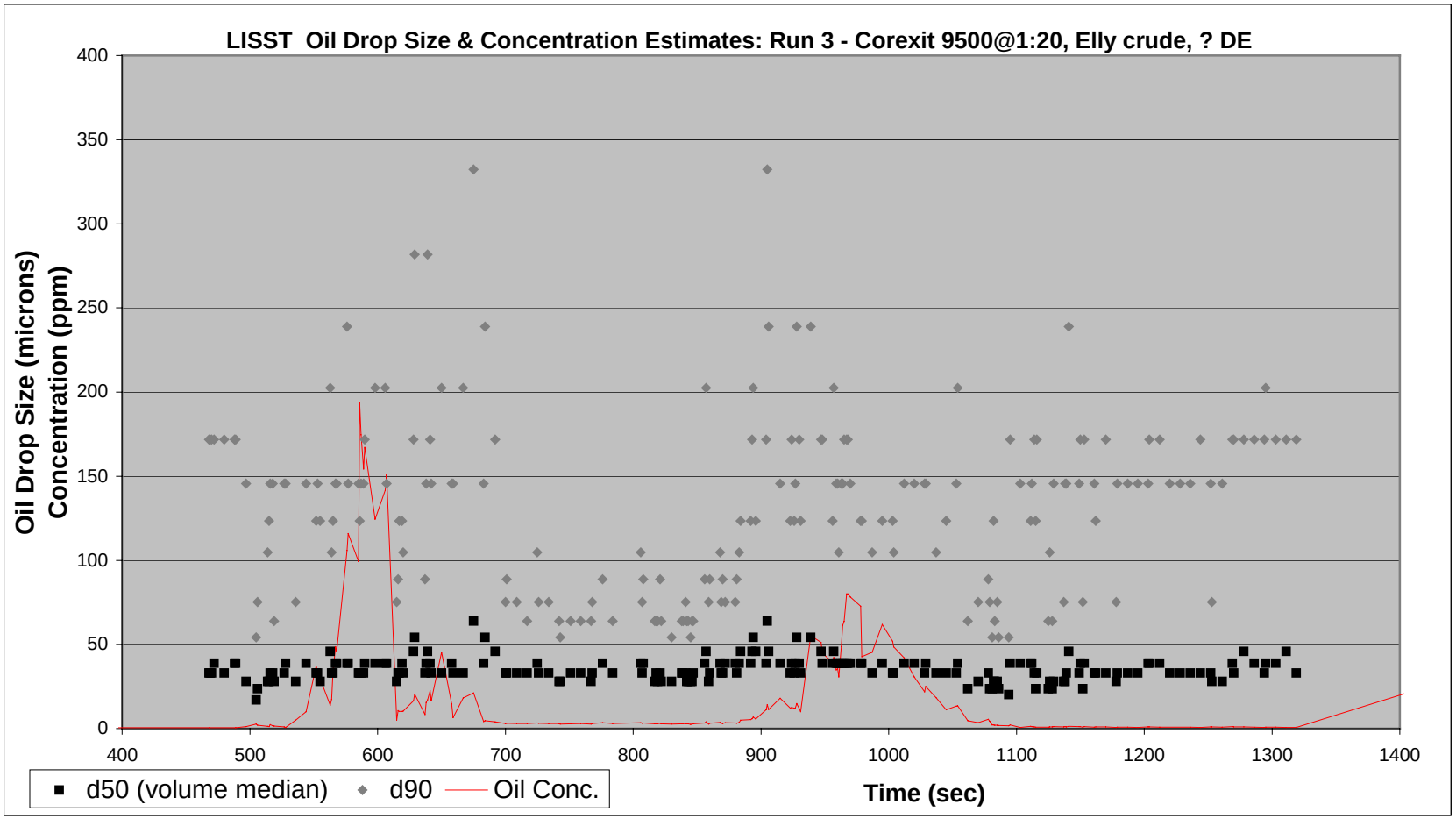
SL Ross. 2006. Dispersant Effectiveness Testing On Viscous, U.S. Outer Continental Shelf Crude Oil. Report to U.S. Minerals Management Service, January 2006.

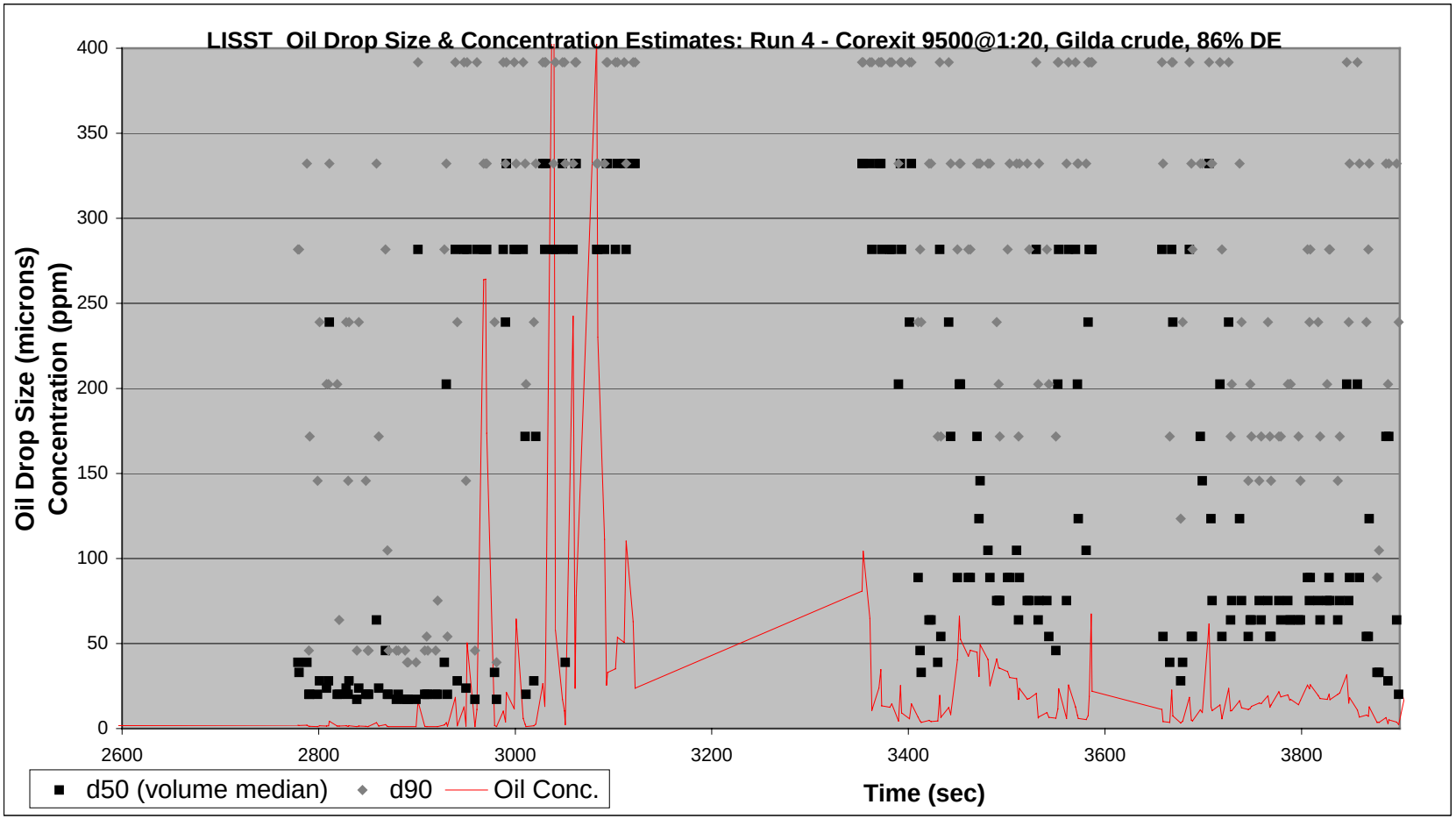
SL Ross. 2007. Tank Tests to Evaluate the Effectiveness of Dispersants in Water of Varying Salinity. Report to ExxonMobil Upstream Research Company. December 2007.

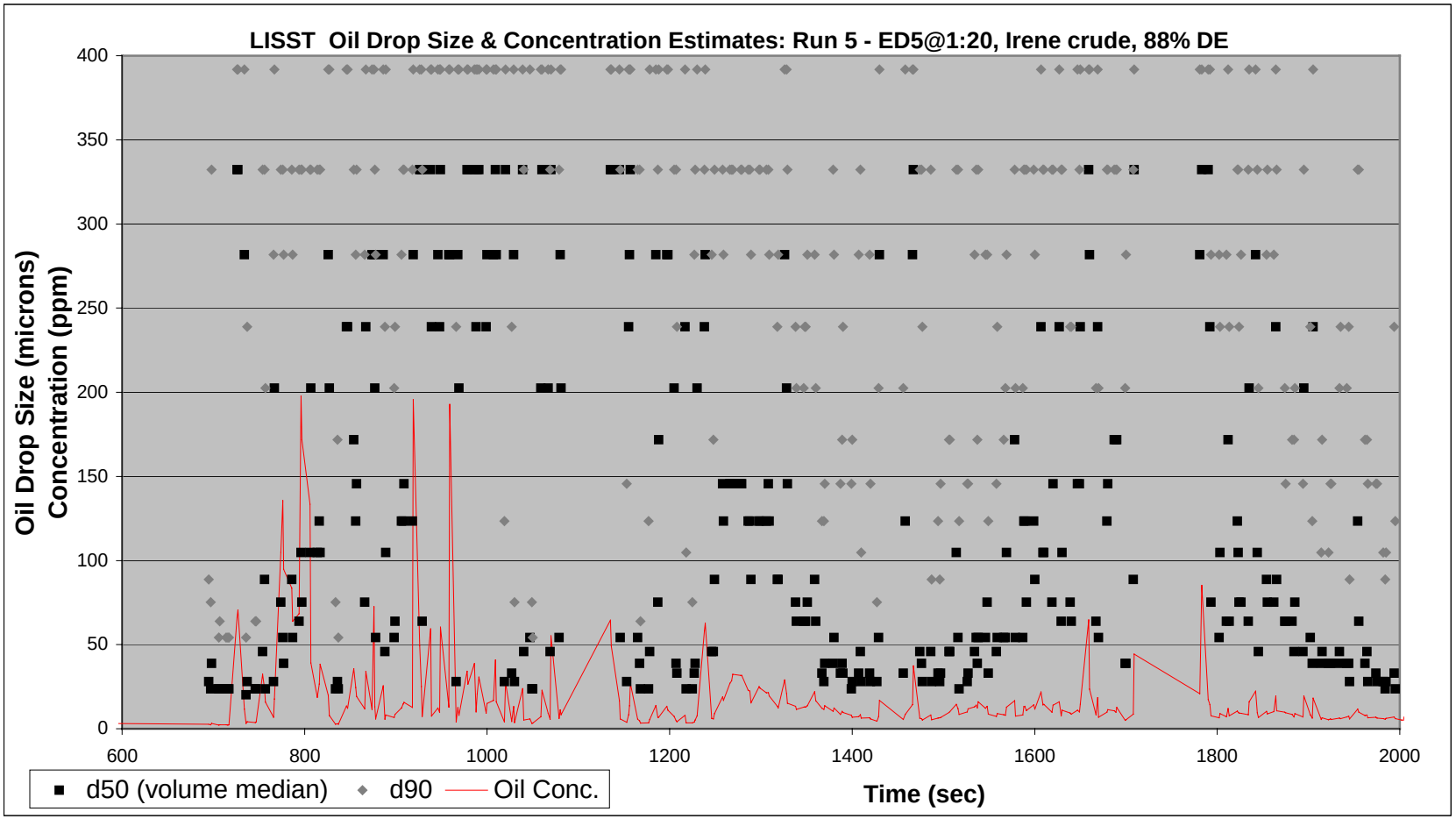
7.0 Appendix A. In-Water Oil Characterization

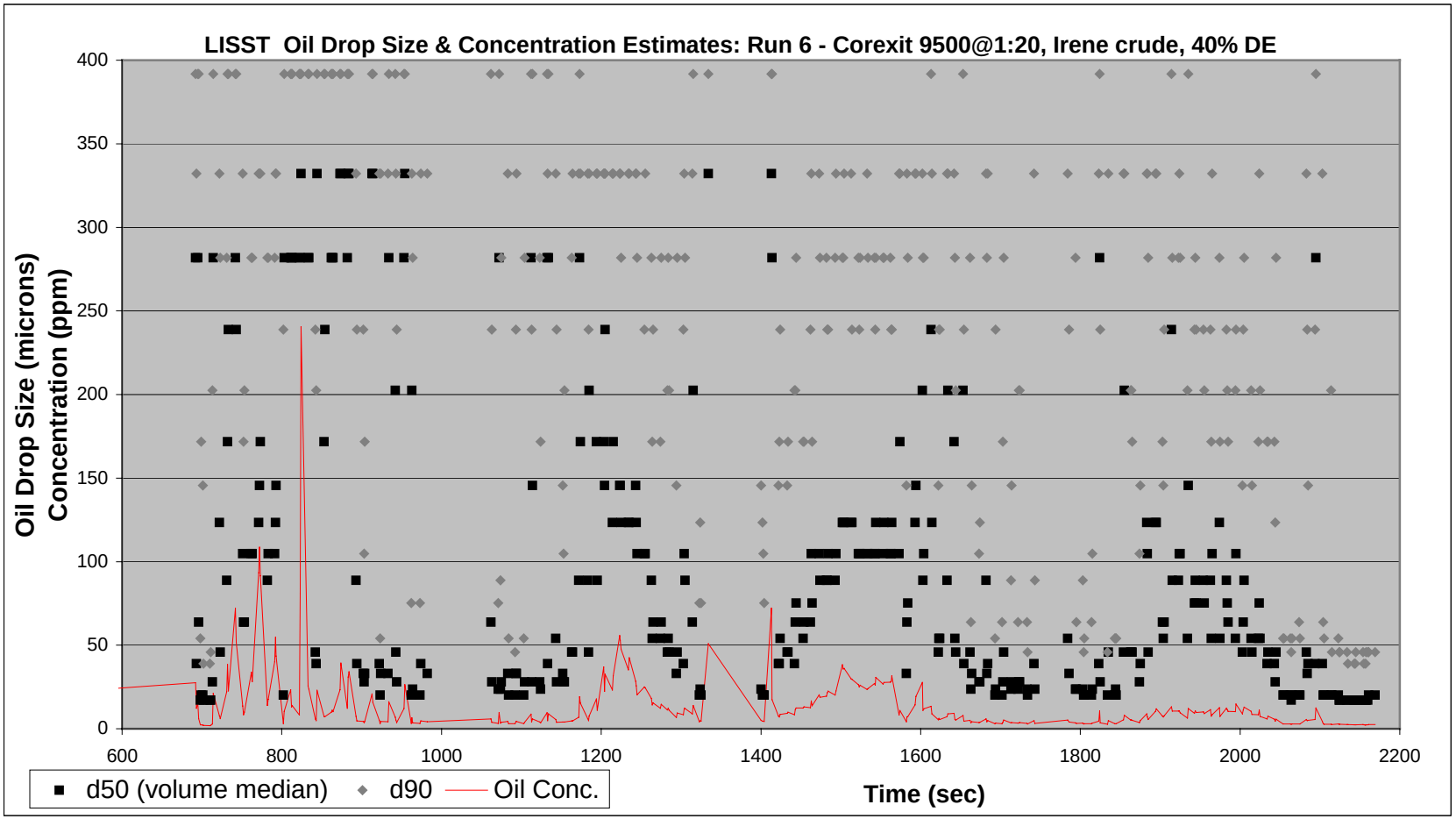


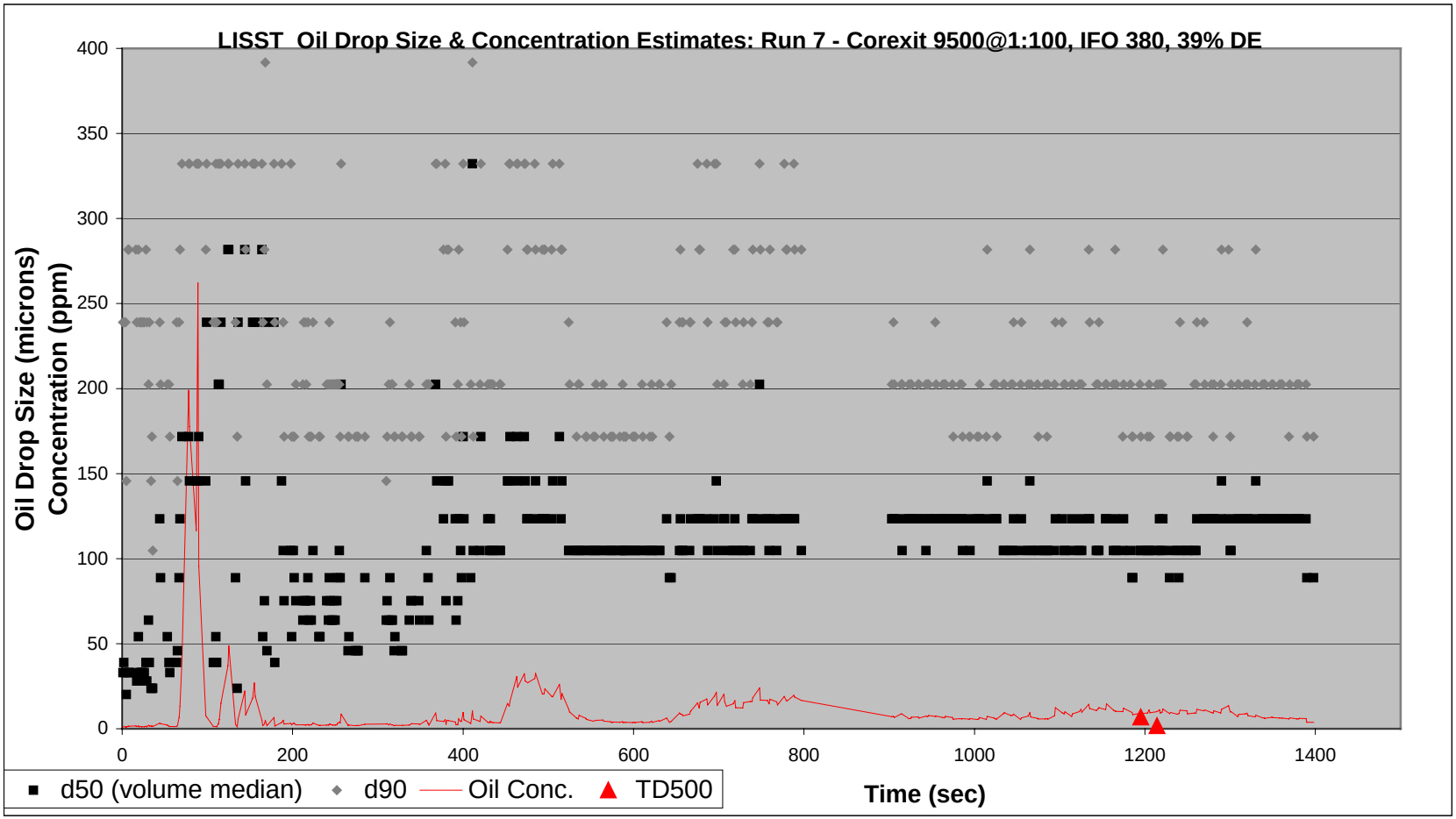

LISST Oil Drop Size & Concentration Estimates: Run 2- ED5@1:20, Elly crude, 91% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
Time (sec)
d50 (volume median)
d90
Oil Conc.

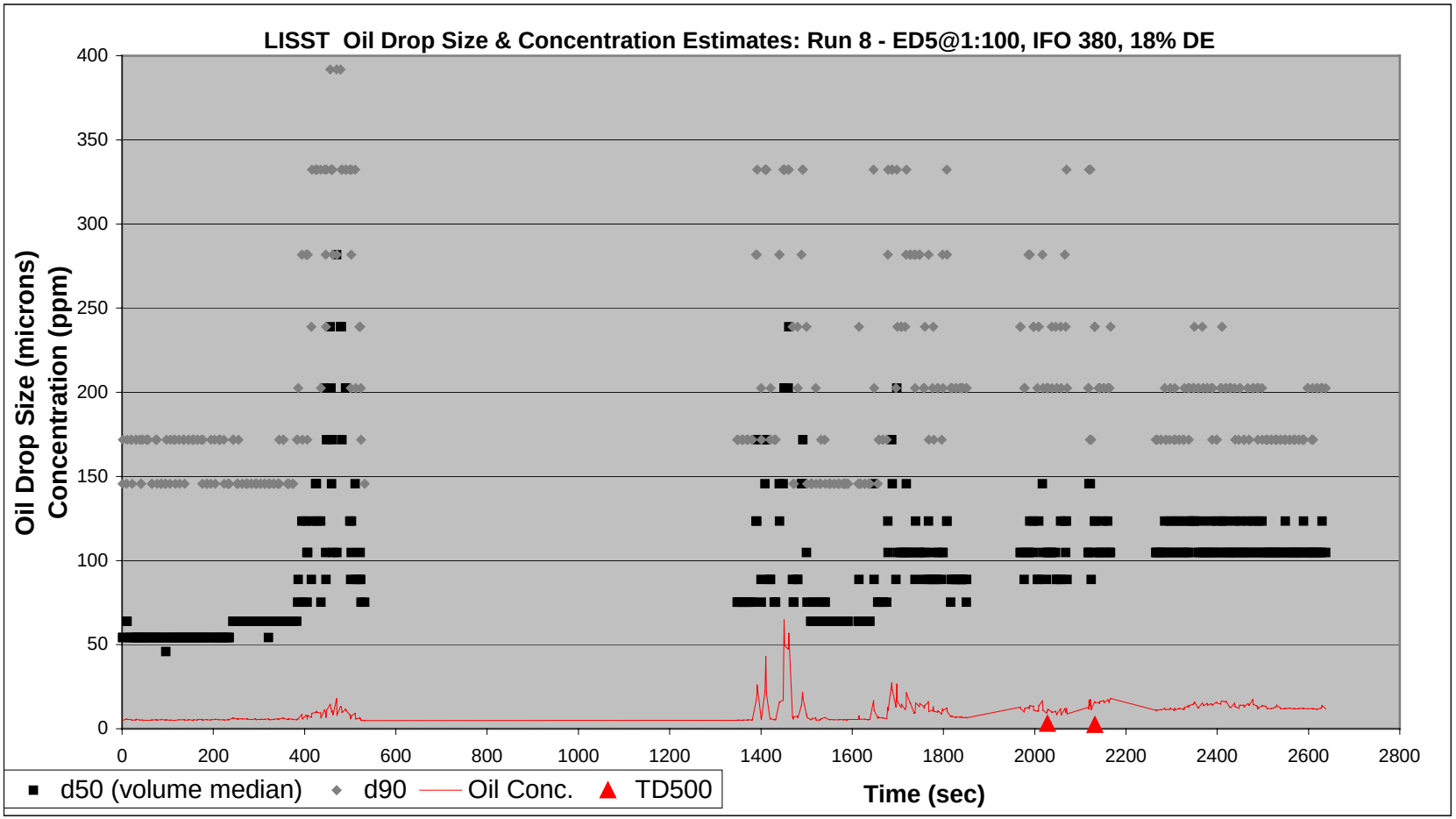

LISST Oil Drop Size & Concentration Estimates: Run 3 - Corexit 9500@1:20, Elly crude, ? DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
400
500
600
700
800
900
1000
1100
1200
1300
1400
Time (sec)
d50 (volume median)
d90
Oil Conc.

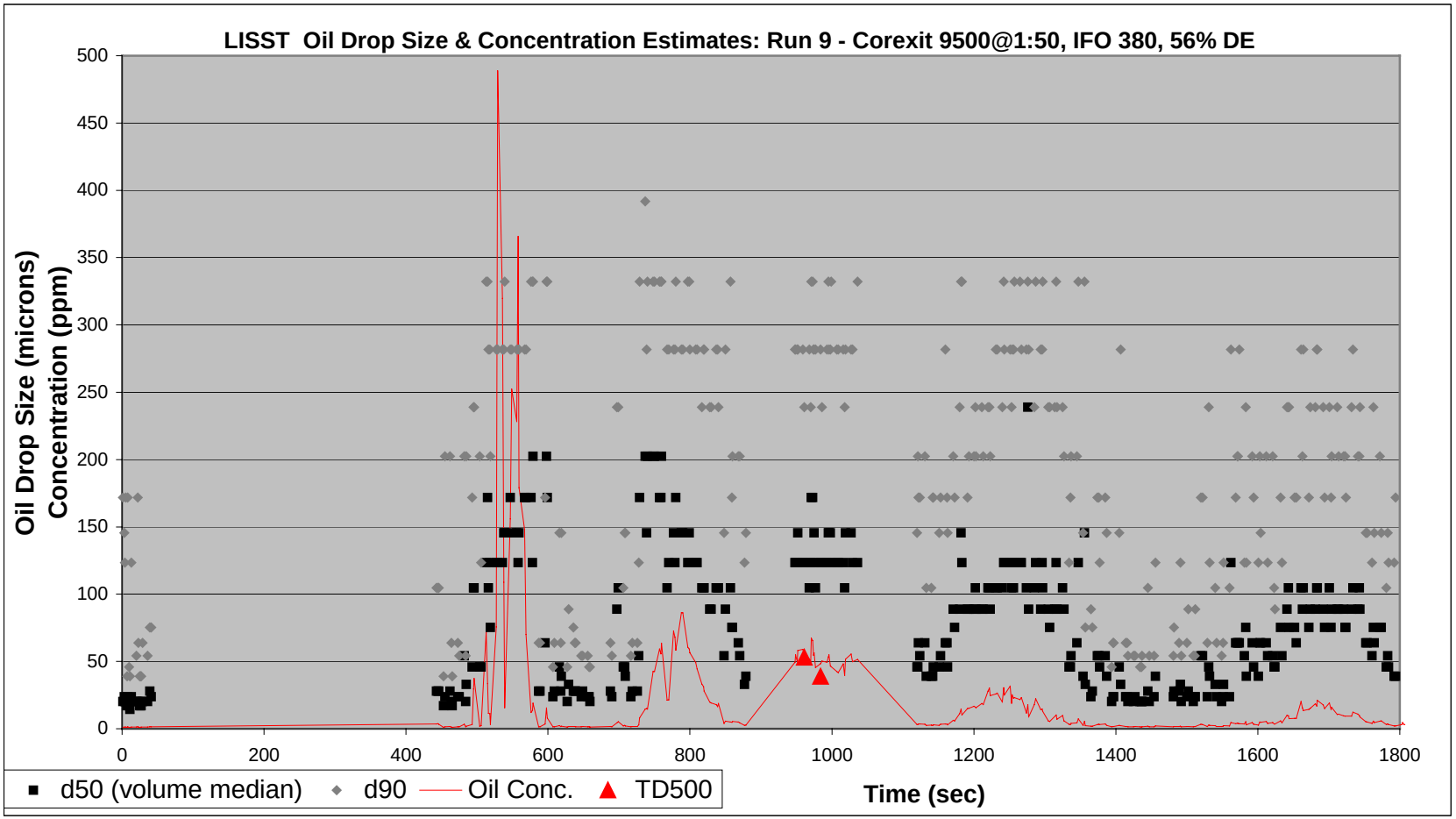

LISST Oil Drop Size & Concentration Estimates: Run 4 - Corexit 9500@1:20, Gilda crude, 86% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
2600
2800
3000
3200
3400
3600
3800
Time (sec)
d50 (volume median)
d90
Oil Conc.

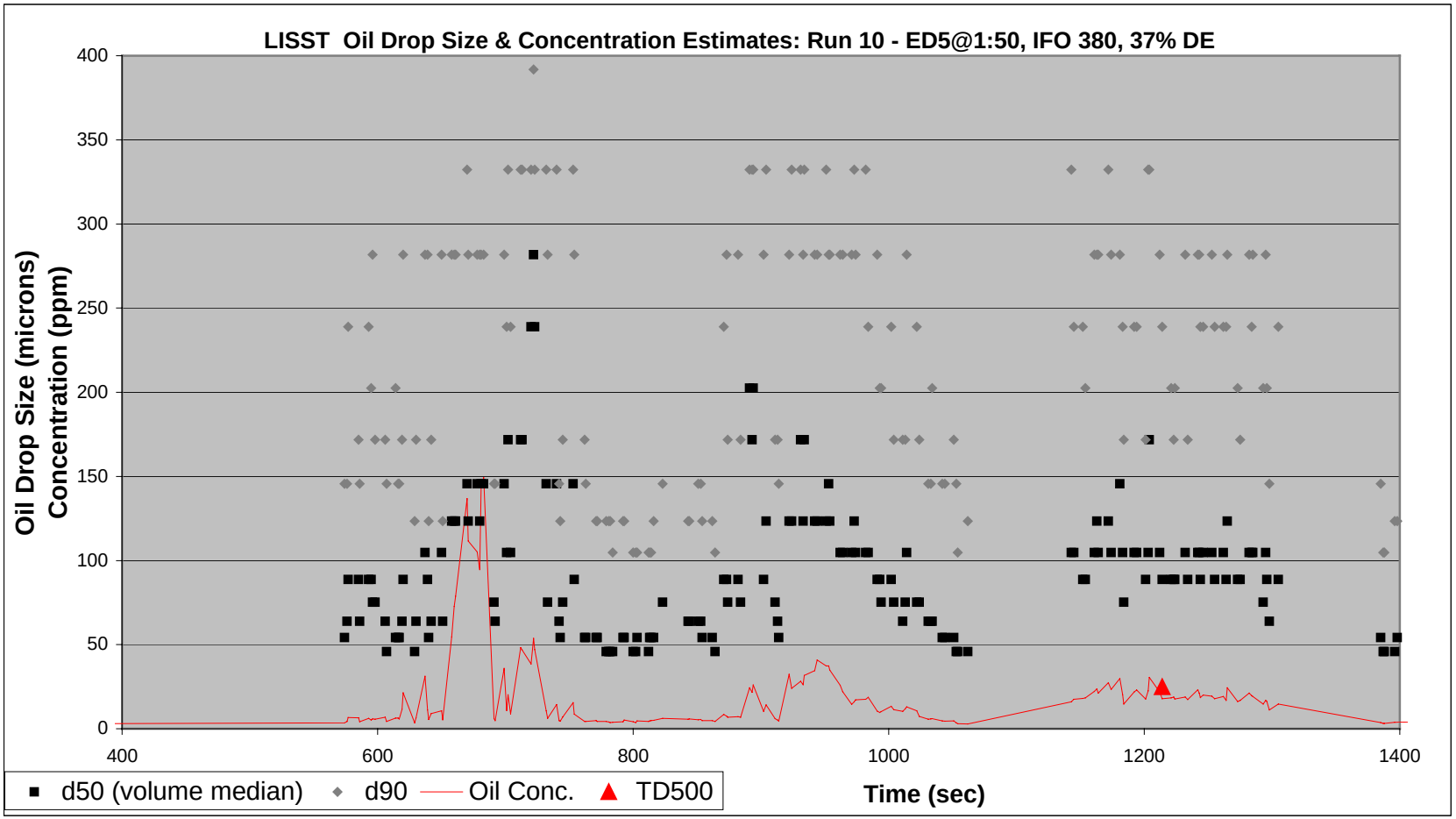

LISST Oil Drop Size & Concentration Estimates: Run 5 - ED5@1:20, Irene crude, 88% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.

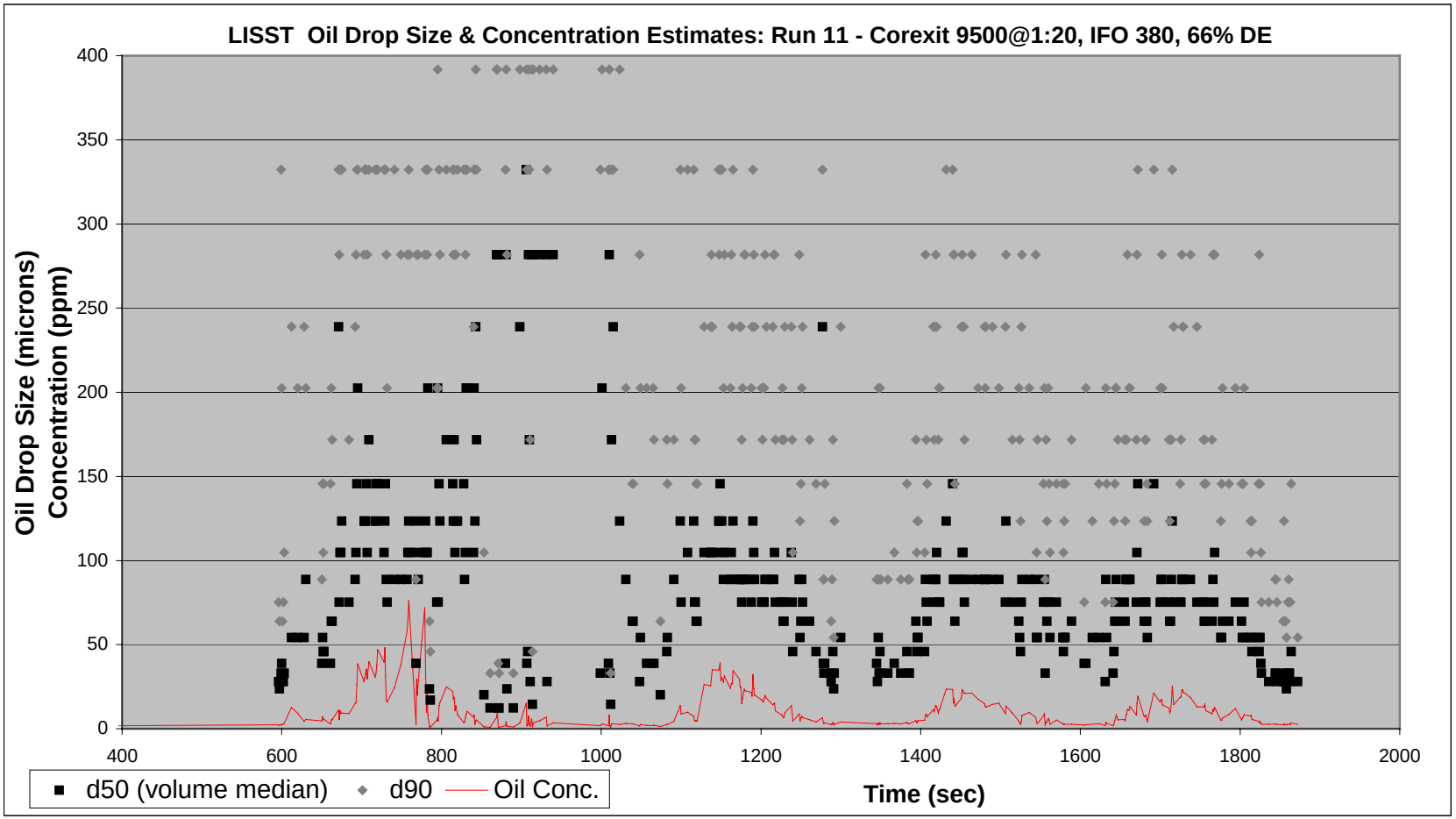

LISST Oil Drop Size & Concentration Estimates: Run 6 - Corexit 9500@1:20, Irene crude, 40% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
2200
Time (sec)
d50 (volume median)
d90
Oil Conc.

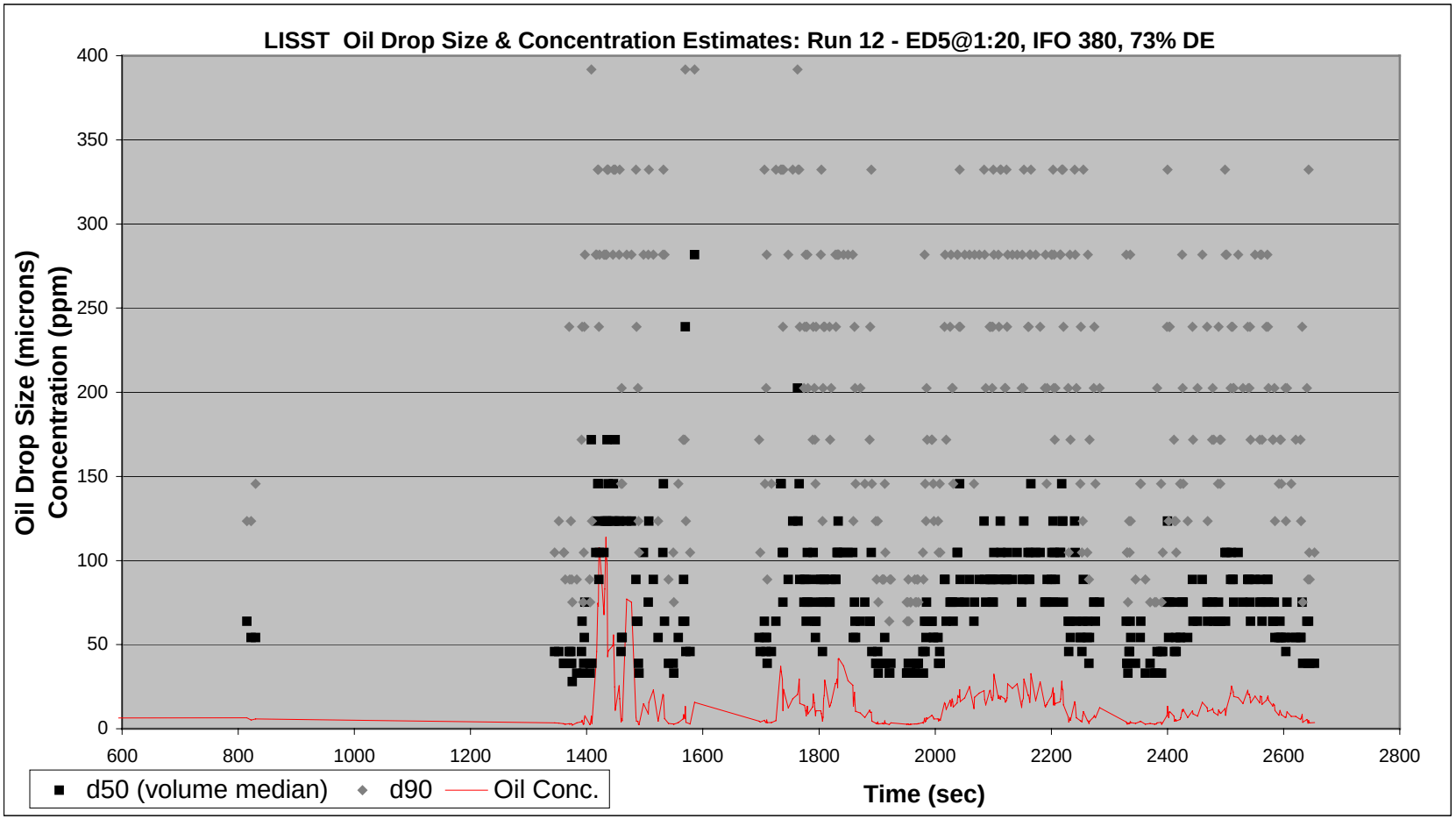

LISST Oil Drop Size & Concentration Estimates: Run 7 - Corexit 9500@1:100, IFO 380, 39% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500

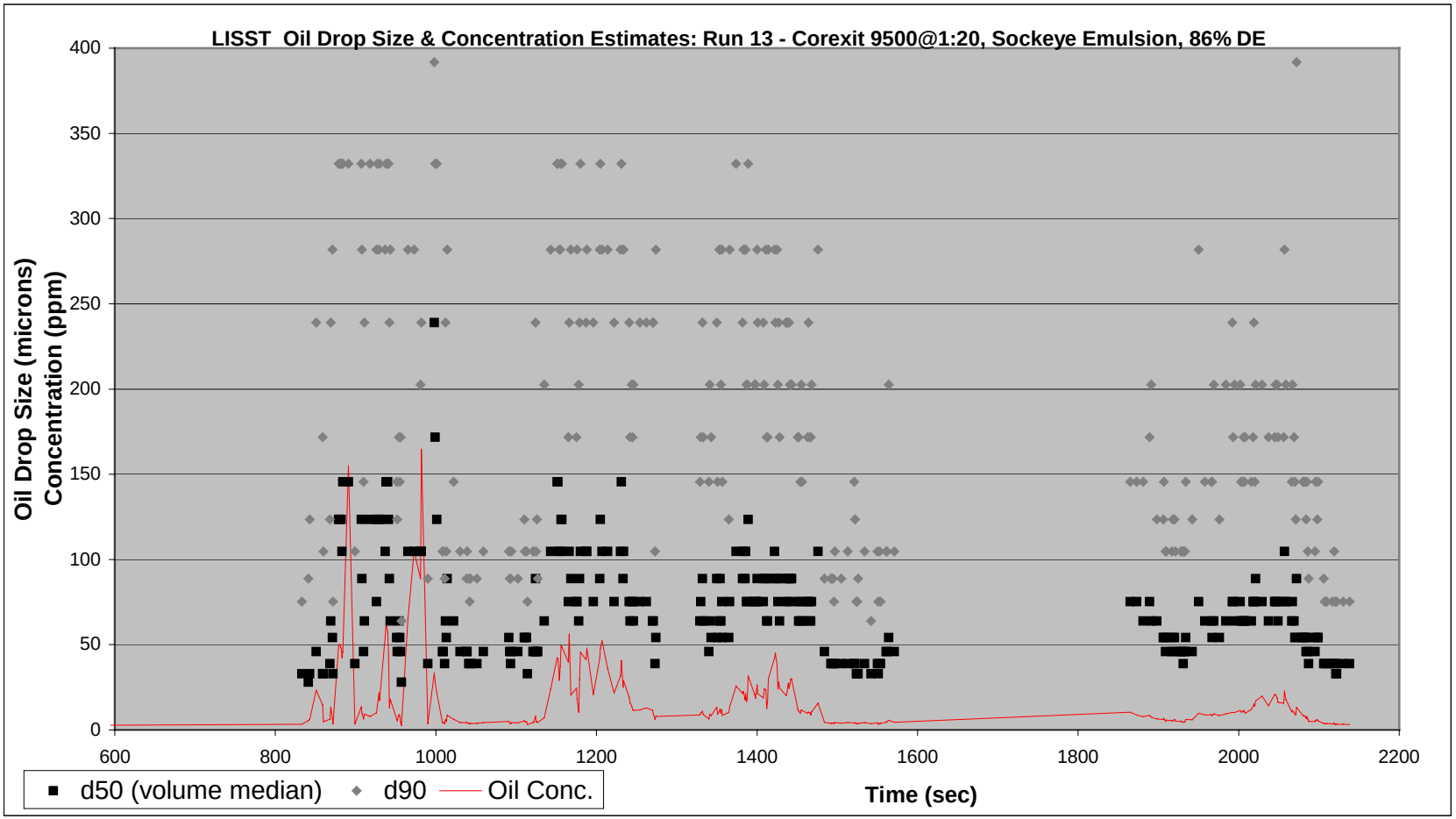

LISST Oil Drop Size & Concentration Estimates: Run 8 - ED5@1:100, IFO 380, 18% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500

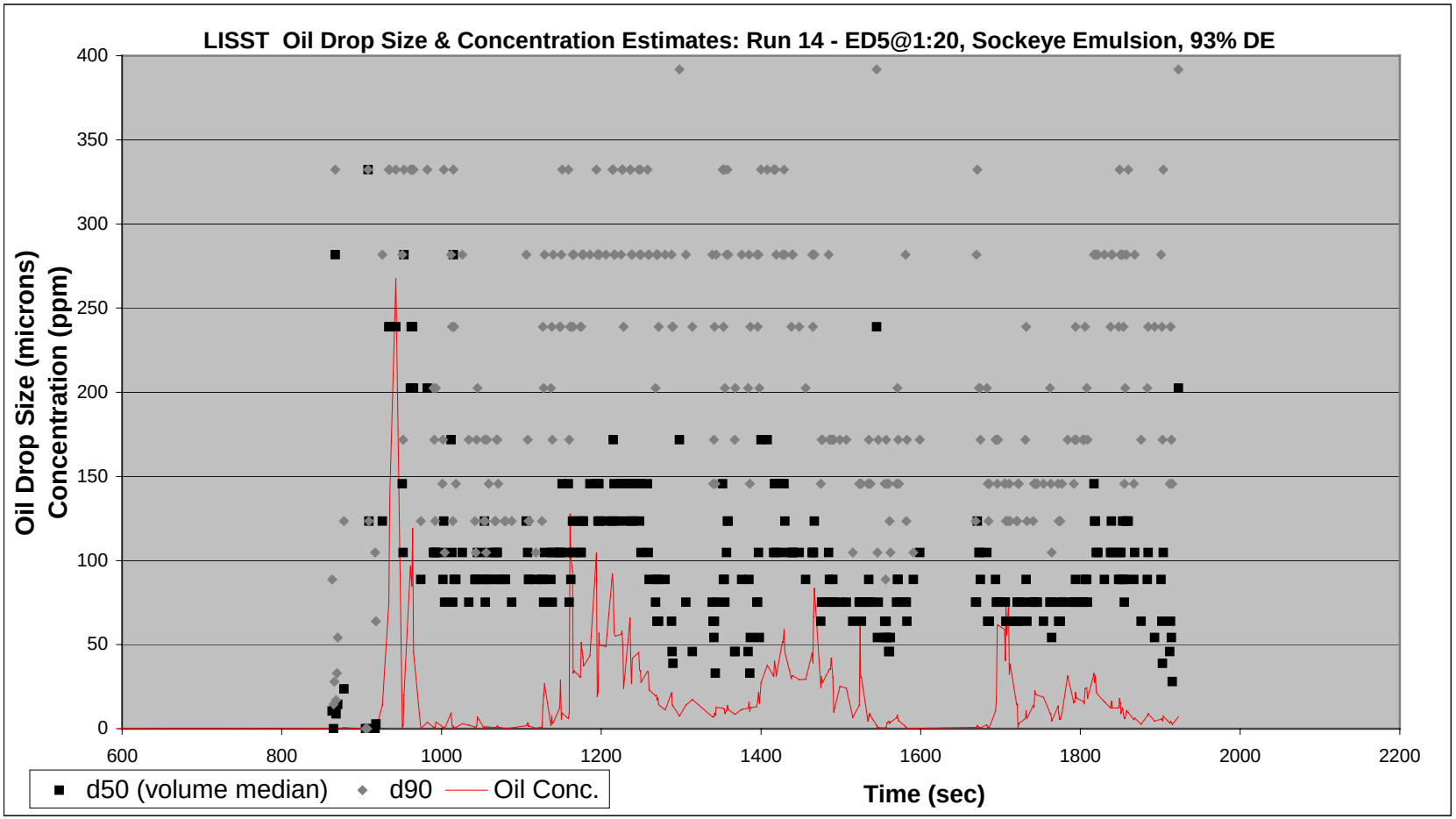

LISST Oil Drop Size & Concentration Estimates: Run 9 - Corexit 9500@1:50, IFO 380, 56% DE
Oil Drop Size (microns)
Concentration (ppm)
500
450
400
350
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
1600
1800
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500

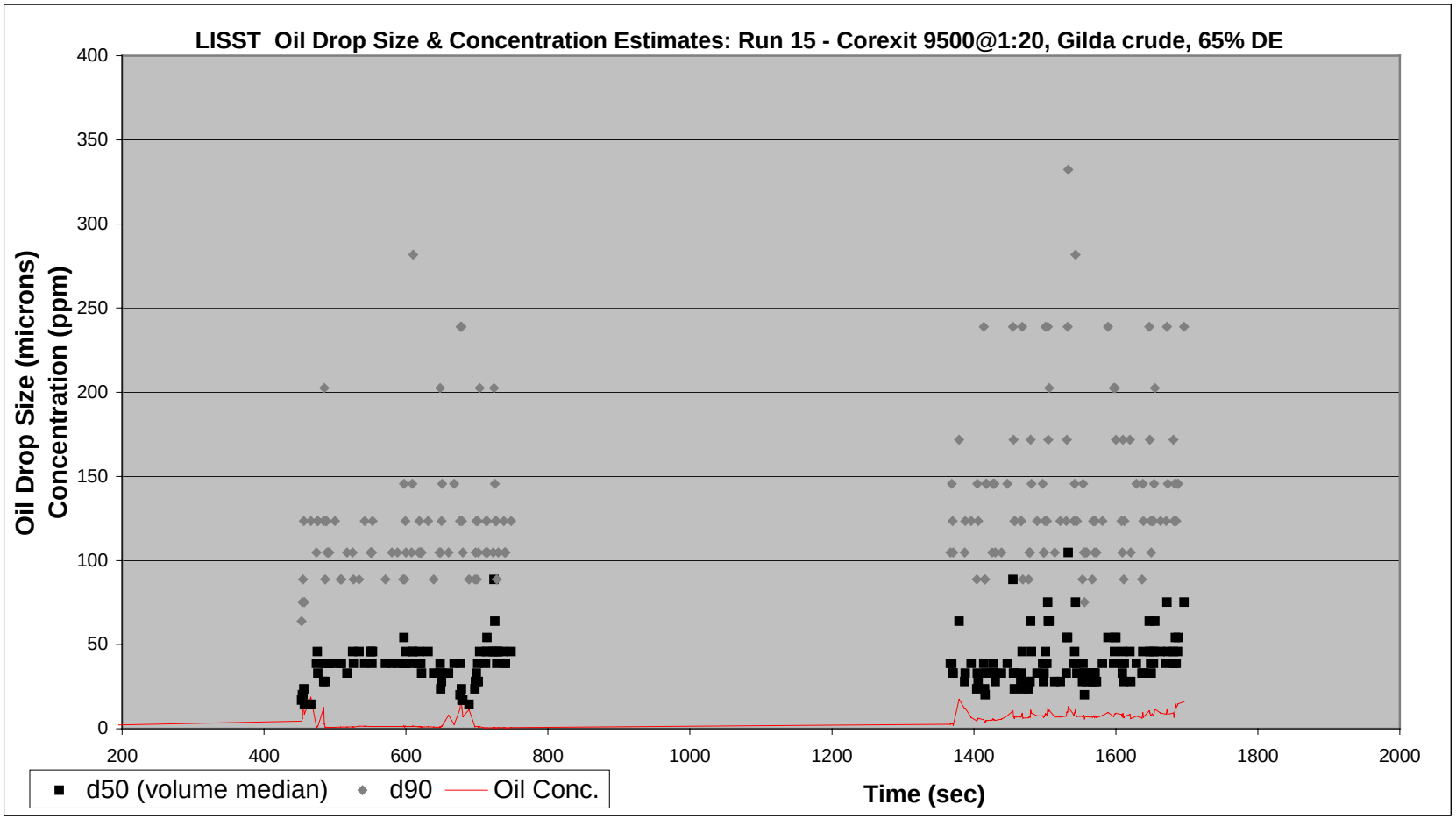

LISST Oil Drop Size & Concentration Estimates: Run 10 - ED5@1:50, IFO 380, 37% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
400
600
800
1000
1200
1400
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500

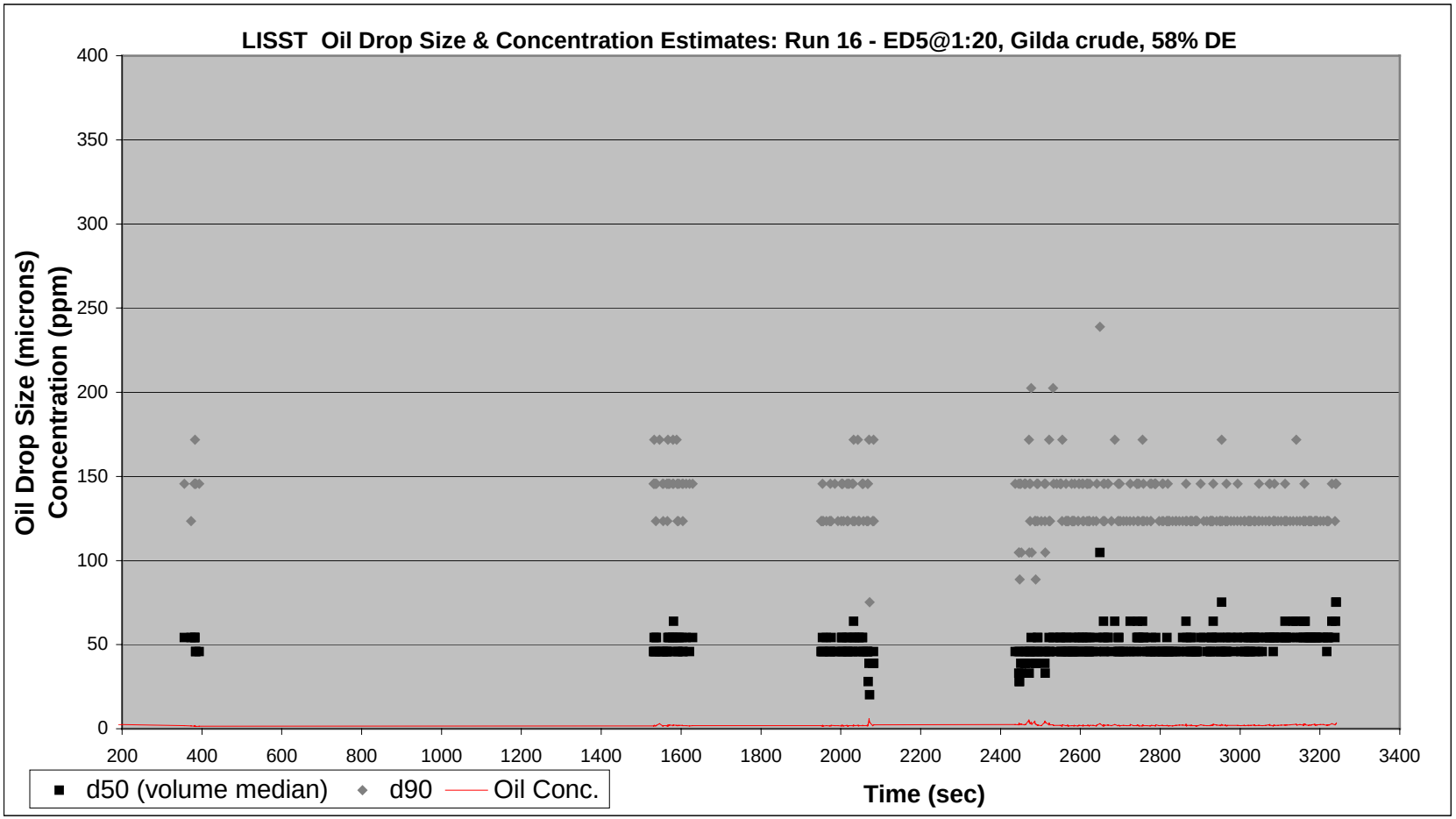

LISST Oil Drop Size & Concentration Estimates: Run 11 - Corexit 9500@1:20, IFO 380, 66% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
400
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 12 - ED5@1:20, IFO 380, 73% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 13 - Corexit 9500@1:20, Sockeye Emulsion, 86% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
2200
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 14 - ED5@1:20, Sockeye Emulsion, 93% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
2200
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 15 - Corexit 9500@1:20, Gilda crude, 65% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.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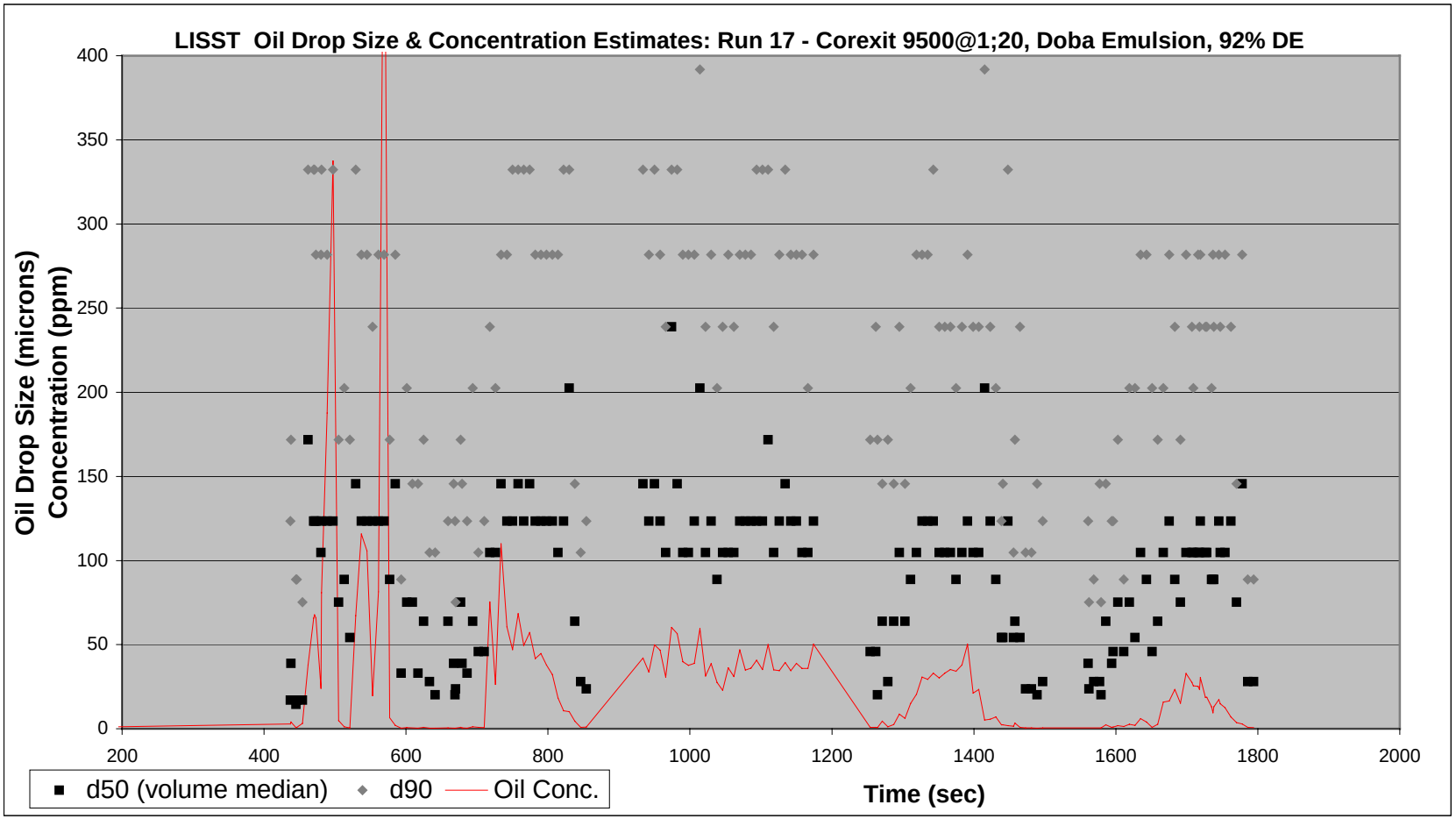
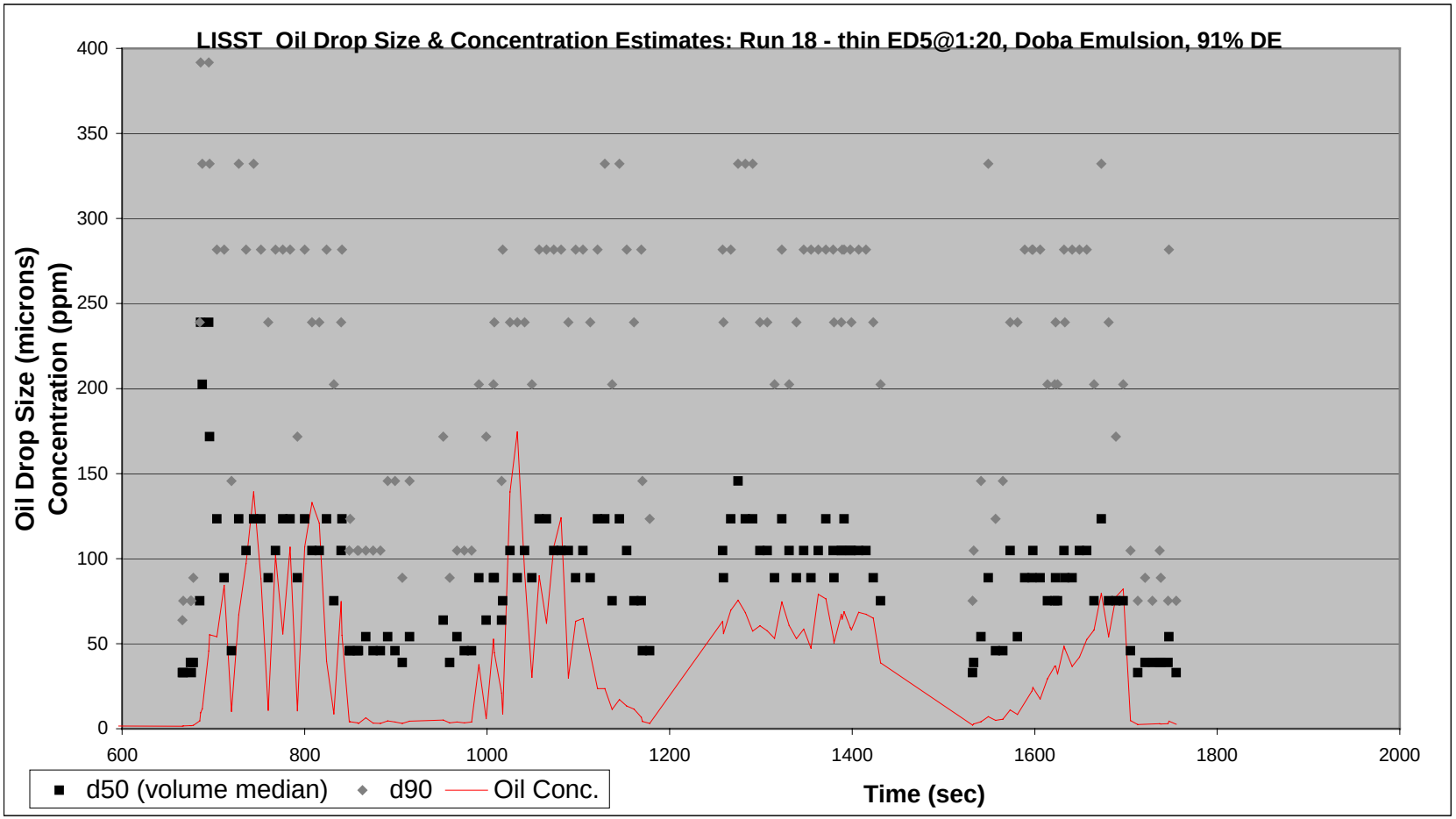
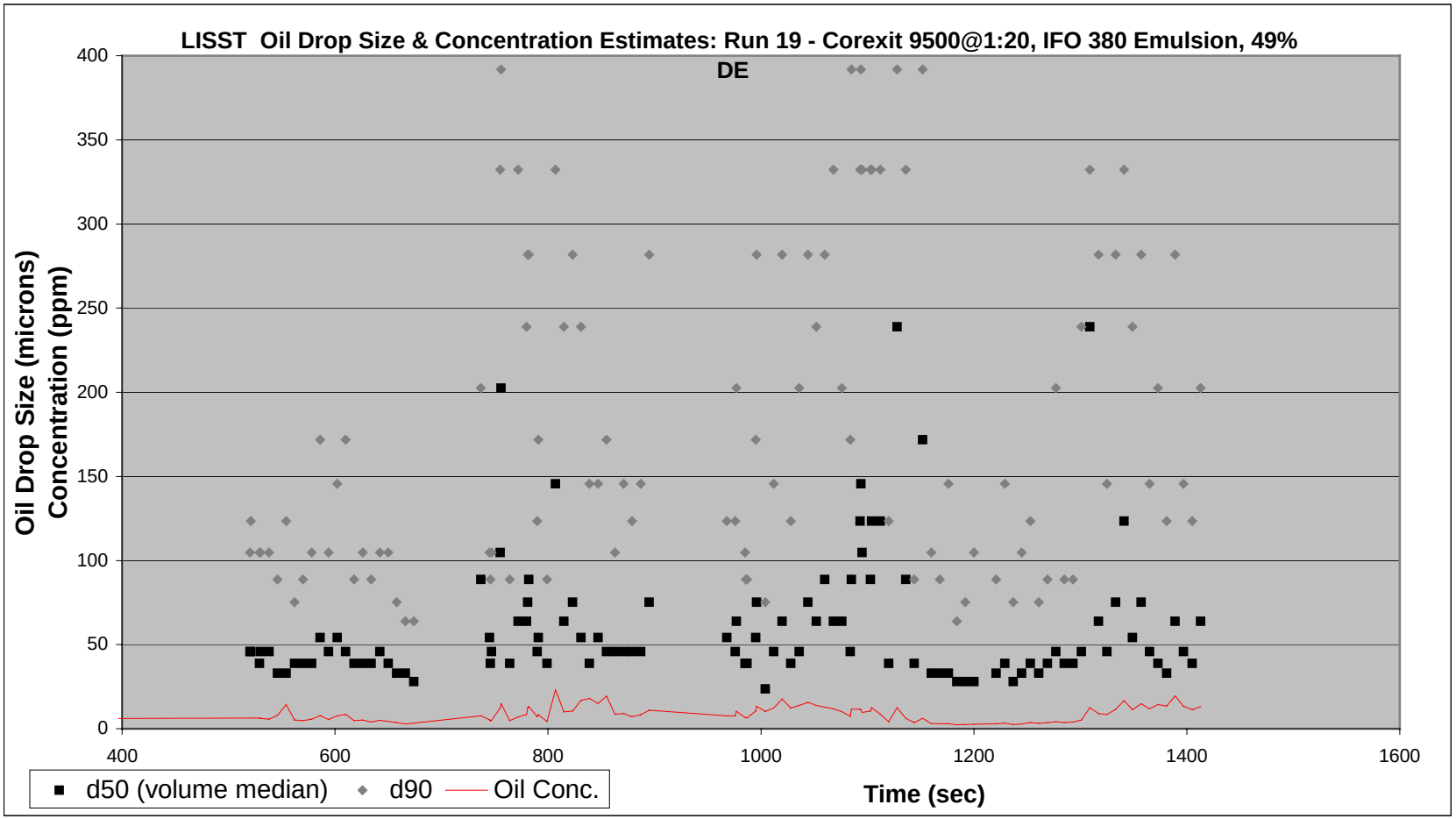
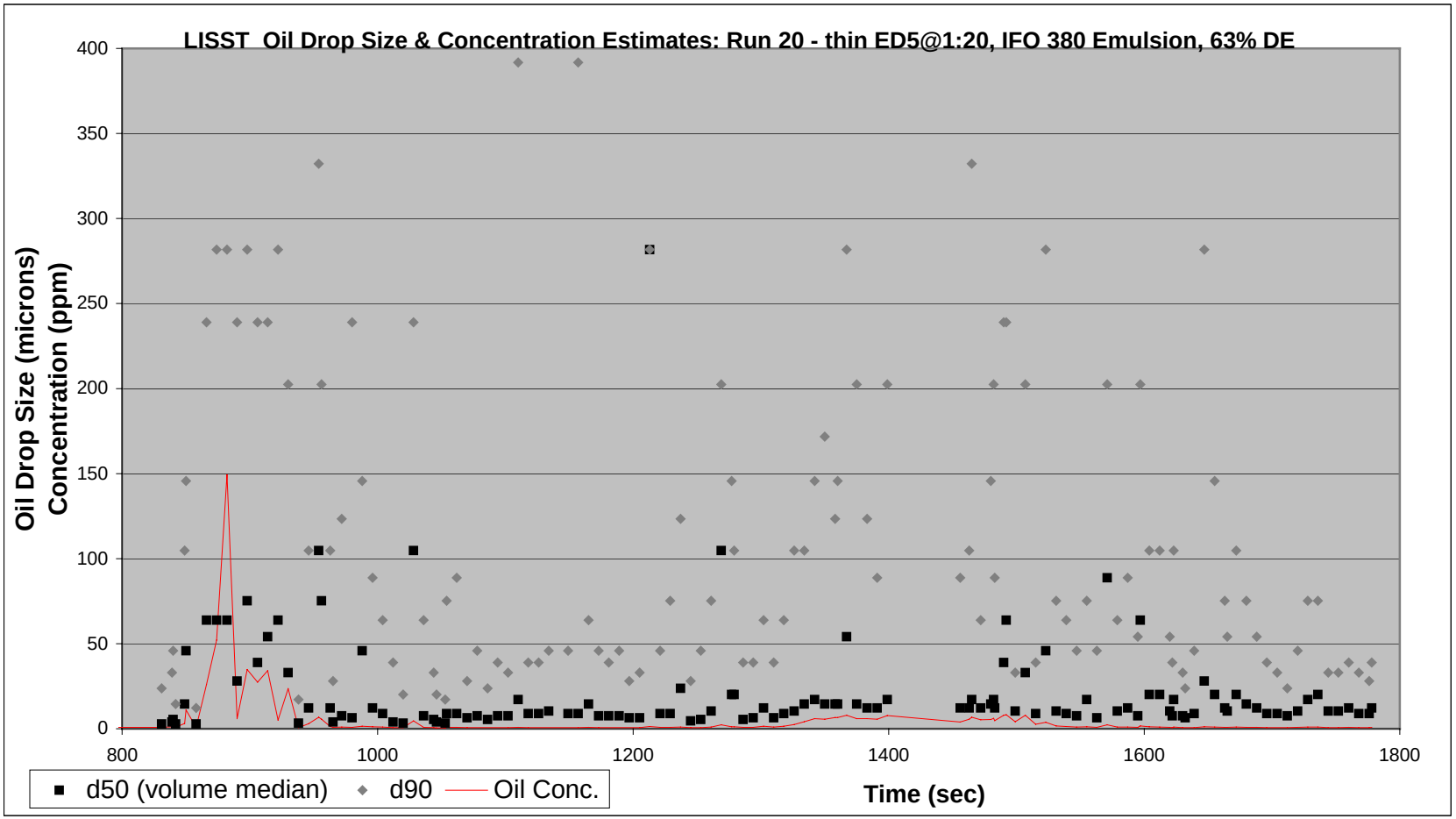
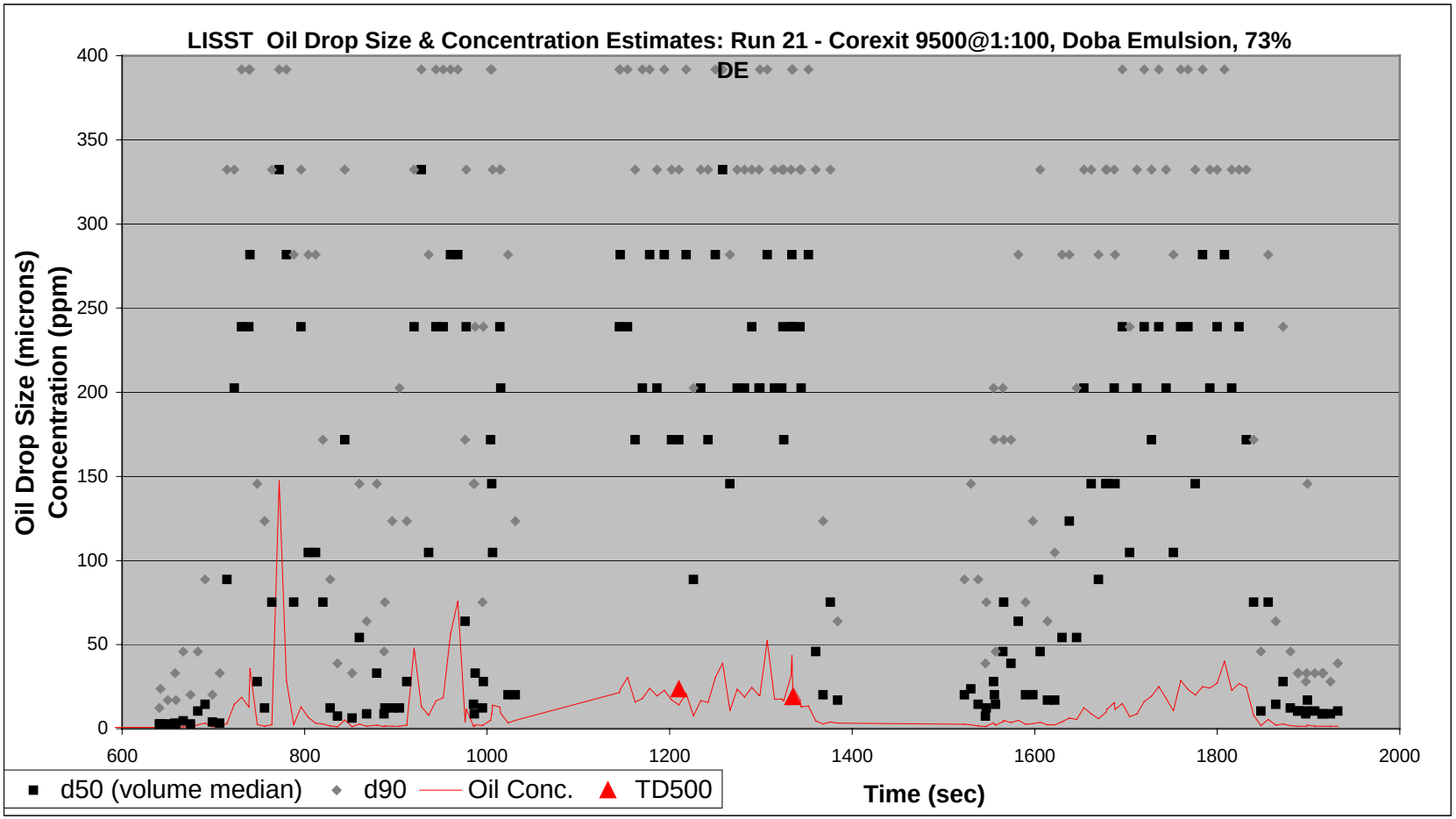
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
Time (sec)
d50 (volume median)
d90
Oil Conc.

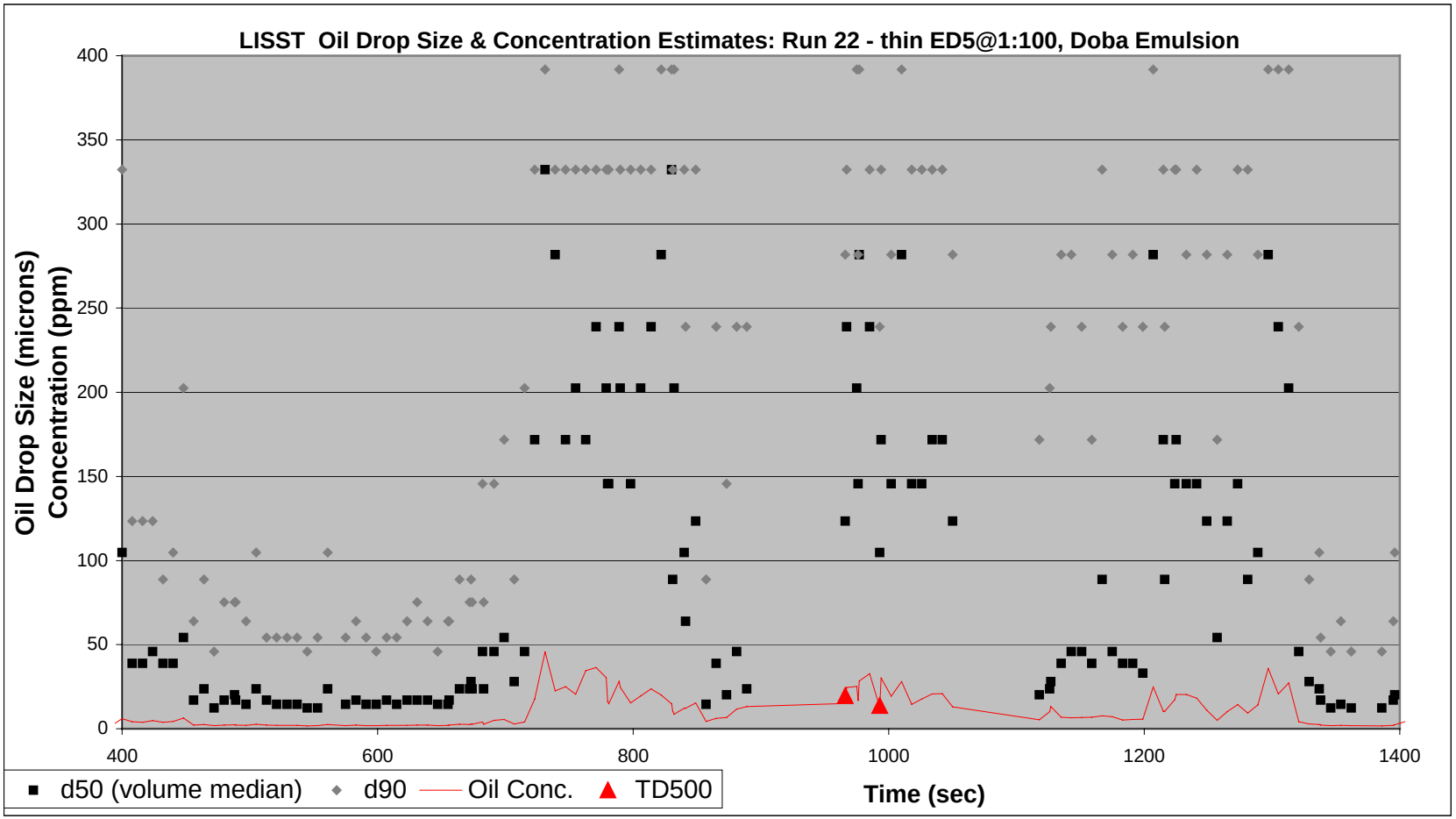

LISST Oil Drop Size & Concentration Estimates: Run 17 - Corexit 9500@1;20, Doba Emulsion, 92% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.

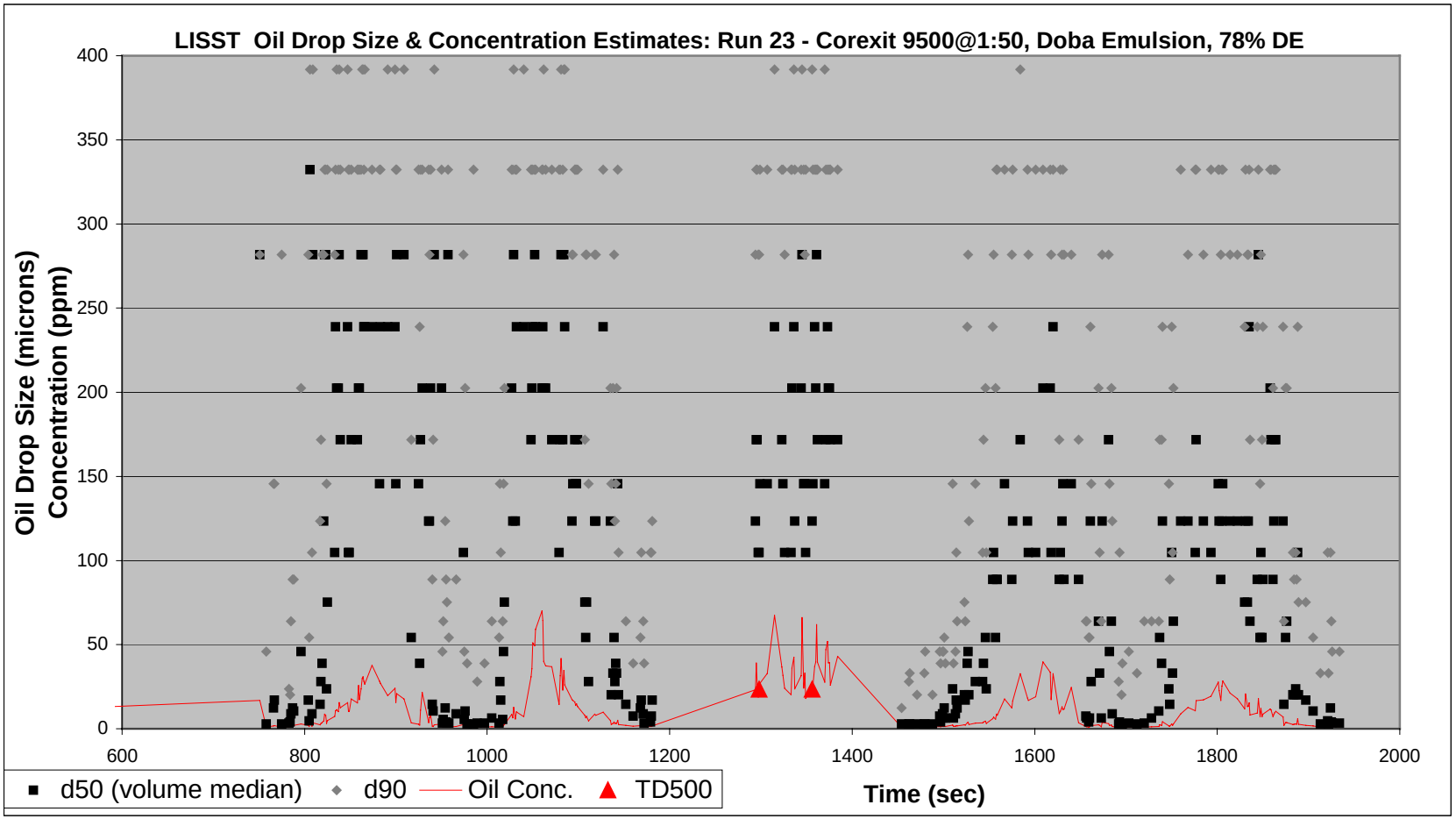

LISST Oil Drop Size & Concentration Estimates: Run 18 - thin ED5@1:20, Doba Emulsion, 91% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.

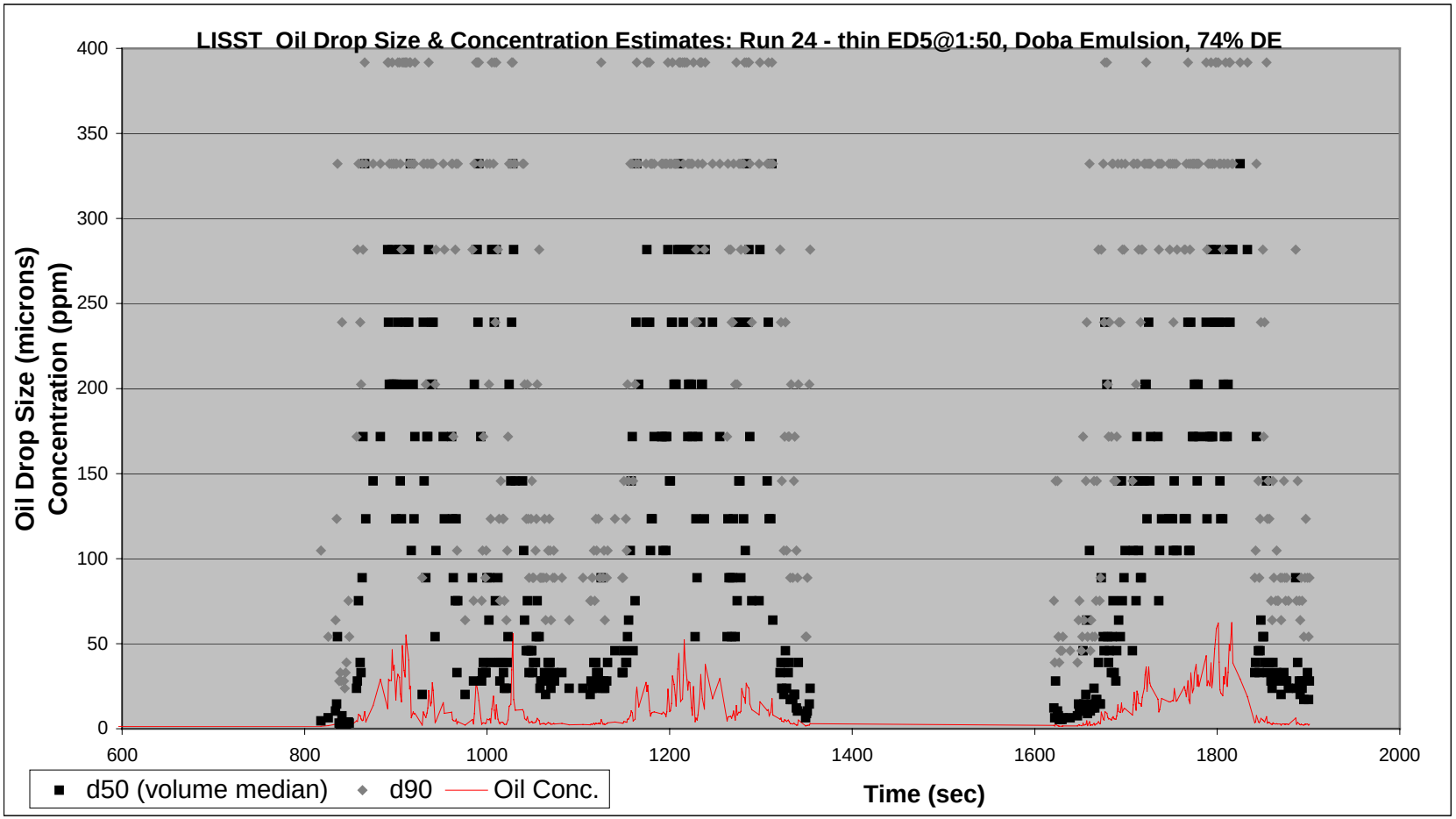

LISST Oil Drop Size & Concentration Estimates: Run 19 - Corexit 9500@1:20, IFO 380 Emulsion, 49% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
400
600
800
1000
1200
1400
1600
Time (sec)
d50 (volume median)
d90
Oil Conc.

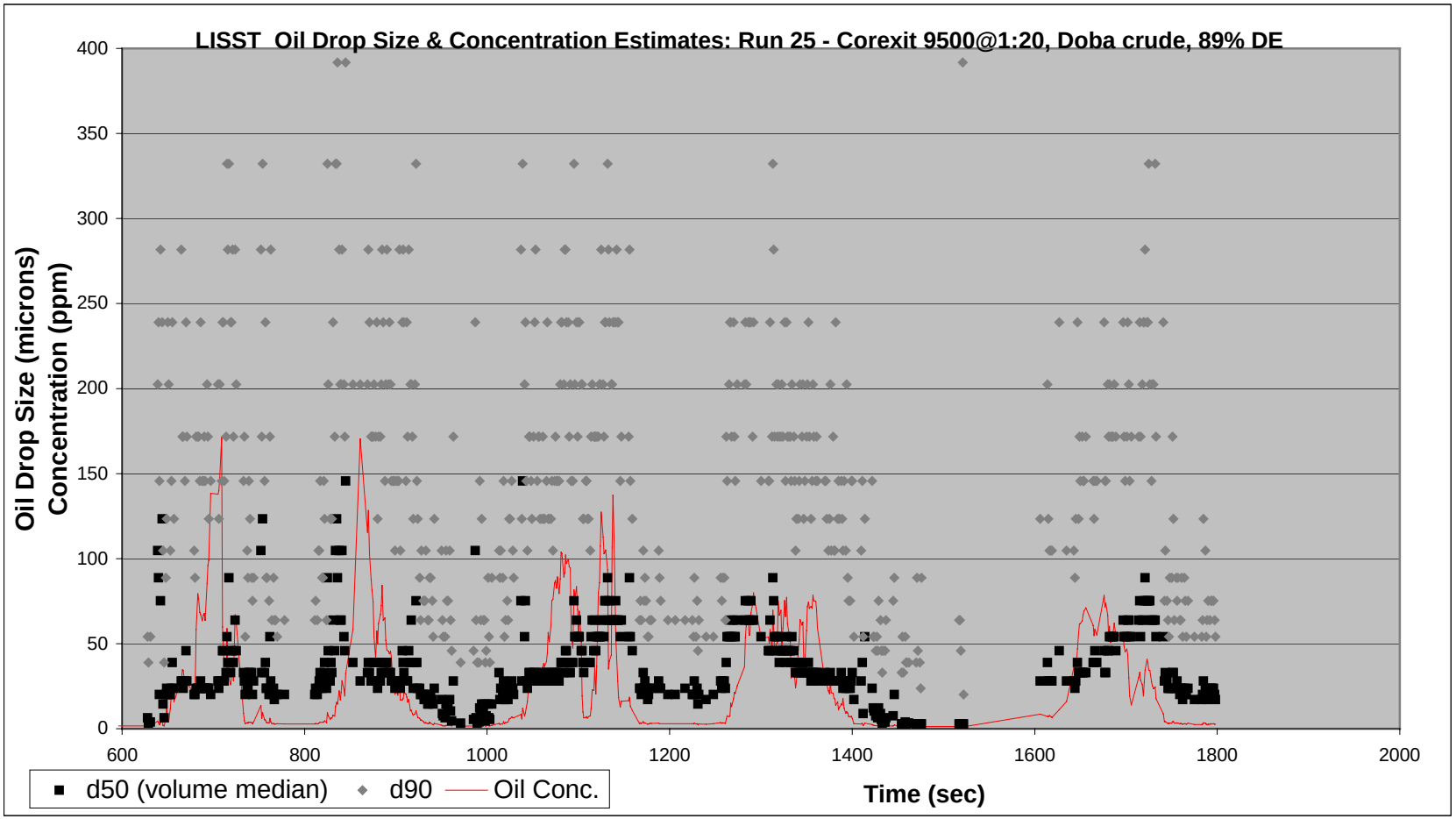

LISST Oil Drop Size & Concentration Estimates: Run 20 - thin ED5@1:20, IFO 380 Emulsion, 63% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
800
1000
1200
1400
1600
1800
Time (sec)
d50 (volume median)
d90
Oil Conc.

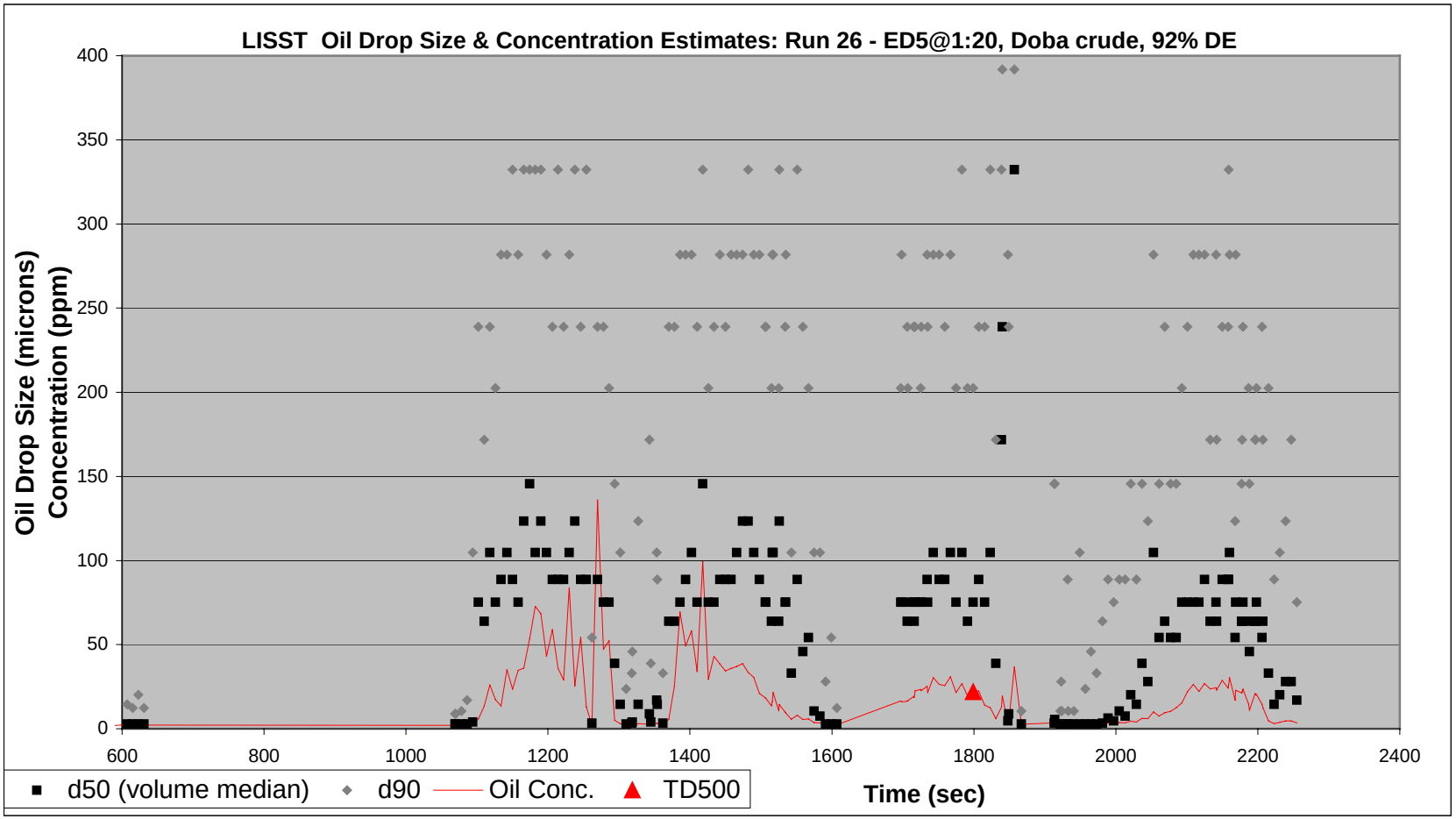

LISST Oil Drop Size & Concentration Estimates: Run 21 - Corexit 9500@1:100, Doba Emulsion, 73% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500

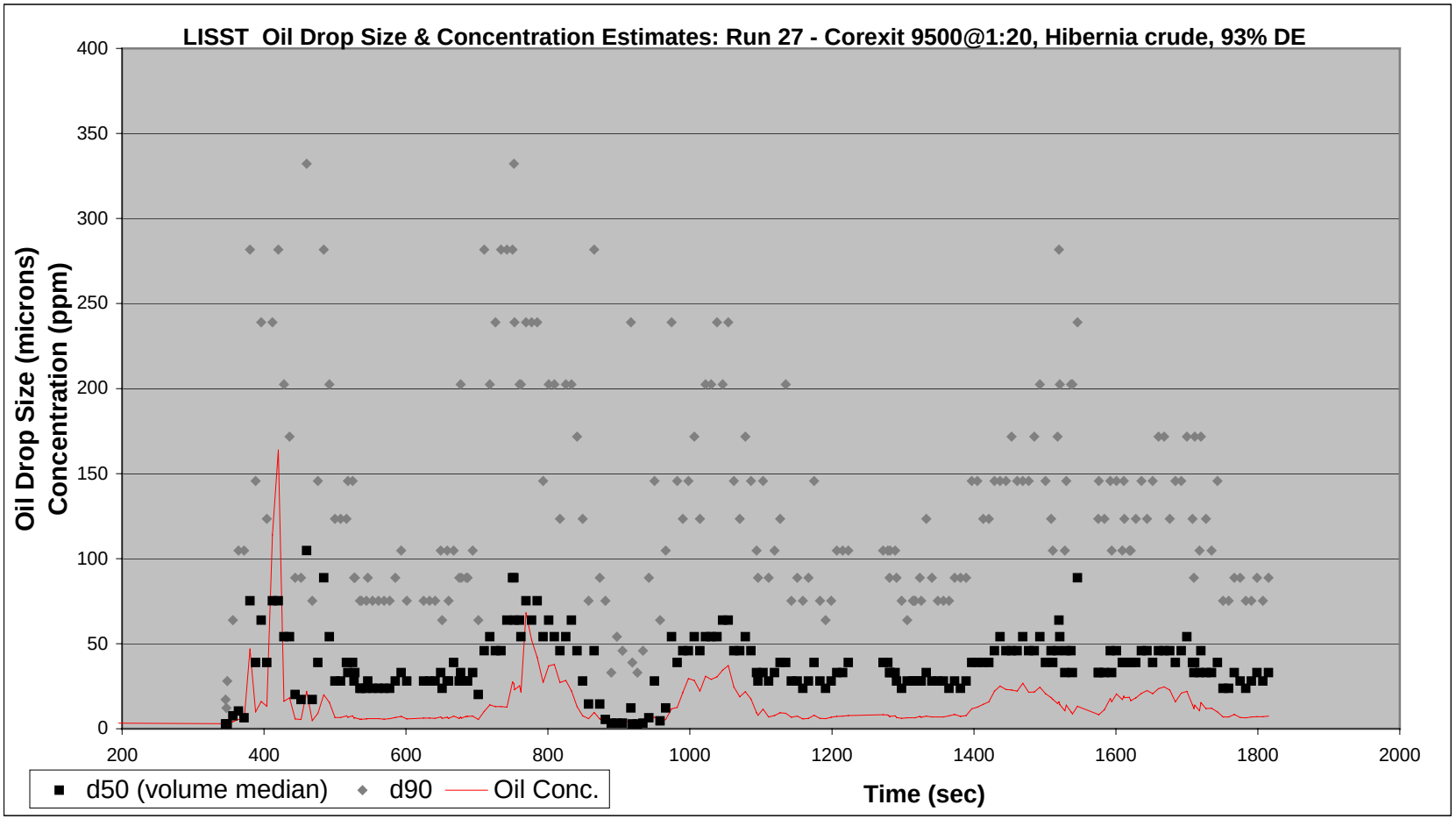

LISST Oil Drop Size & Concentration Estimates: Run 22 - thin ED5@1:100, Doba Emulsion
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
400
600
800
1000
1200
1400
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500


LISST Oil Drop Size & Concentration Estimates: Run 23 - Corexit 9500@1:50, Doba Emulsion, 78% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500


LISST Oil Drop Size & Concentration Estimates: Run 24 - thin ED5@1:50, Doba Emulsion, 74% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 25 - Corexit 9500@1:20, Doba crude, 89% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.


LISST Oil Drop Size & Concentration Estimates: Run 26 - ED5@1:20, Doba crude, 92% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Time (sec)
d50 (volume median)
d90
Oil Conc.
TD500


LISST Oil Drop Size & Concentration Estimates: Run 27 - Corexit 9500@1:20, Hibernia crude, 93% DE
Oil Drop Size (microns)
Concentration (ppm)
400
350
300
250
200
150
100
50
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (sec)
d50 (volume median)
d90
Oil Conc.