Comparison of Small-Scale Dispersant Testing Methods to Ohmsett:

Effect of Dispersant Type and Oil Properties

for:

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Executive Summary

Dispersant effectiveness estimates were made for four different dispersant brands using small-scale dispersant effectiveness apparatus and were compared against estimates made in the large wave tank at Ohmsett. All dispersants were tested against three oils of different viscosities. Dispersant effectiveness was ranked by product type and the relationship between dispersant effectiveness and oil viscosity in each apparatus was investigated.

At the outset six dispersant products listed on the National Contingency Plan Product Schedule were screened for this study and four products were selected for testing, namely: Accell® Clean DWD (Accell); Corexit® EC9500A (Corexit); Dispersit SPC 1000™ (Dispersit); and Nokomis 3-AA (Nokomis). Dispersants were tested using the Baffled Flask Test (BFT) and EXDET apparatus, as well as the Ohmsett protocol. Three United States Outer Continental Shelf crude oils of different viscosities were used in the testing: Endicott crude oil; PER-038 and PXP-01 with viscosities of 120, 2977 and 9400 cP, respectively. This spans the viscosity range of oils shown to be dispersible in earlier Ohmsett studies.

The work has showed that small-scale BFT and EXDET produced dispersant effectiveness rankings that agree. Within the limitations of the study, rankings of the small-scale tests agree with those at Ohmsett. As an example, the BFT ranked the dispersant brands Corexit > Accell > Dispersit > Nokomis, but differences between Accell and Dispersit were small.

It was equally clear that oil viscosity influenced the effectiveness estimates in all three apparatus. Dispersant effectiveness declined with increasing oil viscosity in all apparatus and differences in effectiveness between products were clearly evident.

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Introduction

In this project, effectiveness rankings for dispersant brands were made using small-scale dispersant test apparatus and were then compared to rankings made under simulated at sea conditions at Ohmsett. The relative effectiveness of different dispersant brands has always been of interest to operators and government personnel alike for many reasons. A variety of testing methods have been developed to compare product effectiveness. Historically different apparatus have produced somewhat inconsistent product rankings and rankings have not related well to dispersant performance at sea. In recent years several new dispersant effectiveness testing apparatus have been developed and testing under simulated at-sea conditions in large wave tanks (e.g., Ohmsett) has been used as a surrogate for at-sea testing. In this project a number of dispersant products were tested against oils of different viscosities in two bench-scale test apparatus and at Ohmsett. Both the product rankings and the product –oil viscosity interactions from bench-scale testing were compared to those from Ohmsett.

In the early days of dispersants, products were tested at sea (e.g., Martinelli 1984). However, for a number of reasons workers quickly turned to small-scale or bench-scale testing to compare effectiveness of different dispersant brands. Many different test apparatus were developed. In the early 1980s Meeks (1981) reviewed the numerous methods available at the time and pointed out that in order to be useful, test methods should produce results that could be related to product performance at sea. According to Meeks, bench-scale methods should either:

a) Simulate at-sea conditions; or

b) Be known to produce effectiveness rankings that could be related to those at sea.

Experimental work conducted during the 1980 and 1990s met with limited success in relating small-scale apparatus to dispersant performance at sea. Daling and Lichtenthaler (1986/87) found that there was poor correlation among rankings made using three laboratory test apparatus or between rankings made in small scale apparatus and those from field trials. Byford and Green (1984), on the other hand, found good agreement between results of the MNS test and Labofina apparatus. They believed that while both apparatus had some usefulness in predicting dispersant performance at sea, each apparatus had shortcomings. They believed that until there was more information about dispersant performance at sea, little progress was possible in improving the state of the art of small-scale testing. That situation continued to be a problem through the late 1990s (Fiocco and Lewis, 1999). A series of BSEE-funded studies in 2003 to 2005 underscored the challenges of relating small-scale bench tests to at sea performance (Belore et al, 2005,Clark et al. 2005, Trudel 2005). However, that work demonstrated the advantages of using studies in large wave tanks as a surrogate for at sea testing for purposes of calibrating bench scale test methods. This study built on that work.

The need for credible testing of the relative effectiveness of dispersant products was highlighted recently during the Deepwater Horizon spill (Belore et al 2011). Routine dispersant effectiveness testing at sea was still not possible, so dispersant planners continued to use bench-scale methods to compare effectiveness of different dispersant brands (Belore et al., 2011, Holder, 2011; Venosa and Holder 2013). In recent years however, authors developed protocols for dispersant effectiveness testing under simulated at sea conditions in large wave tanks (BSEE, DFO/EPA). A recent major BSEE-funded study provided critical baseline information for five modern test apparatus by comparing the oil viscosity-effectiveness curves for each apparatus to Ohmsett for

15 widely different oils and a single dispersant, Corexit 9500 (Belore et al. 2011). That study showed that certain apparatus agreed well with Ohmsett and others did not. The present study compares two of the best-performing apparatus from that study to Ohmsett based on their ability to rank effectiveness of various dispersant brands.

General Approach and Methods

The general approach was to compare the effectiveness rankings produced in Ohmsett tests against those produced in two bench scale tests for a number of dispersant brands. Beside the dispersant brand itself, the most important variable determining dispersant effectiveness is the viscosity of the oil, so oil viscosity is a critical operational variable. For that reason, dispersants were tested against three oils of greatly differing viscosities that were known to be dispersible in Ohmsett tests. The dispersants tested were chosen from the NCP product schedule and were selected based on preliminary laboratory testing. The project involved four sets of tests.

a) First the relative effectiveness of six dispersant products from the NCP Product Schedule were tested using the EXDET Method against a single medium-viscosity oil. Four products were selected for further testing.

b) Those four products were tested against three dispersible crude oils of widely different oil viscosity using the EXDET method.

c) The relative efficiencies of the four selected dispersants were tested at Ohmsett against the same three test oils. Effectiveness rankings were compared against results of EXDET testing in Phase 1.

d) Finally, effectiveness of the four dispersants was tested with the BFT using the same four oils.

e) Results of the EXDET and Baffled Flask Test were compared to results from OHMSETT tests.

Dispersants and Oils

The dispersants selected for screening were COREXIT® EC9500A, ACCELL® CLEAN DWD, DISPERSIT SPC 1000™,NOKOMIS 3-AA, FINASOL OSR 52 and SEA BRAT #4 (Table 1). They were selected because:

a) All were listed on the EPA NCP Product Schedule at the time of testing (September 2011 to July 2012).

b) Some had been included in an earlier study (Belore 2011).

The oils used in this study were crude oil samples collected from producing wells on the US Outer Continental Shelf. In 2009 samples of selected produced oils on the US OCS were collected, analysed for oil spill-related properties and stockpiled at Ohmsett for research purposes. Three oils were selected from among these for this project based on their viscosities and apparent dispersibility based on earlier studies. Their properties are summarized in Table 2 below. These oils were selected because they span the range of viscosities that are dispersible at Ohmsett.

a) Endicott (fresh) is a relatively low-viscosity oil that has been shown in previous tests at Ohmsett using Corexit 9500 to disperse quickly and completely producing a fine café-au-lait colour dispersion.

b) PER 038 is a low- to intermediate-viscosity oil (2977 cP at 15deg C) and represents oils that disperse completely, but form coarse black dispersions some of which may resurface during testing.

c) PXP-01 is an intermediate to heavy oil (viscosity 9400 cP at 15 deg C) and represents oils that resist dispersion to a degree, but dispersed partially during the course of past tests with Corexit 9500.

The properties of the test oils are provided in Table 2, below.

Table 1. Dispersant products used in this study.

Dispersant Name	**Supplier**	**Name Used Here**
ACCELL® CLEAN DWD	Advanced BioCatalytics Corp 18010 Skypark Circle, #130, Irvine, CA, 92614	Accell
COREXIT® EC9500A	Nalco Environmental Solutions LLC 7705 Highway 90-A, Sugar Land, TX 77478	Corexit
DISPERSIT SPC 1000™	U.S. Polychemical Corp. 584 Chestnut Ridge Rd, Chestnut Ridge, NY 10977	Dispersit
NOKOMIS 3-AA	Mar-Len Supply, Inc. 23159 Kidder Street, Hayward, CA 94545	Nokomis
FINASOL OSR 52	TOTAL FLUIDES 24 cours Michelet La Défense 10, 92069 Paris La Défense Cedex, France	OSR
SEA BRAT #4	Alabaster Corp. 6921 Olson Ln., Pasadena, TX 77505	Sea Brat

Table 2. Properties of oil samples used in this project.

Oil Name	Viscosity (cP, at 15 °C)	Measured Density (g/cm^3 at ~15°C)	Pour Point (°C)	Source of Oil
Endicott –fresh	120 @$100s^{-1}$	0.896	-2	Alaska
PER 038 (Ellen (038)	2,977 @$100s^{-1}$	0.956	- 21	California OCS
PXP 01 (Irene Lompoc)	9,400 @$10s^{-1}$	0.951	- 9	California

EXDET Testing

Tests using the EXDET method involved:

a) an initial screening of a number of dispersants to select products for testing in this project; and

b) testing the selected oils against the two additional oils used in this study.

The initial screening of dispersant involved testing six dispersant brands against PER038 crude oil, a medium-viscosity oil (viscosity = 2977 cP @ 15 ºC). Based on the screening, four products were selected for testing in the Baffled Flask Test (BFT) and at Ohmsett, as well as in further EXDET tests. The EXDET method was chosen for this phase of the study because the test is commonly used in North America; correlated well with Ohmsett in an earlier study (Belore et al, 2011); is well suited for testing a number of different oils and is quick and simple to perform. In the earlier study.

Methods

The EXDET method is described in detail in Appendix A. In brief, the test uses 250 ml separatory funnels clamped in a Burrell wrist-action shaker. Approximately 250 ml of seawater was placed in each separatory funnel, filling the funnel to its widest point. One ml of test oil was deposited on the water surface in each funnel with a pipette, forming an oil lens. A 0.04-ml volume of dispersant was then deposited on the oil lens for a dispersant-to-oil ratio of 1:25. The funnels were stoppered and shaken for 20 minutes. Sorbent pads are added to the water surface at the 15-minute mark to absorb oil droplets large enough to resurface during the test. At the 20-minute mark, the water phase was drained from the separatory funnels without stopping the shaking and the oil was extracted from the water with solvent. The non-dispersed oil on the sorbent pad and remaining in the funnel was also extracted using the solvent. The two batches of solvent were made up to a constant volume and the oil content of each was determined using a spectrophotometer operated at an appropriate wavelength (in this case 460 nm). The ratio of dispersed oil to dispersed plus undispersed oil was determined for each of the funnels and the average and standard deviations of the percent dispersed oil were reported for the test run.

Water temperatures during tests ranged from 23 to 25 degrees C.

Results

The results of initial screening test are in Table 3. Average values for the dispersant effectiveness against the PER 038 oil ranged from as low as 3.7% to 84.9 %. There were clear differences among dispersant products with OSR 52 and Corexit showing the highest effectiveness, Sea Brat showing the least and overall ranking of OSR 52=Corexit>Accell=Dispersit>Nokomis>Sea Brat. Based on these results the following were selected for further testing: Corexit, Dispersit, Accell and Nokomis. Finasol OSR 52 was not included because its performance was similar to Corexit. Sea Brat was not included because it appeared to be completely ineffective against an oil that was dispersible at Ohmsett and in other apparatus.

The results of further EXDET testing of those four dispersants are summarized in Table 4 and Figure 1. Average effectiveness values for the dispersant-oil combinations ranged from as low as 5% to as high of 92 %. Figure 1 shows that some clear differences in effectiveness were evident among brands for each of the three oils tested. Corexit 9500 produced the highest effectiveness and Nokomis the lowest of all brands with all three oils. The type of oil used in the test influenced the average effectiveness of dispersants; effectiveness was greatest for the least viscous oil (Endicott) and declined with increasing oil viscosity.

Figure 1 shows that with the low-viscosity Endicott oil (viscosity = 120 cP at 15°C), all dispersants produced a high level of effectiveness. Corexit produced a slightly higher effectiveness than other brands, but there was no clear difference among the other brands. Tests with the intermediate viscosity PER 038 oil (viscosity = 2977 cP at 15°C) produced generally lower levels of effectiveness than the Endicott oil and produced the greatest differences in effectiveness among the dispersant brands. Corexit 9500 was clearly most effective (82.3%), Accell and Dispersit were somewhat less effective at (58.9%) and (55.4%) effectiveness respectively, but were very similar to one another. The Nokomis clearly produced the lowest effectiveness (19.7 %). Effectiveness with the most viscous PXP-01 oil (viscosity = 9,400 cP at 15°C) was lowest for all products. Corexit 9500 produced clearly higher effectiveness (41.8%) than the other brands (5to 6%). There was little apparent difference in effectiveness among the other brands.

The numerical effectiveness data reflected the visible behaviour of oil in the tests. In the Corexit 9500 x Endicott test, the oil sheared immediately into a café-au-lait coloured dispersion of very fine oil droplets and remained dispersed throughout the test. In Endicott tests with Accell and Dispersit the oil also sheared quickly into dispersions of apparently fine droplets. In the Endicott x Nokomis test the oil sheared into visibly coarse droplets initially, which appeared to grow finer with time through the 15-minutes of the test, prior to addition of the sorbent.

Visually, the PER038 x Corexit oil sheared quickly into a fine brown-black-coloured dispersion as in the Endicott test. On the other hand, with in the Accell and Dispersit tests, the PER 038 oil did not shear immediately. Rather the oil remained as a single lump for some minutes. After a few moments of mixing, the lump of oil sheared first into many fine strings, then sheared further into coarse droplets. The PER 038 x Nokomis oil produced some fine strings of oil as with Accell and Dispersit, but large blobs of oil persisted through the test.

Finally, in the PXP 01 x Corexit test, the oil formed into a lump initially after which some strings of oil formed with time. In tests with other brands, the oil did not shear, but remained as a lump throughout the tests with no apparent shearing, stringing or dispersion.

In short, all dispersant products produced high and relatively similar levels of effectiveness in tests with the non-viscous Endicott oil (120 cP), though the Corexit 9500 was slightly more effective. Tests with the intermediate viscosity PER 038 oil (2977 cP) produced the greatest differences among the dispersants with Corexit producing the highest effectiveness, Nokomis clearly the least. Accel and Dispersit produced clearly an intermediate effectiveness and were similar. With the PXP-01 oil, Corexit produced some effectiveness, but the other brands did not.

Table 3. Summary of Dispersant Screening Tests Using the EXDET method

Oil	Dispersant	Test Temperature °C	Dispersant Effectiveness	Standard Deviation
PER038	OSR-52	25	84.9	5.0
PER038	Corexit	24.5	82.3	1.1
PER038	Accell	24	58.9	14.4
PER038	Dispersit	24.5	55.4	7.7
PER038	Nokomis	23	19.7	3.9
PER038	Sea Brat	23	3.7	0.40
Oil Viscosity at 15 °C = 2,977 cP @100s and at 24 °C = 1900 cP @100s				

Table 4. Summary of effectiveness test results using the EXDET method

Oil	Dispersant	Oil Viscosity (cP @15°C)	Dispersant Effectiveness	Standard Deviation
Endicott	Accell	120 @100s	82.6	1.2
Endicott	Corexit	120 @100s	92.6	1.12
Endicott	Dispersit	120 @100s	84.8	1.3
Endicott	Nokomis	120 @100s	81.8	5.0
PER038	Accell	2,977 @100s	58.9	14.4
PER038	Corexit	2,977 @100s	82.3	1.1
PER038	Dispersit	2,977 @100s	55.4	7.7
PER038	Nokomis	2,977 @100s	19.7	3.9
PXP 01	Accell	9,400 @10s	5.6	3.9
PXP 01	Corexit	9,400 @10s	41.8	8.2
PXP 01	Dispersit	9,400 @10s	6.1	1.7
PXP 01	Nokomis	9,400 @10s	5.3	3.9

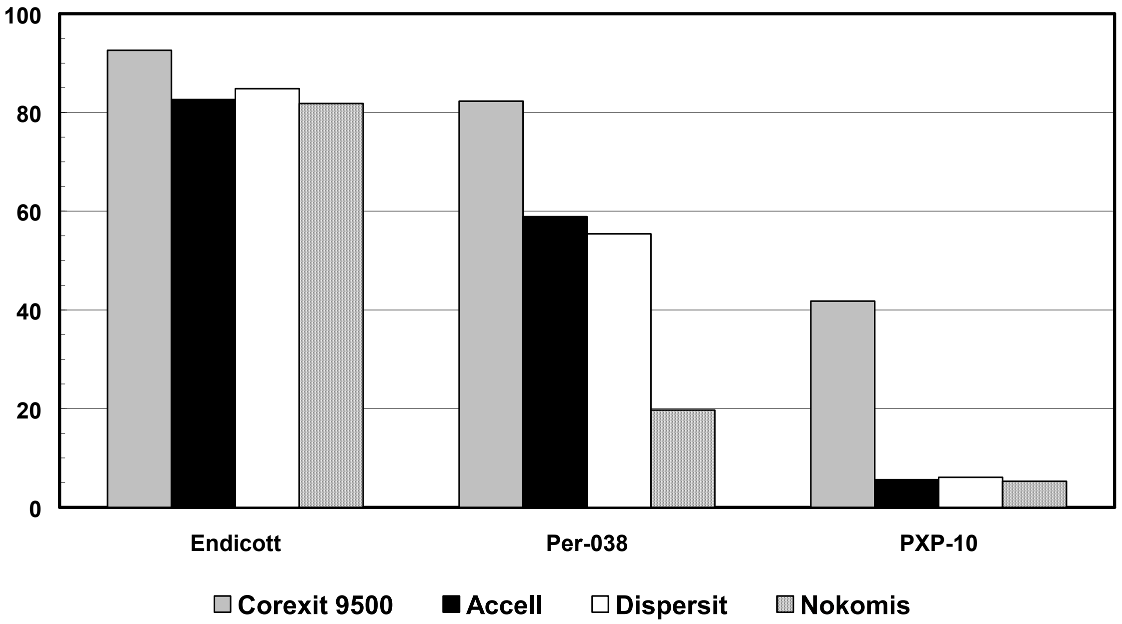

Figure 1. Dispersant effectiveness on the three test oils in EXDET testing

Ohmsett Testing

Large-scale dispersant effectiveness (DE) testing of the Accell, Dispersit and Nokomis dispersants against Endicott, PER 038 and PXP-01 oils was completed in the Ohmsett test tank in the week of July 1-13, 2012. It was not possible to test all four dispersants against all three oils in the single week available for testing. For that reason it was decided to omit tests of Corexit 9500 and substitute data from an earlier series involving the same three oils (October 26th through November 2, 2010).

Methods

A photograph of the Ohmsett facility is provided in Figure 2. In short, Ohmsett is a wave tank 200 m in length, by 20 m in width and 3 m in depth containing approximately 9,841 m^3 (=2.6 million U.S. gallons) of seawater. A wave paddle is located at the south end and a wave-dampening beach at the north end. Three movable bridges span the width of the tank. The standard dispersant effectiveness (DE) test protocol is described in detail in previous publications (SL Ross et al 2000, 2003, 2004, 2006). In brief, the procedure was as follows.

1. An oil testing/containment area in the tank was established by placing booms across the north and south ends of the Ohmsett tank. These booms contain all the undispersed oil between them. The oil and dispersant were loaded into their respective supply tanks on the main bridge deck (called Tow Bridge in Figure 2).
2. The main bridge was positioned at the southern quarter point within the boomed area. The wave paddle was started and the waves were allowed to develop to a stage just prior to the formation of breaking waves (4 to 5 minutes).
3. The wave paddle setting used in all of these tests was a 3.5-inch stroke and 34 to 35 strokes per minute.
4. The bridge was moved south at a pre-determined speed to achieve proper slick dimensions and dispersant application dosage (either 1 or ½ knot (0.5 or 0.25 m/s) for this test series).
5. Oil was discharged at the required rate onto the surface through the discharge manifold mounted on the south side of the bridge (nominally 20 gpm for one minute in this test program).
6. The dispersant was immediately sprayed onto the oil slick using the spray bar system mounted on the north side of the bridge in the same pass as the oil discharge.
7. The behaviour of the treated oil was observed as the bridge was moved over the treated slick.
8. Slicks were agitated by the breaking wave-field for 30 minutes after which waves were stopped.
9. Throughout the 30-minutes of the test, a LISST particle size analyzer and a Turner C3 fluorometer were towed repeatedly along the length of the tank through the cloud of dispersing oil for in-water dispersed oil characterization. The instruments were towed from the main bridge at 1.5 m depth during the mixing period. Generally 3 to 5 passes were made in each test. Visual observations of the oil were also made during each pass.
10. At the end of the test, the wave maker was turned off and waves permitted to subside for a few moments, before surface water currents developed by the water spray from the bridge fire monitors were used to sweep any remaining surface oil to a common collection area at one corner of the containment boom.

11. The oil was then removed from the water surface using a double-diaphragm pump and suction wand or a hand ladle and was placed in a 55-gallon (208L) collection drum or a 5-gallon (20L) pail.
12. The collected emulsion was permitted to stand at least overnight to allow the oil and water to separate before most of the free water was drained from the bottom of the collection container.
13. The remaining oil and water were well mixed and a sample was taken for water content and physical property determination.
14. The volume of the oil-water mixture was measured and the amount of oil determined by subtracting the amount of water as determined using the 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.
16. Each test was video taped for future visual reference.

The tank water temperatures during the July 2012 tests were 27 to 29 ºC and for October/November 2010 tests (Corexit tests) were 14 ºC. Air temperatures ranged from 25 to 30 ºC and 10 to 15 ºC for the respective periods. Tank water salinity was approximately 32 ppt.

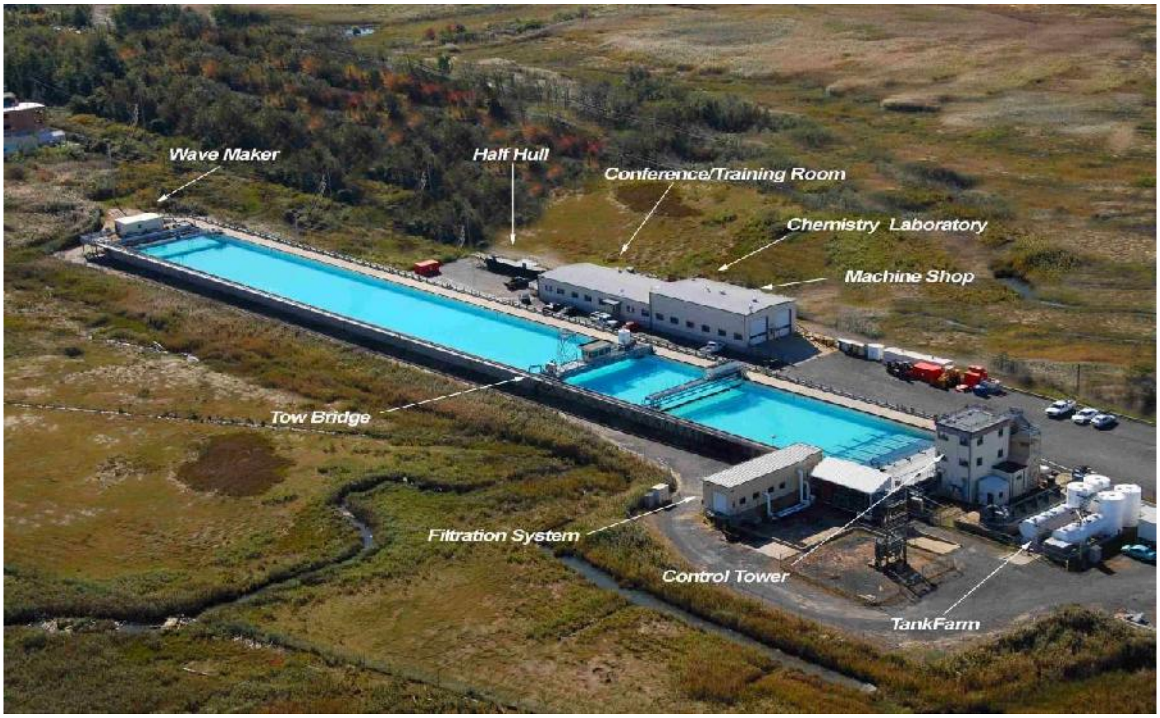

Figure 2. Ohmsett - The National Oil Spill Response Research & Renewable Energy Test Facility

Results

Dispersant Effectiveness

The test conditions and estimated dispersant effectiveness (DE) for all of the Ohmsett tests are summarized in Table 5 and Figure 3. The DE values in the table were determined using the following formula:

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

DE values ranged from as low as 41.7% to 98.9 %, a smaller range than in the bench-scale tests. Quality assurance test pairs (# 6, 7 and #10, 11) showed that repeatability was greater in tests producing high DE values (Endicott x Dispersit [98.9, 98.9]) and less in tests with lower DE values (PER 038 x Nokomis [41.7, 53.7]).

There were clear differences in effectiveness among dispersant brands with each of the oils. Overall effectiveness appears to decline with increasing oil viscosity for each dispersant brand, other than Nokomis.

As mentioned above, for scheduling reasons, it was decided to forgo retesting of Corexit during the July 2012 test period in order to allow time to test the Accell, Dispersit and Nokomis with all three test oils, as well as complete the duplicate QA/QC tests. When the test data became available weeks after testing had been completed, it was clear that effectiveness results for Dispersit and Accell from the July 2012 tests clearly exceeded those for Corexit from the November 2010 tests. This was inconsistent with the EXDET results and results of an earlier project. After re-examining the test records for the two sets of tests, it was evident that the Nov 2010 tests of Corexit had been completed at much lower temperature (14 ºC) than the July tests of the other brands (27-28 ºC). This large difference in temperatures between the two tests meant that the oil viscosities in the Corexit tests was much greater than for the Accell/Dispersit /Nokomis tests due to the difference in temperatures (See oil viscosity data in Table 5 and Appendix D). As a consequence the data sets were not directly comparable, so the Corexit results could not be considered here.

Among the dispersants tested under identical conditions, there were clear differences in effectiveness of the three brands and the rankings of the brands were the same for all oils: Dispersit>Accell>Nokomis. Effectiveness of Accell and Dispersit were similar with the non-viscous Endicott oil. Differences among brands appeared to be greatest with the PER 038 oil and less with the PXP-01. DE values for Accell and Dispersit were consistently greater than with Nokomis for all oils.

Oil Dispersion Behaviour

The behaviour of the oil in each of the Ohmsett test runs in July 2012 was observed and is summarized and related to the numerical DE values Table 6. This provides insight as to how numerical DE values may relate to oil behaviour during the test and perhaps at sea. Features of oil behaviour that are observable in Ohmsett dispersant tests include:

a) The proportion of oil slick dispersing from the surface. All or part of the test slick may be dispersed.

b) The appearance of the dispersed oil cloud in the water. The dispersed oil may form a light brown cloud, black cloud or no dispersion at all.

c) The amount of dispersed oil resurfacing while the test is in progress. In some cases the oil appears to disperse completely in the early phases of the test, but patches of thick oil reform later in the test and are no re-dispersed by breaking waves.

In this study oil behaviour ranged from "Rapid, complete and permanent dispersion of all oil producing a light brown cloud of dispersed oil' to "No visible dispersion". The combination of Endicott oil treated with Accell and Dispersit produced "Rapid, complete and permanent dispersions that form light brown clouds of dispersed oil that persist in the water throughout the test". The combination of Endicott and Nokomis produced some black-brown dispersion in the water but patches of thick undispersed oil remained visible on the surface throughout the test.

Treating the more viscous PER038 oil with Accell and Dispersit produced rapid and complete dispersion initially. Small amounts of oil with the appearance of "tea leaves" were observed on the surface later in the tests. The "tea leaves" may be a small amount of dispersed oil that resurfaced later in the test. The combination of Nokomis and PER038 produced some dispersion in the water, but patches of thick undispersed oil remained clearly visible throughout the test.

Accell and Dispersit applied to the viscous PXP01 oil appeared to cause rapid and complete dispersion initially, producing black-colored dispersed oil clouds in the water column. However, thick patches of oil were clearly visible on the surface later in the test. PXP01 treated with Nokomis appeared to produce no visible dispersion. Thick patches of oil were visible through the test and little dispersed oil was visible in the water after the slick was mixed with breaking waves.

Dispersed Oil Concentrations and Drop Size Distributions

The oil conditions in dispersed oil clouds generated during each test were monitored using a Sequoia Scientific LISST 100X particle size analyzer (LISST) and Turner Cyclops C3 *in-situ* fluorometer (C3). During each 30-minute test, the two instruments were towed side-by-side, through the cloud at a depth of 1.5 m for five or 6 passes. Oil droplet size and oil concentration data are reported in tables 7 and 8, below. The instrument output from this monitoring is provided in Appendix A.

As pointed out above, effectiveness was on average greatest with Dispersit and least with Nokomis. Average oil concentration at a depth of 1.5 metres in the dispersed oil clouds during the first 5 minutes of testing ranged from 11.4 to 54.2 ppm depending on the dispersant and oil combination being tested. Both average and peak oil concentrations declined with declining dispersant effectiveness. Average oil droplet diameter values (volume mean diameter) ranged from 15.6 to 90.6 microns. Average diameter increased with decreasing effectiveness, regardless of whether the change in effectiveness was related to dispersant type or oil viscosity.

Table 5. Summary of effectiveness test results using the Ohmsett method

Oil	Dispersant	D O R	Water Temp °C	Air Temp °C	Oil Viscosity (cP @15°C)	Oil Visc (cP @ test temp°C)	Oil Volume (liters)	DE %	Test #	Test Date
PXP 01	Nokomis	1:14	27.5	27.0	9,400 @10s	3200@10s	78.0	63.8	1	10/7/12
PXP 01	Dispersit	1:16	27.4	28.1	9,400 @10s	3200@10s	76.8	81.2	2	10/7/12
PXP 01	Accell	1:19	27.8	24.3	9,400 @10s	3200@10s	79.5	73.4	3	11/7/12
PER038	Dispersit	1:18	28.2	29.6	2,977 @100s	1400@10s	81.0	90.2	4	11/7/12
PER038	Accell	1:24	28.5	29.5	2,977 @100s	1400@10s	82.2	79.9	5	11/7/12
PER038	Nokomis	1:17	28.9	27.7	2,977 @100s	1400@10s	79.5	41.7	6	11/7/12
PER038	Nokomis	1:15	28.1	25.1	2,977 @100s	1400@10s	89.7	53.7	7	12/7/12
Endicott	Nokomis	1:32	28.1	27.6	120 @100s	120 @100s	82.1	58.6	8	12/7/12
Endicott	Accell	1:22	28.3	29.7	120 @100s	120@100s	125.7	93.7	9	12/7/12
Endicott	Dispersit	1:27	28.7	29.6	120 @100s	120@100s	83.7	98.9	10	12/7/12
Endicott	Dispersit	1:30	27.5	25.3	120 @100s	120@100s	86.3	98.9	11	13/7/12
Endicott	C 9500	1:30	14.2	13.7	120 @100s	197 @10s	71	95	6	Oct/2010
PER038	C 9500	1:29	14.0	13.1	2,977 @100s	4100@100s	80 L	66	5	Oct/2010
PXP01	C9500	1:24	14.3	13.0	9,400 @10s	13,600 @1s	76 L	60	3	Oct/2010

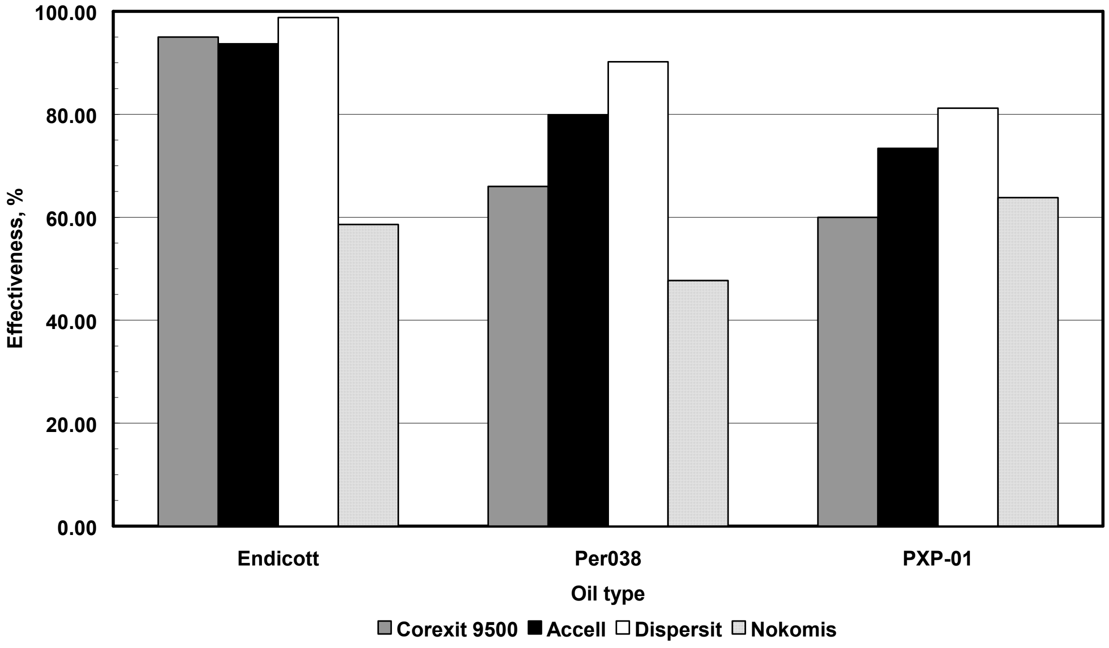

Figure 3. Dispersant effectiveness on the three test oils in OHMSETT testing (note: Corexit 9500 tests conducted at 14 °C versus 28 °C for all other dispersants)

Table 6. Description of oil behaviour during tests

Test #	Oil	Disp.	DE (%)	Oil Viscosity (cP @ 15°C)	Visual Appearance of oil behaviour
1	PXP-01	Nokomis	63.8	9,400 @10s	No visible dispersion. Thick oil slicks visible throughout the test. No dispersed oil visible in water under slick.
2	PXP	Dispersit	81.2	9,400 @10s	All oil dispersed initially as black cloud. Some oil resurfaces to form thick patches of oil.
3	PXP	Accell	73.4	9,400 @10s	All oil dispersed initially as black cloud. Some oil resurfaces to form thick patches of oil.
4	PER038	Dispersit	90.2	2,977 @100s	Rapid and complete dispersion of slick. All slick disperses. Brownish black cloud of dispersed oil forms and persists through test. Small amount of tea leaves resurface.
5	PER038	Accell	79.9	2,977 @100s	Rapid and complete dispersion of slick. All slick disperses. Brownish black cloud of dispersed oil forms and persists through test. Small amount of tea leaves resurface.
6	PER038	Nokomis	41.7	2,977 @100s	Difficult to see into water. Some or most thick oil survive on surface. Little dispersion visible.
7	PER038	Nokomis	53.7	2,977 @100s	Water cleaner. Some oil disperses as black cloud (no brown seen). Some thick oil left on surface.
8	Endicott	Nokomis	58.6	120 @100s	Some black-brown dispersion, but some oil,left on surface. Thick oil visible on surface through the test.
9	Endicott	Accell	93.7	120 @100s	Rapid and complete dispersion causing light brown cloud in water. No oil resurfaces through test.
10	Endicott	Dispersit	98.9	120 @100s	Rapid and complete dispersion causing light brown cloud in water. No oil resurfaces through test.
11	Endicott	Dispersit	98.9	120 @100s	Rapid and complete dispersion causing light brown cloud in water. No oil resurfaces through test.
	Endicott	C 9500	95	197 @10s	No data
	PER038	C 9500	66	4100@100s	No data
	PXP01	C9500	60	13,600 @1s	No data

Table 7. Summary of Test Conditions and In-Water Monitoring Data from Ohmsett Testing

Test #	**Oil**	**Disp.**	**DOR**	**DE (%)**	**Ave. Elevated Oil Conc. by LISST (ppm)**	**Oil Drop Size (Average D50) (microns)**	**LISST Peak Oil Conc. (ppm)**	**Oil Viscosity (cP @ 15°C)**	**Testing Date**	**Water Temp.**	**Links to Oil Drop Size / Conc. Graphs**
1	PXP-01	Nokomis	1:14	63.8	11.4	127.7	37.2	9,400 @10s	10/7/12	27.5	FigA1
2	PXP	Dispersit	1:16	81.2	23.9	49.3	145.4	9,400 @10s	10/7/12	27.4	FigA2
3	PXP	Accell	1:19	73.4	17.3	76.9	84.2	9,400 @10s	11/7/12	27.8	FigA3
4	PER038	Dispersit	1:18	90.2	54.2	21.3	213.3	2,977 @100s	11/7/12	28.2	FigA4
5	PER038	Accell	1:24	79.9	44	39.0	164.3	2,977 @100s	11/7/12	28.5	FigA5
6	PER038	Nokomis	1:17	41.7	19.6	57.1	45.2	2,977 @100s	11/7/12	28.9	FigA6
7	PER038	Nokomis	1:15	53.7	15.3	78.4	64.2	2,977 @100s	12/7/12	28.1	FigA7
8	Endicott	Nokomis	1:32	58.6	15.1	65.7	47.3	120 @100s	12/7/12	28.1	FigA8
9	Endicott	Accell	1:22	93.7	41.3	20.	142.2	120 @100s	12/7/12	28.3	FigA9
10	Endicott	Dispersit	1:27	98.9	40.2	15.6	128.4	120 @100s	12/7/12	28.7	FigA10
11	Endicott	Dispersit	1:30	98.9	39.9	16.2	142.3	120 @100s	13/7/12	27.5	FigA11
	Endicott	C 9500	1:30	95	59	29	168	197 @10s	Oct 2012	14.2	FigA12
	PER038	C 9500	1:29	66	78	126	647	4100@100s	Oct 2012	14.0	FigA13
	PXP01	C9500	1:24	60	50	161	742	13,600 @1s	Oct 2012	14.3	FigA14

Table 8. Oil concentrations and droplet sizes as a function of oil and dispersant type.

Oil type	**Dispersit**	**Accell**	**Nokomis**
	Average oil concentration, ppm		
Endicott	40.2	41.3	15.1
PER038	54.2	44.0	19.6
PXP01	23.9	17.3	11.4
Mean	**39.4**	**34.2**	**15.4**
	Peak oil concentration, ppm		
Endicott	142.3	142.6	47.3
PER038	213.3	164.3	64.2
PXP01	145.4	84.2	37.2
Mean	**167.0**	**130.4**	**49.6**
	Average oil droplet diameter, microns		
Endicott	15.6	20.0	65.7
PER038	21.3	39.0	78.4
PXP01	49.3	76.9	127.7
Mean	**28.7**	**45.3**	**90.6**
	Dispersant Effectiveness, DE		
Endicott	98.9	93.7	58.6
PER038	90.2	79.9	47.7
PXP01	81.2	73.4	63.8
Mean	**90.3**	**82.3**	**56.7**

Baffled Flask Testing

Baffled Flask Testing (BFT) was completed in the SL Ross laboratory from February 11 to 28, 2013.

Methods

The BFT procedure used was that described in Venosa and Holder (2011). For each test, four modified trypsinizing flasks (Baffled Flask) containing 120 mL of synthetic seawater, equilibrated to the desired temperature were placed on a stationary orbital shaker. Exactly 100 uL of oil was dispensed directly onto the surface of the synthetic seawater in each flask using an Eppendorf pipette with a 5 mL syringe tip. Four uL of dispersant were then dispensed onto the center of the oil lens, giving a dispersant-to-oil ratio of 1:25. The orbital shaker was then turned on and operated for 10 minutes at a rotational speed of 200 rpm. After 10 minutes the shaker was stopped and the four oil suspensions were allowed to settle for 10 minutes. At the end of the settling time, 2 mL of the oil suspension was drained from the stopcock and discarded. Then a 30 mL sample was collected in a 50 mL measuring cylinder, transferred to a 125 mL separatory funnel and then extracted three times with 5 mL aliquots of dichloromethane. The three aliquots were combined, made up to final volume of 20 mL and transferred to a 25-ml glass vial with a tight fitting screw cap and Teflon liner. These vials were stored at 4º C until analysed. In addition to the dispersant/oil tests, oil alone control runs were also completed. All tests were completed at 23 to 25º C.

Results

The dispersant effectiveness data (DE) for all Baffled Flask test runs are in Table 9 and Figure 4. The data presented here are the average dispersant effectiveness values and are not adjusted by subtracting the control values as in Venosa and Holder (2011). In this way they are more directly comparable to results from other test methods. They correspond to the "Average Oil Dispersed" values reported in Venosa and Holder (2011). DE values range from 10% to 75%. There were some differences among dispersant brands for each of the oils. Also, while there were differences in overall effectiveness among oils, the trend toward declining effectiveness with increased oil viscosity was not evident. This is discussed below.

There were some clear differences in effectiveness among dispersant brands with each of the oils. On average Corexit ranked highest followed by Accell, Dispersit and Nokomis. As with EXDET and Ohmsett differences among dispersant brands were most clearly evident with the intermediate viscosity oil, PER038. Differences among Corexit, Accell and Dispersit were obscured for the least viscous (Endicott) and most viscous (PXP) oils, but all three performed better than Nokomis with all oils.

In both the EXDET and Ohmsett test average effectiveness (of all dispersants) was greatest with the Endicott oil and declined with increasing effectiveness oil viscosity. In the BFT series, however, effectiveness with Endicott was markedly lower than with PER038. This lower than expected effectiveness with Endicott may reflect a potential problem with the BFT method as used in this study. Because of the small amount of oil used (100 uL) in each test, when the non-viscous oil was tested the oil spread to form a very thin slick. As the dispersant was added, the first drop virtually always penetrated the slick, herded the oil to the sidewalls and some dispersant was lost to the water rather than mixing with the oil. This herding problem was much less pronounced with the more viscous oils and may have resulted in a lower than expected dispersant-to-oil ratio in Endicott tests. The possibility of under-dosing in the Endicott tests was tested by premixing Corexit with the Endicott in one test. The result was an increase in effectiveness in the Corexit-Endicott test to over 80% effectiveness, from the 65% value obtained by adding dispersant dropwise. This suggests that the Endicott results for all dispersants should be higher making the results overall results for the BFT more similar to the EXDET.

Table 9. Summary of effectiveness test results using the Baffled Flask method

Oil	Dispersant	Oil Viscosity (cP @15°C)	Nominal Dispersant Effectiveness Mean %	Standard Deviation	Control	Corrected
Endicott	Accell	120 @100s	66.4	2.4	10.7	55.7
Endicott	Corexit	120 @100s	65.4	4.6	10.7	65.4
Endicott	Dispersit	120 @100s	41.4	1.6	10.7	30.7
Endicott	Nokomis	120 @100s	20.7	4.1	10.7	10
PER038	Accell	2,977 @100s	64.2	2.5	4.3	59.9
PER038	Corexit	2,977 @100s	75.9	2.4	4.3	71.6
PER038	Dispersit	2,977 @100s	55.2	2.1	4.3	50.9
PER038	Nokomis	2,977 @100s	46.3	11.0	4.3	42
PXP 01	Accell	9,400 @10s	29.7	3.4	1.1	28.6
PXP 01	Corexit	9,400 @10s	34.8	0.9	1.1	33.7
PXP 01	Dispersit	9,400 @10s	35.3	7.6	1.1	34.2
PXP 01	Nokomis	9,400 @10s	10.0	3.2	1.1	8.9

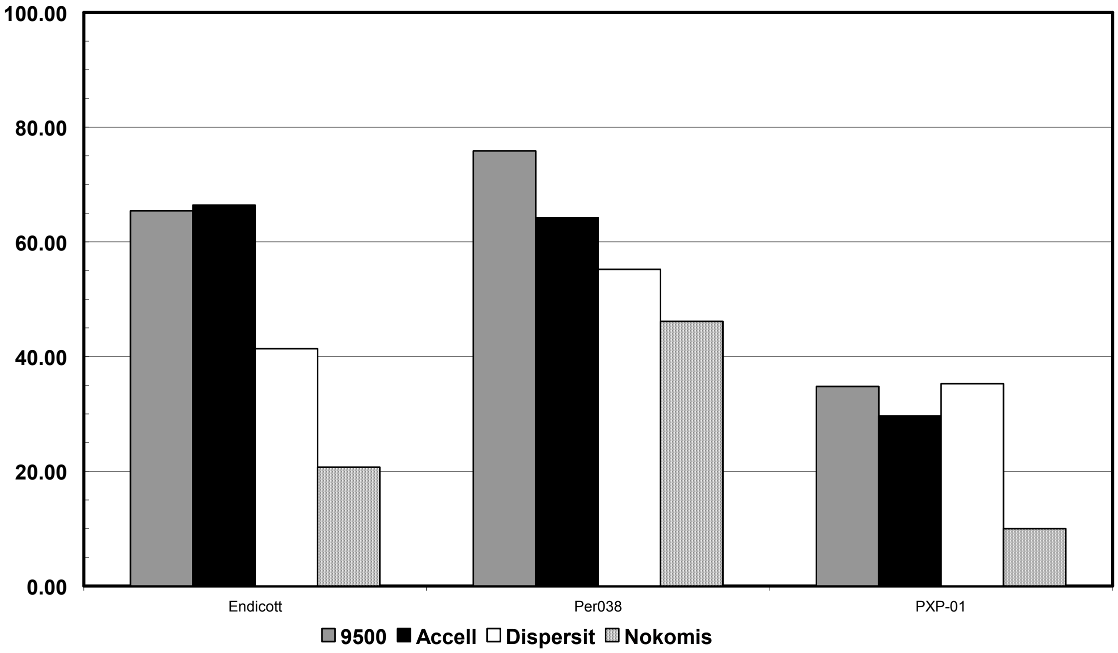

Figure 4. Dispersant effectiveness on the three test oils in Baffled Flask apparatus

Comparison of Methods

Effectiveness data produced by all three methods are compared in Figure 5.

Baffled Flask Test and EXDET Method

Both Baffled Flask and EXDET methods showed differences among dispersant brands and oil types. The two methods produced almost identical rankings for the dispersant brands. BFT ranked the brands Corexit 9500>Accell>Dispersit>Nokomis. EXDET produced a similar ranking with the exception that it did not distinguish between Accell and Dispersit with any oil.

In the EXDET method the influence of oil viscosity on effectiveness was greatest of any of the methods. Effectiveness values were uniformly high (82 to 92%) with the least viscous oil (viscosity 120 cP) and little between-brand variation was evident. Effectiveness declined with increasing oil viscosity and the effect of viscosity was greater with some brands than others. Effectiveness was eliminated for three of the brands in the most viscous oil (viscosity = 9400 cP). Only Corexit showed effectiveness in the most viscous oil. Differences among brands were greatest with the intermediate viscosity oil.

EXDET and Ohmsett

As stated above the Ohmsett method produced the same product ranking for all oils: Dispersit>Accell>Nokomis. The EXDET method was consistent with this except that EXDET showed negligible differences between Dispersit and Accell for any oil.

While EXDET produced a similar product ranking to Ohmsett, the methods differed in two important ways. First, effectiveness in Ohmsett tests changed less with oil viscosity over the range tested. In EXDET, effectiveness declined from > 80% to near zero for the same products over the same range. The difference between the two methods might be due to higher mixing energy at Ohmsett, which might override influences in oil viscosity over this range.

Baffled Flask Test and Ohmsett

As stated above, the Ohmsett method showed differences among brands for all oils and produced the same ranking for each: Dispersit>Accell>Nokomis. Differences between Dispersit and Accell were small, but consistent across all oil types. By comparison the BFT ranking was Accell>Dispersit>Nokomis. The Accell/Dispersit ranking varied with oil type and differences between the two were small. The difference between Nokomis and Accell/Dispersit was clear.

While the BFT produced a similar product ranking to Ohmsett, effectiveness levels in BFT were generally lower than for Ohmsett for all oil-dispersant combinations. The overall interaction of product effectiveness with viscosity is not clear because of the apparent under dosing problem with the Endicott oil in the BFT tests. The BFT was more similar to the EXDET than Ohmsett in that effectiveness declined markedly at a viscosity of 9400 cP.

Summary

In short, for these dispersant products and oils, the two bench-scale test methods produced product rankings that are largely consistent with Ohmsett. With Ohmsett there was a small, but clear influence of oil viscosity on overall effectiveness over the range of viscosities tested and there were clear and consistent differences in effectiveness among products over this range.

In EXDET, effectiveness was strongly influenced by oil viscosity to the point that differences among some dispersants were completely obscured for low and high viscosity oils. Differences in effectiveness among products were most evident with the intermediate viscosity oil (viscosity = 2911 cP). Results of the BFT are similar to Ohmsett and EXDET only insofar as product rankings are consistent. BFT resembles EXDET more than Ohmsett in that effectiveness declines markedly in the most viscous oil.

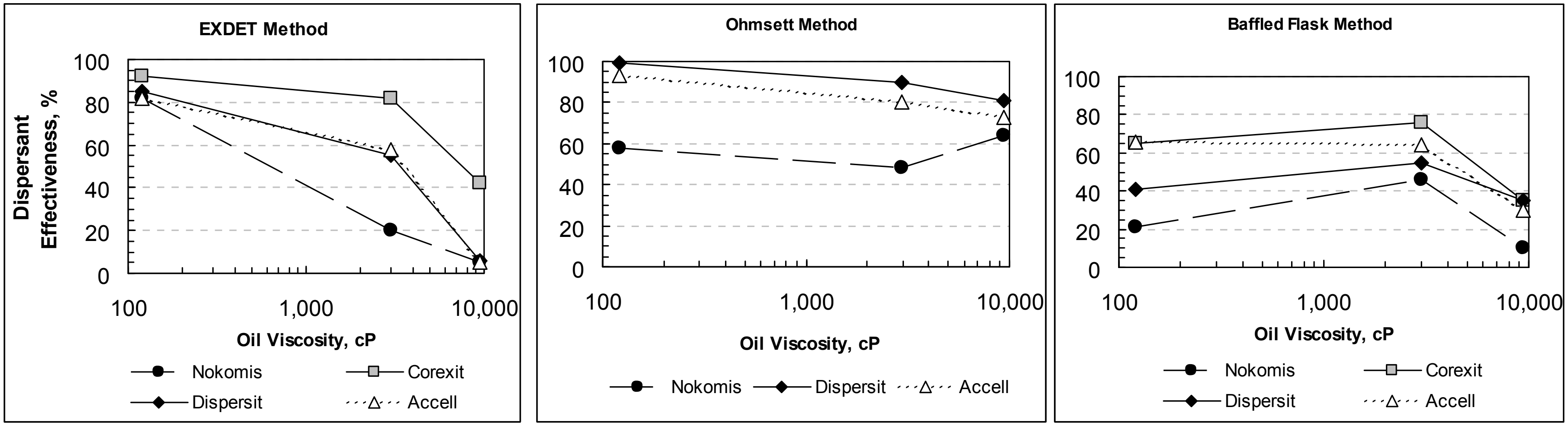

Figure 5. Comparison of the EXDET and Baffled Flask Results to Ohmsett

Discussion

Using small-scale tests to compare dispersant brands according to their relative effectiveness at sea has always been a challenge. This study used Ohmsett as a surrogate for at sea testing in order to:

a) Determine whether effectiveness rankings made using bench-scale tests might agree with rankings made at Ohmsett; and

b) Determine whether patterns of dispersant product-oil viscosity interactions in bench-scale tests correlated with Ohmsett.

This study showed that both the BFT and EXDET produced product effectiveness rankings that agree with Ohmsett for the products tested. On the other hand, the product-effectiveness versus oil-viscosity relationship shown in the EXDET and BFT tests are not consistent with Ohmsett over the oil viscosity range studied.

Baffled Flask and EXDET methods produced rankings that were almost identical to each other. BFT ranked the brands Corexit 9500>Accell>Dispersit>Nokomis, with differences among Corexit, Accell and Dispersit being small. The relative ranking of Dispersit and Nokomis in this study were consistent with Venosa and Holder (2013) who used the BFT and South Louisiana crude oil. The EXDET rankings were similar to the BFT in this project, though differences could not be detected between Accell and Dispersit with any oil.

Oil viscosity influenced the effectiveness estimates in all three apparatus. At Ohmsett, effectiveness declined somewhat with oil viscosity, but differences in effectiveness were clearly evident and product ranking remained constant across the range of oil viscosities (120 cP to 9400 cP). On the other hand, in the EXDET apparatus dispersant effectiveness were very high (80% and above) with the low viscosity oil, but declined markedly with increasing oil viscosity. Differences in effectiveness among dispersant brands were clearly evident with the intermediate-viscosity oil, but were obscured in tests with the lower and higher viscosity oils. The rankings with the intermediate viscosity oil agreed with Ohmsett.

In the BFT, effectiveness with the low-viscosity Endicott oil was markedly lower than with PER038. This lower than expected effectiveness with Endicott may reflect a potential problem with the BFT method as it was used in this project. As described above, the Endicott oil tests may have been under dosed with dispersants thereby artificially lowering overall effectiveness for that oil. The BFT may be influenced by viscosity in the same way as EXDET, but this cannot be shown with the existing data set.

As discussed above, tests with Corexit were excluded from the Ohmsett comparison for this report because those tests had been completed at much lower temperatures that made the results not comparable to tests for other products. The lack of a direct comparison among Corexit, Accell and Dispersit based on Ohmsett testing is an important knowledge gap because:

a) For purposes of this study, the two bench-scale apparatus ranked Corexit consistently highest in effectiveness over the full range of oil viscosities tested. If this ranking is realistic it will be important to verify that the superior performance of Corexit occurs under simulated at sea conditions at Ohmsett.

b) For practical purposes it will be essential to demonstrate: i) whether or not Corexit can actually outperform its nearest competitors under at sea conditions; or ii) if other products outperform Corexit, identify the conditions under which they do so.

c) Corexit is a critical product in the U.A., both in terms of its apparent superior performance and its dominance in dispersant stockpiles in North America. It will be important for researchers to have a benchmark set of dispersant performance data for Corexit and several competitor products gathered under simulated at sea conditions at Ohmsett. These benchmark data could be used by workers to develop new and better testing apparatus or refine old ones, so that results can be related to at-sea conditions (simulated at sea conditions).

Summary and Recommendations for Future Work

This work compared product effectiveness rankings made using small-scale dispersant tests against those made using the Ohmsett protocol. Four dispersant products were tested: ACCELL® CLEAN DWD, COREXIT® EC9500A, DISPERSIT SPC 1000™ and NOKOMIS 3-AA. The Baffled Flask Test and EXDET tests were used in addition to Ohmsett. Three US OCS crude oils of different viscosities were used in the testing, namely Endicott crude oil, PER-038 and PXP-01. These oils spanned the range of oil viscosities that were shown to be dispersible at Ohmsett.

This work has shown that BFT and EXDET test produced dispersant effectiveness rankings that agree. Within the limitations of the study, rankings of the small-scale tests agree with those at Ohmsett. It would be useful to retest Corexit on the three oils at Ohmsett at the same temperature conditions to produce a complete and comparable data set.

It was equally clear that oil viscosity influenced the effectiveness estimates in all three apparatus. At Ohmsett average effectiveness declined with oil viscosity, but differences in effectiveness were clearly evident and product ranking remained constant across the range of viscosities used in the study (120 cP to 9400 cP). In EXDET the viscosities of the test oils had a marked influence on the outcomes. Effectiveness was very high with the low viscosity oil, but declined markedly with increasing oil viscosity. The differences in effectiveness were clearly evident with the intermediate-viscosity oil, but differences in effectiveness among some products were obscured in tests with the higher and lower viscosity oils. It may be that the BFT may be influenced by viscosity in the same way as EXDET, but this cannot be proven with the existing data set.

Future Work

Future Ohmsett studies should include the following:

a) Retesting of Corexit and some of the dispersants and oils tested in this study to fill the gaps in this study.

b) The relative performance of the BFT and Ohmsett should be elaborated using the full range of available dispersant products listed on the US EPA National Contingency Plan Product Schedule.

c) The interaction of oil viscosity and dispersant brand effectiveness should be explored to assess the potential merits of using less effective (possibly less toxic or expensive) products in spills of non-viscous oils, reserving the more effective products for spills of more viscous or emulsified oils.

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Appendix A: LISST and C3 Measurements

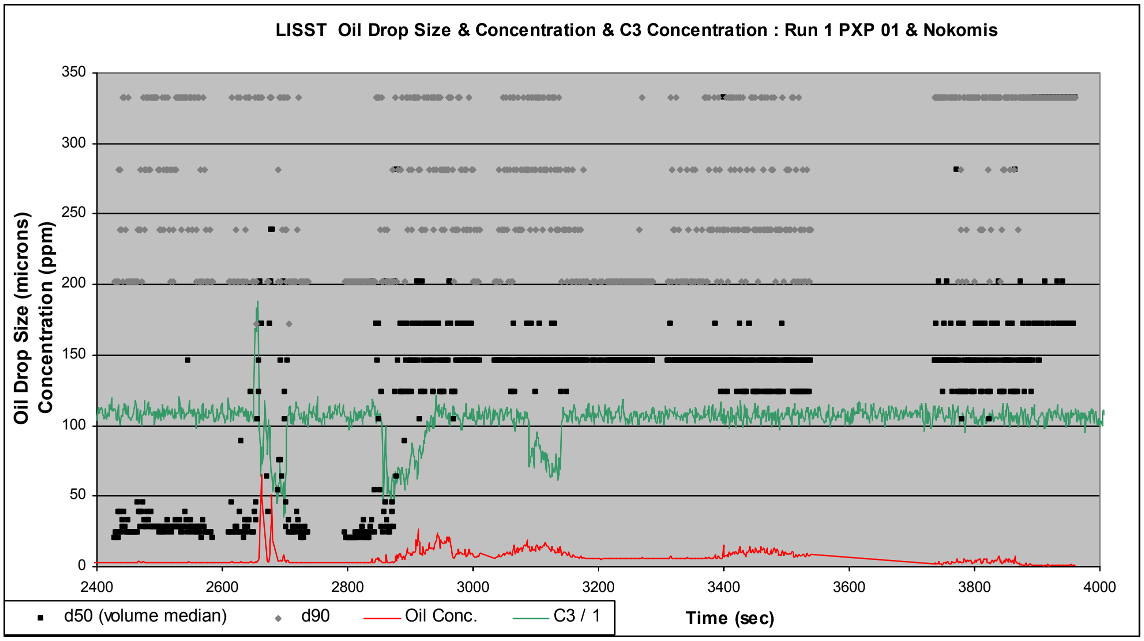

Figure A1: Oil Drop Size and Concentration Data: Test #1, PXP 01 x Nokomis

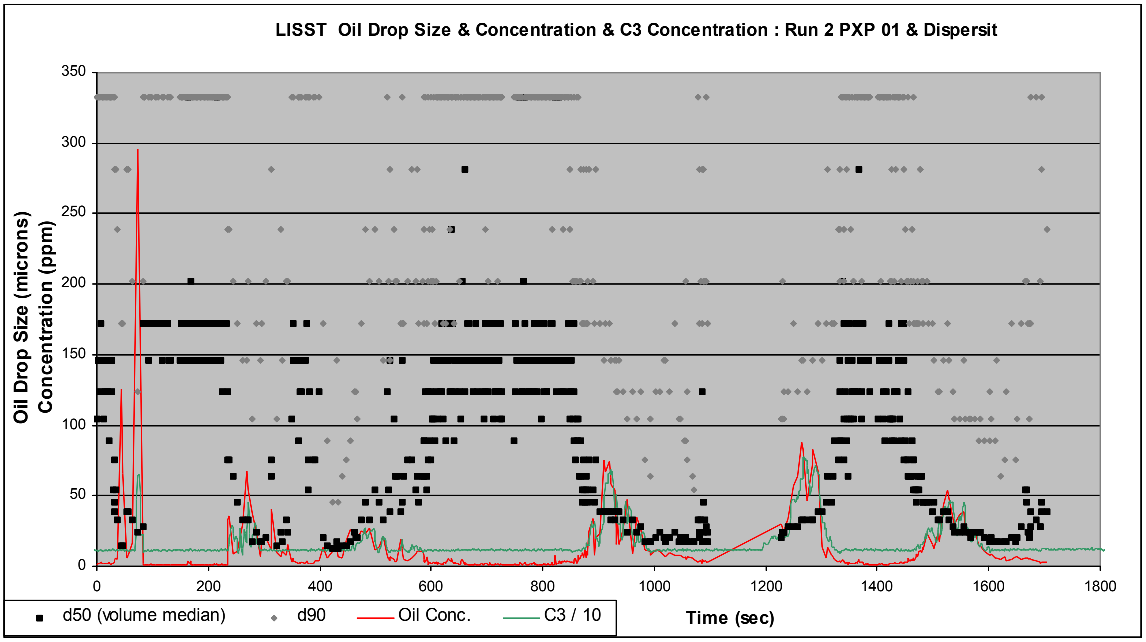

Figure A2: Oil Drop Size and Concentration Data: Test #1, PXP 01 x Dispersit

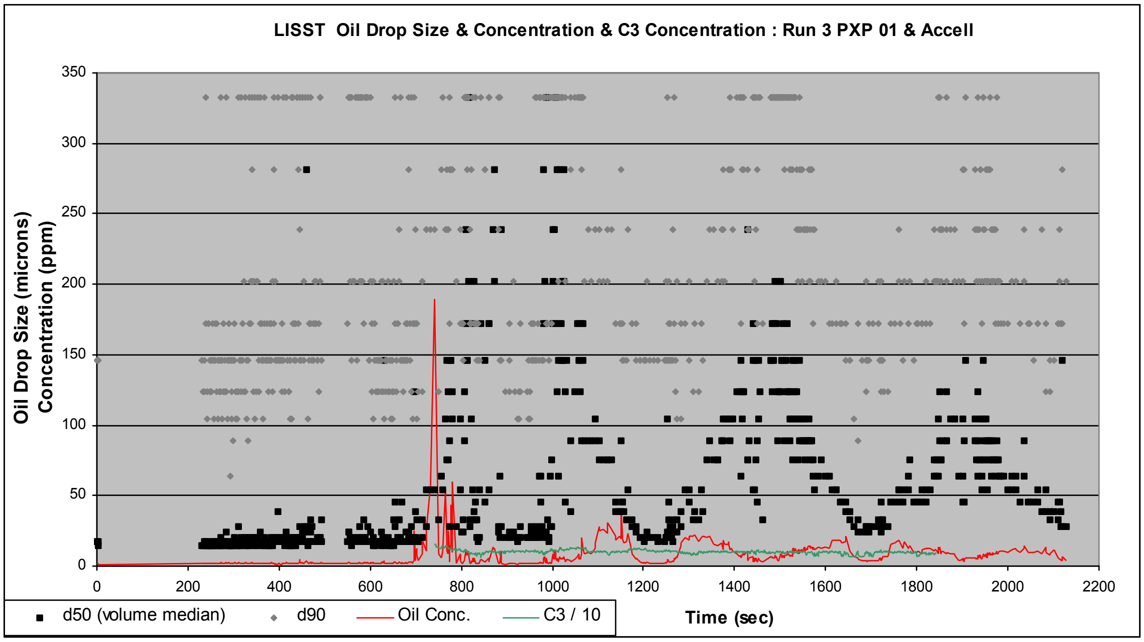

Figure A3: Oil Drop Size and Concentration Data: Test #1, PXP 01 x Accell

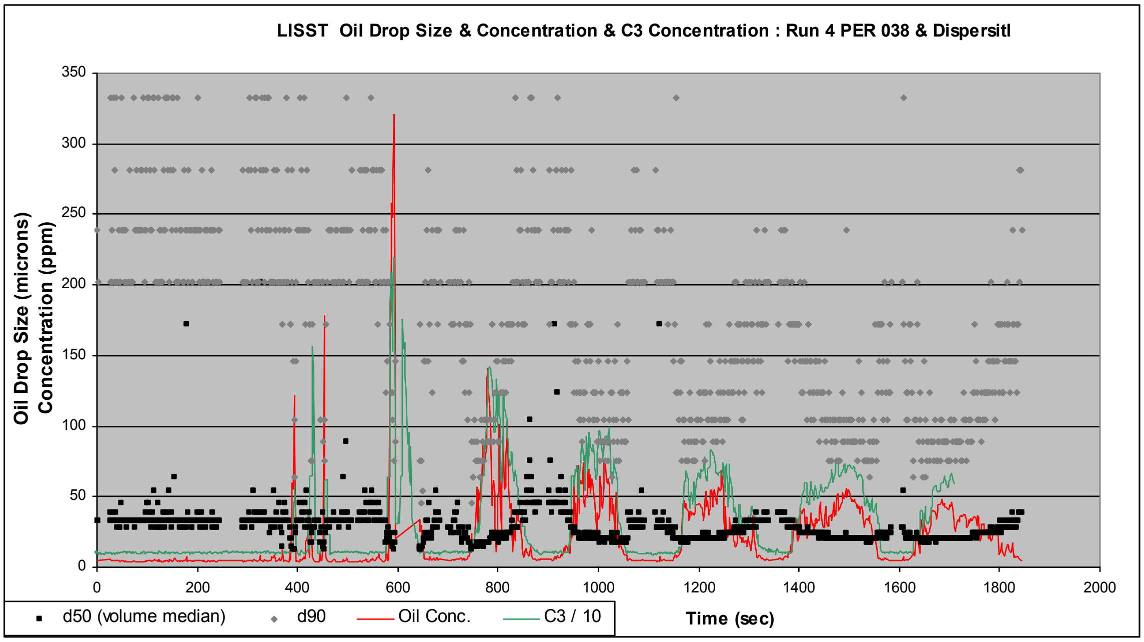

Figure A4: Oil Drop Size and Concentration Data: Test #1, PER 038 x Dispersit

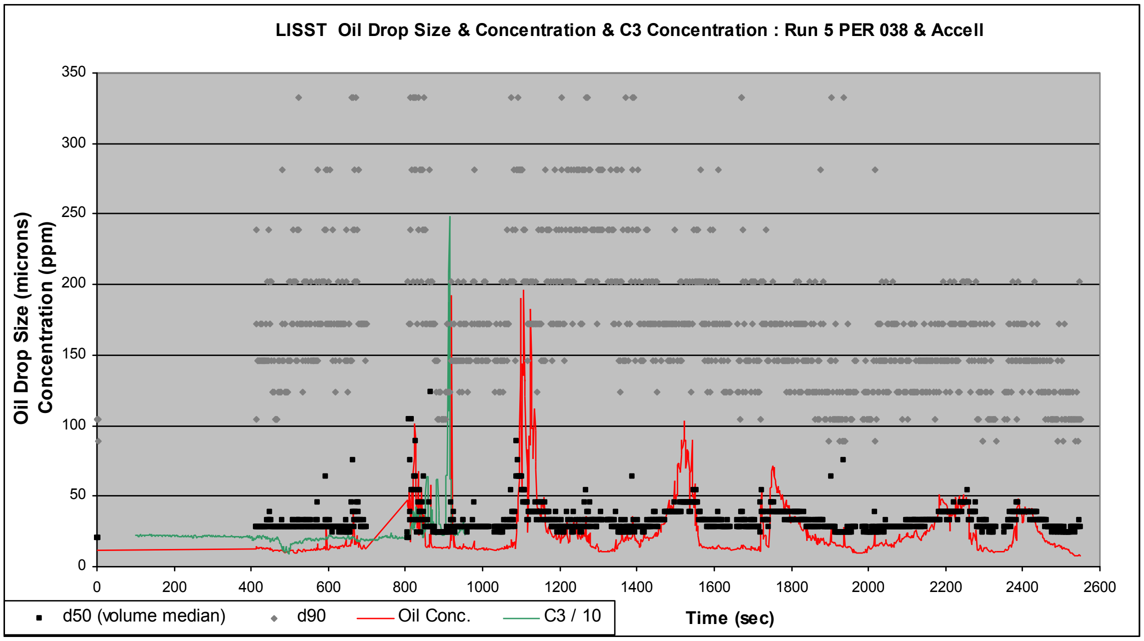

Figure A5: Oil Drop Size and Concentration Data: Test #1, PER 038 x Accell

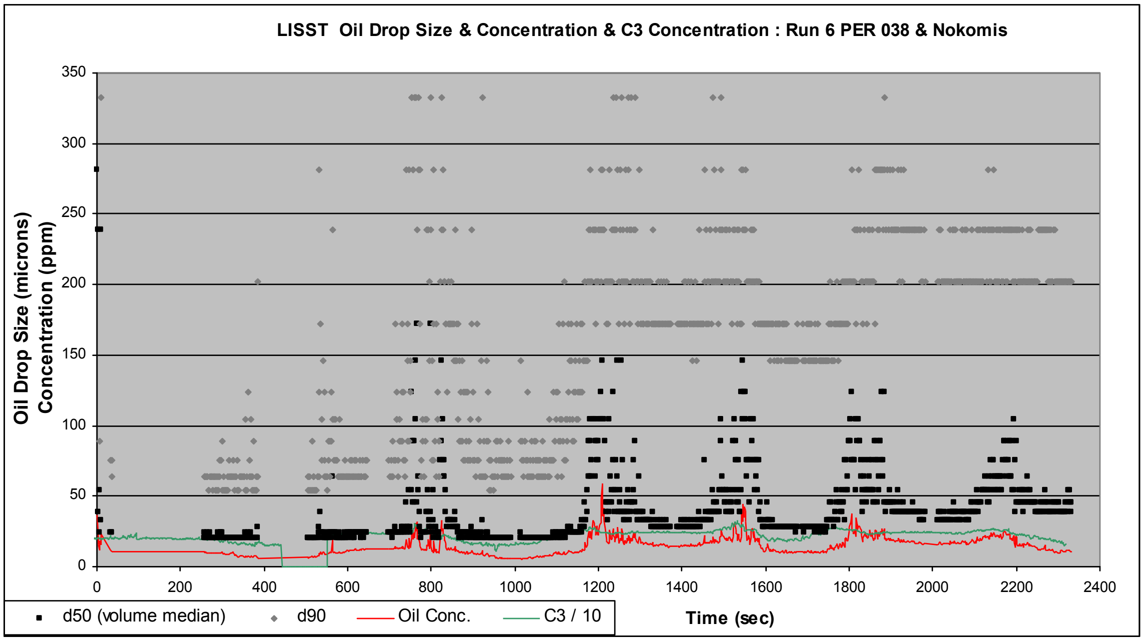

Figure A6: Oil Drop Size and Concentration Data: Test #1, PER 038 x Nokomis

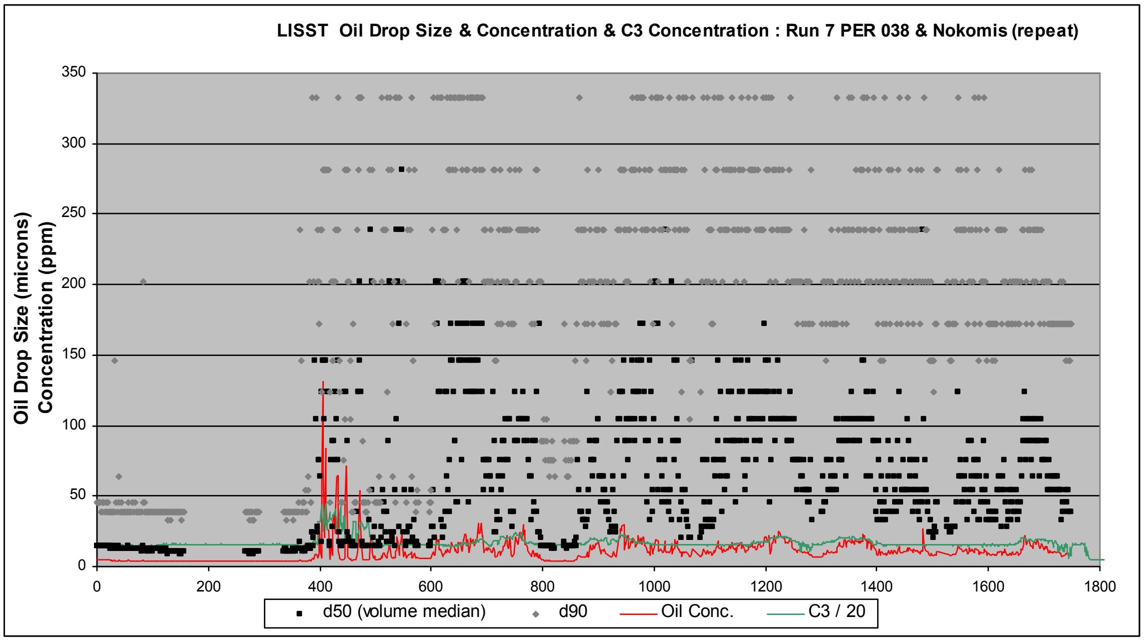

Figure A7: Oil Drop Size and Concentration Data: Test #1, PER 038 x Nokomis (repeat)

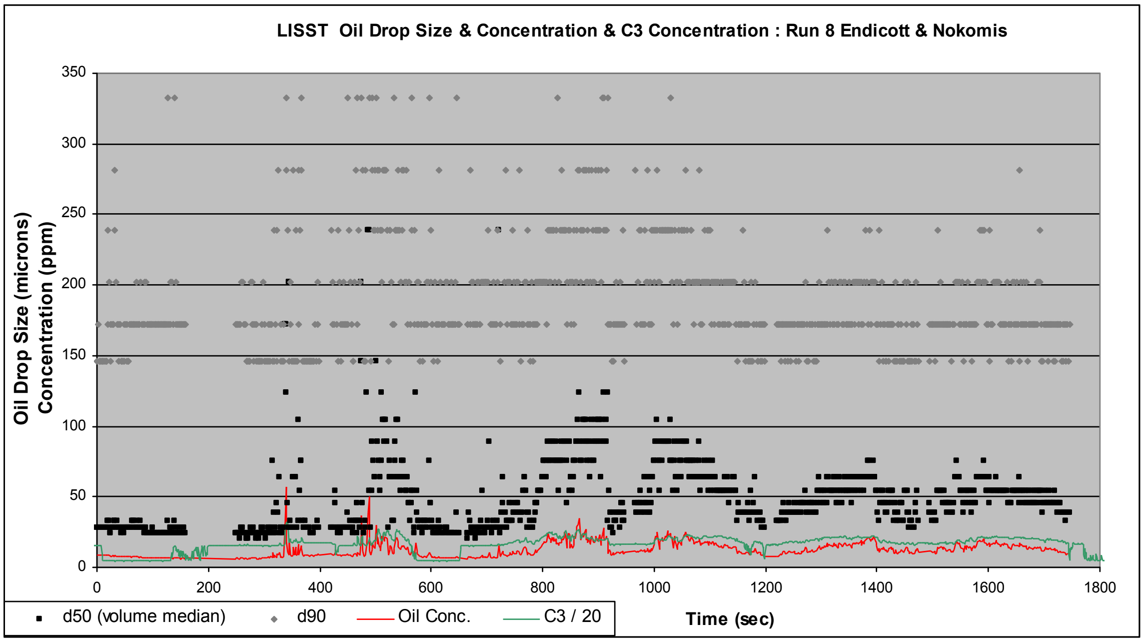

Figure A8: Oil Drop Size and Concentration Data: Test #1, Endicott x Nokomis (repeat)

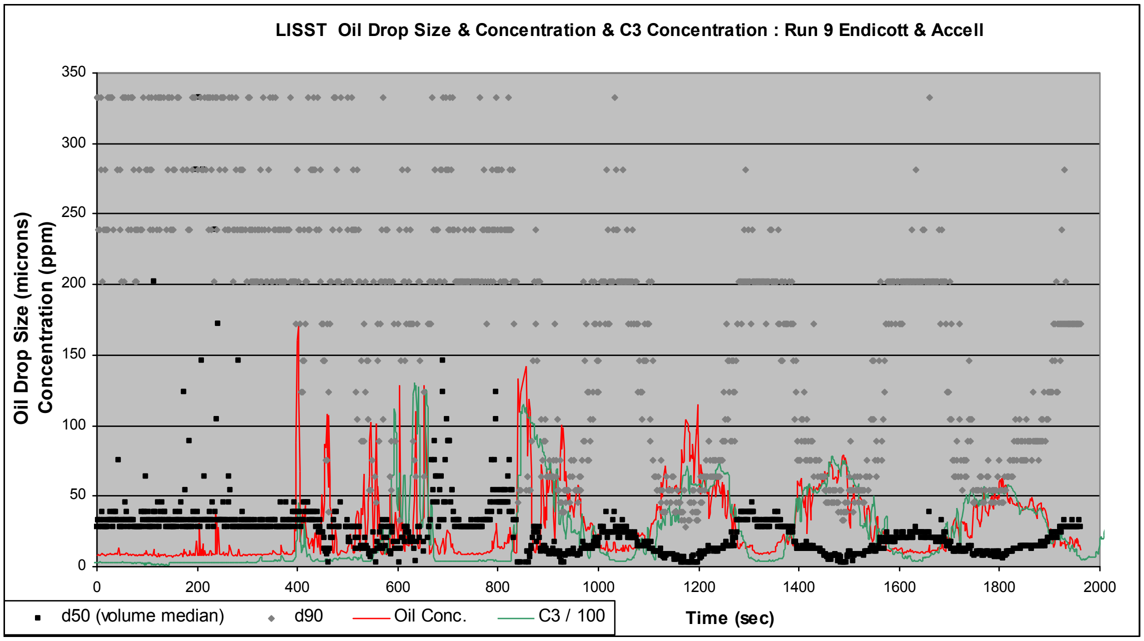

Figure A9: Oil Drop Size and Concentration Data: Test #1, Endicott x Accell

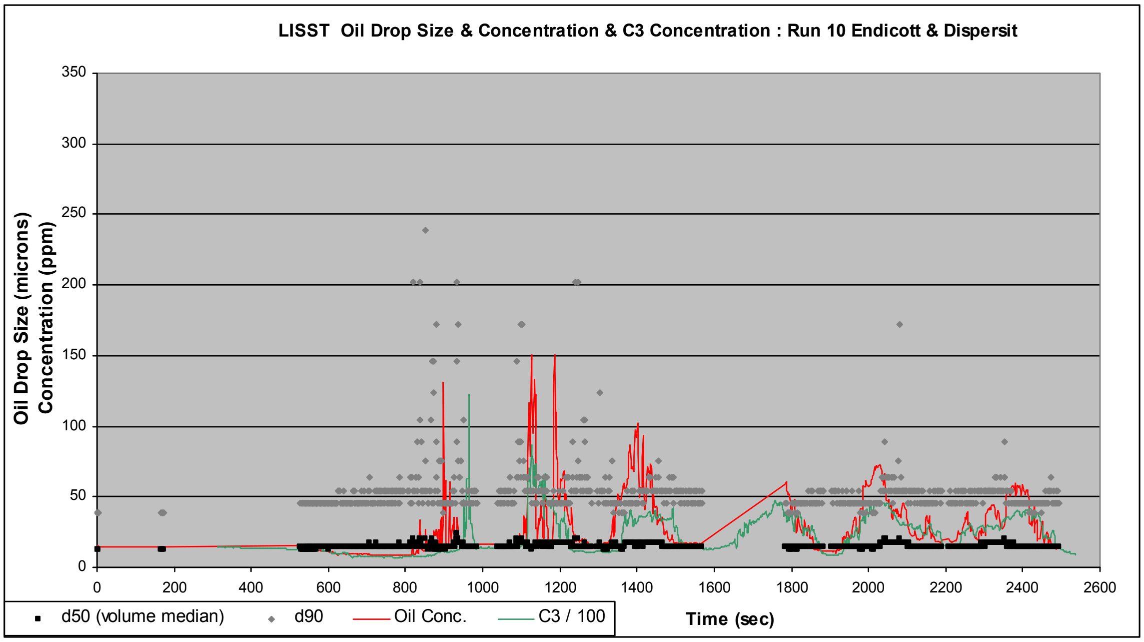

Figure A10: Oil Drop Size and Concentration Data: Test #1, Endicott x Dispersit

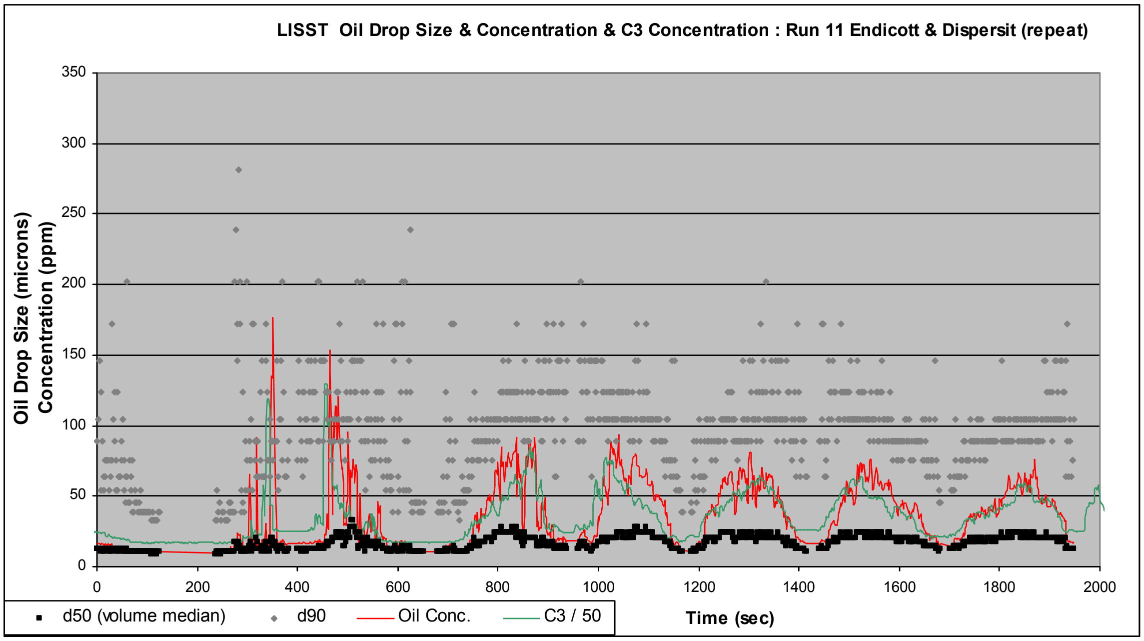

Figure A11: Oil Drop Size and Concentration Data: Test #1, Endicott x Dispersit (repeat)

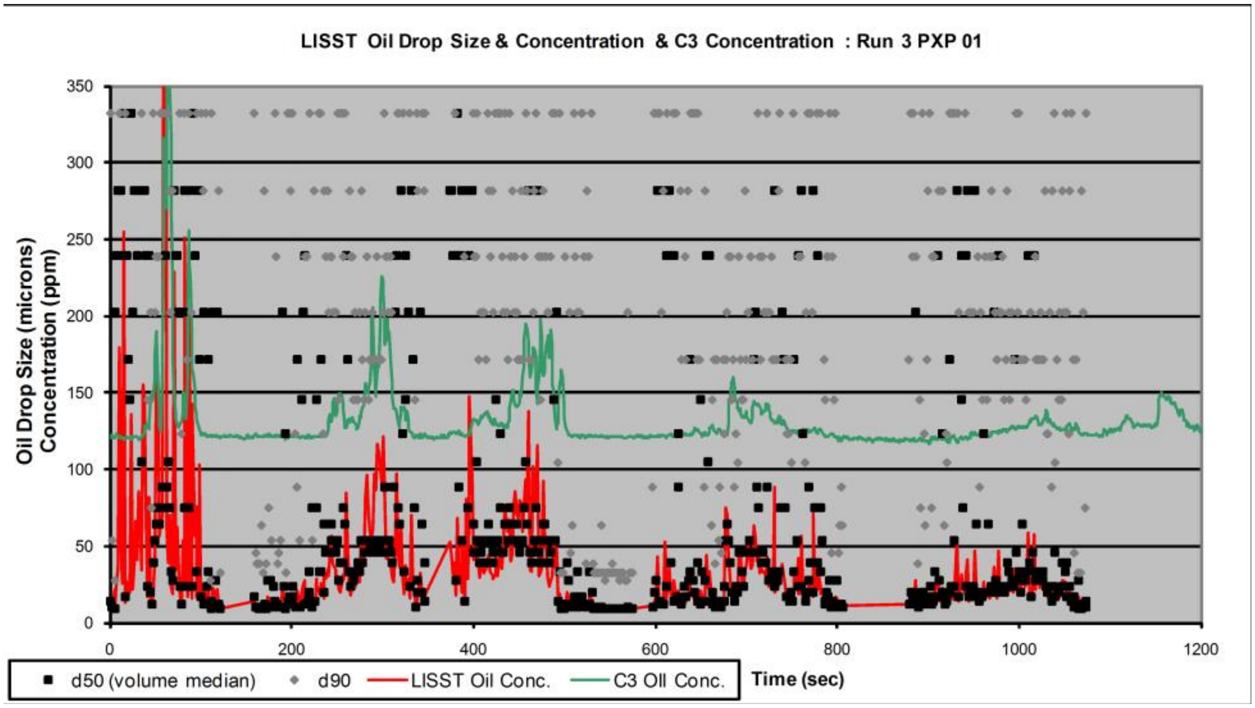

Figure A12: Oil Drop Size and Concentration Data: Test #3 (Oct 2012), PXP 01 x Corexit

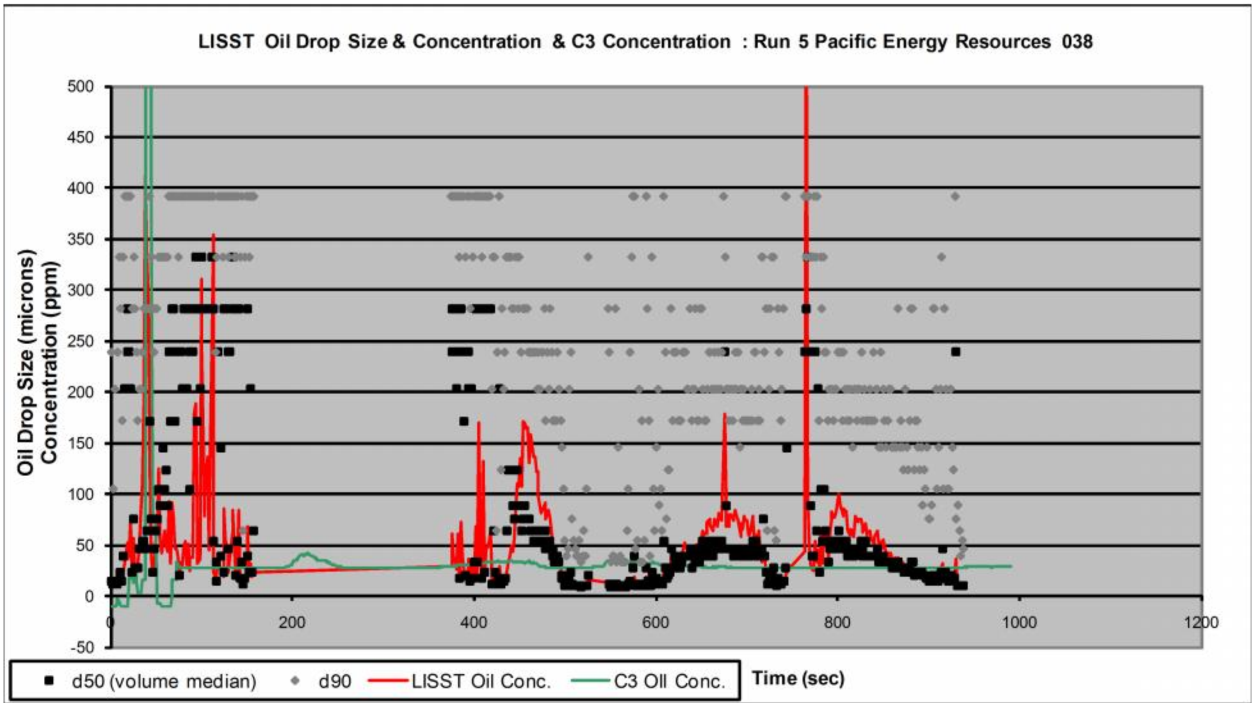

Figure A13: Oil Drop Size and Concentration Data: Test # (Oct 2012), PER 038 x Corexit

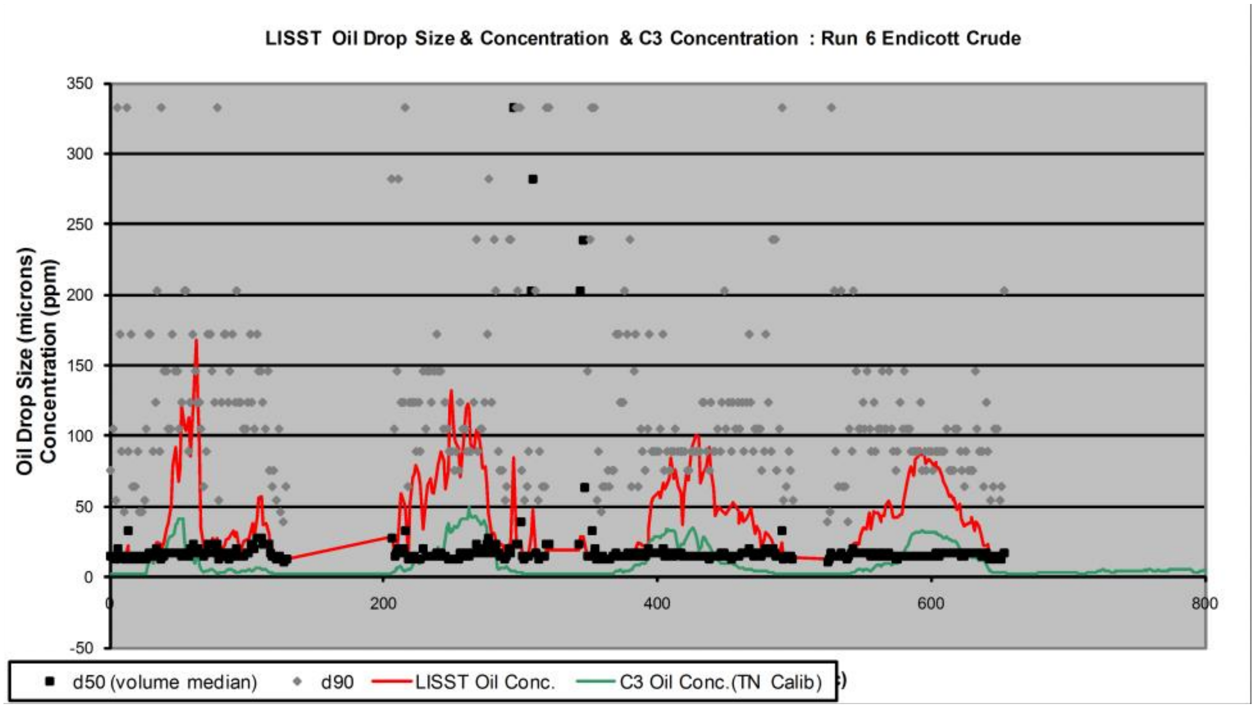

Figure A14: Oil Drop Size and Concentration Data: Test #6, Endicott x Corexit

Appendix B. EXDET Test Method

The procedure used here was from Becker 1993.

Equipment and supplies.

- Four 250 mL glass separatory funnels (such as Fisher 10-437 -1OC) for clamping onto the shaker-the 250 mL line should be approximately at the widepoint of the flask. (Funnels that are about 8 in from neck base to stopcock are recommended rather than shorter, pear-shaped separatory funnels.) Each funnel is stoppered to prevent splash-out.
- Four 16 oz glass jars (per test) for draining dispersed oil-in-water samples (Optional: see note A at the end of this appendix:)
- Eight 4 oz glass jars (per test) for solvent extracts
- Four 500 mL separatory funnels with glass stoppers for extracting the dispersed oil-in-water samples
- 100µL and 1000 µL Drummond Digital Microdispensers (pipettes)
- Bausch and Lomb Spectrophotometer (Spectronic 21), and adequate supply of appropriately matched sample tubes (cuvettes)
- Chloroform or methylene chloride, as a solvent, for extraction (Fisher certified Optima, for HPLC, spectrophotometer, GC, Fisher C297-4)
- Sea water, as needed (Sea Salt ASTM D-1141-52, Lake Products Co., Maryland Heights, Missouri, recommended for artificial sea water)
- Polypropylene sorbent pads (3M sorbent sheets cut into 1.5 in squares)
- Bottletop dispenser, 50 mL (Fisher 13-688-70); optional, for dispensing aliquots of solvent when many tests are being run
- Burrell Wrist-Action Shaker, Model 75 (Fisher 14-260), with arms holding two double clamps on each side (which can hold a total of eight separatory funnels)-For convenience, it is best to use only the four front clamps.

Initial Procedure

Shaker setup. The arms of the wrist-action shaker must be level, that is, the 250 mL separatory funnels must be in an upright, non-slant position before starting each group of tests. The funnels are clamped to the shaker just above the stopcock. To assure a secure and stable clamping action, rubber or latex laboratory tubing can be fitted over the fingers of the clamp, and/or olypropylene padding wrapped around the lower part of the funnel where the clamp grips. Add artificial sea water (approximately 250 mL) to reach the widest part of each test funnel. Mark this level on each test funnel for future runs.

Calibration. Use the adjustment handle to set the shaker deflection angle amplitude to between 1.5° and 1.6°. To measure the amplitude, a rod with pen attached to the end is clamped perpendicular to the shaker shaft, and the pen deflection is measured. For example, a pen deflection of 6 mm at a 218 mm distance from the center of the shaft to the tip of the pen (tangent 1.57° = 6/218) is set using the adjustment handle. The oscillation frequency of the current Burrell shaker is approximately 390 cycles per minute. This can be checked by recording the pen deflections on a chart recorder. Older Burrell shakers run at a lower frequency (approximately 310 cycles per minute) and should be set for a slightly greater deflection amplitude, such as 2.1°.

Detailed test method

If testing a premixed sample, prepare the desired dispersant/oil (D/O) mixture, for example, 1 part of dispersant to 25 parts of oil.

1. Fill each test funnel with artificial sea water to the widest part of the funnel (approximately 250 mL). Using the 1000 µL pipette, carefully add the test oil or D/O mixture (about 1 mL) to the top of the water in each test funnel. Then, if using the direct application method, carefully add the desired amount of dispersant to the oil. Stopper the funnels, start the shaker, and allow toshake for 15 minutes. Then, without stopping the shaker, add one sorbent pad to each test funnel, replace the stopper, and continue shaking for 5 minutes more. The sorbent will collect the undispersed oil.
2. Do not stop the shaker, but remove the stoppers from each funnel, and drain the dispersed oil/water mixture from each funnel into 16 oz glass jars or 500 mL separatory funnels (see Note A). The sorbent pad remains in the funnel. Be sure to shut the stopcock immediately after the water drains to prevent any of the oil clinging to the sides of the test funnel from draining oil.
3. Stop the shaker, and add 50 mL of solvent to each funnel to extract the oil from the sorbent pads. Be sure to "wash" the sides of the funnel with solvent when adding the first 50 mL aliquot. Shake for 5 to 10 minutes, and then drain the oil/solvent mixture from each test funnel into separate 4 oz jars, squeezing the pad against the side of the glass jar to remove as much oil as possible. Repeat this procedure with a second 50 mL aliquot of solvent, adding the drainage to the first extract in the respective 4 oz jars. A total of 100 mL of solvent is used for each undispersed oil sample (see Note B). The shaking funnels are left in place at the end of the experiment, and, after rinsing with water, are ready for the next run.
4. While the pads are being extracted, the extraction of the dispersed oil/water fractions can begin. If 16 oz jars were used in Step 3, transfer each of these fractions to a set of 500 mL separatory funnels. Rinse each of the 16 oz jars with 50 mL of solvent, and add this to the respective separatory funnels. Stopper, and shake the funnels vigorously by hand. After allowing the contents to separate completely, draw off the lower fraction into a set of 4 oz jars. Repeat the procedure with a second 50 mL aliquot of solvent for each sample, until the top fraction is clear of oil. A total of 100 mL of solvent is used for each dispersed oil sample (see Note B).

These procedures result in two 4 oz jars (100 ml) of extracts for each test funnel, one of dispersed oil from the water, the other of undispersed oil from the sorbent pads.

5. The extracts are examined in the spectrophotometer at an appropriate wave-length setting, such as, 460 millimicrons. The extracts may have to be diluted to fall in the linear range, 0.1 to 1.1, of the spectrophotometer. If an undiluted sample is too low, select a wavelength to obtain a reading in this range if possible, and use this same setting for both extracts. The dilution can be carried out in the cuvettes used in the spectrophotometer, using pipettes to add known amounts of extract and pure solvent.
6. Zero the spectrophotometer with a solvent blank. Read the absorbance of each pair of test samples, both water extract and sorbent pad extract.

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

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

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

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

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

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

Equation 1 can be simplified to:

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

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

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

Notes.

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

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

Appendix C. EPA Baffled Flask Method

The method used here was modified from Venosa and Holder (2011).

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

Figure 1. Photograph of the baffled trypsinizing flask.

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

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

Major Ion	Salt Composition, % total weight	Salt Composition at 34 ppt Salinity, mg/L
Chloride (Cl$^-$)	47.470	18,740
Sodium (Na$^+$)	26.280	10,454
Sulfate (SO$_4^{-2}$)	6.600	2,631
Magnesium (Mg^{+2})	3.230	1,256
Calcium (Ca^{+2})	1.013	400
Potassium (K$^+$)	1.015	401
Bicarbonate (HCO^{-3})	0.491	194
Boron (B^{3+})	0.015	6
Strontium (Sr^{2+})	0.001	7.5
Solids Total	86.11%	34,090
Water	13.88	--
Total	99.99%	--

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Appendix D. Temperature-Viscosity Curves for Oil Samples