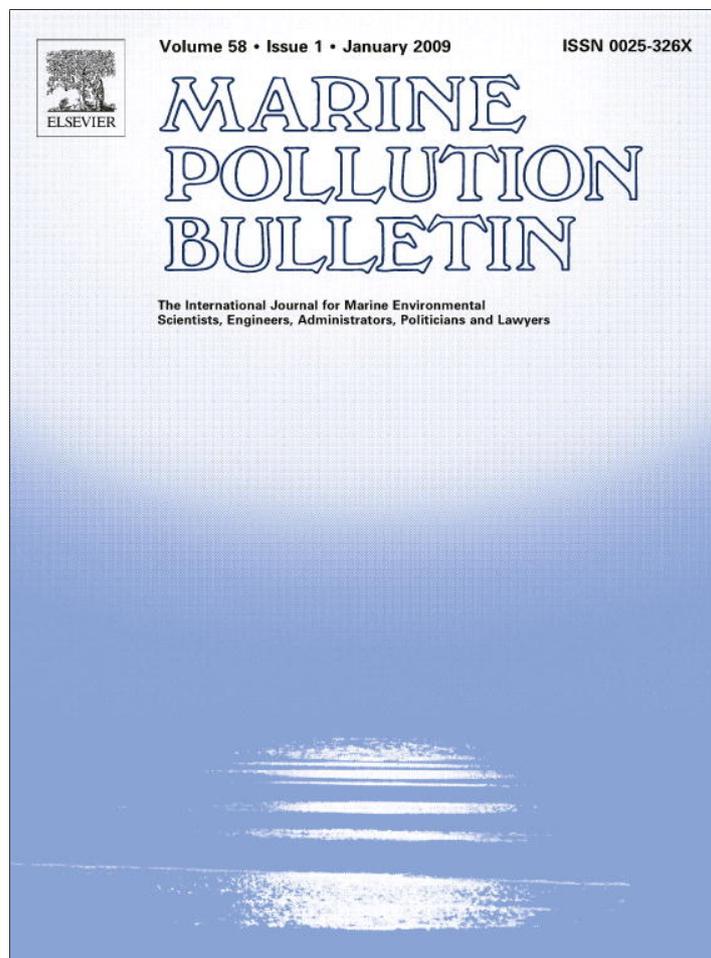


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Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants

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ABSTRACT

There continues to be reluctance in some jurisdictions to use chemical dispersants as a viable countermeasure for accidental oil spills. One argument used by some opponents to dispersant use is that “chemical dispersants do not work effectively in cold water”. To address this issue, the U.S. Minerals Management Service (MMS) funded and conducted two series of large-scale dispersant experiments in very cold water at Ohmsett – The National Oil Spill Response Test Facility, located in Leonardo, New Jersey in February–March 2006 and January–March 2007. Alaska North Slope, Endicott, Northstar and Pt. McIntyre crude oils and Corexit 9500 and Corexit 9527 dispersants were used in the two test series. The crude oils were tested both when fresh and after weathering. Results demonstrated that both Corexit 9500 and Corexit 9527 dispersants were 85–99% effective in dispersing the fresh and weathered crude oils tested at cold temperatures. The MMS expects that results from these test series will assist government regulators and responders in making science based decisions on the use of dispersants as a response tool for oil spills in the Arctic.

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1. Introduction

Considerable skepticism exists concerning the viability of using chemical dispersants on crude oils spills in very cold-water conditions. There are regional concerns that dispersants may not be effective on spills of Alaskan crude oils in cold water, especially those that could take place in the colder months and that dispersants should not be or cannot be used in these conditions. The general misconception is that cold temperatures inhibit dispersant effectiveness (DE). Colder temperatures do increase the viscosity of the spilled oil and dispersant product. Dispersants have been formulated to be relatively non-viscous in cold temperatures and can be successfully applied in cold weather. The viscosity of spilled oil will be higher at low temperature, but possibly not too high for effective chemical dispersion.

A number of bench-scale test programs that investigated the effect of cold temperatures on chemical dispersant effectiveness were completed in the 1980s. Tests completed by Harris and Wells

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(1980) and Mackay et al. (1980) both showed reduced dispersant effectiveness with colder temperatures. Cox et al. (1981) used similar test apparatus and methods and found that cold dispersant applied to warm oil-water systems worked better than warm dispersant and concluded that dispersants could be effective in cold arctic environments. MacKay and Hassain (1982) studied interfacial tensions in dispersant-oil-sea water systems using a spinning drop technique and found that oil-water interfacial tensions were higher in cold-water thus suggesting that dispersants might be less effective in cold conditions. However, Mackay also stated that the overall effect of temperature on DE would be very complex due to dispersant-oil mixing and interfacial tension modification processes as well as oil viscosity issues. Farmwald and Nelson (1982) conducted tests using cold air (4 to –40 °C) over 1 °C water and DE was not impaired even at the lowest temperature. He concluded that low air temperature should not govern the decision to use dispersants. The results from bench-scale tests conducted by Byford (1982), Byford et al. (1983) suggested that the optimization of a dispersant formulation for one crude oil at low temperature may not result in optimal results for another crude. Byford also suggested that higher oil viscosities due to cold temperatures might reduce oil re-coalescence of dispersed oil drops and the higher density of the oil reduces buoyancy; both factors resulting in better dispersion with cold temperatures. Cold temperatures did not significantly reduce DE in these tests. He found poor

correlation between different test apparatus and attributed the differences in results to different mixing energies used in each apparatus. Lehtinen and Vesala (1984) tested DE at various salinities and temperatures and found reduced effectiveness at low salinities and low temperatures. Mackay et al. (1985) proposed mechanisms for chemical dispersion of oil slicks, based on results from bench scale testing and observations, and concluded that chemical dispersion under cold marine conditions is only marginally more difficult or requires only marginally more dispersant unless there is a marked increase in the oil viscosity because the temperature is less than the oil's pour point. Brandvik et al. (1992) achieved 10–90% DE in small-scale tests at 0 °C for a range of dispersants on various weathered oil and water-in-oil emulsions.

Tests were conducted in a large outdoor wave tank, in cold-water conditions (1–13 °C), by Esso Resources Canada (Brown et al., 1985 and Brown et al., 1986). The tests showed that dispersants could be effective in cold conditions under breaking waves (1%–77% DE) and to a lesser extent (3%–33% DE) in non-breaking waves of 10–20 cm in height. The DE estimates were based on extensive in-water oil concentration measurements taken 20 h after the wave action was terminated. The authors noted that the DE measurements under-estimated likely field effectiveness since the waves were not left on during the 20 h prior to measurement and some oil drops rose to the surface under these quiescent conditions whereas they would remain in the water column in the presence of normal turbulence in typical field conditions. Mackay (1995) completed cold-water (4 °C) dispersant effectiveness tests in both a bench scale apparatus (EXDET test) and in the ESSO Resources Canada outdoor test basin using Alaska North Slope Crude oil and Corexit 9527. The bench scale results showed a slight decrease (from 90% to 80%) in effectiveness as the temperature increased from 4 °C to 15 °C suggesting that the cold conditions slightly improved the dispersant performance. The tests completed in the outdoor basin resulted in measured DE values between 80 and 97% for weathered ANS crude oil subjected to breaking waves immediately after the application of dispersant.

In summary, various small- and large-scale DE tests have been completed at cold temperatures in the past with somewhat mixed results. Generally, the results have indicated that chemical dispersants can be effective in cold conditions, but several factors might reduce their effectiveness in the cold.

The goal of this research was to determine if typical Alaskan crude oils are amenable to chemical dispersion in near-freezing temperatures. Large-scale experiments that simulate at-sea conditions were conducted to eliminate the concerns posed when extrapolating laboratory test results to offshore conditions. The mixing energies generated by surface waves in the large tank more closely simulate offshore mixing conditions when compared to bench-scale test systems and full-scale dispersant application equipment can be used to apply the dispersant to realistic slicks. The National Research Council (NRC) strongly supported the use of wave-tank testing in their recent review of chemical dispersants as evidenced in the following quote from the report "... wave-tank tests are an important tool that can be used to tie the artificialities of laboratory studies to the operational realities of dispersant use in spill response" (NRC, 2005).

The DE test series were conducted at Ohmsett – The National Oil Spill Response Test Facility, located in Leonardo, New Jersey, USA. More information regarding the capabilities of this research facility can be found at <http://www.ohmsett.com>. Twenty-five large-scale dispersant effectiveness experiments were completed in the winter of 2006 using Corexit 9527 (SL Ross, 2006b), the dispersant product presently stockpiled in Alaska. Twenty-one large-scale tests were conducted in the winter of 2007 using Corexit 9500 (SL Ross, 2007), the dispersant that would most likely be used

to replace the Corexit 9527 stockpiles if they were depleted. Alaska North Slope, Endicott, Northstar and Point McIntyre crude oils were used in both test programs. Detailed project reports for these two research projects can be acquired from the Minerals Management Services web site (<http://www.mms.gov/tap/home/>).

2. Methods

2.1. Overview of test procedure

A test is conducted by laying down a uniform slick of a known quantity of oil on the surface of the Ohmsett tank, spraying the oil with dispersant at a pre-determined dose, subjecting the oil to wave action (breaking waves) for 30 min and then collecting the oil remaining on the surface at the end of the mixing period. The oil discharge and dispersant spraying operations are completed from opposite sides of a moving bridge in a single-pass operation.

A comparison of the oil collected with the oil released provides an estimate of the effectiveness of the dispersant. Control tests are conducted without the application of dispersant to determine potential oil losses by processes other than chemical dispersion, such as sidewall adhesion, evaporation and natural dispersion/dissolution. Dispersant effectiveness (DE) estimates are compared to the oil losses in the control tests to determine if the application of chemical dispersant has a significant or only marginal impact on the survival of the surface oil.

Time is provided between tests (usually between 1.5 and 2 h) to allow large oil drops from a previous test to surface prior to completion of the next test. Immediately before each test, the test area was cleared of oil on the water surface, tank sidewalls and end booms by sweeping it down the tank using the spray from fire nozzles and out of the test area. It has been determined that the dispersant in the water from a previous test has no effect on the outcome of a subsequent test unless the dispersant concentration in the water is greater than about 400 ppm (SL Ross, 2000a). Dispersant concentrations in the tank never exceeded 10 ppm in either of the test programs. 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, 2004a, 2006a) and the National Research Council (NRC) review comments (NRC, 2005).

Ideally, oil in the water column (both particulate and dissolved), on the water surface, on tanks side walls and booms and the amount of oil evaporated should be measured to permit the determination of a mass balance of oil before and after each test to be certain that all of the oil has been accurately accounted for. Unfortunately, completing the measurements necessary to arrive at oil mass balance determinations is not a feasible option in a test of this size. The primary difficulty is in accurately determining the quantity of oil present in the water column during or immediately after a test. The spatial and temporal variability of the dispersed oil in the water column makes it virtually impossible to accurately measure the amount of oil in the water column at a point in time. The number of sensors or sampling points needed to measure the oil concentrations at a sufficient resolution to confidently establish the amount of oil in the water column is economically and logistically unmanageable. This difficulty in measuring the in-water oil present in large-scale test facilities or offshore experiments has been well documented by other researchers (Brown et al., 1987; Goodman, 2004). Goodman stated that "at any scale greater than the size of laboratory apparatus the measurement of mass balance is truly a myth using existing technologies". Bonner (Bonner et al., 2003) attempted

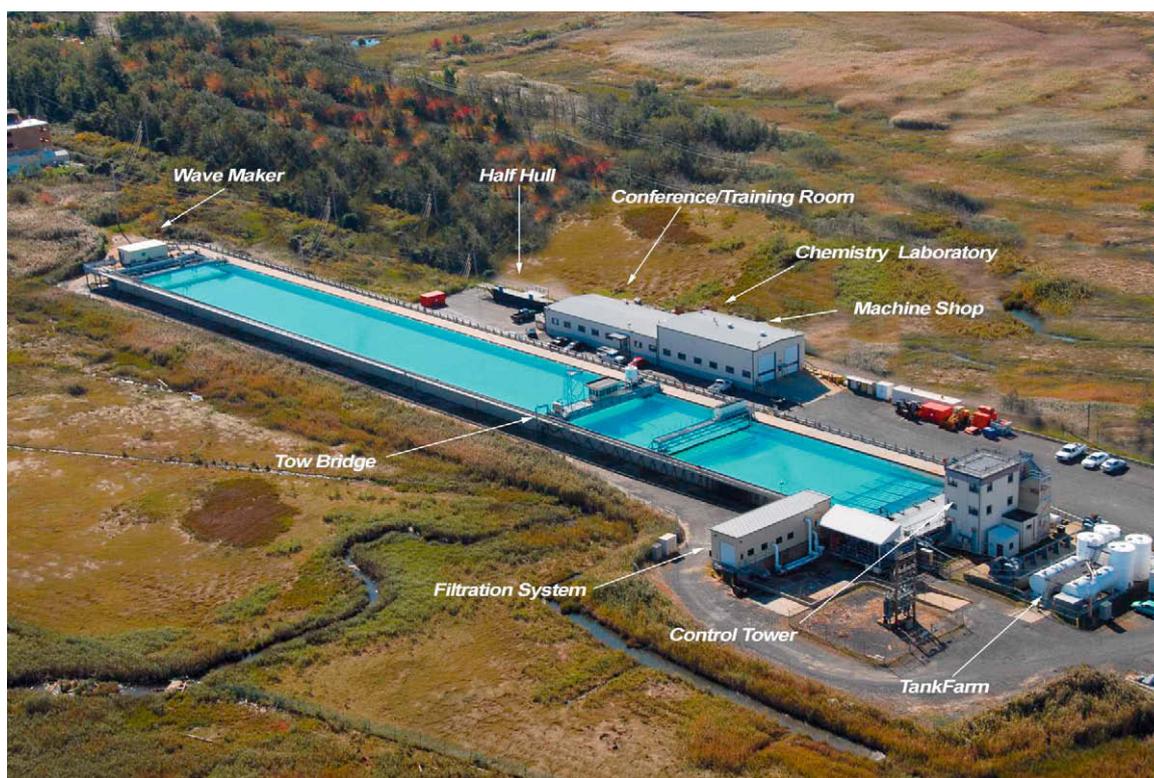


Fig. 1. Ohmsett – the National Oil Spill Response Test Facility.

to achieve a mass-balance measurement in a meso-scale dispersant effectiveness test without success. Depending on the instrumentation used to measure in-water oil quantities up to 30% of the oil was un-accounted for. Only one test was completed in this study, presumably due to the high cost associated with attempting to achieve a mass-balance on the oil.

2.2. Major test equipment components

The key component of the test facility is the outdoor, above ground, concrete test tank, seen in Fig. 1, which measures 203 meters long by 20 m wide, by 3.3 m deep. The tank is filled with 9.8 million liters of clear saltwater, is maintained at oceanic salinity (32–35 ppt) and is filtered and treated to maintain water clarity. Ocean waves are simulated with a wave generating system and a wave dampening artificial beach. The wave paddle was operated with a stroke of 7.6 cm (three inches) and a frequency of 35 rpm for these experiments. This wave setting generates significant wave heights ($H_{1/3}$) of 20–50 cm over the surface of the tank (Asher, 2005) with wave periods between 1.8 and 2.2 s.

The main moveable bridge spans the width of the tank and is used as a platform to discharge the oil and dispersant, to tow oil measuring devices through the dispersed oil clouds and to house personnel and equipment used to monitor the behavior of the spilled oil during an experiment.

The DE experiments are conducted over the full width of the tank and over 150 m of its 203 m length. Containment booms are placed across the tank in front of the wave paddle at the south end and the beaches at the north end to contain the oil during the test and to facilitate collection of oil. Oil was discharged using a progressing cavity pump and a discharge header positioned just above the water surface. Dispersant was applied at 50 psi using a gear pump and Spraying Systems Company flat fan T-jet nozzles (model Nos. 80015 or 8004) mounted on a spray bar positioned approximately one metre above the water surface.

2.3. Oil measurement

2.3.1. Surface oil

The quantity of oil discharged was determined by measuring the change in oil depth in the supply tank. After the waves were stopped at the end of each test, the remaining surface oil was herded to a collection point at the end of the tank using local currents induced by the spray from fire monitors and skimmed from the surface. The oil and water mixture collected was decanted to remove excess water and the remaining emulsion was analysed for water content to determine the amount of oil collected at the end of the test. Evaporative losses in the control tests were accounted for by comparing the collected oil densities to density versus percent evaporation curves prepared for the test oils.

2.3.2. Dispersed oil

In-water oil concentrations were estimated using three or four different techniques depending on the experiment. The oil concentrations were measured to identify when elevated oil concentrations existed to verify that the chemical dispersants were having an effect and to characterize the drop size distributions of the oil dispersions when they occurred. Various methods were deployed in the two test programs primarily to identify the most appropriate method and equipment package for use in future test programs. A Turner 10AU flow-through fluorometer, a LISST 100 particle size analyzer and a Turner Designs TD500D oil-in-water analyzer were used in all of the 2006 tests and a Wet Labs in-situ fluorometer also was used in a few of the early 2006 test runs. In the 2007 test program, only the LISST 100 and a TD3100 oil-in-water analyzer were deployed for in-water oil characterization. The LISST 100 device, the WET Labs *in situ* fluorometer and the water pump feeding the Turner 10AU and water grab-sampling ports were all positioned at 1.5 meters below the calm water level in both test programs. Technical details for these four oil-in-water measuring systems can be found at the following web sites: <http://>

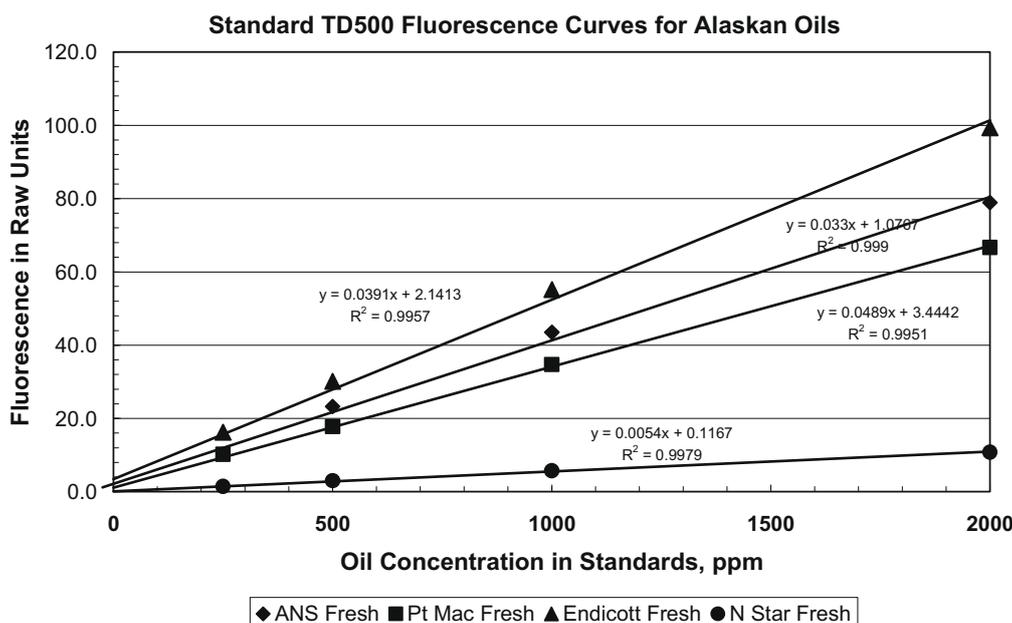


Fig. 2. Standard calibration curves for fresh Alaskan oils using TD500.

www.sequoiasci.com, <http://www.oilinwatermonitors.com>, <http://www.wetlabs.com>.

The Turner 10AU flow-through fluorometers were fitted with a 10–046 lamp, a 034–0860 excitation filter (254 nm), a 1/16" attenuator plate and a 10–050R emission filter. The emission filter is broad enough to measure anything from diesel through #6 fuel oil. Prior to the testing the sensitivity and range of the 10AU's were set using standard dispersions of ANS crude oil (pre-mixed with dispersant at a 1:50 dispersant to oil ratio) in salt water. The systems were then calibrated using standard ANS crude and dispersant (pre-mixed 1:50 DOR) dispersions ranging from 10 to 1000 ppm. The 10AU's outputs were regularly checked by injecting them with standard oil-in-water dispersions of 200 ppm. The flow-through cells required periodic cleaning to maintain accurate readings.

The Turner Designs TD500D and TD3100 generate raw fluorescence measurements for solvent (heptane) extracted samples. The raw values are then converted to oil concentration based on calibrations with known oil-in-solvent concentrations. The sensitivity of these devices were set prior to the test programs to ensure that a linear response to oil concentration in the range of 0–2000 ppm was possible. Calibration curves (see Fig. 2) were established for all of the oils tested. One hundred ml water samples were taken during the experiments and the oil was extracted with 10 ml of heptane. Raw fluorescence measurements from each sample extraction were then converted to oil concentrations using the calibration curves.

The WET Labs *in situ* fluorometer was used as configured to measure raw fluorescence.

Dispersed oil drop size distributions were measured using the LISST 100 particle size analyzer. The LISST 100 is a laser diffraction device that measures angular scattering distribution in 32 ring detectors corresponding to drop size ranges from 2.5 to 500 μm . The operating status or health of the instrument is checked by recording the background scatter using distilled water. If the scatter matches the factory settings, the glass surfaces are clean and the device is working properly. There are no user adjustments for device calibration only the need to keep the glass surfaces clean during operation. This device also generates an estimate of oil concentration based on the oil drop information gathered.

3. Dispersants and oils used in test programs

Corexit 9527 dispersant was used in the 2006 testing and Corexit 9500 was used in 2007.

Four Alaskan crude oils were tested in both 2006 and 2007. They were Alaskan North Slope (ANS), Endicott (End), Pt. McIntyre (PtMc), and Northstar (NS) crude oils. ANS is a blend of crude oils from the various Alaska North Slope fields and is the oil that is exported from Alaska by tankers, whereas the other oils are specific to their Alaskan production areas. In the 2006 test program oils were tested fresh, weathered by removal of light ends using air sparging and weathered by placing the oils on the tank in breaking wave conditions (high-energy 34–35 cpm waves) and non-breaking waves (low-energy 28 cpm waves) long enough for the oil to reach a volume percent loss similar to the air sparged oils. The on-tank weathered oils were weathered on the tank and then collected and stored in drums at 0 °C until used in a test. The oils were weathered, collected and then re-released using the oil discharge header to facilitate the control of the dispersant dosage and to ensure that a similar test method was used in all tests. Only fresh oils and oils weathered by air sparging were used in the 2007 test program.

Air sparging is a standard procedure to weather crude oils that is used by researchers worldwide (SL Ross, 2007). The target evaporative loss for the oils used was 15% by mass for the ANS, Endicott and Pt. McIntyre oils and 30% for the Northstar crude.

One objective of the 2006 testing was to compare the process of on-tank weathering (light-end losses only without significant water-in-oil emulsion formation) to that of air sparged weathering. The goal was not to generate water-in-oil emulsions in the on-tank weathering, but to match the light-end loss achieved in the air sparging process as close as possible. The physical properties of the oils used in the two test programs are shown in Table 1. No oils were weathered "on-tank" in the 2007 test program.

The Endicott oil was not subjected to on-tank weathering in the 2006 program due to time constraints. The on-tank weathered oils formed water-in-oil emulsions of varying water contents and stabilities. Although this was not intended, it was inevitable. The water contents of these oils at the time they were used in the dispersant application testing in the 2006 experiments are shown in Table 1.

Table 1
Physical properties of test oils

Oil	2006 Program				2007 Program		
	Density (mg/l)	Viscosity (cP) 100 s ⁻¹ , 1 °C	Oil Loss (% Volume)	Water Content (%)	Density (mg/l) @20 °C	Viscosity (cP) 100 s ⁻¹ , 1 °C	Oil Loss (% Volume)
<i>Alaska north slope</i>							
Fresh	0.863	22	0	0	0.862	65	0
Air sparged	0.887	93	15.3	0.2	0.893	200	15
Air sparged	–	–	–	–	0.900	300	22
On-tank lo-Energy	0.901	203	25.1	5	–	–	–
On-tank hi-energy	0.903	200	26.5	16	–	–	–
<i>Endicott</i>							
Fresh	0.9018	270	0	0.2	0.901	350	0
Air sparged	0.917	644	20.1	0	0.916	520	18
<i>Northstar</i>							
Fresh	0.8025	7.6	0	0	0.814	6	0
Air sparged	0.839	36	34.5	0	0.842	30	30
On-Tank Lo-Energy	0.842	116	37.6	40	–	–	–
On-tank hi-energy	0.843	143	38.6	48	–	–	–
<i>Pt. McIntyre</i>							
Fresh	0.861	34	0	2	0.862	45	0
Air sparged	0.880	76	12.5	0.5	0.898	400	15
On-tank lo-energy	0.884	214	15.9	45	–	–	–
On-tank hi-energy	0.898	695	27.6	48	–	–	–

4. Test results

4.1. Test conditions and raw dispersant effectiveness estimates

The test conditions measured during the experiments (oil viscosities, oil water contents, oil and water temperatures, oil volumes spilled, and dispersant to oil ratios) and estimated Dispersant Effectiveness (DE) without adjustment for control experiment losses are summarized in Tables 2 and 3, respectively.

The “% collected” data in Tables 2 and 3 are the volume percentages of the oil spilled that were collected from the surface after each test (after accounting for water contents in both the discharged and collected oils).

The “% Dispersed/Lost” data are the percentages of oil not accounted for by collection or evaporation estimates. In the “dispersant applied” tests, the “% Dispersed/Lost” estimates were all very high in both the 2006 program that used Corexit 9527 dispersant and the 2007 program that used Corexit 9500. In 2006, there were ten tests with 95% or higher values, four tests with 90% or higher and one test at 85%, with this being the lowest value. In the 2007 program there were nine tests with 95% or higher values and two tests with 90% or higher values.

The “% Dispersed/Lost” values recorded for the control runs (no dispersant applied) in both the 2006 and 2007 programs were generally in the 10 to 25% range meaning that 75–90% of the spilled oil in the control experiments was accounted for by either oil collection or evaporation estimates. The high “% Dispersed/Lost” values in the dispersant applied experiments can thus be confidently attributed to the effect of the applied chemical and not to “natural dispersion” of the oil or adhesion of the oil to tank side walls or booms. Fig. 3 shows a graphical comparison of the “% Dispersed/Lost” results for the dispersant applied and control tests for both the Corexit 9500 (2006 test program) and the Corexit 9527 (2007 test program) results. Due to cost and time constraint inherent in large-scale testing, it was not possible to do replicate testing for the various test combinations that were studied in these test programs. As a result, statistical significance testing on the data results is not possible.

Higher oil losses (38–60%) were encountered in the Northstar control runs than in control runs with all other oils in both 2006 and 2007. This can be attributed to the natural dispersion/dissolu-

tion of this very light oil. The reason for the unusually high oil loss recorded for control test #17 for ANS crude oil in the 2007 test program is unknown. The data collected for the control test for the Pt. McIntyre on-tank, high-energy weathered oil in 2006 (test #22) is suspect due to a number of operational difficulties experienced in this test.

There was no difference in the dispersibility of the air sparged versus the on-tank weathered oils in the 2006 test program.

4.2. Visual records

All of the experiments were videotaped from the observation tower located on the main bridge. The video was edited to show the progression of the test from the beginning to the end. The complete sets of video summaries for each report are available online at <http://www.mms.gov/tarphome>.

4.3. Dispersed oil concentrations and drop size distributions

Up to four passes were made down the length of the test tank with the main bridge after the oil was discharged to measure in-water oil concentrations and drop size distributions. These measurements were made to confirm the presence of oil in the water column and to characterize the form of the oil (drop size distribution). Graphs of the oil drop size distributions and concentrations recorded in all of the tests are provided in the project reports that can be acquired from the MMS web site referenced earlier. Two examples of these graphs are provided to illustrate the types of measurements that were made during the test programs.

Figs. 4 and 5 show the oil drop size distributions and in-water oil concentration measurements for the 15% air-sparged ANS tests completed in 2007. The “continuous” traces on these plots are from the LISST 100 device that sampled both oil concentration and oil drop size every few seconds as the bridge was moved back and forth dragging the device through the water. The high concentration zones correspond to the times that the LISST sensor was in the dispersed oil cloud. In the control experiment (Fig. 4), elevated oil concentrations (30–50 ppm) were recorded under the slick, but the oil drop sizes in the zones of high oil concentrations were large (volume median diameters (VMDs) or d50's of 250–350 μm). In the dispersant applied case (Fig. 5), the oil drop size distributions were

Table 2
2006 dispersant effectiveness (DE) test conditions and results summary: Corexit 9527 dispersant

Oil	Initial oil viscosity (cP)	Initial oil water content (%)	Air temp °C	Water temp °C	Oil temp °C	Dispersant temp °C	Oil volume (liters)	Oil thickness (mm)	DOR	% Collected	% Evaporated	% Dispersed / lost	Test #
<i>Alaska north slope</i>													
Fresh	22	0	-2.7	-2	7.8	-	74.8	0.9	Control	60.3	19.3	20.4	2
Fresh	22	0	1.2	0.3	-1.7	3.9	75.7	1.2	1:38	5.3	-	94.7	3
Air sparged	93	0.2	3.3	-0.6	-0.6	-	75.9	1.1	Control	77.9	9.6	12.6	5
Air sparged	93	0.2	6.2	0.0	2.2	5.0	50.4	1.1	1:26	2.7	-	97.3	6
On-Tank	203	5	-1.9	0.0	-4.4	-1.7	69.7	2.8	1:28	2.6	-	97.4	10
Lo-Energy													
On-tank hi-Energy	200	16	0.5	0.0	-0.6	3.3	62.8	2.6	1:25	3.4	-	96.6	9
On-tank hi-lo Mix	256	14	8.6	2.8	3.3	7.2	65.2	1.2	1:21	1.1	-	98.9	23
<i>Endicott</i>													
Fresh	270	0.2	0.5	0.0	0.0	-	72.5	1.2	Control	61.8	24.7	13.5	8
Fresh	245	0.2	7.1	2.8	3.3	7.2	79.8	3.3	1:27	0.4	-	99.6	17
Air sparged	772	0	-0.7	0.0	-1.1	-	73.4	3.2	Control	71.5	5.7	22.8	7
Air sparged	644	0	-0.1	0.0	-2.8	0.0	73.4	3.8	1:40	14.9	-	85.1	11
Air sparged	644	0	15.7	3.3	10.6	13.9	77.0	2.5	1:17	8.9	-	91.1	25
<i>Northstar</i>													
Fresh	7.6	0	5.6	1.7	0.0	-	80.2	1.6	Control	31.9	45.0	23.1	13
Fresh	7.6	0	7.3	1.7	2.2	9.4	69.4	1.5	1:25	3.7	-	96.3	14
Air sparged	36	0	7.3	1.9	-1.7	0.6	75.7	3.2	1:43	8.9	-	91.1	15
On-Tank	116	40	2.8	1.1	-1.7	-	47.9	1.9	Control	49.4	12.3	38.3	12
Lo-Energy													
On-tank hi-energy	143	48	1.6	-2.8	-2.8	-	39.9	1.7	Control	24.2	17.2	58.6	18
On-tank hi-energy	143	48	5.6	2.2	0.0	1.7	38.3	2.4	1:23	1.7	-	98.3	16
<i>Pt. McIntyre</i>													
Fresh	34	2	-2.0	0.0	7.8	-	66.4	2.2	Control	76.3	12.2	11.5	1
Fresh	34	2	7.6	3.3	5.0	11.7	68.4	1.1	1:18	0.7	-	99.3	21
Air sparged	76	0.5	0.6	-0.4	-0.6	-	75.3	1.1	Control	68.4	9.4	22.2	4
Air sparged	76	0.5	5.8	2.8	2.2	8.3	67.8	2.1	1:18	0.7	-	99.3	20
On-tank lo-energy	214	55	13.7	2.8	2.8	16.7	33.6	1.9	1:28	1.0	-	99.0	24
On-tank hi-energy	695	48	7.8	2.8	2.2	-	28.0	0.9	Control	19.6	3.8	76.7	22
On-tank hi-energy	695	48	3.9	2.8	0.6	4.4	39.7	3.5	1:25	5.9	-	94.1	19

Table 3
2007 dispersant effectiveness (DE) test conditions and results summary: Corexit 9500 dispersant

Oil	Initial oil viscosity (cP)	Air temp °C	Water temp °C	Oil temp °C	Dispersant temp °C	Oil volume (liters)	Oil thickness (mm)	DOR (Corexit 9500 unless otherwise noted)	% Collected	% Evaporated	% Dispersed / lost	Test #
<i>Alaska north slope</i>												
Fresh	65	-6.1	-4.4	-7.2	-	80	1.06	Control	41	13	46	1
Fresh	65	19.2	7.2	15.6	16.7	69	1.63	1:25	2	-	98	19
Air sparged 15%	200	-2.2	-4.4	0.0	-	78	0.90	Control	77	5	18	4
Air sparged 15%	200	0.9	-3.3	0.0	12.8	77	1.04	1:17	1	-	99	5
Air sparged 22%	300	14.2	5.6	13.3	-	78	1.39	Control	41	8	51	17
Air sparged 22%	300	14.6	5.6	13.9	15.0	71	1.46	1:24	3	-	97	18
<i>Endicott</i>												
Fresh	350	1.7	-2.2	1.7	-	75	1.12	Control	76	5	19	3
Fresh	350	20.7	9.4	19.4	18.3	76	1.62	1:24	2	-	98	21
Air sparged 18%	520	8.1	2.8	7.8	-	76	1.59	Control	69	10	24	14
Air sparged 18%	520	10.1	3.9	7.8	11.7	74	1.12	18	6	-	94	16
Air sparged 18%	520	12.1	4.4	11.1	10.6	71	1.38	1:21 (C9527)	7	-	93	15
<i>Northstar</i>												
Fresh	6	1.1	-1.1	-0.6	-	78	0.95	Control	52	36	11	9
Fresh	6	3.2	-0.6	3.9	10.0	78	0.97	1:18	1	-	99	10
Air sparged 30%	30	-1.7	-2.2	-2.2	-	85	1.04	Control	49	11	38	6
Air sparged 30%	30	1.1	-2.8	-0.6	10.0	77	1.15	v20	1	-	99	7
Air sparged 30%	30	1.7	-2.2	-0.6	8.9	73	1.15	1:19 (C9527)	1	-	99	8
<i>Pt. McIntyre</i>												
Fresh	45	-1.7	-4.4	1.1	-	77	0.95	Control	62	15	24	2
Fresh	45	16.0	7.2	14.4	15.0	78	1.62	1:19	1	-	99	20
Air sparged 15%	400	-7.7	-5.0	-3.3	-	67	1.10	Control	68	9	23	11
Air sparged 15%	400	-7.9	-6.1	-8.3	4.4	69	1.34	1:23	1	-	99	12

small (d50's less than 25 μm) in the high oil concentration zones (50–150 ppm). Elevated oil concentrations were measured in both the control and dispersant applied tests, but much smaller oil drop sizes were detected in the dispersant applied case. Dispersed oil

drops less than 70–100 μm in diameter are generally considered permanently dispersed in a typical offshore environment (Lunel, 1993; Neff, 1990). A theoretical study (Li and Garrett, 1998) of oil drop breakup under typical offshore breaking wave conditions

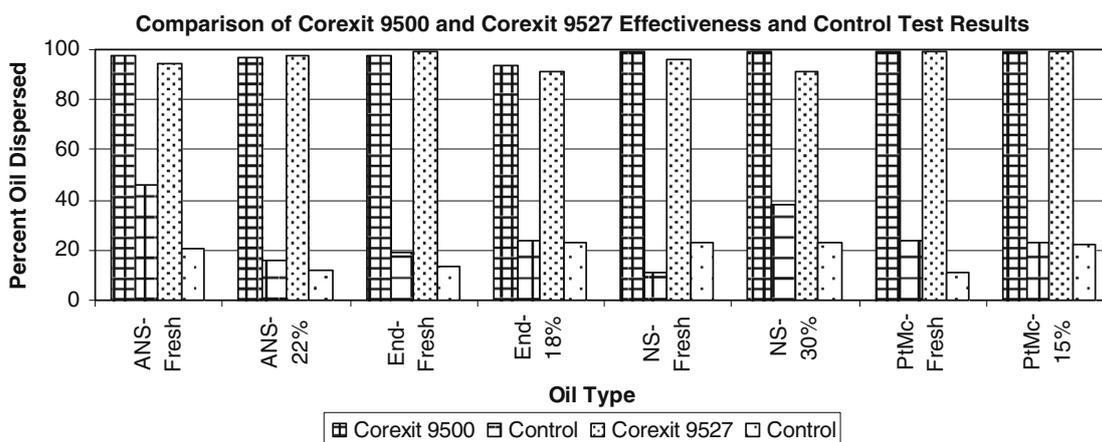


Fig. 3. Comparison of effectiveness results for Corexit 9500 and Corexit 9527.

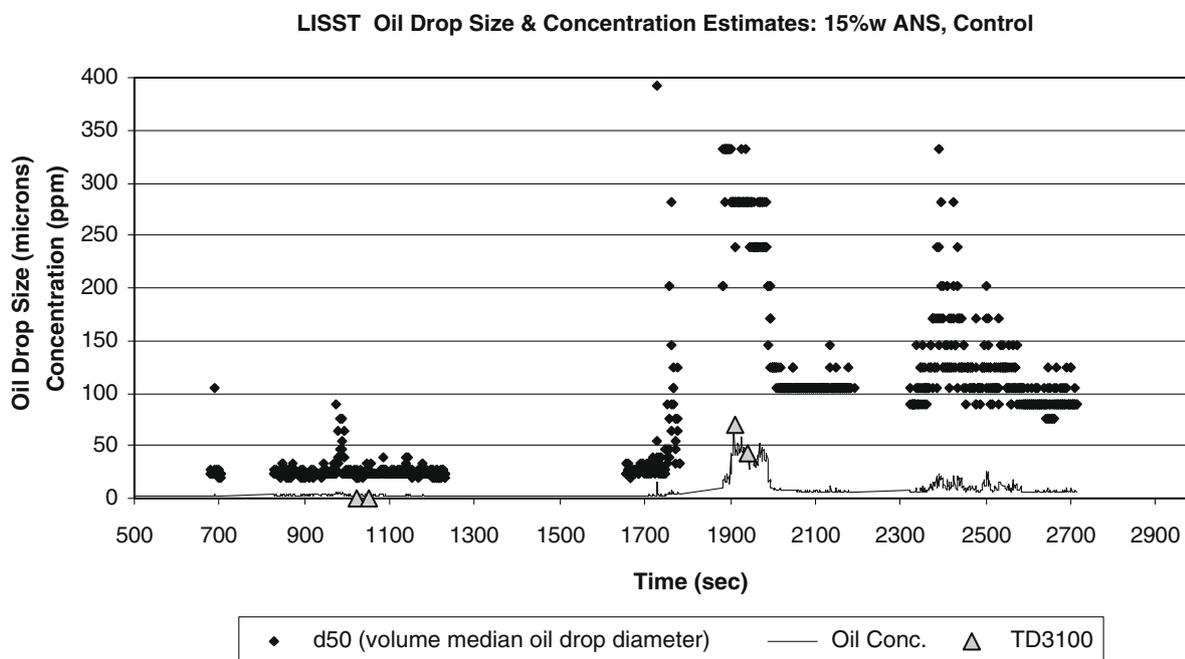


Fig. 4. Oil drop size and oil concentration measurements from a control experiment: no dispersant.

has shown that untreated oil slicks of Prudhoe Bay crude oil will likely be broken into drops between 150 and 1000 μm and treated oil into drops between 10 and 150 μm . These values are supported by the work of Lunel and Neff and are similar to the drop size ranges measured in the control and treated tests in the current study. The drop size results from the control run (Fig. 4) suggest that much of the naturally dispersed oil will not likely be permanently dispersed. The small oil drops recorded in the dispersant applied test (Fig. 5) suggest that the dispersant was effective in generating dispersed oil in small enough drops to be permanently dispersed. The in-water oil characterizations qualitatively support the measurements of oil lost from the surface that are used to determine dispersant effectiveness.

4.3.1. Oil drop size analysis and adjusted DE estimates

The oil drop size data collected for each experiment (described above) has been analysed to determine one) the average VMD drop size, and two) the volume percent of the oil present in the form of oil drops less than 70 μm in diameter. The detailed results of this

analysis for both test series are presented in Table 4. The VMD drop size for the control test dispersions were consistently and significantly higher than for the dispersant applied runs in both test programs. The volume of oil present in the water column in the form of drops less than 70 μm in diameter was also much higher in the dispersant tests (70–77%) when compared to the controls (18–34%) in both test series. This would be expected since the role of surfactants in chemical dispersants is to reduce the oil/water interfacial tension and promote the formation of smaller droplets of oil under a given mixing energy. As previously discussed, oil in drops 70 μm in diameter or less were permanently dispersed in offshore dispersant tests (Lunel, 1993; Neff, 1990). These measurements indicate that a high percentage of the dispersed oil in the chemically treated tests in both of these programs would likely remain dispersed in an ocean setting.

The average oil drop VMDs in the control tests of 2006 were consistently smaller than in the 2007 (composite average of 130 μm in 2006 versus 186 μm in 2007: see Table 4) study even though the oil viscosities and temperatures in the two studies were

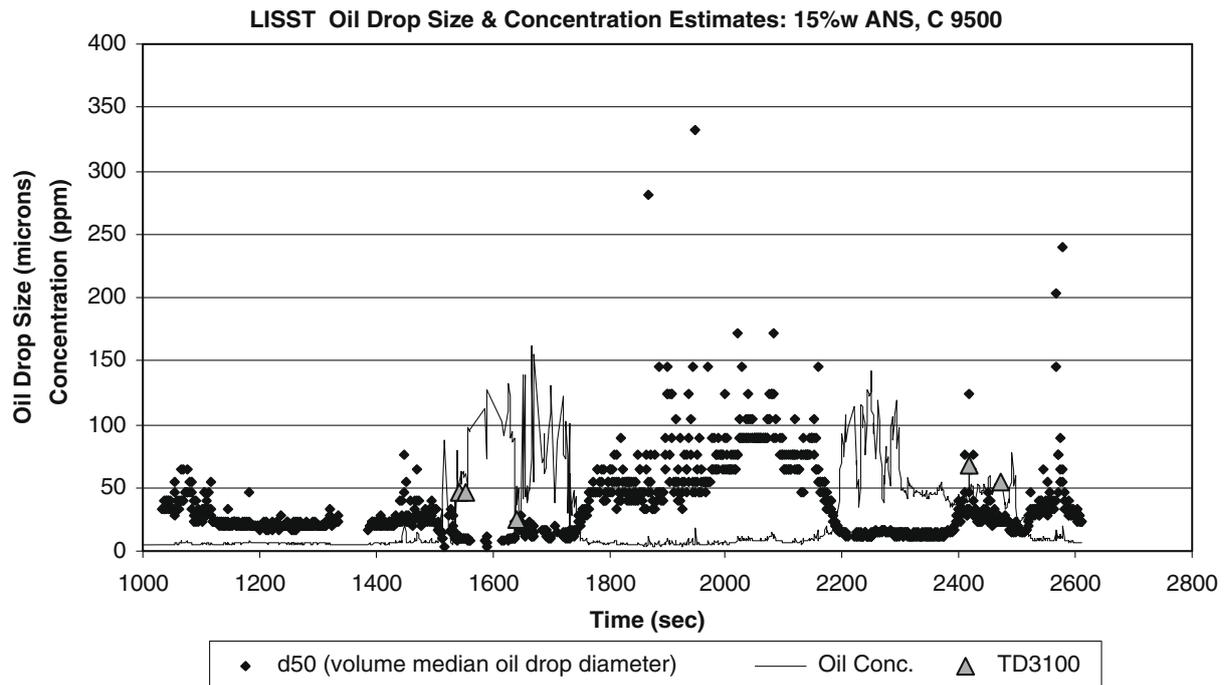


Fig. 5. Oil drop size and oil concentration measurements from a dispersant applied experiment.

similar. This suggests that the energy levels present in the 2006 test program may have been slightly higher than those used in 2007. The oil drop VMDs in the dispersant applied tests were consistently lower in the 2007 tests with Corexit 9500 than in the 2006 test where Corexit 9527 was used (composite average of 35 μm in 2007 versus 50 μm in 2006: Table 4). This, combined with possibly lower energy levels used in 2007, suggests that the

Corexit 9500 generated smaller oil drops than Corexit 9527 and was therefore somewhat more effective.

The “volume percent less than 70 micron” values computed for each dispersant applied test and reported in Table 4 have been multiplied by the raw DE values shown in Tables 2 and 3 and Fig. 3 as a method to account for the possible resurfacing of large

Table 4
Oil drop size distribution summaries

2006 Test program (Corexit 9527)				2007 Test program (Corexit 9500)			
Test #	Test type	Average VMD (μm)	Vol% < 70 (μm)	Test #	Test type	Average VMD (μm)	Vol% < 70 (μm)
1	Control	123	27.0	1	Control	176	8.1
2	Control	82	56.2	2	Control	198	14.5
4	Control	115	41.8	3	Control	173	28.9
5	Control	130	33.8	4	Control	151	19.0
7	Control	147	35.2	6	Control	225	9.7
8	Control	136	26.8	9	Control	166	20.3
12	Control	98	44.6	11	Control	249	9.2
13	Control	133	29.0	14	Control	209	9.8
18	Control	117	36.3	17	Control	125	42.8
22	Control	214	13.3		Averages	185.8	18.0
	Averages	129.5	34.4		Std. dev.	38.4	11.5
	Std dev	35.2	11.7				
				5	dispersant	47	70.8
3	Dispersant	80	51.8	7	dispersant	24	83.3
6	Dispersant	23	85.9	8	Dispersant	38	77.3
9	Dispersant	80	68.6	10	Dispersant	32	79.2
10	Dispersant	42	82.4	12	Dispersant	47	67.0
11	Dispersant	43	75.8	15	Dispersant	60	64.5
14	Dispersant	73	54.8	16	Dispersant	72	58.3
15	Dispersant	46	70.6	18	Dispersant	9	91.1
16	Dispersant	74	55.4	19	Dispersant	11	86.5
17	Dispersant	24	80.9	20	Dispersant	25	82.8
19	Dispersant	76	50.7	21	Dispersant	20	89.7
20	Dispersant	18	78.5		Averages	35.0	77.3
21	Dispersant	17	81.1		Std. dev.	20.0	10.8
23	Dispersant	17	81.2				
24	Dispersant	87	62.9				
	Averages	50.0	70.0				
	Std dev	27.3	12.7				

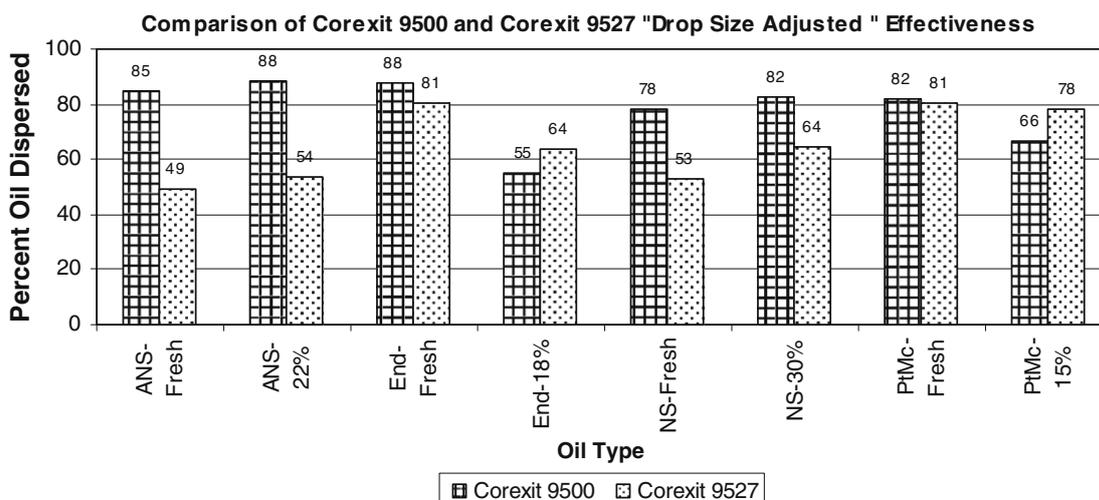


Fig. 6. Comparison of Corexit 9500 and Corexit 9527 "drop size adjusted" effectiveness.

oil drops over time and to estimate a conservative DE value. It should be noted that this adjusted DE may be an underestimate of effectiveness because the oil present in the larger drops held in the water during wave activity may have re-surfaced shortly after the waves were stopped and prior to oil collection and were thus already accounted for in the raw DE estimates. The final "drop size" adjusted DE estimates for the tests are provided in Fig. 6 where the results for the two different dispersants are compared. The adjusted DE results vary from about 50 to 90%. Corexit 9500 appears to have worked better than Corexit 9527 on the ANS (35% higher DE) and Northstar (about 20% higher DE) crude oils (both fresh and weathered) but produced about the same DE on the Endicott and Pt. McIntyre oils (DE values within 10%).

The primary physical oil property that affects dispersant performance is oil viscosity. The drop size adjusted DE values in the two test programs were plotted against initial oil viscosity to determine if there was any correlation between viscosity and DE. There was

no trend identified in either test program for the range of viscosities tested. The lack of correlation may be due to the combination of high mixing energy employed (full-scale breaking waves) in the testing and the relatively narrow oil viscosity range tested (5–700 cP).

4.3.2. Oil concentration data: comparison of measurement methods

As previously discussed, four methods were used to document the in-water oil concentration in the 2006 test program; the Turner A10U and Wet Labs fluorometers, the LISST 100 and the Turner TD500. The measurements of in-water oil concentration in the Ohmsett dispersant effectiveness test protocol are made only to provide verification of the presence of dispersed oil in the water column and not to quantify the volume present and, as such, these measurements are of secondary importance. The different measurement methods were deployed in 2006 to permit a qualitative assessment of the various methods for future use in dispersant

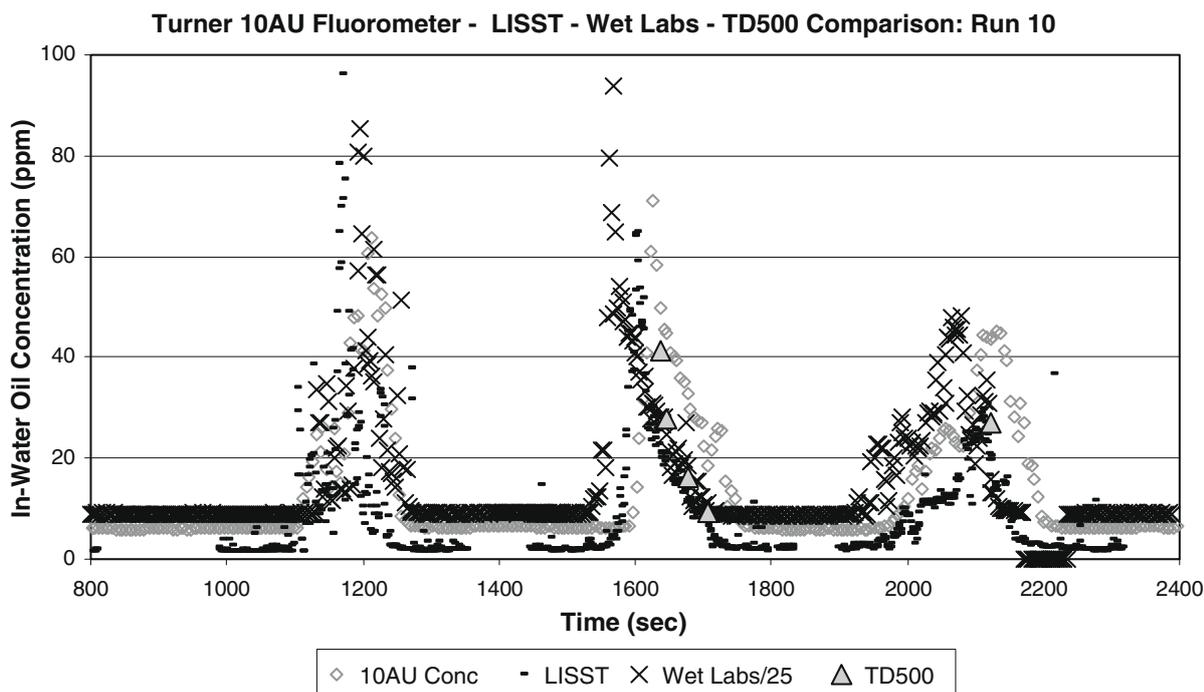


Fig. 7. Comparison of four methods for in-water oil concentration measurement.

testing programs at Ohmsett. Fig. 7 shows a comparison of the four methods used to measure the in-water oil concentration for experiment #10 in 2006. As can be seen in Fig. 7 there was reasonable agreement between the results from the four methods. The TD500 results can be considered the most accurate of these results since a more rigorous oil extraction and calibration procedure was used in determining the oil concentrations by this method.

The Turner 10AU, TD500, TD3100 and Wet Labs fluorimeters all require calibration to the specific oil being measured before they can provide estimates of actual oil in-water oil concentrations. Without such calibrations, their outputs provide only relative oil concentration levels within a test. The difficulty of accurately measuring in-water concentrations of dispersed oil using various techniques has been reported elsewhere (Lambert et al., 2001).

The LISST 100 provided a reasonable estimate (similar to the TD500 results) of in-water oil concentration without the need for time-consuming instrument calibration, water sampling, solvent extraction and analysis. The LISST also provides oil drop size distribution information and is therefore a more versatile instrument. Based on the assessments of the various oil concentration measurement techniques used in the 2006 program the LISST 100 was selected for use in subsequent dispersant testing at Ohmsett (including the 2007 test program).

5. Discussion

Caution must be used when comparing the results from different DE testing programs because the specific crude oil and dispersant combination used can result in very different DE results. Very seldom is the exact same crude oil used in two independent test programs as even crude oils from a given source (production field or pipeline) constantly change with time. It is known that the properties of ANS crude oil as shipped from Valdez have changed over the past twenty years with a steady decline in both density and viscosity and a decline and then increase in pour point (SL Ross, 2004b). Nevertheless, other researchers have completed dispersant effectiveness tests using fresh and weathered ANS crude oil (of various vintage) and Corexit 9527 and 9500 dispersants under cold conditions. The work that most closely matches that completed in the Ohmsett test basin is the study by (Mackay, 1995) in the ESSO Resources outdoor test basin in cold-water (4 °C) using Alaska North Slope Crude oil and Corexit 9527. The tests completed in this outdoor basin resulted in measured DE values between 80 and 97% for weathered (10–20% evaporated) ANS crude oil that was subjected to breaking waves immediately after the application of dispersant. These results compare very favorably to the “raw” DE estimates recorded in the current study.

The results from other studies that used small bench scale testing do not always correlate to the large scale test results. Mackay (1995) also completed bench scale tests using the Exxon Dispersant Effectiveness Test (EXDET). DE results in the 80%–95% range were recorded using this test on fresh and weathered ANS crude oil at 4 °C. These results are similar to the outcomes recorded in the Ohmsett test series. Moles et al. (2002) used Environment Canada's swirling flask test (SFT) (Fingas et al., 2000) to test the effectiveness of these dispersants on fresh and 20% evaporated ANS over a range of water salinities and temperatures. The SFT results for the both the fresh and weathered oil were below the detection limit of the test (<10%) at the lowest temperature (3 °C) and highest salinity (32 ppt) tested; the conditions that most closely matched those present during the Ohmsett test programs. This is in sharp contrast to even the 50%–90% drop size adjusted DE measured in the Ohmsett test program. The likely explanation for the difference in results is in the degree of mixing energy present in the two test environments. Moles provided the

following caution when reporting his results “because our laboratory tests were conducted at low mixing energy, considerable caution should be used in extrapolating these laboratory studies to field conditions”. Similar bench scale testing by Fingas et al. (2006) used a slightly modified SFT procedure where only the final oil extraction and detection procedure were modified. Tests were completed on fresh ANS crude oil at 5 °C in 20–30 ppt salinity water and the measured DE ranged from 55 to 65%. These results were considerably higher than those reported by Moles but still not quite as high as the results from the large-scale Ohmsett tests. (Fingas et al., 1991) also reported a SFT DE of only 7% on Prudhoe Bay crude oil, presumably at room temperature, using the SFT procedure. The likely reason for the considerably lower test result compared to his 2006 work is due to the different oil properties of the Alaskan oil in the 15 years between tests.

A comparison of results from various bench-scale DE test methods on heavy fuel oils by Clark et al. (2005) has shown that the swirling flask test (SFT) can generate significantly lower DE estimates than other common bench scale test methods under the same test conditions with the same oils and dispersants. The difference in results is generally attributed to a lower mixing energy in the SFT. Venosa et al. (2005) measured energy dissipation rates in the SFT, EPA's new baffled flask test (BFT), and in the meso-scale wave tank operated by the Canadian Department of Fisheries and Oceans. The energy dissipation rates measured by Venosa et al. in the SFT test were similar in magnitude to those recorded during typical non-breaking wave conditions in the wave tank and the energy dissipation from the BFT were similar in magnitude to those recorded during breaking wave conditions in the tank. While Venosa suggests that this indicates that the BFT test mimics turbulent conditions similar to breaking waves, the work by Mukherjee and Wrenn (2007) indicates that the measurement of energy dissipation alone may not be adequate to describe the differences in dispersant effectiveness and the characteristics of the dispersions that have been observed in experimental systems. These results emphasize the need to be very careful when extrapolating bench-scale DE test results to large-scale or field behavior and supports the use of large scale testing such as that completed in this study to bridge the gap between bench-scale and field-scale testing. This is further supported by Daling and Lichtenthaler (1986) who found poor correlation between the results from three different laboratory DE tests to the results from field tests using the same oils and dispersants.

6. Conclusions

The two dispersants tested, Corexit 9527 and Corexit 9500, were both effective (85%–99% raw DE and 50%–90% drop size corrected DE) in dispersing the fresh and weathered Alaskan oils in the large-scale tests completed at the Ohmsett test facility in winter conditions. There was no apparent difference in DE on fresh or weathered oil within the relatively narrow range of viscosities tested (5–700 cP). The results demonstrate that chemical dispersants may be effective in dispersing oils in near freezing water and energetic breaking wave conditions in the offshore environment.

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dispersants. However, no official endorsement from any of these organizations should be implied.

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