

**UPDATING THE SMART DISPERSANT MONITORING  
PROTOCOL:  
Review of OHMSETT Results from 2001-2007**

**Final Report**

**For**

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## Executive Summary

This project analyzed monitoring data from five dispersant studies completed at Minerals Management Service's National Oil Spill Response Test Facility (Ohmsett). In these studies, instrumental monitoring data were gathered in all projects and visual monitoring data were gathered in some. The study focused narrowly on verifying the usefulness of instrumental methods for monitoring dispersant efficacy under the protocol, "Special Monitoring of Applied Response Technologies (SMART)" (USCG et al 2006).

In the SMART protocol, dispersion effectiveness is assessed primarily by visual means with in-water instrumental measurements of oil behavior being used for support and verification. The instrumental measurements involve comparing oil concentrations under treated and untreated sections of the slick (SMART Ratio). The SMART Ratios calculated for all of the Ohmsett tests have been plotted against levels of effectiveness (DE) in [Figure S-1](#). Based on Ohmsett dispersant tests, there is very little correlation between the SMART Ratio and DE for the range of conditions studied. In addition, Ohmsett results suggest that the use of the "five-times" guideline for determining effective dispersion might result in a large number of both false positive and negative outcomes. This finding reinforces the protocol admonishment that "five-times" is a general guideline only and that it should not be used as an action level for turning on or off dispersant operations.

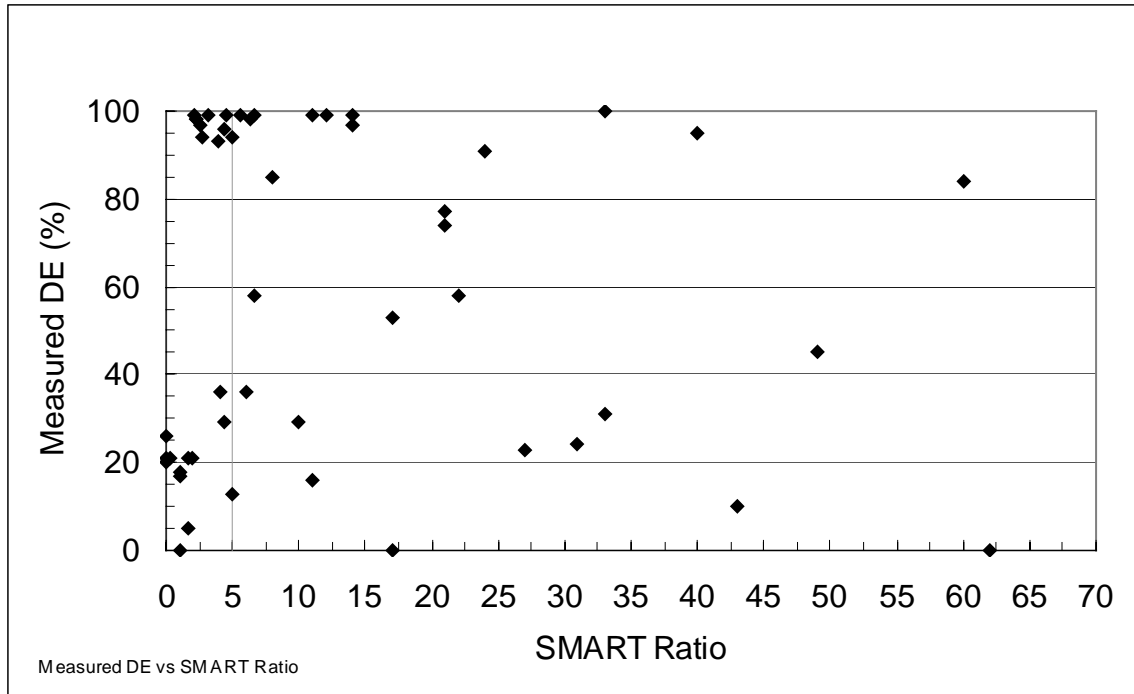
In the projects analyzed, DE values ranged from 0 to 77% in control tests and 0 to 100% in dispersant treated tests. Studies of dispersibility of Alaskan oils provided the best insights into monitoring of oil behavior. In both the 2006 and 2007 studies of Alaska oils, the dispersant-treated tests yielded high effectiveness levels (85 to 100%) suggesting that the SMART Ratio should be above the "five-times" guideline in all cases. In both series, oil concentration measurements made under slicks with the laser particle-size analyzer (Sequoia LISST-100X) and fluorometer (Turner 10AU) correlated well to effectiveness, though the concentrations varied between studies. The SMART Ratios calculated in paired tests (where untreated and dispersed tests were carried out on identical oils under identical conditions) exceeded the "five-times" guideline in 9 out of 11 pairs of oils tested in 2006, but in only 4 out of 11 pairs in 2007. The size of particles in oil clouds beneath untreated and treated spills was strongly correlated to effectiveness. Average diameter of oil particles (volume-mean diameter (VMD)) under untreated

slicks ranged from 83 to 226 microns in both sets of tests, while in chemically dispersed oil clouds were much smaller, ranging from 10 to 83 microns.

In short, in Alaskan oil tests, assessments of effectiveness based on the SMART Ratio using oil concentration in the water under slicks led to incorrect conclusions in some cases in the 2006 tests and more than half of the tests in 2007. On the other hand, similar assessments made based on particle size would have led to no errors. This suggests that droplet size might be a more reliable indicator of effectiveness than oil concentration. It is tempting to conclude that assessments of effectiveness might be made based on droplet-size alone, but this is not true. Background values for droplet size vary widely making particle size data misleading. Rather, the Ohmsett data suggest that particle size information should be used in combination with oil concentration data to achieve the most reliable results. Data from the Alaska oils studies showed that very low oil concentration under slicks (indistinguishable from background) is a strong indicator of low effectiveness. On the other hand, elevated oil concentrations always occur in effective applications, but also occur in some ineffective ones. When elevated concentrations occur, the size of drops causing the elevated oil concentration is an unambiguous indicator of effectiveness, with large droplets (VMD >83  $\mu\text{m}$ ) indicating low effectiveness and small droplets (VMD < 83  $\mu\text{m}$ ) indicating high effectiveness. This is consistent with Lunel (1993) who concluded that oil droplets generated from slicks at sea would be permanently dispersed if their droplet diameter was less than 70  $\mu\text{m}$ , while those with diameters greater than 70  $\mu\text{m}$  were temporarily suspended in the water column, but would ultimately rise to the sea surface.

In the 2006 tests, comparisons were made between the instrument currently being used by SMART practitioners, the Turner 10AU fluorometer (T-10AU), and the more modern instruments that might be considered to replace it, namely the WetLabs WETStar fluorometer or the Sequoia LISST-100X laser particle analyser (LISST). The correlation between T-10AU and LISST measurements varied with oil type, with LISST and T-10AU values being similar for ANS and Endicott oils, while the LISST gave lower concentration estimates for North Star and Pt McIntyre oils than did the T-10AU. Output of the WETLabs WETStar (CDOM) sensor corresponded well to those of the LISST and T-10AU. When the LISST and T-10AU measurements were compared to oil concentrations determined by extraction and detection of oil from water grab samples, the LISST results generally provided a closer fit to the more accurate grab-sample concentrations. In summary, under Ohmsett conditions, LISST-determined

concentrations are more consistent with our best estimates of in-water concentrations than the T-10AU even when the T-10AU had been calibrated to the specific oil spilled. The possible reasons for this are discussed in the report.



**Figure S-1.** Measured DE versus Smart Ratio: All Ohmsett Test Data Analyzed

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## 1 Introduction

The objective of this project was to analyze the instrumental monitoring data collected during recent dispersant research projects at Minerals Management Service's National Oil Spill Response Test Facility (Ohmsett) to test the reliability of dispersant effectiveness monitoring protocols described in, "Special Monitoring of Applied Response Technologies (SMART)" (USCG et al., 2006). The SMART dispersant effectiveness protocol and its predecessor SROMP (NOAA Hazmat and USCG Gulf Strike Team 1994) were developed in the 1990s as a means of assessing whether or not dispersant applications on spills at sea were effective. SMART has been updated from time to time based on experience in spills and drills (e.g., USCG et al. 2006). In 2001 a dispersant testing protocol was developed for Ohmsett ([Figure 1](#)). Since that time nine major dispersant research projects have been conducted at Ohmsett ([Table 1](#)). These projects sought to: a) estimate the level of dispersant effectiveness likely to be encountered in responses to spills at sea; or b) measure the influence of important variables on effectiveness in general (e.g., oil properties, emulsification, dispersant type, wave energy). During these experiments dispersant effectiveness (DE) was measured directly by measuring the amount of oil remaining on the surface of the tank at the end of each test and comparing this amount to the amount spilled. In addition, behavior of the oil was monitored by visual means during the test and by making in-water oil-measurements using instruments similar to those outlined in the SMART protocol. The instrumental measurements were intended to:

- a) Verify the presence of dispersed oil in the water column and measure oil droplet size to assess the potential for long-term dispersion;
- b) Obtain information about the behavior of dispersed oil; and
- c) Acquire experience with instruments and procedures under simulated at sea conditions.

The objectives of the present project were to analyze the results of these instrumental monitoring exercises to:

- a) Verify the usefulness of the SMART protocols, in general;
- b) Verify usefulness of thresholds specified in the protocol for assessing effectiveness;
- c) Compare the performances of different instruments that are currently used or may be used in the future for assessing effectiveness; and

- d) Identify potential opportunities for improvement in the SMART protocol.

In the present study, results from the following tests were analyzed:

- a) Dispersibility of Alaska crude oils (SL Ross 2003, 2006, SL Ross and MAR 2007);
- b) Correlating OHMSETT and at-sea tests (SL Ross et al. 2005); and
- c) Testing dispersibility of water-in-oil emulsions (SL Ross et al. 2006).

Other Ohmsett dispersant studies were not included because either data were not collected using monitoring instruments or levels of effectiveness were not high enough to be useful in the present study. Visual monitoring results were not included here because formal visual monitoring using teams of observers was not conducted in all studies.

### **1.1 Ohmsett Large Outdoor Wave Tank**

In recent years dispersant effectiveness tests conducted in large wave tanks have replaced bench-scale tests for some aspects of dispersant research and for addressing controversial operational questions surrounding the dispersibility of specific oils (e.g., Alaska crude oils). Ideally many of these questions should be addressed by testing at sea under actual operational conditions (dispersant applied by spraying on slicks, mixing added by waves), but this is seldom possible due to cost and permitting considerations. Large scale testing of effectiveness in wave tanks offered a possible alternative to at-sea testing. Minerals Management Service's National Oil Spill Response Test Facility (Ohmsett) has been used extensively for this purpose ([Figure 1](#)).

Ohmsett is located at the Naval Weapons Station Earle in Leonardo, New Jersey. It is a large, outdoor, aboveground test tank measuring 203 m long by 20 m wide by 3.4 m deep and is filled with 2.6 million gallons of seawater. The tank's wave generator creates realistic sea environments needed for dispersant research and equipment testing. The facility makes safe testing possible in a cost-effective way under controlled, reproducible simulated at-sea conditions without the need for marine discharge permits. The facility allows:

- a) Oil slicks to be laid down in a controlled, reproducible and realistic way;
- b) Dispersant to be sprayed at controlled doses in a realistic, reproducible way using actual dispersant spraying gear;
- c) Treated slicks to be agitated in a realistic way with breaking or non-breaking waves;



- d) Dispersant performance to be measured directly by collecting the oil remaining undispersed on the water surface at the end of the test; and
- e) Replicate control and experimental tests to be conducted under similar test conditions.



**Figure 1.** Minerals Management Service's National Oil Spill Response Test Facility, Ohmsett.

## 1.2 Approach

The SMART protocol assesses effectiveness of a dispersant application by observing the behavior of slicks before and after treatment and attempting to discern changes in oil behavior linked to dispersant use. The most recent revision of SMART contains the following guidance for interpreting results of instrumental measurements of in-water oil concentrations.

“Persons reviewing the [oil concentration] data should look for trends and patterns providing good indications of increased hydrocarbon concentrations above background. As a general guideline only, a fluorometer signal increase in the dispersed oil plume of five-times or greater over the difference between the readings at the untreated oil slick and background (no oil) is a strong positive indication.” (USCG et al. 2006)

In the present project a SMART-like approach was used in that in-water oil conditions were examined under slicks in control (no dispersant) and chemically treated tests. Average oil concentrations and droplet sizes were measured in the dispersed oil plume (treated tests) and under the untreated slicks (control tests). These were corrected for background conditions and were then related to the level of effectiveness for each test. In each study, pairs of tests conducted on identical oils<sup>1</sup> under identical test conditions<sup>2</sup> were analyzed in detail. In particular, the “five-times” guideline suggested in SMART was verified by calculating the ratio (SMART Ratio) between oil concentration in the dispersed oil plume (corrected for background) and the oil concentration under the untreated slick (corrected for background)<sup>3</sup>. Similar ratios were calculated for droplet size distributions. The objectives here were:

- a) To verify that oil concentrations in dispersed oil plumes always exceeded concentrations under untreated slicks by five-times or more in effective dispersant operations regardless of oil or dispersant tested or instrument used to measure oil concentration;
- b) To determine whether there was a relationship between SMART Ratio and level of effectiveness.

Details of testing and monitoring methods used in each study are described in the results sections. In-water oil conditions were monitored using several different instruments

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<sup>1</sup> oil type, batch, degree of weathering

<sup>2</sup> wave energy, temperature, dispersant type and dose

<sup>3</sup> For tests where the measured oil concentration under the control slick minus the measured background concentration was less than 1 ppm, the background-adjusted control slick oil-in-water concentration was assigned a value of one (1) for the purpose of identifying a reasonable SMART ratio (otherwise inflated ratios or divide by zero situations arise).

including, Turner T-10AU, Sequoia LISST-100X, and WETLabs WETStar (CDOM). The latter was operated as part of a BUBA Buster<sup>4</sup> integrated system. Results were analyzed on a project-by-project basis, to ensure that tests of effects of dispersant on any given oil involved identical oils, under identical conditions (wave energy, temperature) and that monitoring was done using the same instruments, instrument set-up and personnel. Results were analyzed considering the following:

- a) What oil concentrations and oil particle size distributions were generated in the upper water column (mixing zone) in control and experimental tests?
- b) What was the relationship between oil concentrations and particle sizes in the water-column under untreated and dispersant treated slicks when high levels of effectiveness were observed in treated tests? Was there a clear relationship between effectiveness and the SMART Ratio?
- c) In tests that were highly effective, did application of the SMART Ratio and “five-times” standard always led to a correct assessment of effectiveness?
- d) How did instruments (Turner, LISST, WETLabs WETStar) compare in terms of their ability to measure oil and detect differences between control and experimental runs?
- e) Did the combination of oil concentration and particle size distribution correlate well with dispersant effectiveness?

Operators must exercise care in interpreting monitoring measurements, such as SMART Ratios, in operations at sea and in tests in wave tanks because a number of factors, not just dispersion effectiveness, influence the concentrations of oil in the water and the SMART Ratios computed from them. These factors include variables such as slick thickness, wave energy and dispersant-to-oil ratio (DOR), among others. The “five-times” standard that was set for the SMART Ratio can be achieved only when slicks are moderately thick, there is moderate mixing energy, and slicks are fully dosed with dispersant (DORs near 1:20).

During actual spills conditions will vary widely and the range of in-water oil concentrations

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<sup>4</sup> Biochemical Underwater Bay Analyzer (BUBA) Buster is an instrument package containing a fluorometer (WETLabs WetStar (CDOM) fluorometer), Global Positioning System (GPS) and software that allow the output of both to be integrated and displayed graphically on a laptop computer for ease of interpretation. The system was developed and tested at the Shoreline Environmental Research Facility at Texas A&M University in Corpus Christi, Texas (Texas A & M 2007).

and SMART Ratio values that are possible vary as well. All available information, including direct observations and knowledge of the dispersibility of a particular oil, needs to be used in dispersant usage decisions.

NRC (2005, pp.90-91) points out that dispersant experiments in wave tanks offer realism not available in laboratory studies, but even tanks have physical limitations (shallow depths, limited wave conditions, wall effects, etc) that limit the obtainable results. In addition, the test protocol itself introduces artificialities and limits for scientific and operational reasons. For example, test conditions at Ohmsett are standardized and use only one combination of thickness, wave energy and ODR, so Ohmsett results do not necessarily reflect the full range of results that might be encountered in the field. Some of these conditions tend to maximize potential SMART Ratios (e.g., shallow mixing depth), while others may minimize them (e.g., test slicks limited to 1 mm thickness). It is important to recognize that these factors are acting when interpreting test results in this study.

**Table 1.** Summary of projects, Monitoring methods used and oils tested at Ohmsett from 2001 to date.

	Date	Methods Applied							Oils Tested																
		Visual	Video	Direct Measurement	In-Situ UVF (One depth)	In-Situ UVF (Two depths)	WETLabs WETStar	LISST-100X	Post Calibration	IFO-30	IFO-120	IFO-180	IFO-380	Sundex 2000	Sundex 10,000	GA 209 GOM	EB 873 GOM	WD 30 GOM	Harmony CA	Pt. Mac AK	N. Star AK	ANS AK	Endicott AK	Sockeye CA	
Ohmsett Studies																									
Ohmsett Dispersant Protocol Development	2001	x			x	x							x	x											
Testing of Dispersants On Alaskan Oils in Cold Water	2003		x	x	x	x		x	x										x	x	x	x			
Correlating Ohmsett w At-Sea	2003	x	x	x	x						x	x	x												
Testing Dispersibility of Viscous OCS Crude Oils		x	x	x																					
Testing on Water-in-oil Emulsions	Sept 2006	x	x	x				x		x	x												x	x	
Testing of Dispersants On Alaskan Oils in Cold Water	July 2006	x	x	x	x			x	x	x										x	x	x	x		
Dispersant Application on Calm Seas	2006		x	x				x		x						x	x								
Dispersant Application in Non-Breaking Waves	2006		x	x				x								x	x	x	x						
Testing of Dispersants On Alaskan Oils in Cold Water	2007		x	x				x	x											x	x	x	x		

## 2 Results

### 2.1 Alaskan Oils 2003

The objective of the 2003 tests on Alaskan oils was to assess the potential dispersibility of a number of environmentally important crude oils from Alaska under near-at-sea conditions at freezing temperatures (SL Ross 2003). Four crude oils were tested, including three production oils: North Star (NS), Point McIntyre (Pt McI), and Endicott (END), as well as the commercial pipeline/tanker blend, Alaska North Slope (ANS) crude oil. The dispersant used, Corexit 9527, was the dispersant stockpiled in Alaska at the time. Oils were tested fresh (unweathered) and weathered to a state of evaporation that varied from oil to oil ([see Appendix 1](#)).

All tests (dispersed or untreated) involved discharging approximately 100 L of the test oil through a 5-m wide header that was moved down the tank, creating a slick approximately 20 m long by 5 m wide and 1 mm thick. In the dispersant-treated tests, the slick was sprayed immediately with dispersant at an oil-to-dispersant ratio (ODR) of approximately 20:1. Slicks were photographed to assess patchiness, so that an accurate ODR could be estimated. Slicks were immediately agitated with breaking waves for 30 minutes. In control tests (no dispersant), breaking waves broke up the slicks into patches, mixing some oil into the water creating localized, short-lived black clouds of oil droplets in the upper mixing zone. In the dispersant-treated tests, the first breaking waves dispersed all or part of the slick, creating light brown clouds of dispersed oil in the water column. Oil concentrations in the water were monitored by towing samplers for the two T-10AU fluorometers along the tank passing under slicks in the untreated tests or through the patches of dispersed oil in the treated tests. Two to four instrument passes were made per test. An initial pass was made when the slicks were laid down to assess background conditions at the start of the test. Oil concentrations were measured at 1 and 2 meters below the calm surface of the tank<sup>5</sup>. Fluorometers were calibrated using standard methods and a suspension of chemically dispersed Alaska North Slope crude oil as a standard. Fluorometer output was reported in units of ppm hydrocarbons. For purposes of this study, fluorometry output was analyzed for all runs. For each, an average oil concentration was estimated for the main oil cloud during each pass and the values were averaged to yield a single concentration value for each test.

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<sup>5</sup> Experience indicates that the mixing zone in the Ohmsett tank extends to 1.5 meters below the calm water surface.

Results are summarized in [Table 2](#). Matching control tests were not completed for the weathered oils tested in this study thus making this sub-set of tests unsuitable for the present purpose. However, for two oils [Endicott (END Fr), Point McIntyre (Pt. McI Fr)] control and experimental tests were conducted on identical samples of fresh oils, making direct comparisons possible ([Table 2](#)). In these tests, dispersion effectiveness values<sup>6</sup> (DE) in control tests for Pt McIntyre and Endicott were 43 and 14 %, respectively. When slicks were treated with dispersants DE values rose to 77% and 74%, respectively, indicating that dispersant application was somewhat effective on both oils. As mentioned above, the fluorometers in this study were standardized using suspension of chemically dispersed ANS oil, so output was reported in terms of ppm of crude oil. In the Point McIntyre (Fresh) control tests, tank background oil concentrations (background fluorescence) and oil concentrations measured under the slick at a 1 m depth were 0.5 and 1.1 ppm, respectively. The calculated background-corrected oil concentration under the control slick was 0.6 ppm. At the 2 m depth the background-corrected oil concentration was 0.8 ppm. As discussed earlier, a value of 1 ppm has been used to determine the final SMART Ratios in these cases where the background corrected value is less than 1.0 ppm to eliminate exaggerated or undefined ratios. In the dispersant treated Point McIntyre (Fresh) tests, corrected oil concentrations were higher, 20.7 ppm (1-m) and 3.7 ppm (2-m). Similarly, in tests with the heavier more viscous Endicott (Fresh) oil, corrected oil concentrations in the control test peaked at less than 1 ppm at both 1- and 2-m depths, and at 20.7 ppm (1-m) and 8.5 ppm (2-m) in the treated tests. Clearly oil concentrations in the water column were dramatically higher in the dispersant-treated tests for both oils, with oil concentrations in the upper water column increasing by more than 20 times at the 1-m depth and 4 and 8 times at the 2-m depth. The SMART Ratios for the Endicott and Point McIntyre tests (ratios of peak fluorometer output treated versus untreated) were 21, at 1-m depth and 4 & 8 at 2-m. Results from this set of tests clearly suggested that highly effective dispersant operations might be distinguished from ineffective operations by taking oil concentration measurements in the upper mixing zone, at depths of 1 and 2 meters.

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<sup>6</sup> Dispersion Effectiveness or DE = Volume of oil spilled at start of test minus the volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.

### **2.1.1 Diagnostic value of measurements**

The chemically treated slicks in the two cases analyzed were determined to be effective dispersions (77% and 74%) by the direct measurement of the quantity of oil remaining on the surface at the end of the tests. As such, the SMART Ratios should be about 5 or higher to verify a successful application. The SMART Ratios calculated for the two test pairs from 1 m depth oil concentration measurements were both 21, verifying the usefulness of the “five-times” guideline for measurements taken at 1 m. The SMART Ratios for the 2 m oil concentration measurements (4 and 8) were also consistent with the SMART Ratio, although just approaching the criteria in one of the two cases.

Please note that in the following discussions, oil concentrations presented refer to values that have been corrected for background. Again, it is important to note that when the calculated background-corrected concentrations under control slicks fell below 1 ppm they have been adjusted to 1 ppm to eliminate exaggerated and undefined SMART Ratios.



**Table 2. Peak Concentrations of Oil in Tank Water in  
2003 Tests of Alaska Oils**

Sampling Depth, m			1 meter				2 meter				Test No.
Oil <sup>a,b</sup>	ODR <sup>c</sup>	DE <sup>d</sup> %	Oil Concentration, ppm <sup>e</sup>								
			Back-ground, Ppm	Mean Peak Concentration Ppm	Corrected Mean Peak Conc. Ppm	SMART <sup>f</sup> Ratio	Back-ground, Ppm	Mean Peak Concentration Ppm	Corrected Mean Peak Conc, ppm	SMART <sup>f, g</sup> Ratio	
ANS Fr	0	3	.3	.7	.4	nd	.4	.6	.2	nd	7
ANS Fr	0	31	.3	.8	.5	nd	.5	.7	.2	nd	4
ANS 17%	25	86	.3	30	29.7	nd	.3	4.3	4.0	nd	9
North Star Fr	0	7	.3	2	1.7	nd	.5	2.0	1.5	nd	5
North Star 29%	19	8	.4	3.2	2.8	nd	.2	.4	0.2	nd	10
<b>Pt Mcl Fr</b>	<b>0</b>	<b>43</b>	<b>.5</b>	<b>1.1</b>	<b>1</b>		<b>1.5</b>	<b>2.3</b>	<b>1</b>		<b>13</b>
<b>Pt Mcl Fr</b>	<b>29</b>	<b>77</b>	<b>1.0</b>	<b>21.7</b>	<b>20.7</b>	<b>21</b>	<b>4.0</b>	<b>7.7</b>	<b>3.7</b>	<b>4</b>	<b>12</b>
<b>End Fr</b>	<b>0</b>	<b>14</b>	<b>.1</b>	<b>.5</b>	<b>1</b>		<b>.1</b>	<b>.2</b>	<b>1</b>		<b>6</b>
<b>End Fr</b>	<b>31</b>	<b>74</b>	<b>.3</b>	<b>21</b>	<b>20.7</b>	<b>21</b>	<b>.5</b>	<b>9.0</b>	<b>8.5</b>	<b>8</b>	<b>8</b>
End 11%	22	3		16.7	15.7	nd	2.	4.3	2.3	nd	14

- a. ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil,
- b. Fr = Fresh oil (unweathered), x% = indicates the percent lost by air sparging by weight
- c. ODR = oil to dispersant ratio
- d. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.
- e. This is actually an index of oil concentration as the T-10AU units were calibrated using only Alaska North Slope crude oil, They were not calibrated separately for each oil in each test.
- f. SMART Ratio is the ratio of mean peak oil concentrations in dispersed oil cloud versus that under untreated slick as corrected for background.
- g. Nd = no data

## 2.2 Correlating OHMSETT Results with At-Sea Tests 2003

This project related the level of dispersion obtained in tests at Ohmsett to those observed in comparable tests at sea. For purposes of the present study, data from some of the tests were used to verify the SMART Ratio's relevance. The at-sea study (Lewis 2004) tested dispersibility of two marine fuel oils, IFO 180 and IFO 380, using three dispersants (Corexit 9500, Superdispersant 25 and Agma 273) at Beaufort Sea States 3 and 4 (i.e., wind speeds of 7-10 knots and 11-14 knots). The tests showed that, in general, oil-type, wind speed and dispersant type all influenced dispersant performance. The Ohmsett tests sought to use identical oils, dispersants and dispersant-to-oil ratios (ODRs) as in the UK tests and produced similar trends. (SL Ross et al., 2005).

In the Ohmsett tests, the oils and dispersants from the at-sea tests were re-tested under three wave conditions as determined by the frequency setting on the Ohmsett wave generator. Two of these wave conditions, 33- and 35-wave paddle cycles per minute (cpm), produced breaking waves and one, 30 cpm, produced regular, non-breaking waves. Effectiveness was measured as in the 2003 Alaska oils tests and oil behavior was monitored visually and by measuring oil concentrations at two depths using T-10AU fluorometers. Transects were completed as the slick was being laid/sprayed and after waves had begun to agitate the slick over the 30 minutes of the test. Fluorometer output was reported in raw fluorescence units (RFU). For reasons related to the spreading of these viscous oils, the ODRs in these tests were well below the intended levels of 20:1 to 50:1. As a result some dispersant applications were only partially effective in these tests. Results in [Table 3](#) show that, in general, all dispersant applied tests in non-breaking waves (wave maker set to 30 cpm) produced low DE values. Both control tests and 30-cpm dispersant-applied tests produced raw fluorescence levels in the water that were similar to background thus resulting in background-corrected concentrations of zero. These concentrations have been set to 1 ppm for the purpose of determining SMART Ratios. No control tests were completed using the 30-cpm wave setting for either oil, or the 33-cpm wave setting for the IFO 380 oil, but it is reasonable to assume for the purpose of this study that the background concentrations that would be generated under these lower wave energies would also be less than 1 ppm, as was the case for the 33- and 35-cpm control tests on the same oils. SMART Ratios have been determined using the above assumptions and are provided in [Table 3](#). For the low energy (30-cpm) tests the SMART Ratios

were less than five for all but 2 of the eight tests. The two tests with Ratios of 5 and 6 (tests #7 and #19) were both tests with Corexit 9500 that had been applied at the highest ratio achieved in the test program (65:1), so a higher DE might be expected for these two tests. For test #19 the measured DE was significantly higher than the other low energy tests (36% versus 17 to 21%). However, test #7's measured DE was low even though the SMART Ratio met the "five-times" criteria. In the 33-cpm tests with IFO 380, SMART Ratios of 11 and 10 were calculated for tests with relatively low DEs of 16% and 29%, respectively. In the 33-cpm tests with IFO 180, DE values in the experimental runs with Agma, Super 25 and Corexit 9500 were 24, 45 and 84%, respectively. The corresponding SMART Ratios at the 1 m depth for these tests are 31, 49 and 60.

Two tests were completed at 35 cpm using IFO 380 oil. DE values of 58% and 16% and corresponding SMART Ratios of 22 and 11 were measured for these tests.

A plot of DE versus SMART Ratio has been constructed using the data from this study and is provided as [Figure 2](#). Within each oil type and wave energy grouping there are obvious trends in the DE versus the SMART Ratio; generally the higher the DE the higher the Ratio as would be expected. However, a specific SMART Ratio value cannot be selected from this graph that would indicate that a successful dispersion has occurred for the range of oil types and energy levels being considered. The "five-times" standard would certainly generate false positive identifications of effective dispersion for a number of the cases identified in this analysis.

**Table 3. Peak Concentrations of Oil in 2003 Ohmsett Tests – Correlating Ohmsett with At-Sea**

Oil Type <sup>a</sup>	Dispersant Type <sup>b</sup>	ODR <sup>c</sup>	Waves, CPM <sup>b</sup>	DE <sup>d</sup>	Oil Concentration, RFU <sup>e</sup>								Test No.
					1 meter				2 meter				
					Back-ground, Ppm	Mean Peak Concentration Ppm	Corrected Mean Peak Conc Ppm	SMART Ratio	Back-ground, Ppm	Mean Peak Concentration Ppm	Corrected Mean Peak Conc ppm	SMART Ratio	
<b>IFO 380</b>	<b>Control</b>	<b>0</b>	<b>35</b>	<b>30</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>nd</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>nd</b>	1
IFO 380	9500	180	35	58	3	25	22	22	3	6	3	3	2
IFO 380	Agma	100	35	16	4	15	11	11	8	14	6	6	8
IFO 380	Super 25	171	33	29	5	15	10	10	9	12	3	3	9
IFO 380	Super 25	104	33	53	5	22	17	17	10	17	7	7	20
IFO 380	9500	195	33	34	nd	nd	nd	nd	13	9	0	0	3
IFO 380	9500	153	30	26	8	6	0	0	8	9	1	1	4
IFO 380	Super 25	144	30	18	8	9	1	1	8	10	2	2	5
IFO 380	Super 25	67	30	20	4	4	0	0	7	7	0	0	6
IFO 380	9500	65	30	13	5	10	5	5	10	15	5	5	7
<b>IFO 180</b>	<b>Control</b>	<b>0</b>	<b>33</b>	<b>2</b>	<b>4</b>	<b>4</b>	<b>1</b>	<b>nd</b>	<b>6</b>	<b>6</b>	<b>1</b>	<b>nd</b>	10
IFO 180	Agma	148	33	24	4	35	31	31	3	27	24	24	12
IFO 180	Super 25	106	33	45	2	52	49	49	5	42	37	37	15
IFO 180	9500	106	33	84	40	100	60	60	40	90	50	50	16
IFO 180	Agma	105	30	17	3	4	1	1	6	6	0	0	11
IFO 180	Super 25	129	30	21	2	2	0	0	2	2	0	0	13
IFO 180	9500	101	30	21	2	4	2	2	3	4	1	1	14
IFO 180	9500	63	30	36	2	8	6	6	4	7	3	3	19

- a. IFO 180 and IFO 380 are two standard grades of commercially available intermediate fuel oil used in marine diesel engines
- b. Agma = Agma 273 and Super 25 = Superdispersant 25 dispersant products that are approved for use in UK waters but not in US.
- c. ODR = oil to dispersant ratio calculated as volume of oil / volume of dispersant applied.
- d. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.
- e. This is actually an index of oil concentration as the T-10AU units were calibrated using only Alaska North Slope crude oil, They were not calibrated separately for each oil in each test.
- f. SMART Ratio is the ratio of mean peak oil concentrations in dispersed oil cloud versus that under untreated slick as corrected for background.

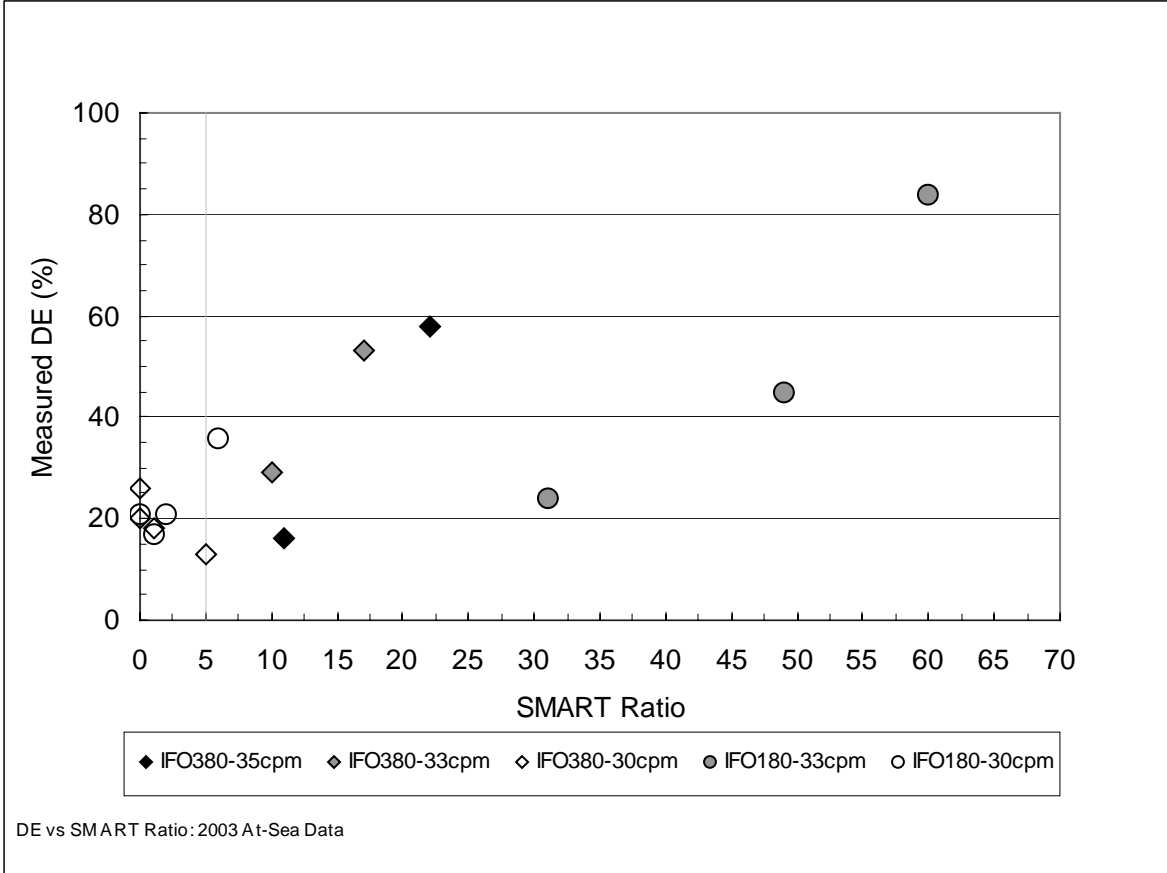


Figure 2. Dispersant Effectiveness versus SMART Ratio: Correlating Ohmsett with At-Sea

### 2.3 Alaskan Oils 2006

The 2006 experiments on Alaskan oils involved re-testing the oil-types used in the 2003 tests employing refined methods and improved oil-handling equipment (SL Ross 2006). For purposes of the present study, data from this project allowed an examination of:

- a) SMART Ratio,
- b) Direct measurement of concentrations of oil in the water;
- c) Comparison of Turner and LISST in measuring oil concentrations in the water column;  
and
- d) Oil droplet size determination.

The objective of the 2006 study was to assess the potential dispersibility of Alaskan crude oils at freezing temperatures using Corexit 9527 under near-at-sea conditions with breaking waves. New samples of the original oil types (sampled in 2005) were used and oils were tested both fresh and weathered (evaporated) by air sparging as in 2003. In addition, some oil samples were weathered on the tank using breaking- and non-breaking waves before testing to simulate weathering conditions at sea. Properties of the oils tested are in [Appendix 1](#). Dispersant effectiveness was measured directly, as in 2003. Oil behavior was also monitored visually and in-water oil conditions were monitored as in the 2003 tests, except that<sup>7</sup>:

- a) In addition to the T-10AU<sup>8</sup>, oil in the water was monitored using the Sequoia LISST-100X<sup>9</sup> and WETLabs WETStar/BUBA Buster integrated system in a similar fashion to the 2003 tests; and
- b) Measurements were made at a single depth, 1.5 m.

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<sup>7</sup> Grab samples taken of the effluent from the Turner were analyzed for total oil content by extracting the oil-water mixture with heptane and measuring the total oil content in the extract by fluorometry using the Turner TD500. These results are included in [Appendix 2](#).

<sup>8</sup> For this work the Turner 10AU was calibrated using a suspension of chemically dispersed Alaska North Slope crude oil.

<sup>9</sup> The LISST-100X model used in this work measures the amounts of oil present in a range of droplet sizes from 2.5 to 500  $\mu\text{m}$ . Data are recorded in terms of numbers of droplets in each of 32 size range bins that span the 2.5 to 500  $\mu\text{m}$  range. In the OHMSETT studies, the instrument was set up to sample continuously and output as 10-second averages. Measurements were reported in terms of volumes of oil in each of the 32 size-range bins, total particle concentration (total volume of droplets present, ppm (volume)) and average droplet size (volume mean diameter, VMD50).

Results are summarized in Tables [4](#), [5](#) and [6](#). In control tests, DE values ranged from 11 to 76%, while dispersed runs yielded very high DE values ranging from 84 to 100%, averaging 95%. In controls, the vast majority of oils had DE levels < 25%, but two tests, NS On-Tank Hi and Pt McIntyre On-Tank Hi, showed DE values that were considerably higher than the others, 59% and 77%, respectively. The causes of these high control values were not apparent, but they did correlated to higher concentrations of oil in the water column than in other control tests. This in turn did influence the interpretation of results as discussed below.

The use of the LISST allowed for direct quantification of oil droplet concentrations and size distributions in the water. In controls, oil concentrations in the water at 1.5 m depth, ranged from 1 to 12 ppm, averaging 6 ppm. In the chemically dispersed oil clouds, peak oil concentrations were much higher than in controls, ranging from 8 to 53 ppm, with an average of 31 ppm. The in-water droplet size distributions have been characterized using volume mean diameter (VMD). The VMDs measured in the dispersed oil cloud have been averaged to provide an overall indicator of the oil drop sizes. In controls, the VMDs varied from test to test, ranging from 83 to 226  $\mu\text{m}$  and averaged 157  $\mu\text{m}$  for all tests. The VMDs for chemically dispersed oil clouds were dramatically smaller, ranging from 10 to 83  $\mu\text{m}$  and averaged 36  $\mu\text{m}$ .

### **2.3.1 Turner versus LISST Comparison**

For both controls and treated runs oil concentrations measured using the T-10AU (and reported as ppm ANS Fr equivalents) correlated well to the LISST values. For controls, T-10AU values ranged from 0 to 34 ppm, with an average of 7 ppm compared to the LISST, which recorded values ranging from 1 to 12 ppm and averaging 6 ppm. In treated runs the T-10AU values ranged from 5 to 147 ppm (averaging 50 ppm) compared to LISST results of 8 to 53 ppm (averaging 31 ppm). On the whole, the LISST appeared to yield somewhat lower concentrations than the T-10AU. When comparisons were made on an oil-by-oil basis, the relationship between T-10AU and LISST measurements varied with oil type. LISST and T-10AU values were similar for ANS and Endicott oils, while the LISST gave lower concentration estimates for North Star and Pt McIntyre oils than did the T-10AU ([Figure 3](#)). Because the T-10AU was calibrated using ANS oil, it is not surprising that T-10AU measurements of ANS should be similar to those made using another technology. Since other oils would fluoresce differently from ANS, it is not surprising that T-10AU measurements might not agree with other measurements as well as for ANS.

Periodic water grab samples were taken from the T-10AU sampling stream during most of the tests. Samples were extracted with 10-ml aliquots of n-heptane and total hydrocarbons were measured using the Turner Designs TD500 handheld fluorometer. The instrument was calibrated using standard curves prepared using fresh and weathered samples of each of the oils tested. The calibration curves for the fresh oils are shown in Figure A-1. Analysis for oil concentration using this method eliminates problems associated with oil type and oil particle size that are encountered with the Turner 10AU. As such, the concentrations determined by the grab sample extraction and analysis must be considered more accurate than those from the T-10AU. The concentration measurements recorded by the Turner 10AU and LISST equipment at the same time as the water grab samples were taken have been plotted against the oil concentration measured from the grab samples (Figure 4). Based on the slopes of the best fit lines for these comparisons the T-10AU results generally over-estimated the oil concentrations by more than 4 times. The LISST results were not as wide spread and generally were only slightly higher than the grab-sample concentrations (1.1 times higher). Based on this assessment it appears that, for the oils tested and under the test conditions encountered at Ohmsett, the LISST appeared to provide a more accurate estimate of the actual oil concentration than the T-10AU.

Results in [Table 5](#) show that output of the WETLabs WETStar (CDOM)<sup>10</sup> sensor calibrated with ANS crude oil correspond well to those of the LISST and T-10AU.

### **2.3.2 Comparison of Paired Tests**

The 2006 study included 10 pairs of tests in which controls and treated tests were conducted on identical oils. Oil concentration and drop size measurements from these tests are summarized in [Table 6](#). All but two of the controls had DE values less than 23%. The controls produced in-water oil concentrations < 7 ppm based on the LISST and < 8 ppm based on the T-10AU. The SMART Ratios based on T-10AU results ranged from 4 to 40. Eight of the ten SMART values were consistent with the “five-times” SMART guideline for these highly effective dispersions, while two were not. As mentioned above, two control runs had rather high DE values, 59% and 77%, and produced somewhat higher than average in-water oil concentrations. One of these resulted in a low value for the SMART Ratio. The other low SMART Ratio value occurred in tests of the unweathered North Star oil (NS Fr), in which the control test for this light oil

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<sup>10</sup> WETLabs WETStar (CDOM)<sup>10</sup> is the WETStar model configured to detect colored dissolved organic matter (CDOM)



produced much higher than average in-tank oil concentrations, which in turn contributed to the low SMART Ratio value. Corresponding results based on LISST oil concentration data yielded SMART Ratios ranging from 1 to 22. SMART Ratios for seven of the nine pairs exceeded the “five-times” guideline. Results using the two instruments show that the “five-times” SMART Ratio guideline has some usefulness, but fails in some cases. These failures are significant because since they occur in tests where measured dispersion was at or near 100%.

It is clear from the results of paired test data in [Table 6](#) that there was virtually no overlap in droplet size ranges of dispersed and untreated tests. Within each pair of tests, VMD values for the control run was at least 2 times of that in the corresponding dispersed test (last column in [Table 6](#)); some were 10 to 20 times larger than the dispersed test.

### **2.3.3 Diagnostic Value of Measurements**

In short, results from the instruments tested here provide several possible approaches for diagnosing effectiveness based on in-water oil measurement. This data set is useful for the present purpose as it contains only results from the extreme ends of the effectiveness spectrum; on one hand control tests produce little effectiveness and produce only a small amount of physically-dispersed oil, while on the other hand the treated tests were very highly effective driving virtually all of the test oil into the water. In addition, the data set includes tests on oil spanning a range of viscosities from 7 to 772 cP. Based on the comparisons of paired tests, LISST-based oil concentration values are strongly indicative of the level of effectiveness. In the treated tests oil concentrations in the dispersed oil clouds ranged from 8 to 53 ppm, with most values >20 ppm. This overlapped only minimally with concentrations under untreated slicks that range from 1 to 12 with most <7. In this study the output of the ANS-calibrated T-10AU, was reported in terms of oil concentrations and these concentrations alone were strongly indicative of effectiveness. The T-10AU-measured concentrations in controls ranged from 0 to 34 ppm with all but one result <8 ppm, while in treated tests, concentrations ranged from 5 to 92 ppm with all but two >18 ppm. This suggests that assessments of dispersant effectiveness might be based on the absolute values of oil concentrations recorded under treated and untreated slicks rather than using concentration ratios. The 2006 test results indicate that if measured oil concentrations were 5 ppm or less the dispersant would be considered ineffective and if oil concentrations were 15 ppm or greater they would be deemed successful. However, results of this kind would not be possible using the T-10AU under the current SMART protocol because the latter requires the T-

10AU to be calibrated using fluorescein dye with its output presented in units of raw fluorescence rather than oil concentration. The SMART Ratios and “five-times” guideline showed some promise, particularly when applied using the output of the LISST. Based on LISST data, SMART Ratio values for the paired tests ranged from 1 to 22, with seven of the nine values being greater than or equal to the “five-times” guideline. The two low values resulted from higher than average concentrations in the untreated tests in one case and lower than average concentrations in the treated test on the other. The SMART Ratio results based on T-10AU results showed a similar pattern to the LISST.

The droplet size results show great promise from a diagnostic perspective. Average VMD values for highly effective treated runs showed virtually no overlap with controls ([Table 4](#)). In addition, results from paired tests showed that average VMD values for dispersed tests were less than ½ of control values. It is important to recognize that in the present study, decisions based on droplet size would have been correct 100% of the time, while those based on SMART Ratios and oil concentrations would have been in error in some cases. It is tempting to conclude that assessments of effectiveness might be made based on droplet-size alone, but this is not true. In-tank background particle VMDs varied from 10 to 325 µm over the two-week test program making particle-size data alone misleading. Rather, particle size information should be used in combination with oil concentration data. Data from this study show that very low oil concentrations under slicks (indistinguishable from background) are most often indicative of low effectiveness. Elevated oil concentrations occur in effective applications, but also occur in some ineffective applications. When elevated concentrations occur, the size of drops causing the elevated oil concentration are an unambiguous indicator of effectiveness, with large droplets (VMD >83 µm) indicating ineffective application and small droplets (VMD < 83 µm) indicating a high level of effectiveness. This is consistent with the work of Lunel (1993), who concluded that oil droplets generated from slicks at sea would be permanently dispersed if their droplet diameter was less than 70 µm, while those with diameters greater than 70 µm were temporarily suspended in the water column, but would ultimately rise to the sea surface.

**Table 4. Summary of Results of 2006 Tests on Alaska Oils**

Oil <sup>a</sup>	ODR <sup>b</sup>	DE <sup>c</sup> %	Viscosity cP	Run No.	Turner Oil concentration (ppm) <sup>d</sup>			LISST Oil Concentration (ppm)			LISST Droplet Diameter (VMD, μm)	
					Back- ground, Ppm	Mean Peak Conc Ppm	Corrected Mean Peak Conc Ppm	Back- ground, Ppm	Mean Peak Conc Ppm	Corrected Mean Peak Conc Ppm	Back Ground Droplet Diameter, mm	VMD in Areas of Elevated Oil Conc, mm
Pt Mcl Fr	0	12	34	1	3	9	6	3	15	12	150	200
ANS Fr	0	20	22	2	3	4	1	3	7	4	140	167
Pt Mcl Air Sparged	0	22	76	4	5	13	8	4	11	7	20	156
ANS Air Sparged	0	13	93	5	7	10	3	5	11	6	30	150
END Air Sparged	0	23	772	7	5	5	0	3	4	1	10	150
End Fr	0	14	270	8	5	5	0	3	6	3	20	83
NS On-tank Lo	0	38	116	12	5	10	5	4	8	4	325	226
NS Fr	0	23.1	7	13	8	42	34	6	13	7	150	142
NS On-tank Hi	0	59	143	18	15	23	8	5	15	10	20	100
Pt Mcl On-tank Hi	0	77	695	22	30	30	0	20	23	3	nd	197
ANS Fr	38	95	22	3	3	43	40	5	33	28	50	75
ANS Air Sparged	26	97	93	6	7	48	41	5	36	31	30	13
ANS On-tank Hi	25	97	200	9	7	37	30	3	47	44	10	23
ANS On-tank Lo	28	97	203	10	8	32	24	3	31	28	20	23
END Air Sparged	40	85	644	11	8	16	8	8	30	22	35	50
NS Fr	25	96.3	7	14	20	167	147	10	50	40	20	58
NS Air Sparged	43	91	36	15	10	107	97	5	37	32	20	37
NS On-tank Hi	23	98	143	16	20	38	18	10	18	8	20	50
End Fr	27	99	245	17	10	43	33	8	38	30	20	20
Pt Mcl On-tank Hi	25	94	695	19	15	20	5	10	27	17	20	84
Pt Mcl Air Sparged	18	99	76	20	15	107	92	15	53	38	20	10
Pt Mcl Fr	18	99	34	21	40	120	80	20	45	25	20	20
ANS On-tank Hi-Lo Mix	21	99	256	23	30	93	63	20	73	53	50	10
END Air Sparged	17	91	644	25	30	54	24	nd	nd	nd	nd	nd

- a. ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil, Fr = Fresh oil (unweathered), Lo = weathered on tank in non-breaking waves; Hi = weathered on tank in breaking waves.
- b. ODR = oil to dispersant ratio calculated as volume of oil / volume of dispersant applied.
- c. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.
- d. This is actually an index of oil concentration as the T-10AU units were calibrated using only Alaska North Slope crude oil, They were not calibrated separately for each oil in each test.

**Table 5.** Comparison of Oil Measurement Instruments - 2006 Tests on Alaska Oils

Oil <sup>a</sup>	ODR <sup>b</sup>	DE	Viscosity, cP	Test No.	Corrected Mean Peak Oil Conc		
					ppm		
					T-10AU	LISST	Wetlabs
END Air Sparged	0	23	772	1	5	4	5
End Fr	0	14	270	8	5	6	7
ANS Air Sparged	0	13	93	5	10	11	23
END Air Sparged	40	85	644	11	17	33	23
ANS On-tank Lo	28	97	203	10	32	31	40
ANS On-tank Hi	25	97	200	9	37	47	35

a. ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil, Fr = Fresh oil (unweathered), Lo = weathered on tank in non-breaking waves; Hi = weathered on tank in breaking waves.

b. ODR = oil to dispersant ratio calculated as volume of oil / volume of dispersant applied.

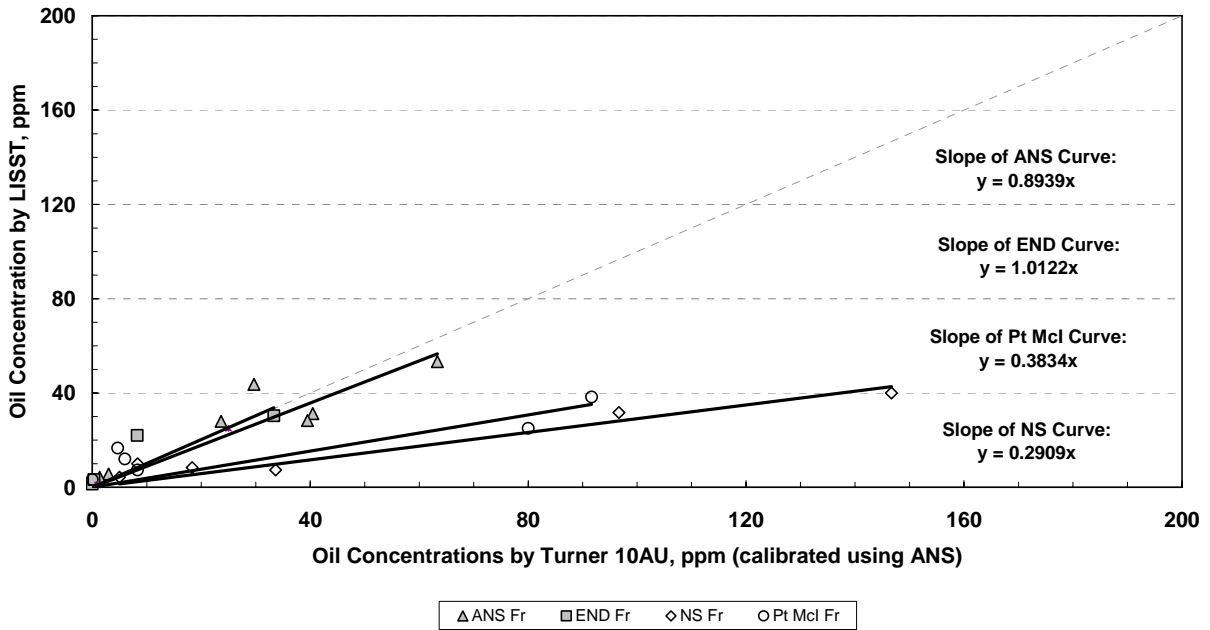
c. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.

d. This is actually an index of oil concentration as the T-10AU units were calibrated using only Alaska North Slope crude oil. They were not calibrated separately for each oil.

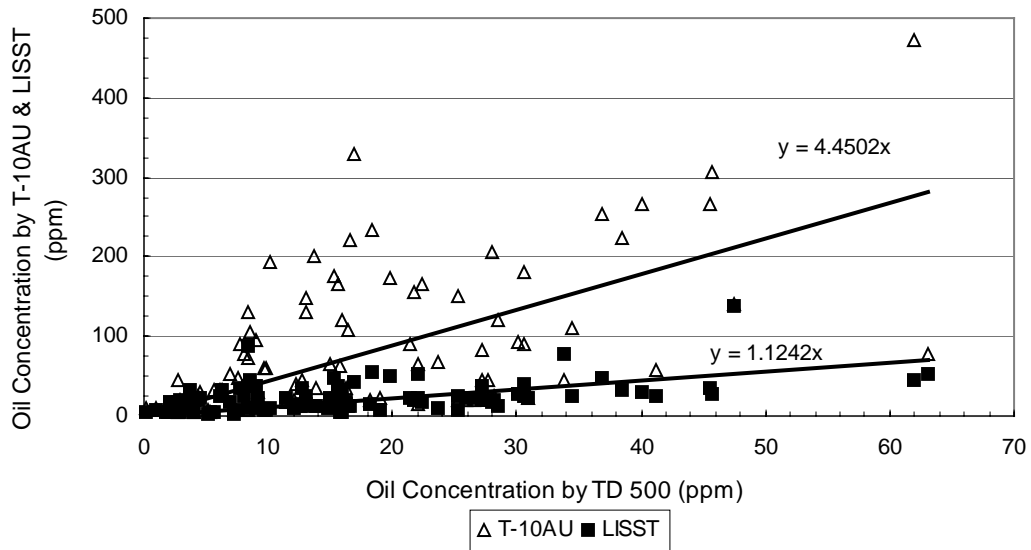
**Table 6.** Summary of Paired Test Results on Alaskan Oils 2006

Oil <sup>a</sup>	DE <sup>b</sup>		Turner Oil Conc (ppm) <sup>d</sup>				LISST Oil Conc (ppm)				LISST Drop Dia $\mu$ m (VMD)			
	Untr <sup>c</sup>	Disp <sup>c</sup>	Bkgd <sup>c</sup>	Untr <sup>c</sup>	Disp <sup>c</sup>	SMART Ratio <sup>c</sup> Disp/Untr	Bkgd	Untr	Disp	SMART Ratio Untr/Disp	Untr	Disp	SMART Ratio	
													Disp/Untr	Untr/Disp
NS Tank Hi	59	98	15	8	18	2	5	10	8	1	100	50	.5	2
Pt. Mcl Fr	12	99	3	6	80	14	3	12	25	2	200	20	.1	10
ANS Air	13	97	7	3	41	14	5	6	31	5	150	13	.09	11
Pt. Mcl Air	22	99	5	8	92	12	4	7	38	5	156	10	.06	17
Pt. Mcl Tank Hi	77	94	30	1	5	5	20	3	17	6	197	83	.42	2
NS Fr	23	96	8	34	147	4	6	7	40	6	142	58	.4	2
ANS Fr	20	95	3	1	40	40	3	4	28	7	167	75	.44	2
END Fr	14	100	5	1	33	33	3	3	30	10	83	20	.24	4
END Air	23	85	5	0	8	8	3	1	22	22	150	50	.33	3
END Air	23	91	5	1	24	24	3	1	nd	nd	150	nd	nd	Nd

- ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil, Fr = Fresh oil (unweathered), Air = air sparged, Tank Hi = weathered on tank at high wave energy
- DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.
- Untr = untreated (no dispersant control), Disp = treated, Bkgd = tank background, SMART Ratio = value for treated run (corrected for Bkgd) / value for untreated run (corrected for Bkgd)
- Turner oil concentration = Turner output in ppm when as calibrated using suspension of chemically-dispersed Alaska North Slope crude oil
- VMD = droplet size as volume mean diameter in microns.



**Figure 3.** In-tank Oil Concentrations by LISST versus T-10AU, Alaska Oils 2006



T-10AU & LISST Oil Conc vs TD500: Alaska 2006

**Figure 4.** Comparison of Tuner 10AU & LISST Concentrations with TD 500 Results

## **2.4 Alaskan Oils 2007**

The 2007 Alaskan oils project involved tests of fresh and evaporated oils treated with Corexit 9500 rather than Corexit 9527 (SL Ross and Mar 2007). These tests were intended to verify that Corexit 9500 was as effective against Alaskan oils as Corexit 9527 and involved testing new samples of the oils tested earlier. Fresh and weathered (air-sparged) samples of oils were tested and effectiveness measured using procedures similar to 2006. Monitoring was by measuring in-water oil concentrations using the LISST only. The T- 10AU fluorometer was not used.

Results are summarized in Table [7](#) and [8](#). DE values for controls ranged from 22 to 59% and were markedly higher than in the 2006 tests. As in the 2006 work, most treated slicks dispersed almost completely yielding DE values of 93 to 100%, with most in the 99-100% range. For controls, oil concentrations in the water ranged from 5 to 27 ppm. In dispersant-applied tests oil concentrations were greater than for controls, ranging from 21 to 95 with most being >45 ppm ([Table 7](#)). Oil concentrations in all untreated and treated tests were markedly higher than in the 2006 tests. By contrast droplet size data for the 2007 tests were consistent with the 2006 results. VMD values for the controls ranged from 107 to 330  $\mu\text{m}$ , while those for the effectively treated tests ranged from 17 to 87  $\mu\text{m}$ .

The LISST concentration measurements have been plotted versus oil concentrations determined from water grab samples (see [Figure 5](#)) as was done with the Alaska 2006 work. A Turner Design Model 3100 bench scale fluorometer was used to analyze the oil extractions. Based on the slope of the best-fit curve for the data the LISST generally underestimated the oil concentration in this test series by a factor of 1.7.

### **2.4.1 Comparison of Paired Tests**

The 2007 tests included 11 pairs of tests conducted on identical oils ([Table 8](#)). The control tests had DE values ranging from 22 to 59%, which were somewhat higher than in 2006. DE values for the treated tests were near maximal as they were in 2006. There is no apparent explanation for this difference between years. SMART Ratio values computed from LISST-measured oil concentrations ranged from 2 to 11. Of the 11 pairs of tests in this project, all of which involved highly effective treated tests, SMART Ratio values were greater than or equal to the “five-times” standard in only four of eleven cases. This differs from the results of the 2006 tests, where

SMART Ratio values met the “five-times” standard in most, though not all test pairs. It was noted above that the DE values in controls in 2007 were higher than in 2006 and the average in-water oil concentrations in both control and treated tests were greater in 2007 than in 2006. A partial explanation of this apparent difference in SMART Ratios between years is that while the oil concentrations for all tests was higher in 2007 than in 2006, the concentrations in the Control tests increased proportionately more than the treated tests, so it is only to be expected that in general the SMART Ratios in 2007 might be less than in 2006. The reason for the consistent shift in measured oil concentrations between years is not clear.

As mentioned above, droplet size values for dispersed tests were markedly smaller than for untreated tests and there was no overlap between droplet size ranges in dispersed and untreated tests. The VMD of the oil drop distributions in the control tests were at least 2 times higher than those in the matching dispersed tests (see last column in [Table 8](#)).

#### **2.4.2 Diagnostic value of measurements**

As with the 2006 data set with Alaska oils, the 2007 data set was useful in that it contained only results from the extreme ends of the effectiveness spectrum; ineffective control tests on one hand and highly effective treated tests on the other. The results demonstrated the potential usefulness of the combination of oil concentration and droplet-size measurements over oil concentrations alone for assessing effectiveness. In one sense, the data set supported the use of oil concentration values alone for assessing effectiveness as oil concentrations from control and treated tests fell into mutually exclusive ranges. On the other hand, the concentration ranges from the 2007 control tests overlapped somewhat with the highly effective treated tests in 2007, showing that concentration values may shift under the influence of environmental variables and may not be unambiguously related to effectiveness. The 2007 data set suggested strongly that the SMART Ratio “five-times” standard may not be a useful criterion for identifying effective dispersion as SMART Ratios from only 4 out of 11 pairs of tests exceeded the standard. It was mentioned above that tank conditions or the test protocol itself might influence monitoring results. In these tests virtually all of the 1-mm-thick treated oil slicks were fully dispersed into the water. If the treated and untreated slicks had been thicker, SMART Ratio values might conceivably have been larger.



The droplet size data however, appeared to be as consistently related to effectiveness in the 2007 study as in the 2006. Average VMD values from control and treated tests fell into completely separate ranges in the 2007 tests and these ranges are consistent with those of the 2006 tests. In addition, SMART Ratios for droplet size are also consistently lower than 0.5 in 2007 as in 2006. Both the 2006 and 2007 data sets suggested that oil concentration coupled with droplet size might have important advantages for assessing effectiveness. The usefulness of using a combination of oil concentration and droplet size to assess effectiveness was illustrated by considering a pair of tests on 22% weathered Alaska North Slope crude oil (ANS 22%) (in [Figure 6](#)) The upper graphic (Run 17) shows results of five passes during the control test (DE=68%). The first pass at 0 to 100 seconds showed the background conditions of oil concentration and droplet size as they existed while the oil slick was being laid down, namely approximately 5 ppm and 30  $\mu\text{m}$ , respectively. The second pass at 300 to 600 seconds showed oil concentrations had increased to 10 - 20 ppm with spikes to 30 ppm, which might have indicated dispersion. This increase was accompanied by oil droplet sizes increasing from background to as much as 200  $\mu\text{m}$ , indicating that elevated oil concentrations were due to entrainment of large droplets that would not remain permanently dispersed. Subsequent passes showed similar oil behavior. The lower graphic (Run 18, DE=97%) showed the results of six passes during the test of treated ANS 22%. The pass at 0 to 100 seconds shows background conditions during the oil discharge similar to those in the control run. The next pass (400 seconds) showed conditions in the cloud of dispersed oil that are characteristic of high levels of effectiveness, that is elevated oil concentrations of 100 ppm due to droplets of 10  $\mu\text{m}$  diameter or less, reflecting entrained oil of small droplets that would remain permanently dispersed. These conditions are repeated in the four subsequent passes. This figure illustrates the potential usefulness of the combination of oil concentration and droplet size in distinguishing between ineffective and effective dispersant applications.

**Table 7. Summary of Results of 2007 Tests on Alaska Oils**

Oil <sup>a</sup>	ODR <sup>b</sup>	DE <sup>c</sup>	Viscosity, cP	No.	LISST Oil Concentration (ppm)			LISST Droplet Volume Mean Diameter (VMD) $\mu$ m	
					Back ground, ppm	Mean Peak Concentration, ppm	Corrected Mean Peak Concentration, ppm	Background Droplet Diameter, $\mu$ m	VMD in Areas of Elevated Concentration, $\mu$ m
NS 30%	0	51	30	6	10	20	10	10	167
Pt Mcl 15%	0	32	400	11	15	20	5	10	107
ANS 22%	0	59	300	17	5	30	25	40	117
NS Fr	0	59	6	9	20	37	17	10	167
END 18%	0	31	520	14	5	23	18	5	223
ANS 15%	0	22	45	4	5	22	17	30	237
END Fr	0	24	350	3	3	15	10	75	240
Pt. Mcl Fr	0	38	45	2	5	25	20	100	280
ANS Fr	0	59	65	1	2	24	22	200	330
NS Fr	18	99	6	10	15	50	35	10	17
NS 30%	19	99	30	7	5	50	45	20	27
ANS Fr	25	98	65	19	20	70	50	30	20
NS 30%	20	99	30	8	10	77	67	10	30
ANS 22%	24	97	300	18	5	71	66	30	17
END 18%	18	94	520	16	5	53	48	5	87
ANS 15%	17	99	200	5	5	100	95	25	47
END Fr	24	98	350	21	10	73	63	10	20
Pt. Mcl Fr	23	99	400	20	10	73	63	10	30
Pt Mcl 15%	23	99	400	12	20	75	55	10	63
END 18%	21	93	520	15	5	77	72	25	63

a. ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil, Fr = Fresh oil (unweathered), Air = air sparged, Tank Hi = weathered on tank at high wave energy

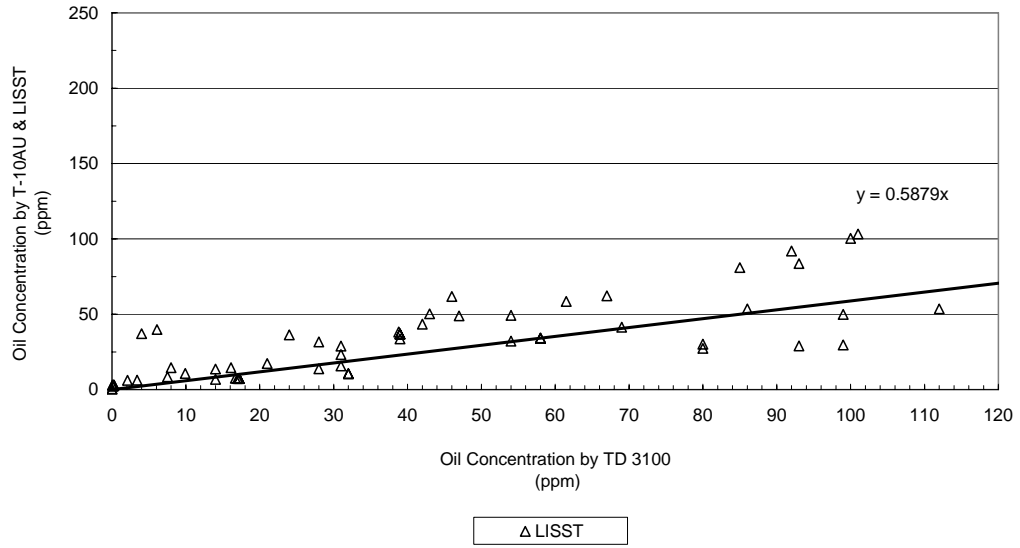
b. ODR = oil to dispersant ratio (volume of oil/volume of dispersant)

c. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.

**Table 8. Results of Paired Tests on Alaskan Oils 2007**

Oil	DE (%)		LISST Oil Concentration (ppm)				LISST Drop Diameter <sup>c</sup> (VMD), $\mu\text{m}$			
	Untr	Disp	Bkgd <sup>c</sup>	Untr	Disp	SMART Ratio	Untr	Disp	SMART Ratio	
									Disp/Untreated	Untreated/Disp
NS Fr	59	99	20	17	35	2	167	17	.1	10
ANS Fr	59	98	2	22	50	2	330	20	0.06	17
ANS 22%	59	97	5	25	66	3	117	17	0.15	7
END 18%	31	94	5	18	48	3	223	87	0.39	3
Pt. Mcl Fr	38	99	5	20	63	3	280	30	0.11	9
END 18%	31	93	5	18	72	4	223	63	0.28	4
NS 30%	51	99	10	10	45	4	167	27	0.16	6
ANS 15%	22	99	5	17	95	6	237	47	0.2	5
END Fr	24	98	3	10	63	6	240	20	0.08	12
NS 30%	51	99	10	10	67	7	167	30	.18	6
Pt. Mcl 15%	32	99	15	5	55	11	107	63	.59	2

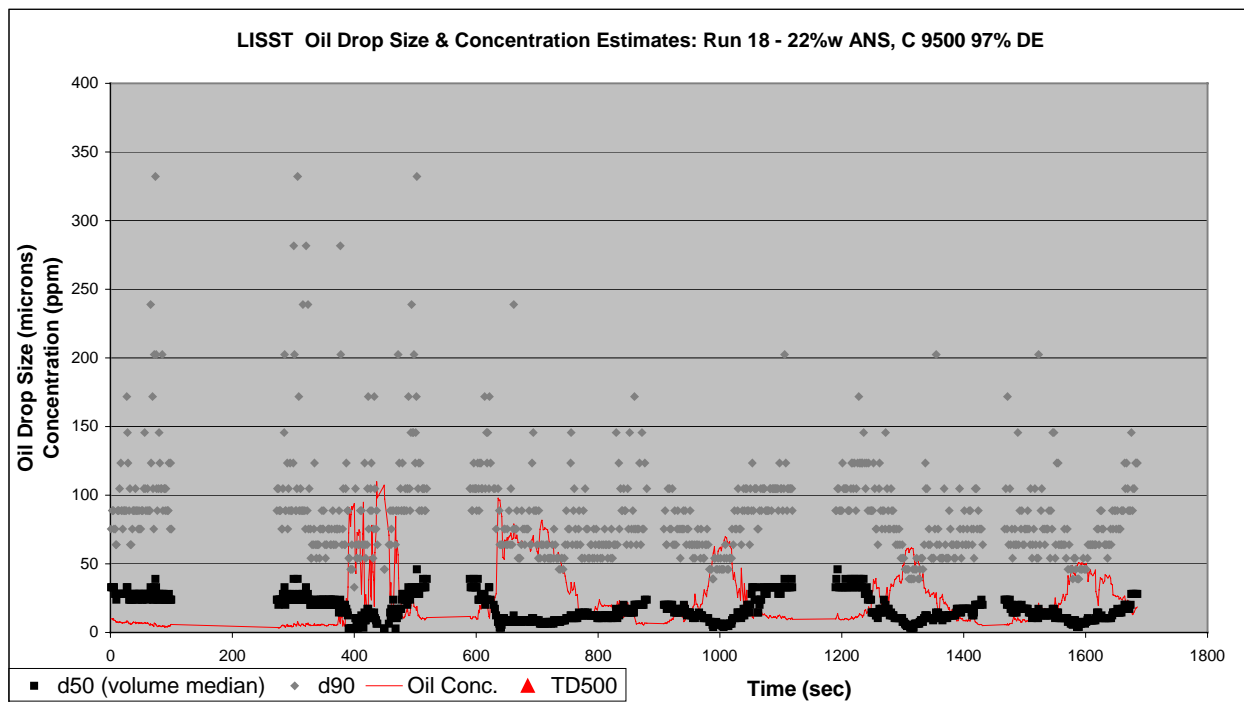
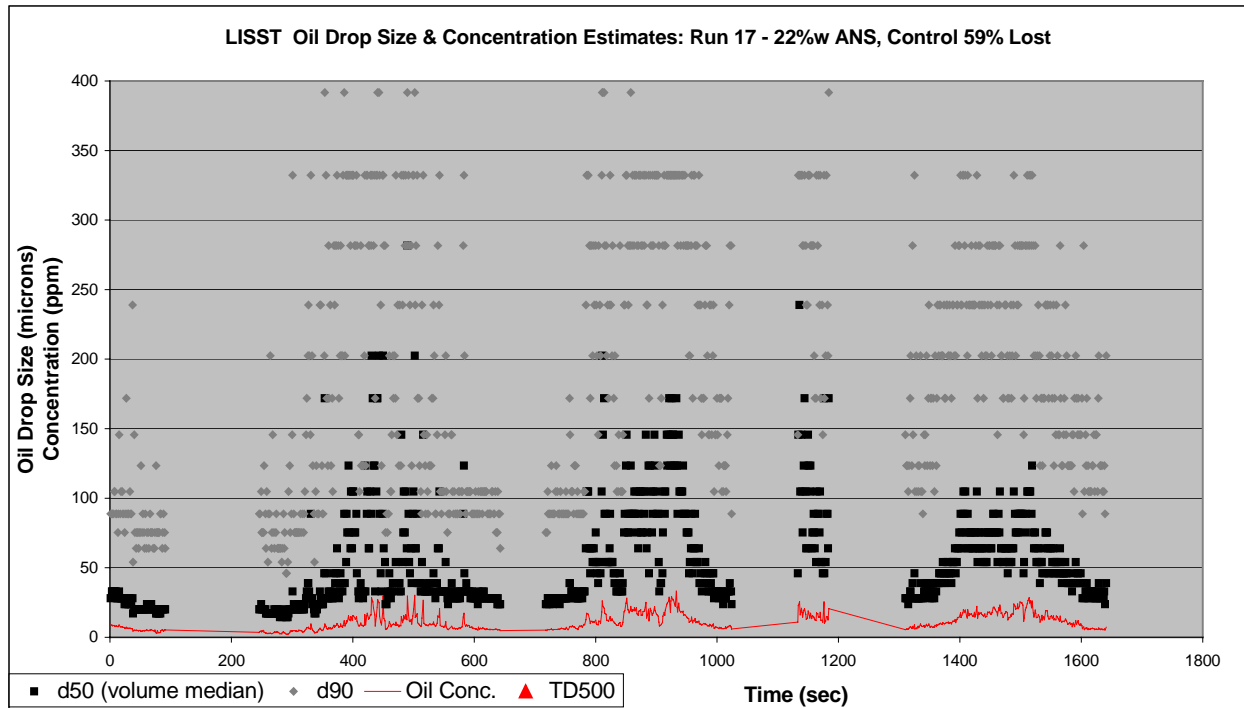
a. ANS = Alaska North Slope crude oil, NS = North Star crude oil, END = Endicott crude oil, Pt Mcl = Point McIntyre crude oil, Fr = Fresh oil (unweathered), Air = air sparged, Tank Hi = weathered on tank at high wave energy  
b. DE = Volume of oil spilled at start of test - volume of oil remaining on the surface of the tank at the end divided by the volume discharged at the start. This is the direct measurement of effectiveness.  
c. Untr = untreated (no dispersant control), Disp = treated, bkgd = tank background, SMART Ratio = value for treated run corrected for bkgd/value for untreated run corrected for bkgd



LISST Oil Conc vs TD3100: Alaska 2007

**Figure 5.** Comparison of LISST Concentration Measurement to TD 3100

Figure 6. In-water Oil Concentration and Droplet Size Results for Control (Upper) and Treated (Lower) Tests on North Star Crude Oil (30% Evaporated)





## 2.5 Dispersibility of Emulsions

The 2006 tests on water-in-oil emulsions involved preparing emulsions with a range of properties and assessing their dispersibility (SL Ross et al 2006). The potential value of this project in the present study was that, unlike most projects discussed above in which dispersant-treated runs yielded very high levels of dispersion, some or all of the dispersant tests in the “emulsions” project yielded only partial dispersion or none at all. As such, this data could potentially have provided insights into the use of monitoring to verify dispersion where only partial dispersion occurred.

Emulsions were prepared by blending water with oil mechanically in a drum and by on-tank weathering in breaking waves. Emulsions spanned a range of viscosities from 4000 cP to 50,000 cP, which were much higher than most oils discussed above. Dispersibility of emulsions was tested using the standard OHMSETT protocol using both Corexit 9500 and 9527 dispersants. Effectiveness was measured directly and oil behavior was monitored visually and in-situ using the LISST. LISST measurements were taken on transects along the tank at a depth of 1.5 m. The T-10AU was not used.

Results are summarized in [Table 9](#). DE values for control tests ranged from 0 to 23%, which was consistent with earlier Ohmsett work. DE values for treated slicks ranged from 0 to 58%, with most DE values lying in the same range as the controls 0 to 23%. Background particle concentration at the beginning of testing was 5 ppm and varied from test to test, ranging from 5 to 20 ppm over the two weeks of testing. Similarly, the background VMD of particles in the tank was approximately 10  $\mu\text{m}$  at the start of the study and varied from test to test ranging from 20 to 100  $\mu\text{m}$  over the test period.

Oil concentration measurements under the control slicks ranged from 5 to 30 ppm, averaging 12 ppm. These were only slightly above background and in the same range as in all earlier studies. Droplet diameter values under control slicks ranged from 15 to 300  $\mu\text{m}$ . In three of the five controls neither oil concentration nor droplet size varied from background. In the other two tests oil concentrations spiked intermittently to >100 ppm accompanied by consistent increases in VMD from background to > 100 microns.

As mentioned above, DE values for treated slicks ranged from 0 to 58%, with values for most runs lying in the same range as the controls, namely 0 to 23%. These values are much lower than

in other studies. Only the least viscous oil showed consistently elevated DE values in treated tests. Average oil concentrations under treated slicks ranged from 7 to 67 ppm, averaging 29 ppm. Most of these appeared to be well above background and most appeared to be greater than the control values for the corresponding oil. They were also consistent with those in the 2006 tests on Alaskan oils. Mean droplet diameter values in treated runs ranged from 17 to 117 ppm. However, in some tests, droplet diameters under slicks or in dispersed oil clouds could not be distinguished from background values.

Most of the treated tests showed some increase in in-water oil concentration, but these were in the form of momentary spikes from 50 to 150 ppm as seen in [Figure 7](#). Broad patches of high oil concentrations like those observed in treated tests in the Alaska oil tests were not observed. In some tests spikes in oil concentration were accompanied by increases in droplet VMD, while in others there was no apparent change from background. In only two tests were concentration increases accompanied by downward shifts in droplet size.

SMART ratios for these tests range from 1 to 62. [Figure 8](#) shows a plot of DE versus the SMART Ratio for these tests. There is no apparent correlation between DE and the SMART Ratio in this data within oil types or in the dataset as a whole. A number of false positive dispersions would be identified if the “five-times” factor were used to identify effective dispersions in these tests.

### **2.5.1 Diagnostic value of measurements**

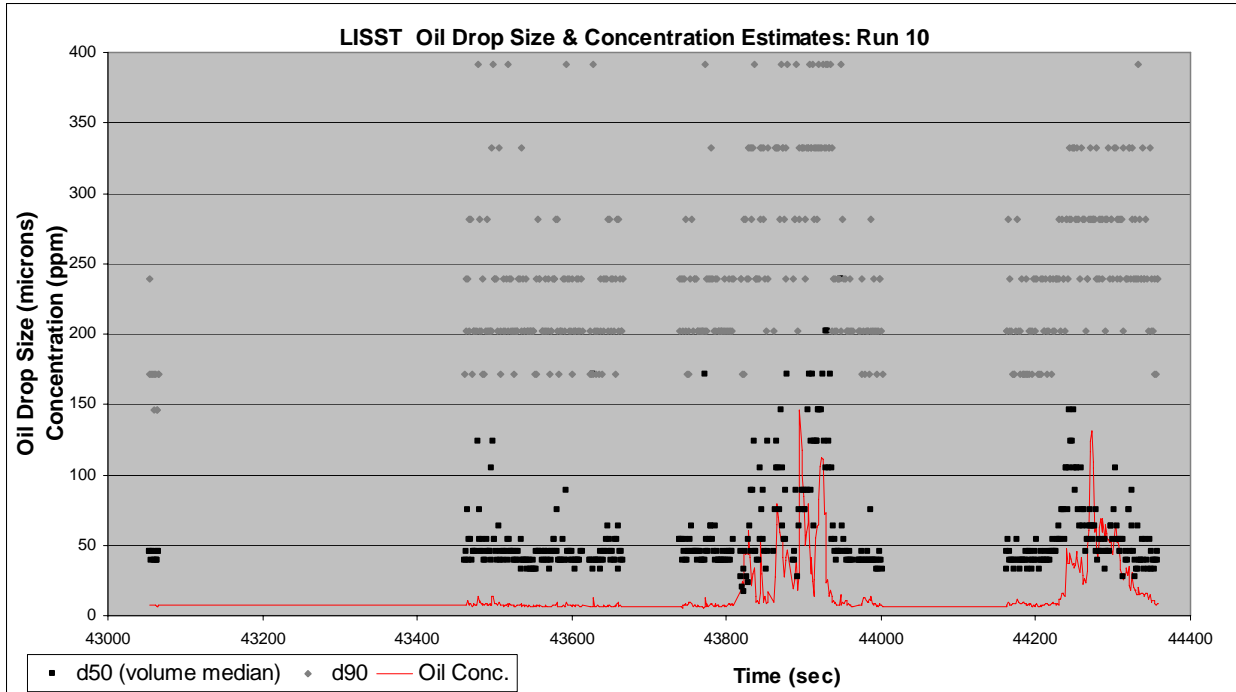
All results of dispersant tests in this project resulted in partial dispersion or no dispersion. However, the calculated SMART Ratios for six of the twelve tests were greater than the “five-times” standard. Three of these six Ratios would have identified false positive dispersions (less than 10% DE was measured for these tests.) Two of the tests where the SMART Ratio was less than five had DE values of approximately 30%, indicating that the application of the SMART Ratio and “five-times” standard may not have detected successful dispersion in these cases.



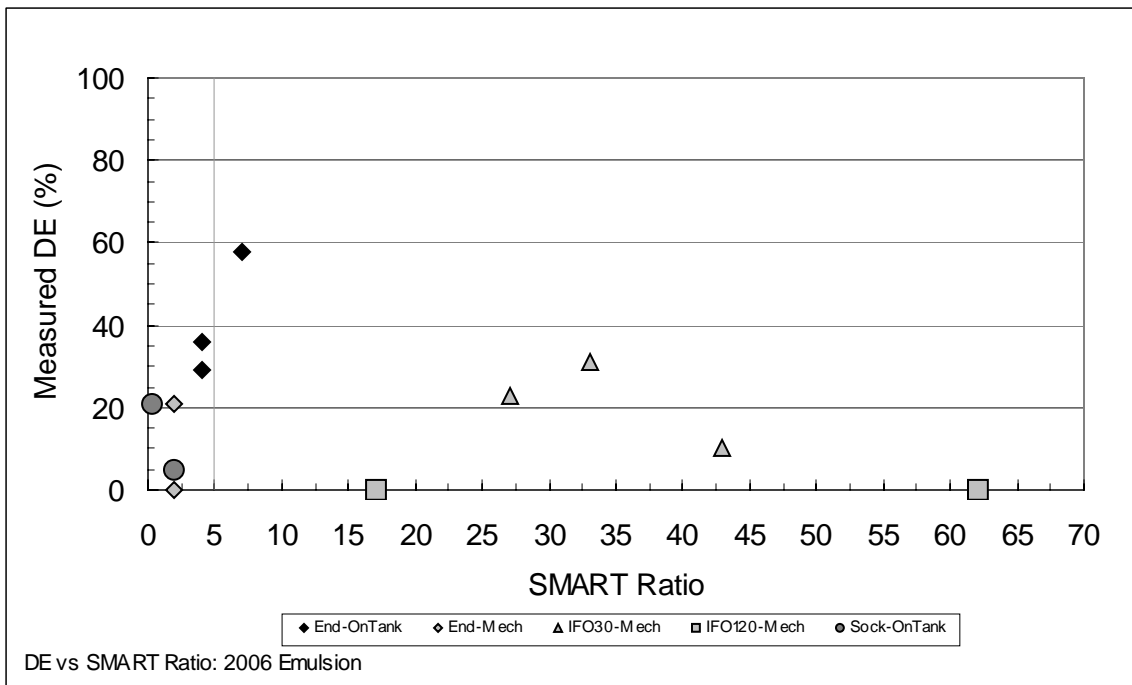
**Table 9.** Summary of Results from Tests on Dispersibility of Emulsions, 2006

Oil <sup>a,b</sup>	Emulsion Viscosity, cP	Dispersant	ODR <sup>c</sup>	DE <sup>d</sup> (%)	Test no	LISST Oil Concentration, ppm				LISST, Drop size, VMD $\mu$ m	
						Back-ground, ppm	Mean Peak Conc ppm	Corrected Mean Peak Conc ppm	SMART Ratio	Background ( $\mu$ m)	VMD in Areas of Elevated Concentration ( $\mu$ m)
<b>Endicott on-tank</b>	<b>3920</b>	<b>Control</b>	<b>0</b>	<b>23</b>	<b>9</b>	<b>5</b>	<b>10</b>	<b>5</b>		<b>20</b>	<b>30</b>
Endicott on-tank	3920	9527	14	58	10	10	43	33	7	40	83
Endicott on-tank	3920	9500	11	29	11	15	37	22	4	30	77
Endicott on-tank	3920	9500	10	36	12	15	35	20	4	30	20
<b>Endicott mech</b>	<b>6069</b>	<b>Control</b>	<b>0</b>	<b>0</b>	<b>2</b>	<b>5</b>	<b>30</b>	<b>25</b>		<b>25</b>	<b>165</b>
Endicott mechl	6069	9527	6	21	4	10	50	40	2	30	30
Endicott mech	6069	9500	12	0	3	5	33	28	2	50	55
<b>IFO 30 mech</b>	<b>7895</b>	<b>Control</b>	<b>0</b>	<b>0</b>	<b>13</b>	<b>5</b>	<b>5</b>	<b>1</b>		<b>30</b>	<b>40</b>
IFO 30 mechanical	7895	9527	21	23	16	20	47	27	27	30	117
IFO 30 mechanical	7895	9500	22	31	14	10	43	33	33	40	13
IFO 30 mechanical	7895	9500	14	10	15	10	53	43	43	20	17
<b>IFO 120 mech</b>	<b>17322</b>	<b>Control</b>	<b>0</b>	<b>0</b>	<b>19</b>	<b>10</b>	<b>10</b>	<b>1</b>		<b>20</b>	<b>15</b>
IFO 120 mech	17322	9527	26	0	18	10	72	62	62	20	13
IFO 120 mech	17322	9500	28	0	17	5	22	17	17	10	17
<b>Sockeye on-tank</b>	<b>45500</b>	<b>Control</b>	<b>0</b>	<b>8</b>	<b>1</b>	<b>5</b>	<b>28</b>	<b>23</b>		<b>100</b>	<b>133</b>
Sockeye on-tank	45500	9527	17	5	5	5	43	38	2	20	30
Sockeye on-tank	45500	9500	18	21	6	20	27	7	0.3	30	23
Sockeye mech	8638	9500	18	4	7	20	37	17	nd	30	77
Sockeye mech	8638	9527	11	20	8	20	43	23	nd	40	87

- a. END = Endicott crude oil, Sockeye crude oil, IFO 30, IFO 120;  
b. On-Tank = emulsion made on tank, mechanical = emulsion made by mechanical stirring with water in a drum  
c. ODR = oil to dispersant ratio (volume of oil / volume of dispersant)  
d. DE = volume of oil recovered at end of test versus volume discharged



**Figure 7.** In-water Oil Conditions in Run 10 Endicott Emulsion Formed On-tank in Dispersibility of Emulsions Study



**Figure 8.** Dispersant Effectiveness versus SMART Ratio: 2006 Emulsion Study

### 3 Summary

This project analyzed the monitoring data from five dispersant studies completed at Ohmsett since 2003, for which suitable instrumental monitoring data had been gathered. The objective was to verify the usefulness of the principles of instrumental monitoring in SMART for distinguishing between effective and ineffective dispersant applications.

The SMART Ratios calculated for all of the tests reviewed have been plotted against DE in [Figure 9](#). It is evident from this figure that there is very little correlation between the SMART Ratio and DE for the range of conditions studied and that the application of the “five-times” guideline for determining effective dispersion would result in a large number of both false positive and negative monitoring outcomes in some cases.

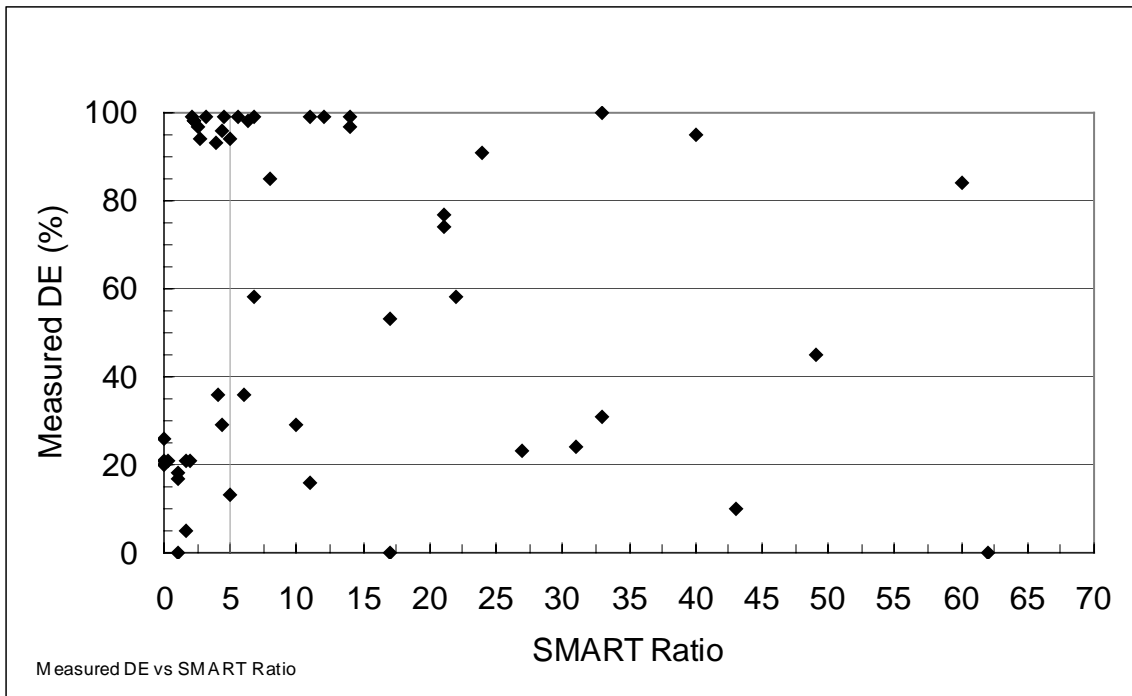
Levels of effectiveness (DEs) ranged from 0 to 77% in control tests and 0 to 100% in dispersant treated tests. Studies of dispersibility of Alaskan oils provided some important insights into oil behavior in untreated and effective dispersant applications. In both the 2006 and 2007 Alaska oils tests, treated tests yielded high effectiveness levels (85 to 100%). It should have followed that the SMART Ratios for these tests should have been above 5, if the “five-times” standard was at all useful. In the 2006 project, oil concentration measurements made under slicks with the laser particle-size analyzer (Sequoia LISST-100X) correlated to a degree with effectiveness, ranging from 1 to 12 ppm (average = 6 ppm) in control tests and from 8 to 53 ppm (average = 30 ppm) in treated tests. Similar trends were observed in the oil concentration data set produced using the Turner 10AU fluorometer (that had been standardized with a dispersion of ANS oil.) The SMART Ratios were also correlated with effectiveness. In paired tests on identical oils in 2006, the ratios of LISST-measured concentrations under treated and untreated spills (SMART Ratios) ranged from 1 to 22, exceeding the “five-times” guideline suggested for making decisions on effectiveness in 9 out of 11 pairs of oils tested. The size of particles (as volume mean diameters or VMD, in  $\mu\text{m}$ ) in oil clouds beneath untreated and treated spills was strongly correlated to effectiveness. Measurements under untreated slicks ranged from 83 to 226  $\mu\text{m}$ , while those in dispersed oil clouds were much smaller, ranging from 10 to 83  $\mu\text{m}$ . Ratios of particle sizes in treated tests were consistently less than half of those in the corresponding untreated tests.

Levels of effectiveness in the treated tests in 2007 were also uniformly high and similar trends were observed in in-water oil concentration ratios and particle sizes. The exception was that oil concentrations in the water column in 2007 were consistently higher than in 2006 in both untreated (5 to 27 ppm) and treated tests (21 to 95 with most being >45 ppm). In paired tests on identical oils in 2007, SMART Ratios were consistently low, ranging from 2 to 11, with only 4 out of 11 pairs exceeding the “five-times” guideline for effectiveness. Particle size ranges under treated and untreated slicks were similar to those in 2006 and ratios of particle sizes in treated tests were consistently less than half of those in the corresponding untreated test, as in 2006.

In short, in the tests on Alaskan oils, assessments of effectiveness based on the SMART Ratio using oil concentrations in the water under slicks would have led to incorrect conclusions in some cases in the 2006 tests and more than half of the tests in 2007. On the other hand, similar assessments made on the basis of particle size would have led to no errors. This suggests that droplet size may be a more reliable indicator of effectiveness than oil concentration. It is tempting to conclude from 2006 and 2007 results that assessments of effectiveness might be made based on droplet-size alone, but this is not true. Background values for droplet size vary widely making particle size data alone misleading. Rather, the Ohmsett data suggest that particle size information should be used in combination with oil concentration data. The studies showed that very low oil concentrations under slicks (indistinguishable from background) are strongly indicative of low effectiveness. Elevated oil concentrations always occur in effective applications, but also occur in some ineffective ones. When elevated concentrations occur, large droplets (VMD >83  $\mu\text{m}$ ) always indicate low effectiveness and small droplets (VMD < 83  $\mu\text{m}$ ) indicate high effectiveness making droplet size coupled with elevated oil concentration an unambiguous indicator of effectiveness. This is consistent with Lunel (1993) who concluded that oil droplets generated from slicks would be permanently dispersed if their diameter was less than 70  $\mu\text{m}$ , while those with diameters greater than 70  $\mu\text{m}$  were temporarily suspended in the water column, but would ultimately rise to the sea surface.

In this work, comparisons were made among the T-10AU, LISST and WetLabs WETStar instruments in the 2006 tests. When comparisons were made on an oil-by-oil basis, the relationship between T-10AU and LISST measurements varied with oil type, with LISST and T-10AU values being similar for ANS and Endicott oils, while the LISST gave lower concentration estimates for North Star and Pt McIntyre oils than did the T-10AU. Output of the WETLabs

WETStar (CDOM) sensor corresponded well to those of the LISST and T-10AU. When the LISST and T-10AU measurements were compared to oil concentrations determined by extraction and detection of oil from water grab samples, the LISST results generally provided a closer fit to the more accurate grab-sample concentrations. In summary, under Ohmsett conditions LISST-determined concentrations are more consistent with our best estimates of in-water concentrations than the T-10AU even when the T-10AU has been calibrated to the specific oil spilled.



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## Appendix 1 - Properties of Oils Tested at Ohmsett

Table A-1. Properties of Oils Tested at Ohmsett					
Test Series	Oil Type <sup>a,b</sup> (% evaporated )	Density (kg / m <sup>3</sup> at 25 °C)	Viscosity ( cP )	Oil-Water Interfacial Tension ( dynes/cm )	Pour Point (°C)
Alaska 2003	ANS (fresh)	873	98 (0 C°)	20.5	< -12
Alaska 2003	ANS (17% )	912	496 (0 C°)	20.9	-12
Alaska 2003	Endicott (fresh)	878	1630 (0 C°)	26.0	-3
Alaska 2003	Endicott (11%)	914	2525 (0 C°)	25.3	3
Alaska 2003	North Star (fresh)	812	101 (0 C°)	14.4	< -9
Alaska 2003	North Star (29%)	864	522 (0 C°)	14.8	12
Alaska 2003	Pt. McIntyre (fresh)	890	740 (0 C°)	22.4	-3
Alaska 2003	Pt. McIntyre (9%)	902	-	-	3
Correlating OHMSETT	IFO 380	983	7100 (16C° )	nd	nd
Correlating OHMSETT	IFO 180	970	2075 (16C° )	nd	nd
Alaska 2006	North Star Fr	803	7 (1 C°)	nd	nd
Alaska 2006	North Star Air Sparged	839	36 (1 C°)	nd	nd
Alaska 2006	North Star On-tank Lo	842	116(1 C°)	nd	nd
Alaska 2006	North Star On tank Hi	843	143(1 C°)	nd	nd
Alaska 2006	Pt McI Fr	861	34(1 C°)	nd	nd
Alaska 2006	Pt McI Air Sparged	880	76(1 C°)	nd	nd
Alaska 2006	Pt McI On Tank Lo	884	214(1 C°)	nd	nd
Alaska 2006	Pt McI On Tank Hi	898	695(1 C°)	nd	nd
Alaska 2006	ANS Fr	873	22 (1 C°)	nd	nd
Alaska 2006	ANS Air Sparged	912	93(1 C°)	nd	nd
Alaska 2006	ANS On-tank Lo	901	203 (1 C°)	nd	nd
Alaska 2006	ANS On-tank Hi-Lo Mix	nd	nd	nd	nd
Alaska 2006	ANS On-tank Hi	903	200 (1 C°)	nd	nd
Alaska 2006	Endicott Fr	902	270? (1 C°)	nd	nd
Alaska 2006	Endicott Air Sparged	917	644 (1 C°)	nd	nd
Alaska 2007	ANS Fr	862	65 (1 C°)	nd	nd
Alaska 2007	ANS Air Sparged	893	200 (1 C°)	nd	nd
Alaska 2007	Endicott Fr	901	350 (1 C°)	nd	nd
Alaska 2007	Endicott Air Sparged	916	520 (1 C°)	nd	nd
Alaska 2007	North Star Fr	814	6 (1 C°)	nd	nd
Alaska 2007	North Star Air Sparged	842	30 (1 C°)	nd	nd
Alaska 2007	Pt. McIntyre Fr	862	45 (1 C°)	nd	nd
Alaska 2007	Pt. McIntyre Air Sparged	898	400 (1 C°)	nd	nd
Dispersibility/ Emulsions	Endicott on-tank	924	3920 (3 C°)	nd	nd
Dispersibility/ Emulsions	Endicott mechanical	nd	6069 (3 C°)	nd	nd
Dispersibility/ Emulsions	IFO 30 mechanical	nd	7895(3 C°)	nd	nd
Dispersibility/ Emulsions	Sockeye mechanical	944	8638(3 C°)	nd	nd
Dispersibility/ Emulsions	IFO 120 mechanical	949	17322 (3 C°)	nd	nd

a. ANS = Alaska North Slope crude oil, IFO = intermediate fuel oil  
b. Value in parentheses is percent weight of oil removed by evaporation by heating and air sparging.



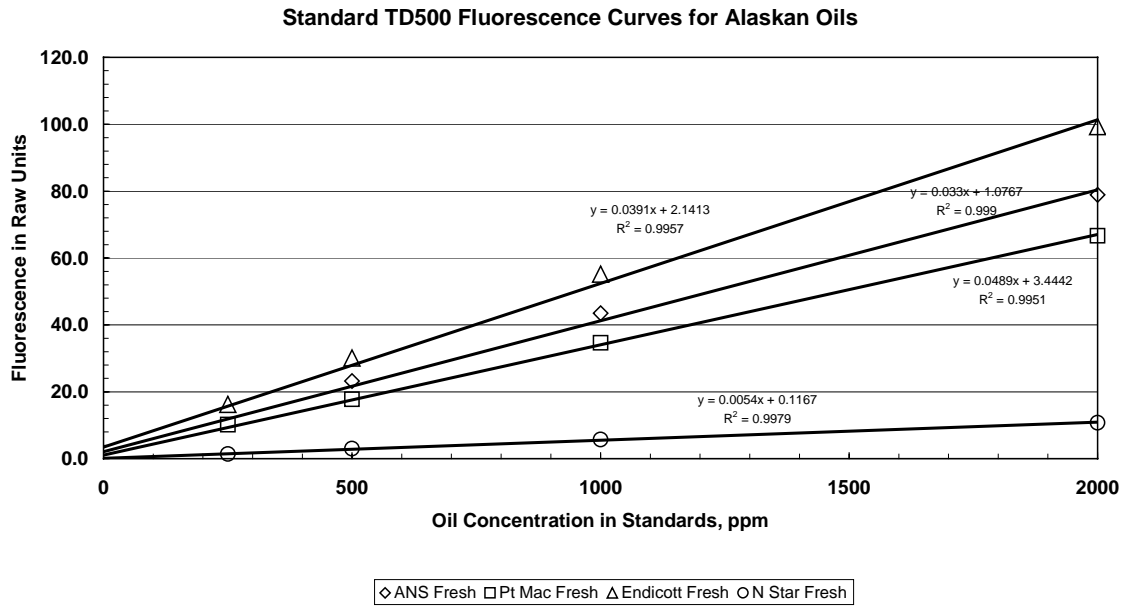
## **Appendix 2 – Alaska Oils 2006: Post Test Calibration Using Grab Samples**

A post-test calibration of the Turner 10AU was conducted in the 2006 Alaskan oils project. Ten to 12 samples (approximately 100 ml) of effluent were taken from the Turner, spanning the range of in-water concentrations observed in the run. Each was extracted with a single 10-ml aliquot of n-heptane and total hydrocarbons were measured using the Turner Designs TD500 handheld fluorometer<sup>11</sup> instrument calibrated using standard curves prepared with fresh and weathered samples of each of the oils tested. The calibration curves for the fresh oils, shown in [Figure A-1](#), show that, in solution in n-heptane, the Endicott oil fluoresced somewhat more than the ANS, while the Point McIntyre and North Star fluoresced somewhat less. Weathering of any given oil was accompanied by some changes in fluorescence, but variation within oils was much less than between oils.

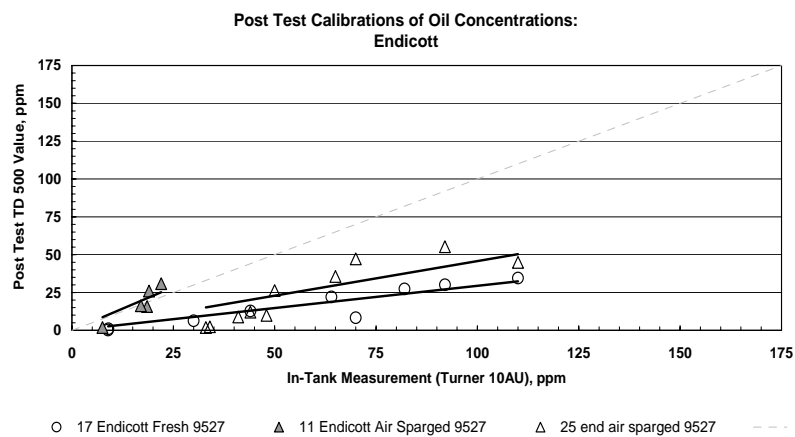
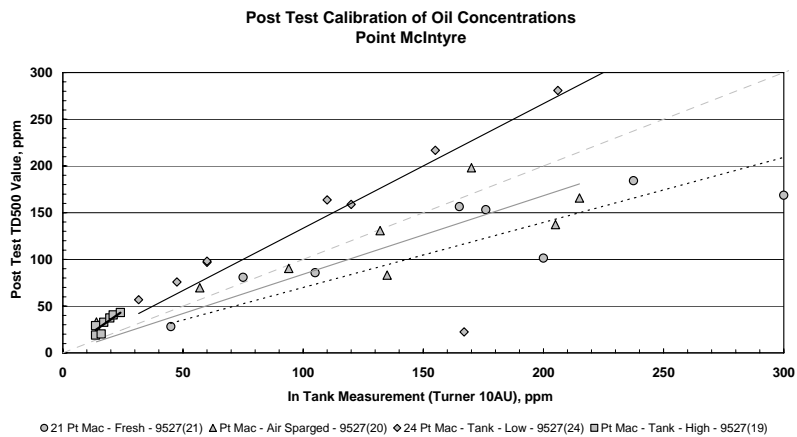
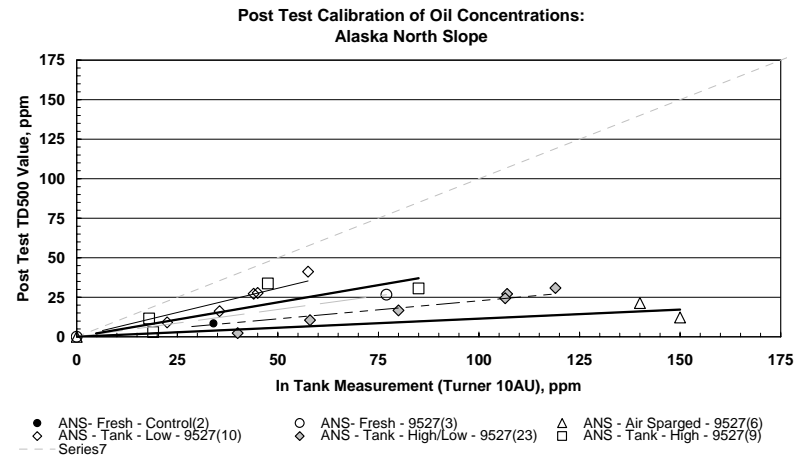
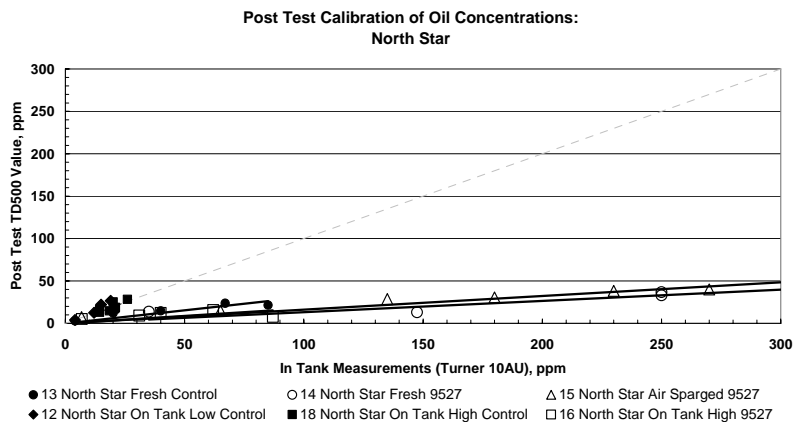
Post-test calibration data are presented in [Figure A-2](#). The diagonal dot line in each of the four graphs shows the slope of the curve expected if the in-situ Turner estimate were equal to the value in the post-calibration sample measured using the TD500. Clearly concentrations of oil measured in the post calibration samples for Point McIntyre oil are somewhat variable, but are consistent with a 1:1 relationship. On the other hand, oil concentration values generated by post-calibration for ANS, Endicott and North Star were well below output values from the Turner 10AU that had been calibrated using a standard suspension of dispersed ANS oil.

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<sup>11</sup> The Turner Designs Hydrocarbon Inc instrument, TD500, is a small, hand-held fluorometer device designed for measuring crude oil and condensates in water in the field. After extracting a water sample with solvent, the hydrocarbon content in the solvent is measured directly by fluorescence after the instrument is suitably calibrated. The instrument has a sensitivity of limit of 1 ppm and an operating range up to 1000-ppm hydrocarbons in the extract according to the manufacturer, Turner Designs Hydrocarbon Instruments of Fresno, CA.



**Figure A-1.** Standard Calibration Curves for Fresh Alaska Oils Using TD500



**Figure A-2** Post-test Calibration of Turner 10AU Estimates of In-Situ Oil Concentrations