DISPERSANT EFFECTIVENESS TESTING ON ALASKAN OILS IN COLD WATER

for

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by

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Executive Summary

Objective

The objective of this study was to determine if Corexit 9500 and Corexit 9527 dispersants are effective in dispersing Alaskan crude oils in cold-water conditions at the National Oil Spill Response Test Facility (Ohmsett).

Background

Dispersant effectiveness experiments completed at Ohmsett, in 2002 (SL Ross 2002) demonstrated that Alaska North Slope and Hibernia crude oils could be successfully dispersed in cold-water conditions. Subsequent to this testing, four Alaskan oils from the Prudhoe Bay area were sampled and tested for *in situ* burning cleanup effectiveness (SL Ross 2003). The Minerals Management Service (MMS) procured an additional 4 drums of each of the crude oils used for the in situ burning test program for dispersant effectiveness experiments. The intent was to collect large-scale test data on both in situ burning and chemical dispersant countermeasures on these crude oils (both fresh and evaporated) to provide better insight into the possible effectiveness of these two clean-up techniques in the event of spills in cold waters. The four Prudhoe Bay crude oils selected for testing were Alaska North Slope (ANS), Northstar, Endicott and Pt. McIntyre. One Cook Inlet crude, Middle Ground Shoals (MGS) was a late addition to the dispersant effectiveness test program and was not included in the *in situ* burning study. All of the crude oils were shipped to Ohmsett for the large-scale test program. Small quantities of each crude oil were also shipped to Ottawa for preliminary, smaller-scale dispersant effectiveness testing used to help plan the more complex and costly large-scale test program at Ohmsett. The degrees of evaporation used in the dispersant effectiveness tests were the same as those used in the *in situ* burning work.

Summary of Results

Preliminary testing in small wave tank tests showed that Corexit 9500 and Corexit 9527 gave similar dispersion effectiveness on all of the oils tested. These results led to the use of only Corexit 9527 for the large tank experiments at Ohmsett. Corexit 9527 was selected because this is the primary dispersant currently stockpiled in Alaska. The small-scale experiments also provided an indication of the Dispersant-to-Oil Ratios (DORs) needed to effect dispersion for each of the oil types at the test temperature ($\sim 0^{\circ}$ C). The DORs ranged from lows of 1:50 to as high as 1:10 for the heavier and evaporated oils.

A total of fourteen large-scale tests were completed at the Ohmsett facility with various combinations of oil type and dispersant-to-oil ratios (DORs). Table S1 summarizes the dispersant tests that were completed. Table S2 summarizes the control test results.

| Oil | % Evap. By Weight | Average Air Temp °C | Average Water Temp °C | Oil Volume Spilled (liters) | Approx. Oil Thickness (mm) | DOR | Max. Dispersant Effectiveness (%) | Links to Video Segments | Test # |
|-----------------|----------------------------|------------------------------|--------------------------------|--------------------------------------|-------------------------------------|-----|--|--|-----------|
| ANS | 17 | -3.1 | -0.6 | 107 | 0.92 | 24 | 85 | <u>1R1.mpg</u> , <u>2R1.mpg</u> , <u>3R1.mpg</u> | 1 |
| ANS | 17 | -1.7 | -0.4 | 1001 | 0.97 | 25 | 86 | <u>1R9.mpg, 2R9.mpg, 3R9.mpg, 4R9.mpg, 5R9.mpg, 6R9.mpg</u> | 9 |
| Endicott | 0 | -2.1 | -0.4 | 113 | 1.1 | 31 | 74 | <u>1R8.mpg, 2R8.mpg, 3R8.mpg, 4R8.mpg, 5R8.mpg, 6R8.mpg</u> | 8 |
| Endicott | 11 | -1.9 | -0.6 | 94 | 0.91 | 22 | 3 | <u>1R14.mpg, 2R14.mpg, 3R14.mpg, 4R14.mpg</u> | 14 |
| Northstar | 0 | -4.4 | -0.4 | 78 | 0.75 | 18 | ~100 | <u>1R2.mpg</u> , <u>2R2.mpg</u> , <u>3R2.mpg</u> | 2 |
| Northstar | 29 | -7.4 | -0.7 | 105 | 1.1 | 19 | 8 | <u>1R10.mpg, 2R10.mpg, 3R10.mpg</u> | 10 |
| MGS | 0 | -6.1 | -0.5 | 98 | 0.95 | 24 | 82 | <u>1R11.mpg</u> , <u>2R11.mpg</u> , <u>3R11.mpg</u> , <u>4R11.mpg</u> , <u>5R11.mpg</u> | 11 |
| MGS | 20 | -5.3 | -1.1 | 105 | 0.90 | 27 | 80 | <u>1R3.mpg, 2R3.mpg, 3R3.mpg, 4R3.mpg, 5R3.mpg</u> | 3 |
| Pt. McIntyre | 0 | -5.6 | -0.5 | 103 | 1.0 | 29 | 77 | <u>1R12.mpg</u> , <u>2R12.mpg</u> , <u>3R12.mpg</u> , <u>4R12.mpg</u> , <u>5R12.mpg</u> , <u>6R12.mpg</u> | 12 |

Table S1. Cold-Water Dispersant Effectiveness Test Results Summary

It was clear from visual observations alone which experiments resulted in a significant dispersion of oil and which did not. The visual observations were supported in three separate ways. First of all, a numerical estimate of the dispersant effectiveness (DE) was made for all tests by recovering and measuring the surface oil remaining at the end of the test period. Secondly, inwater oil concentration measurements were made using two flow-through fluorometers and analysis of water grab samples using IR spectrophotometry. Finally, oil drop size distributions were recorded using a laser particle size analyzer suspended in the tank.

| Oil | % Evap. By Weight | Average Air Temp °C | Average Water Temp °C | Oil Volume Spilled (liters) | Approx. Oil Thickness (mm) | DOR | % of Spilled Oil Recovered from Surface | % Evap. from Collected Oil | Links to Video Segments | Test # |
|-----------------|----------------------------|------------------------------|--------------------------------|--------------------------------------|-------------------------------------|-----|---|--|---|-----------|
| ANS | 0 | -4.3 | -1.0 | 96 | 0.93 | 0 | 69 | 12 | <u>1R4.mpg</u> , <u>2R4.mpg</u> , <u>3R4.mpg</u> , <u>4R4.mpg</u> | 4 |
| ANS | 0 | -1.4 | -0.9 | 108 | 1.1 | 0 | 97 | 5 | <u>1R7.mpg, 2R7.mpg, 3R7.mpg,</u> <u>4R7.mpg, 5R7.mpg</u> | 7 |
| Endicott | 0 | 2.8 | -1.0 | 103 | 1.0 | 0 | 84 | 4 | <u>1R6.mpg, 2R6.mpg, 3R6.mpg,</u> <u>4R6.mpg, 5R6.mpg</u> | 6 |
| Northstar | 0 | -3.6 | -1.8 | 103 | 1.0 | 0 | 93 | 27 | <u>1R5.mpg</u> , <u>2R5.mpg</u> | 5 |
| Pt. McIntyre | 0 | -3.7 | -0.8 | 104 | 1.0 | 0 | 58 | 20 | <u>1R13.mpg</u> , <u>2R13.mpg</u> , <u>3R13.mpg</u> , <u>4R13.mpg</u> , <u>5R13.mpg</u> | 13 |

Table S2. Large-Scale Control Test Results

After each test the oil remaining in the containment area was collected and its volume determined. The collected volume was compared to the quantity of oil discharged in the test to determine the maximum possible dispersion efficiency (DE) of the experiment. The DE values measured in the test program ranged from 3 to 100%, as reported in Table S1. The chemically dispersed runs resulted in high percentages (75 to ~100%) of oil dispersing into the water column, with the exception of tests 10 (evaporated Northstar) and 14 (evaporated Endicott). The DE trends identified in the smaller scale testing were mirrored in the large-scale test results. The heavily evaporated Northstar and evaporated Endicott crude oils were resistant to chemical dispersion in both the small-scale and Ohmsett experiments. A higher percentage of the fresh Endicott crude oil was dispersed in the Ohmsett experiments when compared to the small-scale results (74% vs 20 to 30%). This may be due to additional mixing energy present in the Ohmsett tests, in the form of breaking waves that do not develop in the small tank tests.

The oil concentration measurements taken at the 1-meter depth were the largest measured and the most variable in all of the experiments, especially on the first pass of the fluorometers through the dispersed oil cloud. The concentrations at 1-meter depth tended to decline and stabilize on subsequent passes, presumably due to the diffusion of the dispersed oil cloud and/or the rise of larger oil drops to the surface. The concentrations measured at the 2-meter depth were generally lowest on the initial pass and often increased on subsequent passes. These results suggest an initial dispersion of oil in the upper water layer with a gradual diffusion of the cloud to depth. Plots of these measurements are provided in Appendix E and are accessible through the following hyperlink (Appendix E).

It was found that the oil concentration estimates made using the flow-through fluorometers were in general 4 to 5 times lower than the concentration estimates made using IR spectrophotometry. However, the relative concentrations measured with the fluorometers provide a valid picture of the change in oil concentration over time and space.

Particulate matter in the water column was measured at the 2-meter depth using a laser particle size analyzer. The data was adjusted to account for the presence of background particles prior to each experiment. The measured drop size distributions suggest that a high percentage (average of all experiments was 78%) of the oil mixed into the tank, in the cases where dispersant was applied, would remain dispersed under typical ocean mixing conditions (all oil drops less than 100 μ m in diameter assumed permanently dispersed). Only about 30% (average of all experiments) of the oil present in the water column in the control experiments was in the form of drops that could be considered permanently dispersed. The concentrations of oil in the water column during the control experiments were also generally much lower than for the chemically dispersed cases.

The percentage of oil recovered from the surface was measured for each control experiment (no dispersant applied). The oil remaining in the containment boom at the end of each experiment was collected and the total volume, water content and density (of parent oil not oil and water mixture) of the collected emulsions were measured. The parent oil density data were used to estimate the amount of oil that evaporated over the duration of each control experiment. The amounts collected and losses attributable to evaporation are shown in Table S2. Between 80 to 120% of the spilled oil was accounted for in the control experiments indicating that the test protocol achieved a mass balance accuracy of about $\pm 20\%$.

A small, undetermined amount of oil splashed over the north-end containment boom in the first control experiment (test #4). No oil loss over the end containment was seen in the first three experiments (tests #1, #2 & #3) as most of the oil dispersed within minutes of the application of dispersant. After test #4, a second end barrier was installed approximately ten feet south and parallel to the original barrier to improve the oil containment. Loss of oil outside of the second containment barrier was not observed in any of the subsequent experiments. Between 80 to

120% of the oil discharged in the control experiments was recovered or accounted for through evaporation losses at the end of the test periods. The in-water oil concentration measurements from the fluorometers did not show any significant quantities of oil in the water column for any of the control experiments.

The Ohmsett tank water temperature stayed between -0.4 to -1.8 °C throughout all of the experiments without the need to use artificial chilling. This was due to the unusually cold weather experienced during the test period. Average air temperatures during each test ranged from 2.8 to -7.4 °C. The average wave amplitude for the tests ranged between 5.9 and 8.6 inches and the average period was between 1.8 and 2.2 seconds.

The concentration of dispersant in the water at the end of the experiments was about 7 ppm. A total of about 70 liters of dispersant was sprayed into the 10 million-liter tank during these experiments. The dispersant added to the Ohmsett tank water during the test program did not affect the results of experiments; dispersant concentrations on the order of 400 ppm are the lowest at which dissolved dispersant in the water begins to affect DE test results.

Recommendations

A double north-end containment boom should be used in all future tests to eliminate the loss of surface oil from the containment area by splash over.

The air-actuated valves used to start and stop the oil flow through the discharge piping should be serviced prior to any additional cold-water dispersant effectiveness testing. These valves mal-functioned in the cold weather experienced during the test period.

The effect of oil drop size on the measurement of the fluorescence of oil-in-water dispersions, using the Turner Fluorometers, should be investigated if direct, absolute oil concentration measurements are of interest. Alternatively, the results from the fluorometers should be adjusted based on the results of IR-Spectophotometry measurements of water grab samples taken in conjunction with the fluorometry readings.

The use of continuous flow through fluorometry to monitor in-water oil concentrations and *in situ* laser particle size measurement provided valuable insight into the dispersion process and could be used in future dispersant effectiveness tests when budgets permit.

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Disclaimer

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DISPERSANT EFFECTIVENESS TESTING IN COLD WATER

1. Objective

The objective of the study was to evaluate the effectiveness of Corexit 9500 and Corexit 9527 dispersants on Alaskan crude oils in cold-water conditions at the National Oil Spill Response Test Facility (Ohmsett).

2. Background

Dispersant effectiveness experiments completed at Ohmsett, in 2002 (SL Ross 2002) demonstrated that Alaska North Slope and Hibernia crude oils could be successfully dispersed in cold-water conditions. Subsequent to this testing, four Alaskan oils from the Prudhoe Bay area were sampled and tested for in situ burning cleanup effectiveness (SL Ross 2003). The Minerals Management Service (MMS) procured an additional 4 drums of each of the crude oils used for the *in situ* burning test program for dispersant effectiveness experiments. The intent was to collect large-scale test data on both in situ burning and chemical dispersant countermeasures on these crude oils (both fresh and evaporated) to provide better insight into the possible effectiveness of these two clean-up techniques in the event of spills in cold waters. The four Prudhoe Bay crude oils selected for testing were Alaska North Slope (ANS), Northstar, Endicott and Pt. McIntyre. One Cook Inlet crude, Middle Ground Shoals (MGS) was a late addition to the dispersant effectiveness test program and was not included in the *in situ* burning study. All of the oils were shipped to Ohmsett for the large-scale test program. Small quantities of each crude oil were also shipped to Ottawa for preliminary, smaller-scale dispersant effectiveness testing used to help plan the more complex and costly large-scale test program at Ohmsett. The degrees of evaporation used in the dispersant effectiveness tests were the same as those used in the in situ burning work.

3. Test Methods

Two series of dispersant effectiveness experiments were completed on the crude oils. Initial small-scale tank experiments were completed at the SL Ross laboratory in Ottawa. The goal of these experiments was to determine the likely effectiveness of both Corexit 9500 and 9527 dispersants on each of these oils prior to the more complex and costly large-scale test program at Ohmsett.

3.1 Small-Scale Tank Test Methods

A detailed description of the test procedures used in the small-scale tank experiments at the SL Ross facility in Ottawa is provided in Appendix A. An abbreviated description of the test method is provided below.

The test method uses the SL Ross indoor wave tank that is 10 meters long by 1.2 meters wide by 1.2 meters deep and is fitted with a wave-generating paddle at one end and a wave-dissipating beach at the other. This relatively large tank allows the use of full-scale spray nozzles for dispersant application. Tests are completed with the tank filled to a depth of 85 cm with 32 ppt salt water. A photo of the test tank is shown in Figure 1.

Oil is held in the middle of the tank using an air bubble curtain. The rising air bubbles from this submerged diffuser system entrain water that in turn creates an inflow of water at the surface. This inflow herds the oil to the center of the area above the rectangular diffuser. The oil remains within this confinement zone even when waves are introduced.

Dispersant is applied using an overhead spray boom mounted to the ceiling above the center of the test tank. The dispersant is applied through Spraying System Company flat-fan nozzles. These are the same type of nozzles used in full-scale, vessel-based dispersant application systems.



Figure 1. Test Tank

The amount of dispersant applied per unit area of surface is measured for each test by collecting the spray in a tray suspended just above the water surface at one edge of the oil containment zone.

The final estimate of dispersant effectiveness for each test is made by sorbing the oil left in the containment area at the end of the test and comparing the amount sorbed with the amount used in the test.

The key elements of the test method or procedures can be summarized as follows.

1. The dispersant spray apparatus is prepared by fitting the appropriate nozzles to the spray boom, putting the selected dispersant in the application pressure vessel, adjusting the air

pressure used to spray the dispersant and setting the boom drive motor to the appropriate speed.

- 2. The underwater lights, dispersant measurement tray, video camera and air bubble barrier are readied.
- 3. The oil is placed within the containment zone, the dispersant applied, the dispersant measurement tray removed and weighed and the wave paddle started.
- 4. After 20 minutes the wave paddle is stopped and the oil remaining in the containment zone is sorbed to estimate the dispersion efficiency.

3.2 Ohmsett Dispersant Effectiveness Test Method

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

3.2.1 Major Test Equipment Components

The main equipment components of the DE test procedure include the Ohmsett tank, the wave making system, the main equipment bridge, the oil distribution system, the oil containment boom and the dispersant spray system. Photos of these components are provided in Figures 2 through 8. Additional details concerning this equipment can be found in SL Ross 2000. Dispersed oil was characterized using flow-through fluorometry, dispersed oil particle size determination and water sampling (for Total Petroleum Hydrocarbon (TPH) determination).



Figure 2. Ohmsett Test Tank with Oil Containment Boom



Figure 3. Ohmsett Tank Wave Paddle System



Figure 4. Main Bridge with Dispersant Spray Bar in Foreground, Oil Distribution Behind



Figure 5. Oil Distribution System



Figure 6. Oil Delivery Pump and Supply Drum



Figure 7. Dispersant Supply Tank and Pump



Figure 8. Dispersant Spray Bar in Operation

3.2.2 Dispersed Oil Measurement Methods

The presence of dispersed oil in the water column was measured using three techniques:

1. In-water oil concentrations were measured using two flow-through fluorometers (Turner Design model AU-10 fluorometers, <u>AU-10 Specifications</u>) to which water was pumped from 1-meter and 2-meter depths. The pumps were suspended by chain from the bridge rail and were moved laterally in each test so they passed through the main dispersed oil cloud or under the main surface slick, if no cloud was visible. Calibration curves were developed for each of the oils for the two fluorometers over the range of 6.25 to 100 ppmv. The calibration standards were made by thoroughly mixing 1 ml of oil (that was premixed with 0.1 ml of Corexit 9527) into 10 litres of salt water. The standards were light brown in color with little or no visible dark oil droplets indicating that the oil was present in the form of very small droplets. The 100 ppmv standard was serially diluted to

achieve concentrations as low as 6.25 ppmv. Instructions for the basic operation of the AU-10 fluorometers can be viewed in the following document <u>10au_manual.pdf</u>. The calibration curves for the two fluorometers are provided in Appendix D and can be immediately viewed by using the following link <u>(Turner Calibrations)</u>. The calibration curves were linear over the range of concentrations considered.

- 2. Water samples were also taken from the fluorometer water streams during the experiments for total petroleum hydrocarbon determination (TPH) using CCl₄ extraction and infrared spectophotometry.
- 3. Dispersed oil drop-size distributions were recorded using a Sequoia LISST 100 particle size analyzer (LISST Specifications). This device was suspended by chain from the bridge rail and moved in each experiment to ensure that it passed through the main dispersed oil cloud or under the main surface slick, if no dispersed oil cloud was evident.

3.2.3 Ohmsett Dispersant Effectiveness Test Procedure

The following steps, were completed for each experiment.

1) Set up boom / oil distribution system / dispersant spray bar and pump.

2) Clear entire tank and inner boom area of oil. Remove tramp oil slicks from the tank or isolate them from the test area using the auxiliary bridge boom.

3) Set up fluorometer and particle size instrumentation. Deploy fluorometer pumps shortly before start of test to prevent freezing of water lines. Pumps were left running in a tank of water on deck (with flow re-cycling into the on-deck tank) to ensure proper flow at test time.

4) Transfer oil to open top drum on main bridge. Fill the oil discharge manifold with oil. Measure and record the depth of oil in the drum.

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5) Fill dispersant supply tank and keep warm with immersion heater to ensure proper spray pattern.

6) Test spray bar operation to ensure even spray from all nozzles (visual confirmation). Measure and record the depth of dispersant in the supply tank. Leave dispersant spray pump running and re-circulate the dispersant through the supply return line to keep supply line contents warm.

7) Position main bridge north of the center of the boomed area.

8) Start data collection for fluorometers and particle size analyzer just prior to starting the discharge and spraying of the oil to provide background readings.

9) Move bridge to the south at 1 knot (0.5 m/s).

10) Start oil pumping when the bridge is a few meters south of the center of the boomed area and continue pumping for 35 to 40 seconds at 40 gpm. Time the duration of the oil discharge and measure and record the depth of oil in the drum at the end of the discharge.

11) Start wave paddle at 35 cycles per minute (cpm) with 3-inch stroke at same time that oil discharge is started.

12) Start dispersant spray at start of oil pumping and continue spraying until 1 m past last surface oil (spray pressure 45 to 55 psi). Time the duration of the dispersant spraying and measure and record the depth of dispersant in the supply tank at the end of the spraying operation.

13) Rotate the oil distribution bars up away from the water surface to prevent contact with waves or the end containment booms.

14) Videotape and photograph the test with emphasis on providing a good overview of the development (or lack thereof) of any dispersed oil cloud that forms.

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15) Ten minutes after the formation of the first breaking waves, move the bridge over the main dispersed oil cloud (or surface slick if no cloud is evident) at a speed of 0.25 knots and collect oil concentration data (fluorometer readings and water grab samples) and particle size data. Move the instrument chain so the fluorometer pumps pass through the center of any dispersed oil cloud. The duration of the sampling run should be about 8 minutes.

16) Repeat in-water sampling passes 30 and 50 minutes after the start of waves.

17) Stop the wave paddle 60 minutes after the start of breaking waves.

18) Flush the oil remaining within the boom to the down-wind end of the boom and collect either using a ladle or a suction tube.

19) Decant free water from the collected oil and measure the quantity of oil (or emulsion) collected.

20) Completely mix the collected material and take a 500 ml sample of the product oil for water content and density determination. This data is used to determine total quantity of oil collected.

21) Clean and prepare the tank for the next test.

Figure 9 shows a typical control test (no dispersant applied) in cold water shortly after the onset of wave cresting. The photo provides a good indication of the wave energies used in the tests and illustrates the behavior of a typical oil slick with no dispersant applied.

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Figure 9. Control Test (no dispersant), Surface Oil an Cresting Wave

Figure 10 shows surface oil remaining at the end of a test after herding to a central collection area using the main bridge fire monitors.



Figure 10. Oil herded to End of Double Boom for Collection

The oil remaining in the boomed areas at the end of each test was pumped from the surface, using a diaphragm pump and suction tube, into a decant drum.

4. Test Results

4.1 Small-Scale Tank Experiments

A total of 16 small-scale tank experiments were completed on four of the five crude oils. The degrees of weathering used in the tests were the same as those used in the *in situ* burning work completed on these oils in a parallel MMS research project (SL Ross 2003). Slightly different degrees of evaporation were used in the small-scale versus the large-scale tests for the Northstar crude oil (33.8% vs 29%) and the Endicott crude oil (9% vs 11%), due to the difficulty in reaching a specific end point when evaporating a large quantity of oil. Table 1 shows the basic physical properties of the oils tested in the large-scale tests were very similar to those reported in Table 1, all other oil properties apply to both the small and large-scale tests. Detailed viscosity data are provided in the Lab Analysis section of MAR Inc.'s data summary report delivered under separate cover. All experiments were completed with water temperatures between 0 to 2°C. The oil thickness in these experiments ranged from 0.9 to 1.1 mm, with the exception of test 2 where the oil was estimated to be 0.75 mm thick.

| Oil Type (% evaporated) | Density (kg/m ³ at 25 °C) | Viscosity (cP at 0 °C) | Oil-Water Interfacial Tension (dynes/cm) | Pour Point ¹ (°C) |
|----------------------------|---|---------------------------|---|---------------------------------|
| ANS (fresh) | 873 | 98 | 20.5 | < -12 |
| ANS (17%) | 912 | 496 | 20.9 | -12 |
| Endicott (fresh) | 878 | 1630 | 26.0 | -3 |
| Endicott (11%) | 914 | 2525 | 25.3 | 3 |
| NorthStar (fresh) | 812 | 101 | 14.4 | < -9 |
| Northstar (29%) | 864 | 522 | 14.8 | 12 |
| Pt. McIntyre (fresh) | 890 | 740 | 22.4 | -3 |
| Pt. McIntyre (9%) | 902 | - | - | 3 |
| MGS (fresh) | 856 | 36 | 26.9 | <-18 |
| MGS (20%) | 914 | 3180 | 25.4 | 0 |

Table 1. Physical Properties of Test Oils

¹ Pour Points reported are from historical records for these oils with the exception of MGS. Pour point shown for MGS is from recent analysis of oil used in the current test program.

Small-scale tank tests were not completed for the ANS crude oil because large-scale results were already available from previous Ohmsett tests (SL Ross 2002). The small-scale tank test results are summarized in Table 2. The small-scale testing provided insight into two main areas.

| | | End | icott | | | | | |
|----------------|------------------|--------------|-----------------|--------------|--|--|--|--|
| | Fre | esh | 9.1 % Ev | vaporated | | | | |
| | Corexit 9500 | Corexit 9527 | Corexit 9500 | Corexit 9527 | | | | |
| DOR | 1:14 | 1:11 1:23 | 1:27 | 1:21 | | | | |
| Efficiency (%) | 8 | 20 33 | 0 | 0 | | | | |
| | | Nort | hstar | | | | | |
| | Fre | esh | 33.8 % E | vaporated | | | | |
| | Corexit 9500 | Corexit 9527 | Corexit 9500 | Corexit 9527 | | | | |
| DOR | 1:33 1:52 | | 1:20 | 1:19 | | | | |
| Efficiency (%) | 96 | 99 | 0 | 19 | | | | |
| | Cook Inlet (MGS) | | | | | | | |
| | Fre | esh | 20 % Evaporated | | | | | |
| | Corexit 9500 | Corexit 9527 | Corexit 9500 | Corexit 9527 | | | | |
| DOR | | 1:58 | | 1:26 1:14 | | | | |
| Efficiency (%) | | 99 | | 74 77 | | | | |
| | | Pt. Mc | eIntyre | | | | | |
| | Fre | esh | 9.1 % Ev | raporated | | | | |
| | Corexit 9500 | Corexit 9527 | Corexit 9500 | Corexit 9527 | | | | |
| DOR | 1:54 | 1:58 | 1:16 | 1:16 | | | | |
| Efficiency (%) | 99 | 96 | 37 | 8 | | | | |

Table 2. Small-Scale Tank Dispersant Effectiveness Test Results

The first is that Corexit 9500 and Corexit 9527 give similar effectiveness results on all of the oils tested. Because Corexit 9527 is the dispersant presently stockpiled in Alaska in the largest quantities and would be the most likely product to be used on a spill, it was selected for use in the Ohmsett testing to minimize the number of tests required. It can be inferred from the small tank results that Corexit 9500 would generate similar results at Ohmsett to those achieved with Corexit 9527.

The second piece of information gained from the small-scale experiments was an indication of the Dispersant-to-Oil Ratio (DOR) needed to effect dispersion for each of the oil types. For the fresh Northstar, Point McIntyre and MGS crude oils, DORs of 1:50 (or less) provided sufficient chemical for complete dispersion of the oil. The fresh Endicott crude oil was only partially dispersed (20 to 30%) with DOR's as high as 1:11. The small-scale tank test results also indicate

that the weathered oils were not easily dispersed with dispersant applied in DORs in the 1:15 to 1:20 range. The evaporated MGS crude oil showed promise for chemical dispersion (about 75% dispersion) and evaporated ANS was shown to be dispersible in the previous Ohmsett trials. Chemical dispersion of the remaining evaporated oils was poor in the small-scale tank experiments with effectiveness results ranging from 0% for Endicott to 37% for Pt. McIntyre.

4.2 Large-Scale Tank Experiments at Ohmsett

A total of fourteen experiments were completed with various combinations of oil type and Dispersant-to-Oil Ratio (DOR). Table 3 summarizes the tests that were completed, ordered by oil type. The physical properties of the oils used in the tests can be found in Table 1. Oils were evaporated by bubbling air through heated drums. A series of video clips have been captured for each run. They can be accessed through the hyperlinks in the Table 1. In most of the dispersant tests the video images show the early dispersion of oil and formation and growth of a dispersed oil cloud. The control test videos feature distinct surface slicks throughout the tests.

The air temperature during the test period ranged from 2.8 to -7.4 °C. The water temperature during each test was constant and the average water temperatures for the 14 experiments ranged between -0.4 to -1.8 °C. With the exception of one test, the estimated average oil thickness for the oil slicks were very close to the 1 mm design thickness. Only test 2, that used light Northstar crude, had a significantly different thickness of about 0.75 mm.

It was clear from visual observations which tests resulted in significant dispersion of oil and which did not. Additional efforts were also undertaken to characterize the dispersion in each test. A quantitative estimate of the amount of oil dispersed was made by comparing the oil collected from the surface at the end of the test to the amount initially spilled. In-water oil concentrations were measured using two flow-through fluorometers and the analysis of oil content from water samples taken during each test. The oil droplet size distributions were also measured during each test. Discussions of these efforts and the results are provided below.

| Oil | % Evap. By Weight | Average Air Temp °C | Average Water Temp °C | Oil Volume Spilled (liters) | Approx. Oil Thickness (mm) | DOR | % Oil Recovered from Surface | Max. Dispersant Effectiveness (%) | Links to Video Segments | Test # |
|-----------------|----------------------------|------------------------------|--------------------------------|--------------------------------------|-------------------------------------|-----|---------------------------------------|--|---|-----------|
| ANS | 17 | -3.1 | -0.6 | 107 | 0.92 | 24 | 15 | 85 | <u>1R1.mpg, 2R1.mpg, 3R1.mpg</u> | 1 |
| ANS | 17 | -1.7 | -0.4 | 1001 | 0.97 | 25 | 14 | 86 | <u>1R9.mpg, 2R9.mpg, 3R9.mpg,</u> <u>4R9.mpg, 5R9.mpg, 6R9.mpg</u> | 9 |
| Endicott | 0 | -2.1 | -0.4 | 113 | 1.1 | 31 | 26 | 74 | <u>1R8.mpg, 2R8.mpg, 3R8.mpg, 4R8.mpg, 5R8.mpg, 6R8.mpg</u> | 8 |
| Endicott | 11 | -1.9 | -0.6 | 94 | 0.91 | 22 | 97 | 3 | <u>1R14.mpg, 2R14.mpg,</u> <u>3R14.mpg, 4R14.mpg</u> | 14 |
| Northstar | 0 | -4.4 | -0.4 | 78 | 0.75 | 18 | 0 | ~100 | <u>1R2.mpg, 2R2.mpg, 3R2.mpg</u> | 2 |
| Northstar | 29 | -7.4 | -0.7 | 105 | 1.1 | 19 | 92 | 8 | <u>1R10.mpg, 2R10.mpg,</u> <u>3R10.mpg</u> | 10 |
| MGS | 0 | -6.1 | -0.5 | 98 | 0.95 | 24 | 18 | 82 | <u>1R11.mpg, 2R11.mpg,</u> <u>3R11.mpg, 4R11.mpg,</u> <u>5R11.mpg</u> | 11 |
| MGS | 20 | -5.3 | -1.1 | 105 | 0.90 | 27 | 20 | 80 | <u>1R3.mpg</u> , <u>2R3.mpg</u> , <u>3R3.mpg</u> , <u>4R3.mpg</u> , <u>5R3.mpg</u> | 3 |
| Pt. McIntyre | 0 | -5.6 | -0.5 | 103 | 1.0 | 29 | 23 | 77 | <u>1R12.mpg</u> , <u>2R12.mpg</u> , <u>3R12.mpg</u> , <u>4R12.mpg</u> , <u>5R12.mpg</u> , <u>6R12.mpg</u> | 12 |
| Cantual | | | | | | | | | | |
| Tests | | | | | | | | | | |
| ANS | 0 | -4.3 | -1.0 | 96 | 0.93 | 0 | 69 ^a | - | <u>1R4.mpg</u> , <u>2R4.mpg</u> , <u>3R4.mpg</u> , <u>4R4.mpg</u> | 4 |
| ANS | 0 | -1.4 | -0.9 | 108 | 1.1 | 0 | 97 | - | <u>1R7.mpg</u> , <u>2R7.mpg</u> , <u>3R7.mpg</u> , <u>4R7.mpg</u> , <u>5R7.mpg</u> | 7 |
| Endicott | 0 | 2.8 | -1.0 | 103 | 1.0 | 0 | 84 | - | <u>1R6.mpg</u> , <u>2R6.mpg</u> , <u>3R6.mpg</u> , <u>4R6.mpg</u> , <u>5R6.mpg</u> | 6 |
| Northstar | 0 | -3.6 | -1.8 | 103 | 1.0 | 0 | 93 | - | <u>1R5.mpg</u> , <u>2R5.mpg</u> | 5 |
| Pt. McIntyre | 0 | -3.7 | -0.8 | 104 | 1.0 | 0 | 58 | - | <u>1R13.mpg, 2R13.mpg,</u> <u>3R13.mpg, 4R13.mpg,</u> <u>5R13.mpg</u> | 13 |

Table 3. Cold Water Dispersant Effectiveness Test Results Summary

^a This control test was completed with only a single end containment barrier. All other control tests had a double boom in place at the north end of the tank to improve oil containment.

4.2.1 Oil Residue Volumes and Properties

For those tests where quantities allowed (all but test #2), the crude oil remaining in the containment boom at the end of the test was collected for volume, water content, and density (of parent oil, not oil and water mixture) measurement. Table 4 summarizes these data as well as the initial oil characteristics.

As would be expected, the densities of the crude oils generally increased over the duration of the tests. Of primary interest is the density of the oils for the control tests and the inefficient dispersant tests where, in both cases, significant quantities of oil were recovered at the end of the

test period. This oil was subjected to weathering processes over the full one-hour test period and therefore would have had an opportunity to lose significant volume through evaporation. The density measurements have been used, in concert with evaporation-density curves for the oils, to estimate the likely loss of oil through evaporation for the control and poor dispersion tests. This has then been added to the estimate of the volume of oil collected on the surface to provide an approximate accounting of the oil spilled in each test. The same type of calculation cannot be made for the tests where significant dispersion did occur.

| Pre-T Prop | Fest O pertie | Dil s | Post Test Oil Volumes and Properties | | | | | | | | |
|----------------------|------------------|---|--|--------------------------------------|----------------------------|--------------------|--|-----------------------------------|--|-----------|--|
| Oil Type | % Evap. | Density @ 25 °C (kg/m ³) | Vol of Emul. Recovered (liters) | Water Content of Emul. % | Vol. of Oil (liters) | % Oil Recovered | Parent Oil Density @ 25 °C (kg/m ³) | Estimated Additional % Evap | Oil Recovered + Evaporated % | Test # | |
| ANS | 17 | 912 | 31.6 | 48 | 16.4 | 15 | 922 | na | 15 | 1 | |
| ANS | 17 | 912 | 15.5 | 8 | 14.3 | 14 | 933 | na | 14 | 9 | |
| Endicott | 0 | 878 | 31.4 | 8 | 28.9 | 26 | 949 | na | 26 | 8 | |
| Endicott | 11 | 914 | 107 | 15 | 91 | 97 | 912 | 0 | 97 | 14 | |
| Northstar | 0 | 812 | 0 | - | 0 | 0 | - | na | 0 | 2 | |
| Northstar | 29 | 864 | 120.7 | 20 | 96.6 | 92 | 874 | 6 | 98 | 10 | |
| MGS | 0 | 856 | 19 | 9 | 15.4 | 18 | 899 | na | 18 | 11 | |
| MGS | 20 | 914 | 31.4 | 35 | 20.4 | 20 | 907 | na | 20 | 3 | |
| Pt. McIntyre | 0 | 890 | 25.1 | 5 | 23.8 | 23 | 932 | na | 23 | 12 | |
| | | | | | | | | | | | |
| Control Tests | | | | | | | | | | | |
| ANS | 0 | 873 | 101.5 | 35 | 66.0 | 69 | 899 | 12 | 81 | 4 | |
| ANS | 0 | 873 | 107.7 | 2.8 | 104.6 | 97 | 882 | 5 | 102 | 7 | |
| Endicott | 0 | 878 | 140.5 | 38 | 87.1 | 84 | 903 | 4 | 88 | 6 | |
| Northstar | 0 | 812 | 159.5 | 40 | 95.7 | 93 | 861 | 27 | 120 | 5 | |
| Pt. McIntyre | 0 | 890 | 65.2 | 7.2 | 60.5 | 58 | 918 | 20 | 78 | 13 | |

Table 4. Oil Residue Volumes and Properties at End of Tests

na - not known as considerable quantities of fresh oil dispersed early in the test.

In test 14 (11% weathered Endicott), the oil density remained virtually constant over the test period (913 kg/m³ and 914 kg/m³) indicating that the pre-evaporated oil did not evaporate further during the test. About 97% of the spilled oil was recovered from the surface at the end of the test.

The density of the recovered oil for test #10 (29% weathered Northstar) indicates that the oil evaporated an additional 6% from its start point. A total of 98% of the oil in this test is accounted for through collection of residue and evaporation estimates.

In the first ANS crude oil control test (#4), the density increased from a fresh oil value of 873 kg/m³ to 899 kg/m³. This would suggest that about 12% of the oil was lost through evaporation over the test period. Over 80% of the spilled oil in this test can be accounted for by adding the evaporated amount to the amount of oil recovered (12% + 69%). In the second ANS control test (#7), the density of the collected oil (882 kg/m^3) indicates an evaporative loss of about 5%. The total volume of emulsion collected and the measured water content of the emulsion accounts for 97% of the oil spilled. Slightly over 100% of the oil (102%) of the oil is "accounted for" when these two numbers are summed.

In the Endicott control test (#6), the density increased from 883 kg/m³ to 903 kg/m³, suggesting an evaporative loss of about 4%. When this is added to the estimate of the collected oil 88% of the total quantity of the spilled oil is accounted for.

The oil residue data collected for the Northstar control test (#5) are problematic. The volume of emulsion collected and water content measurement suggests that 93% of the spilled oil was collected at the end of the test. However, the 861 kg/m³ density recorded for the collected oil from this test would suggest that the Northstar oil evaporated by about 27%. This is based on the extrapolation of the available evaporation/density curve for Northstar. It would appear that the estimate of collected oil volume is high for this test since significant evaporation (20 to 30%) would be expected for this relatively light oil.

The density for the Pt. McIntyre control test (#13) increased from 890 to 918 kg/m³, suggesting approximately 20% loss due to evaporation. About 60 % of the oil was recovered from the surface at the end of the test resulting in an accounting for about 80% of the spilled oil.

When the collected oil amounts and evaporation estimates are combined a mass balance accuracy of approximately $\pm 20\%$ was achieved in the control and ineffective dispersant tests (tests 4, 5, 6, 7, 10, 13, 14).

4.2.2 Dispersant Effectiveness Estimates

A numerical estimate of the dispersant effectiveness (DE) was made for all tests. After each test the oil remaining in the containment area was collected and its volume determined. The collected volume was compared to the quantity of oil discharged in the test to determine the maximum possible dispersion efficiency (DE) of the test. Loss of oil through evaporation was not accounted for when determining the maximum DE values. In the chemically treated tests the oil disperses within about 10 minutes after the application of dispersants and wave energy. Only a small amount of oil could evaporate during this short time frame, especially for the oils that were pre-evaporated prior to the test. The maximum DE values for the test conditions studied are reported in Table 3. Effectiveness values ranging from 3 to 100% were recorded.

With the exception of tests 10 (evaporated Northstar) and 14 (evaporated Endicott), all of the chemically dispersed tests resulted in high percentages (75 to \sim 100%) of oil dispersing into the water column. The effectiveness trends identified in the smaller scale testing were mirrored in the large-scale test results. The heavily evaporated Northstar crude and evaporated Endicott crude were resistant to chemical dispersion in both the small-scale and Ohmsett tests. A higher percentage of the fresh Endicott crude oil was dispersed in the Ohmsett tests when compared to the small-scale results (74% vs 20 to 30%). This may be due to additional mixing energy in the Ohmsett tests, in the form of breaking waves that do not develop in the small tank tests.

Only test 2 (fresh Northstar) yielded dispersant effectiveness estimates above 90%. The initial Northstar crude oil slick was thinner (due to lighter oil characteristics and spreading tendency) than the other oils and thus received a somewhat higher estimated dispersant dosage. The lighter oil characteristics and higher dispersant dosage may account for the complete dispersion and the absence of visible oil on the water surface at the end of this test.

The significant dispersion present in many of the tests was observed by those who attended the tests and is extensively documented in the video clips provided for each of the tests. These can be viewed by clicking on the hot links in Table 3.

4.2.3 Control Test Results

The percentages of oil recovered from the surface at the end of each control test (no dispersant applied) are presented at the bottom of Table 4. A small, undetermined amount of oil splashed over the north-end containment boom in the first control test (#4). No oil loss over the end containment was seen in the first three dispersant applied tests (tests #1, #2 & #3) as most of the oil dispersed within minutes of the application of dispersant. After test #4, a second end barrier was installed approximately ten feet south and parallel to the original barrier. It was hoped that this boom would dampen the occasional waves that were splashing oil over the north containment zone and provide a secondary collection area, between the two end booms, for any oil that was splashed over the interior boom. The addition of the second boom appeared to provide the desired result, as loss of oil over the second boom was not observed in the remaining tests.

Between 78 to 120% of the oil discharged in the control tests was either recovered from the surface at the end of the test or accounted for by evaporation estimates. The "over-accounting" of oil for test #5 is likely due to errors in estimating the volume of collected oil, possibly due to poor decanting or an unrepresentative sample used in the water content determination. The evaporation estimate for test #5 seems reasonable for this light oil.

While the control tests did not provide a perfect accounting of the oil released in each test, the results indicate that the test set up and procedure consistently accounts for at least 80% of the released oil. For the chemically treated spills where the dispersant was seen to be effective, between 74 to 100% of the released oil was not recovered at the end of the test. Even if 20% of this oil loss were deemed attributable to experimental error (poor control etc) the dispersant would still have been between 54 and 80% effective in all but the heavily weathered oil tests.

4.2.4 Dispersed Oil Concentration Measurements

Water samples were pumped from one and two meter depths for hydrocarbon concentration measurement. Continuous, flow-through fluorometer measurements and dispersed oil particle

size distributions also were measured in all tests. The results of these activities assist in confirming the presence or absence of dispersed oil in the water column during each test and help to characterize the dispersed oil.

The raw fluorescence data collected by the Turner fluorometers for each test were first adjusted based on the calibration curve developed for the oil used in the testing. (The ability to properly calibrate the flourometers to measure absolute concentrations of oil droplets in the water is discussed below.) The data for each run was then normalized such that the lowest concentration value recorded (background) was subtracted from the remaining reading. The fluorometer concentrations presented in this report are relative to the background concentration and to standards prepared with unknown oil drop size distributions. For most tests (Runs 5 through 14) the 1 and 2-meter deep fluorometers were operated during the oil discharge and on two or three other passes through the containment zone at approximately 10 to 15 minute intervals. Less data was collected for runs 1 through 3 because only one fluorometer was in operation during these tests. The oil concentration data from all runs has been plotted as a function of the approximate distance from the north containment boom. The oil slick and dispersed oil cloud generally moved from the south to the north during the test duration. These oil concentration plots are provided in Appendix E and can be accessed through the hyperlinks provided in Table 5.

A general trend is evident in all of these plots. The oil concentration measurements taken at the one meter depth were the highest measured and the most variable, especially on the first pass. The concentrations at 1-meter depth tended to drop and stabilize on subsequent passes, presumably due to the diffusion of the dispersed oil cloud and/or the rise of larger oil drops to the surface. The concentrations measured at the 2-meter depth were generally lowest on the initial pass and often increased on subsequent passes. These results suggest an initial dispersion of oil in the upper water layer with a gradual diffusion of the cloud to depth.

Columns 7 and 9 in Table 5 show the maximum oil concentration measured by the fluorometers in each of the runs. These highest concentrations were generally recorded at the 1-meter level on the first pass of the fluorometers following the oil discharge. The first pass following the oil discharge occurred about 15 minutes after the onset of wave action. In the tests where the DE was high (>70%) the oil concentrations measured were also high (20 to 300 ppm above

background levels). In test 10 where the DE was low (8%), the maximum oil concentrations measured were 4 ppm at the 1-meter level and only 0.5 ppm at the 2-meter level. These low concentration values are consistent with the control run measurements shown at the bottom of Table 5. The results of test 14, the other poor dispersion test (only 3% DE), are puzzling. The fluorometers detected significant amounts of oil at both the 1 and 2-meter depths over the course of the test even though a poor overall dispersion was recorded.

| Oil | % Evap. By Weight | Oil Volume Spilled (liters) | DOR | 1m Depth Fluorometry Links | Maximum ¹ Conc. At 1 m Depth (ppmv) | 2 m Depth Fluorometry Links | Maximum ¹ Conc. At 2 m Depth (ppmv) | Test # |
|----------------------|----------------------------|--------------------------------------|-----|----------------------------------|---|-----------------------------------|---|-----------|
| ANS | 17 | 107 | 24 | Not recorded | - | <u>Run 1 - 2m</u> | 304 | 1 |
| ANS | 17 | 101 | 25 | <u>run 9 - 1m</u> | 55 | <u>run 9 - 2m</u> | 8 | 9 |
| Endicott | 0 | 113 | 31 | <u>run 8 - 1m</u> | 38 | <u>run 8 - 2m</u> | 12 | 8 |
| Endicott | 11 | 94 | 22 | <u>run 14 - 1m</u> | 45 | <u>run 14 - 2m</u> | 6 | 14 |
| Northstar | 0 | 78 | 18 | <u>run 2 - 1 & 2 m</u> | 65 | <u>run 2 - 1 & 2 m</u> | 45 | 2 |
| Northstar | 29 | 105 | 19 | <u>run 10 - 1m</u> | 4 | <u>run 10 - 2m</u> | 0.5 | 10 |
| MGS | 0 | 98 | 24 | <u>run 11 - 1m</u> | 45 | <u>run 11 - 2m</u> | 14 | 11 |
| MGS | 20 | 105 | 27 | <u>run3 - 1 m</u> | 18 | Not recorded | - | 3 |
| Pt. McIntyre | 0 | 103 | 29 | <u>run 12 - 1m</u> | 35 | <u>run 12 - 2m</u> | 13 | 12 |
| | | | | | | | | |
| Control Tests | | | | | | | | |
| ANS | 0 | 96 | 0 | <u>run 4 - 1 m</u> | 9 | <u>run 4 - 2 m</u> | 0.8 | 4 |
| ANS | 0 | 108 | 0 | <u>run 7 - 1m</u> | 0.9 | <u>run 7 - 2m</u> | 0.5 | 7 |
| Endicott | 0 | 103 | 0 | <u>run 6 - 1m</u> | 0.8 | <u>run 6 - 2m</u> | 0.2 | 6 |
| Northstar | 0 | 103 | 0 | <u>run 5 - 1m</u> | 2.5 | <u>run 5 - 2m</u> | 2.5 | 5 |
| Pt. McIntyre | 0 | 104 | 0 | <u>run 13 - 1m</u> | 1.8 | <u>run 13 - 2m</u> | 3.2 | 13 |

Table 5. Hyperlinks to Fluorometry Data Plots

¹ Concentrations reported here are likely low by a factor of 3 to 4 based on IR analysis of water grab samples.

Water samples were also taken during the tests as backup and verification of the fluorometer measurements. The fluorometer reading was recorded just prior to taking the water samples that were taken from the same flow lines that fed the fluorometers. The concentration of oil in each water sample was determined using extraction and IR spectrophotometry. Comparisons of the oil concentration measurements by fluorometry and by IR analysis are shown in Table 6 and Figure 11. As seen in Table 6, the concentration results from the water sample analyses do not closely match the fluorometer results. When the two data sets are linearly correlated (see Figure 11) it is evident that the concentration estimates by the fluorometer are about 4 to 5 times lower than the IR determined values. While there is considerable scatter in the data, especially for the 1 m depth, it is fairly obvious that the fluorometers show consistently lower concentrations than the IR analysis. A similar discrepancy between fluorometer readings and TPH concentration from IR

analyses of water samples was reported in a Dutch field trial (Delvigne 1983). In the Dutch field trial, fluorometry readings ranged from 0.1 to 2 ppm while TPH by IR analyses ranged from 1 to 100 ppm. One possible explanation for this discrepancy might be the way the calibration curve is established for the fluorometer. If the drop size distribution in the calibration standard is much finer than the oil drop distribution found in the field then the fluorometer could read higher fluorescence in the standard than for a similar oil concentration (but with larger drop sizes) in the field. Subsequent estimates of concentration in the field setting would then be lower than that identified with the calibration curve. Oil concentration measurements using solvent extraction and IR analysis would not be affected by the oil drop size distribution in the sample. It is quite likely that the oil concentration in the water. However, the fluorometer readings reported and the plots in Appendix E do provide valid records of the relative amounts of oil in the water column both spatially within the tank and over time.

| | % | Max. Dispersant Effectiveness t (%) | One] | Meter Depth | Two Meter Depth | | |
|--------------|-----------------------|--|-----------------------------|--|-----------------------------|--|----|
| Oil | Evap. By Weight | | TPH by IR Spec. (ppm) | Oil Concentration by Fluorometry (ppm) | TPH by IR Spec. (ppm) | Oil Concentration by Fluorometry (ppm) | # |
| Pre-Test | - | - | 4.1 | 1.5 | - | - | |
| ANS | 17 | 85 | - | - | - | - | 1 |
| ANS | 17 | 86 | 79.5 | 15 | 55.0 | 12 | 9 |
| Endicott | 0 | 74 | 72.7 | 11.7 | 31.9 | 7.0 | 8 |
| Endicott | 11 | 3 | 72.8 | 24.5 | 21.2 | 4.9 | 14 |
| Northstar | 0 | ~100 | - | - | - | - | 2 |
| Northstar | 29 | 8 | 15.6 | 7.3 | 11.0 | 0.4 | 10 |
| MGS | 0 | 82 | 21.8 | 13 | 10.2 | 2.5 | 11 |
| MGS | 20 | 80 | - | - | - | - | 3 |
| Pt. McIntyre | 0 | 77 | 78.0 | 21 | 64.6 | 5.5 | 12 |
| | | | | | | | |
| Control | | % Oil | | | | | |
| Tests | | Recovered | | | | | |
| ANS | 0 | 69 | 10.9 | 4.5 | 7.3 | 0.0 | 4 |
| ANS | 0 | 97 | 23.8 | 0.1 | 6.2 | 0.01 | 7 |
| Endicott | 0 | 84 | 2.4 | 0.4 | 2.7 | 0.0 | 6 |
| Northstar | 0 | 93 | 6.7 | 0.0 | 7.9 | 0.0 | 5 |
| Pt. McIntyre | 0 | 58 | 8.4 | 1.2 | 9.2 | 1.1 | 13 |

Table 6: Comparison of TPH by IR Spectrophotometry vs Fluorometry

Note: valid water samples were not collected for runs 1 through 3.



Figure 11. Comparison of Oil-in-Water Concentration Measurements

Increased fluorescence with a decrease in drop size may have been demonstrated in a series of tests completed by Environment Canada (Lambert 2001). In these tests dispersed oil and water containing dispersant was re-circulated by pump from a reservoir through a fluorometer over a period of several hours. The fluorescence increased by a factor of between 3 to 4.5 in these tests with no change in oil quantity in the closed system. One possible explanation for the increase in fluorescence, with the same total quantity of oil, is that the oil drops were sheared by the pumping process to smaller and smaller diameters thus increasing the effective surface area that could fluoresce (Lambert 2003, pers comm). Drop sizes were not measure so this cannot be confirmed.

4.2.5 Oil Drop Size Distributions

Particle size distributions were collected during the runs, using the Lisst particle size analyzer discussed earlier. Interpretation of the results was complicated by the presence of background particles of oil from earlier tests, sediments from the tank bottom and other materials that may have entered the water through the air or other means. Initial readings in the tank prior to any

addition of oil or tank agitation indicated that there was some material in the tank with a mean diameter of about 300 microns. We have speculated that this background is due to a spore from the marsh grasses that are extensive next to the Ohmsett facility. The particle size distribution detected in these background measurements can be seen by accessing the following link (background contaminant particle distribution). Further complicating the interpretation of the drop size data is the fact that this specific background signature did not persist during the test period. This seems to indicate that the material was removed from the tank during the initial dispersion tests, possibly by adhesion to dispersed oil drops that then rose to the surface when the wave energy was stopped.

To account for background contaminants in the water prior to each test, the particle size data collected for each test was processed, as follows. A number of representative background particle size distributions (20 to 30 samples) were selected from the beginning of each dataset. The selected distributions were averaged for each drop size range captured by the LISST system. The average values from each concentration range was then subtracted from the remaining particle size distributions collected in the run to remove the background signal from the data. The adjusted data sets that contained significant quantities of oil particles (concentrations identified by the LISST device to be significantly above the background signal) were then analyzed to determine an average value for the volume percent of particles less than 75 microns in diameter, less than 100 microns in diameter, less than 200 microns in diameter and greater than 200 microns in diameter. This data is provided in Table 7.

The drop diameter cutoffs in Table 7 (75 and 100 microns) were selected because other researchers have specified these values as the maximum drop size that could be considered permanently dispersed in an ocean environment (75 micron, Lunel 1993 and 100 micron, Neff 1990). In the dispersant cases, 58 to 86% (average of all tests was 78%) of the oil was present in drops less than 100 microns in diameter. Approximately 70% (average) of the oil was in drops of 75 microns or less.

The average amount of oil in the control tests in drops less than 100 microns in diameter was about 32%. The volume percent of oil in drops less than 75 microns in diameter was about 24%.

| | | % Oil | Max. | Averag | ge Particle I | Diameter St | atistics |
|----------------------|------|-----------|------------|----------|---------------|-------------|----------|
| Oil | Test | Recovered | Dispersant | (Vol | ume % in I | Diameter Ra | nge) |
| | # | From | Effect. | Volume % | Volume % | Volume % | Volume % |
| | | Surface | (%) | < 75µm | < 100µm | < 200 µm | > 200 µm |
| Evaporated ANS | 1 | 15 | 85 | 70 | 81 | 92 | 8 |
| Evaporated ANS | 9 | 16 | 86 | 81 | 86 | 91 | 9 |
| Fresh Endicott | 8 | 36 | 74 | 54 | 58 | 62 | 38 |
| Weathered Endicott | 14 | 97 | 3 | 72 | 82 | 90 | 10 |
| Fresh Northstar | 2 | 0 | ~100 | 70 | 81 | 93 | 7 |
| Evaporated Northstar | 10 | 92 | 8 | 65 | 73 | 83 | 17 |
| Fresh MGS | 11 | 18 | 82 | 75 | 81 | 87 | 13 |
| Evaporated MGS | 3 | 20 | 80 | 62 | 78 | 91 | 9 |
| Fresh Pt. McIntyre | 12 | 23 | 77 | 79 | 86 | 91 | 9 |
| Control Tests | | | | | | | |
| Fresh ANS | 4 | 69 | - | 49 | 57 | 64 | 34 |
| Fresh ANS | 7 | 97 | - | <1 | <2 | 6 | 94 |
| Fresh Endicott | 6 | 84 | - | 12 | 17 | 33 | 67 |
| Fresh Northstar | 5 | 93 | - | 32 | 46 | 74 | 26 |
| Fresh Pt. McIntyre | 13 | 58 | - | 27 | 39 | 58 | 42 |

Table 7. Drop Size Distribution Analysis (data recorded at 2 meter depth)

The drop size distributions measured for the dispersant tests revealed a higher percentage of oil in the smaller drop ranges when compared to the control tests. 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. The measured drop size distributions also suggest that a high percentage (70 to 80% minimum) of the oil mixed into the tank in the dispersant applied cases would remain dispersed under typical ocean mixing conditions.

The results from test 14 indicate a low dispersant effectiveness but a high percentage of the measured oil in the form of small drops. This may be due to a small amount of oil being affected by the dispersant and subsequently being detected by the LISST sensor.

All of the particle size distributions collected during the test program have been provided with the CD version of this report along with a copy of the software needed to view the distributions. These files can be found in the LISST directory on the CD. Run the Lisst.exe program and select the "Open Particle Distribution File" menu item in the main File option of the program menu. Select one of the *.psd files to view the measured particle distributions. The *.asc files provided in the LISST directory are ASCII file formats of the same data in the raw data format described in the <u>List Specifications</u> in Appendix C.

4.2.6 Environmental Conditions

The Ohmsett tank water temperature stayed between -0.4 to -1.8 °C throughout all of the experiments without the need to use artificial chilling. This was due to the unusually cold weather experienced during the test period. Air temperatures ranged from 2.8 to -7.4 °C. Detailed weather data sheets, daily test logs and bridge operator logs can be found in MAR Inc.'s test data binder prepared for the project.

Wave amplitude and period measurements were made during each test. Considerable noise is present in this data so short sections of the records were analyzed for average wave amplitude and period and the results are shown in Table 8. The average wave amplitude for the tests ranged between 5.9 and 8.6 inches and the average period was between 1.8 and 2.2 seconds.

| T4 | Measured Wave Characteristics: Cold Water Tests | | | | | | | | | | |
|---------------------|---|----------|------------|---------|--|--|--|--|--|--|--|
| l est Idontifion | Amplitude | (inches) | Period (s) | | | | | | | | |
| Identifier | Average | Std Dev | Average | Std Dev | | | | | | | |
| 1 | 5.9 | 3.0 | 2.1 | 0.33 | | | | | | | |
| 2 | 8.6 | 3.0 | 2.1 | 0.23 | | | | | | | |
| 3 | 6.6 | 3.3 | 2.0 | 0.25 | | | | | | | |
| 4 | 6.4 | 3.1 | 2.1 | 0.22 | | | | | | | |
| 5 | 7.6 | 3.1 | 2.2 | 0.23 | | | | | | | |
| 6 | 7.2 | 2.9 | 2.0 | 0.21 | | | | | | | |
| 7 | 7.4 | 3.4 | 2.1 | 0.23 | | | | | | | |
| 8 | 7.6 | 2.6 | 2.2 | 0.21 | | | | | | | |
| 9 | 7.0 | 3.7 | 2.1 | 0.27 | | | | | | | |
| 10 | 7.8 | 3.6 | 2.2 | 0.21 | | | | | | | |
| 11 | 8.3 | 1.9 | 1.8 | .014 | | | | | | | |
| 12 | 7.5 | 3.3 | 2.1 | 0.15 | | | | | | | |
| 13 | 7.5 | 3.7 | 2.1 | 0.22 | | | | | | | |
| 14 | 6.5 | 2.7 | 2.1 | 0.23 | | | | | | | |

Table 8: Measured Average Wave Amplitudes and Periods
5. Summary of Experimental Results

Preliminary experiments completed in a small wave tank demonstrated that Corexit 9500 and Corexit 9527 give similar dispersion effectiveness on all of the crude oils tested. This led to the use of only Corexit 9527 for the large tank tests at Ohmsett. Corexit 9527 was selected because it is the primary dispersant currently stockpiled in Alaska. The small-scale experiments also provided an indication of the Dispersant-to-Oil Ratios (DORs) needed to effect dispersion for each of the oil types at the low test temperatures (~0°C). The DORs ranged from lows of 1:50 to as high as 1:10 for the heavier and evaporated oils.

In the large-scale tests in the Ohmsett facility it was clear from visual observations which experiments resulted in a significant dispersion of oil and which did not. Verification of this was accomplished using several methods. A numerical estimate of the dispersant effectiveness (DE) was made for all tests. After each test the oil remaining in the containment area was collected and its volume determined. The collected volume was compared to the quantity of oil discharged in the test to determine the maximum possible dispersion efficiency (DE) of the test. In-water oil concentration measurements were made using two flow-through fluorometers and analysis of water samples using IR spectrophotometry. Oil drop size distributions were also recorded using a laser particle size analyzer.

The chemically dispersed runs resulted in high percentages (75 to ~100%) of oil dispersing into the water column, with the exception of tests 10 (evaporated Northstar) and 14 (evaporated Endicott). The DE trends identified in the smaller scale testing were mirrored in the large-scale test results. The heavily evaporated Northstar and evaporated Endicott crude oils were resistant to chemical dispersion in both the small-scale and Ohmsett tests. A higher percentage of the fresh Endicott crude oil was dispersed in the Ohmsett tests when compared to the small-scale results (74% vs 20 to 30%). This may be due to additional mixing energy present in the Ohmsett tests, in the form of breaking waves that do not develop in the small tank tests.

Test 2 (fresh Northstar), was the only test where no visible oil was present on the surface at the end of the test. The initial Northstar crude oil slick was thinner (due to lighter oil characteristics and faster spreading tendency) than the other oils and thus received a somewhat higher

dispersant dosage. The lighter oil characteristics and higher dispersant dosage may account for the complete dispersion and the absence of visible oil on the water surface at the end of this test.

The oil concentration measurements taken at the one meter depth were the largest measured and the most variable in all of the tests, especially on the first pass. The concentrations at 1-meter depth tended to drop and stabilize on subsequent passes, presumably due to the diffusion of the dispersed oil cloud and/or the rise of larger oil drops to the surface. The concentrations measured at the 2-meter depth were generally lowest on the initial pass and often increased on subsequent passes. These results suggest an initial dispersion of oil in the upper water layer with a gradual diffusion of the cloud to depth. It was found that the oil concentration estimates made using the flow-through fluorometers were generally 4 to 5 times lower than the concentration estimates made using IR spectrophotometry. However, the relative concentration over time and space.

Particulate matter in the water column was measured at the 2-meter depth using a laser particle size analyzer. The data was adjusted to account for the presence of background particles prior to each test. The adjusted data sets that contained significant quantities of oil particles (concentrations significantly above the background signal) were then analyzed to determine an average value for the volume percent of particles less than 75 microns in diameter, less than 100 microns in diameter and greater than 200 microns in diameter. Previous research has suggested that oil drops less than 75 to 100 microns in diameter will be permanently dispersed in an ocean environment. The drop size distributions measured for the dispersant tests revealed a higher percentage of oil in the smaller drop ranges when compared to the control tests, as would be expected. In the dispersant applied cases, 58 to 86% (average of all tests was 78%) of the oil was present in drops less than 100 microns in diameter. Approximately 70% of the oil was in drops of 75 microns or less. The average amount of oil in the control tests in drops less than 100 microns in diameter was about 32%. The volume percent of oil in drops less than 75 microns in diameter was about 24% for the control tests. The measured drop size distributions also suggest that a high percentage (70 to 80% minimum) of the oil mixed into the tank in the dispersant applied cases would remain dispersed under typical ocean mixing conditions.

The oil remaining in the containment boom at the end of each control test was collected and the total volume, water content and density (of parent oil not oil and water mixture) of the collected emulsions were measured. The parent oil density data were used to estimate the amount of oil that evaporated over the duration of each control test.

A small, undetermined amount of oil splashed over the north-end containment boom in the first control test (test #4). After this test, a second end barrier was installed approximately ten feet south and parallel to the original barrier to improve the oil containment. Loss of oil outside of the second containment barrier was not observed in any of the subsequent tests. Between 80 to 120% of the oil discharged in the control tests was recovered or accounted for through evaporation losses at the end of the test periods. The in-water oil concentration measurements from the fluorometers for all of the control tests also did not show any significant quantities of oil in the water column in these tests.

The water temperature during each test was constant and the average water temperatures for the 14 experiments ranged between -0.4 to -1.8 °C. The Ohmsett tank water remained cold throughout all of the testing without the need to use artificial chilling. This was due to the unusually cold weather experienced during the test period. Air temperatures ranged from 2.8 to -7.4 °C. The average wave amplitude for the tests ranged between 5.9 and 8.6 inches and the average period was between 1.8 and 2.2 seconds.

6. Recommendations

A double north-end containment boom should be used in all future tests to eliminate the loss of surface oil from the containment area by splash over.

The air-actuated valves used to start and stop the oil flow through the discharge piping should be serviced prior to any additional cold-water dispersant effectiveness testing. These valves mal-functioned in the cold weather experienced during the test period.

The effect of oil drop size on the measurement of the fluorescence of oil-in-water dispersions, using the Turner Fluorometers, should be investigated if direct, absolute oil concentration measurements are of interest. Oil-in-water dispersions, used to establish calibration standards for these fluorometers, may require similar oil drop size distributions as would be present in the tank, to enable the devices to accurately measure absolute in-water oil concentrations. Alternatively, the results from the fluorometers should be adjusted based on the results of IR-Spectophotometry measurements of water grab samples taken in conjunction with the fluorometry readings.

The use of continuous flow through fluorometry to monitor in-water oil concentrations and *in situ* laser particle size measurement provided valuable insight into the dispersion process and could be used in future dispersant effectiveness tests when budgets permit.

7. References

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8. Appendix A. SL Ross Dispersant Effectiveness Test Method

8.1 Objective

The objective of the work is to conduct dispersant effectiveness tests with selected crude oils using a large test tank at the SL Ross Laboratory.

Work Statement

The following test parameters or conditions are generally used in the testing.

Test Conditions

- 1. Oil thickness— one thickness: 3mm
- 2. Energy level—non-breaking waves with 15 cm amplitude and 1.5 second period
- 3. Oil type— as determined by client
- 4. Oil weathered state— fresh oil and weathered oil as required by client
- 5. Dispersant type— as specified by client
- 6. Dispersant to Oil Ratio (DOR)— determined by preliminary tests involving oil samples pre-mixed with dispersant to determine the minimum DOR needed to achieve 100% dispersion at above energy level
- 7. Temperature— 0° C to 30° C; as required

8.2 Test Procedure

The SL Ross test tank and the procedure used for dispersant testing is detailed below.

8.2.1 Test Tank

The test involves the SL Ross indoor wave tank. Using this relatively large tank allows the use of full-scale spray nozzles for dispersant application. The test tank is 10 meters long by 1.2 meters wide by 1.2 meters deep and is fitted with a wave generating paddle at one end and a wave dissipating beach at the other. Tests usually involve filling the tank with 32 ppt salt water to a depth of 85 cm. Two 12 volt, sealed beam, automotive headlights are mounted at the bottom of the tank and their beams directed up to the water surface to improve the visibility of the surface oil slicks. A photo of the test tank is shown in Figure 1.



Figure 1. Test Tank

8.2.2 Oil Containment

Oil is held in a 1.0 m by 0.75 m rectangular area in the middle of the tank using an air bubble curtain constructed from $\frac{1}{2}$ inch copper pipe, as seen elevated above the water surface in Figure 2. The rising air bubbles from this submerged diffuser system entrain water as they rise which in turn creates an inflow of water at the surface above the rectangular barrier. This inflow herds the oil to the center of the area above the rectangular diffuser. The oil remains within this confinement zone even when waves are introduced.



Figure 2: Air Bubble Barrier Piping

8.2.3 Dispersant Application System

Dispersant is applied using an overhead spray boom mounted to the ceiling above the center of the test tank. Over-spray from the boom is collected by plastic sheeting that extended from the ceiling to short lengths of eaves trough that were suspended just below the arc of the spray nozzles. The boom is counter-weighted and powered using a rope and pulley system. On the end of one rope is a weight that holds the boom in its start position. The other rope is attached to a "take-up" spool driven by a variable speed electric motor and clutch mechanism. The motor speed is set to achieve the required boom speed and allowed to run up to speed. Then, the clutch is engaged to pull the boom through its arc over the center of the tank to apply the dispersant. The overhead boom, plastic sheeting and rope-pulley system are shown in Figure 3.



Figure 3. Dispersant Spray Boom

The dispersant is applied through Spraying System Company flat-fan nozzles. These are the same type of nozzles used in full-scale, vessel-based dispersant application systems. The dispersant is held in a small stainless steel pressure vessel connected to another tank that is charged with air to the pressure required for the spray application (40 to 80 psi). An electrically controlled valve is mounted at the outlet of the dispersant supply tank to start and stop the dispersant supply to the spray nozzles. A photo of the dispersant delivery system is shown in Figure 4. The spray is turned on and allowed to stabilize for a few seconds and then the boom take-up spool is started to cause the boom, and spray nozzles, to pass over the test slick. The spray nozzles release the dispersant from a height of about 1.8 meters above the oil slick. The plastic sheeting and eaves trough capture the excess spray at either end of the boom travel to minimize dispersant over-spray.

An estimate of the spray boom speed needed to achieve proper slick dosing for a given oil thickness, design dosage, nozzle type and flow pressure is made prior to each test. These

approximate speed estimates are adjusted on the basis of the results of the "cookie tray" measurements (see below), to achieve the proper final spray quantity.



Figure 4. Dispersant Spray Pressure Tanks and Valve

The amount of dispersant applied per unit area of surface is measured for each test by collecting the spray in a "cookie" tray suspended just above the water surface at one edge of the oil containment zone as seen in Figure 5. The tray is weighed before and immediately after the application to determine the quantity of dispersant applied.



Figure 5. Dispersant Measuring Tray

8.2.4 Preliminary Test System "Calibration"

Appropriate dispersant dosages for the dispersants being tested are determined prior to the start of the spray application tests. Small volumes of the oil to be tested are pre-mixed with various quantities of dispersant to identify suitable dispersant dosages. These samples are placed in the test tank and the resulting dispersion efficiencies observed when subjected to wave energy. From past experience it is known that the amount of dispersant required to achieve full dispersion when pre-mixed with oil is usually much less than the recommended field dosage. For this reason dosages of 1:50, 1:75 and 1:100 are generally used in this assessment. Visual observations are used to identify the minimum dispersant dosage required to achieve full dispersion. This minimum dosage becomes the starting point for the spray application tests.

The system powering the spray boom's movement is also calibrated prior to starting the final test

matrix. The variable speed motor is run at different speeds and the boom's speed calculated for each setting. This then allows an estimate of the motor's speed setting to be made for each test, given the oil thickness being treated, the dispersant amount required, and the flow rate of the nozzles being used in the testing.

The final estimate of dispersant effectiveness for each test is made by sorbing the oil left in the containment area at the end of the test and comparing the amount sorbed with the amount used in the test. To remove water sorbed with the oil the sorbents are left to drip-dry overnight and weighed the next day. To correct for evaporation loss, both during the time the oil is on the water surface and while drying overnight, a quantity of oil (about 1.0 liter) is placed on the tank in the containment area and allowed to "weather" for 30 minutes (duration of all tests). This oil is then sorbed from the surface and allowed to drip-dry. The weight of the sorbents and oil is measured after 24 hours to determine the approximate amount of oil loss through evaporation when this test protocol is followed.

8.2.5 Test Method

The key elements of the test method or procedures can be summarized as follows.

- 5. The dispersant spray apparatus are prepared by fitting the appropriate nozzles to the spray boom, putting the selected dispersant in the application pressure vessel, adjusting the air pressure used to drive the dispersant boom and setting the boom drive motor to the appropriate speed.
- 6. The underwater lights, dispersant measurement tray, video camera and air bubble barrier are started or put in place.
- 7. The oil is placed within the containment zone, the dispersant applied, the dispersant measurement tray removed and weighed and the wave paddle started.
- 8. After 30 minutes the wave paddle is stopped and the oil remaining in the containment zone is sorbed to estimate the dispersion efficiency.

9. Appendix B. Turner Designs Fluorometer Specifications



10-AU Field Fluorometer

Typical Field Configurations

Continuous-Flow Field Studies. A 10-AU equipped with the 25 mm one-piece continuous flow cell, a waterlight case. internal data logging, and the 12 Volt DC Power & Signal cable is an ideal instrument for field studies. Temperature-compensation is strongly recommended for dye studies. If the instrument will be transported or shipped between field sites, a transport case is recommended.

A 10-AU equipped with an indoor case and the discrete sampling system for 13 mm or 25 mm test tubes allows the instrument to function well in an enclosed field setting, such ais an ocean vessel research laboratory or field station.



The 10-AU configured with the 25 mm One-Piece Film Cell, a garden hose, and a 12 VDC cuble for continuous field operation.

Discrete Sample Studies Sampling Options

One-Piece Flow Cell. The 25 mm One-Piece Flow Cell is easy to clean, eliminates flow cell leaks and sample compartment flooding, and simplifies calibration. Designed with a Luer lock port for injection of discrete samples into the flow cell, calibration can be accomplished quickly without switching between sample systems. For cleaning, a built-in port provides easy access to the flow cell. Flow cells of boroslicate glass or Suprasil quartz are available

Narrow Diameter Flow Cells. For special applications, one-piece continuous-flow cells with diameters of 10 mm. 3 mm, and 1 mm are available.

25 mm and 13 mm Cuvette Systems. The cuvelle systems change easily. The 25 mm holder allows sampling with 25 x 150 mm fest lubes. Simply insert the 13 mm adaptor into the 25 mm holder to accommodate 13 x 100 mm test tubes. Test tubes of borosilicate glass. or Suprasil quartz are available.

10 x 10 mm Adaptor System. For applications where small sample volumes are required, the 10 x 10 mm adaptor system accommodates 10 x 10 mm square cuvetles, 100 µJ vials, and 9 µJ capillary tubes.



Configured for discrete sumpting, the 10-AU is also an excelent laboratory instrument.

Data Handling Options

Internal Data Logging Package. With internal data logging, up to 64,800 data points can be stored in the instrument's memory. This eliminates the inconvenience and expense associated with transporting, operating, and maintaining additional data collection equipment. Downloading data stored in the fluorometer and converting data into ASCII format is a simple process. The ASCII data can be imported directly into a standard spreadsheet program for manipulation. Using the fluorometerkeypad, parameters such as the data collection interval can be selected. Also, with the addition of the temperature compensation leature, sample temperatures can be recorded.

Electronic Chart Recording Package. Graphically view the internally logged data without downloading with Electronic Chart Recording. By viewing 240 data points at a time and scroling through the data, the user can observe trends in the field without processing the data on a computer. Internal Data Logging must be installed to use this feature.

Temperature Compensation Package. As the lempenature of fluorescent samples rises, the fluorescence decreases. Serious errors can result if lemperature changes are ignored. The temperature oompensation package includes a temperature probe that mounts onto the flow cell and software that compensates for changes in sample temperature. Using the keypad, the appropriate temperature coefficient can be entered directly into the fluorometer, so there is no need formanual correction for temperature changes.

Hardware Options

Instrument Cases. The waterlight case is designed for rugged use out-of-doors and is factory-installed on the fluorometer to ensure a waterlight seal. The indoor case provides protection for the instrument when used in enclosed or protected environments.

Optical Kits. Optical kits with appropriate filters and tamps are available for applications including. In vivo & extractive chlorophyll, extractive chlorophyll a (acidification or non-acidification methods), in vivo chlorophyll a, Rhodamine WT dye, fluorescein dye, refined petroleum, and crude oil. Individual filters and lamps can be purchased as replacements or to customize the fluorometer for other applications.

Applications Include

- OceanographicStudies
- Chlorophyll Analysis
 - Lake and Reservoir Management
- Fluorescent Tracer Studies
- EmergencyOilSpill Response



Ruggest and watertight, the 10-AU is the instrument of choice for keld studies

Instrument Transport

Case. To protect the fluorometer and accessories during shipment, the instrument transport case is recommended. Designed specifically for the 10-AU, it is equipped with wheels for easy maneuvering.

10-AU Field Fluorometer

About Fluorescence

Certain compounds absorb light of one wavelength and re-emit light at a longer wavelength. Using the proper optical litter and lamp combination, a filter fluorometer can measure. this light and quantify select compounds. Filter fluorometry is often chosen. over other analytical lochniques because of its superior sensitivity, high selectivity, and low cost.

Option Specifications

Power, DC (optional): 11-16 V; 2.5 amperes

Internal Data Logging (optional): From 18,510 to 64,500 data points. Intervals: 1; 2, 3, 5, 10, 20, or 30 seconds, or 1, 2, 3, 6, 10, 20, or 30 mitubes

Electronic Chart Recording (optional with Internal Data Logging): 243 data points wed at a time

Temperature Compensation leptionate: Calsius or Fatners heil degrees. Temperature methaent Linear, 0 - 15.0000 %PC or *F, Exponential, 0 15.0000% / *C or *F. Long-term stability +F. 0.10*F. Nonknewith +1-0.30# (from -50 to 300#)

10.00

Instrument Specifications

Sensitivity: 10 parts per trillion of Rhodamine WT in potable water, 50 parts per trition of extracted chlorophyll at 10 parts per billion of crude oil in pure water

mer Design Lightennerton

errology

Dual Beam Optics: Compensate for drift in lang intensity and/or photomuliplier chill

Watertight Filter Paddles: Ealily removable littler paddles make excitiation and emission litter changes guick and convenient

Auto-Ranging: Manual or automatic range changing in response to changing concentration lawets (user selectable)

Ranges; 3 tanges, each a factor of 10 more sensitive than the next, 0 to 9999 999 Fluorescent Signal Units.

Blank: Reads and subtracts blank (uper selectable).

Operating Temperature: 10 - 55°C: 32 - 131°F campion0

Setware: Meru-driven microprocessor-controlled.

Digital Output: 100% ASCII formal through a 9-pin RS-232 cenal paties at 4800 or 9600 lists per second (tips)

Analog Output: Full scale voltage: 0.1, 1, 2, or 5 volts (user India Mathéri

Readout: Direct Concentration of Raw Fluorescence.

Detector: Factory installed photomultiplier tube Standard: 300-660 nm; Optional: Red Senative 185-870 nm

Discrete Sample Averaging (user selectate): Pre-averaging delay: 1 to 60 seconds, Averaging period: 2 to 60 seconds.

Lamp: Low Pressure Mercury Vapor Lamp (4 watts, 8000 hours lamp life). Several different wavelengths are evaluable.

Alarm: Auditie and visible when fluorescence of sample fails below or exceeds user selectable imits (user may disable aliam) Alarm delay time: 10 to 3600 seconds.

Diagnestics: Diagnosito activen displays status of internal instrument electronics for easy troubleshooting

Display: 40 x 8 character, backstLCD (152 mm x 59 mm).

Keypad: 4 x 5 keys (3" x 2 7"; 7.6 on x 6 8 on)

Power, AC: 100-130 V: 200-340 V, 5060 Hz, 30 watts

Physical Characteristics: Dimensions and weight vary with instrument configuration. Maximum: 24 cm H (9:46°) a 55 cm W (21.65°) x 34 on D (13.39°)

Weight 15.6 Kg (34.5 lbs)

Warranty: One year warranty

TURNER DESIGN! Approvals: TUV, VDE & CE

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10. Appendix C. LISST 100 Specifications

Technical Specifications

- Parameters measured/derived Particle Size distribution Total Volume Concentration Optical Transmission Depth Temperature
- An external analog input (0-5V)
- Two external digital I/O ports (5V logic)
- Optical path length: 5 cm standard, 2.5 cm optional
- Optical transmission: 12 bit resolution
- Particle size range: Type B: 1.25 250 micron diameter, Type C: 2.5 500 micron
- Resolution: 32 size classes, log-spaced
- Data storage memory: 512K (6500 samples) expandable to 2 MB (26,000 samples)
- Maximum sample speed: 1 size distributions per second (standard)
- Temperature-sensor range: -10 to 45°C resolution: 0.01° C
- Depth Sensor range: 0 to 300 m of H_2O , resolution: 8 cm of H_2O
- Dimensions: 13 cm (5") dia x 81 cm (32")
- Weight in air: 12 Kg (25 lb)
- Weight in water: 4 Kg (8.5 lb)
- Depth rating: 300 m (standard)
- Connector Endcap screws: Socket head cap screws #8-32 3/4" long
- Endcap O-ring: Parker Part # 2-244



Size Ranges, Angles of Observation and Data Storage Format

Size RangesThere are 32 size ranges logarithmically placed from 1.25 - 250
microns in diameter, or 2.5 - 500 microns (the upper size in
each bin is 1.180 times the lower).The table below shows the median size of each size class. For
clarity the table is shown with multiple rows. In the output data

file the data for each size class is oriented in one row from small to large.

Type B Instruments - 1.25 to 250 micron size range

| 1.36 | 1.60 | 1.89 | 2.23 | 2.63 | 3.11 | 3.67 | 4.33 |
|------|------|------|------|------|------|------|------|
| 5.11 | 6.03 | 7.11 | 8.39 | 9.90 | 11.7 | 13.8 | 16.3 |
| 19.2 | 22.7 | 26.7 | 31.6 | 37.2 | 44.0 | 51.9 | 61.2 |
| 72.2 | 85.2 | 101 | 119 | 140 | 165 | 195 | 230 |

Type C Instruments – 2.50 to 500 micron size range

| 2.73 | 3.22 | 3.80 | 4.48 | 5.29 | 6.24 | 7.36 | 8.69 |
|------|------|------|------|------|------|------|------|
| 10.2 | 12.1 | 14.3 | 16.8 | 19.9 | 23.5 | 27.7 | 32.7 |
| 38.5 | 45.5 | 53.7 | 63.3 | 74.7 | 88.2 | 104 | 128 |
| 157 | 186 | 219 | 259 | 293 | 332 | 391 | 462 |

Angles

The median angles (in Degrees) for the VSF measurement are shown in the table below.

Type B Instruments – 1.25 to 250 micron size range

| 0.106 | 0.125 | 0.148 | 0.174 | 0.206 | 0.243 | 0.287 | 0.338 |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.40 | 0.47 | 0.56 | 0.66 | 0.77 | 0.91 | 1.08 | 1.27 |
| 1.50 | 1.77 | 2.09 | 2.46 | 2.91 | 3.43 | 4.05 | 4.78 |
| 5.64 | 6.65 | 7.85 | 9.26 | 10.93 | 12.90 | 15.22 | 17.96 |

Type C Instruments – 2.50 to 500 micron size range

| 0.053 | 0.063 | 0.074 | 0.087 | 0.103 | 0.121 | 0.143 | 0.169 |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.20 | 0.24 | 0.28 | 0.33 | 0.39 | 0.46 | 0.54 | 0.64 |
| 0.75 | 0.89 | 1.04 | 1.23 | 1.45 | 1.72 | 2.02 | 2.39 |
| 2.82 | 3.33 | 3.93 | 4.63 | 5.47 | 6.45 | 7.61 | 8.98 |

Raw Data StorageThe values in the raw data file are stored in the order shown in the
table below.

| Elements | Parameter |
|----------|--|
| 1:32 | Light intensity on detectors 1 through 32 |
| 33 | Laser transmission Sensor |
| 34 | Battery voltage in raw counts |
| 35 | External Auxiliary input 1 (0 to $5V = 0$ to 4096) |
| 36 | Laser Reference sensor |
| 37 | Pressure in raw counts |
| 38 | Temperature in units of 100ths of degrees C |
| 39 | (Day*100 + Hour) at which data taken |
| 40 | (Minutes*100 + Seconds) at which data taken |

Processed DataThe values in the processed data file are stored in the order shown**Storage Format**in the table below. Each sample is stored in one row.

| Elements | Parameter |
|----------|---|
| 1:32 | Volume concentration (in ul/l) for size class 1 through 32 |
| 33 | Laser transmission Sensor |
| 34 | Battery voltage in calibrated units |
| 35 | External Auxiliary input 1 in calibrated units |
| 36 | Laser Reference sensor in calibrated units |
| 37 | Pressure in calibrated units |
| 38 | Temperature in calibrated units of degrees C |
| 39 | (Day*100 + Hour) at which data taken |
| 40 | (Minutes*100 + Seconds) at which data taken |
| 41 | Computed % Optical transmission over path |
| 42 | Computed Beam-C in units of 1/m |

Example Particle Size Distribution of Background Contaminant in Ohmsett Tank Prior to Dispersant Tests



11. Appendix D. Turner Fluorometer Calibration Curves

Calibrations for the fluorometer used in the

11.1 One-meter depth measurements











Calibrations for the fluorometer used in the

11.2 Two-meter depth measurements


























































