Oil Spill Dispersant Effectiveness Testing in OHMSETT
February – March 2006

for

Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Anchorage, Alaska

by

Merv Fingas
Ottawa, Ontario

and

Elise Decola
Nuka Research and Planning Group

May, 2006

Abstract

This paper is a review of some recent dispersant testing at OHMSETT. These tests were designed to measure the effectiveness of dispersant on Alaskan oils at low temperatures. The oil and water temperatures were close to the freezing point.

Ten dispersant tests were observed, 5 dispersant tests and 5 control tests. The dispersant tests showed good initial dispersion and subsequent observation showed much of the oil from these tests re-surfaced, about half within about one to two hours and most of it by next morning.

The testing method was viewed with respect to concerns raised earlier from observing and analysing other tests. First, a report sponsored by PWS RCAC, had raised 18 concerns about dispersant tank testing. The following are 18 critical factors, identified in an earlier study, that need to be considered and included in any test for measuring the effectiveness of dispersants in a tank in order for that test to achieve useful results. These factors are reviewed in this assessment.

1. Mass balance
2. Proper controls
3. Analytical method
4. Differential plume movement
5. Time lag and length of time plume followed
6. Mathematics of calculation and integration
7. Lower and upper limits of analytical methods
8. Thickness measurement
9. Behaviour of oil with surfactant content
10. Surfactant stripping
11. Recovering surface oil
12. Background levels of hydrocarbons
13. Fluorescence of dispersant
14. Herding
15. Heterogeneity of the oil slick and the plume
16. True analytical standards
17. Weathering of the oil
18. Temperature and salinity

The National Academy of Sciences reviewed dispersant testing and noted the following concerns:

1. Wave-tank tests should be judged primarily on the basis of their additional realism – over laboratory studies – that is incorporated into their test design while remaining sufficiently controlled to allow replication and collection of quantitative information.
2. Studies should also investigate the evolution of the physical-chemical characteristics and the operational dispersability, as oil weathers in a slick.
3. Effectiveness of dispersants on blended emulsions should be tested under more realistic field conditions. The rheological and chemical properties of the test emulsions should be characterized and compared to data from emulsified oil samples collected during actual oil spills. The dispersability of the artificially generated emulsions should be tested over a range of temperatures, including cold, subarctic conditions.
4. Measurement of effectiveness as a function of dispersant droplet-size distributions

and impact velocity should be carried out if this parameter is of consideration.

5. Mixing energy should be measured over a range of mixing energies that span the range that can be realistically expected in the environment of interest. The wave energies used in the experimental system should be scaleable to actual sea states. and

6. The effects of temperature and ice on dispersed oil droplet size, coalescence and resurfacing should be investigated.

In addition, there were several concerns raised by PWS RCAC:
1. heating of the oil,
2. artificial weathering of the oil,
3. use of booms in testing field,
4. re-surfacing of the oil,
5. tank contamination,
6. use of oils which are not typically transported,
7. herding, and
8. uncontrollable natural factors.

Although many of the initial concerns were taken into account in re-designing the protocol for the current trial round, this report shows that there remain some concerns:

1. The experiment is ended at the peak of dispersion and before extensive re-coalescence occurs. Extensive re-surfacing of the oil can readily be seen after the experiment is terminated and within 1 hour of the start of the experiment.

2. No mass balance is attempted and data collected are not used to attempt mass balance.

3. Some oil was collected to presumably determine amount dispersed, however this was always collected within 45 minutes of the trail and major re-surfacing occurred after this collection. The spraying action caused a great deal of re-dispersion. Further it would be impossible to be quantitative as the sweeping operation is not completely effective and there is much oil around the tank before and after the sweeping operations.

4. The use of instrumentation was increased several-fold, however calibration of these methods and use of data remains at the initial level. and

5. There was no quantitative measure of sea energy. Wave data was collected as before with somewhat more precision.

Alternative procedures are given that take into account lessons learned during the detailed work conducted at the Imperial Oil tank in Calgary, Alberta and the SERF tank in Corpus Christi, Texas. These procedures will make it possible to reasonably estimate the effectiveness of dispersants in a large test tank.

The recommendations are that several points need attention:
1. Quantitative method of determining effectiveness,
2. Correct analytical procedures,
3. Necessity to take measurements for at least 6 hours, and
4. Ability to recover surfactant-treated oil

List of Acronyms

ANS - Alaska North Slope - Usually referring to the crude oil mixture at the end of the pipeline

ASMB - Alberta Sweet Mixed Blend - a crude oil from Alberta often used as a reference

PAH - Polynuclear Aromatic Hydrocarbons

PWS - Prince William Sound

PWSRCAC - Prince William Sound Regional Citizens' Advisory Council

TPH - Total Petroleum Hydrocarbons - A measurement of total oil in a sample

WAF - Water-Accommodated Fraction - The sum total of oil in a water sample including physically dispersed and soluble oil

Acknowledgements

Table of Contents

1.   An Overview of Tank Testing

There are several concerns about the behaviour of oil and dispersants as it relates to tank testing. First, oil, treated or untreated, will move into several 'compartments' such as into the water, onto the tank walls, or evaporation. Therefore, without proper mass balance calculations, it could be presumed that the oil has dispersed. Second, little treated oil remains on the surface whether significant dispersion occurs or not. This is because it will go into the various compartments as noted in point one. Third, it is very difficult to get a synoptic view of all the oil dispersed because of the heterogeneity of the oil distribution in the water. Furthermore, the dispersed droplets are still somewhat buoyant and are therefore not distributed equally with depth. Fourth, the dispersed oil destabilizes and re-surfaces and the amount dispersed decreases with time. The measurement is therefore time-dependent. Fifth, the presence of surfactant alters the behaviour of oil as well as causing dispersion. It spreads the oil out on the surface of the tank, often past visibility. Due to these and many related complications, careful procedures must be developed to measure the amount of oil actually dispersed at a given point in time.

The only reasonably accurate way to measure effectiveness in the water is to measure the oil concentration in the water at least 6 hours after the dispersant application. Brown et al. (1987) suggested that the value was only accurate after 24 hours. The longer time would allow the oil concentration to be more homogeneous around the tank.

Lessons on tank testing can be taken from Imperial Oil in Calgary, Alberta (Brown et al., 1987; Brown and Goodman, 1988). Testing was developed in the Imperial Oil tank over a period of 7 years. The mass balance problems were particularly noted during these tests. In recent years, the SERF facility in Texas went through similar difficulties and many of their lessons are incorporated into this paper (Bonner et al., 2002). In addition to mass problems, Bonner et al. noted that the wave energy, spectrum, and several other factors in the tank required measurement and adjustment. Both the difficulties with mass balance and wave energy developments lasted about 5 years.

2.   The February-March 2006 Dispersant Tests

A round of experiments was conducted at OHMSETT beginning on February 28, 2006 and continuing for 2 weeks. The authors of this report observed trials on the first week of tests between February 28 and March 3, 2006.

2.1   Test Protocol

The protocol provided by the OHMSETT staff follows:

a. Crude Oils to be Tested
Alaska North Slope, Endicott, Northstar and Pt. McIntyre crude oils.

Fresh and weathered crude oils were used in the experiments. Weathering was carried out by air sparging and on-tank exposure.

b. Dispersant
Corexit 9527 applied with a target Dosage of 1:20.

c. OHMSETT Dispersant Test Protocol

- Basic Pre-Test Setup Requirements

Three sets of boom are to be mounted across the tank, two sets separated by about two to three meters at the beach end and one set at the wave paddle end. Exact positions of booms will be the same as in previous dispersant tests to maximize the length of the study zone.

Dispersant spray gear will be mounted on the main bridge. System will be flushed with water and all nozzles thoroughly cleaned and calibrated in preparation for the tests.

The oil discharge hopper, pump and hose are placed on the main bridge.

Oil discharge header will be mounted on the main bridge and connected to the oil spill pump and hopper.

Video camera and scale will be mounted under the main bridge for recording dispersant spray and oil slick characteristics.

A vertical pole (as fabricated for use in an earlier test program) will be mounted on the main bridge for attachment of the Sontek velocity probe and a data acquisition laptop readied for connection to the Sontek.

One submersible pump and garden type hose will be mounted on the main deck to supply water from one to two meters depth to one Turner fluorometer to be placed in the main bridge house. Hose and pumps from previous tests to be used if available.

Desk or shelf space will be readied to place one Turner fluorometer, three data acquisition laptops (fluorometer, LISST and Sontek) with enough space remaining to service the LISST between tests.

Oil weathering for some experiments will be by air bubbling. Specific weight or volume loss for each oil to be specified.

All oils delivered for testing to be stored at 0 to 5° C so they are at or near test temperature when needed.

- Control Tests: No Dispersant

LISST, Fluorometer, Sontek velocity probe and under-deck video camera are put in position and readied for use.

Oil is placed in the discharge hopper and the discharge system is charged with oil.

The test area is swept clean of oil using fire-monitors.

The bridge is positioned for an oil discharge run. Location within the boomed test area will depend on wind speed and direction.

Waves are started at the appropriate stoke and frequency (3.5 inch and 35 cpm).

After four to five minutes of wave development (just prior to onset of breaking waves) the oil is laid down. Bridge speed and oil pump rate will be determined on a case-by-case basis (between 0.25 and 1 knots and 10 to 40 gpm depending on the test oil).

LISST, Sontek and Fluorometer are operated during a minimum of three passes through the center of the tank during the test for oil detection and characterization.

Waves are left on for twenty minutes.

Once the surface has calmed, the remaining oil in the boomed area is swept to a central collection location.

The oil is pumped from the water surface into open-top drums using a double diaphragm pump.

Water collected in the drums is decanted. The remaining oil and water is thoroughly mixed with a small amount of demulsifier and allowed to sit overnight. Water is decanted from the drum again and the depth of oil left in the drum is measured to determine the quantity of oil and water remaining. The drum is thoroughly mixed again and a 500 ml sample of the oil is taken for water content, viscosity and density determination. The amount of oil collected is determined after subtracting the % water content determined by solvent extraction. Oil density measurement is used to estimate the oil volume lost by evaporation.

The amount collected at the end of the test minus the evaporation estimate is compared to the amount discharged to determine approximate oil losses to the water column, tank walls and booms in a test when no dispersants have been applied.

- Dispersant Applied Experiments

Dispersant spray gear is readied by mounting the appropriate nozzles for 1:20 application on the target slick and filling the dispersant supply basin with dispersant.

All steps identified in the control test protocol are completed with the following additional steps.

Dispersant is applied to the surface oil during the oil discharge pass. Oil is laid down on the south side of the bridge and dispersant is applied from the north side as the bridge travels from north to south.

The dispersant-to-oil ratio is determined by estimating the thickness of oil and dispersant sprayed. The oil width, percent of water surface covered with oil, oil discharge rate and bridge speed are used to estimate the oil thickness. The spray width, bridge speed and volume of dispersant discharged are used to estimate the dispersant thickness. An under-bridge mounted video camera is used to provide oil and dispersant spray widths and oil surface coverage.

Dispersant effectiveness is determined by collecting the surface oil from the tank at the end of the test as outlined in the control test, accounting for losses as determined in the control test and then estimating the amount lost due to the application of dispersant.

2.2   The observed protocol

The protocol that was used during the time of the visit is described here. An overview of the tank is shown in Figure 1. The instruments that were mounted and used include: a Turner flow-through fluorometer, a Wet Labs fluorometer, a Sequoia LISST particle size analyzer, a Sontek Horizon Acoustic Doppler velocimeter, a Turner TD500D oil-in-water analyzer and various cameras. The computers controlling and logging the data are shown in Figure 2. Oil was loaded from a refrigerated container onto the movable bridge of the tank. The temperature of the oil and the water in the tank were near freezing. From the drums, the oil was pumped into a hopper tank and dispensed via a positive-displacement pump through nozzles about 1 metre wide just over the water. Figure 3 shows the oil discharge during an actual run. Figure 4 shows the hopper tank and the positive displacement pump. Figure 5 shows the spray operation. The amount of oil put out was gauged by taking measurements inside the hopper tank before and after the tests.

A typical run began with a sweep of the tank with the two fire nozzles to remove oil into the boomed area at the one of the tank. Oil appeared to accumulate beyond the third boom, the whole time we were there, the accumulated oil at that point was not removed. Some oil was removed from in front of the first boom. Figure 6 shows recovery of some oil. It should be noted that oil was often not physically removed and measured during the time that we were at the site. The stated procedure was that oil was to be pumped from the tank after a given test and placed in drums for later quantitation. Sweeping oil rarely resulted in quantitative oil removal, especially right after chemical dispersion. The sweep largely resulted in re-dispersion of oil in this case. Figure 7 shows such a sweeping operation which resulted in extensive re-dispersion.

Once the tank was swept, the bridge was positioned about 100 from the far end boom, and the waves started. Once the waves were well-established and breaking waves could be seen down the tank, the bridge was started at a speed of 1 knot. Oil was discharged for one minute and this covered about 100 feet of lineal track. Twenty gallons of oil was generally discharged. Light oils would spread out to about 6 to 8 feet. The width of the dispersant spray is 10 feet. Heavy oils would spread out to only about 4 to 6 feet. The approximate initial slick areas for a light oil would be about 700 square feet (yielding a slick thickness of about 1 mm) and for a heavy oil about 400 square feet (yield a slick thickness of about 2 mm). As the winds were generally from the west, many of the slicks moved to the east end of the tank.

After the pass to spill the oil, the bridge remained at the south end of the spill area for about 5 minutes. After this the first of 3 test passes were made. Fluorometric and other readings were recorded. Each pass took about 5 minutes with approximately a 5 minute pause between passes. The experiment was considered to be over in 30 minutes and the first sweep with the fire nozzles took place. There generally was not enough oil to recover after these passes, unless the test was a control. A second sweep was usually carried out before the next experiment.

The typical timing and sequence of events during the experiments was as follows: At time of the laying of the slick, dispersants were applied at the same time as the slick laying, just on opposite sides of the moveable bridge; This took place on the south end of the tank over a100-foot track; then after a short pause, a fluorometric run was

Figure 1 An Overview of the OHMSETT Tank with the Waves Falling after a Test

Figure 2 A View Inside the Moveable Bridge Showing the Fluorometer in the Foreground and Laptops which are Used to Collect Data

Figure 3 The Discharge Outlet. The Oil Typically Spread from 4 Feet to About 6 Feet

Figure 4 The Hopper Tank and Pump Used to Deliver Oil to the Discharge Outlet

Figure 5 The Dispersant Spray System. Note that Some Herding is Occurring Here. The Width of the Spray System is about 10 Feet and the Current Oil Slick is about 5 Feet Wide

Figure 6 Recovery Operation. The Oil is Picked up Using a Cup on a Pole. Note that There is an Extensive Slick Forming on the Tank Behind the Recovery Operation

carried out – this was done from about 5 to 9 minutes after laying the slick; a run took about 4 to 5 minutes to complete; A second fluorometric run was done from 12 to 15 minutes after slick laying and a third about 16 to 20 minutes after. The slick was swept with fire hoses to the downwind side (typically the north end of the tank) at times ranging from 33 to 45 minutes. The fluorometric peak occurred typically on the first run or from 5 to 9 minutes after the slick laying, but sometimes occurred on the second run, about 12 to 15 minutes after slick laying.

Merv took samples on the first or second fluorometric run for control experiments, but took samples on both the first and second fluorometric runs for dispersant experiments. The peak fluorometric recordings typically occurred during the second run. Fluorometric ranges and peaks were recorded by Merv. The samples were extracted with dichloromethane shortly after they were taken and samples placed in the refrigerator. Samples were shipped by courier back to the Environment Canada laboratory where they were analyzed for TPH.

Some samples were taken by the test crew and were presumably analyzed by a separate procedure. This was not documented at the time of the writing of this report.

At the end of each experiment (after 30 minutes) the tank was swept with fire hoses and all prepared for the next experiment. Typically 3 experiments could be conducted in one day. The background fluorometric readings would rise somewhat through the trial series and more and more residual oil was seen floating around the tank.

2.3 Summary of Experiments
During the four days we were at OHMSETT, we observed 10 tests. Each will be summarized separately below, but the general features of each were the same. In the dispersant tests it was possible to observe a "dispersed oil plume spreading down into the water and expanding horizontally. After these dispersant trials one could see an increasingly-thickening slick over the entire tank. In the absence of wind this remained intact, however with wind, a pool of oil would form in the downwind areas. Estimations of these oil pool volumes ranged from 5 to 10 gallons. This is significant in that only 20 gallons of oil were put out and first recovery attempts often recovered 5 gallons 45 minutes after a test. The observations on the tests are also given in Decola and Fingas (2006).

Test 2 – February 28 – ANS control test – the oil was driven to the downwind wall by the strong winds. Observations in the windows into the water column showed a high degree of natural dispersion, more than most experienced observers had previously seen. Figure 8 shows the natural dispersion from test number 1.

Test 3 – February 18 – Fresh ANS with Corexit 9527 – The oil was again driven toward the wall, and after about 10 minutes, some plumes were noted. After 20 minutes there was more dispersion. Figure 9 shows the dispersion at about 8 minutes. Our visual estimates were that 20 to 40% of the oil was dispersed. The oil was flushed to a collection centre about 45 minutes after the slick was laid. Figure 10 shows sheen and dispersant floating about the tank about the time that the flushing was taking place. Figure 11 shows re-surfaced sheen about 35 minutes after the experiment was terminated and about 10 minutes after the sweep was completed. After 2 hours we went up to the tank and noted that the tank was entirely covered with sheen and small patches of oil, despite the fact that it supposed had been cleared about ¾ of an hour earlier. It appeared

Figure 7 Sweeping Operation. Note that Extensive Re-dispersion is Occurring and Only a Small Amount of Oil is Being Swept in Front of the Water Spray from the Fire Hoses

Figure 8 A View of the Second Test Involving Fresh ANS Oil. Note that this Oil Spread Readily Over much of the Tank. Significant Natural Dispersion Was Also Noted.

Figure 9 Test 3 – Dispersion of Fresh ANS Oil. This Picture was Taken about 8 Minutes After Dispersant Application. Dispersion is Occurring at the Edges of the Slick, Although Some Oil is Leaving as a Sheen
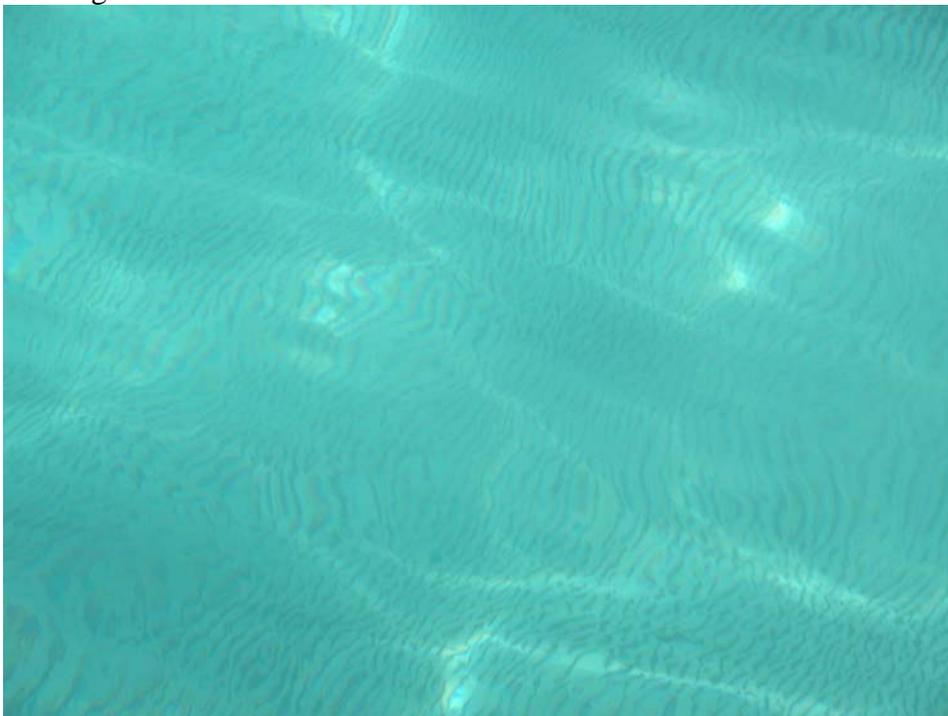
Figure 10 A View of the OHMSETT Tank About 45 Minutes After Dispersion and About 10 Minutes After Waves Were Turned Off. Note the Sheen and White Dispersant Trails.

It appeared that a very large portion (up to 90%) of the oil had resurfaced within this time. This is shown in Figure 12. Note the black oil resurfaced on the opposite end of the tank from where the photo was taken. We re-visited the tank next morning before the tank was again re-swept. There was a major oil slick from re-surfaced oil in the downwind corner. This slick contained between 10 to 15 gallons and had a surface area of about 200 square feet. This slick is shown in Figure 13. In addition to this slick there were several small slicks along the downwind edge of the tank and a sheen covering most of the tank. The slicks along the wall are seen in Figures 14 and 15.

Test 4 – March 1 – Weathered Point McIntyre – 10% weathered by air sparging – Control Experiment - the oil was driven by the winds of about 10 mph toward the opposite wall. Some natural dispersion was observed in the windows in the tank. This slick is shown in Figure 16.

Test 5 – March 1 – Weathered ANS – 16% weathered by air sparging – Control Experiment - the oil was driven by the winds of about 10 mph toward the opposite wall. Some natural dispersion was observed as noted in Figure 17.

Test 6 – March 1 - Weathered ANS – 16% weathered by air sparging – Dispersant Experiment – The oil and dispersed oil was driven to the side wall by a wind of about 15 mph. A lesser amount of dispersant was put on the slick. The tank is shown in Figure 18. In Test 2 about a 2 inch displacement was observed in the dispersant tank, and in Test 6 about a 1 inch displacement. A small localized dispersed plume formed beside the wall and the fluorometric readings through this small plume of about 20 feet long by about 10 feet wide ranged up to 180 relative fluorometric units. Our visual estimates were that about 50% was dispersed. The oil was swept with fire hoses 30 minutes after the experiment. We noted that in addition to flushing oil down the tank, the spray re-dispersed the oil and spread it more over the tank. This can be seen in Figure 7 which was taken during this trial. The peak dispersion is shown in Figure 19. We performed a walk around the tank and found significant re-surfacing within 45 minutes. We again did a walk around the tank after one and a quarter hours and found that even more was resurfaced. There was about a 3 foot band of re-surfaced oil all along the downwind side of the tank for about 400 feet. A portion of this slick is illustrated in Figure 20. In the morning, we again re-surveyed the tank and found a heavy layer of oil on the downwind side of the tank – an estimate of the amount of oil in this slick was 13 gallons or about 70% of the oil put out in the last test. The estimate ranged in accuracy plus or minus 50%.

Test 7 - March 2 – Weathered Endicott – 11% (by volume) weathered by air sparging – control experiment - the oil remained largely intact and little natural dispersion was observed. As the wind was light, and from the East, the oil remained between the centre and the side wall of the tank. Figure 21 shows this slick.

Test 8 - March 2 – Fresh Endicott – control experiment - the oil remained largely intact and little natural dispersion was observed. As the wind was light, and from the East, the oil remained between the centre and the side wall of the tank. Sheen appeared to spread over the whole tank. Throughout the experiments an acoustic Doppler velocimeter was used and Figure 22 shows the typical output screen from this instrument.

Figure 11 Resurfacing of Oil After Test 3, Fresh ANS Dispersed. This is About 55 Minutes After Dispersant Application and About 25 Minutes After Waves Were Turned Off.

Figure 12 A View of the Tank After About 60 Minutes After Dispersant Application and About 35 Minutes After Waves Were Turned Off. Note the Thicker Black Oil Slick Resurfaced on the Opposite Wall and the Coverage of the Tank by Sheen

Figure 13 Oil Resurfaced Overnight from Test 3 – Dispersed Fresh ANS

Figure 14 Oil Resurfaced Overnight from Test 3 – Dispersed Fresh ANS. Much of the Downwind Side of the Tank Was Covered with This Density of Slicks

Figure 15 Oil Resurfaced Overnight from Test 3 – Dispersed Fresh ANS

Figure 16 Slick from Test 4 – Control Slick, 10% Weathered Point McIntyre. This is Immediately After Deposition

Figure 17 The Slick from Test 5 – 16% Weathered ANS – About 10 minutes After Slick Laid. Note There is a Small Amount of Natural Dispersion

Figure 18 A View of the Dispersant Tank and Pickup Pipes

Figure 19 The Slick from Test 6 - Dispersion of 16% Weathered ANS – This is About 10 Minutes After Dispersion. Note Dispersion of Portions of the Slick and Others Which Are Not.

Figure 20 Resurfaced Oil From Test 6 - 16% Weathered ANS – Photo Taken About 50 Minutes After Dispersion. The Downwind Wall had Oil of This Density Along Most of Its Length

Figure 21 The Slick from Test 7 – Control Using 16% Weathered Endicott. This Photo is Right After The Slick Was Laid
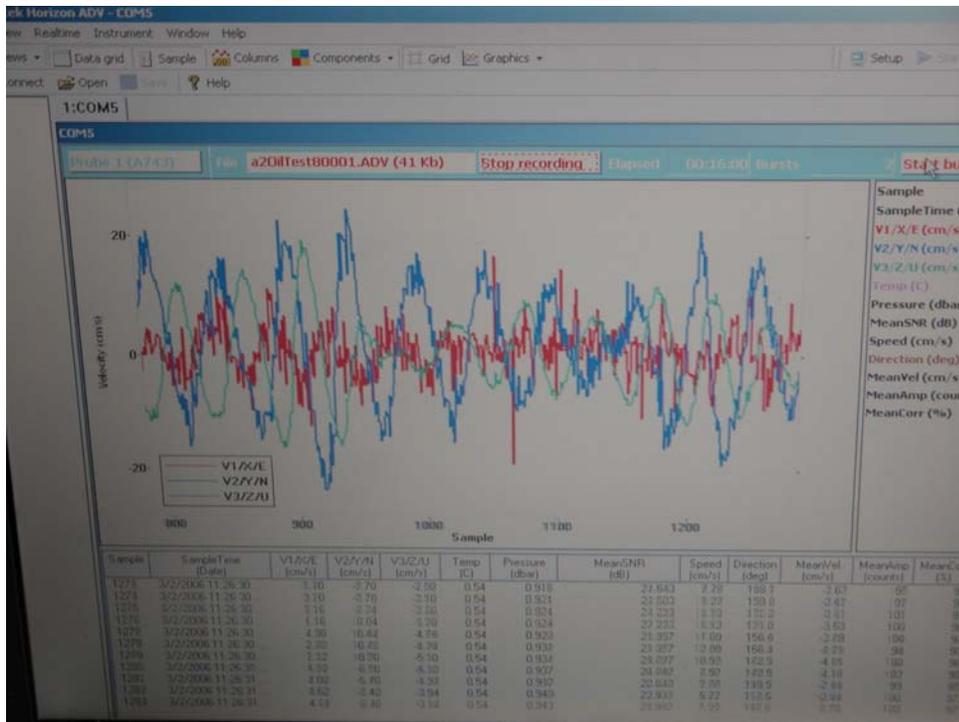

Figure 22 A View of the Screen of the Computer Logging the Acoustic Doppler Velocimeter Output

17

Test 9 – March 2 - Weathered ANS – 15% weathered by placement on tank surface – Dispersant Experiment – The oil was laid to the North central part of the tank as the wind was from the North. The oil dispersed visually to about 50%. Figure 23 shows the dispersion of this slick at the peak of the dispersant effectiveness, about 15 minutes after dispersion. After the experiment, (30 minutes) the crew swept the tank with fire hoses and recovered about 5 gallons of oil with water, estimating that 4 of it was pure oil. Figure 24 shows the oil recovered during this sweep operation. We observed that the entire tank was covered with a sheen of darker gray colour. I estimated that about 10 gallons or more of the oil was in this sheen. The next morning, we found that there was about 5 gallons of oil in a heavy slick near the south end of the tank as would be expected from the wind direction. Figure 25 shows some of this oil from test 9. There was other oil on the tank. Because oil behind the booms was not cleaned out, it is not known which experiment the oils in the tank or behind the booms were derived from.

Test 10 – March 3 - Weathered ANS – 15% weathered by placement on tank surface but with low sea energy– Dispersant Experiment – The oil was laid to the North central part of the tank as the wind was from the North west. Figure 26 shows the oil very shortly after deposition and dispersant spraying. It should be noted that much of the dispersant didn't mix with the oil and can be seen as white streaks in this figure. The oil dispersed visually to about 50%. Figure 27 shows the dispersed plume at the point of maximum effectiveness. After the experiment, (30 minutes) the crew swept the tank with fire hoses and just before the second time this was done, we observed that the east side of the tank had a column of oil all along it with some concentrations. A portion of this oil is shown in Figure 28. This oil was estimated to be 10 gallons, in volume. This did not count the oil removed on the first sweep which was estimated to be 5 gallons. Another sweep was carried out later and this yielded still another 5 gallons. The origin of all this oil was not known as there was oil left behind booms from previous experiments. It should be noted that the dispersant observed as not mixing in Figure 27 is again visible in Figure 28, again not well mixed with the oil.

Test 11 – March 3 – 10 % weathered Endicott - The oil was laid to the north central part of the tank as the wind was from the northwest at about 25 mph. Again, the dispersant was seen as mixing poorly into the oil as can be seen in Figure 29. The oil dispersed visually to about 40%. After the experiment, (30 minutes) the crew swept the tank with fire hoses and just before the second time this was done, we observed that the East side of the tank had a column of oil all along it with some concentrations. This re-surfacing oil is seen in Figure 30, along with residual dispersed oil in the water column. Before the second sweep an additional 5 gallons was estimated on the sweep. This was a total of about 10 gallons of oil. A third sweep was done, however we did not observe the oil on this occasion.

The tests carried out are summarized in Table 1.

Figure 23 Dispersion from Test 9 – Dispersed 15% On-Tank Weathered ANS About 15 Minutes After Spraying

Figure 24 Oil Recovered from Test 9 – Dispersed 15% On Tank Weathered ANS. This is after the First Sweep About 50 Minutes after Dispersion

Figure 25 Resurfaced Oil From Test 9 – 15% Weather ANS – As Seen Next Morning

Figure 26 The Slick from Test 10 – Dispersed 15% On-Tank Weathered ANS – About 5 Minutes After Dispersion. Note that Dispersion is Just Beginning (Brown Areas) and That There is Some Dispersant Streaking

Figure 27 The Slick from Test 10 – Dispersed 15% On-Tank Weathered ANS – About 15 Minutes After Dispersion. Note that Dispersion is Relatively Wide Spread

Figure 28 Resurfaced Oil From Test 10 – Dispersed 15% Weathered ANS About 45 Minutes After Dispersion. Note that There Still Are Unmixed Dispersants In the Area

Figure 29 The Slick from Test 11 – Dispersed 10 Weathered Endicott – About 5 Minutes After Dispersion. Note that Dispersion is Some Dispersant Streaking

Figure 30 Resurfaced Oil From Test 11 – Dispersed 10% Weathered Endicott About 45 Minutes After Dispersion. Note that There Are Unmixed Dispersants in the Area

Table 1 Summary of Dispersant tests at OHMSETT

Test	Date	Oil type	Dispersant	Visual Results	Fluorometer Peak	Oil Resurfaced	Fluorometer Background
2	28-Feb	fresh ANS	control	good natural dispersion	7		1.7
3	28-Feb	fresh ANS	1:10	20 to 40%	80	most	1.7
4	01-Mar	10% Pt. Mc	control	some natural dispersion	18		4.6
5	01-Mar	16% ANS	control	some natural dispersion	28		4.7
6	01-Mar	16% ANS	1:20	50%	170	most	4.7
7	02-Mar	11% W Endicott	control	little natural dispersion	5.1		4.3
8	02-Mar	fresh Endicott	control	little natural dispersion	5		4.3
9	02-Mar	15% ANS tank weathered	dispersant	50%	169	most	4.7
10	03-Mar	15 % ANS weathered on tank/ low energy	dispersant	50%	72	most	4.6
11	03-Mar	10 % Endicott	dispersant	40%	25	most	7.1

Peak Fluorometer values were monitored with the time taken. This is shown in Figure 31. This indicates that peak fluorometric values, and probably the peak dispersion, is obtained at 15 minutes after the dispersant was applied. Fluorometric values typically declined to less than half the peak value at about the 30 minute time level.

Figure 32 shows the background fluorometric readings throughout the test series. The fluorometric values did not rise significantly except for between tests 2 and 3. This shows that the dispersed oil did not accumulate in the water. It also shows that the dispersed oil was diluted and re-surfaced over the course of the experiments.

2.4 Sample Analysis

During the progress of the ten tests observed, 16 water samples were collected from the output of the Turner fluorometer which was pumping from the depth of 1.5 metres. The fluorometer readings during the sample taking were recorded. Table 2 shows the samples and the relevant data on each samples. One hundred millilitres of the water sample were extracted with dichloromethane within 10 minutes of when they were taken. The DCM extras were then stored in a refrigerator until they were sent to Environment Canada for analysis. The shipment to Environment Canada was two months later, however the samples were preserved in DCM and in sealed containers. The analytical results are shown in Table 2.

The samples were analysed according a standard procedure. This method uses a high resolution capillary GC equipped with a flame ionization detector (GC/FID) for the determination of normal alkanes (Wang et al., 2004).

It is relevant to compare the fluorometric data with the TPH data. Figure 33 shows all sample results compared to the fluorometric reading at the time that the sample was taken. It can be seen that there is a great deal of scatter. If the control and background sample TPH results are plotted versus the fluorometric data, as shown in Figure 34, the relationship is somewhat better. On the other hand, the dispersed experimental results show extensive scatter as shown in Figure 35. This is well-known that the fluorometer readings of dispersed oil are hard to relate to TPH (Lambert et al., 2001a, 2001b). The reason for this is that there are different abundances of fluorescing compounds in the water over time.

Table 2   Samples Taken During Dispersant tests at OHMSETT

Test	Date	Oil type	Dispersant	Sample number	Type	Fluorometer	Fluorometer range	Fluorometer Peak	TPH	
				1	background	1.7	1.68 to 1.71		1.1	
2	28-Feb	fresh ANS	control	2	control	4	3.9 to 4.4	7	4.6	
3	28-Feb	fresh ANS	1:10	3	dispersed	6	5.5 to 6.5	80	2.2	
				4	dispersed	42	41 to 43		15.7	
4	01-Mar	10% Pt. Mc	control	5	control	13	17.6 to 12	18	5.8	
5	01-Mar	16% ANS	control	6	control	5.5	5 to 6	28	3.6	
6	01-Mar	16% ANS	dispersant	7	dispersed	63	60 to 67	75	8.3	
				8	dispersed	146	155 to 140	169	29	
7	02-Mar	Endicott 11% weathered	control	9	control	4.8	4.7 to 4.8	5.1	1.2	
8	02-Mar	fresh Endicott	control	10	control	4.95	4.9 to 5	4.95	3.8	
9	02-Mar	ANS 15% on tank weathered	dispersant	11	dispersed	80	75 to 101	169	17.8	
				12	dispersed	22	23 to 21	84	6.9	
10	03-Mar	ANS 15% low energy on water	dispersant	13	dispersed	19	16 to 22	65	32.6	uncertain
				14	dispersed	68	65 to 71	72	23	
11	03-Mar	Endicott 10% weathered	dispersant	15	dispersed	15	13 to 17	27	15.3	
				16	dispersed	20	18 to 22	25	20.7	

This data clear shows that fluorometric data cannot be used alone as an absolute measure of the hydrocarbon content of a dispersed system. Absolute laboratory measurements are required to ascertain the amount of hydrocarbons in a given system.

Calculations can be made to provide estimates of effectiveness given a certain concentration at depth (Fingas, 2002). The slick is assumed to be either equally distributed to the depth of 1 m (roughly the sampling depth in this case) or exponentially distributed over the same depth. These calculations are very simple arithmetic calculations presuming the distribution being either equal or exponential. The estimations are shown in Table 3 and graphically in Figure 36. The situation that is believed to be closest to these tests is the 1 mm slick and the exponentially-distributed case. This shows that given the exponential distribution and a 1 mm thickness that the actual effectiveness would be no greater than 1 to 20%.

Table 3   Estimation of Effectiveness Based on Oil Concentration

|						Estimated Effectiveness %				
						slick	1 mm	1 mm	2 mm	2 mm
Test	Date	Oil type	Sample number	Fluorometer Reading	TPH	Equal distribution	Exponential	Equal distribution	Exponential	
3	28-Feb	fresh ANS	3	6	2.2	0	1	0	1	
			4	42	15.7	2	7	1	3	
6	01-Mar	16% ANS	7	63	8.3	1	3	0	1	
			8	146	29	3	20	1	3	
9	02-Mar	ANS 15%	11	80	17.8	2	7	1	3	
			12	22	6.9	1	3	0	1	
10	03-Mar	ANS 15%	13	19	32.6	3	20	2	7	
			14	68	23	2	7	1	3	
11	03-Mar	Endicott 10%	15	15	15.3	2	7	1	3	
			16	20	20.7	2	7	1	3	

24
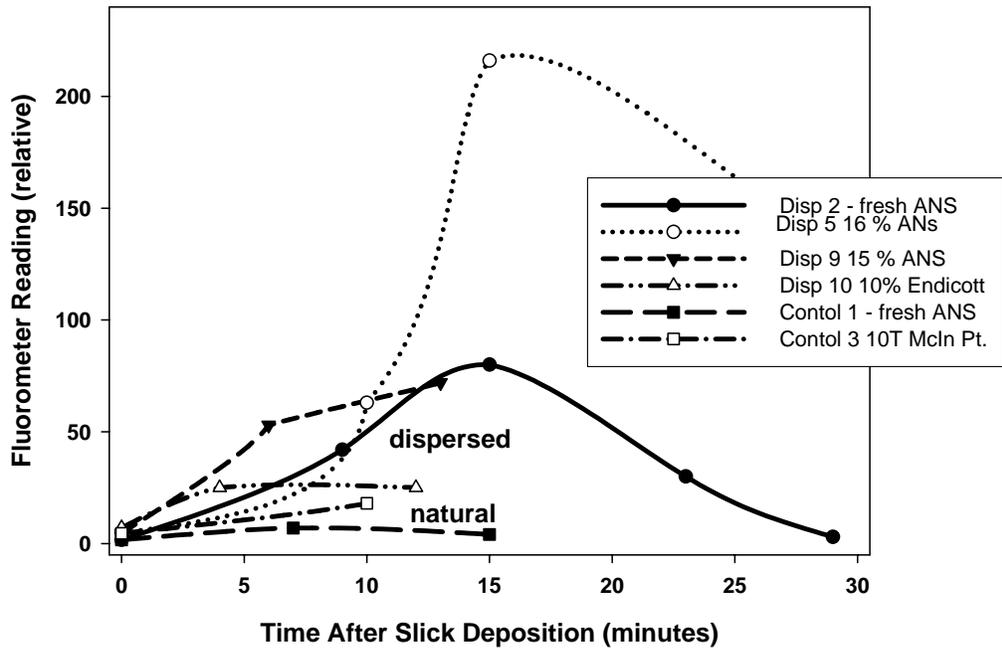
Figure 31   Peak Fluorometry Values With Time
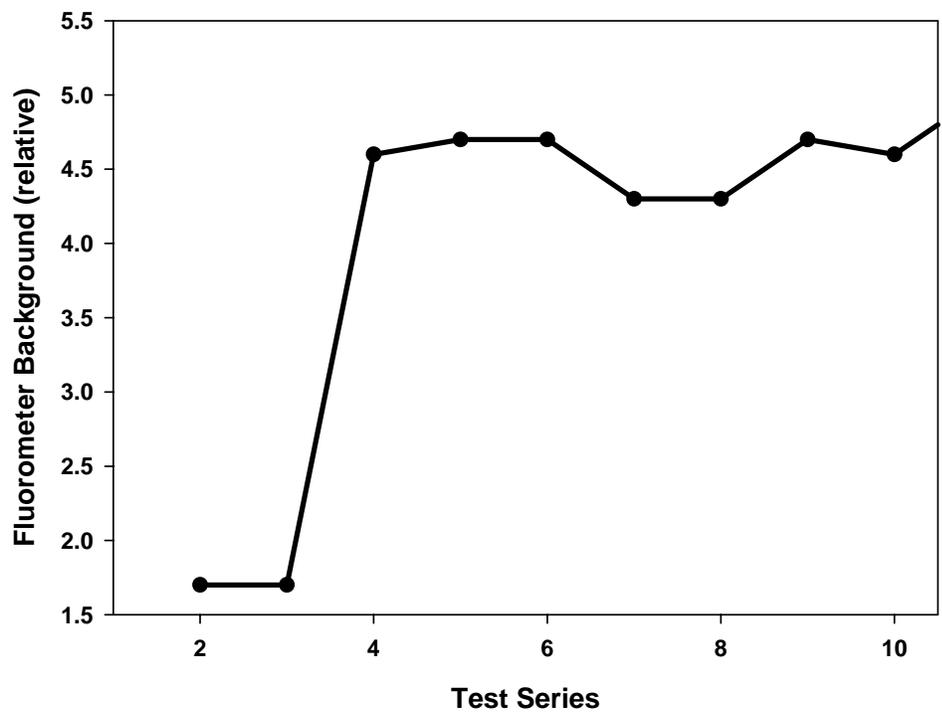
Figure 32 Background Fluorometry Values Throughout the Tests
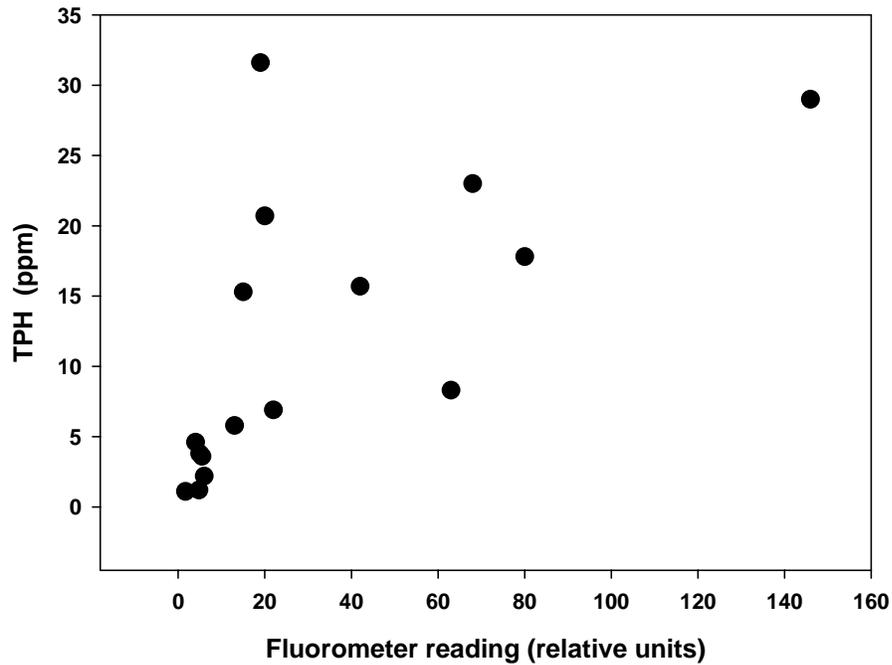
Figure 33   Comparison of TPH data with the fluorometric reading at the same time, all data included
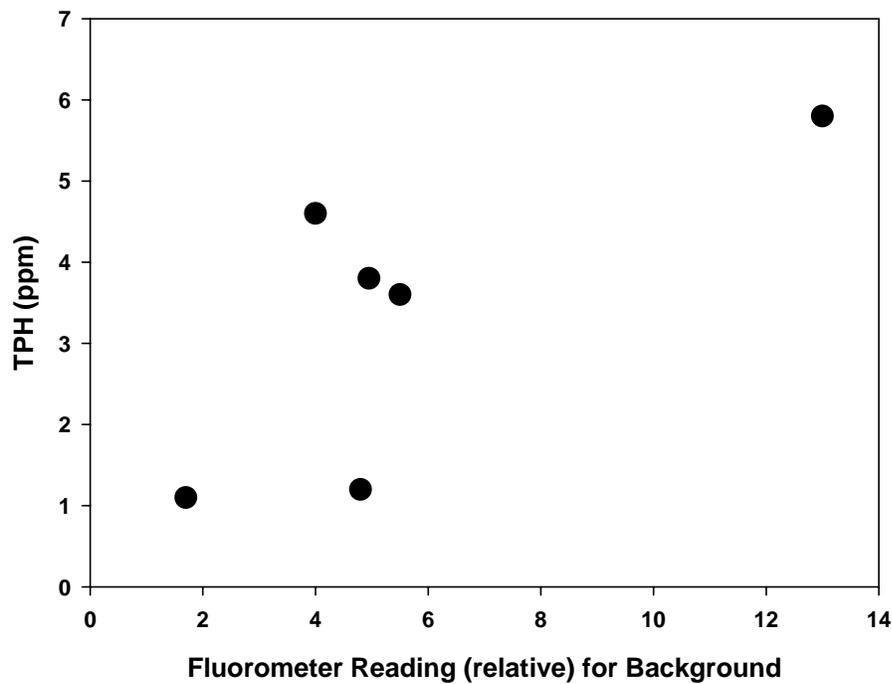
Figure 34   Comparison of TPH data with the fluorometric reading at the same time, this includes background and control test readings only
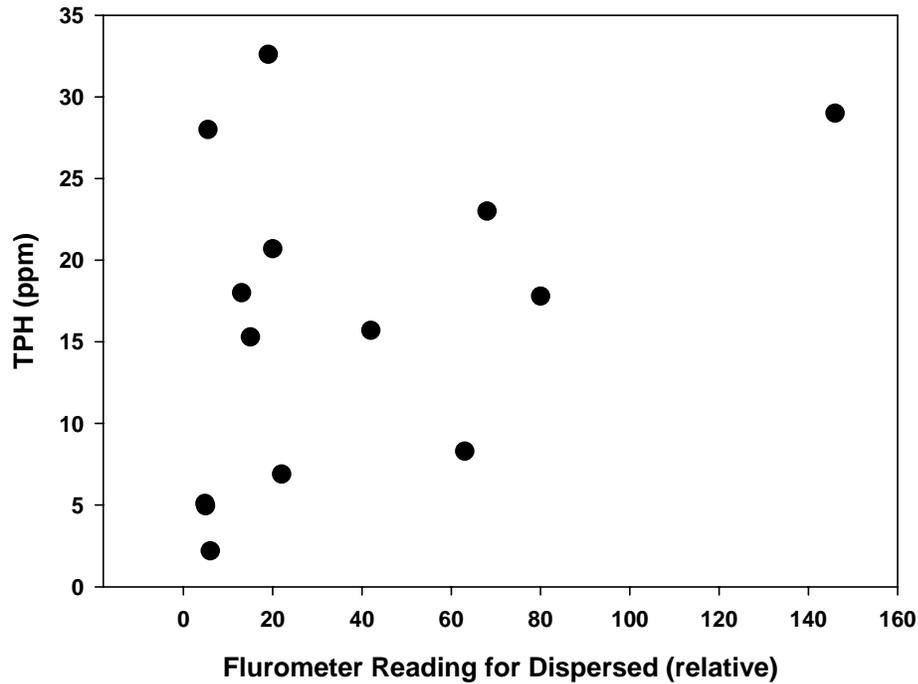
Figure 35   Comparison of TPH data with the fluorometric reading at the same time, this includes data only from the dispersed experiments. This shows the high scatter expected if one were to use fluorometer readings as an absolute measure.
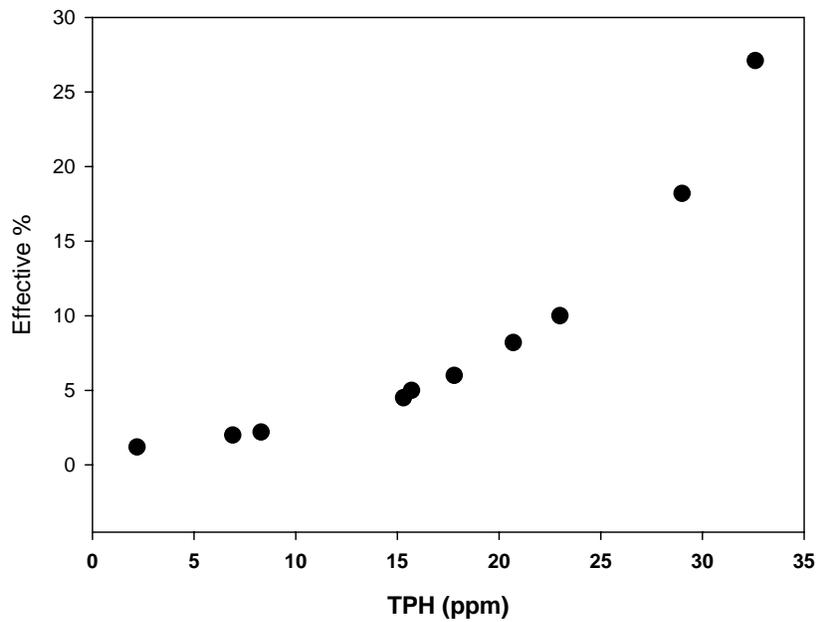

Figure 36   Prediction of Effectiveness % Assuming Exponential Distribution of the Oil to Sampling Depth of 1.5 m

3.   General Measurement of Dispersant Effectiveness in Tanks
        This section will deal with concerns about tank testing as raised by Fingas, the National
Academy of Sciences and by the Prince William Sound Regional Citizens' Advisory Council.

3.1   Items on Tank Testing from the Fingas Report
        A study on field testing provided an overview of the requirements for testing in the field
or large tanks (Fingas, 2002). The key points in this report, as they relate to tank testing, are
summarized here.

3.1.1   Mass Balance
        Mass balance is very difficult to achieve. In the 1993 North Sea dispersant trials, the
dispersed oil in the water column measured shortly after the dispersant treatment accounted for
only 1.8 to 3.5% of the initial volume of the oil released (Lunel, 1994a, b). Similarly, only 0.1 to
0.2% could be accounted for under the control slick, so the difference between the two was
emphasized, e.g., 16 to 27 times the amount of oil. It should be noted that the amount of oil
remaining on the surface was not accurately measured, nor are there techniques for performing
this precisely.
        Even in enclosed test tanks, it is very difficult to establish a mass balance. Brown et al.
(1987) reported on tank tests of dispersant effectiveness. Effectiveness was measured in two
ways: by accumulating the concentrations of oil in the water column by fluorometric
measurements and by removing and weighing oil on the surface. The results of these two
measurements, the amount of oil unaccounted for, and the difference between the two
measurements are shown in Table 4.

Table 4   Results of Tank Effectiveness Tests and Mass Balance Determinations

Dispersant Oil Combination	Results of Effectiveness by Different Methods		Percentage Unaccounted for	Percent Difference Between Methods
	Water Column - 3 hour	Surface removal		
1	9	53	38	44
2	24	77	-1	53
3	33	77	-10	44
4	9	76	15	67
5	11	39	50	28
6	14	43	43	29
7	16	16	68	0

        These data show that between 0 and 68% of the oil in the tank can be unaccounted for.
Furthermore, in two cases (2 and 3 in the table), the amount of oil was over-calculated. This
shows the difficulty in attaining a mass balance, even in a confined test tank. It was noted by
Brown et al. (1987) that the problem was accentuated by the heterogeneities in oil concentration
in the tank. Some of the unaccounted oil may have been in regions where the concentrations of
oil were higher than average. It should also be noted that surface removal exaggerated the
amount of oil dispersed from a factor of 1 to 8, with an average of 4 times.
        Another example of mass balance is the efforts of the SERF facility in Texas to account

for the oil in their tank (Page et al., 1999). Initially the group was able to account for only 10 to 33% of the oil originally placed in the tank. After considerable effort, the mass balance was improved to about 50 to 75%.

Mass balance is very important in test situations because the reliability of the data relates directly to the mass balance. If the mass balance is not accounted for, the numbers are meaningless. The above examples show that mass balance even in the more controlled tank tests can vary from a few percent and higher. If the measurement made does not account for the discrepancies in mass balance, then very high errors result. A typical example of this is using only the oil remaining on the surface as an indicator of dispersant effectiveness. Table 1 shows that in a very highly controlled test series, this number can be from 0 to 67% greater than the oil actually dispersed.

A question that must be dealt with is, as in the title of the Brown et al. (1987) paper, "where has all the oil gone?" In summary, the mass balance problems revolve around analytical problems; loss of oil through thin, invisible sheens; calculation difficulties; loss to tank walls and also in the presence of large heterogeneities in oil concentrations in the water column.

The recent round of OHMSETT tests again did not try to establish a mass balance. A mass balance is needed to properly assign effectiveness ranges to the oil dispersion effectiveness at given points in time. It is important here to stress that as the oil is continually rising, an effectiveness value is truly relevant only at a given point in time.

3.1.2 Proper Controls

A proper control is needed in order to accurately assess a dispersant field test. The control slick must be treated equally to the test slick in every respect except for the application of dispersant. The importance of the use of a control slick can be illustrated by two field dispersant trials, the treatment of emulsified oil at the *Exxon Valdez* oil spill and the Beaufort Sea Trial.

In the *Exxon Valdez* test of dispersant application to an emulsified oil slick, two slicks were chosen in the Gulf of Alaska, south of Seward. One was left as a control and the other was treated with large amounts of dispersant. Sampling was conducted from a ship and from aircraft, some equipped with remote sensing gear. The slicks were observed for about 6 hours. The dispersant failed to break the emulsion or to disperse the oil. Coincidentally, the control slick broke up somewhat after about 5 hours. This was probably due to its greater exposure to waves as it was up-sea of the treated slick. Without a control, the experimental results could have different interpretations.

In the case of the Beaufort Sea experiment, three slicks were laid and two were left as controls (Swiss et al., 1987). Two days later, three slicks were found at sea and each had the same orientation and general geometry as one on the first day of the experiment. The largest slick was the dispersed slick, although the oil content was not known. The interpretation of the results would have been quite different if there were no controls and if the slick had not been followed for days.

Controls were carried out for every test at OHMSETT during this February-March round, however, sometimes the controls were not carried out on the same days – hence this would result in different conditions. As was noted in some of the foregoing discussion, the energetic conditions changes very much from day to day in this tank.

3.1.3 Analytical Method

There are few analytical methods that can be used in field situations. Very early in the field testing program, fluorometers, particularly Turner fluorometers, were used. In early years before GPS, it was difficult to assess the position at which samples were taken. Now accurate GPS data coupled directly to fluorometer data can provide reasonable positional data for the fluorometric readings.

Some of the earlier trials used grab samples which were subsequently taken for analysis by UV or IR absorption (Fingas, 1989). These methods are notoriously inaccurate and have long since been replaced by gas chromatography methods. The use of fluorometry in the field has been examined in detail (Lambert et al., 2000, 2001a, 2001b). These studies show that fluorometry is a sensitive, but not necessarily accurate, means of oil determination. A fluorometer uses UV or near UV to activate aromatic species in the oil. The UV activation energy is more sensitive to the naphthalenes and phenanthrenes, whereas the near UV is more sensitive to large species such as fluorenes. The composition of the oil changes with respect to aromatic content as it weathers and is dispersed, with the concentration of aromatics increasing. Thus, the apparent fluorescent quantity increases in this process.

The calibration of fluorometric readings is critical (Lambert et al., 2000, 2001a, 2001b). The most important factor is how the oil is introduced to the fluorometer and the subsequent readings made. The physical factors that influence how much of the oil the fluorometer sees are the solubility and dispersibility of the particular oil and the subsequent evaporation/volatilization of the oil. A typical procedure is to add oil and dispersant to a container (e.g., a bucket) and then pump this through a flow-through fluorometer. Most often, that amount of oil added is taken as the amount of oil read by the fluorometer. The problem with this method is that most of the oil is not dispersed into the water column and that a large amount of soluble species are present, which would not be the case in the sea. Tests of these types of methods show that the fluorometer calibration curve is generally between 5 and 10 times greater than is the actual case. Thus, a reading of 15 ppm in the field is actually a reading of somewhere between 1.5 to 3 ppm. As this was generally the case in most past field trials, the actual ppm readings provided are far too high and cannot simply be converted into actual values.

A better method of calibrating a fluorometer is to use weathered oil (to about the percentage expected in the field) and introduce this to a closed container. After about 15 minutes of pumping, take a sample and analyze it by a good GC method (Lambert et al., 2001b). Then continue the addition, increment at a time and the sampling and analysis at each increment. After the numbers are collected, this will form a relatively good calibration curve. But because of the differences in chemical composition, this calibration curve could also give results as high as twice that of actual concentration.

The most reliable method of calibrating a fluorometer is to perform the above calibration procedure, but repeat it throughout the actual experiment. Almost simultaneous samples are relatively easy to collect from the fluorometer as the flow from the output of the fluorometer can be captured and preserved for later analysis. This is generally done when the fluorometer reading is relatively stable to ensure correspondence between the sample and the fluorometric value. The actual values and the previously prepared calibration curve can be compared to examine the differences in composition. It should be noted that this method was followed in the Protecmar V and VI trials in France. Examination of this data shows the lower oil concentrations actually achieved in a dispersant application.

The effects of running probes into the water column have not been fully examined. Several devices have been created in the past to examine the sub-surface water column, however the standby usually ends up being weighted hose. Tests show that there is significant retention on Tygon tubing and that pumping for up to one hour may be required to clear this line to the point of background measurements. Teflon tubing appears to show a lesser effect, although less testing has been conducted on this. There may be a serious effect on measurements depending on how the tubes or sampling devices are deployed. Tests conducted by the French during the Protecmar trials showed that there was a significant hull effect. This hull effect consisted of portions of the oil-in-water plume being driven downwards by a boat (Bocard et al., 1986). The solution found by the French group was to run a sampler far from the boat hull using a specially built device. Subsequently, a Canadian group ran a fixed probe in front of a sampling vessel to overcome the hull effect problem (Gill et al., 1985).

Another complication to sampling is the retention of surface oil on the sampling tubes, weights, and pumps that are lowered into the water. As the equipment goes through the surface slick, which is always present, some of the surface oil will be retained on the sampling equipment and will be read as oil concentration at that depth. Some experimenters have dragged the submerged sampling train to the next sample point to avoid this problem, however, this action may also drag oil on the outside of the sampling gear.

In summary, fluorometry is a practical technique for measuring concentrations of oil in the water column. The errors encountered all increase the apparent value of the oil concentration in the water column. Incorrect calibration procedures can distort concentration values up to 10 times their actual value. Correct calibration procedures have been defined (Lambert et al., 2001b) and involve performing accurate GC measurements both in the laboratory and in the field during the actual experiment. Furthermore, water sampling gear must be deployed in such a way as to avoid disturbing the underwater plume or carrying oil from one level or area to another.

Although water samples were taken by the experimenters at OHMSETT, they were often left for long periods of time, up to a day, and then the methods by which they were analyzed was not specified at the time this was written. The samples taken by the present author could be used to provide a more accurate means of tying the readings from the Turner fluorometer to actual values. It should be noted that each oil and whether the oil was chemically dispersed or not gave a slightly different reading. Thus there would be no universal calibration.

The hoses used for the fluorometers were automotive rubber hoses and may have retained significant amounts of oil.

3.1.4   Differential Plume Movement

The dispersed oil plume can move in a different direction than the surface slick (Fingas, 2000). Furthermore, its geometry generally has no relation to the surface slick. Locating sample probes and later trying to quantify the oil in the plume, the extent of which is unknown, become major problems. The best solution in the test tank is to let it equilibrate over 24 hours and then take samples at several points and average the results (Brown et al., 1987).

During this round of OHMSETT tests, the location of the slick was not a large issue as the fluorometers were at fixed locations on the bridge and there was no attempt to correlate the mass of oil with the visual slick. This would have been a better method of estimating dispersant effectiveness had it been done.

3.1.5 Time Lag and Length of Time Plume is Followed

There are certain time characteristics to the dispersion process that must be understood. First, the time to visible action after an actual dispersant application varies from 15 to 90 minutes. In the OHMSETT tank, the dispersant action occurs more rapidly due to the thinner slick put out and the close proximity of the dispersant application. The second item of timing to note is that the dispersant may continue to act for up to an hour after application. Thirdly, the movement and dispersion of the plume are generally slow, although the plume is generally visible for about 3 hours and is never visible past about 8 hours. Finally, the oil in the plume will resurface slowly over the next several hours. Since the resurfaced oil is usually thinner than the visibility limits, this will not be noticed unless there is little differential movement between the slick and the dispersed plume.

It is important to track and follow the un-dispersed oil, the control slick, and the dispersed plumes for as long as possible. The Beaufort Sea experiment is again a good example. Three slicks were laid and two left as controls (Swiss et al., 1987). Two days later, three slicks were found at sea and each had the same orientation and geometry as one on the first day of the experiment. The largest slick was the dispersed slick, although the oil content was not known. The interpretation of the results would have been quite different if the slick had not been followed for days.

Brown et al. (1987) noted that they had to measure their test tank after 24 hours to yield a reasonable result. Measurements before about 6 hours were found to be of little value.

This was, in the current authors' opinions, a serious deficiency in the current experimental plan. The experiments were terminated at 30 minutes and sweeping operations were then carried out. Generally, the first sweep operation was carried out within 45 minutes after the dispersion was started. This occurred during a time of rapid re-surfacing and one could observe an increasing thickness of sheen covering the entire tank. Even with sweeping operations there was oil on the tank the next morning. Typically there were thicker slicks downwind and the entire tank would often have a sheen over the entire tank. Figure 31 shows the time after dispersion that fluorometric values were taken. This shows that the peak fluorometric values occurred about 15 minutes after dispersion.

A better way to perform the experiments would be to put out the oil and then collect the remaining oil on the next morning to assess the effectiveness. The difference between picking up the control oil and the amount put out could serve as one indicator of effectiveness of recovery, although the information in the surfactant section below should be noted.

3.1.6 Mathematics of Calculation and Integration

Several examples of the effects of integrating and averaging incorrectly are given in a former paper (Fingas, 1989). This effect is exacerbated if no zero-oil concentration values are measured in areas outside of the plume. This was again illustrated by a figure in a recent paper (Fingas, 2002).

To date, there was no attempt to integrate oil values from the fluorometers taken during the recent OHMSETT trials. At least 3 fluorometer instruments could have been used to provide integration of oil in the plumes at a given time.

3.1.7 Lower and Upper Limits of Analytical Methods

The lower and upper limits of the analytical methods applied are another important

factor, especially in the field situations. If the lower limit is exceeded, the use of these values can result in serious errors as shown in Section 3.6. The lower analytical limit should be taken as twice the standard deviation or about 0.3 ppm for an older fluorometer or about 0.1 ppm for a newer unit. The use of double the standard deviation is standard laboratory practice and, in fact, newer practices sometimes advocate three times the standard deviation. Values below this should be taken as no-detect levels and not zero, but for calculation purposes, zero is the only choice.

The upper limit is equally important since the amount of oil in the water column could exceed the upper limit of some analytical procedures. If this were to occur in practice, the effectiveness would be underestimated. Fluorometers are non-linear in concentrations approaching or exceeding about 100 ppm oil-in-water and therefore very high concentrations might be missed, although such high concentrations have never been measured in the field or lab.

An issue might be the background levels of hydrocarbons in the tank at OHMSETT. Before the first run the background level was about a fluorometric reading of 2, after the first day the background level stayed at a level of about 4 to 5 fluorometric units on the Turner fluorometer. If dispersion was highly effective the readings should have constantly increased during the 4 days of trials and they did not. Typically, the background readings were the same during most of the trials. This is shown in Table 1, and illustrated in Figure 32.

3.1.8   Thickness Measurements

Several researchers have tried to estimate the amount of oil remaining on the surface by estimating thickness. One of the most common means to do this was by touching the surface with a sorbent. The amount of oil in the sorbent was determined by a number of means such as colorimetric or IR analysis. This was then presumed to relate directly to the oil thickness. Careful laboratory tests of these techniques have shown that they do not yield a good quantitative thickness result (Goodman and Fingas, 1988, Louchouarn et al., 2000).

The removal of oil from the surface is not necessarily total for several reasons. The edges of the sorbent may trap more oil, it may not be possible to calibrate the sorbents in the laboratory, and there may be poor extraction from the sorbent. Sorbents cannot be 'calibrated' in the laboratory because it is very difficult to get a uniform thickness of oil in a vessel in the lab. Oil often does not spread uniformly and can form blobs interconnected by sheen. Oil will be herded to one side even by the minimal air circulation in the laboratory. Also, most oils will form a concave lens with more oil on the edge.

The use of sampling tubes and other similar devices is fraught with similar difficulties. In summary, the thickness of oil on the surface of the test tank cannot be measured. Therefore, thickness cannot be measured as one way to determine dispersant effectiveness. Recent work by Bonner et al. (2002) has resulted in thin slick estimation methods as a means to examine mass balance.

The thickness of the oil on the tank during the recent OHMSETT trials was estimated by comparing the volume spilled to the visual estimate of area.

3.1.9   Behaviour of Oil with Surfactant Content

Oil behaviour other than dispersion that is strongly affected by surfactant content includes lesser containment capability and lower adhesion. These also affect the ability to measure oil remaining on the surface.

If the oil were to be contained, dispersant applied, and the remaining oil measured, errors as large as an order-of-magnitude would occur because the oil would pass under the boom. The value that is important is the critical velocity of containment. The critical velocity of containment is the velocity at which oil is lost under the boom through several failure mechanisms. The critical velocity of containment can be given by (Lee and Kang, 1997):

$$U_{cr} = \{2 [g\ T_{o/w}(\rho - \rho_o)]^{1/2} (\rho + \rho o)/(\rho\rho_o)]^{1/2} \qquad (1)$$

where:

U$_{cr}$ is the critical velocity

T$_{o/w}$ is the interfacial tension between oil and water

ρ is the water density

ρo is the oil density.

A very low ratio of dispersant or surfactant (about 1:100) will lower the interfacial tension to about half its previous value (Fingas, 2000). Thus, according to the equation, this would lower the critical velocity to about 0.7 of the previous value. If an experiment were set up that measured the oil left behind a containment boom where the oil was being held close to critical velocity, even a small amount of dispersant would release the oil. If the oil left were measured as the effectiveness of the dispersant, this effectiveness value would be highly exaggerated and would represent containment failure and not dispersion.

The other factor changed by adding dispersant to oil is the adhesion of the oil. While quantitative studies have not been performed on this, practical tests have shown that it is difficult, if not impossible, to remove the remaining oil after dispersant application using a sorbent surface skimmer (Brown et al., 1987). Such a skimmer relies on the adhesion of the oil to remove it from the water surface. Again, because of the effect of the dispersant, the oil remaining on the surface is likely to be underestimated, leading to an increase in the apparent effectiveness of the dispersant. While this effect is not felt to be as large as that of containment failure, it is significant nevertheless.

The combination of errors resulting from using contained oil slicks and lack of mass balance is at least a factor of 4 as noted in Brown et al. (1987) and is possibly as large as no dispersion at all even though the surface appears to be clear.

Although the method at OHMSETT had been changed to avoid direct use of booms, some effort was made to sweep the oils and then quantitatively recover these. The foregoing discussion clearly shows that this is a futile effort as the surfactant content will not be conducive to oil sweeping. Further, it was clearly observed that the use of the fire hoses re-dispersed some of the oil due to its surfactant content. This is illustrated in Figure 7.

The less adhesive nature of surfactant-treated oil also leads to poor recovery of that oil compared to untreated oil. One must be careful not to make a direct comparison, however, the longer the oil has been on the water, the less surfactant in it, so a comparison at the 24 hour level is likely to be less disparate than at the one-hour point.

3.1.10 Surfactant Stripping

It is relatively well known that there is an exchange of surfactants between the target droplet and the surrounding water (Heimenz and Rajagopalan, 1997; Fingas, 2006). This results

in de-stabilization of the emulsion. In situations where the water is a large ratio to the droplet concentration, surfactant is largely lost and destabilization is relatively rapid. In laboratory tests, the ratio of the oil to water then becomes important in simulating the conditions at sea. In the swirling flask test used here, the oil-to-water ratio is 1:1200 which may be somewhat representative of a more open situation. The relationship of the energy, the dilution, and other factors in the laboratory test to open water conditions is not well understood at this time.

As noted above, consideration of resurfacing was not done at OHMSETT during this round of testing. Further, experiments were terminated at 30 minutes, with sweeping taken place before about 45 minutes. Figures 10 to 14 show a time progression in resurfacing after a dispersant test in OHMSETT.

3.1.11 Recovering Surface Oil

Some experimenters have tried to recover surface oil in an attempt to directly determine effectiveness by presuming that the entire remainder is dispersed. This is incorrect because the loss from the surface includes the amount evaporated, the amount in very thin (often invisible) slicks, the amount that is physically unrecoverable, oil adhered to booms or other surface objects, errors in the amounts of all the oil compartments, and oil that is simply unaccounted for.

Controlled tests in a test tank have shown that the difference between oil accounted for in the water column and the amount on the surface can vary from 0 to 80% (Brown et al., 1987; Brown and Goodman, 1988). This again represents the typical error of trying to perform a surface-only measurement. Once oil is treated with dispersant, it becomes less adhesive and therefore much more difficult to recover from the surface using typical skimmers and sorbents. This fact can contribute to the error.

Some experimenters have recovered surface oil (Page et al., 1999, Tissot et al., 2000). While a very good experimental procedure, it should be noted for the reasons described above, that this number is fraught with error and great care must be taken to ensure good recovery as well as subsequent interpretation of the results.

Again, this was not considered in the recent test at OHMSETT. After every dispersant trial, oil was to be recovered, but as noted above, one could see re-dispersion and resurfacing right behind the sweeping operation. Further the ratio of the area between the slick and the rest of the tank was that was used is about 1:60. So if the approximately 1 mm slick is spread out over the entire area with no or little dispersion, the slick thickness would be approximately 15 micrometres. The oil appearance on some occasions may have indeed been that thick.

3.1.12 Background Levels of Hydrocarbons

The background level of hydrocarbons is important for several reasons, some of which are noted above. A good background value is needed first to subtract concentration values and second to know when to terminate integration of the spill. It is suggested that the same techniques, along with the grab samples for calibration, be applied in the area before dispersant application and also after, if practical, to determine the range of background values in the area. These values can then be judged for use in correcting the values and for ending integration.

Another problem associated with the background levels is that hydrocarbons will adhere to sample tubes and equipment. This will result in higher than background values at the end of a run through the plume. There is no easy solution to the problem. One of the solutions is to examine the values and look at where the signal drops off significantly, probably at the end of

the plume, and use this value as a 'corrected' background. Some experimentation at the scene of the measurements can be used to define the carry-though of hydrocarbons in the system. It should be noted that, if the carry-through is not corrected for, gross errors could occur in the amount of oil calculated.

The background levels at the OHMSETT trials appeared to remain about the same after the first day of testing. They were recorded and would presumably be taken into account for the reports that would follow. Figure 32 shows that the background fluorometer values remained relatively constant throughout the experiments over 4 days. This indicates that the dispersed oil did not stay dispersed and the background remained relatively stable.

3.1.3   Fluorescence of the Dispersant

While the dispersant mixtures, per se, should not fluoresce, most of them show a significant signal when placed in a Turner Fluorometer (Lambert et al., 2001a). The reason for this fluorescence is the reflection of UV and other light into the detection path and the actual fluorescence of small amounts of fluorescent material in the dispersant or picked up through the system. Most experimenters have ignored the fluorescence of the dispersant in the past because it was presumed that there was no contribution. Furthermore, in an actual application or experiment, the pickup of even a small amount of oil by the dispersant will result in a significant signal. While this is difficult to correct for, one way is to correct all the readings to accurate GC analytical results.

The fluorescence of the dispersant would not be taken into account. It would have been useful to conduct a dispersant-only experiment to see how this would produce readings on the instruments used during the test.

3.1.14   Herding

Herding is the phenomenon that occurs when the oil is pushed aside by the dispersant (Merlin et al., 1989). This occurs because the spreading pressure of the dispersant can be more than that of the oil slick, especially when the oil slick is thin. The dispersant must directly contact the water surface in order to cause herding. This readily occurs with thin oil slicks because aerially applied droplets are generally 300 to 1200 µm in size, while the oil slick could easily be as thin as 100 µm (appearing as a thick slick) (Merlin et al., 1989).

There are several problems with herding, the major one being that often little dispersion occurs if the oil is herded. The larger droplets will land on the surface first and cause herding if the conditions are correct and then much of the dispersant that follows in smaller droplets can land directly on the water.

Herding was observed during the recent tests at OHMSETT, however, because the dispersant was applied at such close proximity, herding should not have been a factor in aspects of this test.

3.1.15   Heterogeneity of the Slick and Plume

As slicks are rarely homogeneous in thickness, the dispersant applied may be insufficient in areas or may break through and cause herding in other areas (Merlin et al., 1989, Payne et al., 1993). Furthermore, slick heterogeneities will result in heterogeneities in the dispersant plume, which will again result in difficulties integrating the plume. Using peak values will result in over-estimating the dispersant effectiveness and vice versa. This difficulty can be mitigated by

36

integrating very small areas of the sub-surface plume. In tanks, this can be overcome somewhat by continuing circulation for 24 hours and then measuring (Brown et al., 1987).

The fluorescent values were very heterogeneous during the OHMSETT tests and as tests were concluded within 30 minutes, homogeneity would not have been achieved. It is not known how the fluorescence data would be used in producing a quantitative report.

3.1.16 True Analytical Standards

There now exist certified laboratories that use certified petroleum hydrocarbon measurement techniques. These should be used for tank studies. One of the most serious difficulties in older field and tank trials occurred when inexperienced staff tried to conduct chemical procedures. Analytical methods are complex and cannot be conducted correctly without chemists familiar with the exact procedures.

Furthermore, field instrumentation such as fluorometers require calibration using standard procedures and field samples during the actual trial. These samples must be taken and handled by standard procedures. Certified standards must be used throughout to ensure good Quality Assurance/Quality Control (QA/QC) procedures.

The current OHMSETT tests did not use certified analytical procedures or quality control procedures.

3.1.17 Weathering of the Oil

Dispersant effectiveness decreases with weathering of the oil. The weathering trend is characteristic of that oil, but every oil shows this decrease (Fingas et al., 2001). The oil used for any dispersant test should be weathered to an extent that it would represent a realistic situation, e.g., equivalent to about 1 day. The weathering of the oil will also assist in maintaining a more correct mass balance.

Some of the oil was weathered in three ways, by air sparging, by placement on the OHMSETT tank with breaking waves and by placement on the OHMSETT tank with low energy. The fresh ANS used during the demonstration day on day 1 was not weathered.

3.2 The National Academy Points on Tank Testing

The National Academy of Sciences reviewed a variety of aspects of dispersant testing in 2005 (NAS, 2005). The major recommendation stated: " Relevant state and federal agencies and industry should develop and implement a detailed investigation of wave-tank studies that specifically address the chemical treatment of weathered oil emulsions" (NAS, 2005, p. 7). Specific recommendations include: a)"wave-tank tests should be judged primarily on the basis of their additional realism – over laboratory studies – that is incorporated into their test design while remaining sufficiently controlled to allow replication and collection of quantitative information" (NAS, 2005, p. 91);   It is felt that this recommendation was not fully met in the current OHMSETT tests as there was no mass balance attempts and thus little control to allow replication. A further complication is that OHMSETT is subject to variable winds and these cause forces on the water surface that are not repeatable. Sometimes the winds predominate in determining the slicks movement and this also influences dispersion.
b) "Structural effects ….wave-tank tests that can simulate oil weathering as would occur at sea … should be conducted. These studies should also investigate the evolution of the physical-chemical characteristics and the operational dispersability, as oil weathers in a slick" (NAS,

2005, p. 91); During the present tests there was no effort to simulate at-sea dispersion. Dispersants were applied directly to the oil a few feet away from the laying of the slick. While this is not realistic, this is also the only way to maintain control of where the dispersant is applied and ensure that it hits the oil. It also eliminates this as a variable from the test.

One way to avoid this lack of reality would be to test the effect of dispersant application in separate tests. This should be done in the future.

c) "In this regard, the formation of water-in-oil emulsions is particularly important in inhibiting dispersant effectiveness. To date, large wave tanks have not been used to examine the performance of dispersants on water-in-oil emulsions generated from weathering of oil on the sea surface. Ideally these emulsions could be generated in adjacent wave tanks or other systems that can provide continuous mixing of oil and water for hours to days. The effectiveness of dispersants on these blended emulsions should be tested under more realistic field conditions. The rheological and chemical properties of the test emulsions should be characterized and compared to data from emulsified oil samples collected during actual oil spills. The dispersability of the artificially generated emulsions should be tested over a range of temperatures, including cold, sub-arctic conditions. If this approach is successful, it could be expanded to investigate dispersant effectiveness on water-in-oil emulsions in the presence of ice." (NAS, 2005, p. 91-92): Tests were conducted on emulsions in a previous test. The effectiveness of dispersants on these was not good.

d) "Dispersant application …Dispersant application efficiency is affected by dispersant droplet size and velocity. If this aspect of operational effectiveness is to be investigated in wave tanks, the dispersant application system should simulate the droplet size distributions and impact velocities that are characteristics of specific application methods …. These parameters should be measured to verify that the desired characteristics have been achieved. The dispersant distribution over the target area also should be characterized at some point during these tests. …. Although it is unlikely that the characteristics of real dispersant application systems can be accurately reproduced in a wave tank …, measurement of effectiveness as a function of dispersant droplet-size distributions and impact velocity may provide information that can be used as input to dispersant effectiveness models" (NAS, 2005, p. 92);

Dispersant application parameters were not included as parameters in these tests.

e) "Mixing energy …. Mixing energy is one of the most important factors determining dispersant efficiency. …. As with effectiveness tests at laboratory scales, mixing energy should be measured over a range of mixing energies that span the range that can be realistically expected in the environment of interest. The wave energies used in the experimental system should be scaleable to actual sea states." (NAS, 2006, p. 92);

An acoustic Doppler velocimeter was used in the experiments. This answers a part of the questions, eg. wave height and some information on the waves. It does not measure specific energy. There is a wide variance of surface conditions at OHMSETT due to high variance in winds and wind directions.

f) "Coalesence and resurfacing of dispersed oil droplets….The effects of temperature and ice on dispersed oil droplet size, coalescence and resurfacing should be investigated to evaluate

38

the range of conditions under which dispersants are likely to be effective, and these investigations would probably be realistic in very large wave tanks where dilution more closely approximates natural conditions." (NAS, 2005, p. 93);

The effect of coalescence and resurfacing was not investigated during these tests. Efforts by the current author were somewhat focussed on investigating these phenomena in the absence of these in the experimental plan. Very significant re-surfacing was observed in all dispersant tests (five of these). Weathered oils showed significant re-surfacing very quickly after the initial dispersion. The oils that showed very rapid resurfacing were 10% weathered Endicott and 15% weathered ANS. These were dispersed in experiments 10 and 9, respectively. Once could see slicks along the downwind walls within 45 minutes after the initial dispersion.

3.3 Points Raised by PWS RCAC

In addition, there were several concerns raised by PWS RCAC:
1. heating of the oil,
2. artificial weathering of the oil,
3. use of booms in testing field,
4. use of booms in testing field,
5. re-surfacing of the oil,
6. tank contamination,
7. use of oils which are not typically transported,
8. herding, and
9. uncontrollable natural factors.

4. Further Analysis of the OHMSETT Trials

Table 5 shows information gathered during the trials. This includes temperature, etc.

Table 5 Details of the Dispersant Tests at OHMSETT

Test	Date	Oil type	Dispersant	Visual Results	Water Temp °C	Oil Temp °C	Fluoro-meter Peak	Oil Re-surfaced	Fluorometer Background	Time of sample runs	Peak Fluorometer at sample run	Length of oil slick (ft)	Estimated width of slick	Estimated Area behind Bridge	Estimated average dispersant width	Estimated Dispersion area (ft2)	Estimated Dispersion volume	Volume in M cubed	Concentration if evenly distributed (ppm)*	Ratio of concentration to Peak*
2	28-Feb	fresh ANS	control	good natural dispersion	0	-2.2	7		1.7	0	1.7	100	6	600	20	2000	2000	60	70	30
										7	7									
										15	4.1									
3	28-Feb	fresh ANS	1:10	20 to 40%	-1.7	-1.6	80	most	1.7	0	1.7	100	6	600	10	1000	6000	170	400	10
										9	42									
										15	80									
										23	30									
										29	3									
										34	sweep									
										84	significant oil on surface									
4	01-Mar	10% Pt. Mc	control	some natural dispersion	-0.3	-3.3	18		4.7	0	4.6	100	6	600	8	800	800	20	200	40
											18									
5	01-Mar	16% ANS	control	some natural dispersion	-0.5	-2.8	28		4.7	0	4.7	100	6	600	8	800	800	20	200	20
											28									
6	01-Mar	16% ANS	1:20	50%	2.2	-2.2	170	most	4.7	0	4.7	100	6	600	8	800	4800	130	600	10
										10	63									
										15	216									
										27	148									
										45	sweep									
										24 hours 10 to 20 gallons on tank surface										
7	02-Mar	11% V Endicott	control	little natural dispersion	-1.6	-1.6	5.1		4.3	0	4.3	100	6	600	20	2000	2000	60	70	220
										10	5.1									
8	02-Mar	fresh Endicott	control	little natural dispersion	0	0	5		4.3	0	4.3	105.5	6	633	20	2110	2110	60	70	250
										6	4.8									
										16	5									
9	02-Mar	15% ANS	dispersant	50%	-0.2	-1.6	169	most	4.7	0	4.7	106.4	6	638.4	8	851.2	5107.2	140	500	10
										8	169									
10	03-Mar	15 % ANS	dispersant	50%	-4.4	-4.4	72	most	4.6	0	4.6	102	6	612	20	2040	12240	340	200	10
										6	53									
										13	72									
										45	sweep	about 10 gallons on surface								
										60	third sweep	about 5 gallons / sweep								
11	03-Mar	10 % Endicott	dispersant	40%	-1.5	-2.2	25	most	7.1	0	7.1	104	6	624	10	1040	6240	170	400	60
										4	25									
										12	25									
										46	sweep	5 gallons along wall								

* Indicates that this estimation applies to actual TPH

Table 5 is described as follows: column 1gives the designated test number, column 2 the date on which the test was held, the oil type is listed in column 3 and the test type in column 4. The observers visual results are noted in column 5, the water temperature as taken by the OHMSETT operators is given in column 6, the oil temperature in column 7 and the peak fluorometer reading in column 8. The observer's estimate of the amount of oil surfaced in column 9, the fluorometer background reading in column 10 and the time (after dispersion) of the sample run is given in minutes in column 11. Column 12 gives the peak fluorometer reading during the relevant sample run. The length of the oil slick (in feet) taken from the lineal readings on the bridge are given in column 13, the width of the slick is estimated from is passage under the bridge and is given in column 14. These slick dimensions are then used to calculate areas, given in column 15, combined with the estimated dispersion width (the average width of the dispersed oil near the surface) in column 16 to yield the estimate dispersion area in column 17 and the estimated dispersion volume (in cubic feet) in column 18 and converted to cubic metres in column 19. The expected concentration of the oil is given in column 20, assuming that this oil is evenly distributed throughout this volume. Column 21 then gives the ratio of the peak measured concentration (from the fluorometer readings adjusted to the measured values) to the calculated concentration.

Column 21 shows the ratio of the measured concentrations to the peak concentrations. These values are fractions of the peak concentration ranging from 1/3 to 1/100. This would indicate that effectiveness might be expected to range no higher than 1 to 33%.

5. How a Test Tank Could be Used to Measure Dispersant Effectiveness

In part 3 of this paper, the following 18 factors were noted as being relevant to the proper measurement of dispersant effectiveness in a tank.

1. Mass balance
2. Proper controls
3. Analytical method
4. Differential plume movement
5. Time lag and length of time plume followed
6. Mathematics of calculation and integration
7. Lower and upper limits of analytical methods
8. Thickness measurement
9. Behaviour of oil with surfactant content
10. Surfactant stripping
11. Recovering surface oil
12. Background levels of hydrocarbons
13. Fluorescence of dispersant
14. Herding
15. Heterogeneity of slick and plume
16. True analytical standards
17. Weathering of the oil
18. Temperature and salinity

Most of these factors can be taken into consideration or problems avoided if the testing follows the extensive studies of the past. In particular, the tank test studies described by Brown et al. (1987) dealt with several of these issues and showed how dispersant effectiveness could be measured in a test tank. The calibration of tank hydrodynamics and calculation of mass balance are also dealt with extensively in Bonner et al. (2002).

The suggested method is that the fresh, unweathered oil be placed in the test tank. Weathering should be allowed to occur for 12 to 24 hours after placement. Containment of the oil should be used only to enhance contact, not as an analytical method. After the oil is placed, dispersant is applied at the desired ratio. Approximately 6 hours after the application, a series of fluorometers are run through the tank at depths of about 1 m apart and at various spacings across the cross-section. During the sampling, discrete water samples are taken from the fluorometers and the exact readings of the fluorometer recording (best done electronically) during the time that samples are taken. These samples are then correctly preserved and analyzed for TPH. The calibration curve for the fluorometer is derived from these measurements. It is important that sampling, preservation, and analysis be done using certified methods, by certified chemists, and in certified labs.

The 6-hour sampling data are compared to the 24-hour sampling data which are taken in exactly the same manner. The effectiveness is then estimated from integration at the 24-hour mark. The 3-hour sample period is for checking and would be conducted only in the first test or two.

After the 24-hour period, the oil on the surface is driven to one corner where it is recovered with a skimmer for weighing. A mass balance is then achieved by comparing the oil recovered in the whole tank, the amount estimated on the walls, and the amount in the water column. The oil in the water column is the only amount dispersed. The mass balance is used to

judge the validity of the particular run and not the effectiveness of a specific dispersant.

The tank filtration system is turned off during the experiment and is turned on only after the surface oil is recovered. Only about four experiments can be done before all the water must be changed due to the presence of surfactants.

The wave maker can be left on for the full 24 hours.

The hydrocarbon background is also determined in the same way as the dispersant concentration and this is done just before the dispersant experiment.

This method will overcome difficulties and ensure that the 17 critical factors are taken into consideration.

An alternative to this test, although not as robust, would be to use multiple test units such as flourometers. The fluorometers would be adjusted to actual values by taking samples and analyzing them according to certified procedures. At least 4 fluorometers are used, six would be better. The fluorometers are arranged about 2 metres apart with depths of 0.5, 1 and 1.5 m. The data are recorded with position along the tank so that true integration can be achieved. After the values are adjusted to the analytical results an integration of the concentrations can be performed. The results should be reported with time and the experiment should run at least to 6 hours.

5.1   Additional Information on Tank Testing

It is important during any experiment to alter only one variable at a time. Otherwise, the outcome may be a result of the combination of the inputs, leading to confusion as to what the effect was of a given variable.

The experiences of Bonner et al. (2002) show that there are major losses of oil in three areas that historically have not been considered in performing a mass balance. These are adhesion to walls, adhesion to sediments, and formation of invisible slicks. These three losses can account for over 50% of the oil loss in certain cases. Methods for the measurement of each of these oil losses were developed and applied. The adhesion to the walls was measured by placing strips of wall material into the test tank and later removing and quantifying the oil on these strips. It was noted that the age and conditions of these strips were important as the more weathered tank would hold more oil than the newer, unweathered strips.

Bonner et al. (2002) noted that the sediment (even that from the apparently clean tank bottom) must be collected and oil content measured. Oil in thin slicks was measured using a solid-phase extraction disk held by vacuum to retain both the disk and oil adhered to the disk.

Another distinct issue is that of scaling of wave energy (Bonner et al., 2002). Dispersant effectiveness is largely affected by energy inputs and therefore scaling and control of this in a test tank is an important factor. In the laboratory, energy input to the dispersant/oil mixture can be very tightly controlled, but in a test tank it could be highly variable and subject to influences such as winds, etc. Bonner et al. (2002) provide mathematical tests of energy scaling and means to estimate wave reflection, which is another source of variability.

The use of containment while dispersant effectiveness is being measured in a test tank should be reviewed. There is no doubt that this increases the turbulent energy at the boundary between contained and uncontained oil. Since this would not occur at sea or in most laboratory tests, this extra high energy may result in atypical results.

6   Summary of the OHMSETT Tests

Ten dispersant tests were observed, 5 dispersant tests and 5 control tests with Alaskan oils. The dispersant tests showed good initial dispersion and subsequent observation showed much of the oil from these tests re-surfaced, about half within about one to two hours and most of it by next morning.

The testing method was viewed with respect to concerns raised earlier from observing other test. First, a report sponsored by PWS RCAC, had raised 17 concerns about dispersant tank testing. The following are critical factors that need to be considered and included in any test for measuring the effectiveness of dispersants in future tank tests. These factors are reviewed in this assessment.

1. Mass balance
2. Analytical method
3. Time lag and length of time plume followed
4. Behaviour of oil with surfactant content
5. Surfactant stripping
6. Recovering surface oil
7. Background levels of hydrocarbons
8. Fluorescence of dispersant
9. True analytical standards

The National Academy of Sciences reviewed dispersant testing and noted the following concerns which still require addressing at OHMSETT:

1. wave-tank tests should be judged primarily on the basis of their additional realism – over laboratory studies – that is incorporated into their test design while remaining sufficiently controlled to allow replication and collection of quantitative information.
2. studies should also investigate the evolution of the physical-chemical characteristics and the operational dispersability, as oil weathers in a slick.
3. effectiveness of dispersants on blended emulsions should be tested under more realistic field conditions. The rheological and chemical properties of the test emulsions should be characterized and compared to data from emulsified oil samples collected during actual oil spills. The dispersability of the artificially generated emulsions should be tested over a range of temperatures, including cold, sub arctic conditions.
4. measurement of effectiveness as a function of dispersant droplet-size distributions and impact velocity should be carried out if this parameter is of consideration.
5. mixing energy should be measured over a range of mixing energies that span the range that can be realistically expected in the environment of interest. The wave energies used in the experimental system should be scaleable to actual sea states. and
6. The effects of temperature and ice on dispersed oil droplet size, coalescence and resurfacing should be investigated.

In addition, there were several concerns raised by PWS RCAC which remain to be addressed in future tests at OHMSETT:

1. re-surfacing of the oil,
2. tank contamination,
3. use of oils which are not typically transported, and

4. uncontrollable natural factors.

Although many of the initial concerns were taken into account in re-designing the protocol for the current trial round, this report shows that there remain some concerns:
1. The experiment is ended at the peak of dispersion and before significant re-coalescence occurs. Extensive re-surfacing of the oil can readily be seen after the experiment is terminated and within 1 hour of the start of the experiment.
2. No mass balance is attempted and data collected are not used to attempt mass balance.
3. Some oil was collected to presumably determine amount dispersed, however this was always collected within 45 minutes of the trail and major re-surfacing occurred after this collection. The cleaning and spraying action caused a great deal of re-dispersion. Further it would be impossible to be quantitative as the sweeping operation is not quantitative and there is much oil around the tank before and after the sweeping operation.
4. The use of instrumentation was increased several-fold, however calibration of these methods and use of data remains at the initial level. and
5. There was no quantitative measure of sea energy. Wave data was collected as before with somewhat more precision.

Procedures are given that take into account lessons learned during the detailed work conducted at the Imperial Oil tank in Calgary, Alberta and the SERF tank in Corpus Christi, Texas. Alternatives to testing more quantitative are given. These procedures will make it possible to reasonably estimate the effectiveness of dispersants in a large test tank. Ten tests of dispersion, natural and chemically-assisted were observed in the OHMSETT facility. A comparison of the protocol compared to concerns previously expressed noted that many of the literature recommendations have not been adopted. In particular there are several points that need attention:
1. Quantitative method of determining effectiveness,
2. Correct analytical procedures,
3. Necessity to take measurements for at least 6 hours, and
4. Ability to recover surfactant-treated oil

7.   References

Bocard, C., G. Castaing, J. Ducreux, C. Gatellier, J. Croquette and F. Merlin, "Summary of Protecmar Experiments, The French Dispersant Offshore Trials Program", *Oil and Chemical Pollution*, Vol. 3, pp 471-484, 1986/87.

Bonner, J., C. Page and C. Fuller, "Meso-Scale Testing and Development of Test Procedures to Maintain Mass Balance", *Spill Science and Technology*, in press, 2002.

Brown, H.M. and R.H. Goodman, "Dispersant Tests in a Wave Basin: Four Years of Experience", in *Proceedings of the Eleventh Arctic Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 501-514, 1988.

Brown, H.M., R.H. Goodman and G.P. Canevari, "Where Has All the Oil Gone? Dispersed Oil Detection in a Wave Basin and at Sea", in *Proceedings of the 1987 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp 307-312, 1987.

Decola, E. and M. Fingas, *Observer's Report: MMS Cold Water Dispersant Tests, Ohmsett Facility, 28 February – 3 March, 2006*, Prince William Sound Regional Citizens' Advisory Council, 25 p., 2006.

Fingas, M.F., "Field Measurement of Effectiveness: Historical Review and Examination of Analytical Methods", in *Oil Dispersants: New Ecological Approaches*, STP 1018, L.M. Flaherty (ed.), American Society for Testing and Materials, Philadelphia, PA, pp 157-178, 1989.

Fingas, M.F., "Use of Surfactants for Environmental Applications", in *Surfactants: Fundamentals and Applications to the Petroleum Industry*, Laurier L. Schramm, (ed.), Chapter 12, Cambridge University Press, pp 461-539, 2000.

Fingas, M.F., "A White Paper on Oil Spill Dispersant Field Testing", Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, AK, 40 p., 2002.

Fingas, M.F., B. Fieldhouse, L. Sigouin, Z. Wang and J. Mullin, "Dispersant Effectiveness Testing: Laboratory Studies of Fresh and Weathered Oils", in *Proceedings of the Twenty-fourth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 551-556, 2001.

Fingas, M.F., *Stability and Resurfacing of Dispersed Oil,* Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 83 p., 2006.

Gill, S.D., R.H. Goodman and J. Swiss, "Halifax '83 Sea Trial of Oil Spill Dispersant Concentrates", in *Proceedings of the 1985 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp 479-482, 1985.

Goodman, R.H. and M.F. Fingas, "The Use of Remote Sensing in the Determination of Dispersant Effectiveness", *Spill Technology Newsletter*, Vol. 13, No. 3, pp 55-58, 1988.

Heimenz, P.C. and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, Inc., New York, NY, 1997.

Lambert, P., B. Fieldhouse, Z. Wang, M.F. Fingas, M. Goldthorp, L. Pearson and E. Collazzi, "Preliminary Results from the Laboratory Study of a Flow-Through Fluorometer for Measuring Oil-in-water Levels", in *Proceedings of the Twenty-third Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 69-98, 2000.

Lambert, P., M. Goldthorp, B. Fieldhouse, Z. Wang, M. Fingas, L. Pearson and E. Collazzi, "A Review of Oil-in-Water Monitoring Techniques", in *Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp 1375-1380, 2001a.

Lambert, P., B. Fieldhouse, Z. Wang, M. Fingas, M. Goldthorp, L. Pearson and E. Collazzi, "A Laboratory Study of Flow-through Fluorometer for Measuring Oil-in-Water Levels", in *Proceedings of the Twenty-fourth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 23-45, 2001b.

Lee, C.M. and K.H. Kang, "Prediction of Oil Boom Performance in Currents and Waves", Advanced Fluids Engineering Research Centre, Phang, Korea, 24 p., 1997.

Louchouarn, P., J.S. Bonner, P. Tissot, T.J. McDonald, C. Fuller and C. Page, "Quantitative Determination of Oil Films/Slicks from Water Surfaces Using a Modified Solid-phase Extraction (SPE) Sampling Method", in *Proceedings of the Twenty-third Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp. 59-68, 2000.

Lunel, T., "Dispersion of a Large Experimental Slick by Aerial Application of Dispersant", in *Proceedings of the Seventeenth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 951-966, 1994a.

Lunel, T., "Field Trials to Determine Quantified Estimates of Dispersant Efficiency at Sea", in *Proceedings of the Seventeenth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 1011-1021, 1994b.

Merlin, F., C. Bocard and G. Castaing, "Optimization of Dispersant Application, Especially by Ship", in *Proceedings of the 1989 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 337-342, 1989.

NAS, *Oil Spill Dispersants: Efficacy and Effects,* National Academy of Sciences, Washington, D.C., 2005.

Page, C., P. Sumner, R. Autenrieth, J. Bonner and T. McDonald, "Materials Balance on a Chemically-Dispersed Oil and a Whole Oil Exposed to an Experimental Beach Front", in *Proceedings of the Twenty-second Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 645-658, 1999.

Payne, J.R., T. Reilly, R.J. Martrano, G.P. Lindblom, M.H. Kennicutt II and J.M. Brooks, "Spill of Opportunity Testing of Dispersant Effectiveness at the Mega Borg Oil Spill", in *Proceedings of the 1993 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp 791-793, 1993.

Swiss, J.J., N. Vanderkooy, S.D. Gill, R.H. Goodman and H.M. Brown, "Beaufort Sea Oil Spill Dispersant Trial", in *Proceedings of the Tenth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 307-328, 1987.

Tissot, P., C. Fuller, P. Louchouarn, J. Bonner, S. Dellamea and D. Bujnoch, "Quantitative Method for Surface Oil Measurement and Recovery Based on a New Type of Low Impact Skimmer", in *Proceedings of the Twenty-third Arctic Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, ON, pp 353-366, 2000.

Wang, Z., C. Yang, M. Fingas, P-Y. Zhang and W. Sun, "Lab Validation Study for Reference Method for Canada Wide Standard for Petroleum Hydrocarbons in Soil - CCME Tier 1 Method", *Transactions of the Non-ferrous Metals Society of China*, *Vol. 14* (1), pp. 1003-6326, 2004.