CALM SEA APPLICATION OF DISPERSANTS

For

**U.S. Department of the Interior
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By

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Disclaimer

Executive Summary

Oil spill dispersants can be applied to spilled oil in calm sea conditions, but may not cause immediate rapid dispersion of the oil if there is insufficient wave energy. If the oil does not disperse shortly after the application of a dispersant, it is thought that the surfactants, the 'active ingredients' in dispersants, might partition (or 'leach') out of the dispersant-treated oil and into the sea over a period of time, thus reducing the effectiveness of the dispersant application. The objective of the work described in this report was to determine the period of time for which the dispersants would remain with the oil in calm conditions and still be effective when the sea state increases and rapid dispersion can occur.

The work was conducted at three scales:

(i) Laboratory scale tests involving "soaking" dispersant-treated oil slicks on water in aquaria for up to 48 hours, then measuring the change in dispersibility of the slick over time by testing samples of the oil using the Warren Spring Laboratory (WSL) dispersibility test method.

(ii) Tank testing in the S L Ross 1m x 1m x 11 m wave tank, Ottawa, Ontario.

(iii) Large scale tests at the National Oil Spill Response Test Facility (Ohmsett) in Leonardo, New Jersey.

Small-scale laboratory tests were conducted in May and June 2005. The work involved allowing dispersant-treated oil slicks to lay on seawater in calm conditions for up to 48 hours, testing the dispersion tendency of the treated slick at regular time intervals. The oils tested were Alaska North Slope and Ewing Bank Block 873 crude oils and Intermediate Fuel Oil 30 (IFO 30). Results indicated that dispersant performance declined rapidly with time. Dispersant performance on the crude oils that were treated with less than 1 part of dispersant for 20 parts of oil declined quickly during the first 12 hours. Testing with a more viscous fuel oil (IFO 30) showed a slower loss of effectiveness. Most, but not all, of the dispersant performance was lost within 48 hours with all oils tested. Other tests run in parallel with these showed that only a small percentage of the changes in effectiveness were due to weathering-induced changes in the oil, so most were believed to be due to loss of surfactants from the oil to the water.

Tests in the S L Ross wave tank (June 2005), where dispersant-treated oil was soaked on the water surface for a period of 24 hours, also resulted in a substantial drop in dispersant effectiveness at a DOR of 1:50 for the oils tested, but not for the same oils treated with a DOR of 1:20. The decrease in dispersant effectiveness due to oil evaporation and consequent viscosity increase had a very minor effect on dispersant performance.

Tests conducted at Ohmsett involved Galveston 209 and Ewing Bank 873 crude oils, and Intermediate Fuel Oil 30. Corexit 9500 dispersant was pre-mixed into the test oils at recommended dose rates (a DOR of 1:20) and oils were allowed to stand on seawater on the tank under calm conditions for up to six days before dispersibility was assessed by agitating the slicks on the tank with well characterized breaking waves. Ohmsett tests showed that the oils would rapidly and almost totally disperse when exposed to breaking waves after being left on a calm water surface for prolonged periods (up to 6 days for IFO-30 fuel oil or nearly 3 days for Ewing Bank 873 crude oil). There was no reduction in dispersant effectiveness that could be attributed to surfactant leaching at Ohmsett and there was no significant drop in dispersant effectiveness caused by evaporative loss from the crude oils causing an increase in oil viscosity, with the test oils and time periods used in this study.

There were two apparently inconsistent results in the Ohmsett testing. For each of the IFO-30 fuel oil and the Ewing Bank 873 crude oils there was a single test using 50 L of oil (instead of 100L used in most tests) when the oil did **not** disperse after 66 hours and 44 hours, respectively, on the water surface. Unlike the tests with the larger amounts of oil, the 50-L oil slicks in these cases did not cover the entire containment ring and moved over the water surface under the influence of the prevailing winds. This additional movement may have assisted in the leaching of dispersants. Preliminary investigations at Ohmsett using a trolling motor to induce sub-surface currents were not successful in speeding up the dispersant leaching process and did not confirm that a slight water movement would assist in the loss of dispersant from the oil.

On the basis of the information gathered at Ohmsett, it is reasonable to conclude that the surfactants within a dispersant-treated oil (treated at recommended treatment rate of a DOR of 1:20) and left in calm conditions at sea, with no slick drift or under slick water current, will not

leach out to a degree that causes a significant reduction in dispersant effectiveness within 3 to 6 days, and perhaps for much longer. The indications from the smaller-scale tests are that a significant drop in effectiveness, attributable to surfactant loss, can occur at much shorter time intervals of 12 to 24 hours when lower treatment rates (DOR of 1:50) of dispersant are used.

It is recommended that the roles of water movement under slicks and the effect of sub-optimal dose rates be investigated in more detail.

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1. Objective

The objective of the work was to determine the period of time that oil spill dispersants applied to spilled oil in a calm sea will remain effective when the sea state subsequently increases.

2. Background

The use of dispersants to cause spilled oil to disperse at sea, or to enhance the rate of natural dispersion of spilled oil from a very low level to a much higher value, is known to be related to the prevailing 'mixing energy'. Many laboratory studies have concluded that higher 'mixing energy' causes greater levels of dispersion than lower 'mixing energy', but this has yet to be well defined. The recent comparative studies (Kaku et al, 2006) on the turbulence produced in the water of test apparatuses of the SFT (Swirling Flask Test) method and the BSFT (Baffled Swirling Flask test) have highlighted that level of turbulence in the water of a test method is of critical importance in determining the dispersant effectiveness result obtained (Venosa et al., 2002). However, the distinction between the turbulence in the body of the water and the turbulence produced at the interface between the oil and water in a cresting or breaking wave has not yet been made.

2.1 The Dispersion Process

Observation of the dispersion of spilled oil as caused by waves at sea (Colcomb et al., 2005), or in tank tests employing waves (Trudel et al., 2005), reveals that dispersion can be considered to be a two-stage process and both of these processes depend on the prevailing sea conditions for the dispersion process to proceed:

(i)   <u>Oil droplet creation</u>

        The initial stage of dispersion is the formation of oil droplets. The floating slick of dispersant-treated oil may be converted into a plume of oil droplets of a wide range of sizes in the upper water column by the shearing action exerted on the floating oil layer by the action of a cresting, or breaking, wave passing through the slick. Observations made at sea (Lewis, 2004) and previous studies at Ohmsett (S L Ross, 2004) have established that dispersants are much more effective when cresting or breaking waves are present (i.e. in sea states when the wind speed is above 7 – 10 knots (5 m/s, equivalent to Beaufort Force

3, see Table 1) than in the absence of cresting or breaking waves. This first stage of the dispersion process is localized to those areas of the oil slick where cresting or breaking waves pass through the oil. The onset of cresting or breaking waves at Beaufort Force 3 appears to produce a step change in the rate of dispersion of dispersant-treated oil. Dispersion may, or may not, occur slowly at a lower sea state than that caused by Beaufort Force 3 winds and this has been investigated in an allied project (Chemical Dispersibility of OCS Crude Oils At Low Sea States in Non-Breaking Waves: Part 1 – Determining the Limiting Oil Viscosity for Dispersion in Non-Breaking Waves).

(ii)   <u>Dispersion of oil droplets</u>

The second stage of dispersion is the maintenance and subsequent dispersion of the very small oil droplets in the water column. The oil droplets created in the first stage of dispersion will initially be propelled a short distance into the water column the intense turbulence associated with the passage of the cresting or breaking wave. Oil droplets that are sufficiently small (and therefore have a low level of buoyancy, dependant on droplet size and oil density, according to Stokes law, see Table 2) will be maintained in the upper area of the water column by the circular water motion that exists under all waves, whether they are breaking waves or non-breaking waves. The buoyancy of the oil droplet will cause it rise through the water, but the periodic downward water motion will carry the oil droplet deeper in the water. The depth of the well-mixed zone is related to the wavelength of the waves, being approximately 1.5 the average wavelength, and the well-mixed zone extends deeper when long wavelength swells are present than when there is short wavelength 'harbour chop'. The intensity of the downward water motion will be related to wave height with higher waves creating more intense downward (and upward) circulation and, over time, to wave frequency. It is known from measurements (Lunel, 1993) made at sea that the average size of oil droplets maintained in dispersion in a medium sea state is approximately 70 microns in diameter, but the maximum size of oil droplet that can be retained in the water column will be related to sea state; rougher seas are capable of dispersing larger oil droplets.

Table 1 The Beaufort Force Wind Speed Scale and Sea Conditions

Force	Speed			Description	Conditions at Sea
	knots	km/h	mph		
0	< 1	< 2	< 1	Calm	Sea like a mirror.
1	1-3	1-5	1-4	Light air	Ripples only.
2	4-6	6-11	5-7	Light breeze	Small wavelets (0.2 m). Crests have a glassy appearance.
3	7-10	12-19	8-11	Gentle breeze	Large wavelets (0.6 m), crests begin to break.
4	11-16	20-29	12-18	Moderate breeze	Small waves (1 m), some whitecaps.
5	17-21	30-39	19-24	Fresh breeze	Moderate waves (1.8 m), many whitecaps.
6	22-27	40-50	25-31	Strong breeze	Large waves (3 m), probably some spray.
7	28-33	51-61	32-38	Near gale	Mounting sea (4 m) with foam blown in streaks downwind.
8	34-40	62-74	39-46	Gale	Moderately high waves (5.5 m), crests break into spindrift.
9	41-47	76-87	47-54	Strong gale	High waves (7 m), dense foam, visibility affected.
10	48-55	88-102	55-63	Storm	Very high waves (9 m), heavy sea roll, visibility impaired. Surface generally white.
11	56-63	103-118	64-73	Violent storm	Exceptionally high waves (11 m), visibility poor.
12	64+	119+	74+	Hurricane	14 m waves, air filled with foam and spray, visibility bad.

Table 2 "Float Out" Times for Oil Droplets in Still Sea Water

Oil droplet diameter (microns)	Time taken to rise 1 metre in absolutely still water According to Stoke's Law		
	Specific Gravity 0.8500	Specific Gravity 0.9000	Specific Gravity 0.9500
5	5.18 days	7.27 days	12.21 days
10	1.29 days	1.82 days	3.05 days
20	7.77 hours	10.90 hours	18.32 hours
50	1.24 hours	1.75 hours	2.93 hours
100	18.64 minutes	26.18 minutes	43.96 minutes
200	4.66 minutes	6.54 minutes	10.99 minutes
400	1.16 minutes	1.64 minutes	2.75 minutes
600	31.06 seconds	43.63 seconds	1.22 minutes
800	17.47 seconds	24.54 seconds	41.21 seconds
1000	11.18 seconds	15.71 seconds	26.38 seconds

2.2 The Effect of Sea Conditions on the Dispersion Process At Sea

Provided that the dispersant that has been applied to the spilled oil has penetrated into the spilled oil (i.e., dispersant has not been washed off by waves) and that the oil has suitable physical properties for successful dispersion (i.e., the oil viscosity is not greater than a limiting value that is dependent on prevailing sea state), most oils should be dispersible in sea states of Beaufort Force 3 or 4 or higher. Some high viscosity oils may possess enough sufficient cohesion to resist the shearing forces of breaking waves at lower wind speeds in this range. Oils such as high viscosity fuel oils at low temperature can possess an elastic component to their flow behavior that allows them to deform with the shearing action of the cresting waves, rather thanbeing converted into oil droplets. Once these oils have been deformed they can revert to being a coherent slick after the wave has passed through. These oils require a higher sea state – rougher seas – to initiate dispersion when treated with dispersant than lower viscosity oils.

The wind speed, and therefore sea state, that prevails at an oil spill incident is unlikely to be constant over a period of many days and is most likely to vary. These changes will greatly

influence the degree of success of any response measures, including the use of oil spill dispersants.

Response to oil spills that occur in storm conditions (Beaufort Force 10) or higher will always be extremely difficult or impossible. Booms and skimmers will be ineffective and probably destroyed if deployed.

The rate of dispersion of spilled oil will increase with increasing wind speed from Beaufort Force 3 – 4 before dispersant spraying becomes operationally unfeasible at about Beaufort Force 10. Spraying of dispersants from aircraft at high wind speeds, in excess of wind speeds of 40 or 50 knots becomes inherently less safe – flying at the very low altitudes required to accurately apply dispersants in rough weather can be difficult and potentially dangerous. Additionally, the spilled oil in very rough seas will spend a considerable proportion of the time under the sea surface, being temporarily submerged by the waves, and successful dispersant spraying from ships or aircraft would not be possible.

Response to oil spills in calm seas is much easier. Spraying dispersant onto spilled oil in calm sea conditions is operationally feasible, but is unlikely to cause as rapid dispersion as would occur in rougher sea conditions (Delvigne et al., 1988 and 1994). A subsequent increase in wind speed to cause rougher seas may cause rapid dispersion at a later time. This approach of dispersant spraying has certain advantages in some oil spill situations. It is easier to spray dispersants accurately onto the spilled oil in calm sea conditions. The oil is on the sea surface and can be detected and located more easily. The rate of emulsification is slow in calmer seas with an apparent step change in the rate of water-in-oil emulsification occurring at around Beaufort Force 3 to 4 (Walker et al, 1993). Dispersant sprayed onto spilled oil in calm seas will have the opportunity to soak into the spilled oil with a reduced possibility of being washed off by wave action. However, it is essential that the dispersant stays with the spilled oil and is not lost to the sea.

2.3 Surfactant Partitioning

The active ingredients in dispersants are the surfactants. They function because they have a combination of oleophilic ('oil-loving') and hydrophilic ('water-loving') properties combined in the same molecule. When the dispersant is sprayed onto the spilled oil the surfactants migrate through the oil to the oil / water interface. They orient at the oil / water interface and drastically (but temporarily) reduce the oil / water interfacial tension (IFT), thus facilitating dispersion when sufficient energy is present.

Modern oil spill dispersants typically consist of three surfactants; two nonionic surfactants (a fatty acid ester and an ethoxylated fatty acid ester) and an anionic surfactant (typically sodium di-iso octyl sulfosuccinate). The blend of surfactants has been optimized to produce high effectiveness with a range of different oil types and weathered conditions. None of the surfactants are truly soluble in either water or oil, but they will not remain indefinitely at the oil / water interface when dispersant-treated oil is on (or in) the water. In particular, the anionic surfactant will tend to partition into the water phase. It is known from previous studies (Knudsen et al. 1994) that the surfactants, notably sodium di-iso octyl sulfosuccinate, will partition, or 'leach out', from the oil and into the seawater. The surfactant balance in the dispersant formulation will therefore change and become non-optimal for dispersion of the spilled oil.

The rate of this surfactant partitioning, or leaching, will depend on the contact between the dispersant-treated oil and water. The oil will act as a reservoir of surfactants in the dispersant. It is thought that, in totally quiescent water conditions, the rate of surfactant leaching would be proportional to the area of oil surface in contact with the water. The rate of surfactant loss will probably be lower for thicker layers of oil because less oil surface area is exposed to the water than for thinner layers of oil.

In absolutely still water conditions it may be possible for equilibrium to become established between the surfactant concentration in the oil and the surfactant concentration in the water layer next to the oil, but it is likely that in many cases a slight water current will carry the dissolved surfactant away, preventing an equilibrium from becoming established and the surfactant would continue to leach out of the oil. The surfactants may be released from the oil more rapidly if the

oil is dispersed as large oil droplets, which rapidly resurface. However, if the oil droplets are small enough they will be dispersed and remain so since the loss of surfactant will not result in coalescence of the dispersed oil droplets within the water column because of the relatively large distances between individual dispersed oil droplets and the unlikelihood of collisions between them.

In addition to surfactant loss, the evaporation of the more volatile oil components will proceed even in a calm sea and the oil will become less dispersible due to the increased viscosity of the remaining residue. These two effects will cause the dispersant to become potentially less effective after spilled oil has been sprayed with dispersant in calms seas. There is most likely a period of time, before the surfactants have leached out and before the oil viscosity has increased, when the dispersant would still be at least partially effective when wave action is sufficient to cause dispersion of the spilled oil.

Other researchers are studying the potential for surfactant leaching (Nedwed et al., 2006).

3. Study Approach

This work involved study of new processes that had received little prior research and called for development of new experimental procedures at Ohmsett that would allow researchers to "soak" treated slicks in a controlled, reproducible way on the tank for long periods before testing their dispersibility. In order to optimize the use of time in the Ohmsett tank, preliminary testing was completed using bench-scale and wave-tank-scale tests in order to gather preliminary information concerning the processes involved. These preliminary studies were to determine: 1) whether dispersant performance would be influenced by "soaking time" on the 1 to 3 day time scale that was feasible in the Ohmsett tank; 2) what the rate of change in dispersant performance might be; and 3) how the rate of change might be influenced by factors such as oil type, slick thickness and dispersant to oil ratio (DOR). The study approach was to conduct experiments at three scales, bench-scale, small-wave tank-scale and large outdoor wave tank-scale at Ohmsett. The relatively inexpensive bench-scale and wave-tank-scale experiments would: 1) address the three questions stated above, in order to assist in designing the Ohmsett experiments; and b) they would allow us to scale-up results of bench-scale, and wave tank tests in order to predict behavior of dispersant treated oil slicks at Ohmsett and at sea. The major phases of the study were:

1. Identification of OCS crude oils and a marine fuel oil for testing.

2. Completion of aquarium-scale tests to gather preliminary information concerning the influence of spill variables on the rate of change of dispersant performance with soaking time. This work involved laying down 150-200 ml slicks of dispersant-treated (pre-mixed) and untreated oil (weathering controls) on seawater in aquaria for up to 48 hours and testing the dispersibility of oil samples from these slicks after 12, 24 and 48 hours, using a standard laboratory test method (WSL Method). Tests were conducted on several oils.

3. Completion of preliminary, small-scale testing of two crude oils and the fuel oil in the SL Ross wave tank to verify, at a larger scale, the length of time that these oils would remain dispersible if sprayed with dispersants and allowed to sit on calm water before being agitated with cresting waves.

4. The final phase involved large-scale testing at Ohmsett on two crude oils, the PERF oil (if available)[1] and a fuel oil under near-at-sea conditions to determine the length of time that oils remain dispersible if premixed with dispersants and allowed to sit on calm water before being agitated with cresting waves.

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[1] Note the PERF oil, was not tested during the 2005 Ohmsett season as the oil sample did not arrive in time to be tested.

4. Small-scale Laboratory Dispersibility Testing

The objective of the lab bench-scale work was to make an initial assessment of the persistence of dispersants in dispersant-treated oil slicks resting on calm water using a standard, bench-scale method to assess dispersant performance. In this case the method used was the Warren Spring Test Method. For each of the oils, a pre-test was conducted to estimate the relationship between dispersant performance and DOR. DORs ranging from 1:25 to 1:100 were tested. The DOR for subsequent testing was selected based on these tests. Tests were conducted in May and June 2005.

4.1 Oils Used

The oils used in these tests and their physical properties are summarized in Table 3.

Table 3 Summary of Spill-Related Properties of Oils Used in Bench-Scale Testing

Oil Type	Density (gm/ml at 23 ° C)	Viscosity, cP @ 25° C; 10 sec^{-1}
Alaska North Slope crude oil (2005) [a]	0.863	7
Intermediate Fuel Oil 30 (IFO 30)	0.935	200
Ewing Bank Block 873 crude oil	0.914	683[b]
a. low-viscosity oil substituted for the GA 209 oil that had not yet been received at the time of testing		
b. tested @ 15° C and 10 sec^{-1}		

4.2 Methods Used

Dispersant persistence was assessed by premixing Corexit 9500 into 150 ml of each test oil at a known DOR (nominal DOR of 1:20 or 1:50); measuring dispersion performance on samples of the freshly treated mixed oil; applying a slick of known oil thickness (0.5 cm) on seawater in an aquarium; and then removing samples of the slick for at 12, 24 and 48 hours to determine any effect of aging on dispersant performance. The water in the aquarium was pumped through an activated carbon contact chamber for removal of surfactants, with a turnover time of 1/2 hour. This water pumping created a gentle, but significant movement of the water and surface oil during the test duration. Simultaneously, a similar slick of untreated oil (a oil-weathering control) was applied to seawater in the same aquarium. Samples of this oil were removed after 12, 24 and 48 hours to determine the change in oil properties due to weathering and to determine the effect of weathering alone on dispersant performance. The latter was accomplished by pre-

mixing dispersant into the oil at the appropriate DOR and determining the dispersant performance using the WSL method.

4.3 Results of Small-scale Laboratory Dispersibility Testing

The relationships between dispersant-to-oil ratio and dispersant effectiveness seen in Figure 1 were used to select the DORs for the soaking tests. The data in Figure 1 were collected from a series of WSL tests on the fresh oils. The DOR-Effectiveness relationships were similar for the two more viscous oils, Ewing Bank and IFO30. Dispersant performance was greater for the less viscous ANS oil. The DOR's used in the soaking tests are reported in the following sections.
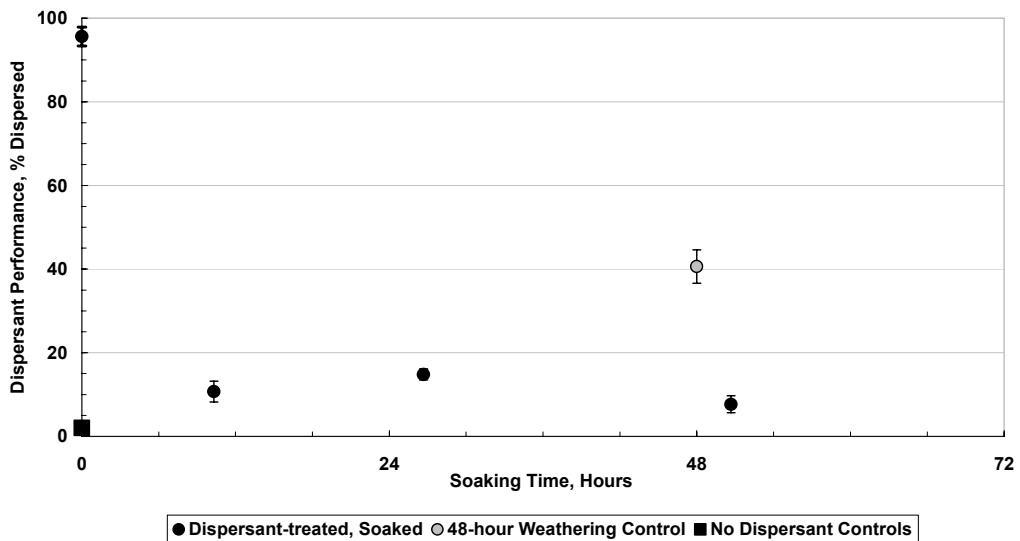
4.3.1 Alaska North Slope Crude Oil

In the preliminary tests, ANS was tested at a DOR of 1:50. In Figure 1, as DOR was reduced below 1:50 effectiveness declined sharply. It was therefore believed that any effect of surfactant loss from the oil on dispersant performance during the "soaking" period might appear sooner and be more reliably detected at this DOR. As can be seen in Figure 2, dispersant performance in the freshly mixed oil-dispersant mixture was high (95% dispersion), but declined rapidly to 10% after 12 hours of "soaking" on calm seawater and further declined to only 7% after 48 hours. Over this 48-hour period the ANS crude oil lost a substantial proportion of volatile components, as shown by the increase in density from 0.863 to 0.918 g/ml. Tests on the "weathering-control" oil sample showed that at least part of the decline in dispersant performance noted above appeared to have been due to the increase in viscosity caused by the loss of volatiles, as shown by the lower reduced dispersant performance (40% effectiveness) in the 48-hour weathering control. However, only part of the 90% reduction in dispersant performance seen in the test sample cannot be accounted for by weathering and may be due to loss of dispersant to the water during "soaking". Note that even after 48 hours of aging on calm seawater the dispersant performance was greater than the no dispersant control.

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Figure 1 Effectiveness versus Dispersant-to-Oil Ratio for All Oils in WSL Tests
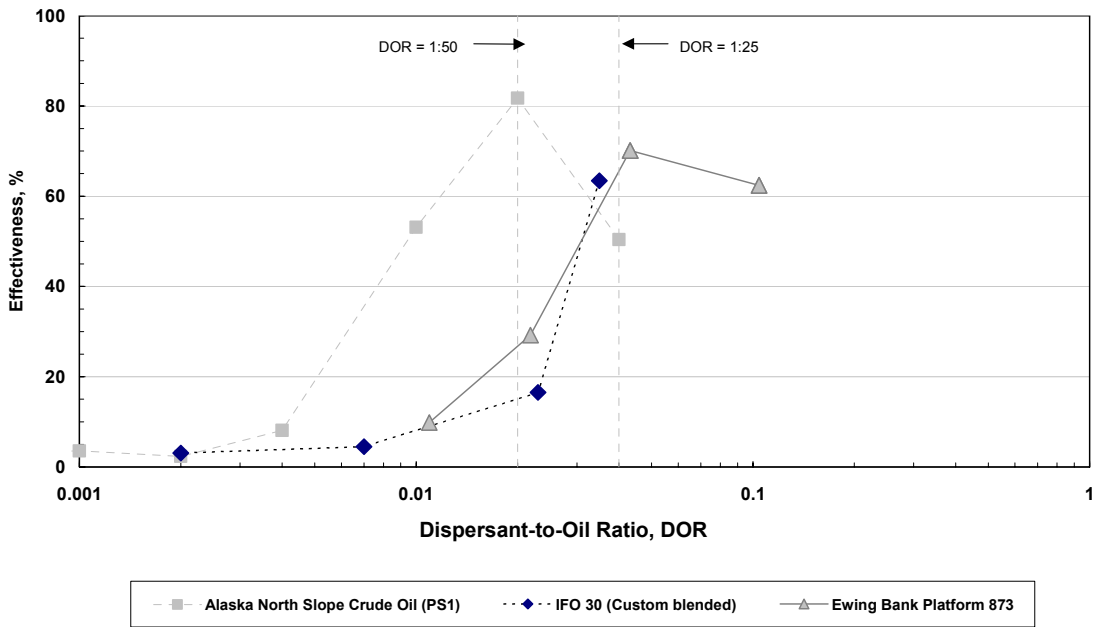
Figure 2 Effect of Soaking Time on Dispersant Performance: Alaska North Slope Crude Oil with DOR of 1:50


Alaska North Slope Crude Oil, DOR = 1:50
a. error bars = 1 s.d.

4.3.2 Ewing Bank Block 873

The behavior of the more viscous Ewing Bank 873 (EB 873) crude oil treated with a DOR of 1:50 (Figure 3) was consistent with that of the ANS, with several notable exceptions. The dispersion of the dispersant treated EB 873 oil prior to soaking was low, only 20% effectiveness, compared to 90% for the ANS. Effectiveness declined significantly to 15% and 8% after 24 and 48 hours of soaking, but the decline was less pronounced and more gradual than in the ANS work. Unlike the ANS results the 48-hour "weathering control" EB 873 sample dispersed to the same degree as the fresh sample.

Dispersant performance on both oils declined from their initial effectiveness to a level of 10% or less over 48 hours. However, in the case of the ANS the decline was precipitous, with most of the effectiveness being lost 12 hours. EB 873 declined to the same level, but the process appeared to be more gradual. To determine whether the pattern of change in effectiveness was due to the oil type alone, a second experiment was conducted with EB 873, but the DOR was increased to 1:20 to increase the initial dispersion performance to more than 60%. In the second EB 873 test the initial effectiveness was much higher (>60%). As in the first test effectiveness declined with soaking time, but in the second test the decline was clearly very rapid, with most of the effectiveness being lost within the first 12 hours (Figure 4). This suggested that regardless of the initial level of effectiveness, effectiveness might be expected to decline to a level of 10 to 15% within the first 12 hours of soaking.

**Figure 3 Effect of Soaking on Dispersant Performance on Ewing Bank 873 Crude Oil (DOR 1:48)**

Ewing Bank 873 oil
a. error bars = 1 s.d.
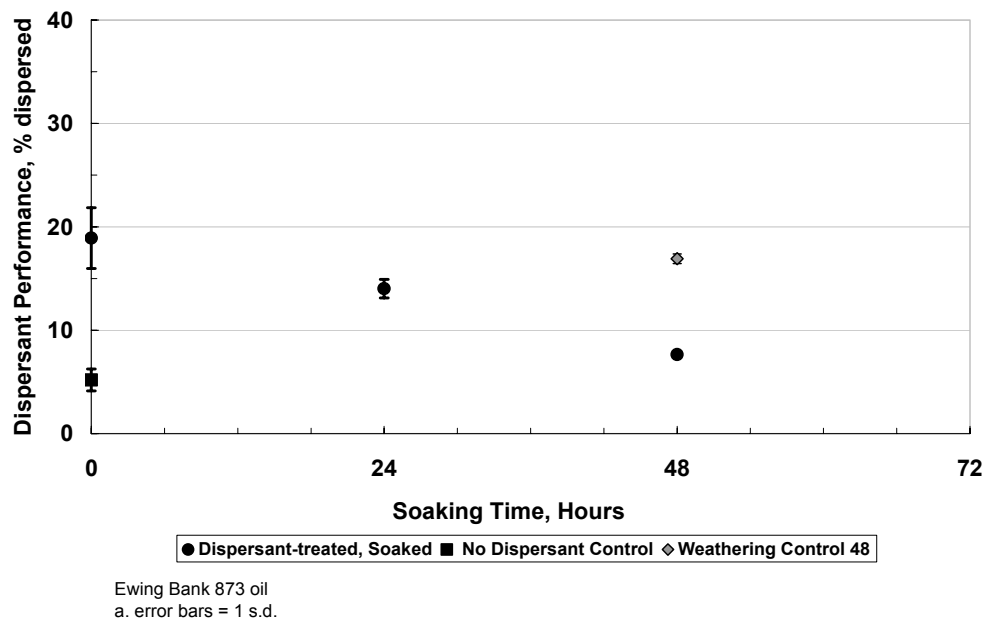
Figure 4 Effect of Soaking on Dispersant Performance on Ewing Bank 873 Crude Oil (DOR 1:20)

Ewing Bank 873, DOR = 1:20
a. error bars are 1 s.d.
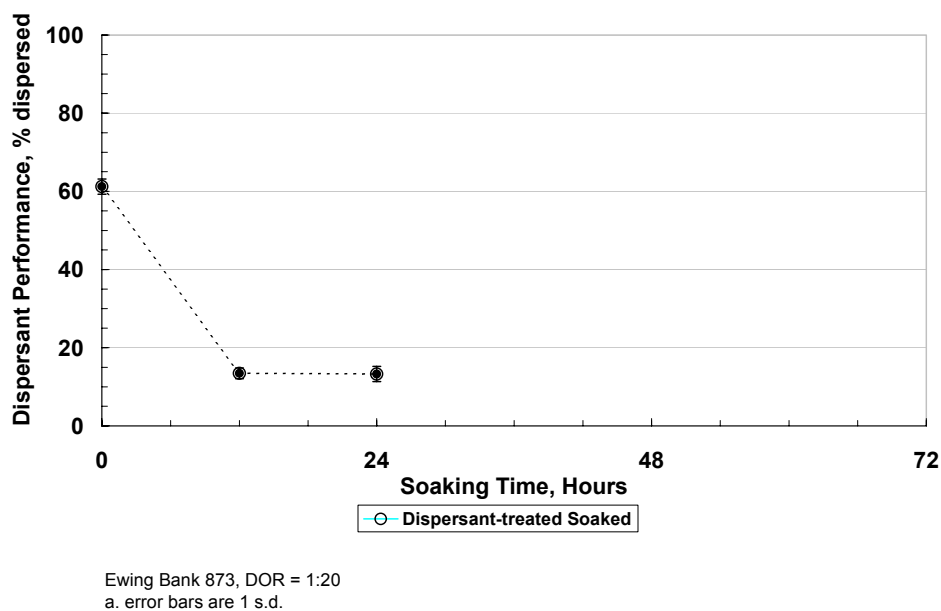
4.3.3 IFO 30 (Custom-blended IFO with Viscosity Approximately 200 cP)

A final test was conducted to confirm the observations in the first two tests that dispersant performance may be high initially, but may be expected to decline to near control levels within 12 hours. In this test the more viscous IFO 30 fuel oil (202 cP @ 15 deg C) was treated with Corexit 9500 at a DOR of 1:20. The initial dispersant performance in the un-aged oil was high (57%), similar to that in the Ewing Bank oil treated at a similar DOR (Figure 5). Dispersant performance declined with soaking on calm water, reaching near control levels within 48 hours. However, the rate of change appeared to be less rapid than in the other two oils, requiring 24 hours, not 12 hours, to reach the 10 to 15 % effectiveness level. The dispersant effectiveness on the weathering-control sample was only slightly less than on the fresh oil. This suggests that the loss in dispersant performance for the "soaked" oil samples is primarily due to dispersant loss and not oil weathering.

Figure 5 Effect of Soaking on Dispersant Performance on IFO 30 (DOR 1:20)

IFO 30; DOR 1:20
a. error bars = 1 s.d
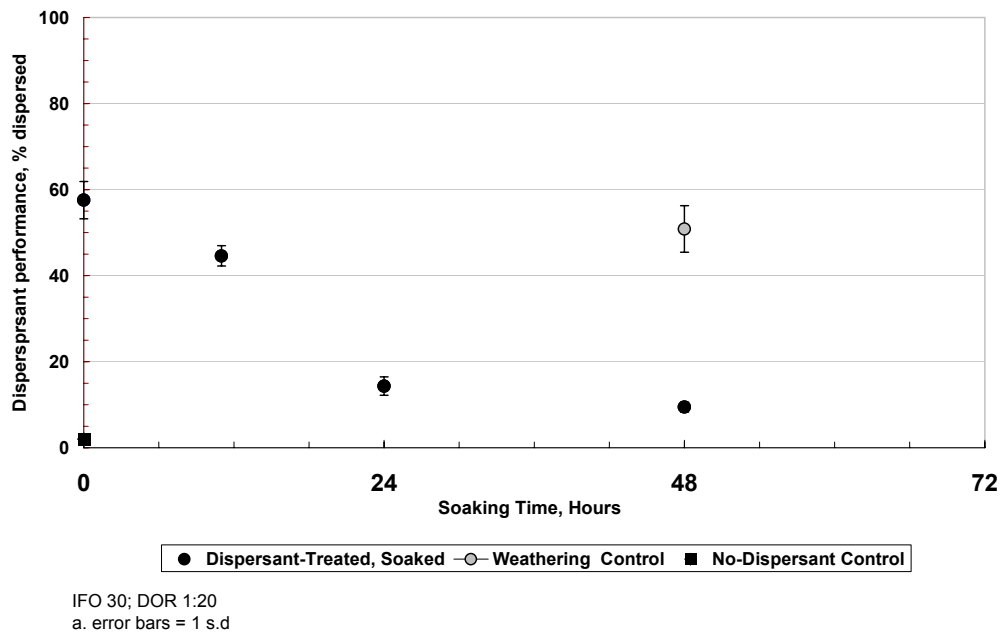
4.3.4 Summary of Small-scale Laboratory Dispersibility Test Results

These preliminary small-scale tests showed the following.

1. Regardless of the initial level of effectiveness observed, much of the effectiveness was lost within 12 to 24 hours of soaking.

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2. In all cases, dispersant effectiveness after 48 hours of soaking was still significantly greater than in no-dispersant controls.

3. Results of the weathering control tests demonstrated that the total loss in effectiveness could not be explained based on weathering-induced changes in oil properties and therefore were probably due to loss of surfactant from the oil to the water.

4. The initial rapid rate of decline of effectiveness seen in the first 12 to 24 hours may have been influenced by oil type.

5. Testing in the S L Ross Wave Tank

The dispersion of oils treated with chemical dispersants and then allowed to soak on quiescent water prior to the addition of mixing energy was tested in SL Ross's wave tank in June of 2005. The goal of the work was to determine if the dispersant initially mixed into the oil would leach out of the oil into the water over time and thus reduce the effectiveness of the dispersant as had been shown in previous small-scale testing.

As oils rest on the water surface they evaporate and their properties change. This property change could also alter the effectiveness of a chemical dispersant. To separate the effect of weathering from that of dispersant leaching, control oils (no dispersant added) were weathered on the tank in trays at the same time as the chemically treated oils "soaked" on the water. Dispersant was then added to these weathered oils and they were tested to allow the differentiation of dispersant effectiveness change between loss of dispersant and oil evaporative loss and property change.

5.1 Oils Tested

The oils tested and their viscosities when fresh are shown in Table 4. These oils were selected for use because they were readily available and their viscosities bracketed the viscosities of the oils that were to be later tested at Ohmsett. The oils tested at Ohmsett were not delivered soon enough for this preliminary testing in Ottawa.

Table 4 Oils Used in SL Ross Wave Tank Tests

Oil	Fresh Oil Viscosity (cP @25 °C and 10^{s-1})
Alaska North Slope (ANS) crude oil	7
IFO 30 (Bunker & Diesel Mix)	200
Harmony crude oil	500

5.2 Methods

In each test, 750 ml of oil were pre-mixed with the appropriate quantity of Corexit 9500 dispersant to achieve the required DOR and placed in a 45 cm diameter containment ring tethered in the middle of the SL Ross wave tank.

An additional 900 ml of the same oil was placed in trays that were floated on the water surface so the oil was subjected to the same temperatures and weathering conditions as the oil floating in the rings. The tank's water filtration system, that includes activated carbon treatment, was operated throughout the test to remove any dispersant entering the water column from the treated oil placed in the containment ring. This filtration system treated the approximately 11 m^3 of water in the test tank every 5 hours. This filtering creates a constant, slow, slug flow of water through the tank.

The oil was left on the surface for between 15.5 and 45.5 hours. The floating trays were removed and the oil in them collected for future tests. A sample of the oil in the containment ring was taken after the soaking period for oil-water interfacial tension determination. The air bubble curtain barrier was then activated and the rigid containment ring lifted to release the oil. The wave paddle was then operated and high-energy waves applied to the oil for a 20-minute period to determine the dispersibility of the oil.

The oil from the weathering trays was collected, analyzed for density, viscosity and interfacial tension. This oil was then treated with dispersant at the same dosage as the oil originally placed in the on-water containment ring. The density, viscosity and interfacial tension of the dispersant and oil mixture were also analyzed for tests 4 and 5, only. The dispersant-treated oils were then placed on the tank within the air-bubble curtain barrier and high-energy wave energy was applied at the same intensity as that used on the oil from the containment ring to determine the effectiveness of the dispersant on the evaporated, chemically treated but "not-soaked" oil.

5.3 Test Results

5.3.1 Change in Physical Properties

The physical properties of the tests oils on the water surface and in the trays progressively changed from that of the 'fresh' oils (Table 4) because of the evaporation of the more volatile oil components, leading to increased viscosity and density. The physical properties of the oils were also modified by the addition of dispersant. The physical properties of the test oils in the condition that they were dispersed are contained in Table 5.

Alaska North Slope (ANS) Crude Oil

The viscosity, density and oil/water interfacial tension (IFT) of the "Oil-On-Water Samples" and the "Oil-In-Tray Sample" (before and after dispersant addition) are contained in Table 4 The viscosity of the Alaska North Slope (ANS) crude oil without dispersant addition (Oil-In-Tray Sample, No Dispersant) had increased from 7 cP for the 'fresh' oil to 56 cP after 15.5 hours, 100 cP after 24 hours and 102 cP after 45.5 hours.

Addition of Corexit 9500 at a DOR of 1:10 to the oil after 15.5 hours in the tray decreased the viscosity from 56 cP to 43 cP. This compares with the 64 cP of the oil that had the dispersant added before soaking on the water surface for the same time.

IFO 30 Fuel Oil

The viscosity of the IFO-30 fuel oil increased from 200 cP to 384 cP after 24 hours in the tray. The IFO-30 "Oil-On-Water Sample" containing Corexit 9500 at a DOR of 1:50 and soaked on the water surface for 24 hours had a viscosity of 258 cP.

Harmony Crude Oil

The viscosity of the Harmony crude oil increased from 500 cP ('fresh' oil) to 2360 cP after 17.75 hours in the tray and was decreased to 662 cP by the addition of Corexit 9500 at a DOR of 1:10. The "Oil-On-Water Sample" had a viscosity of 1400 cP, suggesting that some dispersant had been lost during the soaking.

Table 5 Changes in Physical Properties of Oils Used in Wave Tank Tests

Test #	DOR	Soak Time (hours)	Oil-On-Water Sample			Oil-In-Tray Sample					
						No Dispersant			With Dispersant		
			Viscosity (cP) @25 °C and 10 $^{s-1}$)	Density (g/m^3)	IFT (dyne/cm)	Viscosity (cP) @25 °C and 10 $^{s-1}$)	Density (g/m^3)	IFT (dyne/cm)	Viscosity (cP) @25 °C and 10 $^{s-1}$)	Density (g/m^3)	IFT (dyne/cm)
Alaska North Slope (ANS) crude oil											
5	10	15.5	64	0.91	0.6	56	0.907	19.6	43	0.907	0.6
1	50	24	108	0.919	0.5	100	0.917	n.d.	n.d.	n.d.	n.d.
6	20	45.5	42	0.925	0.6	102	0.918	18.5	n.d.	n.d.	n.d.
IFO 30 fuel oil											
3	10	17.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2	50	24	258	0.939	2.7	384	0.945	n.d.	n.d.	n.d.	n.d.
Harmony crude oil											
4	10	17.75	1400	0.956	0	2360	0.965	57.3	662	0.946	0.9

5.3.2 Dispersion Results

The dispersion results from this set of tests are shown in Table 6. The "Oil-On-Water Sample" is the oil that was pre-mixed with dispersant and soaked on the SL Ross tank water surface prior to the high-energy waves being applied. The "Oil-In-Tray Sample" is the oil that was allowed to lose the more volatile components by evaporation while in a tray floating on the tank water. This oil was removed from the tray, dispersant was added to it, the mixture was placed on the water surface in the tank and subjected to high-energy waves. The difference in dispersant effectiveness between the "Oil-In-Tray Sample" and the "Oil-On-Water Sample" is reported as the "Disp Delta %" value in Table 6. This value represents the decrease in dispersant effectiveness presumed to be due to surfactant loss when the oil was allowed to soak on the water.

Table 6 Dispersion Effectiveness Results from SL Ross Wave Tank Studies

Test #	DOR	Soak Time (hours)	Oil-On-Water Sample % dispersion	Oil-In-Tray Sample % dispersion	Disp Delta (%)
Alaska North Slope (ANS) crude oil					
5	1:10	15.5	100	100	0
6	1:20	45.5	100	100	0
1	1:50	24	12.8	89	76.2
IFO 30 fuel oil					
3	1:10	17.3	74	97	23
2	1:50	24	22.5	89	66.5
Harmony crude oil					
4	1:10	17.75	49	73	24

Results of Alaska North Slope (ANS) Crude Oil Tests

The "Oil-On-Water Samples" of ANS crude oil treated with DORs of 1:10 and 1:20 and soaked for 15.5 and 45.5 hours totally dispersed (100% dispersion). The ANS crude oil that had been pre-mixed with only a DOR of 1:50 and soaked on the tank for 24 hours dispersed to only a low degree (12.8%).

There was no affect attributed to soaking or to evaporation for the ANS crude oils treated with DORs of 1:10 and 1:20. However, there was significant reduction (down to only 12.8% effectiveness) in the degree of dispersion of the "Oil-On-Water Sample" of ANS crude oil pre-mixed with dispersant at a DOR of 1:50. The net effect of soaking the oil on the water surface was an additional loss of effectiveness of about 76% when compared to the weathered only test (Oil-in-Tray Sample).

Results of IFO-30 Fuel Oil Tests

The dispersant-treated IFO-30 fuel oil pre-mixed with dispersant at DORs of 1:10 and 1:50 and soaked on the tank for 17.3 and 24 hours, respectively, showed a marked difference in dispersion; 74% for the DOR of 1:10, but only 22.5% for the DOR of 1:50.

The results from the "Oil-In-Tray Samples" indicate that the actual effect of DOR and oil weathering on dispersant effectiveness was minor; 97% effectiveness for the DOR of 1:10 and 89% for the DOR of 1:50. The effect of soaking the 1:10 treated IFO-30 sample on the tank for 17.3 hours, compared to the "Oil-In-Tray Sample", was an apparent 23% reduction in effectiveness. There was a much greater 66.5% reduction in effectiveness caused by soaking the oil that was treated with a 1:50 DOR. Once again, the major part of the reduction in dispersant effectiveness is associated with the soaking on the water and therefore has been attributed to surfactant loss.

Results of Harmony Crude Oil Tests

The 24% difference between the dispersant effectiveness achieved with the "Oil-On-Water" sample (49%) and with the "Oil-In-Tray" sample (73%) is a clear indication that soaking on the water surface for 17.75 hours reduced the effectiveness of the Harmony oil pre-mixed with dispersant at DOR of 1:10.

5.3.3 Summary of Small-scale Dispersion Testing Results

The small-scale testing in the S L Ross wave tank indicated that soaking on the water surface for a period of 24 hours led to a substantial drop in dispersant effectiveness for ANS crude oil treated with a DOR of 1:50, but not for the same oil treated with a DOR of 1:20. The decrease in dispersant effectiveness due to oil evaporation and consequent viscosity increase was a much

more minor effect. IFO-30 fuel oil and Harmony crude oil showed significant decreases in dispersant effectiveness after soaking on the water surface for 24 hours, compared to the more minor decrease in dispersant effectiveness caused by oil evaporation and consequent viscosity increase. The effect of decreased dispersant effectiveness after soaking on the water surface appeared to be due to surfactant leaching rather than because of changes in oil properties due to weathering.

6. Large-Scale Tank Testing at Ohmsett

6.1 Oils Tested

The oils used for testing at Ohmsett were two crude oils produced in the Outer Continental Shelf area of the United States and an IFO-30 fuel oil. These oils were selected because together they spanned the range of most low- and medium-viscosity oils. The oils selected for use provide commonality with another project, "Determining the Limiting Oil Viscosity for Dispersion in Non-Breaking Waves", being conducted at the same time. The IFO-30 fuel oil provided continuity with previous projects such as the "Correlating the Results of Dispersant Effectiveness Tests Performed at Ohmsett with Identical Tests Performed At Sea" (S L Ross, 2004). The viscosities of the 'fresh' test oils are shown in Table 7. Tests were completed in June, July and August 2005.

Table 7 Physical Properties of Oils Tested at Ohmsett

Oil Type	Viscosity Pa.s (cP) @ 15 °C			
	@ 1 s^{-1}	@ 10 s^{-1}	@30s^{-1}	@ 100 s^{-1}
Galveston 209 crude oil	14	-		-
Intermediate Fuel Oil 30 (IFO 30)			370	340
Ewing Bank 873 crude oil	-	683		773

6.2 Test Methods and Equipment

The dispersant effectiveness testing protocol developed over the past five years at Ohmsett was used in the testing. Detailed descriptions of the test protocol, and its development, and equipment used in the testing can be found in previous publications (SL Ross et al 2000a, 2000b, 2002a, 2002b, 2003a, 2003b, 2004, 2005). The standardized method of dispersant testing described in the above references was modified to achieve the objectives of this study.

Fifty- or 100-litre quantities of test oil, pre-mixed with the appropriate quantity of Corexit 9500 to achieve a DOR (Dispersant to Oil Ratio) of 1:20, were carefully placed in a circular boom (5 metres in diameter with an area of 20 m^2) on the tank in still water conditions. Different quantities of oil were used to try and produce oil layers of different thickness, since the rate of

loss of surfactants from the dispersant was expected to be proportional to the surface area-to-volume ratio of the contained oil slick in contact with the water.

The dispersant-treated oil was allowed to remain in contact with the water under still conditions for the required periods (one to 6 days). Then the circular boom was carefully raised on ropes, to minimize disturbance of the oil, to a position on the underside of the bridge. The waves were then started. The wave paddle settings used in these tests were a 3.5-inch stroke and 33 to 34 strokes per minute for 30 minutes. During the period of wave activity the behavior of the oil was assessed visually and was reported using a four-point dispersion scale (Lewis 2004). The LISST particle size analyzer was towed at a 1.5-metre depth through any visible dispersed oil cloud or under the surface oil slick if a cloud was not visible.

After 30 minutes the wave paddle was stopped and the waves allowed to subside. The water spray from the bridge fire monitors was used to gently sweep any surface oil remaining on the water surface at the end of the test to a common collection area at one corner of the containment boom. The oil was then removed from the water surface using a double-diaphragm pump and suction wand and placed in a collection drum. An emulsion breaker (Drimax™) was mixed into the contents of the drum and the contents were allowed to stand at least overnight. The majority of the free water present was decanted from the drum. The remaining oil and water were well mixed and a sample was taken for water content and physical property determination. The quantity of liquid in the drum was measured and the amount of oil determined by subtracting the amount of water as determined using the water content analysis. The effectiveness of the dispersant was reported as the volume of oil discharged minus the amount collected from the surface all divided by the amount discharged.

In order to complete the test schedule within the allotted time, 'weathering controls' of two oils were prepared in an inflatable paddling pool placed on the tank deck. The 'weathering controls' were oils spread out to the required thickness and allowed to lose their more volatile components by evaporation. This caused an increase in oil viscosity. Dispersant was then added to these oils and they were placed in the circular boom on the water surface of the tank. The purpose of conducting these experiments was to isolate the effect of oil viscosity increase, and therefore

possible decrease in dispersant effectiveness, from a decrease in effectiveness that may have been caused by surfactant loss from the oil.

6.3 Determination of Dispersant Effectiveness (DE) at Ohmsett

The principle used to determine DE (Dispersant Effectiveness) at Ohmsett is to recover the oil that did not disperse from the surface of the water in the tank by manual means (scooped off the water via a double-diaphragm pump into barrels) at the end of the test. This amount is subtracted from the amount of oil placed in the tank and the difference is considered to be the amount of oil that has been dispersed. The expected range of DE would be 0% (no dispersion) to 100% (total dispersion), but there are several potential reasons and circumstances why this is not always obtained with the standard dispersant test protocol:

a).   Some quantity of oil cannot be recovered because it has stuck to the tank walls or to the booms used to contain the oil and cannot be removed by the action of the water-jets used to move it along the water surface for collection by pump and manual means. In addition to losses to the surfaces, it is almost impossible to recover every last bit of oil that remains on the huge area of water surface at Ohmsett; some oil tends to 'escape', despite the best efforts of the water-jet operators and those collecting the oil. Oil that was not dispersed, but could not be recovered because it was stuck to various surfaces or was impossible to recover, will be calculated as having been dispersed and this may artificially <u>increase the DE result</u> obtained by some margin.

b).   The waves must be turned off so that the water surface is calm to allow the oil on the surface to be corralled by the water jets, moved up the tank, collected in one corner of the boom and collected by use of a scoop and then placed into a bucket or barrel. There is a period of time as the wave action subsides and then another period of time with still water as the oil is moved along the tank by the water-jets and then collected. During this time, larger droplets of oil that were dispersed by the wave action will resurface and then will be collected. Oil that was dispersed, but which resurfaced during the quiescent period prior to collection of the surface oil contributes to the non-dispersed oil and this will artificially <u>decrease the DE result </u>obtained by some margin.

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The two effects described above are in 'opposite directions', but will not tend to cancel each other out. Instead, they tend to truncate the DE range from the theoretical 0% to 100% to something like 15% (or higher) to 90 to 95%.

6.3.1 Water in Recovered Oil

Some water is inevitably collected with the recovered oil, even with the most careful manipulation of the scoop on the suction wand. This needs to be separated out of the recovered oil and it can be difficult to do this quantitatively. In order that the vast majority of the oil on the surface is recovered, it is usual to collect an excess of water with it. This oil and water mixture then passes through the double-diaphragm pump en route to the drum. This water content of the oil needs to be determined after an initial water separation stage to remove the 'free' water. Adding Drimax™, mixing and allowing the drum to stand overnight allows the majority of the free water to be decanted from the drum. The remaining oil and water are well mixed and a sample is taken for water content and physical property determination.

6.4 Dispersant Effectiveness Results

The test conditions, visual observations and determined DE for all the tests that were conducted are presented in Table 8.

6.4.1 Tests with IFO-30 Fuel Oil

Six of the eleven tests were conducted with IFO-30 fuel oil that had a viscosity of 180 cP at 15°C and measured at a shear rate of $10s^{-1}$. The control test with no dispersant produced a DE of 27.5% (CS #3).

In test CS #5, IFO-30 was pre-mixed with Corexit 9500 at a DOR of 1:20 and left on the Ohmsett tank for nearly 3 days (70 hours). The oil was totally dispersed (DE of 97%) almost as soon as breaking waves were put through the slick. In test CS #10, IFO-30 weathered for the same period of 70 hours in the paddling pool, mixed with Corexit 9500 at a DOR of 1:20 and then placed on the Ohmsett tank also dispersed to a very high degree (DE of 95%) as soon as breaking waves passed through the slick. In test CS # 1, the same oil treated with the same

dispersant at a DOR of 1:20 and left on the tank for 6 days (149 hours) also dispersed to a very high degree (DE of 85%) as soon as breaking waves were put through the slick.

The conclusion from these tests is that IFO-30 oil pre-treated with Corexit 9500 at a DOR of 1:20 and left undisturbed on the tank for up to 6 days was dispersed as soon as the breaking waves were applied. There was no evidence of extensive surfactant leaching; the oil dispersed to a very high degree after a long period on the water prior to breaking waves being applied.

The single exception to this conclusion was the result from test CS #2. The intention of this test was to use less of the oil (50 L vs 100 L in the earlier tests) to form a thinner oil layer in the boom. This did not happen because the oil spread out to occupy only half of the area within the boom and the oil layer thickness was therefore similar to that in other tests. The oil was pre-mixed with Corexit 9500 at a DOR of 1:20 and was left on the Ohmsett tank for 66 hours. The visual assessment suggested that the oil did not disperse well when breaking waves were applied and the DE of 62% was lower than that of the other tests with dispersant-treated IFO-30. Attempts to repeat this result with test, CS #6, were thwarted when most of the oil leaked out of the boom during the soaking period. The reason for the apparent difference in behavior between the 50 L CS#2 test and the remainder of the IFO 30 tests is not immediately clear. One possible explanation is that during the soaking period the entire surface of the containment area was not covered in oil so the slick was free to move within the ring under the influence of the prevailing wind exposing the oil to more 'clean' water and improving the transfer of surfactant from the oil to the underlying water. Some investigation was undertaken using a trolling motor to induce a current across the underside of the oil slick contained in the boom in an attempt to increase the water exchange, and therefore possibly increase the rate of surfactant leaching, but results of this work are so far inconclusive.

Table 8 Results of Tests at Ohmsett

Test No. CS#	Amount of oil (Litres)	Slick thickness (mm)	DOR	Pre-test oil viscosity (cP 15°C 10s-1)	Duration on tank (hours)	After-test oil viscosity (cP 15°C 10s-1)	Visual observation	Visual rank[a]	DE (%)	Video Links
							IFO-30 tests			
3	77	2.6	None	250	0	513	Oil **not** dispersed in cresting waves.	1	27.5	457 CSS 3.mpg
2	50	5	1:20	250	66	1457	Oil **not** dispersed in cresting waves.	1	62.0	457 CSS 2.mpg
10	50	5	1:20	250	70[b] + 0		Oil totally dispersed in cresting waves.	4	94.5	457 CSS 10.mpg
5	100	5	1:20	250	70.5	3993	Oil totally dispersed in cresting waves.	4	96.9	457 CSS 5.mpg
6	50	5	1:20	250	78	No sample	Most of the oil leaked out of boom.	1	n.d[c].	457 CSS 6.mpg
1	100	5	1:20	250	149	1240	Oil totally dispersed in cresting waves.	4	85.0	457 CSS 1.mpg
							Ewing Bank 873			
7	71	1.7	None	n.d.	0	n.d.	Oil **not** dispersed in cresting waves.	1/2	59.1	457 CSS 7.mpg
8	50	5	1:20		44	n.d	Oil **not** dispersed in cresting waves. Some temporary dispersion of large oil droplets, but majority re-surfaced.	1/2	n.d.	457 CSS 8.mpg
9	50	5	1:20		74	n.d	Oil totally dispersed in cresting waves.	4	n.d.	457 CSS 9.mpg
11	75	5	1:20		70* + 0		Oil totally dispersed in cresting waves.	4	81.6	457 CSS 11.mpg
							Galveston 209			
4	75	3.8	1:20		18		Oil totally dispersed in cresting waves.	4	100.0	457 CSS 4.mpg

a. Visual assessment based on four-point scale of Lewis 2005: 1= no visible dispersion; 2= ; 3= moderate and incomplete dispersion; 4= rapid and compete dispersion.
b. Pre-weathered on paddling pool for 70 hours.
c. n.d. = not determined; viscosity and water contents not determined: samples lost prior to analysis

6.4.2 Tests with Ewing Bank 873 Crude Oil

Four of the eleven tests were conducted with Ewing bank 873 crude oil that had a viscosity of 683 cp at 15°C and measured at a shear rate of $10s^{-1}$. The control test with no dispersant produced a DE of 59.1% (CS #7). This is a very high level of dispersion for a control test.

Two (CS #9 and CS #11) of the remaining three results showed similar trends to those observed with IFO-30; the dispersant-treated oil left on the water surface (or weathered in the paddling pool and then having dispersant added) for nearly 3 days (70 and 74 hours) appeared to be dispersed rapidly and almost totally when breaking waves were applied.

The DE for test CS #11 was 81.6%, which confirms the visual ranking of 4 (indicative of rapid and complete dispersion). The DE result for test CS #9 could not be estimated because the water content of the recovered oil was not measured. A visual ranking of 4 was observed during the test suggesting a similar level of dispersion as for test CS #11.

The exception to these results was test CS #8. The dispersant-treated oil was on the water in the Ohmsett tank for 44 hours and was visually assessed as 1/2 (no visible dispersion or temporary dispersion of only larger oil droplets). A DE value is not available for this test because the recovered oil sample for this test was discarded prior to analysis for water content. In many respects the result from test CS #8 resembles that of test CS #2 with IFO-30; the oil did not totally disperse, unlike the same oils kept on the water surface for much longer periods in nominally identical conditions. As in test CS #2, only about $^{1}/_{2}$ of the containment area was covered in oil in test CS#8 so the slick was free to meander within the ring. This movement may have exposed the oil to more clean water or improved the transfer of surfactant from the oil to the water due to the slick movement and mixing at the oil-water interface.

This unique behavior of tests CS#2 and CS#8 and the fact that both occurred in equally unique tests where slick movement within the containment ring had occurred (no such movement was observed in all other tests where the oil filled the ring completely allowing little movement) has important implications for future work in this area. The definitive reason for this apparently unique behavior is not known, but the results are somewhat consistent with the results of the

bench-scale and small wave tank tests. In the small-scale tests dispersant effectiveness was lost quickly in most tests and in these tests there was clearly a rapid turnover of water under the "soaking" slicks. One could hypothesize that the unique behavior of these two slicks at Ohmsett may have been due to loss of dispersant from oil because a) oil moved around the open space and 'clean' water within the ring, or b) the oil was marginally thinner. The test results do not provide an explanation for these results, but they do suggest that these conditions should be examined in more detail.

6.4.3 Tests with Galveston 209 Crude Oil

Only a single test was undertaken with Galveston 209 crude oil. The oil treated with Corexit 9500 at a DOR of 1:20 was left on the water surface in the Ohmsett tank for only 18 hours before breaking waves were applied. The oil rapidly and totally dispersed based on both visual and DE measurements.

6.4.4 Summary of Ohmsett Dispersion Test Results

The results from testing at Ohmsett indicated that, with two exceptions, the dispersant-treated oils (DOR of 1:20) allowed to stand on calm water for periods of up to 6 days would disperse when breaking waves were applied. There appeared to be no significant detectible decrease in dispersant effectiveness for the test oil, dispersant and treatment rate combinations tested.

The reason for the two exceptional results, where the dispersant-treated oils did not disperse when breaking waves were applied, cannot be definitively explained on the basis of the available information. It is suspected that surface oil movement and/or sub-surface water currents may play a greater part in surfactant leaching than was anticipated in this project. Attempts to induce higher currents or move the surface oil in a systematic way using a trolling motor and a large fan to investigate this were inconclusive.

There were some apparent inconsistencies between the visual observations and the determined DE values. Relatively high DE results were obtained in test CS#2 with the IFO 30 oil and in test CS#7 (the Ewing Bank crude oil control test with no dispersant) and in both cases the oils appeared visually not to be dispersed. The relationship between the visual ranking obtained by observation and the DE determined by analyzing the recovered oil is known not to be linear.

Results obtained during the "Correlating the Results of Dispersant Effectiveness Tests Performed at Ohmsett with Identical Tests Performed At Sea" study (S L Ross, 2004) are presented in Figure 5. The visual ranking scale has no zero; a ranking of 1 indicates no dispersion, and the scale is somewhat subjective. Nevertheless, there is an approximate correlation. For the reasons described in Section 6.3, the DE result determined at Ohmsett tends to be above zero even when no dispersion has occurred and can give slightly low results at very high levels of dispersion. The effect of these systematic offsets in the DE results and the non-linear nature of the visual ranking scale mean that visually obvious dispersions are generally associated with DE values of more than 50%.

6.5 In-Water Oil Concentration Characterization

An in-situ laser particle-size analyzer or LISST was used to monitor in-water oil concentrations and particle size distributions during tests. Measurements were made on along-tank transects at a depth of 1.5 m in the water column, with the detector passing beneath the center of the oil slick. When it was visually obvious that effective dispersion was occurring, the instrument was positioned to pass through the centre of any visible cloud of dispersed oil.

Figure 6 Visual Effectiveness Ranking Versus Direct Measurement at Ohmsett
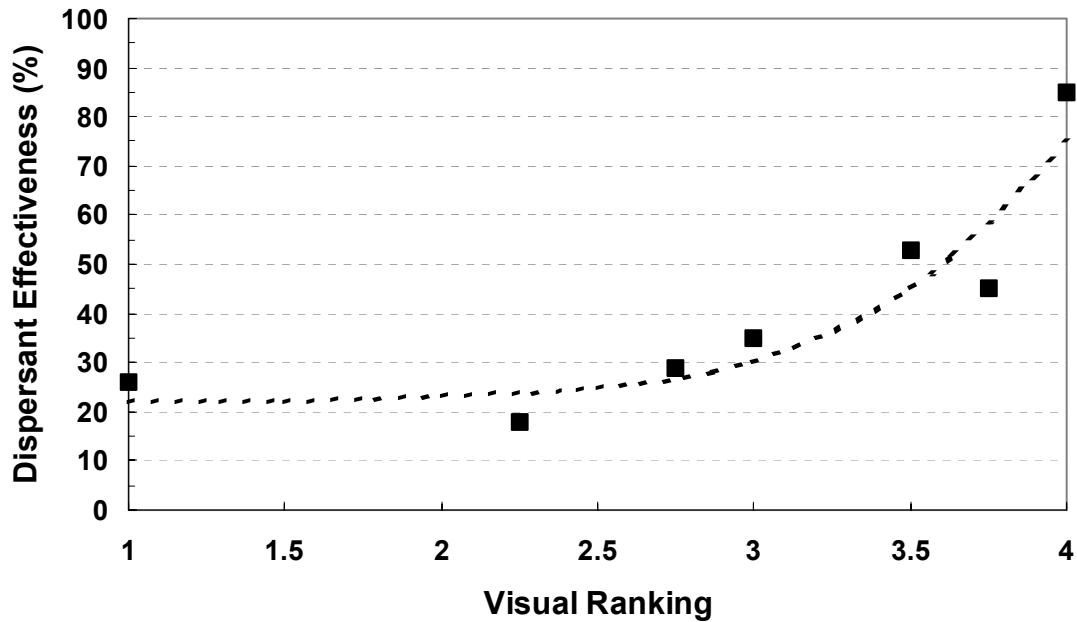
The LISST output from all tests, showing concentrations of particles and 50% volume diameter (VD50) and 90% volume diameter (VD90) are shown in figures in Appendix 1.

Where dispersant application clearly resulted in rapid or moderately rapid dispersion, the LISST output has followed a clear and reproducible pattern during transects through dispersed oil clouds. At the beginning of the transect, while the LISST traversed "clean water" outside of the cloud, the output commonly showed background concentrations of particles (= few ppm or less) and VD50 and VD90 values are highly variable. As the LISST passed through cloud of dispersed oil droplets, the particle concentration increased gradually to peak at several tens to 100 ppm or greater depending on level of effectiveness and degree of spreading of cloud, and then declined to background levels as the list passed out of the cloud. While the LISST was in the cloud, the VD50 and VD 90 values became less variable and showed pronounced shift generally upward (but on occasion downward with lighter oils) compared to background conditions.

7. Conclusions

The conclusions from this study are:

1. The initial indications from the bench-scale-testing (WSL method) and wave tank testing in the S L Ross wave tank were that a significant reduction in dispersant effectiveness, probably due to surfactant leaching out of the dispersant-treated oil, could be reasonably expected over a 12 to 45 hour exposure period on the water surface, particularly if dispersants were used at less than the recommended treatment rate of a DOR of 1:20.

2. The tests conducted at Ohmsett with Corexit 9500 dispersant pre-mixed into the test oils at the recommended rate of dispersant (a DOR of 1:20) showed that the oils would rapidly and almost totally disperse when exposed to breaking waves after being left on a calm water surface for prolonged periods (up to 6 days for IFO-30 fuel oil or nearly 3 days for Ewing Bank 873 crude oil). There was no reduction in dispersant effectiveness that could be attributed to surfactant leaching at Ohmsett and there was no significant drop in dispersant effectiveness caused by evaporative loss from the crude oils causing an increase in oil viscosity, with the test oils and time periods used in this study.

3. For the IFO-30 fuel oil and the Ewing Bank 873 crude oil there was an apparently inconsistent result in each case, in tests where smaller amounts of oil (50 L) were used in place of the larger volumes used in most tests (100L), in that the 50L-tests did not disperse as effectively as did the 100L-tests. The oil slicks in the 50L-tests did not cover the entire containment ring and moved over the water surface under the influence of the prevailing winds. This additional movement may have assisted in the leaching of dispersants. Investigations at Ohmsett using a trolling motor to induce an increased sub-surface current were not successful in speeding up the dispersant leaching process and did not confirm that a slight water movement would assist in the loss of dispersant from the oil.

4. On the basis of the information gathered at Ohmsett, it is reasonable to conclude that the surfactants within a dispersant-treated oil (treated at recommended treatment rates) and left in calm conditions at sea with no slick drift or under-slick water currents will not

leach out to a degree that causes a significant reduction in dispersant effectiveness within 3 to 6 days, and perhaps for much longer.

5. The initial indications from the small-scale work (the laboratory testing and testing in the SL Ross wave tank) are that a fairly rapid and significant decrease in dispersant effectiveness might be expected on prolonged oil exposure to calm sea conditions. These results were not borne out by the testing at Ohmsett. This may be an artifact of the small-scale test methods used, or it may be a systematic difference caused by the low dispersant treatment rates or more rapid turnover or more rapid water movement of the surface waters under the slicks in the smaller-scale tests. The entire quantity of water in the SL Ross test tank was re-circulated through a filter to remove oil and dispersants every 5 hours. The water in the bench-scale tests was treated and re-circulated every half hour. The Ohmsett filtering system treats the tank water once every 24 hours.

6. Earlier dispersant studies at Ohmsett (S L Ross, 2004) have demonstrated that the effects observed and measurements made at Ohmsett are similar to those made under similar conditions at sea and these provide confidence that the results from the Ohmsett testing are valid. However, the standard dispersant test protocol for determining DE (Dispersant Effectiveness) needs to be modified when dealing with dispersant-treated oils that have been 'primed' to disperse, but have not always been subject to sufficient wave energy.

8. Recommendations

The apparent difference in the indications about surfactant leaching from the results of small-scale testing and testing at Ohmsett needs to be rationalized in more detail. It is suggested that further studies be carried out to investigate the role of:

(i) <u>Relative oil and water movement</u>

The dispersant-treated test oil at Ohmsett needs to be constrained within a boom during the prolonged period on simulated calm sea. The possibility that oil movement within a partially-filled boom, with a limited volume of oil attaining its natural terminal thickness and not covering the entire area within the boom, was identified as a possible contributory factor to the two, apparently inconsistent results at Ohmsett. Attempts to induce increased sub-surface currents within the boomed area using a trolling motor were not successful in this study. A more systematic study using both small-scale and Ohmsett testing should be undertaken to further study the effects of slick drift and under-slick water currents on the leaching rate of dispersants from oil slicks

(ii) <u>Sub-optimal dispersant treatment rate.</u>

It is impossible to achieve the recommended dispersant treatment rate of a DOR of 1:20 in real use of dispersants at sea since it is impossible to determine oil layer thickness and localized over- and under-treatment is inevitable. If the results from small-scale testing and the apparently anomalous two results from the Ohmsett testing are indicative that the surfactant 'reservoir' within the oil can, under some conditions, be depleted much more rapidly than was evident in most of the Ohmsett tests, an investigation using a smaller 'reservoir', i.e. lower dispersant treatment rate, should be undertaken at Ohmsett.

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Appendix 1. Dispersed Oil Drop Size Distribution and Concentration

LISST Data Run 1: IFO30 Premixed X Corexit 9500 Standing 6 Days
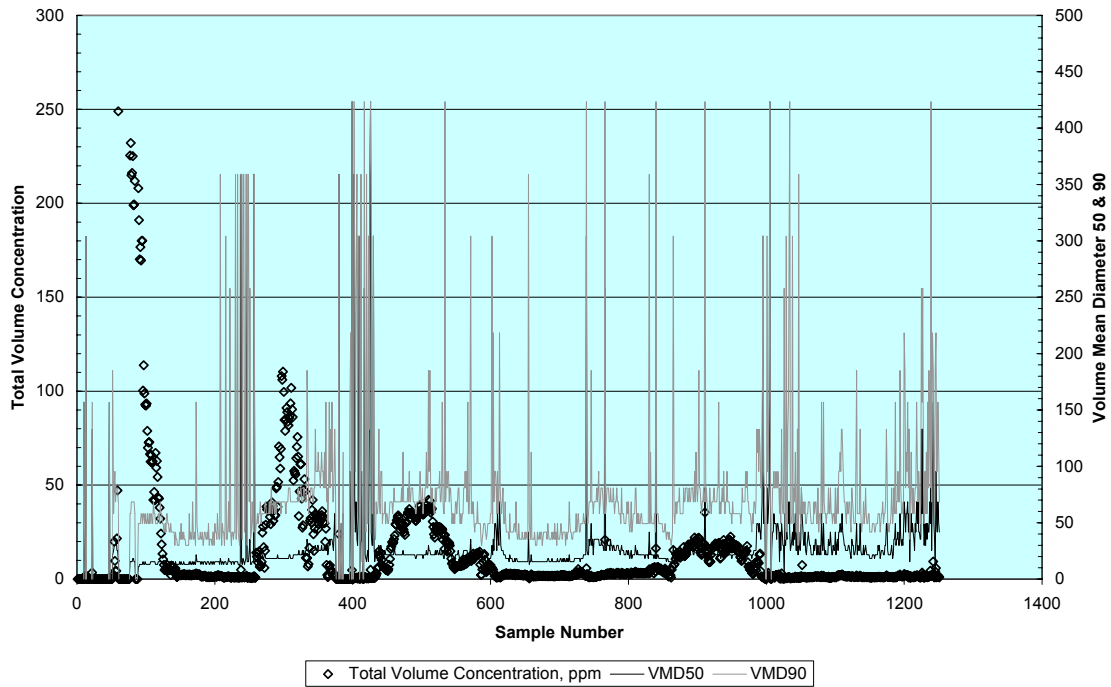
Figure A1.   LISST Data from test CS#1

LISST Data Run 2: IFO30 Premixed X Corexit 9500 Leaching Time = 66 hours
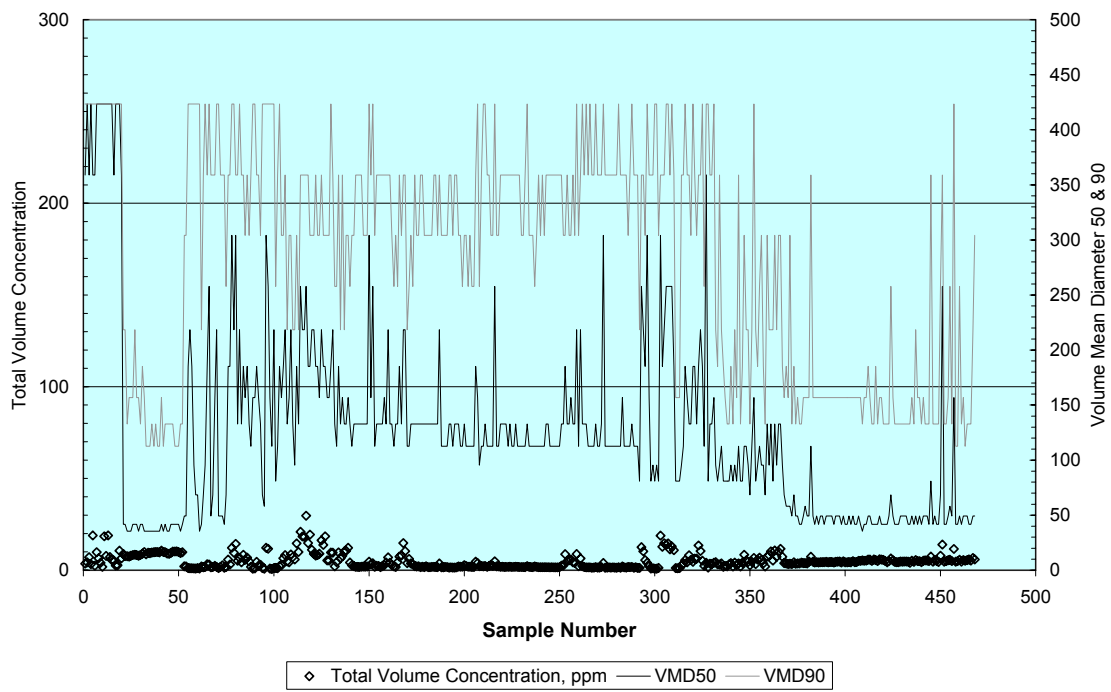
Figure A2.   LISST Data from test CS#2

LISST Data Run 3: IFO30 Control
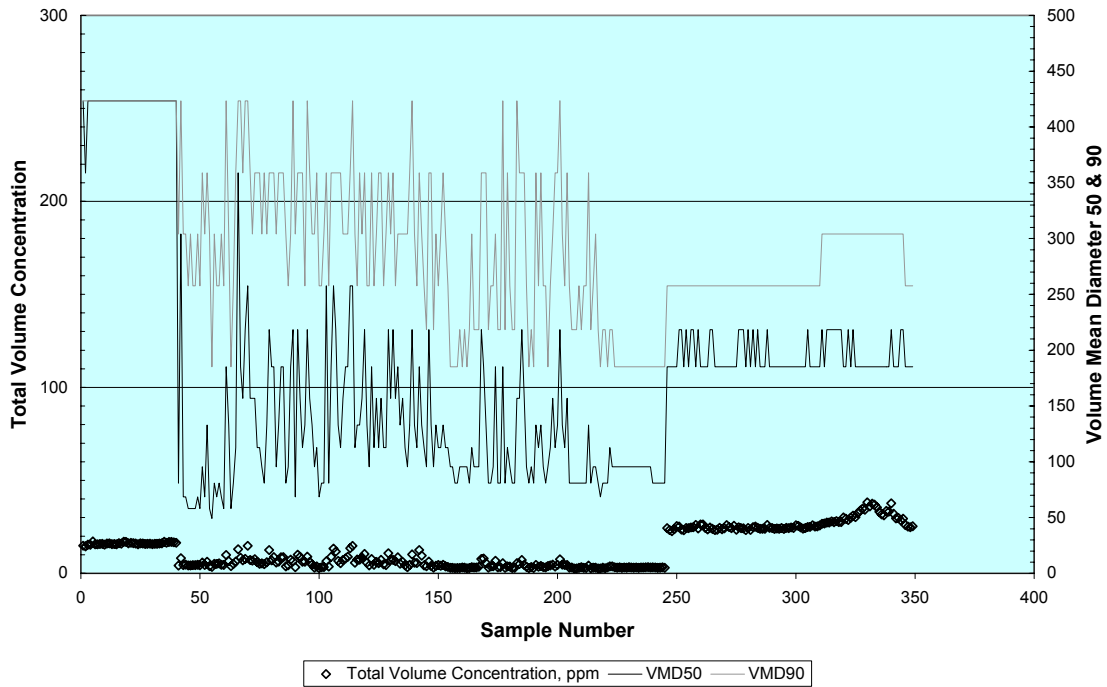
Figure A3.   LISST Data from test CS#3

LISST Data: Run 4: Galveston 209 Crude Oil X Corexit 9500 Leaching Time 17.5 Hours
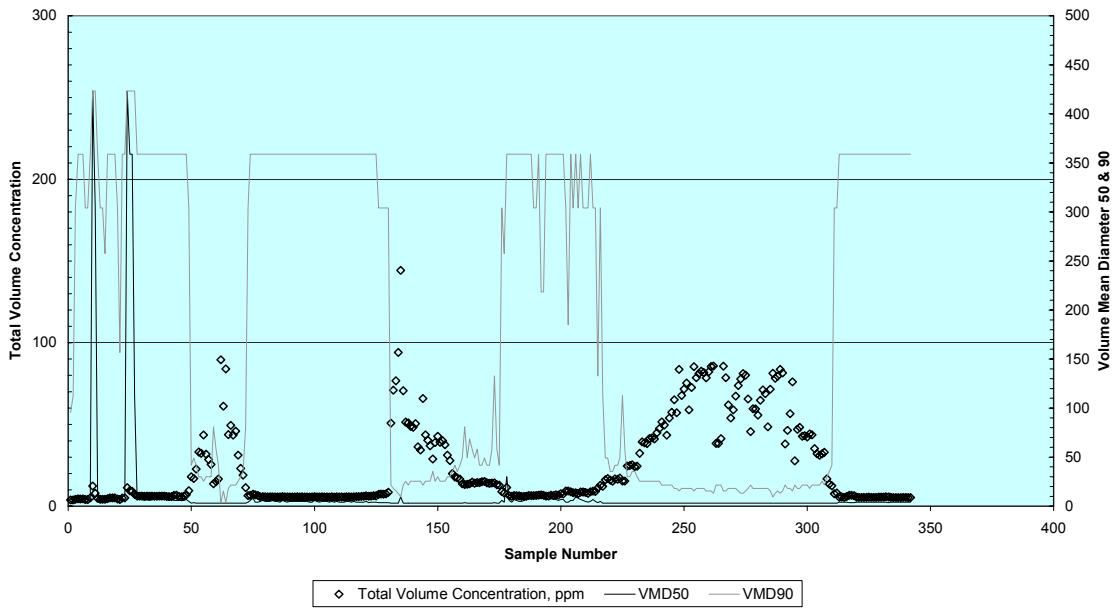
Figure A4 LISST Data from Test CS#4

LISST Data Run 5: IFO30 Premixed X Corexit 9500 70.5 hours
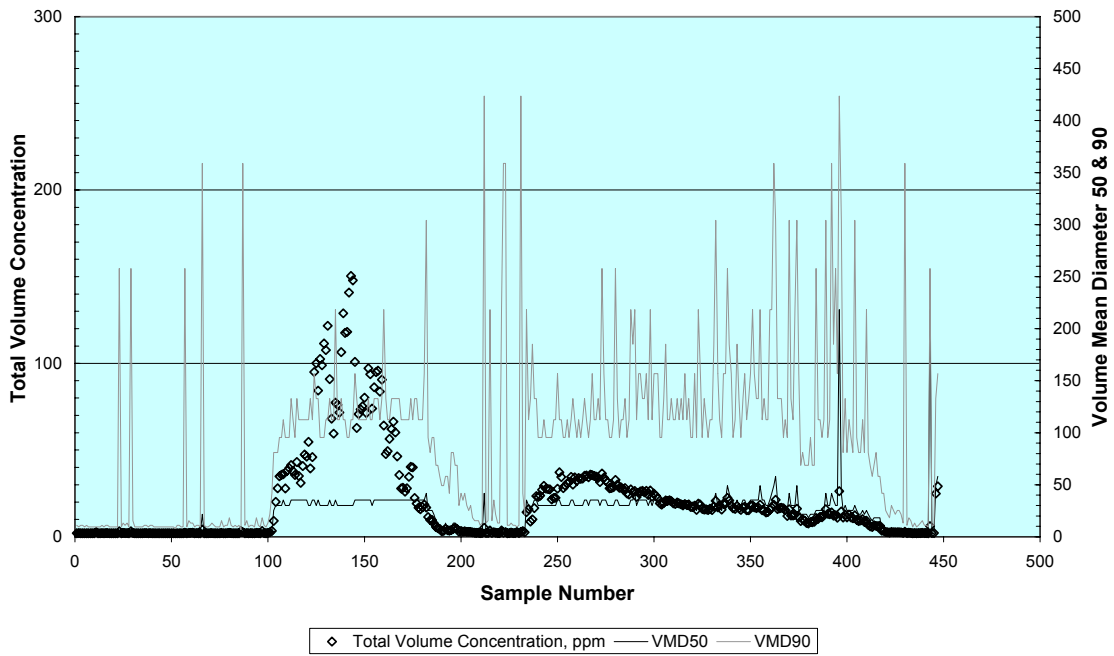
Figure A5.   LISST Data from test CS#5

LISST Data Run 6: IFO30 Premixed X Corexit 9500 Leaching 78 Hours
(most oil lost from ring over weekend)
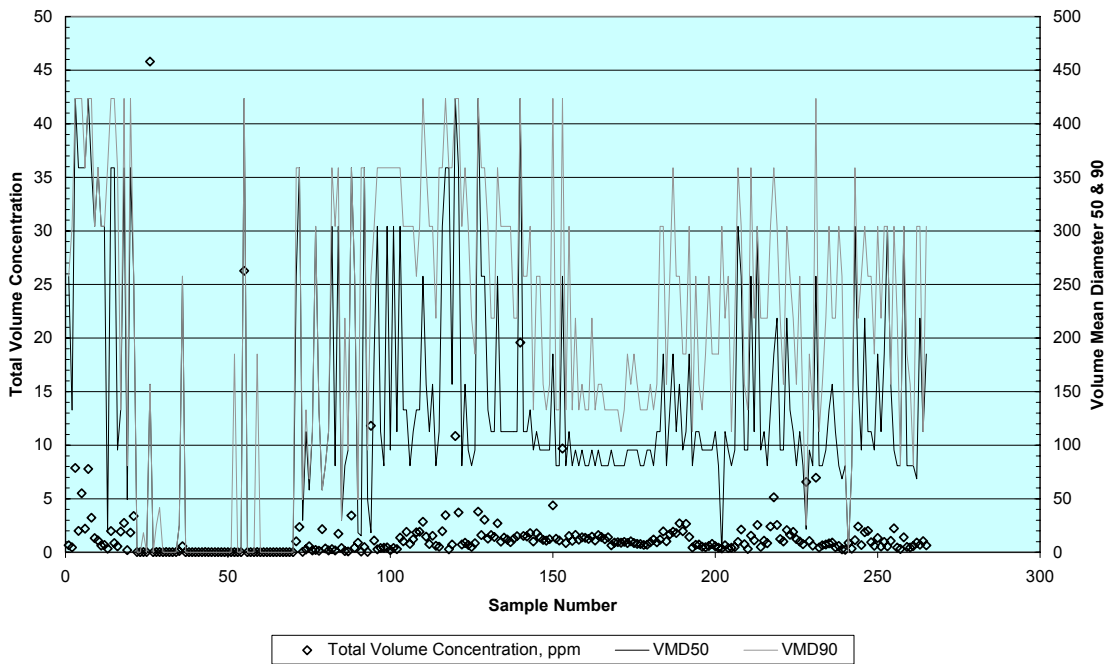
Figure A6.   LISST Data from test CS#6

LISST Data Run 7: Ewing Bank 837 Control
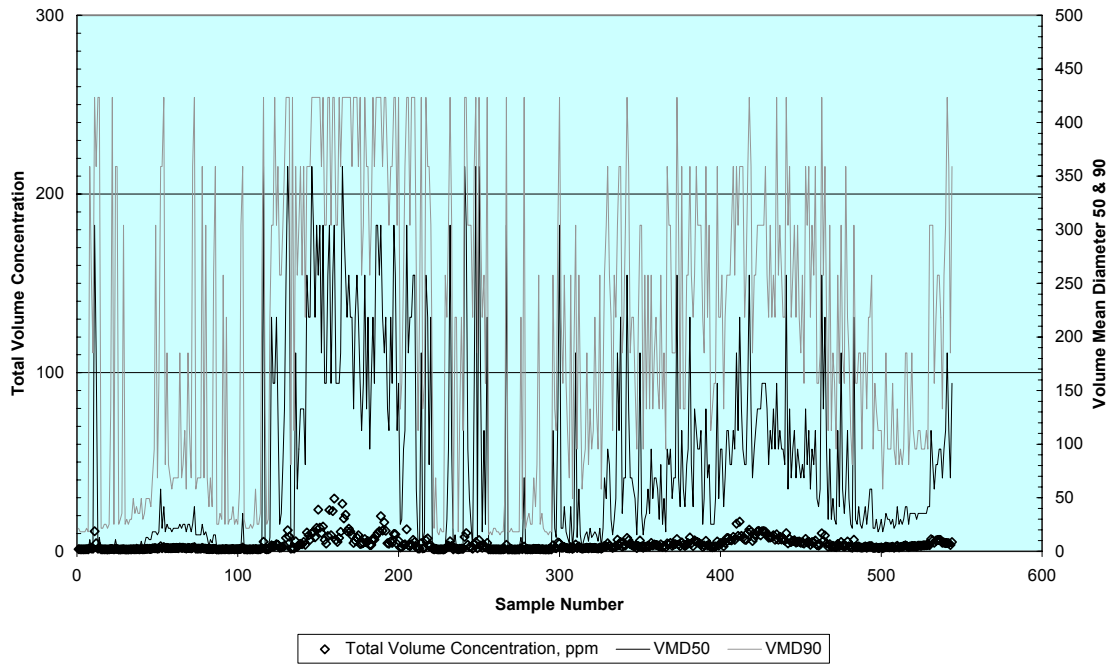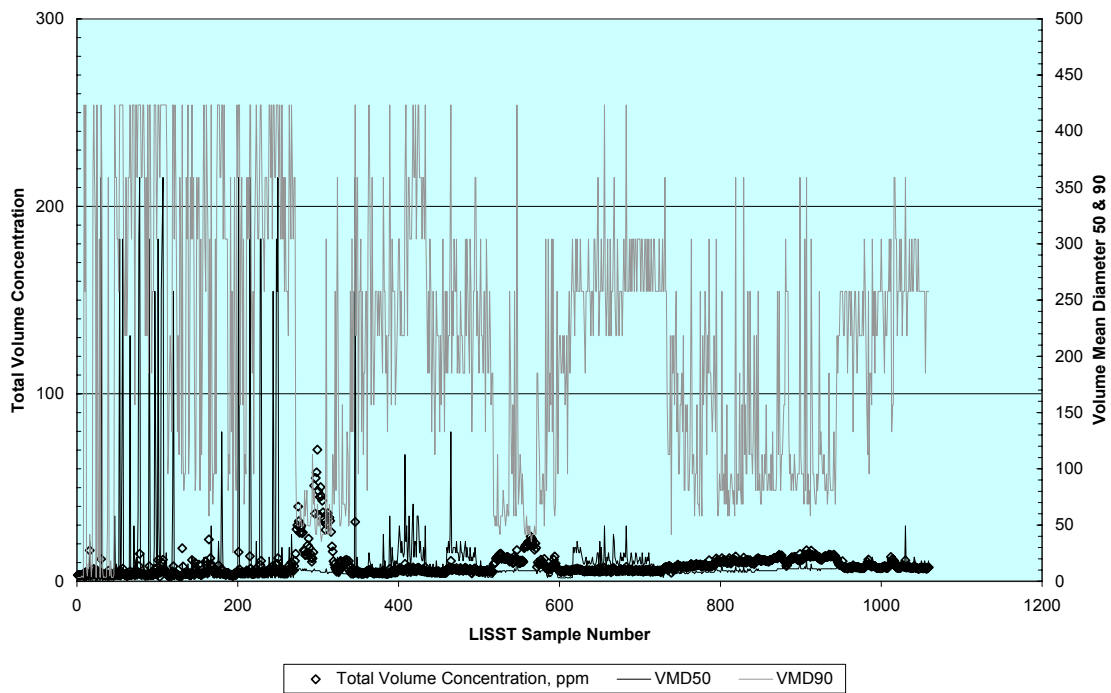

Figure A7.   LISST Data from test CS#7

LISST Data Run 8: Ewing Bank 873 x Corexit 9500 Leaching Time 44 Hours
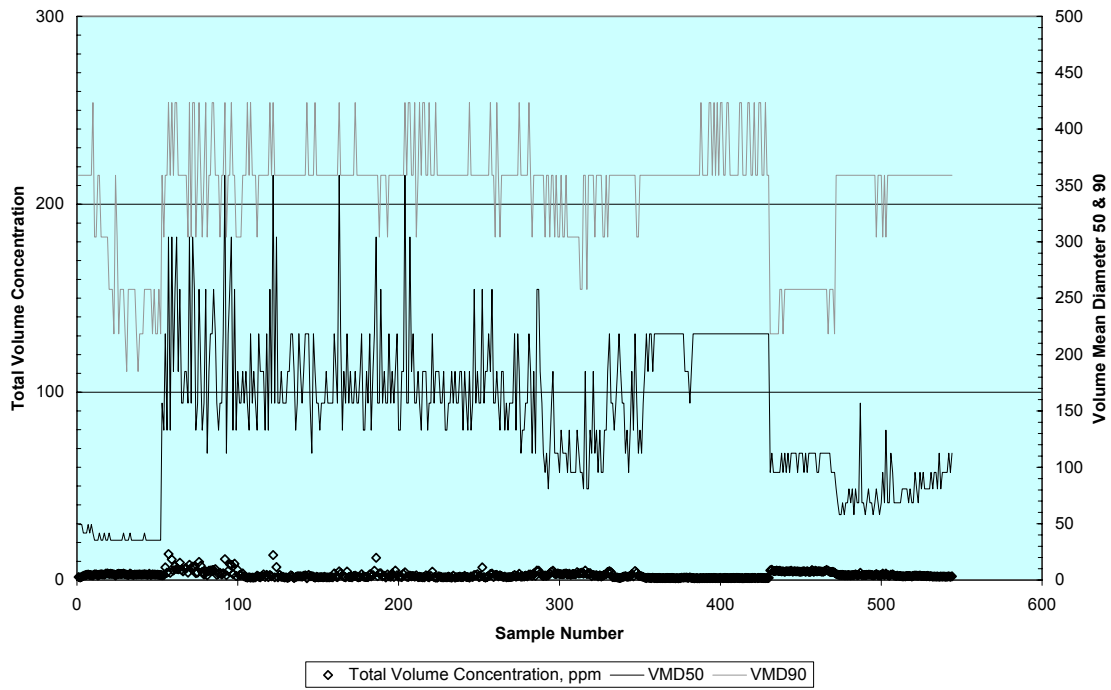
Figure A8.   LISST Data from test CS#8
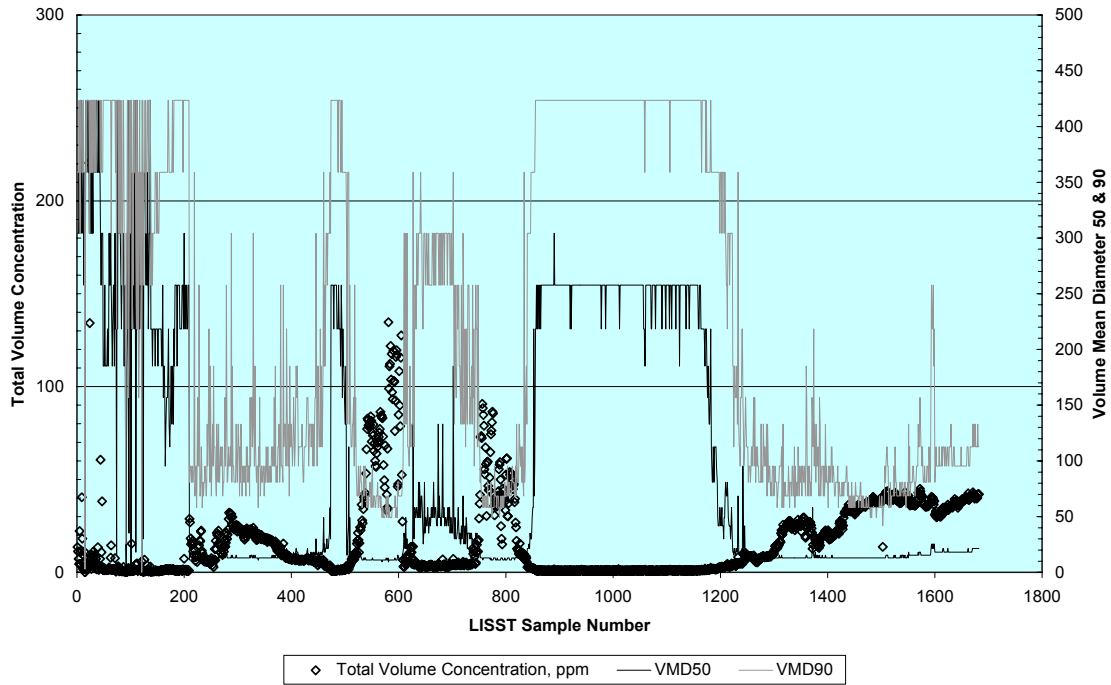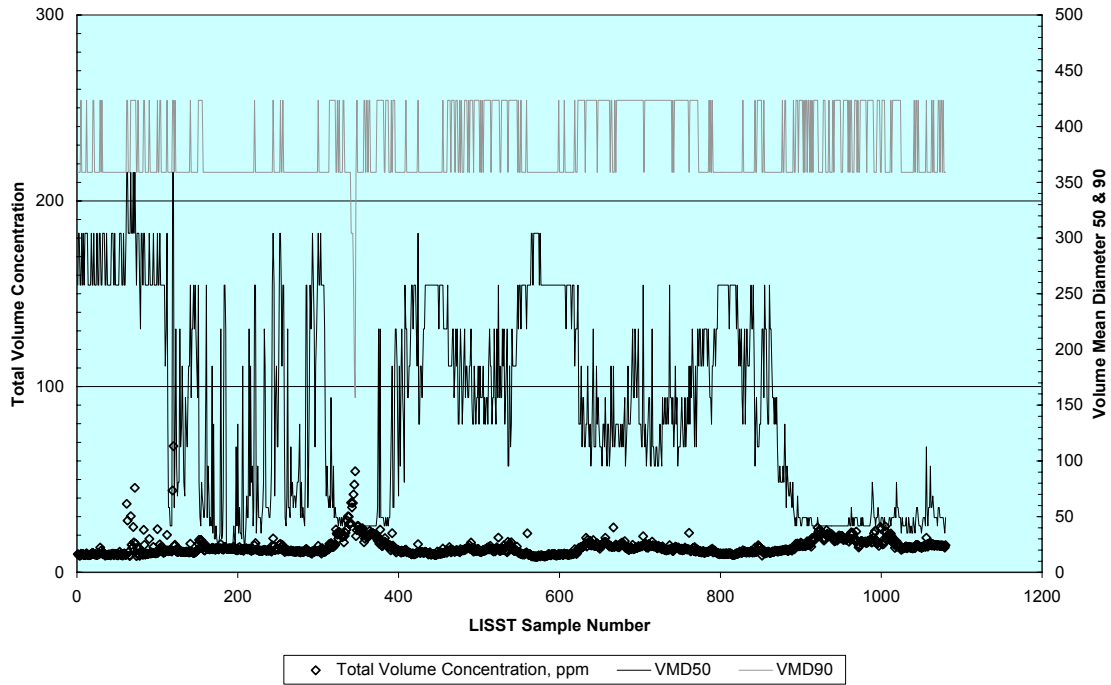
Figure A9.   LISST Data from test CS#9

Figure A10.   LISST Data from test CS#10

Figure A11.   LISST Data from test CS#11