A White Paper on Oil Spill Dispersant Effectiveness Testing in Large Tanks

for

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by

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Abstract

This white paper is a perspective on testing the effectiveness of oil spill dispersants in large tanks. Literature that relates to testing methodology is reviewed.

The following are 17 critical factors 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 be valid. 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
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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

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.

Summary and Issues

There are many issues related to conducting dispersant tests in large tanks. These are described in this report and summarized briefly below. Historical tank trials do form a consistent set of data in that many of the experimental designs are extremely flawed and resulted in a completely incorrect number that bears little resemblance to the real value. The general tendency has been that the lack of mass balance was attributed to dispersion, which results in an exaggeration of dispersion effectiveness by at least 4 times. It is the purpose of this paper to deal with these issues and explain experimental design and measurement methods in order to benefit future trials.

Specific Issues

The following are 17 critical factors 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 be valid. These factors are reviewed in this paper.

1.   Mass balance

Mass balance should be calculated and maintained in the best way possible. Because of the difficulty in accounting for all the oil, dispersant effectiveness should not be taken as the oil unaccounted for. In historical experiments, the oil unaccounted for ranged from -20% (over-accounted) to over 80%. In one set of experiments, Brown et al. (1987) showed that lack of mass balance would exaggerate apparent effectiveness on average by a factor of 4 times.

2.   Proper controls

Dispersant effectiveness must always be directly related to an identical experiment, preferably conducted at the same time under identical conditions as the test with dispersants. It should be noted that dispersants cause other changes in oil behaviour and a simple comparison to an untreated control may not be valid.

3.   Analytical method

There are few analytical methods that can be directly applied outside the laboratory. Fluorometry is one of these, but must be calibrated using standard sample analysis taken at the same time in the field. Furthermore, this calibration must be carried out using certified methods by a certified chemist in a certified laboratory.

4.   Differential plume movement

The geometry and movement of the dispersed oil plume are different than the surface slick and the surface slick cannot be used to guide sampling of the dispersed oil plume.

5.   Time lag and length of time plume followed

There is a time lag of 15 to 90 minutes before significant dispersion takes place. Furthermore, because of resurfacing of oil, the plume loses oil over a 2-day period. These dynamics must be considered in designing experiments.

6.   Mathematics of calculation and integration
        It is shown that several errors can be made in integration. Averages should not be used over wide areas and only the specific dispersant plume should be integrated.

7.   Lower and upper limits of analytical methods
        The analytical methods used must have the dynamic range to cover background levels to the peak dispersant plume value, generally from 0.1 to 100 ppm.

8.   Thickness measurement
        There are no valid and reliable thickness measurement techniques for surface slicks. Thus any value is an estimation and may easily be in error by an order-of-magnitude. This makes it difficult to perform mass balance on the basis of surface measurements. Thin slick quantities have been estimated using specially developed techniques (Bonner et al., 2002).

9.   Behaviour of oil with surfactant content
        Oil with surfactant content behaves differently than oil without. The critical containment velocity is much less. Its adhesion to sorbent-surface skimming devices is poor. Use of containment near critical velocity simply results in the release of oil after dispersant treatment, not dispersion.

10.   Surfactant stripping
        Surfactants partition out of the oil droplets over time, de-stabilizing the dispersed droplets and resulting in oil resurfacing. This occurs slowly and could occur over a wide area. Furthermore, slicks resulting from this phenomena are probably not thick enough to be observed.

11.   Recovering surface oil
        Recovering surface oil to calculate mass balance has a variety of problems including the loss of sheen and invisible sheen as well as evaporation loss. The surfactants also cause poor adhesion. The use of a recovery-enhancer can assist in obtaining a large percentage of the oil.

12.   Background levels of hydrocarbons
        The background levels of hydrocarbons must be used to correct measurements. The levels may vary widely and should be treated with the same caution as actual data.

13.   Fluorescence of dispersant
        The dispersant itself yields a fluorescent value, sometimes as much as 5 ppm. This is largely due to light scattering in the Turner fluorometer and should be corrected for.

14.   Herding
        Herding of oil occurs when larger droplets break through the slick and the surface pressure of the dispersant pushes oil aside. Herding is a major interference in conducting dispersant field trials and should be considered in tank tests.

15.   Heterogeneity of slick and plume
    Neither the slick nor the plume are homogeneous in distribution and concentration. This must be taken into account in the field trial. Measurements over small spatial areas will improve the quality of the final result.

16.   True analytical standards
    There exist certified labs using certified methods with chemists certified to take these measurements. These and certified analytical standards should be used to make the measurements.

17.   Weathering of the oil
    Dispersant effectiveness drops off significantly as the oil weathers. Tank tests of dispersants should use oil that is weathered to such a degree as might be the actual case in an application.

    Each of these factors is important to the appropriate outcome of the dispersant tank experiment. Important factors are the ability to determine a mass balance, the use of proper controls and analytical methods, and avoiding procedures that will result in incorrect results.

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

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1. Introduction
1.1 Objectives

The objectives of this paper are to review the literature related to testing oil spill dispersants in a large tank and to discuss a good method for conducting a tank test of dispersant effectiveness.

1.2 Scope

This paper covers tank testing of dispersant effectiveness and any related literature found.

2.   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 surfactants in dispersants leach out of the oil 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.

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 white paper (Bonner et al., 2002). In addition to mass problems, Bonner et al. note 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.

3. General Measurement of Dispersant Effectiveness in Tanks

A study on field testing provided a good 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, will be summarized here.

3.1 Mass Balance

Mass balance is very difficult to achieve in open field tests and even in large test tanks. 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 1.

Table 1   Results of Tank Effectiveness Tests

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 COSS 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%. This again illustrates the problems of attaining a mass balance.

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.

3.2   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.

3.3   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 successfully. 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. A further problem is that of sample preservation. Samples must be chilled immediately and treated to prevent bacteria growth and hydrocarbon loss. There are standard procedures available, but in early trials these were not applied.

The use of fluorometry in the field has been examined in detail (Lambert et al., 2000,

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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

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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 the only 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.

3.4   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).

Some early experimenters did not recognize the differential plume movement and took measurements under the surface slick. These same experimenters then integrated average concentrations over this large area. This can exaggerate dispersant effectiveness by as much as an order-of-magnitude because the area of the plume is often fractions of the area of the remaining slick.

3.5   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 the dispersant application varies from 15 to 90 minutes. Fast action is herding and not dispersion. The visible action is generally taken as the appearance of a yellow to coffee-coloured plume in the water. 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 days. 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 undispersed 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.

3.6   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).

3.7   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.

3.8   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.

3.9   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):

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

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.

3.10   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). 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.

Chemically dispersed oil has been known to destabilize due to the loss of surfactants to the water column. Once droplets lose a critical amount of surfactant, they are less likely to remain in the water column. This effect was measured in a study using ASMB and ANS crude oils and the dispersants Corexit 9500 and Corexit 9527 (Fingas et al., 2002). Resurfacing was consistent within each group of tests, static and shaken. The values for those samples shaken continuously fit an equation of the form, effectiveness = $a + b\sqrt{time}$. For the static tests, an equation of the form, effectiveness = $a + b/\sqrt{time}$, was the best. A method to generally predict this fall off in effectiveness with time was developed by correlating all the equations and preparing a two-level prediction scheme.

Results show that, under all conditions, significant amounts of oil resurface in the swirling flask after the initial dispersion takes place. While mixing has a tendency to retain more oil in the water column, only about 10% more oil is retained in the water column than if the system is static. The relation of this process to what may occur in the sea has not been determined, however, resurfacing has been noted in several sea trials. Provision should be made to track the plume and test for resurfacing.

3.11   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.

3.12   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.

3.13   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.

3.14   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.

3.15   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 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).

3.16 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.

In this era, it is simply unacceptable not to use certified methods, laboratories, and chemists.

3.17 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.

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

In the first part of this paper, the following 17 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. Elastol can assist in recovering the surfactant-treated oil. 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 is 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.

4.1   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.

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