

# **Review of Monitoring Protocols for Dispersant Effectiveness**

for

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by

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## Abstract

This paper is a review of field monitoring of the effectiveness of oil spill dispersants. The purpose of monitoring is to determine if a dispersant application was relatively effective or not. The most common protocol now is the NOAA SMART monitoring protocol. The protocols currently consist of a visual criteria and often include a surface monitoring program consisting of using in-situ fluorometers to gauge the relative effectiveness of a dispersant application. This report points out that there are many false positives and false negatives with both monitoring techniques. These can be overcome by paying attention to the science and technology.

The following 28 considerations related to the monitoring of dispersants are discussed.

1. Behaviour of the slick or plume
2. Safety
3. Purposes and objectives
4. Misleading indications
  - 4a. False positives visually
  - 4b. False negatives visually
  - 4c. False positives fluorometrically
  - 4d. False negatives fluorometrically
5. Resurfacing
6. Fluorometry
7. Visual surveillance
8. Tracking oil on surface
9. Tracking underwater plume
10. Mass balance
11. Controls
12. Hydrocarbon background
13. Computing values
14. Slick and plume heterogeneity
15. Laboratory data
16. Heterogeneity of slick and plume
17. Mathematics
18. Lower and upper analytical levels
19. Thickness measurements
20. Behaviour of oil with surfactants
21. Recovering surface oil
22. Deposition measurements
23. True analytical standards
24. Training, expertise, and experience

Monitoring by visual or fluorometer means can only yield an estimate of the relative effectiveness of a dispersant application. Specifically, the monitoring produces an estimate of whether the effectiveness of an application is ineffective or somewhat effective. The methods described in this report cannot give degrees or percentages of effectiveness.

It is recommended that a screening test of the dispersant effectiveness be carried out before any test application of the dispersant. This test should show a dispersion of about one-half of the oil. It is suggested that the prime monitoring technique for actual dispersant application is visual. Extensive work is required to produce visual monitoring guidelines and visual aids.

It was also pointed out that monitoring of oil concentrations in the water column would provide useful scientific information. This information may not be useful to the incident commanders, however, because of the complexities of the measurements.

## List of Acronyms

ANS	Alaska North Slope - Usually refers to the crude oil mixture at the end of the pipeline
APSC	Alyeska Pipeline Service Company - The company that operates the Alyeska pipeline and the Valdez terminal
ASMB	Alberta Sweet Mixed Blend - A crude oil consisting of many various low-in-sulphur crude oils
Corexit 9527	Brand name of a dispersant from Exxon
Corexit 9500	Brand name of a dispersant from Exxon
EPA	United States Environmental Protection Agency
IFO	Intermediate Fuel Oil - A mixture of Bunker C and diesel used for ship propulsion
IFP	The French Petroleum Institute - Usually used here as a description of their laboratory test
LC50 or LC <sub>50</sub>	Lethal concentration to 50% of the test population
NOAA	National Oceanic and Atmospheric Administration (U.S.)
PAH	Polynuclear Aromatic Hydrocarbons
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
SERVS	Ship Escort Response Vessel System - A co-op operating in Prince William Sound
SMART	Special Monitoring of Applied Response Technologies
WAF	Water-Accommodated Fraction - The sum total of oil in a water sample including physically dispersed and soluble oil

## **Summary and Issues**

### **Overall**

The monitoring of dispersant applications has been proposed with the purpose of determining if that application was relatively effective or not. The first question is whether such monitoring is necessary. It is suggested that monitoring is necessary, especially the visual component.

The monitoring protocols, such as SMART, currently consist of visual criteria and often a surface monitoring program consisting of using in-situ fluorometers to gauge the relative effectiveness of a dispersant application. This report points out that there are many false positives and false negatives with both monitoring techniques. These can be overcome by paying careful attention to the science and technology.

It is recommended that a screening test of the dispersant effectiveness be carried out before any test application of the dispersant. This test should show a dispersion of about one-half of the oil. It is suggested that the prime monitoring technique for actual dispersant application is visual. It is pointed out that extensive work is required to produce visual monitoring guidelines and visual aids.

Monitoring of oil concentrations in the water column would provide useful scientific information. This information may not be useful to the incident commanders, however, because of the complexities of the measurements.

### **Specific Issues**

The following is a summary of the specific issues and technical concerns related to field monitoring.

#### **1. Behaviour of the slick or plume**

The dispersed oil plume can move in a different direction than the surface slick and the dynamics of this are not easily predicted or tracked.

#### **2. Safety**

The crew of a small sample boat are at risk with aircraft application going on and the potential for a rapid change in weather.

#### **3. Purpose and objectives**

The objective should be to determine if a particular dispersant is relatively effective or not. Some users appear to misinterpret the protocol as actually yielding a judgement regarding effectiveness.

#### **4. Misleading indications**

There are many visual and other indications that may be misleading in terms of determining the effectiveness or lack of effectiveness in a particular application.

### **Visual indications that show more effectiveness than actually occurred**

**Herding** - This is the phenomenon whereby the oil is pushed aside by the dispersant, resulting in a clear path behind the application vehicle.

**Dispersant-only plume** - Once in the water, dispersant forms a whitish plume until it mixes to a

greater extent with the water. Such plumes could be mistaken for dispersed oil as opposed to dispersant only.

**Herding into smaller, unseen strips** - Oil is often herded into small strips that are not visible from the air.

**Spreading** - Dispersants increase an oil's tendency to spread. The surface slick may spread out to thicknesses that are not visible.

**Lacing** - 'Lace' is a sheen of oil with 'holes' in it. The 'holes' are caused by smaller drops of dispersant leading to herding. The 'lace' is usually visible only from the surface and not from the air.

#### **Visual indications that show less effectiveness than actually occurred**

There are also a number of visual indications that would lead one to conclude that little or no dispersion is occurring when in fact there is some or significant dispersion.

**Plume under remaining slick** - It can happen that the dispersed oil plume moves under the remaining slick.

**Plume not developed at time of observation** - The dispersed oil plume can take 15 to 60 minutes to develop to a maximum.

**Poor visibility conditions** - The dispersed plume is not highly visible and can be obscured by haze and some fog. It is unlikely, however, that a test application would be conducted under such conditions.

#### **Fluorescent indications that show more effectiveness than actually occurred**

There are also indications using fluorometers that can be misleading in terms of the effectiveness of a particular dispersant.

**Resurfacing after measurement** - Resurfacing of dispersed oil occurs in every case and, if the fluorometry measurement is taken before much resurfacing takes place, the effectiveness will be over-estimated.

**Repeatedly measuring one part of the plume** - The surface sampling crew does not have a good fixed frame of reference to guide them and it is very easy to repeatedly sample the same small dispersed oil plume.

**Dispersant-only plume** - When aerially applied dispersant lands on heavier or emulsified oils, the dispersant generally runs off without much dispersant penetrating the oil and without any measurable effect on the oil. The dispersant forms a milky mixture that may be mistaken for dispersant effectiveness.

**Dissolved aromatics** - After an oil spill occurs, a significant plume of aromatics forms. These aromatics are the prime target of a fluorometer and will give significant readings.

**Other fluorescent material in the area** - Fluorometers do not discriminate between sources of fluorescence. Fluorometers operating at long wavelengths will readily pick up organic material.

**Dispersant and aromatics only** - A probable occurrence is that dispersants and aromatics from

the oil are in an area and these fluoresce and could be mistaken for dispersed oil.

**Fluorescent indications that show less effectiveness than actually occurred**

**Fluorometer misses plume** - It is very easy to miss the dispersed oil plume with a surface-sampling rig.

**Misdirected by aerial observer** - The surface sampling team could be misdirected by the aerial observers.

**Measurement before plume develops** - The time to visible action after the dispersant application varies from 15 to 60 minutes.

**5. Resurfacing**

Chemically dispersed oil destabilizes due to the loss of surfactants into the water column. Once droplets lose a critical amount of surfactant, they are less likely to remain in the water column.

**6. Review of fluorometry**

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. Two wavelengths are available for fluorometers: the short wavelength is better for fresh crude oils and the long wavelength kit is better for heavy oils. The long wave 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. The apparent fluorescent quantity therefore increases in this process. The calibration method of fluorometric readings is critical if the results are to be used in any quantitative manner. The most reliable method of calibrating a fluorometer is to collect water from the fluorometer output and preserve this for later laboratory analysis. Another complication to sampling is the retention of surface oil on the sampling tubes that are lowered into the water.

**7. Visual surveillance**

The literature is in general agreement that the lower limit of oil visibility ranges from 0.03 to 1.6  $\mu\text{m}$  with a typical average of 0.1  $\mu\text{m}$ . Oil spill observers presume that, if they do not see a slick or sheen, no oil is present. After spreading, which is enhanced by dispersant application, a significant portion of the oil can reside in the 'invisible' sheen.

**8. Remote sensing**

While remote sensing can be useful to assess dispersant trials, some of the data can be misinterpreted. Remote sensing is thought to be a necessary tool for measuring the extent of the surface slick and of the dispersed plume. Colour photography with good time marks is essential, however, nadir-looking, spatially corrected colour imagery is much better.

**9. Tracking of oil on surface**

Tracking is essential to ensure that the geometries and positions of both the plume and surface slick are well established for the airborne and surface crews. Tracking resurfaced oil might be difficult as it is not highly visible. Orion buoys are known to follow surface slicks relatively well.

**10. Tracking of oil underwater**

Technologies to track the underwater plume are not as well tested as those to track oil on the surface, however, success has been recorded using drogued buoys such as the Davis Drifter.

**11. Mass balance**

It is important to note that the SMART document and other monitoring protocols noted do not purport to establish a percentage of effectiveness, nor should they. To achieve a percentage effectiveness, the experiment would have to establish a mass balance. Mass balance is very difficult to achieve in open field tests.

**12. Use of undispersed slick as a control**

In order to properly assess a dispersant field test, a proper control slick is needed. The control must be treated equally to the treated slick in every respect except for the applying of dispersant.

**13. Background levels of hydrocarbons**

A good background value is needed to subtract concentration values and to know when to terminate integration of the spill. The background level of hydrocarbons is generally in the lower parts-per-billion range.

**14. Using and computing values**

SMART and its other counterparts are not intended to result in percentage effectiveness. Despite this, users will inevitably try to use these values to ‘calculate’ effectiveness. This should not be done as it will lead to errors.

**15. Heterogeneity of the slick and plume**

Slick heterogeneities will result in heterogeneities in the dispersant plume.

**16. Review of laboratory and other reports**

There is general agreement on the relative effectiveness with a given dispersant and a given oil between laboratory and field data. It would be useful then to compare laboratory effectiveness data with the relevant field application. It is not likely that an oil that can be effectively dispersed in the laboratory would not be dispersed in the field.

**17. Mathematics of calculation and integration**

SMART does not advocate the calculation of values, however, several users have hinted at doing so. It is relatively easy to miscalculate the effectiveness if one were to attempt a calculation. The SMART protocol notes that a value of about 5 times the background would indicate relative effectiveness. As background levels are generally in the parts-per-billion range, the relative effectiveness would have to be many times - perhaps 100 times - the background level to show even a few percent effectiveness given the typical situation.

**18. Lower and upper limits of analytical methods**

The lower and upper limits of the analytical method should be considered or serious errors could result.

**19. Thickness measurements**

Estimation of surface oil using sorbent pads has been shown to be erroneous. This method would not yield useful information on dispersant effectiveness.

**20. Behaviour of oil with surfactant content**

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

**21. Recovering or estimating remaining surface oil**

Although not recommended in the SMART protocol, other experimenters have attempted to recover surface oil in order to directly determine effectiveness by presuming that the entire remainder is dispersed. This is incorrect because the loss from the surface includes: that amount evaporated, that amount in very thin (often invisible) slicks, that amount that is physically unrecoverable, oil adhered to booms or other surface objects, errors in the amounts of all the oil compartments, and oil simply unaccounted for.

**22. Deposition measurements**

Dispersant deposition measurements would assist in determining the amount of dispersant that caused the dispersion. Deposition measurements are very difficult to perform at sea, however, and would interfere with the dispersant experiment itself.

**23. True analytical standards**

Certified laboratories now exist that use certified petroleum hydrocarbon measurement techniques. These should be used for field applications as well.

**24. Training, expertise, and experience**

A very important factor in implementing any protocol is the training, expertise, and experience of the people performing the monitoring. Training aids are also needed. A review of existing training aids shows that they are not sufficient.



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## **1. Introduction**

### **1.1 Objectives**

The objectives of this report are to review the available field dispersant monitoring protocols and to suggest good monitoring protocols for dispersants in Alaska.

### **1.2 Scope**

This review covers the literature published up to July 2003. The study focuses primarily on literature related to issues of field measurement or monitoring of dispersant effectiveness.

### **1.3 Organization**

The report begins with a summary. The SMART and other protocols are presented in Section 2. In Section 3, the issues and considerations of field effectiveness monitoring are summarized. Section 4 gives the recommendations for future monitoring. Section 5 consists of a summary and conclusions and Section 6 is the list of references.

## **2. Review of Monitoring Protocols**

### **2.1 Introduction to Monitoring**

The purpose of monitoring protocols such as SMART is to determine whether or not dispersant applications are effective. A secondary purpose is to estimate the relative effectiveness, for example to be able to say about half the oil was dispersed. Dispersant effectiveness is defined as the amount of oil that the dispersant puts into the water column compared to the amount of oil that remains on the surface. In the field, effectiveness is visually indicated by the formation of a yellow to coffee-coloured plume of dispersed oil in the water column which is initially visible from ships and aircraft. The monitoring of dispersant effectiveness is largely carried out using visual surveillance or in-situ measurements of oil concentrations.

While it is easier to measure the effectiveness of dispersants in the laboratory than in the field, there are few standard testing procedures and tests may not represent actual conditions. For example, important factors that influence effectiveness, such as sea energy and salinity, may not be accurately reflected in laboratory tests. However, dispersant effectiveness at sea is very difficult to measure and such measurements are subject to many types of errors.

When testing dispersant effectiveness in the field, it is very difficult to measure the concentration of oil in the water column over large areas and at frequent enough time periods. It is also difficult to determine how much oil is left on the water surface as there are no methods available for measuring the thickness of an oil slick and the oil at the subsurface often moves differently than the oil on the surface. The quantitative method is not used in modern monitoring practices. Instead, a relative measure of dispersant effectiveness is made.

Several papers have assessed the techniques used to measure effectiveness in field tests. There is no general consensus that effectiveness and other parameters can actually be measured in the field using some of the current methodologies. All historical tests relied heavily on developing a mass balance of oil in the water column and that left on the surface (Fingas, 2000). Fluorometry has recently been used, but this method is also quantitatively unreliable as it measures only a small and varying portion of the oil (middle aromatics) and does not discriminate between dissolved components and oil that actually dispersed. Furthermore, it is

difficult to calibrate fluorometers for whole oil dispersions in the laboratory without using accurate techniques such as extraction and gas-chromatographic analysis. It is known that the aromatic ratio of the oil changes as a result of the dispersion process (Lambert et al., 2001a).

In early tests, it was not recognized that the plume of dispersed oil forms near the heavy oil in the tail of the slick and that this plume often moves off in a separate trajectory from the slick. Many researchers ‘measured’ the hydrocarbon concentrations beneath the slick and then integrated this over the whole slick area. As the area of the plume is always far less than this area, the amount of hydrocarbons in the water column was greatly exaggerated.

In recent years, many of these factors are being recognized and monitoring is being instituted to simply determine whether a dispersant application had any measurable effectiveness or not. Most of the current monitoring protocols do not try to quantify the effectiveness of dispersants. Furthermore, the purpose of the monitoring is to derive this limited indication of effectiveness because it is also now recognized that there is a potential to have little or no dispersion in actual situations.

In summary, dispersant effectiveness testing in the field is necessary to indicate whether or not the dispersant was effective to some degree. Quantitative measures are difficult because effectiveness values depend on establishing a mass balance between oil in the water column and on the surface. Furthermore, it is difficult to quantify the oil at sea. Because this mass balance and oil concentration values are difficult to achieve, specific quantitative results are questionable. Because of this, recent protocols have focussed on developing relative measures to simply ascertain whether there is some relative effectiveness as compared to little or no effectiveness.

## **2.2 Review of SMART Protocol**

The most common monitoring protocol in the United States is SMART (Special Monitoring of Applied Response Technologies) (SMART, 2003; Barnea and Laferrier, 1999). SMART is a non-regulatory protocol promulgated by the United States Coast Guard and the National Oceanic and Atmospheric Administration (NOAA). The purpose of the protocol is to provide information for decision-making. It is supposed that if the dispersant application were found to be ineffective, that further dispersion would not be carried out.

The SMART protocol proposes three tiers of monitoring:

Tier I is visual monitoring only;

Tier II includes fluorometer monitoring of the underwater dispersed oil plume; and

Tier III includes fluorometer monitoring at several depths and the possibility of performing other in-situ water analysis.

Sampling the water from the fluorometer and subsequent laboratory analysis is suggested although no protocols or standards are given for the laboratory analysis. Detailed procedures are given for on-site work.

For the visual surveillance recommended for all Tiers, the SMART protocol suggests that a visual aid observer such as the “NOAA Dispersant Application Observer Job Aid” be used to provide the user with imagery comparison (Levine, 1999; NOAA, 1999). The protocol also suggests that thermal infrared imaging would provide ‘a higher degree of sensitivity’ in determining dispersant effectiveness.

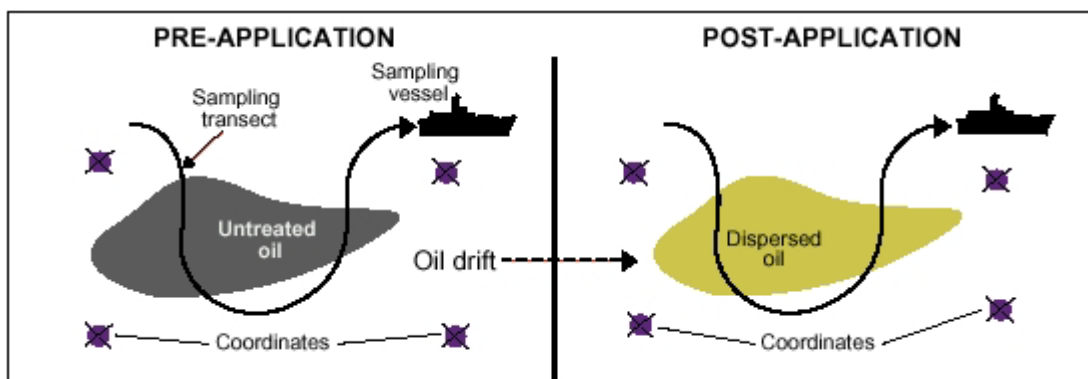
Tier II is the use of a continuous-flow fluorometer and the output from this on a relative basis. The suggestion is that a reading of about 5 times the background level indicates that the

dispersant is working. The data is to be collected at three locations: in a clean area to provide background; under the oiled slick before dispersant was applied; and then after the oil has been treated with dispersants. Data are to be collected both electronically and some on a data log, for which a form is provided. Positions are to be recorded with a GPS. Water samples are taken from the fluorometer output, preserved on ice, and analyzed later. No procedures are given for the subsequent analysis, although sampling procedures are given in detail.

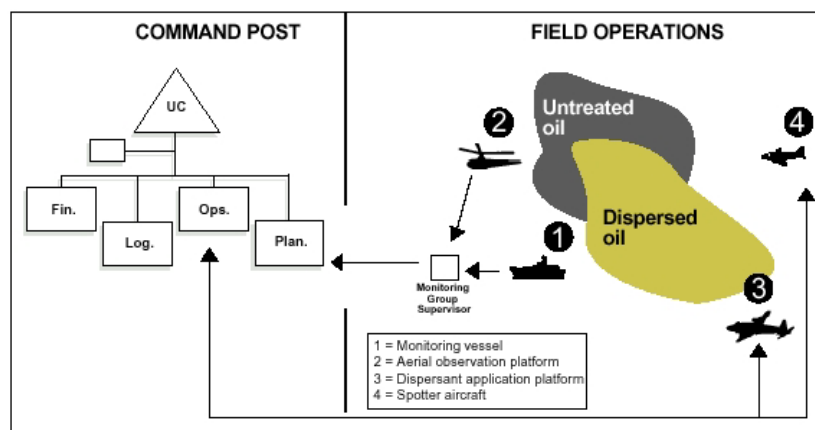
Tier III monitoring has two alternatives: multiple depths with one fluorometer or a transect at 1 and 5 m (or other depths as negotiated) with two fluorometers. Data are treated as before. When one fluorometer is used, the instrument is to be positioned where a high reading is obtained and then readings are taken down as far as 10 m.

The data are to be used only as an indication of the difference between the oil-only and dispersed levels. A level of 5 times is suggested as indicating dispersant effectiveness. Although it is stated that the levels are not to be used for turning a dispersant operation off and on, this is the implication.

The protocol suggests that an s-shaped passage be made though the slick to perform measurements as shown in Figure 1, as drawn from the SMART protocol. The protocol also suggests strong links between the command post and the field sampling and observation platforms as shown in Figure 2.

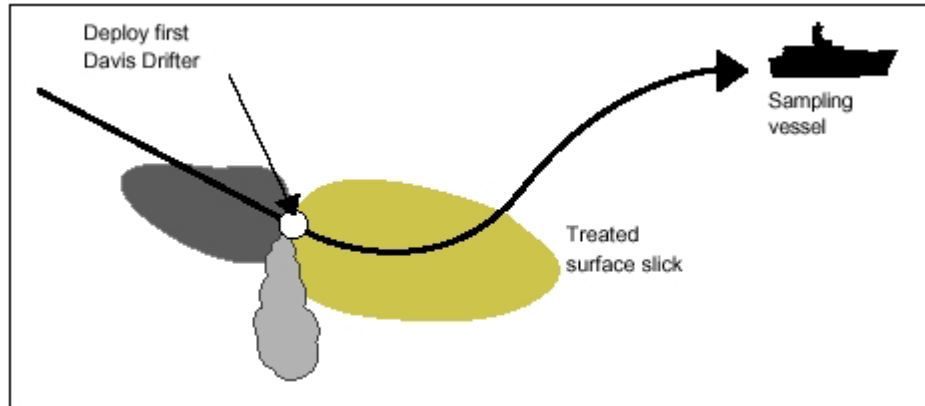


**Figure 1** Sample Path as Recommended in the Smart Document

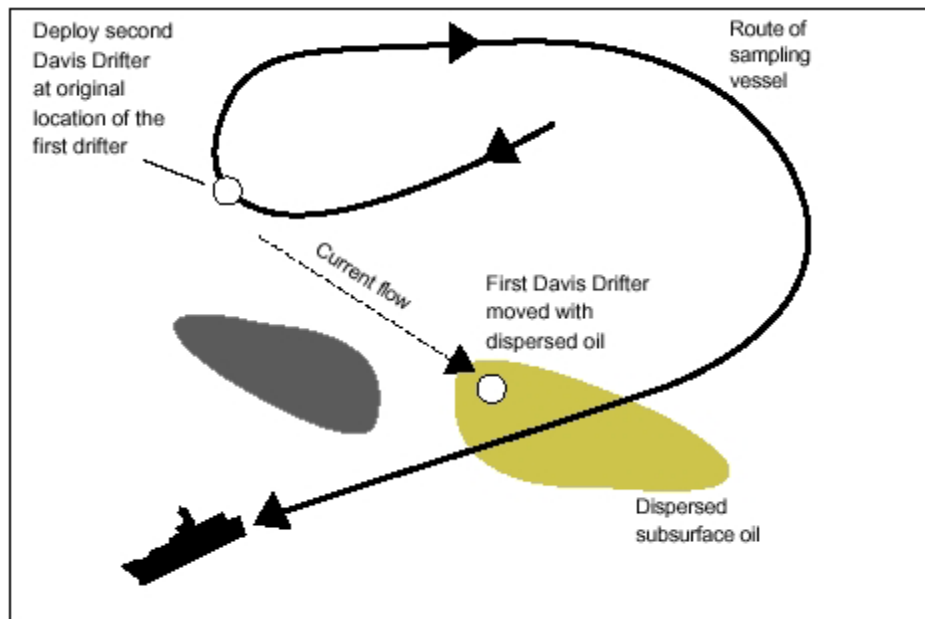


**Figure 2** Communication Between the Field and Command Post.

The protocol recommends that the sub-surface dispersed oil plume be tracked using a Davis Drifter. Figures 3 and 4 show the suggested deployment of Davis Drifters.

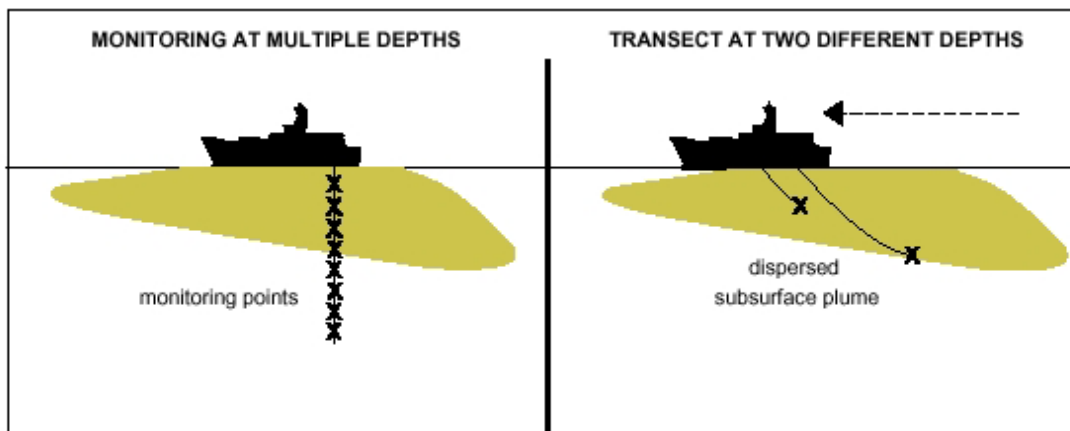


**Figure 3** Suggested Initial Deployment of Davis Drifter



**Figure 4** Deployment of a Second Davis Drifter

The SMART protocol also recommends that in Tier III monitoring, the concentration be measured from 1 to 10 m. This is illustrated in Figure 5.



**Figure 5** SMART Illustration of Sampling Depth

### 2.3 Review of SERVS Protocol

The Ship Escort Response Vessel System (SERVS) of the Alyeska Pipeline Service Company (APSC) has published its own extensive monitoring system (Hillman et al., 1997). The protocol is detailed and includes visual monitoring and on-water monitoring by taking samples as well as by fluorometric data. As with SMART, the procedures are not intended to quantify the amount of dispersant effectiveness or to yield a mass balance. The SERVS protocol is intended to answer the question of whether the application dispersed oil and to provide data for future use, including for scientific purposes.

After the application of dispersant, a vessel held in the vicinity moves to place drogues or markers at the up current and at the down current areas of the dispersed area. Drogues are initially to be rigged to follow currents at the 2-m depth.

The sampling vessel moves to a standby position up-wind and up-current of the dispersant target and outside the oil. Background water samples are taken at this location as are fluorometer data. This location is also marked with a drogue. The locations are marked using the drogues as reference points. The sampling vessel then moves to sample the area under the first dispersant application area. Samples are also taken under the untreated slick. Guidance is provided from the spotter aircraft as well as by reference to the drogues. Detailed instructions are given for each move and operations at each sample point.

The fluorometer is specified as a Turner model 10 with a short-wave light kit. A tube is used to sample at depths of between 0.5 to 5 m. The 2-m depth is recommended for the initial transit. The fluorometer is used to give relative results. The fluorometer is to be calibrated in continuous flow mode before and after each survey. A bench calibration procedure is also prescribed and this includes detailed procedures using Alaska North Slope Crude oil. Very detailed operation and decontamination procedures are given for the fluorometer.

The water grab samples are collected from the outflow port of the fluorometer. Vertical samples are also taken using a Valskon sampler at stations from 10, 5, and 1 m. Two types of samples are taken: total petroleum hydrocarbon samples and volatile aromatic samples. The



former are preserved at 4°C without acid and the latter with acid. Large numbers of samples are taken and up to 30 coolers must be provided to hold these samples.

The VOC samples are measured by purge and trap and injection into a GC/MS. The PHC analysis is conducted by EPA method 602 and 610. This includes TPH and PAH results.

Documentation procedures are given on sampling and fluorometer data-taking. Neither the airborne visual monitoring nor procedures are described in detail.

## **2.4 Review of Other Protocols**

Most jurisdictions in the United States recommend the use of SMART protocols (Texas, 2003; States/BC Task Force, 1998; ADEC, 2003). The SMART protocol has been used in two dispersant applications in the Gulf of Mexico (Stoermer et al., 2001; Gugg et al., 1999). A survey of dispersant regulations in most countries shows that they do not include monitoring protocols (Decola, 2003). The present author could find only the SMART protocol in the United States, the SERVS protocol, and a protocol in the New Zealand dispersant policy.

The New Zealand protocol includes provisions for monitoring (MSA, 2000; Stevens et al., 2001). The protocol is short and consists mostly of a monitoring report form. Two types of monitoring are proposed: visual and fluorometer. Neither guidelines nor values are given for the fluorometer. The visual guidelines are that a coffee-coloured plume indicates effectiveness and a white plume indicates excessive dispersants.

Much of the recent monitoring techniques evolves from British field trials (Lunel and Lewis, 1999; Lunel, 2001). Lunel advocates the dual type of monitoring such as described in SMART, however, the specifications and procedures are somewhat different. Lunel recommends visual monitoring of the dispersed plume (coffee-coloured) and notes that a white plume indicates excess dispersant use. Such monitoring methods are hinted at in Australian documentation, but not required (AMSA, 2003).

## **2.5 Review of Goodman Analysis of SMART**

A critique of the SMART protocol was published in the 2003 AMOP Proceedings (Goodman, 2003). Since this is related to the SMART protocol and monitoring in general, it is important to review this document.

The first point raised is the question of why dispersants and burning, of all the possible countermeasures possible, are the only ones to require monitoring. The second question is that of the possible delay caused by selecting, mobilizing, and deploying the team. Goodman notes that, despite the fact that the document states that such activities should not hold up the dispersant operation, it inevitably will. The third question raised is that of the purpose of effectiveness versus toxicity. Goodman supposes that the main issue is toxicity and notes that SMART does not address this. It is also noted that the SMART protocol would not give a realistic measure of dispersant effectiveness.

Goodman notes that three areas noted in the “Dispersant Application Observer Job Aid” are not covered in SMART (Levine, 1999): 1. time delay in dispersion after application; 2. dispersed oil plume variations; and 3. the occurrence of over- and under-doses of dispersant. Goodman also points out that neither the job aid nor SMART describe how the suggested still and video photography should be done.

The prescription of a water-sampling protocol complicates the issue, according to Goodman. The extra time, logistical support, and arrangements may not result in any

improvement in determining dispersant effectiveness. Goodman states that the problems of interpreting oil concentrations in view of the dynamic nature of the slicks and dispersed oil plume, over the heterogeneities observed and the short time of a traverse is very difficult and may not lead to a correct interpretation of effectiveness. Goodman also notes that fluorometric measures on the open ocean are quite complex and subject to many problems and variations and thus may be unreliable.

Goodman notes that the illustrations in the SMART document portray unrealistic scenarios of the whole slick being treated and the whole slick turning into a dispersed oil plume that is the same size as the oil slick. He further notes that the dispersed plume and the undispersed surface slick may not separate under some circumstances and thus may be missed in the sampling process. Goodman notes that there is no provision in the SMART protocol for compensating for the Eckman spiral, which is the effect of the Coriolis force on the water flow from the direction of the wind at the surface to 90° to the right in the Northern Hemisphere.

Goodman notes that Tier-II sampling at various depths does not solve any problems or limitations of sampling at a single depth. Goodman notes the following three major problems or information needs that SMART should have addressed.

1. The Net Environmental Benefit of dispersant use:
  - i. impact on surface organisms;
  - ii. impact on subsurface organisms; and
  - iii. relative environmental importance of surface and subsurface organisms and their population dynamics.
2. The perceived and actual public acceptance of dispersant use:
  - i. fishery concerns in terms of catch, tainting, and fishing gear contamination;
  - ii. the concern of the public and environmentalists about adding another chemical to the ecosystem; and
  - iii. the cheap factor.
3. The effectiveness of dispersant use compared to other response techniques:
  - i. the amount of oil treated in a given time period;
  - ii. the reduction of surface oil and oiling of shorelines;
  - iii. the response time;
  - iv. the area of the slick covered; and
  - v. the effectiveness of dispersing the oil.

Goodman notes that SMART covers only item 3(v). He suggests that Tier I, visual monitoring, is adequate for this purpose.

### **3. Considerations for Monitoring in the Field**

#### **3.1 Behaviour of the Slick or Plume**

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. Almost any combination of movement and geometry is possible, depending on the differential between surface and sub-surface currents and wind speeds. A major problem is therefore created in locating sample boats and later in trying to quantify the oil in the plume, whose extent is unknown. The best solution to this problem is to perform good aerial surveillance, preferably from a helicopter, or have a series of aerial photographs taken with good time stamps. The

samplers will require direction from a helicopter platform to ensure that measurements are conducted on representative portions of the underwater plume.

Generally, the plume can be seen better from the air. The underwater plume can initially be seen from the surface and the air as a yellow-coloured mass, but later is difficult to see from the surface or air. If the plume moves with the surface slick, neither surface nor airborne observers can see it and it is difficult to develop an accurate measurement and calculation plan to determine the amount of oil in the plume.

### **3.2 Safety**

A prime consideration should be the safety of the operation. The crew in a small sample boat are at risk when an aircraft application is going on and there is the potential for a rapid change in weather. As suggested in SMART or similar protocols, sampling is feasible only in small boats. These small boats should therefore be launched from large, safer vessels that remain in the vicinity while sampling is being done. A compromise to this might be to perform sampling from larger, more seaworthy vessels.

### **3.3 Purpose and Objectives**

The prime purpose and objective of monitoring processes such as SMART appear to be confused. The objective should be to determine if a particular dispersant is relatively effective or not. Some users appear to misinterpret the protocol as actually yielding an effectiveness value. As this report will show, there are many nuances to a dispersant application and thus it is impossible to simply say that a particular application was effective or not. It might be more appropriate to rate the application as somewhat effective, slightly effective, or apparently ineffective. These are probably the three most accurate things that could be said about a particular application.

The next question is whether a monitoring process like SMART could be accurate enough to lead to sound advice as to the continuance of the dispersant operation. In this author's opinion, modifications would be required before SMART would lead to accurate enough information to make this judgement.

Goodman has raised the question of the need for monitoring the dispersant application at all. This report will show that there are many false indications, both from a visual and an analytical point of view. These false indications point to a strong need to properly monitor a dispersant application to see if there was effectiveness or not. Other spill countermeasures do not have false indications such as this and thus do not need the same type of monitoring.

### **3.4 Misleading Indications**

There are many visual and other indications that may be misleading in determining the effectiveness or lack of effectiveness in a particular applications. These are discussed in this section.

#### **3.4.1 Visual Indications that Show More Effectiveness than Actually Occurred**

**Herding** - Herding is the phenomenon whereby 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 in thin oil slicks. In order to cause herding, the dispersant must directly contact the water surface. This readily occurs with thin oil slicks, because aerially applied

droplets are generally 300 to 1200  $\mu\text{m}$  in size, while the oil slick could easily be as thin as 100  $\mu\text{m}$  (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. If the conditions for herding are present, the larger droplets will land on the surface first and cause herding and then much of the dispersant that follows in smaller droplets will land directly on the water. The appearance of open water leads some to believe that dispersion has occurred and not herding. Furthermore, the remaining dispersant appears as a white plume in the open water and can also lead to misimpressions.

**Dispersant-only plume** - Dispersant can run off more viscous oil or can land directly on the water as noted in the description of herding. Once in the water, dispersant forms a whitish plume until it mixes to a greater extent with the water. Such plumes could be mistaken for dispersed oil as opposed to dispersant only.

**Herding into smaller unseen strips** - Herding does not necessarily occur in a broad swath. Oil is often herded into small strips that are not visible from the air. These will respread after a period of time.

**Spreading** - One of the side effects of dispersant is to reduce the oil's interfacial tension and thus increase its tendency to spread. This has been observed at several field trials (Swiss et al., 1987). The result of this is that the surface slick may be spread to thicknesses that are not visible or are not visible under the conditions that apply. This can lead to the assumption that the oil is dispersed into the water column, while it has actually been spread out over a much larger area.

**Lacing** - Another phenomenon that has been observed is the formation of 'lace'. This is a sheen of oil with 'holes' in it. The 'holes' are caused by smaller drops of dispersant leading to herding. The 'lace' is usually visible only from the surface and not from the air. Thus what appears to be sheen disappears after dispersant application, but actually portions of it have been herded by dispersant droplets.

### **3.4.2 Visual Indications that Show Less Effectiveness than Actually Occurred**

There are also a number of visual indications that would lead one to conclude that little or no dispersion is occurring when in fact there is some or significant dispersion. These are discussed here.

**Plume under remaining slick** - The dispersed oil plume may move under the remaining slick. As the surface is never 100% clear of oil under the dispersant application path, the dispersant operation appears to have had no effect. This is unlikely to last for a long time as the plume could emerge from under the remaining slick within about one hour depending on the size of the slick and the plume.

**Plume not developed at time of observation** - The dispersed oil plume can take 15 to 60 minutes to develop to a maximum. Observation may take place before the plume is fully developed leading to a conclusion that there is no plume. This and many other points raised here

emphasize the need for good and continual surveillance during the first few hours after a dispersant application and for at least one hour after a trial dispersion.

**Poor visibility conditions** - The dispersed plume is not highly visible and can be obscured by haze and some fog. It is unlikely, however, that a test application would be conducted under such conditions.

### **3.4.3 Fluorescent Indications that Show More Effectiveness than Actually Occurred**

There are also indications using fluorometers that can be misleading in terms of the effectiveness of a particular dispersant. These are discussed here.

**Resurfacing after measurement** - Resurfacing of dispersed oil occurs in every case (Fingas et al., 2002, 2003). The phenomena will be described in detail in Section 3.5. The point here is that, if the fluorometry measurement is taken before much re-surfacing takes place, the effectiveness will be over-estimated.

**Repeatedly measuring one part of the plume** - The surface sampling crew does not have a good fixed frame of reference to guide them and it is very easy to repeatedly sample the same small dispersed oil plume. This will lead to a large over-estimation of the amount of dispersed oil in the area. This can be prevented by good aerial directions and can be documented by plotting the course of the small boat and the plumes after the operation is completed.

**Dispersant-only plume** - When aerially applied dispersant lands on heavier or emulsified oils, the dispersant generally runs off without much dispersant penetrating the oil and without any measurable effect on the oil. As noted in Section 3.4.1, the dispersant begins to mix with the water and forms a milky mixture that may be mistaken for dispersant effectiveness. This should be noted by direct surface observation to ensure that runoff is not mistaken for dispersant effectiveness.

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, b). 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. In an actual application or experiment, the pickup of even a small amount of oil by the dispersant will result in a significant signal. Although this is difficult to correct for, one way is to correct all the readings to correct GC analytical results.

**Dissolved aromatics** - After an oil spill occurs, a significant plume of aromatics forms. These aromatics are the prime target of a fluorometer and will give significant readings. A dissolved aromatic plume will be as significant as a dispersed oil plume under certain circumstances. There is no way to distinguish this in the field and even in the lab without special analytical procedures.

**Other fluorescent material in area** - Fluorometers do not discriminate between sources of fluorescence. Fluorometers operating at long wavelengths will readily pick up organic material and those at short wavelengths, less so (Lambert et al., 2001a). During a survey of Vancouver

harbour several years ago, this author encountered a large submerged plume of fluorescent material using a Turner fluorometer. Sample analysis and contact with a local refinery showed that this was aromatic material inadvertently released by the refinery.

**Dispersant and aromatics only** - A probable occurrence is that dispersants and aromatics from the oil are in an area and these fluoresce and could be mistaken for dispersed oil.

**3.4.4 Fluorescent Indications that Show Less Effectiveness than Actually Occurred**  
**Fluorometer misses plume** - It is very easy to miss the dispersed oil plume with a surface-sampling rig. As noted before, there are few points of reference for the surface sampling team and their field of view is very narrow. This again points to the need for good aerial support at this type of operation.

**Misdirected by aerial observer** - The surface sampling team could be misdirected by the aerial observers through a series of errors. This is more likely with a fixed-wing aircraft as overpasses might occur at about 15-minute intervals and the aerial observers can easily lose track of where the surface crew was in the past sequence.

**Measurement before plume develops** - Certain time characteristics of the dispersion process must be understood. First, the time to visible action after the dispersant application varies from 15 to 40 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 action of the dispersant may continue for up to an hour after application. Thirdly, the movement and dispersion of the plume are often slow, although the plume is generally visible for about three hours and is never visible for more than about eight hours. Finally, the oil in the plume can resurface slowly over 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, control slick, and the dispersed plumes for as long as possible. The Beaufort Sea experiment is 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 general geometry as 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.

### **3.5 Review of Resurfacing**

It is well known that there is an exchange of surfactants between the target droplet and the surrounding water (Hiemenz and Rajagopalan, 1997). This results in destabilization of the emulsion. When 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; 2003). 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 =  $a + b\sqrt{\text{time}}$ . For the static tests, an equation of the form, effectiveness =  $a + b/\sqrt{\text{time}}$ , 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 that which may occur in the sea has not been determined, however, resurfacing has been noted in several sea trials. Provisions should be made to track the plume and test for resurfacing.

### **3.6 Review of Fluorometry**

There are few analytical methods that can be used in field situations. Very early in the field testing program, fluorometers, particularly Turner fluorometers, were used. In early years without GPS, there was difficulty in assessing the position at which samples were taken. Today, accurate GPS data coupled directly to fluorometer data can provide reasonable positional data for the fluorometric readings. Furthermore, analyzing samples from the fluorometer outputs can provide positive confirmation or better understanding of the readings.

Some of the earlier trials used grab samples which were subsequently taken for analysis by UV or IR (infrared) 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, 2001a, 2001b). These studies show that fluorometry is a sensitive, but not necessarily accurate means of oil determination. A fluorometer uses long-wave 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 that 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, the 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 more 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.

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 Gas Chromatography (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. Because of the differences in chemical composition, however, 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. This data show the lower oil concentrations actually achieved in a dispersant application.

The effects of running probes into the water column have not been fully examined. Although several devices have been created to examine the sub-surface water column, the standby usually ends up being weighted hose. Tests in the present author's laboratory 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, however, 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, which meant that portions of the oil-in-water plume were driven downwards by the boat (Bocard et al., 1986). The solution was to run a sampler far from the boat's 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, although this action may also drag oil onto the outside of the sampling gear.

There is also an issue regarding the use of short- or long-wave emissions in the fluorometer. Both options are available in Turner units. Depending on who is contacted in the manufacturer's or distributor's firms, one or the other is recommended. The discussion can be simplified by stating that the short wavelength is better for fresh crude oils and the long wavelength kit is better for heavy oils (Lambert et al., 2001b). The wavelengths of both kits does include emissions that activate naphthalenes to chrysenes, however, the short wavelength kit has more wavelengths that stimulate naphthalene and phenanthrene emissions as would be appropriate



for lighter crude oils. The long wavelength kit stimulates the chrysenes more than does the short wavelength kit and thus gives better response for heavier oils.

In summary, fluorometry is the only practical technique for measuring oil concentrations in the water column. The errors encountered result in an increase in 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.

### 3.7 Visual Surveillance

Visual surveillance has been a standard tool for examining the effectiveness of dispersants. The primary indicators are the visual appearance of a yellow to coffee-coloured plume in the water from dispersed oil. Indicators of poor effectiveness are the appearance of herding or dispersant-only plumes in the water (whitish).

A very important tool for working with oil spills has been the relationship between the appearance and the thickness of the oil. This relationship is occasionally used to estimate the amount of oil before or after dispersion. Present thickness charts actually date from 1930 (Fingas et al., 1999). Before this, it was already recognized that slicks on water had consistent or nearly consistent appearances. A series of experiments conducted at that time resulted in charts that are still used today. Only a few experiments have been done in recent years.

These appearance factors are very important because they provide the only means of estimating the amount of oil in thin sheens on the sea. There are no means for estimating the amount of thick slicks on the sea.

The only scientific basis for slick thickness related to appearance is the threshold of appearance of rainbow colours (Fingas et al., 1999). The appearance of rainbow colours is the result of constructive and destructive interference of the light waves reflected from the air-oil interface with those reflected from the oil-water interface. The difference in optical path lengths for these two waves depends on the refractive index of the oil. The refractive index of a given wavelength results in a difference in optical path length. This difference can be given as:

$$\Delta L = 2t (\mu^2 - \sin^2 i)^{1/2} \quad (1)$$

where:  $\Delta L$  is the difference in optical path length,  
t is the film thickness,  
 $\mu$  is the refractive index of the film, and  
i is the angle of light incidence.

If  $\Delta L$  contains a whole number of wavelengths, then maximum destructive interference will occur. If  $\Delta L$  contains an odd number of half wavelengths, then maximum constructive interference will occur.

Then the maximum destructive interferences occur at:

$$\lambda = \Delta L/x \quad (2)$$

where:  $\lambda$  is the wavelength under consideration, and  
x is a whole number as 1, 2, 3, 4 etc.

The maximum constructive interferences occur at:

$$\lambda = 2\Delta L/x \quad (3)$$

where: x is a whole odd number as 1, 3, 5, 7 etc.

Tables of constructive and destructive wavelengths can be written. These then result in a colour chart for visible oil as:

thickness less than 0.15  $\mu\text{m}$  - no colour apparent;

thickness of 0.15  $\mu\text{m}$  - warm tone apparent;

thickness of 0.2 to 0.9  $\mu\text{m}$  - variety of colours (e.g., rainbow); and

thickness greater than 0.9  $\mu\text{m}$  - colours of less purity, heading toward gray.

The literature is in general agreement that the lower limit of oil visibility ranges from 0.03 to 1.6  $\mu\text{m}$  with a typical average of 0.1  $\mu\text{m}$  (Fingas et al., 1999). Below this, oil is simply not visible to the human eye and light is transmitted through these thin slicks. Often oil spill observers presume that, if they do not see a slick or sheen, no oil is present. After spreading, which is enhanced by dispersant application, a significant portion of the oil can reside in the 'invisible' sheen. This is another reason that surface measurements are unreliable. These very thin sheens cannot be recovered, seen, or measured at this time.

### 3.8 Remote Sensing

Remote sensing can be useful to assess dispersant trials, however, some of the data can be misinterpreted. Careful use must be made of data and recognition must be given to the physical basis of these data. Very importantly, it should be recognized that no capability exists to measure oil thickness using current airborne sensors. There was a myth that infrared sensors could be used to 'measure' oil thickness, but tests have shown otherwise (Goodman and Fingas, 1988). Furthermore, there were attempts to use sorbent tests to 'calibrate' infrared imagery and this too was shown to be incorrect (Goodman and Fingas, 1988a, b). The only thickness information available to the oil spill worker is the fact that the rainbow appearance has a thickness of between 0.15 and 0.8  $\mu\text{m}$  as described in Section 3.7 (Fingas et al., 1999). This occurs because of multi-path interferences in visible light and is well understood on a physical basis. After the slick becomes thicker, the black/brown appearance has no thickness associated with it.

Remote sensing is thought to be a necessary tool for measuring the extent of the surface slick and of the dispersed plume (Payne et al., 1991). While colour photography with good time marks is essential, nadir-looking, spatially corrected colour imagery is much better.

Infrared (IR) photography can give a picture of the relative thickness, but can be misled by the presence of a dispersed oil plume. Infrared photography was to be the prime measure of effectiveness in the Beaufort Sea trials in 1986 (Swiss et al., 1987). A computer device had been built to directly yield area of thick slicks (i.e., IR 'hot' area). As the trial progressed, the area of the dispersed slick grew rapidly, far beyond that of the two control slicks. While the naive

conclusion would be that dispersants were very ineffective and actually increased the amount of oil on the water surface, the actual fact was that the dispersant increased the area of oil on the surface and the dispersed plume was also hotter than the surrounding water due to the absorption of IR radiation.

There are several reviews of remote sensing technology and which sensors can provide useful imagery (Fingas and Brown, 2001, 2002).

### **3.9 Tracking of Oil on Surface**

Because the long-term effectiveness of the dispersant should be understood as well as the short-term effectiveness (in terms of hours), at sea trials there should be an appropriate plan to track and sample both the slick, the plume, and re-surfaced oil. Technologies exist to monitor the surface slick (Fingas and Lea, 1981; Goodman et al., 1995). Tracking is essential to ensure that the geometries and positions of both the plume and surface slick are well established for the airborne and surface crews. Tracking resurfaced oil might be difficult as it is not highly visible.

The use of GPS can now accurately locate the position of the entire surface track. GPS information can be noted at each sampling station, along with the exact GPS time. Software now exists to readily plot these points onto maps.

### **3.10 Tracking of Oil Underwater**

While technologies to track the underwater plume are not as well tested as those to track oil on the surface, success has been recorded using drogued buoys such as the Davis Drifter (Payne et al., 1991, 1993; SMART, 2003). Both the resurfaced oil and the plume should be tracked using remote sensing or drogue and sampling techniques. Tracking is essential to ensure that the geometries and positions of both the plume and the surface slick are well established for the airborne and surface crews. Sampling of the subsurface plume should be guided by airborne crews as well as by observing the plume and the drogued buoys in the plume. Misplaced sampling can result in under-estimation of the dispersed amount or in large over-estimations if the extent of the plume is over-estimated.

The dispersed oil plume spreads out over time and becomes increasingly more difficult to track. Eventually it becomes invisible to surface and aerial observation, at which time, it can be tracked using fluorometer probes and drogued buoys. The buoys may require repositioning based on fluorometry information as noted in the SMART protocol.

### **3.11 Mass Balance**

It is important to note that the SMART protocol and other monitoring protocols noted do not purport to establish a percentage of effectiveness, nor should they. To achieve a percentage effectiveness, the experiment would have to establish a mass balance. Mass balance is very difficult to achieve in open field tests. 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, 1994b). 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 and techniques for performing this are not available.

Even in enclosed test tanks, it is very difficult to establish a mass balance. Brown et al. (1987) and Brown and Goodman (1988) 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 Showing Mass Balance Problems**

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. 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.

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 field trials (or other 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 in the field and even in the more controlled tank tests can vary from a few percent and higher. If the measurement made does not account for the mass balance discrepancies, 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; and presence of large heterogeneities in oil concentrations in the water column. For all these reasons, a protocol to monitor a real application should not try to establish a percentage, unless the experimenters are prepared to adequately address the large task of establishing a mass balance.

### 3.12 Use of Undispersed Slick as a Control

In order to properly assess a dispersant field test, a proper control slick is needed. The control must be treated equally to the treated slick in every respect except for the applying of dispersant. The SMART protocol suggests that the slick before treatment be used as the control. The importance of the use of a control slick can be illustrated by two field dispersant trials, treatment of emulsified oil from the *Exxon Valdez* and the Beaufort Sea Trial. Both were attended by the author of this report.

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 treated with large amounts of dispersant. Sampling was conducted from a ship and aircraft, some equipped with remote sensing gear, from which the slicks were observed for about 6 hours. The dispersant failed to break the emulsion and did not disperse the oil. Coincidentally, the control slick broke up somewhat after about five hours. This was probably due to its great exposure to waves as it was up-sea of the treated slick. Without a control, the experimental results could be interpreted differently.

In the case of the Beaufort Sea experiment, 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 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 and two left as controls (Swiss et al., 1987).

The use of the same slick as a control as the target slick requires further analysis. The control would in this case act only to compare fluorometric readings on an initial basis. Some smaller slick should be left as a control for comparison over a longer term if the dispersant application is continued.

### **3.13 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. The background of hydrocarbons in the sea varies widely (Henry and Roberts, 2001a, b; Henry et al., 1999; Payne et al., 1993). This is especially true in estuarine and riverine outputs into the sea. These areas are often the same areas that were used for dispersant experiments in the past and possibly also the areas where dispersant may be applied. It is suggested that the same techniques, along with the grab samples for calibration, be applied in the area before dispersant application as well as 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 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 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-through 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.

### **3.14 Using and Computing Values**

SMART and its other counterparts are not intended to result in percentage effectiveness. Despite this, users will inevitably try to use these values to 'calculate' effectiveness. This should not be done as it will lead to errors, as described in Section 3.17.

Another issue is the use of a sampling protocol to determine effectiveness on a trial application. While a useful concept, this author suggests that this is not practical. The cost of

mounting a dispersant operation, be it a trial or not, is too great to stop it after it has begun. In a typical situation, it would not be acceptable to leave the slick with no countermeasures during decision time or to delay countermeasures for further decisions. It may be much more advantageous to obtain a sample of the oil and perform one of the quick bottle tests on the oil as it now is in the field (Fingas, 2000). This would form a better decision point in view of costs and acceptability of approach.

### **3.15 Heterogeneity of the Slick and Plume**

Slicks are rarely homogeneous in thickness and, as a result, the dispersant applied may be insufficient in areas or may break through and cause herding in others (Merlin et al., 1989, Payne et al., 1993). Furthermore, slick heterogeneities will result in heterogeneities in the plume. Plume heterogeneities will again result in difficulties integrating the plume. Using peak values will result in over-estimation of the dispersant effectiveness and vice versa.

### **3.16 Review of Laboratory and Other Reports**

In viewing field applications and laboratory data, it has been noted that there is general agreement on the relative effectiveness with a given dispersant and a given oil. It would be useful then to compare laboratory effectiveness data with the relevant field application. It is not likely that an oil that can be effectively dispersed in the laboratory would not be dispersed in the field.

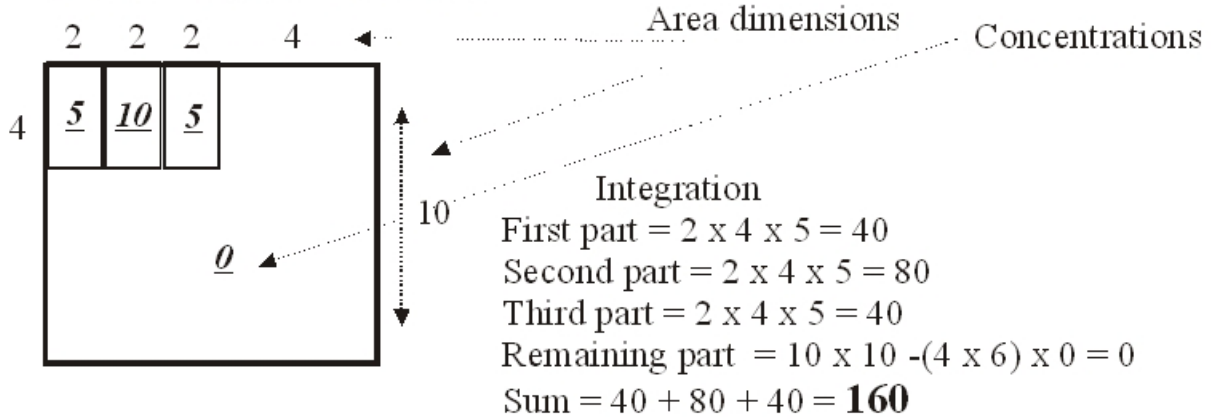
Some laboratory data were compared to the field data by Lunel and co-workers (Lunel et al., 1994a, 1994b, 1995a). While the data correlate somewhat to the field data, with the wide spread in effectiveness numbers and the few data points, this correlation should not be overstated. Another interesting point is that the effectiveness values obtained in the field are lower than the data obtained in the laboratory, indicating that the energy levels may be much higher in laboratory tests than those in the field conditions described here. This is contrary to what was previously thought.

The tests during which these correlations were conducted deserve special mention. The tests were conducted specifically to achieve a mass balance so that effectiveness could be estimated much more accurately than in previous field tests (Lunel et al., 1994b, 1995a, b). The oil was released from a fixed barge which was anchored and a constant volume of oil was discharged down current (about 0.9 m/s). A constant amount of dispersant was sprayed onto this oil. The dispersed oil plume diluted as it moved away from the barge. Since the tidal movement was relatively constant during the test and the oil and dispersant flows were constant, the dispersed oil in any slice cross-plume down current should be constant, that is given that first the dispersant had time to function. Tests of this hypothesis showed that oil amounts were relatively constant beyond 900 m from the discharge vessel (about 15 minutes after release). This constancy was tested at up to 3 times this distance and found to be relatively consistent, although data were not provided.

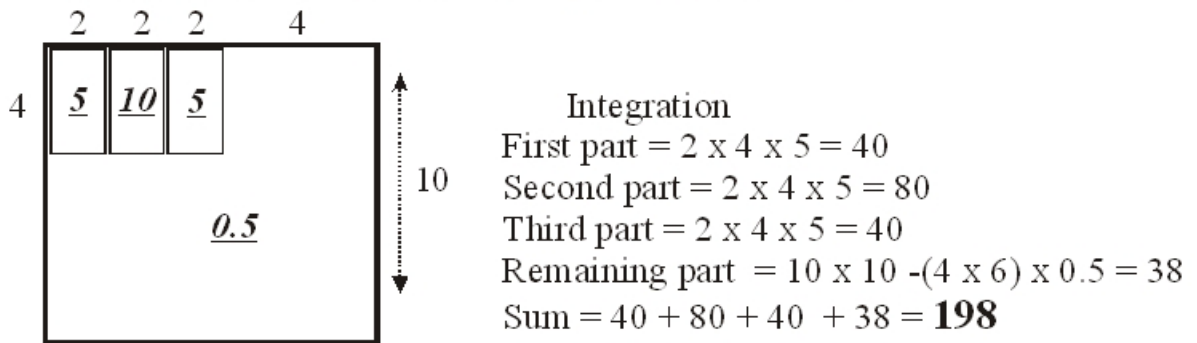
### **3.17 Mathematics of Calculation and Integration**

SMART does not advocate the calculation of values, however, several users have hinted at doing so. Several examples of the effects of integrating and averaging incorrectly were given in the literature (Fingas, 1989). This effect is exacerbated if no zero-oil concentration values are measured in areas outside of the plume. Figure 6 illustrates three cases of integration showing the effect of using non-zero values in the areas outside the plume and the effect of averaging values

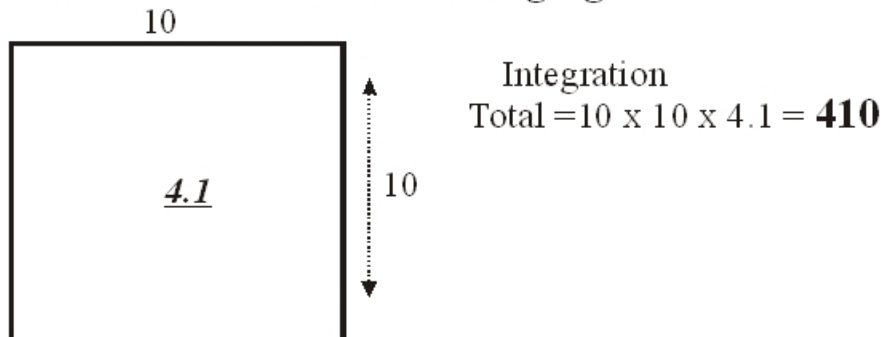
### Case 1 Actual situation



### Case 2 Illustration of taking non-zero values



### Case 3 Illustration of averaging values



**Figure 6 Illustration of the Effect of Integration and Averaging Techniques on the Final Values - A 2-d Example**

over a large area. The difference is over a factor of two for this two-dimensional example and would be a factor of four for a three-dimensional sample. To achieve the most accurate result, small compartments should be integrated and background values subtracted so the volumes outside the plume are not integrated.

Another concern about the mathematics is that related to the use of fixed values to determine effectiveness (Fingas, 1989). Although this method has not been used recently, it was thought to be a reliable means of estimating effectiveness. It is assumed that the slick is evenly distributed in 1, 2 or 3 m of water. Then once the concentration is measured, an effectiveness is assigned. Table 2 illustrates the variances in using this type of scheme. This shows that one concentration could yield a wide range of effectiveness values depending on what assumption one makes. Because one cannot take oil thickness measurements and the depth in mixing is not simply a fixed depth, this type of procedure is not a valid method for determining effectiveness. This table, however, shows the variances in concentration values that might be expected.

**Table 2**                    **Illustration of the Use of Concentration Values and Mixing Assumptions**  
**1 mm slick   1 mm slick   3 mm slick   3 mm slick   10 mm slick   10 mm slick**  
**mixed in 1 m   mixed in 3 m   mixed in 1 m   mixed in 3 m   mixed in 1 m   mixed in 3 m**

<b>Concentration Found in Water</b> ppm	<b>Value of Effectiveness</b> %		<b>Value of Effectiveness</b> %		<b>Value of Effectiveness</b> %	
1	0	0	0	0	1	0
5	1	0	2	1	5	1
10	1	0	3	1	10	1
15	2	1	5	2	15	2
20	2	1	6	2	20	2
25	3	1	8	3	25	3
30	3	1	9	3	30	3
40	4	1	12	4	40	4
50	5	2	15	5	50	5
75	8	3	23	8	75	8

The SMART protocol notes that a value of about 5 times the background would indicate relative effectiveness. Table 2 shows that as background levels are generally in the parts-per-billion range, the relative effectiveness would have to be many times - perhaps 100 times - the background level to show even a few percent effectiveness given the assumptions made in Table 2.

### 3.18 Lower and Upper Limits of Analytical Methods

Another consideration is that of the lower and upper limits of the fluorometric methods applied, especially in the field situations. If the lower limit is exceeded, the use of these values can result in serious errors. The lower analytical limit should be taken as twice the standard deviation or about 0.3 ppm for an older fluorometer or 0.1 ppm for a newer model. 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 the water column could exceed the upper limit of some analytical procedures. If this were to occur in practice, the effectiveness would be under-estimated. Fluorometers are nonlinear 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 either the field or lab.

### 3.19 Thickness Measurements

Several workers 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, 1988a, Louchouart et al., 2000). This is because the removal of oil from the surface is not necessarily total for the following reasons: the edges of the sorbent may trap more oil, the inability to calibrate the sorbents in the laboratory, and 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 by even the light laboratory air circulation. Most oils will form a concave lens with more oil on the edge.

The use of sampling tubes and other similar devices is also fraught with similar difficulties. As noted in Section 3.8, there are no remote sensing means to give thickness data. In summary, thickness of oil on the surface of the sea cannot be measured and thickness therefore cannot be measured to determine dispersant effectiveness.

### 3.20 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.

It has been suggested that a portion of a slick might be contained by using a boom and then trying a dispersant application. If the oil were 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 critical velocity of containment can be given by (Lee and Kang, 1997):

$$U_{cr} = \{2 [g T_{o/w}(\rho - \rho_o)]^{1/2} (\rho + \rho_o)/(\rho\rho_o)\}^{1/2} \quad (4)$$

where:  $U_{cr}$  is the critical velocity,  
 $T_{o/w}$  is the interfacial tension between oil and water,  
 $\rho$  is the water density, and  
 $\rho_o$  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, this effectiveness value would be highly exaggerated and would represent containment failure, not dispersion.

The other factor changed by adding dispersant to oil is the adhesion of the oil. Quantitative studies have not been performed on this, however, practical tests (Brown et al., 1987) have shown that it is difficult, if not impossible, to remove the remaining oil after dispersant application using a sorbent surface skimmer. 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 estimate of the apparent effectiveness. While this effect is not felt to be as large as that of containment failure, it is significant nevertheless.

### **3.21 Recovering Surface Oil**

Although not recommended in the SMART protocol, other experimenters have attempted to recover surface oil in order to directly determine effectiveness by presuming that the entire remainder is dispersed. This is incorrect because the loss from the surface includes: that amount evaporated, that amount in very thin (often invisible) slicks, that amount that is physically unrecoverable, oil adhered to booms or other surface objects, errors in the amounts of all the oil compartments, and oil simply unaccounted for. Controlled tests in a test tank have shown that the difference between oil accounted for in the water column and that accounted for by taking the amount on the surface can vary from 0 to 80% (Brown et al., 1987). 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 just described, 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.

### **3.22 Deposition Measurements**

Dispersant deposition measurements would assist in determining the amount of dispersant that caused the dispersion. Deposition measurements are very difficult to perform at sea, however, and would interfere with the dispersant experiment itself (Giammona et al., 1994). Deposition measurements were tried on the Halifax Trials, however, results show that the dispersant deposition itself is also heterogeneous (Gill et al., 1985). Although, deposition measurements might be a useful instrument to understand effectiveness, they are an additional complication in a very complicated design and measurement scheme. It is not recommended to measure deposition on a field dispersant application.

### **3.23 True Analytical Standards**

Certified laboratories now exist that use certified petroleum hydrocarbon measurement techniques. These should be used for field applications as well. One of the most serious difficulties in older field trials occurred when inexperienced staff tried to conduct chemical procedures. Analytical methods are complex and cannot be conducted correctly other than by 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.

### **3.24 Training, Expertise, and Experience**

A very important factor in implementing any protocol is the training, expertise, and experience of the people performing the monitoring. Training aids have been developed to assist in the process (Levine, 1999). It is suggested that visual observers be trained and have already observed at least two other dispersant applications before leading the observation at a dispersant application scene. Furthermore, it is suggested that the sampling be conducted only by trained and certified chemists and those trained in field work using the fluorometer.

The Dispersant Application Observer Job Aid (NOAA, 1999) is available on the web and the contents include a photograph depicting herding, three photographs of dispersant effectiveness, and several miscellaneous photographs. The photographs in the package are of low resolution. Work is needed to prepare a useful package with many more photographs of the various aspects of dispersant application.

## **4. Recommended Procedures for Monitoring Dispersant Applications**

### **4.1 Overall**

In view of what has already been covered in this report, it should be apparent that there are many nuances to monitoring the effectiveness of a dispersant application. Furthermore, the use of a trial aerial application as a decision point for continuance is questionable in most circumstances. It is suggested that a field test be conducted on a small sample of the oil instead. The aerial application is too expensive to stop if it is not effective. The trial application should only proceed if there is reasonable certainty that the oil is dispersible.

### **4.2 Field Pre-test**

Several tests have been developed and are summarized in Table 3.

The prime purpose of these tests is to screen the effectiveness before application proceeded. No test or agency recommending them, however, suggested any level of effectiveness (even relative) that should be achieved before full application proceeded. The advantage to a pretest is that, before application proceeds, a screen is carried out. This screening takes little logistics and does not interfere with other operations or organization for an actual dispersant application. If the screen test shows that there is potential for dispersant effectiveness, then planning for the next stage could proceed.

The last row of Table 3 shows a recommended test. The concept behind this is that a very simple test would suffice. The procedure for this test is that a sample of the actual spilled oil and a sample of the water in the area are obtained. As soon as practical after the samples are obtained, about 1 L of the water sample is placed into a bottle with a narrower neck (to exaggerate the oil measurement) and filled to the start of the neck. A line is placed at the top of the water level to indicate where the oil would start. This can be done with an etching tool or a special marker. About 1 mL (about 5 drops) of the dispersant to be used is added to 10 mL of oil. This is mixed briefly and then poured into the test vessel. A mark is placed at the top of the oil. The test vessel is vigorously shaken for 1 minute and let stand for 10 minutes and a mark placed at the top

of the new oil level. The criteria suggested is that about half of the oil should be dispersed before proceeding with full-scale dispersant application. For information purposes, the oil and dispersant laboratory effectiveness result should be obtained and compared to this value.

**Table 3 Field Tests for Screening Effectiveness**

Test Sponsor	Reference	Vessel	Water Capacity (mL)	Oil Added (mL)	Oil to Water Ratio	Dispersant Added	Dispersant to Oil
American Petroleum Institute	S.L. Ross, 1989	Battery tester 2 cm d 21 cm long	50	1	1:50	.2 premixed	1:20
Environment Canada	Abbott, 1983	1-L flask	1000	10	1:100	1	1:10
US EPA Test	Diaz, 1987	test tube	5 cm in 1 cm tube (~ 6 mL)	10 drops (~2 mL)	~1:3	1 drop (~0.2 mL)	~1:10
Fina Spill Test Kit	Fina, 1990	Graduated cylinder	100	2	1:50	0.1 0.2	1:10 1:20
Pelletier Screen Test	Pelletier, 1987	25 mL vial	20	0.1	1:200	0.05	2
Suggested	This work	Wine bottle or similar	~1000	~10 (50 drops)	~1:100	~1 (5 drops)	~1:10
		<b>Shake Motion</b>	<b>Shake Time (min.)</b>	<b>Settling Time (min)</b>	<b>Measurement Description</b>	<b>Effectiveness Criteria</b>	
American Petroleum Institute		End-over-end 0.5/second	2	5	Extraction by toluene colorimetric comparison	none	
Environment Canada		Rotated to 140° 30 times	~ 15	3	Visual measurement of oil height	none	
US EPA Test		Vertical 2/second	1	10	Height -O-ring movement light obscuration	none	
Fina Spill Test Kit		Shaking	0.17	0.5	Colour comparison to scale provided	none	
Pelletier Screen Test		Vortex with magnetic stirrer 2000 rpm	1	1	Visual estimation	none	
Suggested		Stopper flask and shake	1	10	Height of lines on bottles top, bottom, after settling of oil	> ~40% of oil gone (about half)	

### 4.3 Visual Surveillance

It is suggested that visual surveillance is a prime method for determining whether or not the initial spray had any effect. The many factors noted in this report must be considered and a good field guide is also needed. As noted in Section 3.24, at least one person with experience should be employed for the visual surveillance to be effective.

It is recommended that buoys be used to track the plume and the remaining slick. Davis Drifters can be used to track the plume and Orion buoys can be used to track the remaining slick. Further visual surveillance on the slicks is necessary for at least one day. The visual surveillance requires documentation by photography. Good quality digital still pictures are the best. The colour quality must be good in order to be able to distinguish between white (dispersant only) and yellow (dispersed oil) plumes. All images require time-coding.

#### **4.4 Measurements from the Surface**

The measurements from the surface, such as by using fluorometry, may provide little additional information over pre-testing and visual surveillance. The basic question to be asked by any monitoring protocol is: “is there significant dispersant effectiveness or not?” Surface monitoring may result in confusing information that is not directly relevant to this question. Therefore, from a strictly monitoring point of view, surface monitoring is not recommended.

For scientific and documentation purposes, however, it is suggested that surface sampling would be extremely useful. Good quality data from surface monitoring could be very useful for future purposes. For this purpose, the protocols as proposed for SERVS are recommended (Hillman et al., 1997). These field procedures and the accompanying lab procedures require updating.

#### **5. Summary and Conclusions**

The monitoring of dispersant applications has been proposed with the purpose of determining if that application was relatively effective or not. The protocols currently consist of a visual criteria and often a surface monitoring program consisting of using in-situ fluorometers to gauge the relative effectiveness of a dispersant application. This report pointed out that there are many false positives and false negatives with both monitoring techniques. These can be overcome somewhat by paying careful attention to the science and technology. It is clear that none of the current published methods including SMART and the SERVS protocols will assure that effectiveness is gauged accurately. There is still potential for answers that are completely opposite to the actual situation. Further the current protocols are very much limited by basic physical and chemical problems so that they are at best, estimates of whether the dispersant application is completely ineffective or somewhat effective.

The current protocols will not yield a measure or even estimate of effectiveness. Both visually and fluorometrically, the indications of a plume could indicate effectiveness as low as a few percent. This is based on calculations and several field trials. These indications should never be confused as being that the bulk of the oil is dispersed unless there are other measures. Even cases where about 30% of the oil is dispersed yields massive underwater dispersed oil plumes, appearance of little remaining surface oil and fluorometer readings over 1000 times that of background.

The SMART protocol suggests that a trial application be conducted but urges that this not be used to decide on further application. Inevitably, such trial applications will be used as a decision point for continuing with further application. It is recommended that a screening test of the dispersant effectiveness be carried out before any test dispersant application. This test should show a dispersion of about one-half of the oil.

The prime monitoring technique for actual dispersant application should be visual. It must be recognized that there are a large number of false positives and negatives. It is pointed out that extensive work is required to produce visual monitoring guidelines and visual aids. The false positives and negatives for visual and fluorometric readings can be summarized as: There are many visual and other indications that may be misleading in terms of determining the effectiveness or lack of effectiveness in a particular application.

#### ***Visual indications that show more effectiveness than actually occurred***

***Herding*** - This is the phenomenon whereby the oil is pushed aside by the dispersant, resulting in a clear path behind the application vehicle.

***Dispersant-only plume*** - Once in the water, dispersant forms a whitish plume until it mixes to a greater extent with the water. Such plumes could be mistaken for dispersed oil as opposed to dispersant only.

***Herding into smaller, unseen strips*** - Oil is often herded into small strips that are not visible from the air.

***Spreading*** - Dispersants increase an oil's tendency to spread. The surface slick may spread out to thicknesses that are not visible.

***Lacing*** - 'Lace' is a sheen of oil with 'holes' in it. The 'holes' are caused by smaller drops of dispersant leading to herding. The 'lace' is usually visible only from the surface and not from the air.

***Visual indications that show less effectiveness than actually occurred***

There are also a number of visual indications that would lead one to conclude that little or no dispersion is occurring when in fact there is some or significant dispersion.

***Plume under remaining slick*** - It can happen that the dispersed oil plume moves under the remaining slick.

***Plume not developed at time of observation*** - The dispersed oil plume can take 15 to 60 minutes to develop to a maximum.

***Poor visibility conditions*** - The dispersed plume is not highly visible and can be obscured by haze and some fog. It is unlikely, however, that a test application would be conducted under such conditions.

***Fluorescent indications that show more effectiveness than actually occurred***

There are also indications using fluorometers that can be misleading in terms of the effectiveness of a particular dispersant.

***Resurfacing after measurement*** - Resurfacing of dispersed oil occurs in every case and, if the fluorometry measurement is taken before much resurfacing takes place, the effectiveness will be over-estimated.

***Repeatedly measuring one part of the plume*** - The surface sampling crew does not have a good fixed frame of reference to guide them and it is very easy to repeatedly sample the same small dispersed oil plume.

***Dispersant-only plume*** - When aeri ally applied dispersant lands on heavier or emulsified oils, the dispersant generally runs off without much dispersant penetrating the oil and without any measurable effect on the oil. The dispersant forms a milky mixture that may be mistaken for dispersant effectiveness.

***Dissolved aromatics*** - After an oil spill occurs, a significant plume of aromatics forms. These aromatics are the prime target of a fluorometer and will give significant readings.

***Other fluorescent material in the area*** - Fluorometers do not discriminate between sources of fluorescence. Fluorometers operating at long wavelengths will readily pick up organic material.

**Dispersant and aromatics only** - A probable occurrence is that dispersants and aromatics from the oil are in an area and these fluoresce and could be mistaken for dispersed oil.

**Fluorescent indications that show less effectiveness than actually occurred**

**Fluorometer misses plume** - It is very easy to miss the dispersed oil plume with a surface-sampling rig.

**Misdirected by aerial observer** - The surface sampling team could be misdirected by the aerial observers.

**Measurement before plume develops** - The time to formation of a substantive plume after the dispersant application varies from 15 to 40 minutes.

Monitoring of oil concentrations in the water column would provide useful scientific information, although this information may not be useful to the incident commanders because of the complexities of the measurements. It must be noted that there are very many fundamental reasons why fluorometry is not a highly accurate measure of oil in the water column. The typical tendency is to exaggerate the water column concentration between 2 and 10 times the actual value with a corresponding decrease in the actual effectiveness value. Fluorometers are, however, rugged and robust field instruments.

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