MASS BALANCE AND DISPERSANT EFFECTIVENESS: ARE NEW TECHNIQUES AND METHODOLOGIES NEEDED?

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ABSTRACT

In order to obtain a scientifically-acceptable measurement of dispersant effectiveness, the oil mass balance must be demonstrated. While this is normal in small-scale laboratory apparatus, it has not been achieved in larger-scale wave basin and open ocean experiments despite the work of a large number of research groups. Five years ago, mass balance was either ignored or losses of up to fifty percent of the applied oil were accepted. In the larger wave basin experiments, recent work has reduced the unknown losses to between ten and fifteen percent. No such reduction has been achieved in the few open ocean tests that have been recently undertaken.

This paper will discuss the limitation of current measuring technologies and experimental techniques. New experimental techniques will be suggested to improve mass balance calculations, such as changing the experimental plan for large wave basins from a Lagrangian description of motion to an Eulerian frame of reference. There are technologies, that can be applied to large wave basins, that are unique to this experimental situation, but are not widely used. These technologies will be discussed.

For the open ocean situation, there are seldomly-used methods, which could be employed to improve the measurement of sub-surface plume characteristics and oil thickness on water. The current limitations of these technologies will be discussed.

INTRODUCTION

Dispersant effectiveness studies have been conducted over the past thirty years at scales varying from small laboratory beakers to open-ocean experiments, all without much success in answering the basic question "Are dispersants a useful oil-spill counter measure?" Why is this? Since dispersants are commonly included as a response option in many contingency plans, why has this basic question not been answered? If it is assumed that the goal of an oil spill response is to reduce the environmental and socio-economic impact of an accidental spill of petroleum hydrocarbons on water, then the concept of "useful" is that the response technique contributes to this goal. The reasons for the lack of success are many, but the main issues are that:

- the wrong question has been asked
- techniques and facilities have guided the experimental program, rather than the development of a proper experimental plan
- publicity and show are more important than understanding and science.

WHAT IS THE QUESTION?

Unless the right question is asked, the answer to that question will be quite useless. For example, if the question is "Are dispersants effective?" the answer is yes and no experimental data is needed. The effectiveness may vary from 0 to 100%, but that was not the question. A better question would be "What is the effectiveness of dispersants?" This question is impossible to answer without knowing the properties of the dispersant, its application method, the relevant parameters of the oil being treated and the environmental conditions under which the dispersant is being used and the methods used to measure the "dispersant effectiveness". In order to answer the latter question, "dispersant effectiveness" must be defined. A common definition of dispersant effectiveness is the ratio of the amount of oil in the water to the total amount of oil being treated. Even this simple definition only generates more questions such as:

- how long must the oil remain in the water: minutes, hours or days?
- where is the oil in the water column?
- how much oil was treated? This volume varies with time due to such weathering processes as evaporation, emulsification and natural dispersion.

SIZE SCALES

Small-scale Experiments

The cost of experimental measurements varies with the scale of the experiment. A large number of small-scale laboratory experiments can be economically undertaken and with suitable experimental procedures, the results of these experiments are highly reproducible and the errors (both systemic and statistical) can be determined. The results of these tests will give a relative ranking of a given dispersant-oil combination under a predetermined environmental condition (Fingas *et al*, 2004). But spills in an enclosed laboratory beaker do not cause an "environmental and socio-economic impact", so how do these measurements solve an actual problem. There is only a very limited understanding of the scaling of a beaker experiment to an actual spill situation, so such work has only a very limited credibility in determining the ability of a dispersant response to reduce the environmental and socio-economic impact of an oil-spill situation.

Meso-Scale Test Basin Experiments

As the size of the experimental test container is increased from the laboratory to the meso-scale test basin, the cost per data point increases by several orders of magnitude, the accuracy and reproducibility of the results is reduced by at least an order of magnitude, and the ability to determine errors and undertake any significant statistical analysis is limited. The scaling problem still exists so that the extrapolation to an actual spill situation is questionable.

Open-Ocean Experiments

This is the size scale at which oil spills are important and have environmental and socio-economic impacts. However, collecting experimental data on the open ocean is very difficult and the quality of the data is low. Even collecting a small amount of qualitative data is very difficult and such data has large errors. Mass balance for these open-ocean experiments is virtually impossible to achieve (Brown *et al*, 1987 and Fiocco *et al*, 1999). The cost per low-quality data point is another order of magnitude more than wave basin experiments. While remote sensing has been suggested as a solution, it can at best only measure the presence of surface oil, and intrinsically cannot be used for mass balance determination (Goodman and Fingas, 1988).

After thirty years of experiments and many million dollars of effort, there is still no universally accepted answer to the simple question "What is the dispersant effectiveness?"

There are many parameters in the dispersant effectiveness equation (which does not exist) and how these parameters interrelate is not well understood. When such a situation has occurred in other areas of science, then the experimental approach generally adopted is to develop a series of experiments that separate the variable and conduct controlled experiments in which only one parameter is varied during the program. After a series of experiments, a matrix involving the relationship between all of the variables in the experimental program that have been measured is obtained and from this a true dispersant effectiveness equation can be defined. Existing data collected over many years, from small-scale experiments, was analysed by (Fingas *et al*, 2003) in order to understand the dispersant equation. However, the variables were not separated in his experiments and the results are derived from equation fitting rather than controlled variable experiments.

Such separation of variables can best be achieved in a controlled environment such as a wave basin when suitable protocols and measurement techniques are used. The development, testing and calibration of program-specific measuring techniques must precede the undertaking of more experiments.

In order to give credibility to the experimental results, the mass balance of the oil must be determined for each experiment. This is a failure of many wave-basin and all open-ocean experiments.

PAST AND CURRENT STATE OF THE ART

Laboratory Studies

Over the past two decades, enhanced experimental procedures and analytical procedure have improved the quality and reproducibility of these experiments. Recently incorporated calibration procedures into these experiments have increased the ability to intercompare results from various laboratories and to produce absolute value data sets. Laboratory data, when used properly, provides a basis for comparison of various dispersant-oil combinations. Some of the variable parameters can be separated in these experiments, thus beginning the complex process understanding and developing the dispersant effectiveness equation. In these experiments, mass balance is readily achieved, which leads to improved confidence in the results.

Meso-Scale Test Basin Experiments

Experimental wave basins have size scales varying from a few metres to tens of metres, and allow the measurement of many more variables (especially water-related parameters) than typical laboratory experiments. In many situations, these basin experiments have been thought to be equivalent to the open ocean, and the design of experiments have been based on this assumption. This has resulted in many experiments in which there have been no attempt to separate variables. The multi-variate nature of the resulting data sets has made their interpretation as difficult as those obtained from open ocean experiments. Three major test facilities have been used in the basin studies of dispersant effectiveness.

Texas

This facility consists of a number of parallel wave basins, which were specifically designed for oil spill experiments. In both their design and commissioning, a great deal of attention was given on studying the hydrodynamics of the basins. This has led to the belief that the relationship between results from these basins and the open-ocean are possible. The long narrow geometry of the basin increases the wall effects and tends to distort the flow geometry. In the experimental design of some studies undertaken at this facility, there has been great attention paid to achieving a mass balance (Page *et al*, 1999 and Bonner *et al*, 2003), a very important parameter in the conducting of a dispersant effectiveness program. In an attempt to emulate the open-ocean situation, the measurement of the sub-surface plume uses a roaming probe, which is only calibrated before and after the experiment. This approach produces a point sample of the oil concentrations, and not a synoptic sample. The dynamics of plume motion are at a time scale much shorter than the resampling time, and hence the size, homogeneity and dynamics of the plume can only be estimated by a model of doubtful skill.

OHMSETT

The OHMSETT facility was designed and is still used for the testing of booms and the training of oil-spill response groups. It has recently been utilized for dispersant testing, but the approach has been quantitative rather than qualitative, and little attention has been given to design programs that separate variables and measure mass balance. In some experimental situations, there is no attempt to measure the amount of oil in the water column or to define the plume shape. While this facility has the potential to undertake a serious study of dispersant effectiveness, it has mostly been used for demonstration programs rather than programs designed to measure, in a reliable manner, dispersant effectiveness.

IOL

The Imperial Oil test basin was initially designed as a facility to measure ice forces and dynamics on structures and was later modified for oil-spill research and is now closed. One of the main limitations of this facility was that the water depth was inadequate (<2 metres) to prevent bottom interactions with the dispersant plume. Its relatively small water volume meant that mounting of sensors and sampling points in the basin was practical. Unlike the other two basins, the experimental design used was to have a number of fixed sampling ports to obtain water samples for external analysis. This methodology provides the capability for continuous calibration of the analytical system.

LIMITATIONS OF CURRENT PRACTICE

Experiments in large-scale wave basins are probably the best venue for undertaking programs to provide data to develop a dispersant effectiveness equation and thus be able to determine dispersant effectiveness and the role of dispersants in oil-spill response.

The main limitation of the current system is a lack of suitable sensors and experimental protocol to determine the size, homogeneity and dynamics of the sub-surface dispersant plume. This limitation essentially eliminates the possibility of achieving a mass balance. A second limitation is one of program design. Many current programs are demonstrative in nature and make no attempt at measuring dispersant effectiveness. This is like the story of Isaac Newton and the falling apple. Newton noticed that the apple fell, and went on to observe that all apples fell. He looked at the sky and found it was blue, and that apples tended to fall when the temperature was above freezing. From this Newton could have concluded that apples fell if the sky was blue and the temperature was above freezing. These are easily observable parameters. Instead, he elected to conduct further experiments from which, after a good deal of effort, his famous three laws of motion were developed. The present state of dispersant effectiveness research is stalemated at observing what is convenient to measure, thus eliminating the possibility of developing the concept beyond simple Linnaean taxometric type descriptions.

From the recent literature, two examples illustrate this point. A study of the use of dispersants in ice was conducted at OHMSETT (Owens and Belore, 2004). Oil was poured on the ice surface, and then dispersant was sprayed on the oil-covered ice. Due to hydraulic action and simple flushing, the oil was removed from the ice surface. While this was interpreted as dispersion, the process is surface cleaning. Pictures showing black oil in or on the water were interpreted as dispersion, but no measurements of the concentration of oil in the water were made. Since only one component of the mass balance was observed, no realistic interpretation of this experiment is possible. The lack of a typical little brown plume of small particles would suggest that dispersion did not occur; but rather the oil was temporarily suspended as large particle in the water column or on the water surface.

A second example is a recent set of experiments at OHMSETT (OHMSETT, 2004) with the headline "New Series of Ohmsett Dispersant Tests To Correlate Open Ocean Results". This experiment used non-quantitative observations in the North Sea and OHMSETT to determine DE (dispersant effectiveness). Is another acronym the answer to the problem? The problem with these experiments is quite simple. How do visual observations, even by experts, quantify dispersant effectiveness? This issue is simply not addressed in the article. What are the values of dispersant effectiveness from either the North Sea or Ohmsett trials and what are the error bands as obtained from the observers or SMART (Special Monitoring of Applied Response Technologies)? The SMART has many limitations (Goodman, 2003) and is not inherently capable of determining sub-surface plume size, homogeneity or dynamics. The two photographs of a researcher poking some type of instrument in or near the surface plume and another picture showing the use of a handheld IR thermometer to measure oil temperature truly illustrate the need for better technology to be developed. How are either of these measurements relevant? The statement "When all these sets of DE experiments are complete, we will have a rare opportunity to get a better understanding of how experiments conducted in the laboratory, and in test tanks correlate and scale with dispersant performance under at-sea conditions" is a desirable objective, but the tests as undertaken at OHMSETT only serve to demonstrate how far away this goal is from reality.

PROPOSED EXPERIMENTAL DESIGN

The proposed experimental program is radically different in both approach and design to most of the previous experiments in that its purpose is to do simplified experiments that focus on the separation of variables rather than simply concentrating on parameters that are convenient and easy to measure. While these do not have the glamour, gee wiz and pizzazz of the traditional experiment, this new approach has the potential to develop an understanding-based dispersant effectiveness equation. This should be the goal, not to have another set of pictures of a coffee-coloured cloud associated with a surface slick and the spraying of dispersants.

The goal of this approach is to develop a defendable equation of dispersant effectiveness, which is based on a combination of experimental measurements, which include mass balance and a complementary theoretical model. Adjustable coefficients should not be part of the equation.

NEW TECHNIQUES NEED TO BE DEVELOPED

New measurement techniques and experimental designs are required if the above objective is to be achieved.

Goal

The goal of this program is to achieve a mass balance in the system which accounts for the oil in the system with an unaccounted for loss of less than 10%. The chief contributors to this mass balance are summarized in Table 1.

This table has been compiled from many databases. The actual values are not important; but it is clear from this table that no reduction in the mass-balance error can be achieved unless errors in dispersion and surface thickness measurements can be reduced. If new technologies can be developed to reduce the errors in these

Table 1. MASS BALANCE PROCESSES

Process	Measurement	Typical Value	Typical Measurement Error	Mass Balance Error
Evaporation	Gas Chromatography	30%	5%	1.5%
Dispersion	Fluorometers	30%	50%	25%
Emulsification	Chemical Analysis	10%	25%	2.5%
Dissolution	Water Chemistry	1%	20%	0.2%
Surface	Oil Thickness	10%	50%	5%
Equipment	Skimmers and Sorbent Pads	19%	20%	4%
Totals		100%		38.2%

two measurements by an order of magnitude, then the mass balance error would be reduced to 15%, which might be marginally acceptable. Reduction of oil adhering to the equipment by good experimental design to a low value or zero value can be achieved by avoiding oil contact with sensors and facility walls. This has the potential to reduce the mass balance error to just over the desired 10%. One way to reduce adhesion is to have all surfaces that are contacted by oil to be water wet.

Due to the dynamics of oil on water, the measurements should be synoptic, since any point sampling method can only be interpolated using a model. This predefines the dynamics and thus forms a circular measurement. The results depend on the results.

New Sensors

The two common methods of measuring oil in or on water involve either the physical collection of a sample with subsequent chemical analysis or by some variation of induced fluorescence of some components of crude oil. In some cases, various forms of electromagnetic sensors, such as visual observations, camera and radar are used to estimate dispersant effectiveness. Acoustic sensing, widely used in medicine, process control and geophysics has the potential to measure both oil-on-water thickness (Goodman *et al*, 1997) and provide a synoptic view of plume dynamics (Hay *et al*, 1984).

Oil-Thickness Measurements

The ability to measure the thickness of an oil film on water has been the subject of many research programs. Techniques varying from the removal of oil from the surface by sorbents (Belore, 1982) to the complex multi-laser LURSOT(Laser Ultrasonic Remote Sensing of Oil Thickness) (Brown *et al*, 1995) system have been developed to measure oil on water thickness. The sorbent techniques are subject to large sampling errors and are not synoptic. The LURSOT system has not been fully developed and tested. One of the advantages of experiments in a wave basin is the ability to install sensors in a fixed geometry. Acoustic imaging systems, such as those used in side-scan sonar, but at a different frequency, have the potential to continuously image the surface slick from below the surface and measure its thickness. Such systems are routinely used in real-time to obtain dynamic foetal images in utro.

Plume Measurements

In addition to measuring oil thickness, acoustics offer the possibility of obtaining three-dimensional images of the sub-surface plume. By mounting two acoustic arrays, orthogonally to each other, on the basin walls and using ranging techniques, a true synoptic and dynamic three-dimensional image of the plume can be obtained. By suitable analysis methods, well develop in geophysics, the time-spatial variation of plume location and oil concentration can be prepared. This instrument, as such, does not exist; but the components and analysis methodology are available from other users of acoustic sensing.

New Experimental Techniques

There are two ways of observing a moving object. One is to follow the object and measure the position as a function of time. This is the Lagrangian approach. The second is to have a fixed set of observers and watch the objects pass these fixed points. This is the Eulerian approach. Wave basins are essentially an Eulerian system, whereas the only practical approach in the open ocean, with no fixed anchor points, is a Lagrangian system. Both the Texas and OHMSETT experimenters use the Lagrangian approach in their desire to emulate an open-ocean experiment. This compromises the data collected due to the large size of the sensor compared to the size of the basin. By using the natural method of observation in a wave basin, the analysis is greatly simplified and the quality of the data can be greatly improved.

CONCLUSIONS

The currently popular methods of measuring dispersant effectiveness have been proven to be ineffective. The lack of mass balance and the inability to measure sub-surface plume dynamics have resulted in, at best, a crude qualitative estimate of the ability of dispersants to be used as a spill response technique.

New measurement techniques and new experimental methods are required before a dispersant effectiveness equation can be developed.

More experiments, which use existing protocols, will not produce any improved understanding of the dispersant process or provide a better measure of dispersant effectiveness. Rather than devote more time and effort to this type of experiment, effort should be spent on new acoustically-based sensors.

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